STUDIES OF SOME SULPHUR RADICALS BY ELECTRON SPIN RESONANCE SPECTROSCOPY

By

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SUMMARY

The occurrence and nature of organic sulphur-containing free radicals in chemical reactions is discussed. The evidence from electron spin resonance spectroscopy for the formation of such species, and the information this technique gives on their structures are reviewed.

The formation of organo-sulphur free radicals by the action of ultraviolet radiation on thiols and disulphides of the C_1 to C_4 alkanes, and certain other sulphur compounds is reported. Diethyl disulphide and di-isopropyl disulphide were found to form secondary radicals by reaction of the initially formed $RS^\bullet$ species by hydrogen abstraction with disulphide molecules. Hyperfine splitting was observed in almost all cases.

The formation of stable aliphatic organo-sulphur free radicals in solution is reported. These species were formed by dissolving aliphatic thiols, monosulphides and disulphides, and N-N'-dithiobisamines in concentrated sulphuric acid. Hyperfine splitting was observed in the esr spectra of these solutions. A structure is suggested for the radicals which is based on a sulphur-containing three membered ring. A mechanism is proposed for the formation of this species. Sulphur itself was found to react in sulphuric acid to form a free radical with hyperfine interaction.

The esr spectra of the sulphuric acid solutions of a range of substituted thiophenols are presented. These solutions were found to contain two radical species, as observed by other workers for thiophenol and 4-methylthiophenol.

The signal at lower g value is due to a radical formed from thianthrene, an oxidation product of thiophenol. The signal at higher g value has previously been attributed to a radical of the type $(C_6H_5S^\bullet)H^+$. Although the spectra from some of the compounds examined are consistent with this, others do not appear so. Other alternative structures are tentatively proposed.

CONTENTS

1. CHEMICAL EVIDENCE FOR THE FORMATION OF ORGANO-SULPHUR FREE RADICALS

The chemical bond consists of two electrons. Fission of the bond can occur in two ways, either heterolytically leading to charged ions, or homolytically, when two species are formed, each having one electron from the bond. These species are free radicals, the electrons from the bond being unpaired and usually conferring high reactivity on the radical species.

The discovery of aryl-substituted carbon, nitrogen, and oxygen radicals, coupled with the discovery of the more reactive and therefore shorter lived alkyl radicals, led to discussion concerning the nature of the chemical bond and to the course of reactions. Many reactions are known which proceed by a radical mechanism, and involve organic compounds containing phosphorus, sulphur, and other elements. Examples thought to involve sulphur are the vulcanisation of rubber (1), the regulating action of many disulphides on the vinyl polymerisation (2,3), and some of the reactions resulting from radiation damage to biological materials such as proteins (4).

The action of ultra-violet radiation on compounds containing the

S-H or S-S bond has been the subject of several papers. It was reported by Skerrett and Thompson (5) that the photolysis of thiols led to cleavage of the S-H link to form the $RS^{\bullet}$ species as a free radical, rather than to split out sulphur.

The effect of light on some thiols, sulphides, cyclic sulphides, disulphides, and thiophenes was investigated with mass spectrometric analysis of gaseous products (6). It was shown that the thiols were decomposed to a greater extent than the other compounds, the major gaseous product being hydrogen. The major products from most sulphides were hydrocarbons, with the cyclic sulphides giving mainly ethene. The authors suggested a reaction sequence for the thiols as:-

$$RSH \longrightarrow R^{\bullet} + HS^{\bullet}$$

$$R^{\bullet} + RSH \longrightarrow RH + RS^{\bullet}$$

$$RS^{\bullet} + RSH \longrightarrow RSSR + H^{\bullet}$$

$$H^{\bullet} + RSH \longrightarrow RS^{\bullet} + H_2$$

The disulphides were cleaved at the C-S bond, producing hydrocarbon products and other unidentified fragments.

The irradiation of disulphides was also known to lead to the formation of thiols. The hydrogen was assumed to be supplied by the solvent. However, thiophenol had been found to be produced by the irradiation of diphenyl disulphide in hydrogen-free solvents (7).

This reaction was further investigated by the same group (8), who showed that thiophenol was not formed from diphenyl disulphide in the dark, even when the active hydrogen donor 9,10-dihydroanthracene was present. They assumed the reaction to be a light-induced rearrangement:-

$$C_6H_5\text{-S-S-}C_6H_5 \longrightarrow 2C_6H_5\text{-S}^\bullet \qquad \text{(I)}$$

$$C_6H_5\text{-S}^\bullet + C_6H_5\text{-S}^\bullet \longrightarrow C_6H_5\text{-S-}C_6H_4\text{-SH} \qquad \text{(II)}$$

$$C_6H_5\text{-S}^\bullet + C_6H_5\text{-S-}C_6H_4\text{-SH} \longrightarrow C_6H_5SH + C_6H_5\text{-S-}C_6H_4\text{-S}^\bullet \qquad \text{(III)}$$

$$C_6H_5\text{-S-}C_6H_4\text{-S}^\bullet + C_6H_5\text{-S}^\bullet \longrightarrow \text{disulphides} \qquad \text{(IV)}$$

This, the authors claimed, was supported by the mean equivalent weight for the thiols in the product, of 170 - intermediate between 110 for thiophenol and 218 for (ortho, para)-mercaptodiphenyl sulphide.

Reaction (II) in the above sequence was blocked by introducing methyl groups at ortho- and para-positions, i.e. using dimesityl disulphide. The photochemically induced reaction of this with diphenylpicrylhydrazyl, a stable free radical, was studied, as was the hydrogen abstraction by species formed by photolysis of dimesityl disulphide with 9, 10-dihydroanthracene, when *o*,*p*-dimethylthiophenol was produced. The photodissociation of dimesityl disulphide was investigated in a variety of solvents, with no direct relation between rate of dissociation and dipole, polarisability, dielectric properties, etc. of the solvent, being found. The rate was, however, found to decrease with increase in the kinematic viscosity of the solvent. Now, dissociation is only complete when the fragments diffuse apart into the solution. The dissociating molecule has to cope with van der Waal's forces in the solvent, and fair correlation was found between reaction rate and activation energy of kinematic viscous flow, indicating that the process was diffusion controlled. This would be expected for a homolytic dissociation.

Rosengren (9) photolysed disulphides in an organic matrix, at 77K, but could not detect thiyl free radical species using uv-visible spectrophotometry. The only detectable overall reaction occurring during photolysis can be represented by:-

$$R_1R_2CHSSCHR_1R_2 \longrightarrow R_1R_2C{=}S + HSCHR_1R_2$$

Both reaction products were found.

The explanation considered simplest was that on photolysis, the disulphide molecule splits symmetrically into two identical thiyl radicals. Subsequent reaction is governed by the close contact between the fragments. Owing to the cage-effect, the free radicals are prevented from diffusing into the hydrocarbon matrix and therefore react with each other or with the matrix molecules. Apparently the α-hydrogen abstraction reaction is the most favourable. Later esr evidence has shown that free radicals are formed under these conditions, (page 51 et seq.)

On photolysing thiols under these conditions, Rosengren (10) found evidence for thiyl radicals. A sharp, stable absorption peak was found at 2.5 MHz m^{-1} at 77K for ethanethiol, isopropanethiol and n-butanethiol. He assumed that the hydrogen atom formed by cleavage of the S-H bond was able to diffuse away. On warming to room temperature, a considerable quantity of disulphide was found in the photolysed thiols, thought to be formed by combination of thiyl radicals.

Free radicals have also been reported when thiols and disulphides have been pyrolysed. Schonberg and Mustafa (11) found that when diphenyl disulphide was heated to 543K, thiophenol and thianthrene were formed. They believed that a free radical process was the most likely, involving the $C_6H_5S^{\bullet}$ species. The hot solutions were found not to obey Beer's Law.

Toluene-ω-thiol, methanethiol and ethanethiol have been thermally decomposed in a flow system (12). Excess of toluene was used as a carrier and free radical trap. The decomposition of toluene-ω-thiol was found to be a first order, homogenous radical reaction, with the dissociation of the C-S bond.

Methanethiol decomposed via a free radical route but the reaction was not simple, involving also the non-radical reaction of the thiol with toluene. Ethanethiol was found to decompose mainly by intermolecular rearrangement to ethene and hydrogen sulphide, although some C-S cleavage occurred, giving $C_2H_5^{\bullet}$ and $HS^{\bullet}$ radicals.

The gas phase thermal decomposition of dimethyl disulphide was found (13), to involve an induction period, after which the primary reaction produced one mole of methanethiol per mole of disulphide, together with a product of low volatility, thought to be thioformaldehyde polymer.

A competing reaction occurred, producing large volumes of H_2S, also hydrocarbons with two or more carbon atoms, sulphur, polysulphides, and carbon disulphides. The decomposition was catalyzed by hydrogen sulphide and also by the "reaction mixture". The overall reactions may be represented as:-

$$\mathrm{CH_3\text{-}S\text{-}S\text{-}CH_3 \longrightarrow CH_3SH + CH_2{=}S}$$

$$\mathrm{nCH_2{=}S \longrightarrow (CH_2S)_n}$$

and

$$\mathrm{CH_3\text{-}S\text{-}S\text{-}CH_3 \longrightarrow H_2S + CH_2{=}CH_2 + S}$$

to account for the formation of H_2S and ethene, but the authors thought a free radical path more likely:-

$$\mathrm{CH_3\text{-}S\text{-}S\text{-}CH_3 \longrightarrow 2CH_3S^{\bullet}}$$

$$\begin{array}{l} \mathrm{CH_3S^{\bullet} + CH_3\text{-}S\text{-}S\text{-}CH_3 \longrightarrow CH_3SH + CH_3\text{-}S\text{-}S\text{-}CH_2^{\bullet}} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathrm{CH_2{=}S + CH_3S^{\bullet}} \end{array}$$

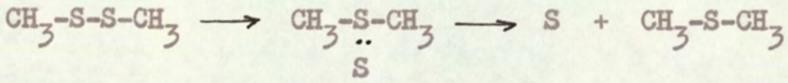
Polymerisation could then occur:-

$$\mathrm{nCH_2{=}S \longrightarrow (CH_2S)_n}$$

or

$$\mathrm{CH_2{=}S + CH_3\text{-}S\text{-}S\text{-}CH_2^{\bullet} \longrightarrow CH_3\text{-}S\text{-}S\text{-}CH_2\text{-}S\text{-}CH_2^{\bullet}}$$

and also



$$CH_3\text{-}S\text{-}S\text{-}CH_3 \longrightarrow CH_3\text{-}\underset{\overset{\cdot\cdot}{S}}{S}\text{-}CH_3 \longrightarrow S + CH_3\text{-}S\text{-}CH_3$$

Further evidence for the occurrence of free radicals of sulphur compounds is found in the reactions of disulphides with radical reagents such as triphenylmethyl (14), metals (15), nascent hydrogen (16), and hydrocarbon radicals present in vinyl polymerisations (16).

Disulphides are also efficient initiators of the free radical polymerisation of acrylonitrile (17) and styrene (18), but only under photolytic conditions (19).

Diazothioesters have also been shown to be useful polymerisation initiators (20), as these produce both reactive carbon radicals and relatively unreactive sulphur radicals, thus giving the advantages of both:-

$$R\text{-}N{=}N\text{-}S\text{-}R' \longrightarrow R^{\bullet} + R'S^{\bullet} + N_2$$

Thiols and trialkyl phosphites have been shown to react at elevated temperatures

$$RSH + P(OEt)_3 \longrightarrow RH + SP(OEt)_3$$

or photochemically at room temperature (21), (22).

The reaction is also initiated by other free radical sources.

Disulphides also react with the trialkyl phosphites

$$RSSR + P(OEt)_3 \longrightarrow RSR + SP(OEt)_3$$

The authors suggested the radical reaction sequence:-

$$RS^\bullet + P(OEt)_3 \longrightarrow RS\text{-}P^\bullet(OEt)_3$$

employing an expanded outer shell of electrons for the phosphorus radical.

Then $$RS\text{-}P^\bullet(OEt)_3 \longrightarrow R^\bullet + SP(OEt)_3$$

$$R^\bullet + HSR \longrightarrow RH + RS^\bullet$$

or $$R^\bullet + RSSR \longrightarrow RSR + RS^\bullet$$

Phenyl radicals were generated from phenylazotriphenylmethane at 330K in a series of aliphatic disulphides (23). The radicals were found to react by attack by hydrogen abstraction to give benzene and by attack on sulphur to yield phenyl alkyl sulphides. The attack was always mainly on sulphur, but the proportion of attack on sulphur decreased as this atom was increasingly hindered. 98% of the total reaction was on sulphur in dimethyl disulphide, only 49% in di-t-butyl disulphide. Reaction of the phenyl radical was found to be 23 times faster with isopropanethiol than with isopropyl disulphide.

A Walden Inversion has been observed in this reaction (24).

A free radical mechanism has been suggested to explain the disproportionation of symmetrical disulphides in the molten state to form unsymmetrical disulphides, and the reverse process (25)

$$\text{R-S-S-R} \rightleftharpoons 2\text{R-S}^{\bullet}$$

$$\text{R-S}^{\bullet} + \text{R}'\text{-S-S-R}' \longrightarrow \text{R-S-S-R}' + \text{R}'\text{-S}^{\bullet}$$

A reaction often used in preparative work is the addition of a thiol to a carbon-carbon double bond, induced by free radical initiators or photolytically. The resulting carbon radical dehydrogenates the thiol to form a sulphur radical which propagates the chain (26)

$$\text{R-S}^{\bullet} + \text{R}'\text{HC=CHR}'' \longrightarrow \text{R}'\text{HC(SR)-C}^{\bullet}\text{HR}''$$

$$\text{R}'\text{HC(SR)-C}^{\bullet}\text{HR}'' + \text{R-SH} \longrightarrow \text{R}'\text{HC(SR)-CH}_2\text{R}'' + \text{RS}^{\bullet}$$

The presence of organic sulphur free radicals has been suggested (27) as the source of some of the colours observed on Jupiter, where, it was thought, $CH_3S^{\bullet}$, $(CH_3)_3CS^{\bullet}$ and other species would be quite stable in the ammonia/methane atmosphere at the ambient temperature of about 120K after being formed by the unattenuated uv or by electrical discharge.

2. ESR EVIDENCE FOR THE FORMATION OF ORGANO-SULPHUR FREE RADICALS

The electron spin resonance spectra obtained from free radicals produced from organic compounds containing sulphur show large differences from the spectra obtained from similar compounds not containing sulphur. These differences arise because of the presence of sulphur in the molecule. They may be summarised as:-

(a) High g-values The g-values of most organic free radicals are close to the free spin value of 2.00229 (28), 2.002319 (29), and do not differ from each other by more than 1% (28). The g-values of free radicals containing sulphur are frequently removed from this free spin g-value by several percent, the largest g-value so far (1970) recorded for an organic sulphur compound being 2.29 for the principal g-value of the free radical formed by irradiating L-cysteine hydrochloride single crystal at 77K with a high energy electron beam (30). The magnitude of the difference of the g-value from the free spin g-value is accounted for by localization of the odd electron on the sulphur atom and the resulting large effect of the spin orbit coupling of the sulphur atom (31), (but see section 3.4., page 113).

(b) Anisotropic g-values The g-values of the sulphur compounds are found to be markedly anisotropic compared to the g-values of carbon, nitrogen or oxygen radicals. The maximum difference between measurements of g-value at different orientations to the external field of a crystal of DPPH is 0.0008. The difference is 0.0069 for gamma-irradiated dimethyl glyoxime, where the odd electron is localised on nitrogen. For the sulphur compound L-cystine dihydrochloride, however, the difference is an order of magnitude larger, being 0.050 (32).

For irradiated thiodiglycolic acid, this difference, or anisotropy, is 0.009 (33), compared to the value of 0.0009 found for irradiated diglycolic acid hydrate (34). This has been taken to show that the odd electrons are localized on the sulphur atoms in the free radicals derived from L-cystine hydrochloride and thiodiglycolic acid.

(c) Small Hyperfine Splitting Constants In most cases, the magnitudes of the hyperfine splitting attributable to interaction with hydrogen atoms in the molecule are small for free radicals formed from sulphur compounds when compared to the splittings measured for carbon radicals, e.g.

alkyl radicals - splitting constants about 20 gauss (35)

benzene anion - splitting constant 3.75 gauss (36)

toluene anion - largest splitting constant 5.45 gauss (37)

9-methylanthracene cation - largest splitting constant 7.03 gauss (38)

thianthrene cation - largest splitting constant 1.30 gauss (39)

thioxanthone-S,S-dioxide anion - largest splitting constant 3.10 gauss (40)

mercaptosuccinic acid, gamma-irradiated - splitting too small to measure (41)

this has been explained (41) by the strong localization of the electron on the sulphur atom, leaving little spin density on any other atom to interact to give hyperfine splitting.

(d) Stability Many of the sulphur containing free radicals prepared to date have been observed to be fairly long lived compared to carbon radicals. Solutions of thianthrene and phenothiazine, for example, in sulphuric acid are stable for many months at room temperature, whereas the related carbon free radicals decay in a few hours or days.

Sulphur radicals may be considered as falling naturally into two groups:-

(1) Compounds with sulphur present in an aromatic ring
(2) Compounds with sulphur not in an aromatic ring, but
    (i) attached to an aromatic system, or
    (ii) attached to an aliphatic system.

Radicals of type (1), where the sulphur forms part of an aromatic ring, have only slightly asymmetric spectra, with, in most cases, fairly well resolved hyperfine structure. The electron is delocalized into the aromatic pi orbital, thus tending to reduce the effect of the spin-orbit coupling of the sulphur atom. As a result of this the g-values tend to be only slightly higher than the g-values of carbon radicals. Examples are:-

Thianthrene cation radical	g = 2.0081 (42)
Phenothiazine cation radical	g = 2.0051 (43)

Anthracene cation radical	g = 2.00249 (44)
Phenanthrene anion radical	g = 2.00269 (44)
Ethyl radical	g = 2.00260 (45)

Radicals of type (2) have the odd electron localized on sulphur to a greater degree. This results in the g-values being higher than for type 1 radicals, and considerably higher than for carbon radicals. This is more marked for compounds of type (2)(ii) than (2)(i). Examples are:-

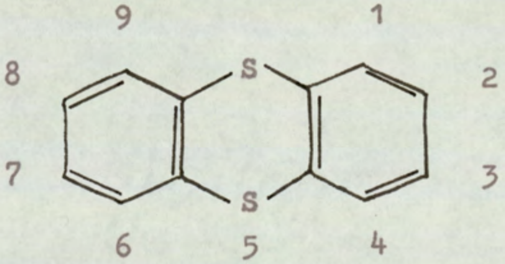
Thiophenol	$g = 2.0151$ (42)
L-cysteine hydrochloride	$g = 2.29$ (30)
Single crystal of L-cystine dihydrochloride	$g_1 = 2.003$ $g_2 = 2.025$ (32) $g_3 = 2.053$

2.1. Compounds with Sulphur Present in an Aromatic Ring

Whilst a considerable number of free radicals of this type have been reported in the literature, a large proportion of the work has involved compounds which can be considered as derived from anthracene as parent -

e.g. Thianthrene (1), Thioxanthone (2), phenothiazine (3), and phenoxathiin (4)

2.1.1. Thianthrene and derivatives

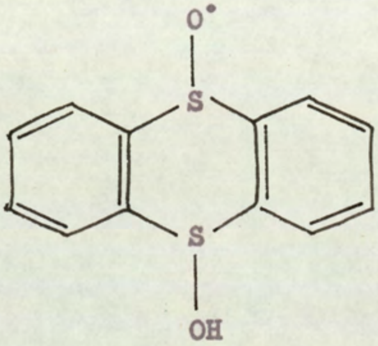


Thianthrene

The first paper on the esr spectra of organic sulphur - containing free radicals was published in 1953 by Fraenkel et al. (46). This reported esr spectra from coloured solutions obtained by dissolving certain compounds in concentrated sulphuric acid. These compounds were thianthrene, thiophenol, p-thiocresol, thio-β-naphthol, and diphenyl disulphide, and it was estimated that about 10% of the solute was present in free radical form. Similarities were noted in the spectra, suggesting that a like species was present in each case. It had previously been shown (47) that thiophenol in solution in sulphuric acid was oxidized to thianthrene, and also to diphenyl disulphide (48). No satisfactory interpretation of the resonances was given, although it was suggested that the signal might be due to some of the solute being in an excited triplet state, in equilibrium with the normal singlet.

Wertz and Vivo (42) later showed that solutions in sulphuric acid of thiophenol and diphenyl disulphide gave paramagnetic resonances due to two separate species. One of these signals was a quintuplet apparently identical to that obtained from solutions of thianthrene in sulphuric acid.

The structure of the thianthrene free radical was investigated by Fava, Sogo and Calvin (49). These workers showed that a wide variety of aromatic sulphides dissolved in sulphuric acid to yield free radicals containing the thianthrene nucleus. From experiments using ultra-violet and visible spectroscopy, and solutions of thianthrene in trifluoroacetic acid as well as in concentrated sulphuric acid, they found that the free radical appeared to have a structure intermediate in oxidation between two oxides, possibly the mono- and di-sulphoxides. This hypothesis was tested by measurements of the relative intensities of the spin resonance absorbtion obtained at equilibrium from different proportions of mono- and di-sulphoxide mixed in solution. The results appeared to support their view that these two oxides were in equilibrium with each other and with the free radical. The structure suggested for the free radical was

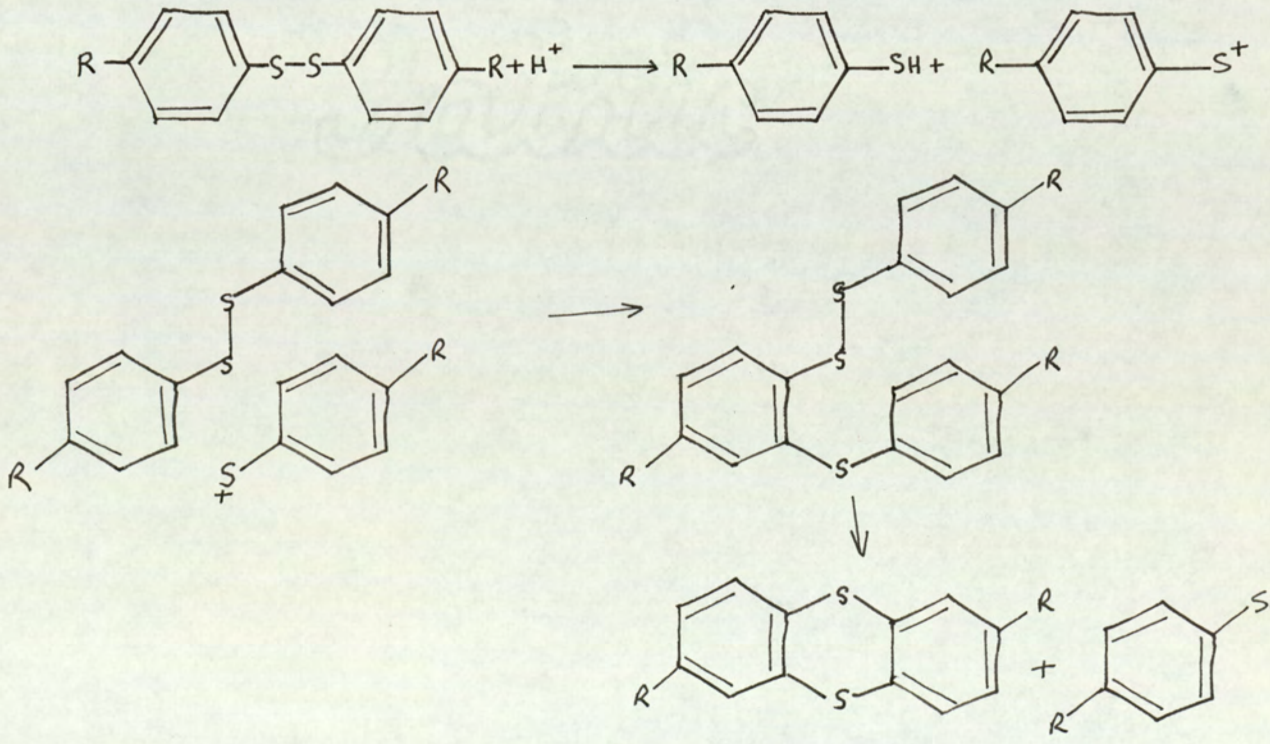


and a mechanism was suggested for the formation of this species. It was observed that free radicals were always formed from thianthrene when dissolved in trifluoracetic acid, which is a non-oxidising solvent, even when all the materials had been thoroughly out-gassed. The authors suggested that some oxygen was always present in thianthrene, possibly as a trans-annular peroxide, and that this would react to form a free radical.

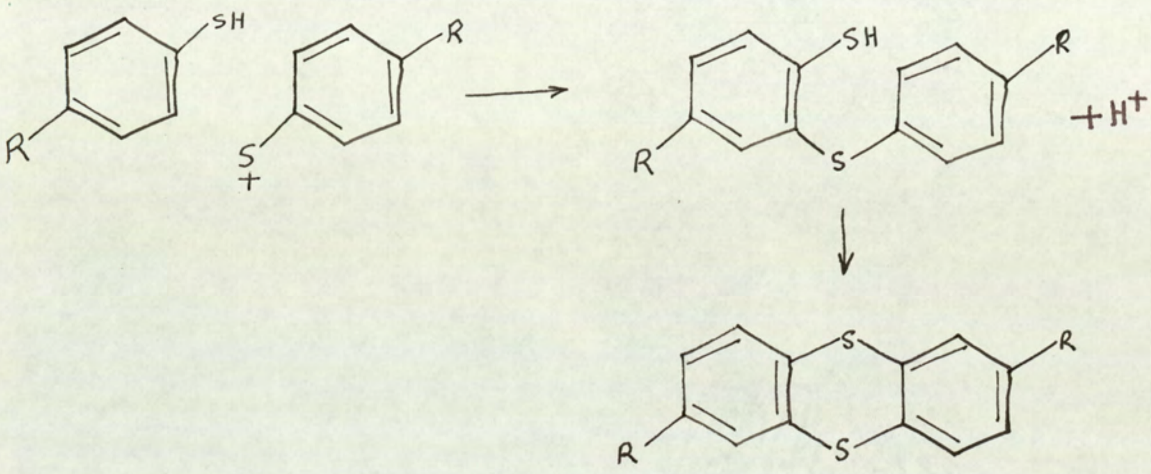
In the esr spectrum, these workers found that the main resonance absorption was a quintuplet of approximately 1 : 4 : 6 : 4 : 1 ratio of intensities. They assumed that this arose from interaction of the electron with four protons, although they thought these to be the 1,3,7,9-protons, which was later shown not to be so (52).

Two groups of five lines, with intensity ratios and splittings identical to the main resonance were found, one at 16 gauss lower field and the other at 16 gauss higher field than the magnetic field for the main resonance. These two resonances were only about 1/500 of the intensity of the main absorption. The authors explained these as a doublet arising from the free radical with the oxygen atom carrying a proton, the proton giving a doublet splitting. It is, however, more likely that these lines were due to splitting by naturally occurring sulphur-33, as found by Shine et al. much later (50).

A reaction sequence was suggested for the reaction of aromatic disulphides and sulphuric acid:-

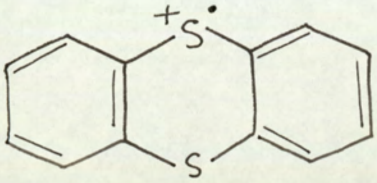


The electrophilic attack may also occur on the thiophenol, when the ring closure and oxidation are simultaneous:-

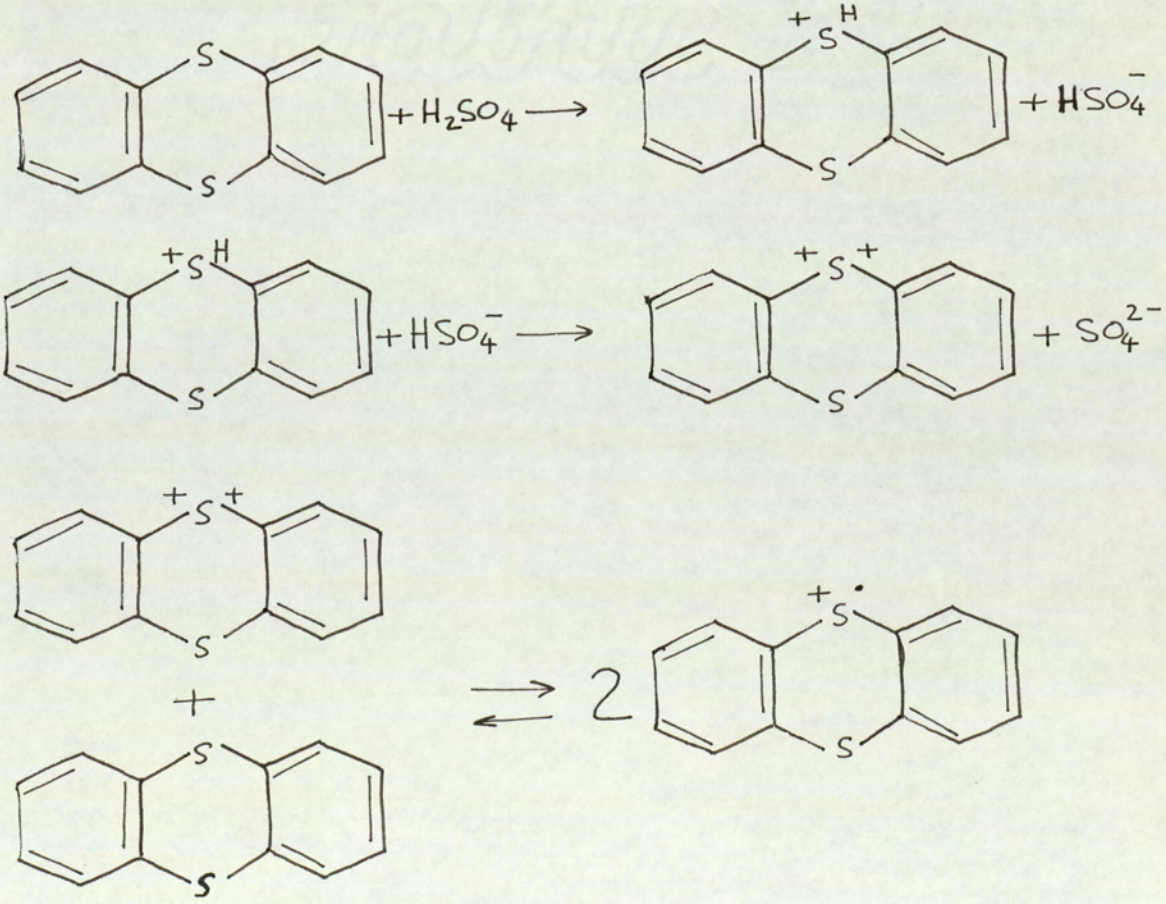


Japanese workers obtained free radicals by mixing certain organic sulphur compounds with another Lewis acid, antimony pentachloride (31, 51). Thianthrene was found to give a solid derivative having an esr spectrum of three broad lines. In solution, this compound had a five-line spectrum, similar to the one obtained from the sulphuric acid solutions.

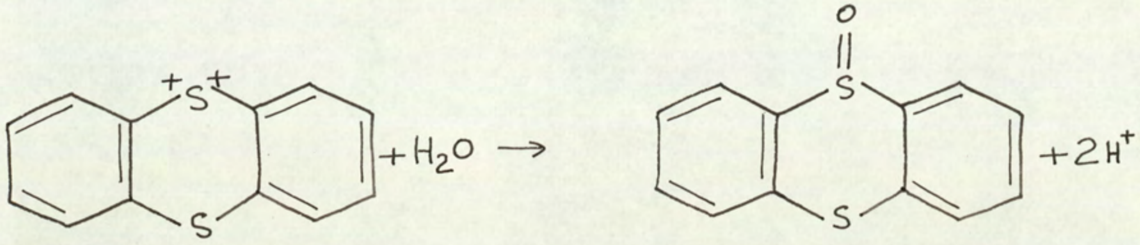
The nature of the free radical formed in sulphuric acid was further investigated by Shine and Piette (52). They examined solutions of thianthrene, the monoxide and cis-dioxide in 96%, 97%, 100%, and fuming sulphuric acid, and also used thianthrene in trifluoracetic acid. They did not agree with the structure of the radical suggested earlier by Fava, Sogo and Calvin (49), and put forward the view that the radical was the simple cation species

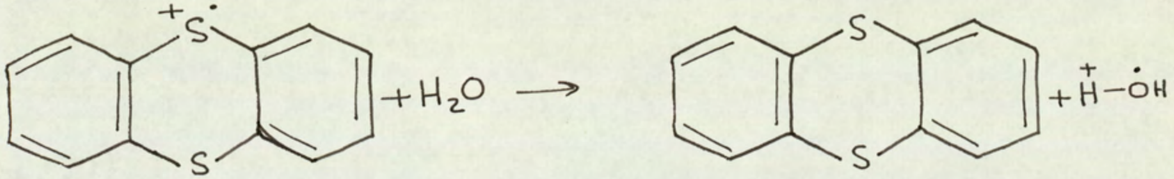


In view of the fact that SO_2 had been noted as evolving from a sulphuric acid solution, it was thought that oxidation occurred. The reaction sequence suggested was



On pouring this equilibrium mixture onto ice, the following reactions would occur:-





resulting in the formation of both thianthrene and its monoxide, in agreement with experiment.

The five line spectrum was explained by interaction with four equivalent protons, shown by substitution to be the 2,3,7,8- set, not the 1,3,7,9-protons previously suggested by Fava, Sogo and Calvin. The other protons were assumed to give a very small, non-resolvable splitting.

From the solutions of the monoxide in sulphuric acid poured onto ice, thianthrene, the monoxide, and another product, a "tan solid" were separated. From the esr signal obtained from sulphuric acid solution of the "tan solid" it was thought to be thianthrene carrying substituents in the 2- or 2,7-positions, but its identity was not determined.

That the protons causing the hfs in the thianthrene cation radical spectrum were the 2,3,7,8-protons was also shown by Rundel and Scheffler (53), who examined the esr spectra of several substituted thianthrenes in solution in concentrated sulphuric acid and also in nitro-methane/perchloric acid mixtures. The substituents were methyl and t-butyl groups. Splitting was resolved from the methyl group protons when the thianthrene was substituted in interacting positions. Methyl proton splitting was observed in these compounds by Shine, Dias and Small (54), who also observed that when two of the interacting protons were replaced by chlorine, the esr spectrum of the cation radical consisted of three lines arising from interaction by the two remaining protons.

The nature of the "tan solid" reported earlier (52) as resulting from the solution of thianthrene monoxide in sulphuric acid was investigated by Shine and Robinson (55). A hydroxythianthrene oxide was isolated from it, and reduced to 2-hydroxythianthrene.

This supported Shine and Piette's (52) suggestion that reduction of a protonated molecule of the monoxide occurs in a reaction involving the transfer-hydroxylation of another molecule of thianthrene oxide.

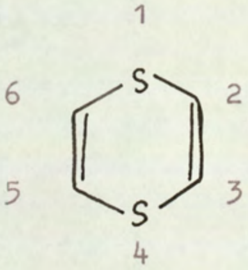
However, Shine and Thompson (56) have since shown by experiments in which the acid solution of thianthrene monoxide was poured onto oxygen-18 enriched ice, prior to isolation of the "tan solid", with subsequent mass spectrometric analysis of the products, that the species thought to be the protonated oxide is actually the doubly protonated thianthrene di-cation.

A large number of substituted thianthrenes were examined in sulphuric acid solution (57) to enable the structure suggested earlier (52) for the cation radical to be tested. The results were all consistent with this structure, arising from a one-electron oxidation of the thianthrene. All the g-values were close to 2.008 - 2.009, except that for the free radical derived from 2,7-dibromothianthrene (g = 2.0101). The small splittings observed (4 to 13 gauss) suggested that the odd electron had a high density on the sulphur atom. This, coupled with the high g-values indicated that spin-orbit coupling was occurring. The spin orbit coupling of bromine probably accounts for the even higher g-value for the dibromo-compound. It was thought that spin-orbit coupling was also responsible for the large hyperfine line widths, compared to those of, say, anthracene in sulphuric acid.

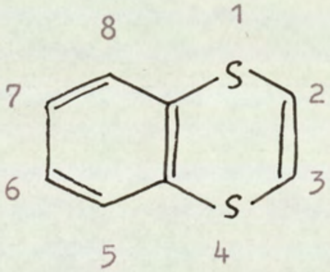
These workers also reported the formation by the anodic oxidation of thianthrene of the same radical species as is present in sulphuric acid solutions of this compound. The half-wave height was found consistent with a one-electron oxidation process, and so this also supports the suggested cation radical structure.

Recently, Shine and Sullivan (50), using the Lewis acid aluminium trichloride in nitromethane, obtained an esr spectrum of the thianthrene cation with much greater resolution, showing hfs from all the protons in the molecule, and also showing splitting resulting from the interaction of the electron with the magnetic nucleus of sulphur-33, occurring in natural abundance.

Lucken (39) prepared and examined the cation radicals of 1,4-dithiin, 1,4-benzodithiin, and thianthrene.



1,4-dithiin



1,4-benzodithiin

He calculated the spin densities both assuming the use of d-orbitals by sulphur and for the case where d-orbitals are not used, and found a better fit with the experimental results for the case using the 3d-orbitals. However, the non-planarity of the radicals might, he suggested, mean that the improvement obtained by including the d-orbitals in the calculations, be partly due to interaction of carbon $2p_z$ orbitals with the antibonding C-S sigma orbitals. He also reported obtaining the same free radicals in nitromethane with antimony pentachloride.

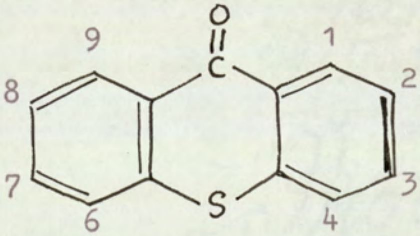
The anions of thianthrene and derivatives have also received attention. The anions of thianthrene-5,10-tetroxide and 2,7-dimethylthianthrene-5,10-tetroxide, formed by reduction of the parent compounds with potassium, were first reported by Kaiser and Eargle (58), but further discussion of this paper is deferred until the section dealing with thiaxanthone (page 26).

Gerdil and Lucken (59) also prepared anion radicals of some sulphur compounds by potassium reduction. They obtained free radicals from dibenzothiophene and diphenyl sulphone. Theoretical calculations for dibenzothiophene gave splitting constants lower than those observed experimentally. When thianthrene was reduced with potassium in dimethoxyethane, the spectrum of the radical anion of dibenzothiophene was observed, thought to arise by elimination of sulphur from the thianthrene.

The radical anions of cis- and trans-thianthrene-5,10-dioxide were found to give different esr spectra (60), showing that the geometrical isomerism is retained in the free radical form. The cis-dioxide spectrum was found to resemble that of the 5,10-tetroxide reported earlier (58), in width and number of lines. The spectrum of the trans-compound, however, was wider and consisted of more lines. This shows that less delocalisation of the odd electron occurs in the trans-compound, indicating that the extent and nature of the delocalization of the odd electron by the sulphur-groups is highly dependent on the stereo-chemistry of the S-O linkage in these compounds.

This aspect was the subject of another paper by these authors (61) in which the spectra of the anion radicals of thianthrene-5-oxide, the trans-5,10-dioxide, cis-5,10-dioxide, -5-dioxide, -5,10-trioxide, and -5,10-tetroxide were described. It was found that the spectra were influenced by the orientation of the S-O bonds. As the oxidation state of the sulphur group increased, a narrowing of the total spectral width was observed. When one sulphone group was present, the effect was found to have reached its maximum.

2.1.2. Thioxanthone and derivatives



Thioxanthone

Using esr, Vincow showed that the blue compound, observed as an intermediate in the thioxanthone-S,S-dioxide, thioxanthenol-S,S-dioxide oxidation-reduction system was a free radical (40). A well resolved spectrum was obtained from thioxanthenol-S,S-dioxide on air oxidation, and also from solutions of thioxanthone-S,S-dioxide reduced with sodium dithionite. The spectra were found to be identical. The spectrum was interpreted as arising from four groups of two equivalent protons. The g-values and splittings were reported to a high order of accuracy. Theoretical calculations were carried out using Moffit's (62) treatment of the conjugation of the π-type sulphone orbitals on the aromatic π system, but good agreement with experiment was not obtained using the simpler methods. However, McLachlan SCF calculations gave good agreement with experiment, and predicted negative spin densities at the 2 and 4 positions. The slight differences found in these negative spin densities were interpreted as indicating that the conjugation is of the charge-transfer type, where conjugation is with an unfilled 3d sulphur orbital.

Kaiser and Eargle's (58) work on the thioxanthone compounds also gave information of the conjugative properties of sulphur groups. They used thioxanthone, thioxanthone-5-dioxide, thianthrene-5,10-tetroxide, and 2,7-dimethylthianthrene-5,10-tetroxide. The radicals were produced by alkali metal reduction.

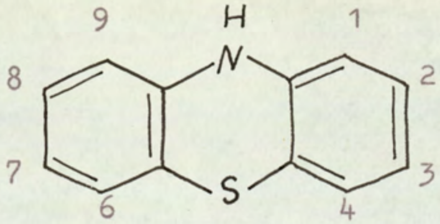
Thioxanthone anion radical was found to give an esr spectrum 17.3 gauss wide, with five major lines each further split into 18. Thioxanthone-5-dioxide under the same conditions gave a narrower spectrum with a markedly different splitting pattern, the narrowing being attributed to a lower spin density in the aromatic system. The tetroxide of thianthrene gave an esr spectrum only 8.9 gauss wide, showing a further reduction in the electron density in the aromatic rings. The spectrum was a quintuplet, the splitting arising from the 2,3,7,8-protons, as shown by the nine line signal obtained from the dimethyl compound. Thus, sulphonyl groups conjugate with the aromatic system to delocalise the odd electron, and are more effective in this than sulphide groups.

A further paper from this group (63) reported the esr spectra of the thioxanthone anion radical, the 2-methyl-, 2,4-dimethyl-, and 1,4-dimethyl- derivatives, the thioxanthone sulphone anion radical, and the 2-methyl-, 2,7-dimethyl-, 2,4-dimethyl-, and 1,4-dimethyl- derivatives of this. The reductions were carried out both by alkali metal in dimethoxyethane and also by basic ethanol, using sucrose or sodium dithionite if necessary. Splitting constants and g-values were reported. The spectrum obtained for thioxanthone sulphone anion radical was different to that reported earlier by Kaiser and Eargle (58). The earlier spectrum was attributed to an impurity present in the sulphone.

Other sulphones, which were reported by Kaiser et al. are best included here. Eargle and Kaiser (64) investigated the anion radicals produced from dibenzothiophen, its sulphoxide, and sulphone, by potassium reduction. They again found a narrowing of the spectrum with increase in oxidation state, indicating an increase of conjugation, as with the thioxanthone/thianthrene compounds.

Kaiser, Urberg, and Eargle (65) obtained esr spectra from diphenyl sulphone and _p,p_'-ditolyl sulphone by treatment with potassium metal in dimethoxyethane at 203K. The spectra were found to be very similar to those from the corresponding hydrocarbons, biphenyl and p,p'-bitolyl, with complex hfs. Results of Huckel M.O. calculations indicated that little spin density would be expected to be withdrawn from the aromatic rings to the sulphone groups by conjugation.

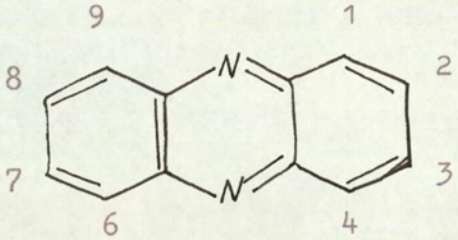
2.1.3 Phenothiazine and derivatives



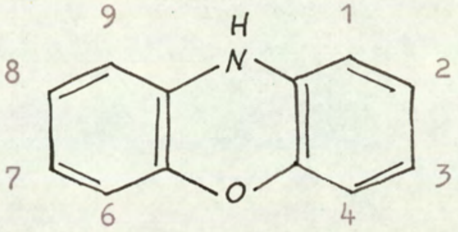
Phenothiazine

Free radicals derived from phenothiazine and related compounds are interesting mainly because of the wealth of detail in the hyperfine structure. Some substituted phenothiazines have found uses as drugs.

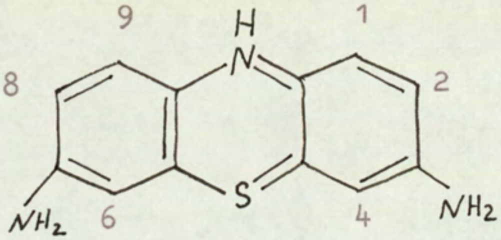
Billon, Cauquis, Combrisson and Li (66) reported the formation of a free radical by the electrochemical oxidation of phenothiazine solutions. They found a spectrum consisting of four lines. A similar spectrum was later obtained by Tuck and Schieser (67) from solutions of phenothiazine in either concentrated sulphuric acid or acidified ethanol. Phenazine, phenoxazine, thionine, and methylene blue also gave esr spectra under these conditions.



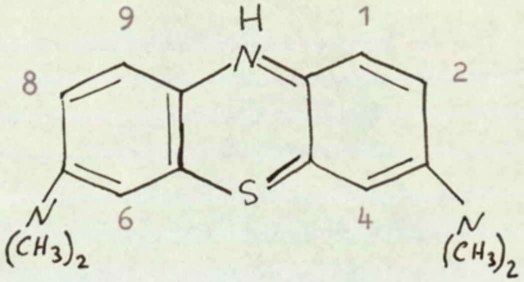
Phenazine



Phenoxazine



Thionine



Methylene Blue

More splitting was then resolved (68) in both electrolytically oxidized samples and also in sulphuric acid solutions. Equivalent splitting was found due to the nitrogen and the hydrogen bonded to the nitrogen, giving the four lines, and also due to the other protons in the molecule, giving further splittings of this basic quartet.

An electron resonance has also been reported (69) from the complex of phenothiazine with iodine, due to strong electron transfer. The spectrum was a single line, the g-value similar to an organic positive ion, as spin-orbit coupling in the iodine negative ion broadens the resonance of this species out of detection.

Negative ion radicals have been prepared by the action of a sodium mirror on phenothiazine and similar compounds in p-dioxan at room temperature (70). Complex hfs was obtained, with a very narrow line width (0.07 gauss).

The electrochemical generation of free radical ions from phenothiazine and its derivatives was further investigated, and it was shown (71) that hfs was observed unless phenothiazine was present in excess, when a single line 5 gauss wide was obtained, due to electron-exchange between the radical ion and the neutral molecule. The spectrum obtained under good conditions had four lines each split into many others.

The spectrum of the free radical ion from N-methylphenothiazine was seen to have six lines under low resolution. Under conditions of greater resolution, evidence for further splitting was found, although this was not completely resolved.

2-methyl-, 3-methyl-, 2,7-dimethyl-, and 2,7,10-trimethylphenothiazines and 2-phenothiazone were oxidized electrochemically to give esr spectra showing hfs.

The spectra expected for the radical cations of phenothiazine and

N-methylphenothiazine were simulated (72) using a computer from spin densities, etc., calculated from molecular orbital theory, and compared with the experimentally observed spectra obtained using electrochemical techniques.

More recently, Norman (43) has obtained the cation radical and neutral radical from phenothiazine. The cation radical was prepared as the perchlorate salt, from phenothiazine, phenothiazine-5-oxide, and perchloric acid. The esr spectrum of this species in acetonitrile solution was recorded, and a complete assignment of the splittings was made.

The neutral species was obtained by the reaction of the cation radical with water buffered at pH 7 and with triethylamine and also deuterium oxide. 3,7-Dimethylphenothiazine showed the same behaviour, although N-methylphenothiazine did not.

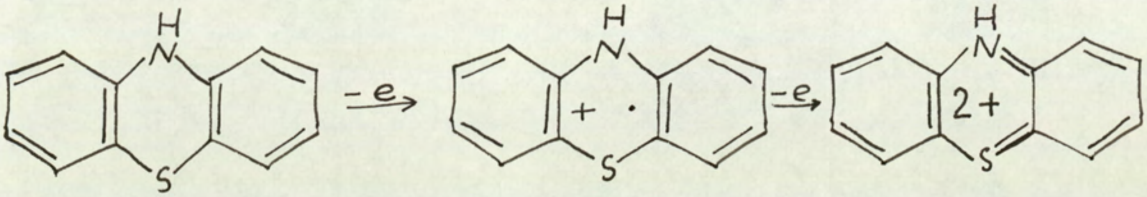
Molecular orbital calculations were made, and fair agreement obtained with the experimentally determined splitting constants, although simultaneous agreement was not found for the 1,9- and 3,7- coupling constants.

The effect of halogen substituents in the phenothiazine molecule on the esr spectrum has been investigated (73). An increase in g-value with degree of substitution was found, the g-value of octachlorophenothiazine free radical being 2.006 compared to the value for unsubstituted phenothiazine of 2.0035. This increase was attributed to a spin-orbit coupling contribution from the halogen. This effect was found to be greater for halogen atoms substituted in the positions for which the calculations of Odiot and Tonnard (72) predicted a high spin density.

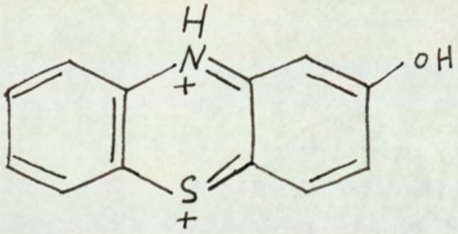
The effect of substituents on oxidation and the stability of the free radicals formed from phenothiazine has been studied by Tozer and Tuck (74). They determined the rate of decay of free radical species in aqueous acetic acid by both esr and visible absorption spectroscopy.

The process was found to be second order, with a rate constant inversely proportional to the acid concentration. The free radical decayed by a rapid one-electron disproportionation by oxidation and reduction. The oxidation product was unstable, and decayed by two processes, either hydrolysis to the sulphoxide, this process being reversible to the addition of acid, or by a two-electron disproportionation to 3-hydroxyphenothiazine. If the parent is substituted on the nitrogen, then the 3-hydroxy-substitution was found to be highly inhibited. The decay rates of 3-substituted compounds were found to obey a Hammett relationship using para-substitution constants, 2,10-substituted compounds were found to require meta-substitution constants to obtain agreement.

A comparative study of free radicals produced from phenothiazine, phenothiazine-5-oxide, and 3-phenothiazone in acid solutions has been carried out (75). Solutions of phenothiazine in 96% sulphuric acid were found to contain cation radicals of the species, which slowly formed protonated phenazothionium ion radicals by further oxidation.

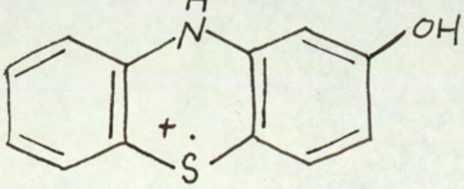


Solutions of the 5-oxide also contained this stable species. Solutions of the ketone were stable, and contained protonated hydroxyphenazothionium ion radicals.



hydroxyphenazothionium ion
(protonated)

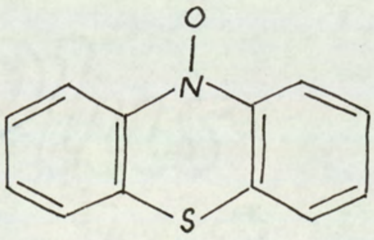
In 59% sulphuric acid, the ketone yielded the hydroxyphenothiazine cation radical.



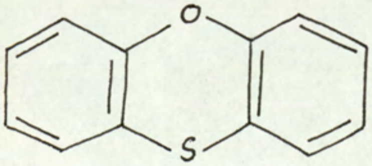
hydroxyphenothiazine cation radical

Some nitrogen-substituted derivatives of phenothiazine of pharmacological interest have been investigated in acid solutions. Schieser and Tuck (76) found that they could not resolve hyperfine structure from the compounds they used, and also that the g-values were all close to that of the free radical derived from phenothiazine itself. Piette and Forrest (77) found complicated hfs in acid solutions of some of these same compounds, and also in other pharmacological phenothiazine derivatives. The hfs is characterised by a basic triplet, differing from the 1 : 2 : 2 : 1 quadruplet observed when the nitrogen carried a proton, which gave a splitting equal to that of the nitrogen (see page 30).

Free radicals have been formed from phenothiazine N-oxide (78), showing splitting from the protons and the nitrogen atom.



2.1.4. Phenoxathiin and derivatives

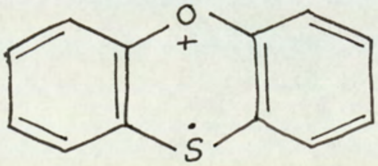


The positive ion radical of phenoxathiin was reported (79) to give an esr spectrum of 31 equally spaced lines, due to interaction of the odd electron with the four sets of protons.

The cation radical was produced by the dissolution in sulphuric acid (96%) of either phenoxathiin or its sulphoxide (80).

The spectrum of the phenoxathiin cation radical has also been published by other workers (81), when it was compared to that derived from thianthrene and dibenzo-p-dioxin.

Free radicals formed by dissolving phenoxathiin sulphoxides in concentrated sulphuric acid gave spectra which on analysis showed that the radicals were based on sulphur (g-factors and line width) (82). A structure was suggested similar to that suggested for the thianthrene cation radical (see page 19 et seq.).

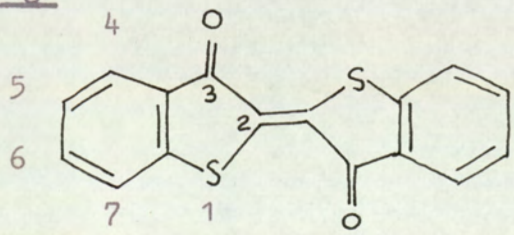


On oxidation of phenoxathiin with stannic chloride and halogen, these workers found that the stable hexachlorostannates of the radical ions were precipitated.

The reactions of phenoxathiin and its sulphoxide with concentrated sulphuric acid have since been investigated in more detail (83). The sulphoxide has been shown to be converted to the cation radical of phenoxathiin in concentrated sulphuric acid. A second free radical is also formed in some acid concentrations, that of 3-hydroxyphenoxathiin. It was suggested by these authors that in the acid solution, the sulphoxide is in equilibrium with protonated sulphoxide and the phenoxathiin dication. The formation of the cation radical occurs by loss of hydroxyl from this protonated species, the hydroxyl being "stored" as hydrogen peroxide or as a peroxysulphuric acid. The reactions leading to the free radical of 3-hydroxyphenoxathiin include a hydroxylation of the aromatic ring by attack of water on either the cation of the protonated sulphoxide or the phenoxathiin dication.

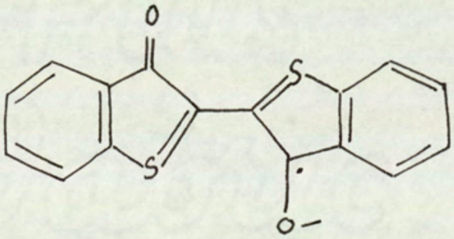
2.1.5. Miscellaneous

Thioindigo

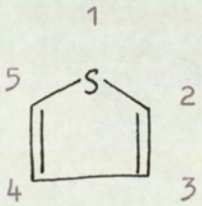


Free radicals were produced from this compound in alkaline ethanol and alkaline acetone (84). The complex spectrum obtained was interpreted as arising from the four pairs of equivalent protons found in this molecule. Differences were found in the splitting constants for the two solvents used, of the order of 29 milligauss (7,7' protons) to 110 milligauss (4,4' protons). The lines in ethanol solution were twice as broad as those in acetone and this was attributed to the difference in viscosity of these two solvents. The differences in the splitting constants were thought to be due to the difference in electric dipole interactions of the ion with the molecules of the two liquids.

The radical was thought to be of the negative ion type,



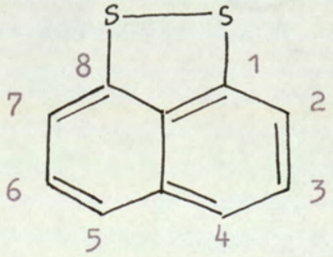
Thiophene



The first free radical species containing the thiophene ring reported was that of thiophene-2-carboxylic acid, prepared by gamma-irradiation (85). Several radical species were observed, some of which were found to disappear on heating to 363K for 40 minutes, leaving one due to the addition of hydrogen to the carbon at position 5. The ring was found to be non-planar, as the coupling constants for the two protons on this carbon atom were different.

Radical anions of 2,2'-dithienyl and 2-phenylthiophene were produced by potassium reduction in oxygen-free dimethoxyethane at 193K (86). The well resolved esr spectrum of the dithienyl was interpreted as arising from two very similar species, present in the ratio of 1 : 4. They were thought to be rotamers of the radical anion, with the two sulphur atoms in a cis- or trans- position, for a sufficient time for each rotamer to give an individual spectrum. In phenylthiophene, the molecule was thought to be locked in a rigid conformation, and different hfs constants were found for the two o-protons and also for the two m-protons.

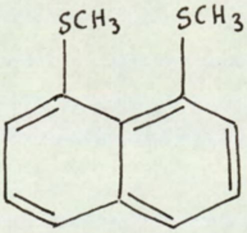
Naphthalene-1,8-disulphide



Free radical species have been produced from this compound by a variety of methods (87). Electrochemical oxidation or solution in sulphuric acid yielded a radical with a signal, of g value 2.0081, interpreted as arising from three pairs of equivalent protons. Reduction with sodium metal in dimethoxyethane gave a spectrum consisting of a single line at g = 2.0110, while electrochemical reduction gave a partially resolved triplet.

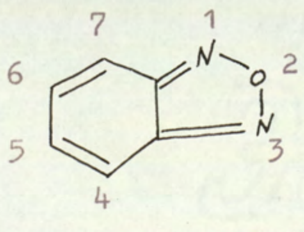
Molecular orbital calculations were carried out by these authors and gave partial agreement with experiment.

Solutions of 1,8-bis(methylthio)naphthalene in sulphuric acid gave, after standing for a few minutes, a spectrum similar to that obtained from the disulphide.

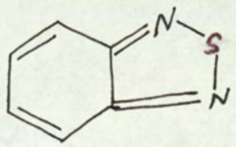


Benzothiadiazole

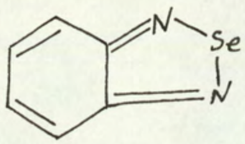
Free radicals have been produced from 2,1,3-benzoxadiazole, 2,1,3-benzothiadiazole, and 2,1,3-benzoselenodiazole by Strom and Russell (88).



2,1,3-benzoxadiazole



2,1,3-benzothiadiazole



2,1,3-benzoselenodiazole

They used an electron-transfer technique, from anions of propiophenone or 9,10-dihydroanthracene in dimethyl sulphoxide and tertiary butanol mixtures containing potassium butoxide.

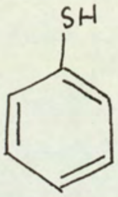
A complex spectrum was obtained from the sulphur compound, consisting of 33 lines. Splitting was observed from both nitrogen atoms, which were found to be equivalent, and from two pairs of equivalent protons. Huckel molecular orbital calculations were performed, giving good agreement with experiment. The p-orbital model was found to be as good as the model using d-orbitals.

On the basis of hfs constants, it appeared that sulphur and selenium in these heterocycles accepted the unpaired electron more readily than did oxygen. From electronegativity considerations, oxygen should be electron-withdrawing relative to carbon, while sulphur and selenium should supply electrons. In conjugated systems, the inductive effect is supplemented by resonance interaction involving the unshared p-electrons of the hetero-atom. If the p-orbital model is used, the lower electron density calculated for sulphur and selenium compared to oxygen could give rise to the greater attraction. However, the d-orbital model of the sulphur atom gives a higher electron density on the sulphur atom than on oxygen, in the parents, and an even higher value for the free radical anion. The authors felt that this behaviour seemed more consistent with the inductive effect associated with mercapto- and alkoxy- substituents in the benzoic acids than the effect predicted using the p-orbital model.

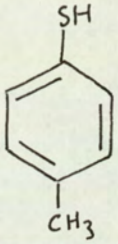
2.2. Compounds with Sulphur Attached to an Aromatic System

Thiophenol and Related Compounds

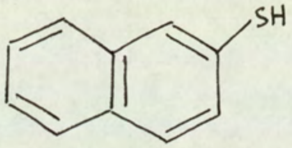
As noted in section 2.1.1. on thianthrene, these compounds were amongst the first to be studied by esr spectroscopy (46). Thiophenol, thiocresol, and thio-β-naphthol were found to form paramagnetic species when in solution in sulphuric acid.



thiophenol



p-thiocresol



thio-β-naphthol

Later (42), thiophenol was observed to give a spectrum resulting from two radical species, one part of this spectrum being identical to that given by thianthrene under the same conditions. It was noted that thiophenol is oxidized to thianthrene by sulphuric acid. This was the first time two radical species in the same solution had been resolved.

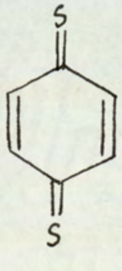
Results have been reported (89) from the oxidation of *p*-methylphenyl sulphide, sulphoxide and sulphone, and other substituted aromatic and alkyl-aromatic sulphones and sulphonic acids with potassium persulphate/concentrated sulphuric acid mixtures. It was concluded that if the sulphinium ions formed by sulphuric acid oxidation of these compounds were formed in the persulphate oxidation, they were very short lived and in low yield. The spectra observed were thought due to more extensively oxidized molecules. The same free radicals were obtained from sulphoxides, sulphones, and sulphonic acids in persulphate/sulphuric acid. Sulphones and sulphinic acids are not normally attacked by sulphuric acid alone. The g values measured were low (2.0035 to 2.0037) compared to those found for aromatic sulphinium ions, in the range 2.007 - 2.01, indicating that these were different species. These workers considered that the species with low g values were hydroxylated molecules, the persulphate in sulphuric acid being such a powerful electrophile that it even hydroxylates sulphones and sulphonic acids (via the sulphate-ester groups). As the range of g values indicated that very little unpaired electron density was present on the sulphur atom, dehydroxylation was thought to have occurred in only one ring of the diaryl substrates, the unpaired electron being confined to that ring.

Japanese workers (90) investigated the variation of the intensity of the signal from thiophenol in sulphuric acid with temperature from liquid nitrogen temperature to room temperature. They found that the intensity decreased with decreasing temperature, in contrast to the signal from DPPH, which increased. On this evidence they considered that the paramagnetic species from thiophenol was in a triplet state.

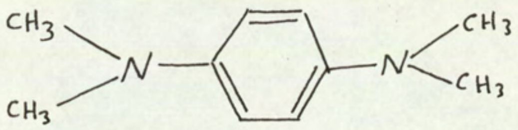
Complexes of this type of compound with various Lewis acids have been found to be paramagnetic (31). The signals consisted of broad lines, some showing hfs, and having high g-values, indicative of sulphur compounds.

Free radicals have been formed from diphenyl disulphides and β,β-dinaphthyl disulphide by pyrolysis in the vapour state, with subsequent condensation of the products on a cold trap (91). The free radicals formed were thought to be the aryl sulphenyl radicals, showing a large g-value anisotropy. This anisotropy was accounted for by spin-orbit coupling, mixing two states of different orbital angular momentum. The spin densities in one of the states were calculated using McLachlan's method. The energy differences of the two states were estimated using M.O. approximation, the results indicating that in the free radical ground state, the unpaired electron is localized in a non-bonding sulphur orbital.

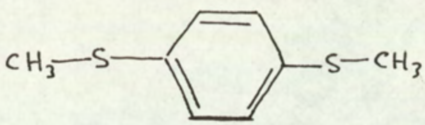
Thioquinone



The compound N,N,N',N'-tetramethyl-p-phenylenediamine, or Wurster's salt, has long been known to form a stable free radical species on oxidation. The sulphur analogue, dithiohydroquinone dimethylether, was shown to undergo one electron oxidation also (92).



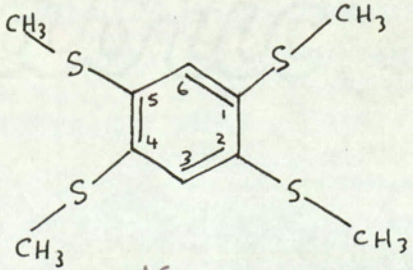
N,N,N',N'-p-phenylenediamine



dithiohydroquinone dimethylether

The deep blue solution of this compound in concentrated sulphuric acid was found to give strong esr signals. The main resonance was one of seven groups of lines from the six methyl protons. On isolating the products from sulphuric acid solutions poured onto ice, the monosulphoxide was found. This gave the same esr signal in sulphuric acid. The spectrum was also obtained on electrochemical oxidation. Each of the seven lines was further split by an even number of protons, thought to be the four ring protons, although resolution was not sufficiently good for unequivocal assignment. The authors suggested that the lack of resolution might be due to the presence of two rotational isomers of the cation radical, resulting in different coupling constants for the ring protons.

This group have also reported the formation of free radicals from 1,2,4,5-tetra(methylthio)benzene (93).



The methods used were electrochemical oxidation in acetonitrile, which gave an esr spectrum with hfs due to interaction of the odd electron with the 12 methyl protons, and solution in H_2SO_4, which yielded a free radical with a strongly asymmetric resonance line having hfs consisting of an odd number of triplets. A solid paramagnetic product was formed with antimony pentachloride, having an anisotropic g value.

HMO and McLachlan SCF calculations were carried out, giving similar results, with no (HMO), or small, negative (SCF), spin density on the 3,6 positions, and equal spin density on the other ring positions and the sulphur atoms. From the splitting constants, $A_H = 0.71$ gauss, and $A_{SCH_3} = 2.57$ gauss, the authors calculated the unpaired electron density on each sulphur atom to be 0.125.

Semiquinones

Although sulphur is not the radical centre in these compounds, they have been included because of the importance of the sulphur atom in their structures.

Aryl- and benzyl-thiosemiquinone free radical species were reported by Lucken (94). These were prepared either by reducing the quinones to the quinols with stannous chloride in acidic alcohol, followed by air oxidation in alkali of the quinol, or by direct action of sodium ethoxide on the quinone in alcohol. These methods were reported to yield identical spectra, although the solutions derived from the quinol were found to be more stable.

Analysis of the spectra and measurement of hyperfine splitting constants indicated that both aryl- and alkyl-thio groups were electron-releasing, in agreement with other physical methods, (Hammett sigma constants, dipole moments, etc.). However, chemical evidence has been interpreted to indicate that these groups are electron-accepting when attached to an aromatic ring. Conclusions based on chemical evidence are open to the objection that in comparing two reactions which are essentially similar, the substituent may alter the energy and entropy of activation in different and not understood ways. Physical methods involve assumptions about the ground and excited states of the molecule, or about the resolution of the dipole into arbitrary directions, etc. The esr spectrum of a free radical, however, gives a method of determining the electron distribution in molecular ground states, and should therefore give evidence upon which more reliance can be placed.

Because of the electron-releasing nature of these groups, the author concluded that it was unlikely that the d-orbitals of the sulphur atom were involved.

Aryl Sulphinic Acids

ArSO.OH

Aryl sulphinic acids have been oxidised to the free radical species $ArSO_2^\bullet$ by ceric ions in a flow system (95). This technique, which has been widely used for other organic compounds, has found little use in the field of sulphur compounds. It involves the mixing of two solutions in, or just before reaching, the sample cavity of the spectrometer. The two solutions react to give a free radical species of short life with a "stationary concentration" great enough to permit their observation. Benzene sulphinic acid was found to give a triplet. Comparison with the spectra of various substituted derivatives showed that the major splitting was by the two ortho protons. Further smaller splittings were found, attributed to the meta and para protons.

Toluene sulphinic acid gave a spectrum of 6 lines, of relative intensities 1 : 5 : 10 : 10 : 5 : 1, due to equivalent splitting by the three methyl and two ortho ring protons.

By comparison with hfs constants for phenoxy and benzyl free radicals, in which the unpaired electron is oriented to hybridise completely with the aromatic pi electron system, and the phenyl radical where the odd electron replaces a sigma C-H bond in the plane of the ring, the authors considered that arylsulphonyl radicals had characteristics of both sigma and pi type radicals. They also found that the $ArSO_2^\bullet$ radicals had more sigma character than the $(ArNO_2^\bullet)^-$ anion radicals. They noted that the radical anion $(SO_3^{\bullet})^-$ is pyramidal, and that calculations of electron density on this species indicated that 62% of the electron spin is associated with the sulphur atom, 13% of the total in its 3s- orbital and 49% in its 3p- orbitals. If $ArSO_2^{\bullet}$ is also assumed to be pyramidal, with respect to the sulphur atom, the spin density in the 3s- orbital of sulphur would give the whole radical a significant degree of sigma character, with respect to the aromatic ring.

2.3. Aliphatic Compounds Containing Sulphur

Compounds which fall into this group and give free radicals which have been studied by electron spin resonance techniques are almost completely confined to disulphides, monosulphides, and thiols.

The method of producing free radicals from these compounds has been to irradiate them with ultra violet radiation, gamma radiation, or charged particles.

This class of compounds fall into two groups:-

A) Simple aliphatic compounds
B) "Biologically interesting" compounds

The simple aliphatic compounds will be discussed first, even though work on these was not published until some considerable time after the first results on the biologically interesting compounds became available. The alkyl compounds are a much simpler system and results gained from their study aids in the interpretation of the spectra of the biologically interesting compounds.

2.3.1. Simple Aliphatic Compounds

The first reported esr results (96) on these compounds involved the gamma-irradiation of dialkyl disulphides at 77K, with spectra recorded from the resulting free radicals held at 103K. Two sample preparation techniques were used, one being to rapidly freeze the material by dropping it directly into liquid nitrogen - referred to as "Ball-Form" material, the other technique was to slowly grow small crystals of the compound and then grind these to a powder (this ensured a random orientation). The two methods were shown to yield material having different crystal structures.

Free radicals present after irradiation of the "Ball-Form" material showed no hyperfine splitting. Dimethyl disulphide gave a signal having a g value of 2.016 and a line width of 33.6 gauss at X-band. This was field dependent. Octyl and octadecyl disulphides gave spectra having an additional resonance at high field (i.e. low g value). This part of the spectrum, about 30% of the total signal, showed hyperfine splittings, which were independent of magnetic field.

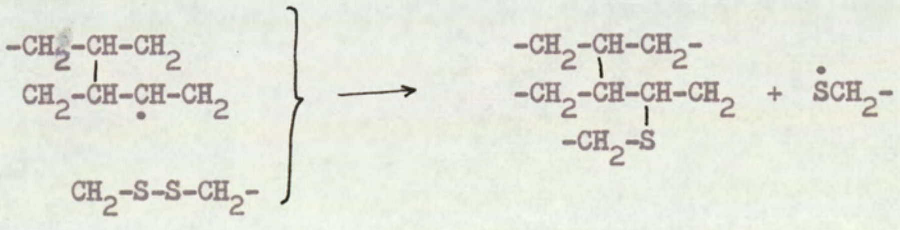
In the slowly crystallized form, compounds from amyl through octadecyl disulphide formed more radicals by C - H breakage than sulphur radicals. Propyl disulphide in this form gave a signal, of which about 10% arose from species formed by C - H fission.

These results are interpreted as being due to energy migration down the carbon chain (as suggested by Gordy, (97), and see section 2.3.2), in the case of the "Ball-Form" samples. This results in localization of energy on the sulphur bond. Some C - H breakage occurs before localization for octadecyl disulphide. For the slowly crystallized material, significant breakage of the C - H bonds occurs for compounds with 5 or more carbon atoms in the alkyl groups. Thus the crystallographic configuration as well as chain length influences the ability of the energy to be localized at the disulphide bond.

Truby has investigated free radicals from n-octadecyl disulphide, n-octadecanethiol (98) and n-amyl disulphide (99). These compounds were gamma-irradiated and examined at 77K, under vacuum (10^{-6}torr).

n-Octadecyl disulphide yielded free radicals having an esr spectrum with a symmetric curve close to the free spin g value and showing hfs, and also a resonance at higher g value which was found to be field dependent. This was interpreted as being due to two separate species, the low g signal arising from a radical formed by cleavage of a C - H bond, which was found to decay when the sample was allowed to warm to room temperature. The high g value signal, which did not decay when warmed to room temperature, was attributed to a "Sulphur radical". This part of the spectrum was shown to be 15% of the total signal intensity.

The decay of the carbon radical was found to occur by two processes. Most of the carbon radicals were found to decay in 2 minutes at 270K. This rapid decay was thought mainly to involve the reaction of free methylene radicals. The remaining alkyl free radicals, 30% of the total initial radical concentration, were more stable and only decayed to half the initial concentration in 12 hours at 270K. These were assumed to be $R\dot{C}H_2$, alkyl type radicals, or crosslinked radicals formed by interaction of a migrating methylene with a double bond also formed as a result of the irradiation. The decay of this more stable species coincided with an increase in the number of sulphur radicals, which appeared to be stable. The total concentration of radical species remained constant after the initial decay of unstable alkyl radicals. From kinetics, a value of 54.3kJ mol^{-1} was found for the formation of $RS^\bullet$, the "sulphur radicals". This is the same as the energy for decay of the more stable alkyl radicals. This leads to the suggestion that the more stable alkyl radical could be a precursor for the sulphur radical, and a mechanism was suggested for this which would be diffusion controlled, involving a crosslinked molecule.



The activation energy was found to be of the right order. This behaviour is different from that of amorphous octadecyl disulphide, where localization of the unpaired electron on sulphur was thought to be due to excitation or electron-hole migration.

After being irradiated at 77K and allowed to warm to 248K, octadecanethiol was found to give an esr signal identical to the high g-value part of the signal obtained from octadecyl disulphide.

Amyl disulphide was gamma-irradiated in vacuum at 77K both in the amorphous state and also in a tetrahydrofuran matrix. In the amorphous state, some hfs was present in the high field (low-g) side of the curve, due to bond breaking in the alkyl group. Another absorption was present at low field, but the largest part, about 70% of the absorption, was due to a third radical. This part of the curve had a dependence of width on field (33.5 gauss at X-band, 70.4 gauss at Q-band) a g value at the cross-over point of 2.018 ± 0.001, and was found to be optically bleached (i.e. the signal decayed on exposure to light) with 300 - 500 nm wavelength radiation. No hfs was found, the other signals were not altered by the decay of the light-sensitive one, and a green colour appeared to be associated with this species. Experiments with thermal ageing showed this species to be ionic rather than neutral, with a threshold energy for bleaching of $(3.36 \pm 0.32) \times 10^{-19}$J.

The compound was studied in a tetrahydrofuran matrix, known to be electron solvating, in order to investigate negative-ion species. Two esr signals were found, the one at high field being symmetrical and showing field-independent hfs, and thought to be due mainly to the solvent. The low field signal had a field-dependent line-width with no hfs, and was removed by optical bleaching, with a threshold energy of $(3.36 \pm 0.32) \times 10^{-19}$J. The signal was axially symmetric, with g tensors of $g_{\parallel} = 2.003$, $g_{\perp} = 2.022$.

The experiment was repeated in methyl tetrahydrofuran with no change in line-width or g values.

From optical absorption studies on mixtures of biphenyl and amyl disulphide in methyl tetrahydrofuran, it was shown that amyl disulphide captures electrons, indicating that the light sensitive species was the negative-ion. From a comparison of line shapes, the amorphous material was shown to contain the positive-ion also. g-Values were calculated for the positive ion, using a model in which the electron-hole was located in a non-bonding sulphur 3p orbital, giving qualitative agreement with the measured values.

Truby et al. (100) have also investigated the migration and localization of energy in gamma-irradiated n-alkyl disulphides in the amorphous state as a function of alkyl chain length, by looking at methyl-, ethyl-, n-propyl-, amyl-, octyl-, and eicosyl disulphides.

They found that all free charge created by the radiation migrated to and localized on the disulphide group. Most excitation also localizes at this group, but some causes C - H cleavage, resulting in an alkyl radical which is believed to react with a disulphide group giving one $RS^{\bullet}$ radical if the disulphide group lies within a distance r, where r was calculated to be 0.34 nm for good agreement of the calculated and measured yields of $RS^{\bullet}$

A comparative study of the production of free radicals from some sulphur compounds and their selenium analogues by irradiation with ultra violet light has been carried out (101). Room temperature irradiation for twenty-four hours produced no esr signals from any of the compounds, although sulphur or selenium formation was observed in some cases. Irradiation at 77K for thirty minutes produced esr signals. Disulphide compounds yielded radicals due to the cleavage of the S-S bond, these gave rise to spectra which were asymmetric and had high g-values. Of the diselenide compounds, dimethyl- and diphenyl- gave no signals, dibutyl diselenide gave a weak signal centred about $g = 2.$* Dibenzyl diselenide gave a spectrum similar to the ones from dibenzyl sulphide and dibenzyl selenide, which were simple curves about 30 gauss wide, at $g = 2.$*

The sulphides gave rise to the "sulphur pattern" observed by Gordy (see section 2.3.2). Di-n-octadecyl sulphide and di-n-dodecyl

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* The g values were quoted by the original authors to this accuracy only.

sulphide also gave an eight line alkyl radical spectrum. Allylmethyl sulphide gave an incompletely resolved spectrum, at $g = 2$,* attributed to an alkenyl radical, with no evidence for a "sulphur pattern".

Di-n-octadecyl selenide and di-n-dodecyl selenide both gave an eight line alkyl radical spectrum and also gave an asymmetric spectrum at high g-value assigned to a selenium radical. Toluene-ω-selenol gave a similar selenium radical spectrum and a triplet with 47 gauss splitting. The selenium radical has an axially symmetric g-factor, the sulphur radicals examined did not.

These facts were interpreted by these workers as:-

uv irradiation of disulphides cleaves the S-S bond,

uv irradiation of diselenides does not cleave the Se-Se bond, but may form radicals at other points in the molecule, usually on a methylene carbon.

uv irradiation of a thiol or selenium analogue cleaves the S-H or Se-H bond. Alkyl sulphides or selenides cleave at the C-S or C-Se bond, yielding both sulphur or selenium radical and alkyl radical.

In the case of dibenzyl sulphide, selenide or diselenide, the C-S or C-Se bond is left intact, and cleavage of C-H occurs in a methylene group. In toluene-ω-selenol, the expected selenium radical $Ph.CH_2Se^\bullet$ is formed, but also a cyclohexadienyl type of radical, formed

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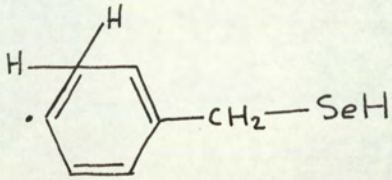
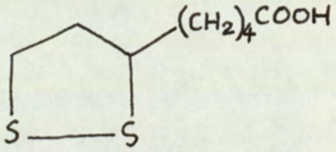
* The g values were quoted by the original authors to this accuracy only.

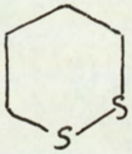
by proton addition to the benzene ring. This has the structure:-



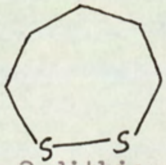
Disulphides have also been uv irradiated by Smissman et al. (102) These workers chose dimethyl disulphide, lipoic acid, o-dithiane and 1,2-dithiepane, and found that the esr spectra were broad lines with no hfs, and had high g-values.



lipoic acid



o-dithiane



1,2-dithiepane

They attributed these spectra to sulphur radicals formed by cleavage of S-S bonds.

Alkyl sulphones and polysulphones have been irradiated with gamma radiation (103), again at 77K. Free radicals produced in the greatest quantity were alkyl radicals, formed by the cleavage of C-S bonds. Sulphur dioxide was detected, indicating that in some cases both C-S bonds were cleaved. Some $R\dot{S}O_2$ radicals were detected, also radicals formed by loss of an alpha hydrogen. The alkyl radicals were destroyed by warming, leaving an asymmetric singlet due to $R\dot{S}O_2$

which was appreciably stable at room temperature. In some cases the concentration of this radical increased as the alkyl radical decayed.

A signal due to $CH_3\dot{C}HSO_2$-C_2H_5 was found in the spectrum from diethyl sulphone, which unexpectedly increased as the alkyl radical (ethyl) decayed. This was thought not to be due to hydrogen abstraction by the ethyl radicals as very little ethane was detected. Hydrogen abstraction by $R\dot{S}O_2$ radicals would not be consistent with the detection of this species as a relatively stable end-product. The authors thought that "hot" $R\dot{S}O_2$ radicals, produced by the exothermic recombination of R and SO_2 (97kJ mol^{-1}) might cause abstraction. The signal due to $CH_3\dot{C}HSO_2C_2H_5$ then decayed slowly at room temperature, leaving the spectrum of $C_2H_5\dot{S}O_2$

The alkyl radicals disappeared by recombination rather than abstraction, shown by the very small amounts of methane and ethane detected.

The spectra from the polysulphones were less well resolved than those from the sulphones, and alkyl radicals formed from them by loss of alpha hydrogen decayed more rapidly than those from the sulphones.

Free radicals have been produced by the uv irradiation in vacuo of some aromatic and aromatic-substituted aliphatic disulphides

$(ArCH_2S)_2$ (104). The resulting $ArS^{\bullet}$ and $ArCH_2S^{\bullet}$ type radicals were stable at 77K and recombined to the disulphides, or formed thiols. Electron donors in the para- position in the nucleus stabilized the sulphur radicals.

Free radicals have been obtained from sulphur itself. Liquid sulphur gives an electron spin resonance signal having a g-value of 2.024 (105). This was thought to be due to the breakage of S-S bonds in polymeric chains. Esr signals have been obtained from solution of sulphur in oleum (105). These have been studied in detail (106), and shown to take on an asymmetric shape when the solutions are frozen, indicating anisotropic g-values. In concentrated (65% SO_3) oleum, one line was observed, of g-value 2.018 with a shoulder at g = 2.003, found to be due to g-value variation, not to hfs. In dilute (20% SO_3) oleum, another line was also present, of g-value 2.032 with a shoulder at g = 2.025. This second line was attributed to polymeric sulphur.

The solutions of sulphur in oleum have received more attention recently (107). In fresh solutions, the species believed to be present were the diamagnetic, yellow S_8^{2+} entity, and the paramagnetic, blue S_4^{+} ion, with g value of 2.0131 at room temperature. On cooling to 90K, the g value was seen to be axially symmetric, the two components being $g_{\parallel} = 2.0004$ and $g_{\perp} = 2.0192$. After two months, the solution was colourless and diamagnetic, only S_4^{2+} being present.

On dilution to less than 40% oleum concentration, the colour of a fresh solution changed from blue through green-brown to brown, with the formation of a second esr signal, of g value 2.0260 at room temperature. This was resolved at 90K into a signal due to 3 g values,

$$g_1 = 2.0024$$
$$g_2 = 2.0311$$
$$g_3 = 2.0421$$

This signal was thought due to an open S_n^+ chain

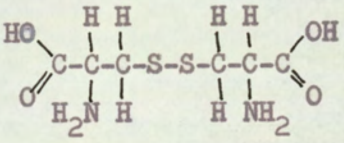
When sulphur was dissolved in amines (108), coloured solutions were often obtained. These were found to be paramagnetic, with a g-value of 2.030. No hfs was seen, but the line showed structure at 77K. It was suggested that homolytic fission of long sulphur chains of polythiobisamines and amine polysulphides occurred, yielding free radicals. Amines are known to catalyse the addition of sulphur to triphenyl phosphine, probably by free radical formation.

Flour (109) was examined for the presence of free radicals after being ground. Paramagnetic species were detected but were found to be carbon radicals, having a g-value of 2.005. Sulphur radicals, although expected, were not detected.

2.3.2. Biologically Interesting Compounds

All of the free radicals in this group have been produced by high energy irradiation. The initial work was done at room temperature, on polycrystalline compounds. This was followed by work at low temperature, and later by work at low temperature using the material in single crystal form.

Various proteins and amino acids were irradiated with 50 kV X-rays (110), and it was noted that proteins containing cystine as one of the units all showed the same resonance, which was that obtained from cystine itself.

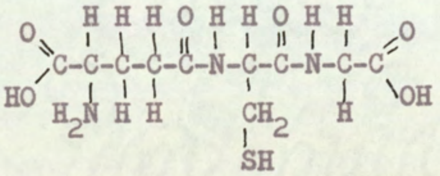


$$HOOC\text{-}CH(NH_2)\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$$

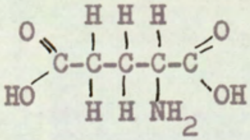
Cystine

No resonance from any other part of the molecule was found. The cystine resonance was asymmetric, and had no hfs, leading to the suggestion that the unpaired electron resided on the sulphur, an electron vacancy in any other part of the molecule migrating to sulphur. A three-electron bond between the two sulphur atoms was postulated. This process was thought to account for the radio-protective action of some sulphur compounds.

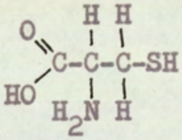
Peptides were next examined (111), as these are intermediate between amino-acids and proteins. Glutathione, a tripeptide of glutamic acid, cysteine and glycine was X-irradiated and found to give esr signals due to cysteine.



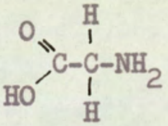
Glutathione



Glutamic acid

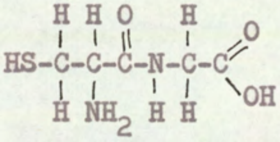


Cysteine



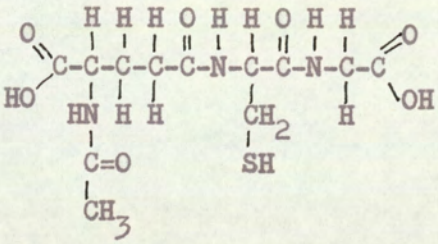
Glycine

Cysteinyl-glycine also gave only a cysteine resonance. Acetyl glutathione and acetyl homocysteine thio-lactone gave spectra which had a cysteine component, although both had another pattern superimposed. In vacuum glycyl methionine and acetyl methionine gave spectra which both had a weak cysteine component, with the major part of the spectrum being very similar to the pattern obtained from glycine. In air, a different pattern was observed.

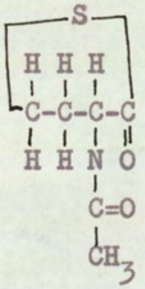


$HS-CH_2-CH(NH_2)-CO-NH-CH_2-COOH$

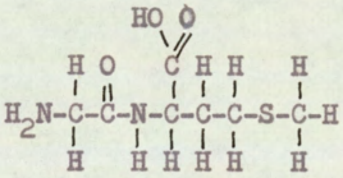
Cysteinyl-glycine



Acetylglutathione



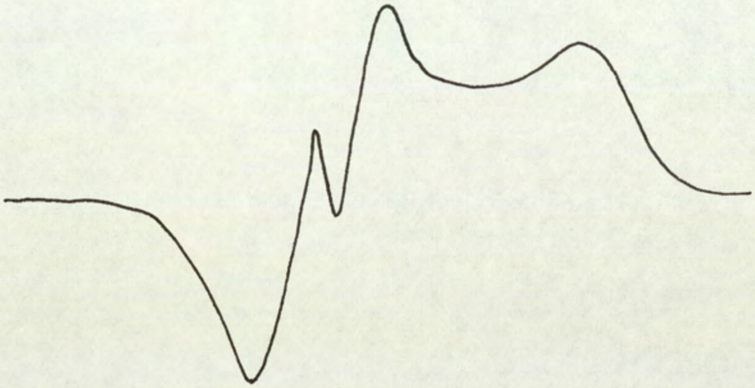
Acetylhomocysteine thiolactone



$H_2N-CH_2-CO-NH-CH(COOH)-CH_2-CH_2-S-CH_3$

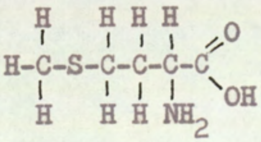
Glycylmethionine

When amino-acids were irradiated by X-rays (112), cysteine, cystine and glutathione all gave similar esr spectra. The structure present was due not to hfs but to an anisotropic g-value, and was found to be field-dependent. This pattern was attributed to a free radical with the odd electron localized on sulphur, and is now known as the "sulphur pattern"



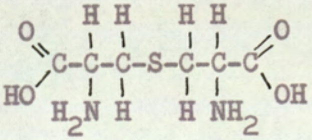
Sulphur pattern

Methionine, lanthionine and djenkolic acid did not give the sulphur pattern (112). These compounds are all similar to cystine in structure, except for the groups attached to sulphur. This is further evidence that the "radical centre" is associated with the sulphur group.



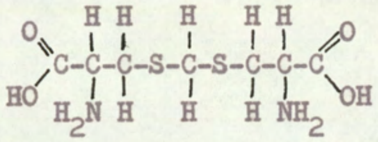
$CH_3-S-CH_2-CH_2-CH(NH_2)-COOH$

Methionine



$HOOC-CH(NH_2)-CH_2-S-CH_2-CH(NH_2)-COOH$

Lanthionine

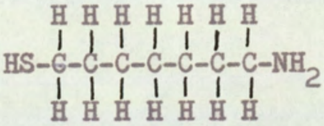


Djenkolic acid

Another worker X-irradiated similar compounds (113) and found that the spectra for cysteamine, cysteine and cystine were similar to each other, but differed from the spectra from 7-aminoheptanethiol and homocystine, which have longer chain lengths, and from penicillamine, which has a branched chain. Substitution in the amino group caused changes in the hfs.

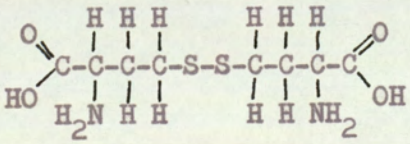
$NH_2CH_2CH_2SH$

Cysteamine

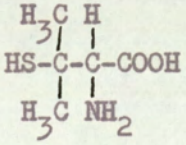


$$HS-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-NH_2$$

1-Mercapto-7-aminoheptane



Homocystine



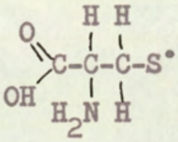
Penicillamine

Polycrystalline glutathione was X-irradiated at room temperature under vacuum, and examined immediately (114). The spectrum resembled that obtained from an equimolar mechanical mixture of the three constituent amino-acids. Over several days, the spectrum changed to that obtained from irradiated cysteine. The authors suggested that paramagnetic centres are produced in each of the three amino acid parts of the reduced glutathione, but then transfer slowly to the cysteine part. This transfer could involve an interaction between the molecular fragments caused by irradiation and undamaged neighbouring glutathione molecules.

The radiation dose required to yield detectable amounts of free radicals was determined (115). In cysteine, a resonance was obtained after only 100r (a sub-lethal dose). It was found that the minimum dose required was dependent on the omnipresence of heavy metals, presumably present as impurity atoms, suggesting that the formation of radicals was by means other than ionizing effects.

The effect of temperature changes on the energy migration process was examined (97). Materials were irradiated with gamma radiation at 77K and examined at this temperature. Different signals were found for different compounds, showing that migration does not occur at this low temperature. The resonances were broad, asymmetric and were probably due to several superimposed signals. They converted to the sulphur pattern of cystine when allowed to warm to room temperature.

Cystine (the disulphide) and cysteine (the thiol) gave the same signal. This was thought to be due to the species:-



Differences were found between the signals from L-cysteine and DL-cysteine irradiated and observed at 77K.

It was suggested that the first process is one of ionisation followed by migration to sulphur, then bond breakage to yield free radicals.

It was shown (116) that the resonance from cystine after irradiation at 77K is an order of magnitude weaker than that from cysteine subjected to the same process. This was thought partly due to the greater probability of recombination in the disulphide case, resulting from the more efficient caging of the RS$^\bullet$ radical than the hydrogen atom. The authors also considered that the S-H bond would break more readily than the S-S bond at low temperatures. It should be noted, however, that the bond dissociation energies at 298K are in the reverse order, being 380 kJ mol^{-1} for the S-H bond and 306 kJ mol^{-1} for the disulphide bond (183).

It was mentioned earlier that djenkolic acid did not give a sulphur pattern when irradiated (112). The spectrum from this compound at room temperature was attributed to a radical formed by loss of a hydrogen from the carbon atom between the two sulphur atoms (djenkolic acid contains the link $-S-CH_2-S-$). It was then found (116) that this species was not produced at 77K, the resonance resulting from the free radical formed at this temperature having no hfs, and was thought to be due to the ionised molecule, with the free spin localized on the sulphur atom.

On irradiation in vacuum at 77K, methionine gave a broad resonance with unresolved structure. When warmed to room temperature, a spectrum with an isotropic g-value and well resolved hfs was obtained. As the g-value was close to the free spin value, this was thought to arise from a carbon-type free radical. On cooling to 77K again, a weak component showing the sulphur pattern was observed. After some hours at room temperature, the signal had changed to a closely spaced triplet. No signal was found when the experiment was conducted in the presence of air. These observations were thought to be due to the initial formation of a carbon free radical, which formed a sulphur free radical when stored at room temperature.

The tripeptide glutathione was also studied. The oxidized form of this contains an S-S bond and therefore corresponds to cystine, while the reduced form corresponds to cysteine, On irradiation at 77K, similar resonances were observed for these two forms, although the resonances differed from that obtained from cysteine and cystine. On warming to room temperature, the pattern from the reduced form became like that from cysteine, while the oxidized form pattern did not, although it did show a cystine like component.

The formation of the sulphur radicals from the primary radicals formed by irradiation was investigated (117). The compounds taken were cysteine, reduced glutathione, and djenkolic acid, all in polycrystalline form. They were irradiated with 220kV X-rays in vacuum, at 77K, 193K and 295K.

When cysteine was irradiated at 77K, a spectrum was obtained having poorly resolved hfs, and a tail at the high g-value side. On annealing at higher temperatures (193K), another signal appeared at a higher g-value, the original signal decaying. The high g-value signal was obtained when the compound was irradiated at the higher temperature. The radiation yield at 77K was greater than at higher temperatures,but very few sulphur radicals were produced, this signal and the yellow colour which was formed being attributed to the carbon radicals.

In the case of reduced glutathione, no sulphur radical resonance was found on irradiation and observation at 77K or 193K. After heat treatment, these samples gave a spectrum showing the presence of sulphur radicals. In air at room temperature, 20% of the resonance was due to sulphur radicals, but the subsequent yield of free radicals was found to be lower, and their formation slower. This is assumed to be due to the formation of peroxy-radicals with atmospheric oxygen, and this was found to be irreversible.

Djenkolic acid, at room temperature, gave a doublet, which changed slowly over a period of months. A sulphur resonance slowly appeared at this temperature. When heated to 383K, the doublet changed to a typical sulphur pattern, without any change in the total radical concentration.

Further work (118) was carried out to investigate the effect of heat treatment on the primary radicals produced at 77K. No, or very few, sulphur radicals were formed in any of the compounds at 77K. There were fewer free radicals formed at 77K than at 295K. Little change was observed in the spectra in the temperature range 77K to 110K, showing that few secondary processes occur in this range. From 110K to 125K decay processes predominate. At higher temperatures, sulphur radicals are formed, the actual temperature required to produce them increasing with complexity of the molecule. Simple thiols and disulphides give rise to sulphur free radicals at 170K, peptides (e.g. glutathione) at about 240K, whilst proteins require temperatures as high as 280K. The formation of sulphur free radicals coincided with an increase in the total free radical concentration:- e.g. in the case of penicillamine, the number of unpaired spins present after annealing to 295K was found to exceed the number present initially at 77K by about 70%. These facts suggested a diffusion controlled intermolecular reaction to produce the sulphur radical from the primary carbon radical. The sulphur radicals were thought to be of the type

$$R - CH_2 - S^{\bullet}$$

with the hfs being temperature dependent. Where the radical is of the type

$$R - CX_2 - S^{\bullet}$$

as in penicillamine (where X = methyl) no hfs is found.

When these compounds were irradiated in vacuum at room temperature, some fraction of the resonance was found to be the sulphur pattern. In some cases only the sulphur pattern was found, e.g. cysteine-hydrochloride, cysteamine, DL-penicillamine.

When D-penicillamine hydrochloride was used, both in polycrystalline and freeze-dried forms, slight differences were found in the spectra of the primary species as were found in the spectra of irradiated polycrystalline and amorphous alkyl disulphides (96). Similar differences were also found for cysteine hydrochloride, cystine, cystamine, and reduced glutathione.

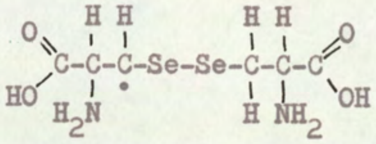
On a purely statistical basis, some sulphur radicals would be expected to be formed at 77K. The fact that in some cases no sulphur radicals are detected, and in other cases very few are found, suggests that some intramolecular migration of radiation energy occurs at 77K, resulting in the selective formation of esr centres.

The total radiation yield was higher at 295K than at 77K, and also higher than in samples irradiated at 77K and heat treated to 295K. If irradiation causes homolytic dissociation, recombination is more likely at low temperatures due to the hindrance of diffusion processes, than at high temperatures, where the fragments can diffuse away before recombination can occur. This indicates that the formation of sulphur radicals may occur as a result of intermolecular reactions. (In experiments on mixtures prepared by freeze-drying, this worker found that unpaired spins were transferred between molecules not covalently bound to each other).

The interactions of solvent radicals with solute molecules was investigated (119) by studying frozen aqueous solutions of some sulphur compounds. The resonance pattern due to the solute was the same as that from the solute when irradiated alone. A resonance was found from the solvent, which was partly due to $\dot{\mathrm{O}}\mathrm{H}$ radicals. Hydrogen atoms were not found to play much, if any, part in forming solute radicals, reacting at 77K. $\dot{\mathrm{O}}\mathrm{H}$ radicals were found to react in the range 100-130K, most disappearing by recombination, only about 15% giving rise to free radicals from the solute. For penicillamine, sulphur radicals were found if the solution was heated above 170K, but no sulphur radicals were formed in glutathione solution even at 210K. In both cases all esr centres were destroyed by heating above 240K.

The effect of uv radiation on free radicals formed by X-irradiation of methionine was investigated (120). A fairly complex spectrum, not a sulphur pattern, was obtained byX-irradiation. If the sample was then irradiated with uv light from a low pressure mercury lamp ($\lambda = 254$ nm), the concentration of unpaired spins was found to fall, reaching a minimum value after thirty minutes, and then to rise again, due to another radical species being formed, with higher g-values. H_2S was also evolved, and the sample turned brown. Radiation with uv of a longer wavelength ($\lambda = 285$ nm) quenched the signal without forming detectable amounts of any new radical species.

In their work on uv irradiation of sulphur and selenium compounds (see section 2.3.1.) Windle et al.(101) irradiated cystine and found the sulphur pattern. Irradiation of selenocystine gave a broad line which they attributed to the radical:-

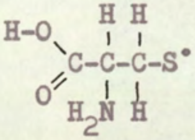


which had a g-value of 2.003. A single line was also found at g = 2.06, but no assignment was made for this.

The g-values for most organic free radicals are anisotropic. This means that the g-factor has different values for different orientations of the radical in the magnetic field. Three values are observed, one for each of the three mutually perpendicular crystal axes. In solution, the g-value measured is the average, due to the rapid tumbling motion of the free radicals. In polycrystalline and amorphous materials, the g-values are not averaged, and broad lines with incompletely resolved hyperfine structure result. Kneubuhl (121) has calculated the line shapes expected from polycrystalline materials containing free radicals with three different g-values, and also for the axially symmetric case, where two of these values are the same, and these shapes agree with those obtained experimentally. This work allows the relevant g-values to be measured from the spectra obtained for the polycrystalline material. In single crystals containing free radical species oriented in a few fixed directions with respect to the crystal axes, a resonance is found for each different orientation of the free radical species. These sometimes overlap, but usually a particular orientation of the crystal in the magnetic field yields a simple pattern.

In some cases, particularly for sulphur radicals, the hyperfine splitting is found to be anisotropic, resulting from an anisotropic component in the Hamiltonian. In solution this is averaged out, due to tumbling, to zero, and the splitting observed is that due to the isotropic Fermi contact term. In polycrystalline materials this anisotropy leads to line broadening and lack of resolution. In single crystals, although the anisotropy is still present, an orientation can normally be found for which the hyperfine splitting can be resolved in sufficient detail. Thus advantages may be gained by examination of single crystals of the material after radiation damage, and information gained which may not be available from the poly-crystalline material.

In the single crystal form L-cystine dihydrochloride has received much attention. It was first gamma-irradiated at room temperature by Kurita and Gordy (32), when a spectrum was obtained which consisted of two doublets. These were interpreted as arising from the same paramagnetic species present in two different orientations. Now, it was known that the unit cell of this compound contained two molecules equivalent in orientation, and that disulphides and thiols both gave rise to the same free radical species under these conditions. The radical was thought to be of the form $RS^{\bullet}$ with the odd electron localized on the sulphur atom. As there are two orientations of the same radical species, radical formation must involve the S - S bond, which is the centre of the molecule. The structure most likely for the radical is therefore:-



The doublet form of each line results from interaction with one proton, which must be attached to carbon, not nitrogen or ogygen, as no exchange was observed with D_2O. To explain this interaction with only one of the two hydrogen atoms on the methylene carbon, it was assumed that the odd electron was located in the p_x orbital, perpendicular to the sp^2 plane ($3sp^2$ are in this plane, the p orbital is perpendicular to it for sulphur). The most stable configuration of the radical leaves the sulphur atom close to the NH_3^+ group, where hydrogen bonding will help to hold this configuration. Thus the orbital containing the odd electron does not rotate about the C - S bond and so may be closer to one proton than the other. The proton removed from the electron may not therefore give a splitting large enough to resolve, with the result that only a simple doublet will be observed from the other proton.

Conflicting results were obtained by Box and Freund (122) when they irradiated single crystal L-cystine dihydrochloride at 77K. They examined the resonance at liquid helium temperature. A single orientation for the free radical was found, indicating that the unpaired electron was associated with the S - S bond and not with the fragments resulting from the cleavage of this bond. These workers suggested that the paramagnetic species formed was the positive ion $(-S-CH_2-CH(NH_3^+Cl^-)COOH\ _2)^+$.

Anisotropy in the g-value was attributed to localization of the odd electron on the sulphur group. The hfs observed came from interaction with the four protons of the CH_2 groups. This can result in 9 lines from two pairs of equivalent protons or 5 lines from 4 equivalent protons. For certain orientations of the crystal in the external magnetic field, there are two equivalent pairs of protons. For other orientations the four protons are all equivalent. Both patterns were therefore found, depending on the orientation of the crystal. The hfs was almost isotropic, the small amount of anisotropy was thought to result from a weak dipole-dipole interaction between the electron and the protons.

A triplet was also found in the spectrum, with an anisotropic g-value. It was suggested that this was the resonance of

$$\dot{S}-CH_2-CH(NH_3^+Cl^-)COOH$$

but Kurita and Gordy (32) have associated this species with a doublet at room temperature. Box and Freund found that the doublet was visible in the spectrum of their sample irradiated at 77K only after extended warming. A background signal was also observed, which decayed after momentary warming, this was thought due to negative ion radicals which disappear on recombination of the ionised electron with the cation.

Akasaka et al. (123) also irradiated this compound at 77K, using gamma radiation and high energy electrons. They found two paramagnetic centres at 77K, which they called alpha-1 and beta-1. Both had anisotropic g-values. On annealing for nine days at 201K, alpha-1 changed to another signal, alpha-2, with a concentration about half that of alpha-1. No change occurred in beta-1. Annealing for ten hours at room temperature caused alpha-2 to change to another signal, alpha-3, almost quantitatively, and beta-1 changed to beta-2 quantitatively.

The structure of these various signals was given as:-

alpha-1	triple-triplet	- almost isotropic
alpha-2	triplet	- almost isotropic
alpha-3	doublet	- isotropic
beta-1	quintet 1 : 2 : 2 : 2 : 1	
beta-2	doublet	

the beta signals were resolved best in only one plane.

All except alpha-1 showed two different orientations. No differences were found for deuterium substituted material, indicating that the splittings were caused by protons bound to carbon only.

Alpha-1 was thought to arise from a free radical with an ionised S-S bond. The hfs was accounted for by assuming two sets of equivalent beta protons from each of the two $-CH_2-$ groups.

Alpha-2. This was present in two orientations and was due to "semi-stable" $R\text{-}CH_2\text{-}\dot{S}^*$. The hfs came from equivalent coupling to the two methylene protons.

Alpha-3. This was the same spectrum as Kurita and Gordy (32) obtained on irradiation at room temperature. It was assigned to the species $R\text{-}CH_2\text{-}\dot{S}$, where the C-S bond has rotated to a stable position to give preferential interaction of the odd electron with one of the two protons in the methylene group. This explains the almost quantitative transformation of the alpha-2 to alpha-3.

Although they were not identified, beta-1 and beta-2 were thought to be due to "sulphur radicals" beacuse of the magnitude of their g-values.

On consideration of g-values, and electronic states from M.O. theory, the radical giving rise to alpha-1 was thought to be the negative ion radical. It was suggested that at low temperatures, electrons ejected from various sites in the molecule, as a result of the radiation, are trapped at the disulphide bond to form the ionised radical. On warming, this breaks to form the unstable species $R\text{-}CH_2\text{-}\dot{S}^*$ which, at room temperature converts to $R\text{-}CH_2\text{-}\dot{S}$, by rotation of the $\text{-}CH_2\text{-}S^{\cdot}$ group accompanied by a change in the electronic state. The species $R\text{-}CH_2\text{-}\dot{S}$ is stable at room temperature.

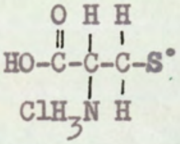
This same compound was again investigated in single crystal form by Box and Freund (124), who irradiated it with X-rays at 4.2K (liquid helium temperature). They found three esr centres, which they called alpha, beta and gamma, in order of increasing g-value.

Alpha was stable at 77K and was thought to be the resonance from the negative ion radical, with hfs arising from two pairs of equivalent protons.

Beta could be observed at 77K, but was less stable than alpha. The line shape varied with the crystal orientation, in some positions it appeared to arise from interaction with four protons. This signal was attributed to the positive ion radical. This is stabilized because sites exist where the electron removed to form this species may be stabilised. These sites are the disulphide groups of other molecules. The magnitude of beta signals relative to alpha signals was thought to suggest some intramolecular transfer of electron vacancies to the disulphide groups.

The origin of the gamma signal was not found. On warming, changes were observed to occur in the spectrum until the resonance reported by Kurita and Gordy (32) was found.

The corresponding thiol L-cysteine hydrochloride, has been examined in single crystal form (30). This was subjected to an electron beam at 77K, when three resonances were found in the spectrum. These were a singlet, a quartet, and a"Double doublet" (Dd)* The double doublet was the largest resonance with a very large anisotropy, the largest principle g-value being 2.29, the largest yet reported for an organic compound. It was axially symmetric, and thought to be the resonance of the species with a nearly degenerate electronic structure with incomplete orbital quenching. The radical was thought to be



$$\mathrm{HO{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{ClH_3N}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}S^{\bullet}}$$

but was unstable at room temperature compared to the radical derived from cystine, the corresponding disulphide. This was explained by assuming a different orientation of the $-CH_2-$ group with respect to the orbital occupied by the unpaired electron.

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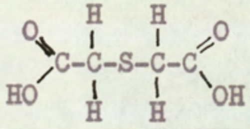
*Original authors terminology.

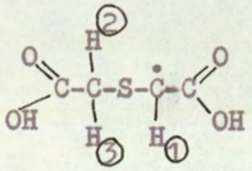
On warming, the signal was observed to broaden, becoming unobservable at about 225K. It reappeared on cooling to 120K, indicating that the spin lattice relaxation time was extremely short, causing broadening. Consistent with this, the signal did not saturate with 100mW microwave power, as do other organo-sulphur and carbon radicals.

A single crystal of thiodiglycolic acid was also gamma irradiated (33) as compounds containing the sulphide link were known to give different patterns to the corresponding disulphides and thiols (101).



Thiodiglycolic acid

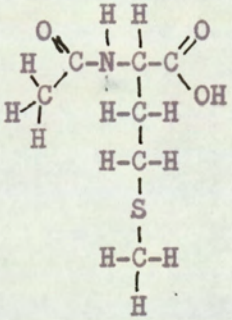
A complex, unresolved spectrum was observed, which, it was thought, was due to the free radical formed by cleavage of a C - H bond.



where H_1 gave a strong, anisotropic interaction, and H_2 and H_3 gave weak nearly isotropic couplings. The odd electron would be in a π orbital, mainly on C and S.

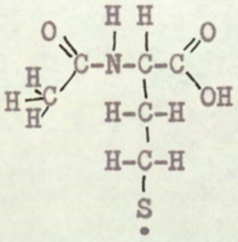
The spin densities showed the unpaired electron to be 60% in the p-orbital of the CH carbon, 2% in the 1s orbitals of the methylene hydrogens, and 22% in the sulphur p-orbital.

N-acetyl methionine was gamma-irradiated at room temperature in single crystal form (125).



N-acetylmethionine

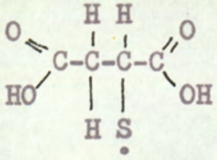
The esr spectrum obtained had two sets of lines, one set was a doublet, with each peak split into two for some orientations, the other set was a multiplet with an almost isotropic g-value. Two chemically equivalent free radicals in slightly different orientations in the crystal were thought to give the doublet. The similarity of the g-value and splitting constants to those of the free radical from cystine dihydrochloride, indicated that the structure of the free radical in this case was:-



formed by loss of the methyl group from the sulphur atom.

The multiplet was probably due to a carbon radical formed by loss of hydrogen from the carbon atom to which the sulphur side chain is attached.

A gamma-irradiated single crystal of mercaptosuccinic acid was found by Hahn and Rexroad (41) to give a spectrum of four lines, interpreted as the resonances of the same free radical in four different orientations in the crystal. The size of the g-value and the absence of hfs were taken to indicate that the radical was based on the sulphur atom, and had the form:-



It should be noted that Kurita and Gordy (32) observed hyperfine structure in the esr absorption of irradiated cystine. The suggested free radical structure for this compound contains the unit CH_2-$S^{\bullet}$ and the hfs results from interaction with one of the two protons. It would therefore be expected that the structure suggested for the free radical formed from mercaptosuccinic acid should give rise to hfs by interaction of the electron with the proton in the group CH-$S^{\bullet}$

2.4. Scope and Objects of Work

The work reported in this thesis falls into three parts.

2.4.1. Photolysis Experiments

Ultraviolet and ionising radiations are known to interact with matter to form, amongst other products, free radical species. Several workers have reported the detection by esr of such species formed by the irradiation of organic compounds containing sulphur (see sections 2.3.1. and 2.3.2.). The compounds investigated have included some simple aliphatic thiols and disulphides, the radiation most often used being γ-radiation. Ultraviolet radiation has been used by two groups of workers, the compounds irradiated were dimethyl, diphenyl, di-n-butyl and dibenzyl disulphides, and toluene-ω-thiol (101), and three cyclic disulphides (102). Free radical species having asymmetric g factors and an absence of hyperfine splitting in the esr spectra were reported.

The work reported here was carried out to investigate the action of ultraviolet radiation on the series of alkane thiols from C_1 to C_4 inclusive, all isomeric forms being used, and the corresponding symmetrical disulphides. Some sulphides were examined, and also compounds containing the group -N-S-S-N-. Certain aromatic disulphides and compounds of use in rubber technology were also irradiated.

Species having asymmetric g factors were found in almost all cases, with evidence for the presence of hyperfine splitting. The spectra observed for diethyl disulphide and di-isopropyl disulphide show additional resonances, with well resolved hyperfine splitting, attributed to species formed by reaction of the primary radicals with disulphide molecules.

2.4.2. Aliphatic Sulphur Compounds in Sulphuric Acid

Solutions of sulphur in oleum have been reported to contain free radical species, detected by esr techniques (105, 106, 107). The signals were thought to be due to two species, one having an axially symmetric g value and thought to be S_4^+; the other, probably an open S_n^+ chain, had three g values. No hyperfine splitting was reported.

Solutions of sulphur in amines are also known to contain free radical species (108), thought to be of the polythiobisamine type, but showing no hfs. No other report has yet been published of the detection of aliphatic organo-sulphur free radicals in solution.

It was found during the course of the work reported here that solutions of sulphur, aliphatic thiols, monosulphides, disulphides, and some dithiobisamines in concentrated sulphuric acid contained appreciable concentrations of free radicals, having esr spectra showing hfs. The esr spectra of a series of such species have been recorded, and analysed in order to identify the structures of the radicals formed.

2.4.3. Aromatic Sulphur Compounds in Sulphuric Acid

The literature contains several reports of paramagnetic species formed by the solution of thiophenols and related compounds in sulphuric acid (sections 2.1.1. and 2.2.). Two different paramagnetic species are present in these solutions, one thought to be the thianthrene cation radical, formed by one-electron oxidation of the thianthrene known to be formed from the thiophenol. The other species has not yet been identified. In order to gain information to aid in the determination of the structure of this species, the solutions in sulphuric acid of a series of substituted thiophenols and some aromatic disulphides and monosulphides have been prepared and their esr spectra recorded and analysed.

3. THEORY OF ELECTRON SPIN RESONANCE SPECTROSCOPY

3.1. The Resonance Condition

Substances showing the phenomenon of electron spin resonance are paramagnetic - i.e. their electronic configurations include unpaired electrons.

The electron spins on its axis, and as it is electrically charged, creates a magnetic dipole. Electron spin resonance spectroscopy is concerned with the study of the re-orientation of such magnetic dipoles by applying electromagnetic radiation in the presence of a suitable magnetic field.

The spin angular momentum of the unpaired electrons may be expressed as

$$\sqrt{S(S+1)}\ \frac{h}{2\pi} \qquad \text{———— 3.1.}$$

where S is the total electron spin quantum number for the atom and h is Plank's constant.

The value of the magnetic moment μ_s of this dipole may be written as

$$\mu_s = -g_e \frac{e}{2mc} \frac{h}{2\pi} \sqrt{S(S+1)} \tag*{3.2}$$

where $\frac{e}{2mc} \frac{h}{2\pi} = \beta$ = the Bohr Magneton

g_e is the g factor for the free electron, and for atoms in S states (when the resultant orbital angular momentum quantum number is 0) is 2.0023. e and m are the charge and mass of an electron, c is the velocity of light.

On substitution in equation 3.1,

$$\mu_s = -g_e \beta \sqrt{S(S+1)} \tag*{3.3}$$

If an external magnetic field H gauss is applied, the magnetic dipoles will orient themselves with respect to the direction of the field. The energy of the magnetic dipoles in the applied field is

$$E_H = E_0 - (\mu_s \cos \theta)H \tag*{3.4}$$

where E_o is the energy of the system in the free field case and is the angle between the magnetic moment and the direction of the external field.

By quantum mechanics, it has been shown that only certain discrete orientations of the magnetic moment relative to the direction of the applied field are permitted. In the case of an atom with one unpaired electron, $S = \frac{1}{2}$, and in the presence of a magnetic field the magnetic quantum number M_s takes the values $\pm \frac{1}{2}$.

The component of the magnetic moment in the direction of the applied field is

$$\mu_H = \mu_s \cos\theta \qquad 3.5$$

$$\therefore \quad \cos\theta = \frac{\mu_H}{\mu_s} \qquad 3.6$$

Substituting from equation 3.6 into equation 3.4 gives

$$E_H + E_0 - \mu_H H \qquad 3.7$$

where $$\mu_H = - g_e \beta M_s \qquad 3.8$$

Substitution for μ_H into equation 3.7

$$E_H = E_0 + g_e \beta M_s H \qquad 3.9$$

For $M_s = + \frac{1}{2}$ the interaction energy of the dipole with the applied field is

$$E_H^{'} - E_0 = g_e \beta M_s H = +\tfrac{1}{2} g_s \beta H \qquad 3.10$$

and for $M_s = - \frac{1}{2}$ it becomes

$$E_H^{''} - E_0 = - \tfrac{1}{2} g_e \beta H \qquad 3.11$$

Thus two states exist, of magnetic energies $-\frac{1}{2}g_e\beta H$ and $+\frac{1}{2}g_e\beta H$.

For a field strength H the energy required for a transition between these two states is given by the equation

$$(E_H' - E_O) - (E_H'' - E_O) = +\tfrac{1}{2}g_e\beta H - (-\tfrac{1}{2}g_s\beta H) \qquad \_\_\_\_\_\_ 3.12$$

If the energy required is supplied as radiation of frequency ν, then

$$E_H' - E_H'' = h\nu \qquad \_\_\_\_\_\_ 3.13$$

$$h\nu = g_e\beta H \qquad \_\_\_\_\_\_ 3.14$$

These transitions are the re-orientations studied by electron spin resonance spectroscopy, the resonant frequency ν being detected by the absorption of energy by the system from that supplied.

Figure 3.1.1.(a) shows diagramatically the transition between $M_s = -\frac{1}{2}$ and $M_s = +\frac{1}{2}$ for a field strength of H' gauss induced by radiation of frequency ν_1.

Figure 3.1.1.(b) shows the resulting absorption.

In the presence of a suitable magnetic field H the magnetic moment due to the unpaired electron precesses about the direction of

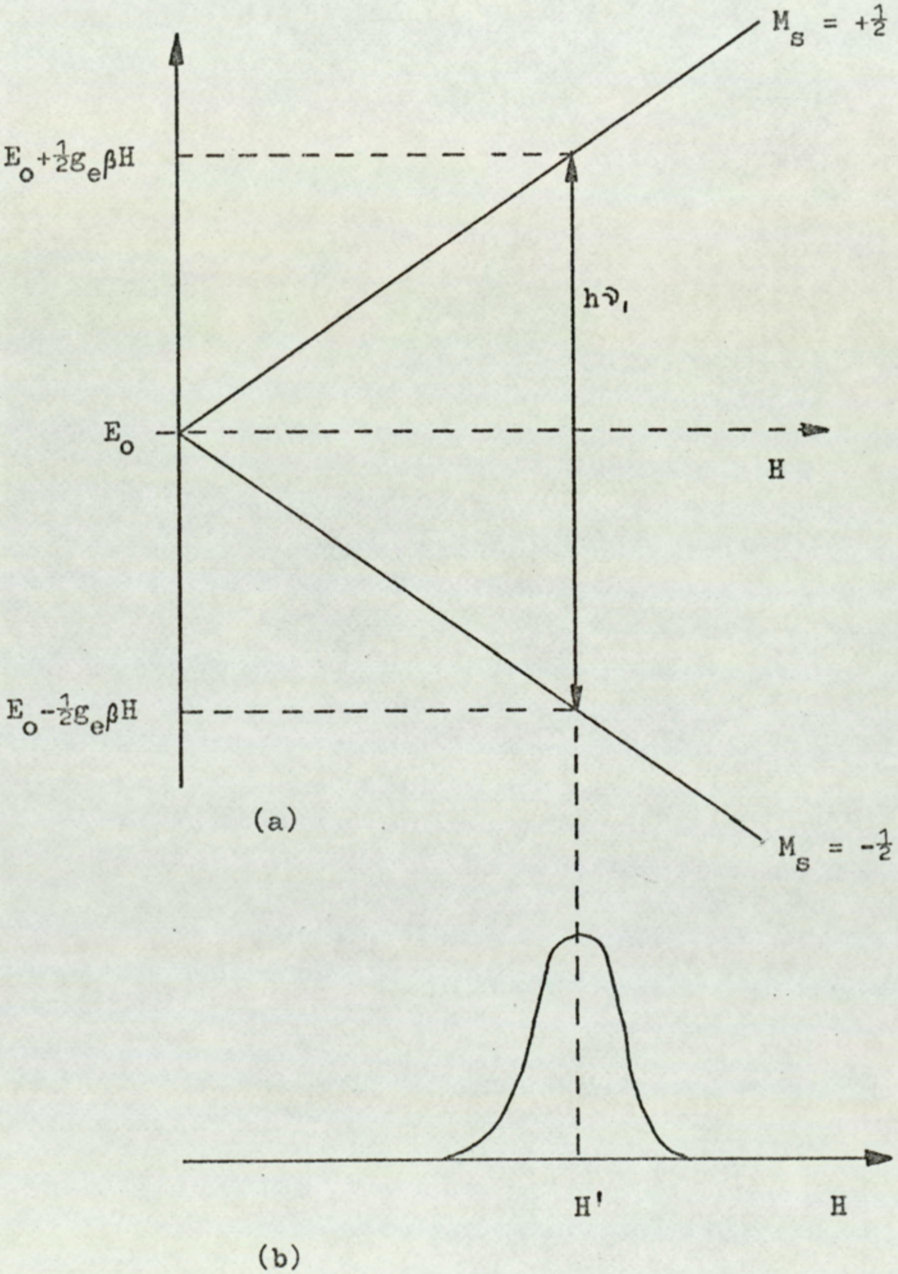


Figure 3.1.1.Transition between $M_s = -\frac{1}{2}$ and $M_s = +\frac{1}{2}$

the applied field with the Larmor frequency ν_L where

$$\nu_L = \frac{eH}{4\pi mc} \qquad 3.15$$

This is shown in figures 3.1.2.(a) and (b) for $M_s = \pm\frac{1}{2}$.

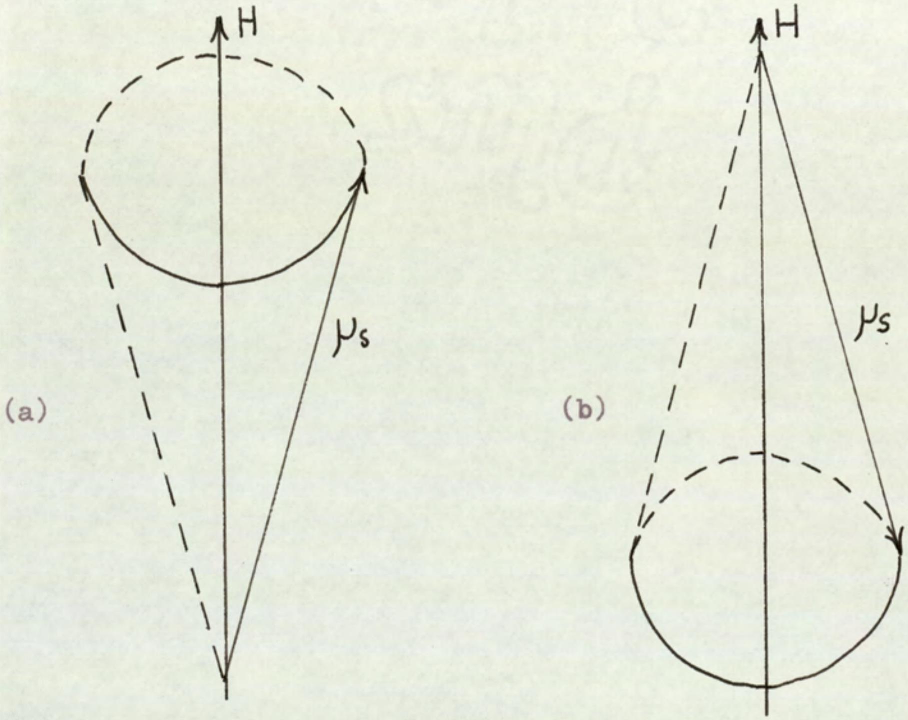


Figure 3.1.2. Precession of electron spin magnetic moment μ_s about applied magnetic field.

The magnetic dipole moment may be resolved into two components, one parallel to H and the other perpendicular. It is through the perpendicular component that the re-orientation of the magnetic dipole moment is accomplished by means of the magnetic field of the electromagnetic radiation supplied, the linear component H_1 of this being perpendicular to H. The magnetic field H_1 may be regarded as being composed of two equal but opposite circulating motions rotating about H. Since the perpendicular component of the magnetic dipole moment is also undergoing a circular motion about H, and as these two circular motions are in the same plane, coupling will occur when these have the same frequency. Re-orientation of the dipole will then occur. If the angular precessional frequency is ω_L, then when the perpendicular field H_1 is revolving at the same angular frequency, the energy exchange is $h\nu$ where

$$2\pi\nu = \omega_L \qquad \text{\_\_\_\_\_\_\_\_}3.16$$

Both absorption and emission transitions occur, but the slight excess population in the lower energy level results in the detection of absorption only.

The ratio of electronic populations of the two states is given by

$$\frac{n'}{n''} = \exp\left(- \frac{h\nu}{kT} \right)$$

where n' and n'' are the population of the upper and lower energy levels respectively, k is Boltzmann's constant and T the absolute temperature.

This gives, for example, a ratio of 0.9984 at 300K and an energy separation corresponding to 3cm wavelength radiation (125). The corresponding ratio at 4K is 0.8772 (126).

Unless some process exists other than stimulated emission whereby the electrons in the upper energy level can lose energy and fall to the lower level, the populations of the two levels will equalize, and absorption of radiation will cease. These processes of energy loss are called relaxation processes, and fall into two classes:

a. Dipolar spin-spin relaxation, when spin energy is shared with other electrons or nuclei.
b. Spin-Lattice relaxation, the spin energy being shared with the thermal vibrations of the lattice or molecule.

These processes will be discussed in more detail later, when the effect on line width will be explained.

3.2. Choice of Resonance Frequency

Electron spin resonance can in principle occur at any frequency, provided that

$$h\nu = g\beta H$$

where g represents the experimentally determined g value.

Now, for high sensitivity, a high value of magnetic field is required, giving a large separation of energy levels. This increases (n''-n'), resulting in a larger net absorption. The frequency of the radiation supplied to the sample must increase with the magnetic field. The intensity of the signal varies as the square of this frequency, but the efficiency of detection falls off if it is too high. A practical limit is also reached with the magnet, it being necessary to produce a highly homogeneous field over 1cm^3. Present magnet technology limits the field to the order of 10K gauss for this degree of homogeneity. This puts the required radiation in the microwave range, supplied from a klystron. There are few klystrons available with a useable output at greater than 40 GHz. The upper limit in practice is 8mm wavelength radiation, corresponding to approximately 36 GHz, with a magnetic field of 13K gauss. This is known as Q-Band radiation.

If the material being studied is liquid or powder, it requires a container. This will occupy a certain amount of the volume of the cavity, both absorbing some of the microwave power, and filling space which would otherwise contain more sample. This container will obviously take up a larger proportion of the volume of a small cavity than a large one, and thus for solution work, a larger, 3cm. wavelength (9GHz) cavity is used, with 3K gauss magnetic field. Klystrons are readily available in this range, which is known at X-Band.

3.3. Origin of Hyperfine Splitting

If the orbit of the electron embraces a nucleus with spin, and therefore magnetic moment, the electron energy levels will be split. The external applied magnetic field at the position of the electron will be modified by that due to the nucleus. Although this is very small compared with the applied field, the electron is very close to the nucleus, maximizing the effect.

The case for splitting by one proton is shown in figure 3.3.1. The proton spin, having the value of $I = \frac{1}{2}$, may only align parallel or antiparallel to the applied field. The effect due to the nucleus therefore either adds or subtracts an amount ΔH to or from the external field felt by the electron. The original resonance is therefore split into two components, one at ΔH upfield, and one at ΔH downfield from the original position. These two components will be of almost the same intensity, as the populations of the two nuclear energy levels are almost equal, being 1 : 1.000007 at 300K in a magnetic field of 10K gauss (127).

Transitions between nuclear energy levels are in general not allowed, giving the selection rules

$$\Delta M_I = 0 \quad \text{and} \quad \Delta M_s = \pm 1$$

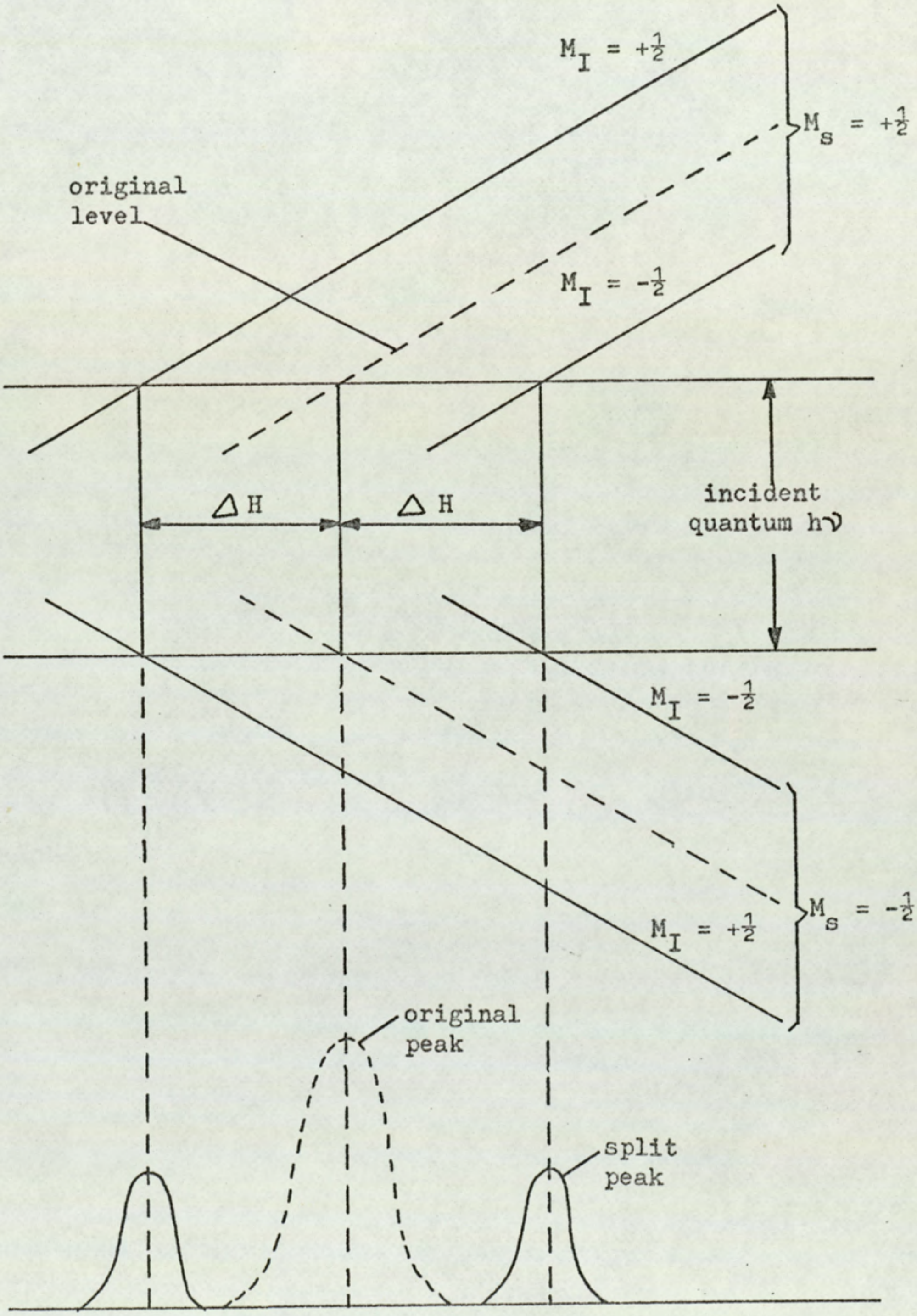


Figure 3.3.1. Splitting by one proton

The transitions in the above case may be described

$$H_1 = \frac{h\nu}{g\beta} - \Delta H$$

and $$H_2 = \frac{h\nu}{g\beta} + \Delta H$$

$$H_2 - H_1 = 2\Delta H$$

and 2 H, the splitting, or difference between the two new levels, is the Hyperfine Splitting.

In general, a nucleus with a spin of I splits a line into (2I+1) components of equal spacing. This simple case is often not found, however, more than one magnetic nucleus usually being involved. Two simple cases may serve to illustrate the general principles:-

a. One nucleus, spin I_1, with large interaction, and a second nucleus, spin I_2, with small interaction.

The nucleus with stronger interaction splits the original absorption into $(2I_1+1)$ components, the weaker interaction then splitting each of these into $(2I_2+1)$ sub-components.

b. Equal coupling to n identical nuclei, of spin I. The result of this is shown in figure 3.3.2., for coupling with 3 protons. The pattern is of overlapping lines, shifted by ΔH w.r.t. each other, giving (2nI+1) lines. These will be of varying intensity, due to the degeneracy of some of the levels. The centre one (odd number of lines) or pair (even number of lines) will have greatest intensity, the others having a symmetrical distribution.

The reason for the degeneracy of some levels is clearly seen from the diagram. The intensities of the lines in this case will be in the ratio 1 : 3 : 3 : 1

The general case for protons:-

n equivalent protons, spin $\frac{1}{2}$ give (n+1) lines, equally spaced, of intensity distribution given by

$$1 : n : \frac{n(n-1)}{2} : \ldots\ldots : \frac{n!}{k!}(n-k)! : \ldots\ldots : n : 1$$

(k varies from 1 to (n-1))

This Hyperfine Interaction arises from two sources, the Anisotropic or classical dipole-dipole interaction, and the Isotropic interaction, originating in relativity theory.

The energy of these interactions is expressed in the Spin-Hamiltonian

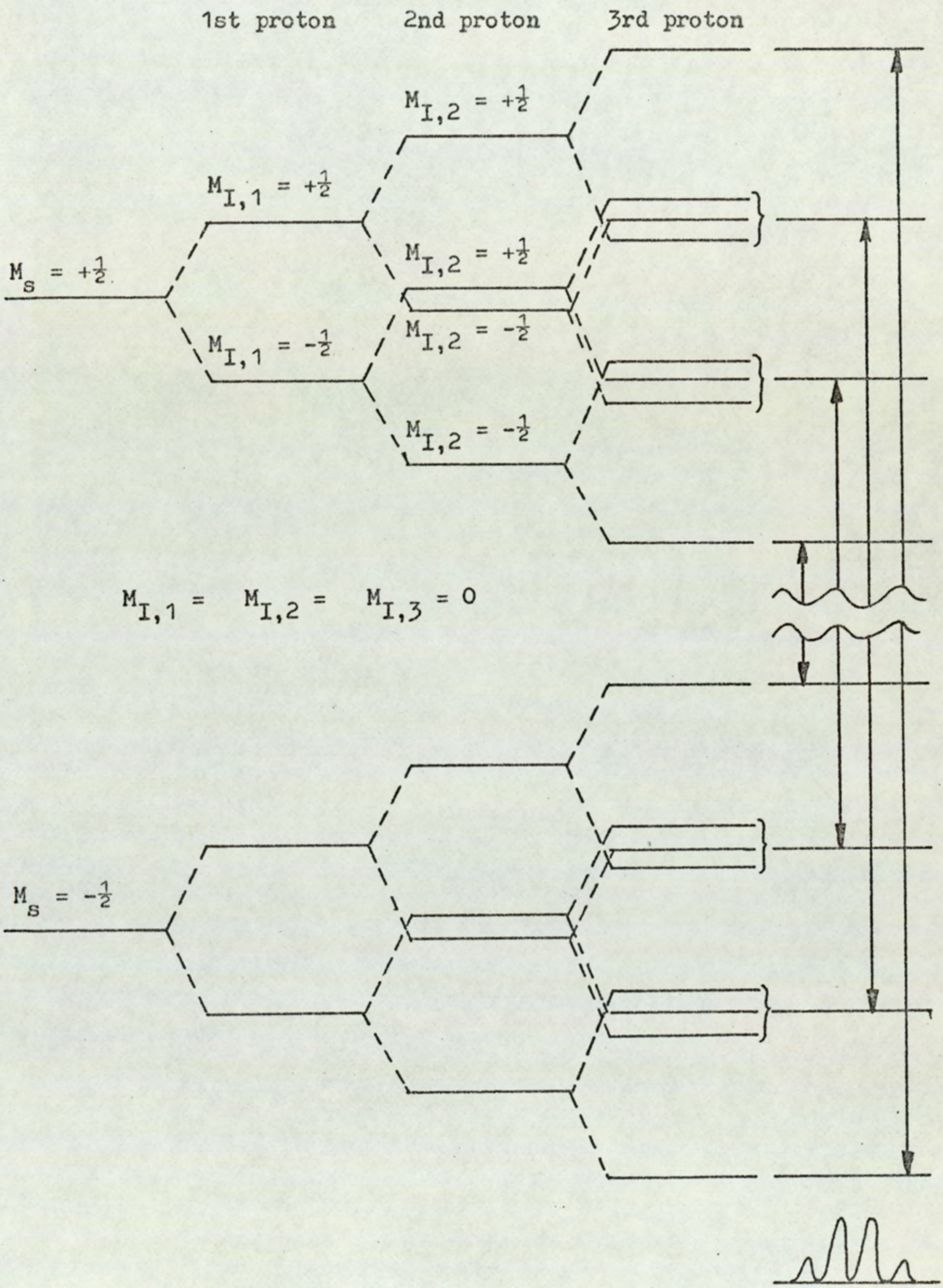


Figure 3.3.2. Hyperfine splitting by three protons

$$\mathcal{H} = g_e g_N \beta\beta_N \left[\frac{S_e I_N}{|r_e - r_N|^3} - \frac{3(S_e r)(I_N r)}{|r_e - r_N|^5} - \frac{8\pi}{3} S_e I_N \,\delta(r_e - r_N)\right]$$

where g_e = g value of the electron

g_N = g value of the nucleus

β = Bohr magneton

β_N = Nuclear magneton

S_e = Electron Spin operator

I_N = Nuclear Spin operator

r_e = vector position of electron

r_N = vector position of nucleus

$\delta(r_e - r_N)$ = Dirac delta function for the distance between the electron and the nucleus, normalized in 3 dimensions.

This expression does not contain the spin-orbit coupling, since this is usually quenched in free radicals, the electron behaving as though it has free spin.

Anisotropic Splitting

This gives rise to the terms:-

$$\mathcal{H}^{\textcircled{1}} = g_e g_N \beta\beta_N \left[\frac{S_e I_N}{|r_e - r_N|^3} - \frac{3(S_e r)(I_N r)}{|r_e - r_N|^5}\right]$$

This will be discussed later, see section 3.3.4.

3.3.1. Isotropic Hyperfine Splitting

$$\mathcal{H}^{②} = g_e g_N \beta \beta_N \left[-\frac{8}{3} S_e I_N \delta(r_e - r_N) \right]$$

This is known as the Fermi contact term, and describes the interactions giving rise to isotropic hyperfine splitting.

In the amorphous or randomly oriented polycrystalline state, the anisotropic component is smeared out by the random direction of the radical bonds with respect to the magnetic field. In solution, the tumbling motion of the molecules will average the anisotropic component to zero, if the tumbling frequency is high compared to that of the hyperfine splitting. Solution spectra are therefore usually well resolved, the splitting being isotropic only.

The Dirac delta function, and hence the Hamiltonian describing the isotropic component, will only be non-zero if the molecular orbital describing the odd electron does not vanish at the position of the nucleus. In the case of single atoms, only the s type orbitals will give rise to splitting, as p,d, and f orbitals have a zero probability of the wave function existing at the nucleus. In the case of organic free radicals, molecular orbitals must be considered. The π orbitals have two lobes pointing in opposite directions, with a zero node at the centre. The σ orbitals have a finite electron density at the nucleus, and therefore may produce splitting.

3.3.2. Configurational Interaction

The above does not explain the splitting found in aromatic compounds, indeed it implies that splitting should not be found when the electron is delocalized into the π electron system.

It is well known that complex and well resolved splitting is obtained from this type of free radical. This splitting is accounted for by configurational interaction. This is the term applied to the mixing of some σ orbital character of an excited state with the pure π character of the unpaired electron's molecular orbital. This gives a finite density for the electron's wavefunction at the edge protons (or other nuclei), and thus produces hyperfine splitting. The quantitative treatment of this process has been discussed by several authors (128, 129, 130, 131).

3.3.3. Hyperconjugation

This is used to account for the splitting caused by, say, the protons of a methyl group attached to an aromatic ring, in radicals where the unpaired electron is delocalized into the aromatic π electron orbitals.

If a methyl substituent is considered, the carbon atom has sp^3 configuration, with lobes overlapping the three 1s hydrogen orbitals and the sp^2 ring carbon lobe. There are no free p orbitals to take part in the π electron aromatic system, and so no unpaired electron density should exist on the methyl protons.

The methyl substituent orbitals may be drawn as shown in figure 3.3.3.

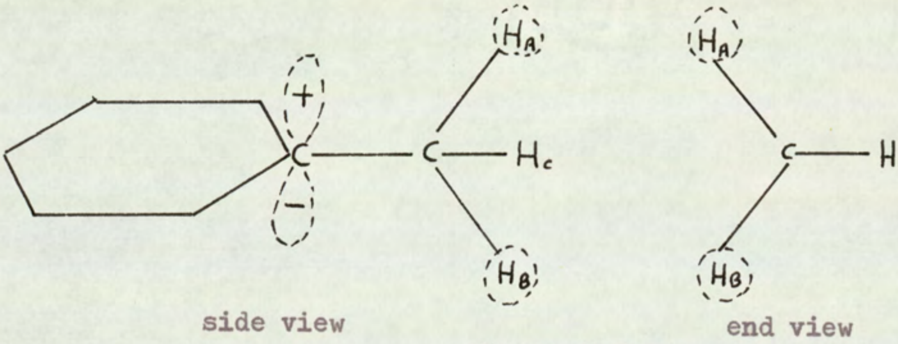


Figure 3.3.3.

If the 1s orbital of proton H_B in the diagram is assumed of negative sign, then the combination of $(h_a - h_b)$, where h_a and h_b are the wave functions of H_A and H_B, will have the same symmetry as the p_z carbon orbital, as drawn. Direct overlap of the ring carbon $2p_z$ with the linear combination of the two proton orbitals may occur, resulting in a mechanism whereby the odd electron in the aromatic π system may have a finite density on the methyl proton. (The three protons will be rotating, thus all will take part in the interaction).

3.3.4. Anisotropic Hyperfine Splitting

In solids, and viscous liquids, the isotropic term is not the only one of importance. Dipolar interaction will also be present either giving rise to splitting or if smeared out by random orientation, giving rise to contributions to the width of the isotropically split lines.

The anisotropic interaction has been given earlier as

$$\mathcal{H}^{\textcircled{1}} = g_e g_N \beta \beta_N \left[\frac{S_e I_N}{|r_e - r_N|^3} - \frac{3(S_e r)(I_N r)}{|r_e - r_N|^5}\right]$$

If this is converted from vector to scalar notation:-

$$\mathcal{H} = g_e g_N \beta \beta_N \sum_k \left(\frac{3\cos^2\theta_k - 1}{r_k^3}\right)$$

which may be simplified

$$\Delta H = B \sum_k \left(\frac{3\cos^2\theta_k - 1}{r_k^3}\right) \quad \text{gauss}$$

B = 28 for proton interaction

r_k = distance between nucleus and unpaired electron in Å averaged over the wave functions concerned.

θ_k = the angle between the applied magnetic field direction and the line joining the electron and nucleus.

If the sample is non-crystalline, the direction of any particular bond is quite random with respect to the direction of the applied magnetic field. The splitting produced will therefore have a range of values which is continuous within the limits of $(3 \cos^2\theta - 1)$. This has a maximum value of 2 when $\theta = 0$, and of 1 when $\theta = \frac{\pi}{2}$. There is only one direction corresponding to $\theta = 0$, but a surface for $\theta = \frac{\pi}{2}$, there will therefore be more molecules with a splitting approaching B/r^3 then $2B/r^3$. The result of adding all values of splitting is to produce a curve with two large peaks, separation B/r^3 gauss, and two subsidiary shoulders, splitting $2B/r^3$ as shown in figure 3.3.4.a.

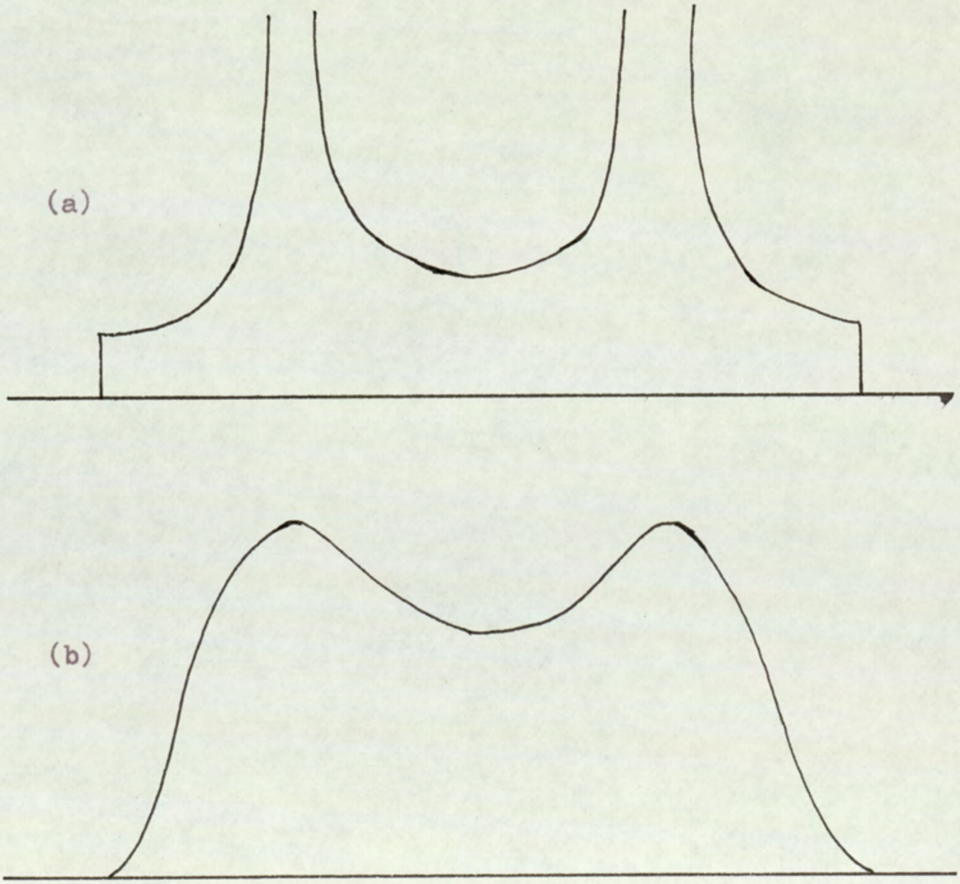


Figure 3.3.4. Anisotropic Splitting

If other forms of broadening are included, the real curve is as shown in figure 3.3.4.b.

The above treatment applies to the interaction with a single proton. In most free-radicals there are several, and the summation must be made over all of them. If all broadening terms are included, all fine detail is lost, and it is not possible to resolve hyperfine lines from dipolar interaction in an amorphous sample unless the interaction is with only one proton.

3.4. g Values

The g value, defined by the equation

$$h\nu = g\beta H$$

is a proportionality constant, relating to the frequency and field at which resonance occurs.

It has been found that the g value for the free electron is 2.002319 (132). The g value of bound unpaired electrons differs from this value, due to magnetic interactions involving the orbital angular momentum of the electron. Since the orbital angular momentum depends on the environment of the electron, the g value must also depend on environment.

Two magnetic interactions of the orbital angular momentum are found to be important.

1. Spin-orbit coupling, or the interaction of the orbital angular momentum with the electron spin. The electron possessing orbital angular momentum is usually thought of as "orbiting" the nucleus. If, instead, we consider the electron as our fixed point, the nucleus "orbits" around the electron. The electron therefore sees a positive charge moving about it. This produces a magnetic field at the electron, which interacts with the magnetic moment of

the electron spin. The interaction is described by the Hamiltonian

$$H_{\text{spin-orbit}} = \zeta \, L.S.$$

where L is the operator of the orbital angular momentum and ζ is a constant called the spin-orbit coupling constant, which can be experimentally estimated from atomic spectra. (This constant is given by the equation

$$\zeta = g_e \beta^2 \langle \psi | \sum_{ij} \left[\frac{z}{2r_j^3} - \frac{1}{r_{ij}^3} \right] | \psi \rangle$$

where r_j is the distance between nucleus and jth electron, r_{ij} is the distance between electrons i and j, z is the effective nuclear charge, $|\psi\rangle$ is the wave function of the atom).

2. The interaction of the orbital magnetic moment with the external magnetic field. The orbital motion of the electron produces a magnetic moment, which interacts with the external field. The Hamiltonian for the interaction is:

$$H = \beta \, L.H.$$

The larger the expectation value of the orbital angular momentum L, the greater the shift of g from the free electron value. The direction of shift is influenced by the sign of the spin-orbit coupling constant, if this is positive, g is usually lower than g_e.

3.5. Line Widths

3.5.1. Dipolar Spin-Spin Interaction

The dipolar spin-spin interaction between the electron and nucleus has been shown above to give anisotropic hyperfine splitting. This is often smeared out, and results in a broadening of the isotropic hyperfine lines. If the equation given above for anisotropic hyperfine splitting is solved for a typical C-H bond of 107pm length, a value of ΔH of 23 gauss is obtained, which is larger than most isotropic hyperfine splitting. This is usually narrowed by other effects to, for example, 10 to 15 gauss for a free radical trapped in a hydrocarbon glass.

Dipolar spin-spin interaction between two electrons is a much stronger interaction, but the nearest unpaired electron is usually much further away than is the nucleus, and the two effects give results of the same magnitude. The electronic case is described by the equation:-

$$\mathcal{H} = g_e{}^2 \beta^2 \sum_k \left(\frac{3\cos^2\theta - 1}{r_k^3} \right)$$

where it is seen that a $(3\cos^2\theta - 1)$ variation of splitting with angle is again found.

In the single crystal case, this has been confirmed. In the amorphous case, a total splitting, integrated over all directions, leads to broadening of isotropic hyperfine lines.

The problem has been treated quantitatively by some authors (133, 134), and an expression for the mean square width of the line developed:-

$$(\Delta H)^2 = \frac{3}{4} \; S(S+1)g^2\beta^2 \sum\left(\frac{1-3\cos^2\theta}{r^3}\right)^2$$

The only parameter in this equation is r, the distance between spins. Electronic spin-spin interaction may thus be reduced by reducing the concentration of the free radicals, until other forms of broadening become more important.

3.5.2. Spin-Lattice Interaction

This term covers all methods by which the electron spins share energy with the molecule, or lattice, as a whole. "Magnetic energy" is converted to "thermal energy", and a relaxation process is produced which results in the electron spins in excited energy levels returning to the ground state.

The most usual form of spin-lattice interaction occurs via the spin-orbit coupling as the thermal vibrations of the molecule (or lattice) will only couple directly to the orbital motion of the electron in the first instance. Kronig (135), has suggested two mechanisms for energy exchange with the lattice, by exchanging a whole quantum directly with a lattice vibration of corresponding frequency, or by scattering a quantum from the lattice, and changing its value. Both of these predict a relaxation time given by

$$T_1 \propto \frac{\Delta^M}{\lambda^2 T^N}$$

where Δ is the splitting to the next orbital level, λ is the spin-orbit coupling coefficient, T is the absolute temperature. M has a value of 4 or 6, N is 1 or 7.

In free radicals, the spin orbit coupling is small, and the orbital motion is strongly quenched by molecular symmetry. This results in Δ being very large, and the relaxation time becomes long, of the order of several seconds. The spin lattice interaction in free radicals is therefore weak, and does not result in much broadening of the lines. In some cases, other processes also occur which cause sharing of the spin energy with the lattice. The tumbling of the free radical in solution allows the transfer from magnetic to thermal energy. Any exchange interaction occuring will also convert magnetic to exchange energy, and then to the lattice thermal energy.

3.5.3. Exchange Narrowing

This occurs when electrons are exchanged between the orbitals of different molecules. It is a direct consequence of the Uncertainty

Principle. This exchange can occur even when there is a negligible amount of chemical binding between the molecules. It is frequently observed in free radical spectra when high concentrations are used.

It has been shown (133, 134, 136, 137), that if the exchange is between similar ions or molecules, it will narrow the absorption line in the centre and broaden it in the wings. The second moment $(\Delta H)^2_{Av}$ is unchanged, but the width measured at half power is reduced. The absorption line from spin-spin interaction alone is Gaussian in shape, the width at maximum slope is 0.852 times the width at half height. Exchange interactions cause the line to change from this to a Lorentzian shape.

Another effect which may be included here is motional narrowing. This is due to the delocalization of the unpaired electrons in a molecular orbital. The electron passes over several atoms, producing an averaging of the dipolar interactions, with a line narrowing similar to that for exchange.

3.5.4. Saturation Broadening

If, as described above, the relaxation interaction is weak, the spins do not return from the excited state to the ground state very quickly. If too high an incident power level is used, the thermal equilibrium may be upset, and the population of the upper, excited, energy level tends to become equal to the population of the ground state. The fraction of the incident power absorbed by the sample therefore decreases, and the absorption line becomes smaller in intensity and broader. This has been treated mathematically (138) in the literature, and shown to take two forms:

a. Homogeneous broadening - where the line is initially broadened by interactions within the spin system, or from an external interaction which is fluctuating rapidly compared with the time taken for a spin-transition - e.g. dipolar spin-spin interactions, spin-lattice interaction, and motional or exchange narrowing.

b. Inhomogeneous broadening - this is caused by interactions external to the spin system, and vary slowly relative to a spin transition. Examples are unresolved hyperfine splitting and inhomogeneities in the magnetic field. In these cases, the observed absorption is the envelope of several absorptions, and saturation will occur separately for each, reducing the peak height of each by the same factor. Thus the line will remain of the same shape and width, but reduce in size.

3.5.5. Modulation Broadening

This is a factor introduced by the method used to detect the absorption (see section 4.3.). A small,oscillating magnetic field is added to the large applied field, allowing the absorbtion to be detected as an a.c. signal instead of a d.c. one. The frequency of the super-imposed field is usually chosen to be 100 kHz. The sample therefore sees a microwave frequency at X band, of 9400 MHz ± 100 kHz, by virtue of the side bands produced modulating the Q of the cavity. This is equivalent to a field inhomogeneity of approximately ± 35 milligauss (2.8 MHz ≡ 1 gauss (139). A line which is theoretically infinitely narrow is therefore broadened to 70 milligauss, thus limiting the resolution of the spectrometer to 70 milligauss. This is due solely to the frequency of the modulation, and is termed modulation frequency broadening.

The amplitude of the modulation may also broaden the lines. If the modulation is one gauss in amplitude, the sample will see a field of H ± 1 gauss. Lines narrower than 2 gauss will therefore be broadened. This is modulation amplitude broadening.

4. EXPERIMENTAL

4.1. Compounds Investigated

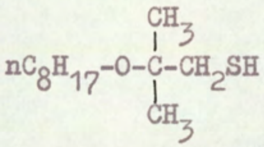
Compounds readily available commercially were purchased, in the purest form available. Their purity was checked using normal spectroscopic and gas-chromatographic techniques.

4.1.1. Aliphatic Thiols

The following materials were purchased:-

Compound	Supplier
Methanethiol	Air Products
Ethanethiol	Koch-Light
n-Propanethiol	"
Isopropanethiol	"
n-Butanethiol	"
Isobutanethiol	"
s-Butanethiol	"
t-Butanethiol	"
2-Propenethiol	"
Trichloromethanethiol	"
Cyclohexanethiol	Hopkins & Williams
Toluene-ω-thiol	"
2-Mercaptoethanol	"

2-Methyl-2-(n-octyloxy)propanethiol



$$nC_8H_{17}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2SH$$

This was prepared using the route outlined below.

1-Chloro-2-methyl-2-propanol (141)

3-chloro-2-methylpropane and 80% sulphuric acid were mixed, with cooling to keep the mixture below 10°C. After stirring, the mixture was poured into ice-water. The product was steam distilled out, and the distillate saturated with salt, causing the organic material to separate. This was collected and re-distilled, the fracting boiling up to 130°C was collected.

1,2-epoxy-2-methylpropane (142)

The chlorocompound prepared as above was added dropwise to a stirred, concentrated aqueous solution of potassium hydroxide. The product distilled out of the mixture. The crude material was distilled, 53-61°C (lit. 57-58°C (142)).

1,2-epithio-2-methylpropane (143)

1,2-epoxy-2-methylpropane was added dropwise, with stirring, to an aqueous solution of potassium thiocyanate. The mixture separated, the top layer was taken and mixed with more aqueous potassium thiocyanate, stirring overnight. The temperature was kept below 40°C. The upper layer was separated, dried over calcium chloride, and distilled, 78-88°C (lit. 84-86°C (143)).

2-Methyl-2-(n-octyloxy)-propanethiol (144)

The sulphide (30g) and n-octanol (78g) were mixed, and 1.0 ml of boron trifluoride complex added. The mixture was heated (steam bath) for twenty hours, then cooled and taken up in ether. The extract was washed with sodium carbonate and sodium chloride solutions, dried, and the ether removed. The material left consisted mainly of n-octanol and the thiol, as shown by ir. and glc. Separation was effected by vacuum distillation, the thiol boiling at 82-94°C/1 torr.

4.1.2. Aliphatic Disulphides

The aliphatic disulphides purchased were:-

Compound	Supplier
Dimethyl disulphide	B.D.H.
Diallyl disulphide	Koch-Light

A small sample of dibenyothiazolyl disulphide and a quantity of tetramethylthiuram disulphide were given by members of the department.

Other aliphatic disulphides were prepared by oxidation of the corresponding thiols (for sources - see section 4.1.1). The method used was as follows:-

0.4 mol of the thiol was dissolved, with stirring, in aqueous sodium hydroxide. The solution was then cooled in an ice bath, and an excess of hydrogen peroxide (Fisons, 30%) was added dropwise over 40 minutes, with stirring. The solution was then made just acid with glacial acetic acid, and extracted with ether (3 x 75 ml). The extracts were combined, dried (Na_2SO_4, anhydrous), and the ether removed. The yellow oil remaining was vacuum distilled, and the colourless product checked for purity by glc on silicone gum columns. For each compound, ir and uv spectra were recorded and compared to those given in the literature. In every case, the purity determined by glc was in excess of 98%.

The disulphides prepared by this method were:-

Compound		b.p./m.p.	lit. value	
Diethyl disulphide	b.p.	56°C/14 torr	46°C/11 torr	(145)
Di-n-propyl disulphide		52°C/3 torr	195°C/760 torr	(146)
Di-isopropyl disulphide		58°C/9 torr	95°C/56 torr	(147)
Di-n-butyl disulphide		102°C/12 torr(i)	116-118°C/20 torr	(148)
Di-isobutyl disulphide		99.5-100.5°C/18 torr(ii)	215°C/760 torr	(149)
Di-s-butyl disulphide		88°C/10 torr	95-7°C/14 torr	(150)
Di-t-butyl disulphide		74°C/10 torr(iii)	73-5°C/10 torr	(151)
Dicyclohexyl disulphide		75°C/4 torr(iv)	288°C/760 torr	(152)
Dibenzyl;disulphide	m.p.	67-69°C(v)	Two forms, m.p. 69-70°C and 70-71°C	(153)

(i) Last two drops of distillate were pink

(ii) Distillate was pale pink, fading (15 minutes) to very pale yellow

(iii) Distilled twice, as low boiling impurity present after first distillation (glc)

(iv) 0.2 mol of thiol used

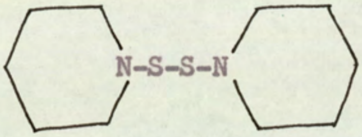
(v) Dibenzyl disulphide was purified by re-crystallising from ethanol, as it is solid at room temperature.

Four disulphides of the dithioamine type were used in this work. They were:-

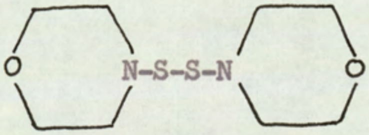
1. N,N'-dithiobis(dibenzylamine)

$$(PhCH_2)_2-N-S-S-N-(PhCH_2)_2$$

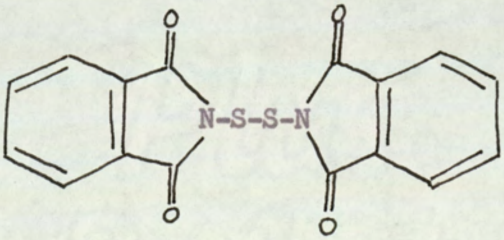
2. N,N'-dithiobis(piperidine)



3. N,N'-dithiobis(morpholine)



4. N,N'-dithiobis(phthalimide)



These compounds were prepared by an undergraduate as part of a final year project (154).

4.1.3. Aliphatic, Aromatic, and mixed Sulphides

Some sulphides were purchased. They were:-

Compound	Supplier
Diethyl sulphide	B.D.H.
Di-n-propyl sulphide	B.D.H.
p-Dithiane	Eastman
Diphenyl sulphide	Hopkins & Williams

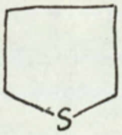
Phenyl isopropyl sulphide was prepared as described in the literature (155). 0.2 mol thiophenol and 0.2 mol potassium hydroxide were dissolved in 50 ml of ethanol. The solution was heated to reflux and 0.2 mol isopropyl bromide was added dropwise. The solution was refluxed for a further 20 minutes, then cooled, water was added, and the solution extracted with ether. The extract was washed with aqueous alkali and water, dried over anhydrous sodium carbonate, and the ether removed. The product was vacuum distilled, 89-90°C/15 torr (lit. 92-94°C/16 torr (156)). It was water-white, and shown by glc to be 99% pure.

Ethyl isopropyl sulphide was prepared similarly from isopropanethiol and ethyl iodide. The product was distilled at 103-107°C (156).

Di-isopropyl sulphide was prepared from isopropanethiol and isopropyl bromide. The product was distilled, 116-122°C (lit. 118-120°C (156)).

Methyl phenyl sulphide was prepared by the reaction between thiophenol and dimethyl sulphate (157). The ester was added slowly to an alkaline solution of the thiol, stirred and cooled in an ice bath. After addition was complete, the mixture was refluxed for two hours, then cooled and ether-extracted. The extract was dried MgSO$_4$), the ether removed, and the product vacuum distilled, 77-79°C/13 torr.

Tetramethylene sulphide



This cyclic sulphide was prepared, using a method described in the literature (158).

The reaction between tetrahydronaphthalene and bromine was used to generate a stream of hydrogen bromide (159). This was bubbled through more tetrahydronaphthalene to remove traces of bromine, and then passed into refluxing tetrahydrofuran until absorption was complete. The product, 1,4-dibromobutane, was taken up in n-hexane, and the solution washed with concentrated sulphuric acid and water, and then dried over calcium chloride. The solvent was removed and the dibromide vacuum distilled, 74-78°C/10.5-11 torr (lit. 76°C/11 torr (158)).

A solution of sodium sulphide nonahydrate (0.4 mol) in water (110 ml) and ethanol (90 ml) was prepared. 100 ml of this was refluxed. The dibromide prepared above (0.27 mol) and the remainder of the sulphide solution were added dropwise to the refluxing solution over 20 minutes. The mixture was refluxed for a further 1½ hours. The product was steam distilled out, and the distillate added to a boiling solution of mercuric chloride in ethanol. Recrystallisation of the mercuric chloride complex to constant melting point (126-127°C, lit. 127-128°C (158)), was followed by decomposition with dilute hydrochloric acid to liberate the cyclic compound, tetramethylene sulphide.

4.1.4. Thiophenol and Derivatives

The following compounds were purchased:-

Compound	Supplier
Thiophenol	Hopkins & Williams
4-Methylthiophenol	"
Toluene-3,4-dithiol	"
2-Methylthiophenol	Aldrich Chemical Co.

Compound	Supplier
3-Methylthiophenol	Aldrich Chemical Co.
2-Mercaptobenzoic acid	B.D.H.
2-Chlorothiophenol	Koch-Light
4-Chlorothiophenol	"
2-Bromothiophenol	"
4-Bromothiophenol	"
Pentafluorothiophenol	"

2,4,6-Tribromothiophenol was prepared by a student as part of an undergraduate project (160).

4-t-Butylthiophenol was prepared by the following series of reactions:-

t-Butyl chloride (161)

t-Butanol and concentrated hydrochloric acid were shaken together. The mixture was allowed to stand, when the halide separated. After washing with aqueous sodium bicarbonate and water, and drying, the product was distilled, 50-52°C (lit. 50-51°C (161)).

4-t-butylphenol (162)

94g phenol and 160g t-butyl chloride were mixed. Anhydrous aluminium chloride (6g) was added and the mixture stirred at 20-30°C. After five hours, the temperature was raised to 65°C and a further 160g t-butyl chloride and 6g aluminium chloride were added. The mixture was stirred for 24 hours. The cooled reaction mixture was then poured onto ice and extracted with ether. The ether layer was washed with water until the washings were neutral, and dried with sodium sulphate. The ether was removed and the resulting dark brown liquid was vacuum distilled. The required product was collected between 92 and 120°C at 10 torr. After re-distilling it was shown by glc to be better than 95% pure. Its ir spectrum was identical to that given for 4-t-butylphenol (163). The material was reserved for use.

Diethylthiocarbamoyl chloride

This was prepared using a method given in the literature (164).

Tetra-ethylthiuram disulphide (0.25 mol) (Robinson Bros.) was melted and poured into a flask fitted with a stirrer, arranged to allow the escape of gas, a gas inlet tube and a thermometer. The flask was placed in a water cooling bath. The molten disulphide was stirred vigorously while chlorine was passed in below the surface. The rate of addition of gas was adjusted to maintain the temperature at 70-75°C. After 6g of chlorine had been absorbed, the temperature was lowered to 50-55°C, and held at this until 18g chlorine had been absorbed. This took about 40 minutes. The stirrer was then replaced with a 6 inch glass-helix packed column and the product vacuum distilled, at 92°C/4 torr (lit. 80-85/1 torr (164)).

O-p-t-butylphenol diethylthiocarbamate was prepared according to the literature (165). p-t-Butylphenol (0.09 mol) prepared earlier was dissolved in 100 ml of dimethylformamide. Sodium hydride (6g of 50% dispersion in oil) was added, and after hydrogen evolution was complete, the mixture was cooled to 10°C, with an ice-bath. Diethylthiocarbamoyl chloride (20g) was added, when the reactants solidified. Slight heating caused reaction to occur, when the temperature was held at 30°C by frequent application of the ice-bath. When the exotherm was complete, the mixture was held at 30-35°C with a water bath for $1\frac{1}{2}$ hours. The products were then poured into water and extracted with benzene-petroleum ether (60-80°C), 2 : 1. The extract was washed with water, 5% aqueous potassium hydroxide and saturated aqueous sodium chloride, then dried with magnesium sulphate. The solvents were removed and the residue distilled, to yield a yellow-orange oil, 154-200°C/3 torr, which slowly solidified.

S-p-t-butylphenol diethylthiocarbamate (165)

The O-p-t-butylphenol diethylthiocarbamate prepared above was heated for 30 minutes at 270°C in a bath of molten potassium nitrate and sodium nitrite (10 : 7) (166). The product was not purified but used for the next reaction:-

4-t-Butylthiophenol (165)

The S-aryl compound prepared above was refluxed under nitrogen with methanol and excess aqueous sodium hydroxide. The solid which separated out was discarded, the solution was neutralised with sulphuric acid and extracted with ether. The combined extracts were washed with water and dried ($MgSO_4$). The ether was removed and the residue, a brown liquid, vacuum distilled. A nitrogen-bleed was used to prevent oxidation. The required product was collected at 98-108°C/6 torr (lit. 102-105°C/7 torr (165)). The ir spectrum of this compound compared well to that given in the DMS index for p-t-butylthiophenol.

3,5-dimethylthiophenol was also prepared, starting from 3,5-dimethylphenol. The O-aryl diethylthiocarbamate was prepared in a manner similar to that described above for O-p-t-butylphenol diethylthiocarbamate. On addition of the diethyl thiocarbamoyl chloride, the temperature rose to 15°C. The ice-bath was removed and the reactants heated to 30-40°C, when the temperature continued to rise, without heat being applied, to 70°C, when cooling was used to maintain this temperature. After pouring into water and extracting with benzene/petroleum ether, the product was distilled under 1 torr pressure at 140-180°C.

This material was pyrolysed at 275°C for 35 minutes to form the S-aryl compound, which was then refluxed with aqueous-alcoholic sodium hydroxide under nitrogen. Neutralisation, extraction with ether, and vacuum distillation, 92-130°C/60 torr, yielded a material having an ir spectrum consistent with 3,5-dimethylthiophenol (lit. value of b.p. 92-100°C/60 torr (167)).

3,5-dimethylthiophenol was also prepared by another route found in the literature (167), as follows:-

Aluminium/mercury couple was prepared as described (168) by shaking aluminium foil with saturated mercuric chloride solution for two minutes. The liquid was decanted and the couple washed with water and ether.

The couple resulting from 0.43g aluminium was placed in refluxing m-xylene (92g), and S_2Cl_2 (20g) was added in portions to maintain reaction at a reasonable rate. When the reaction ceased, a water bath was used to heat the mixture for 1 hour. The brown oil was taken up in ether and washed with water. The sulphur precipitate was separated from the ether layer, which was then dried ($MgSO_4$). The ether was removed and the residue vacuum distilled. A fraction was collected boiling between 88 and 180°C at 40 torr. This was shown by glc to consist of three components, the first being in very low concentration, the second being about 75% of the total. Using preparative glc, a portion of this second fraction was separated out and shown by ir to be 3,5-dimethylthiophenol.

4.1.5. Other Aromatic Thiols

2-Pyridinethiol

This material was prepared, by a series of reactions, from pyridine.

2-Aminopyridine was prepared by the Tschitschibabin reaction from pyridine and sodamide in N,N-dimethylanaline as solvent, the mixture being held at 95°C for 24 hours.

2-Bromopyridine was prepared by a method given in the literature (169) from the 2-aminopyridine prepared above. 160 ml of 48% hydrobromic acid was cooled to 10-20°C, with stirring. 30g of 2-aminopyridine was added over 10 minutes. The temperature of the mixture was then reduced to 0°C and 48 ml bromine was added over 45 minutes. A solution of 55g sodium nitrite in 80 ml water was then added dropwise over 1 hour, the temperature being maintained at 0°C. After stirring for a further 30 minutes, 120g sodium hydroxide in 120 ml water was added, at a rate such that the temperature did not exceed 25°C. The mixture was then extracted with ether (4 x 50 ml) and the extracts combined and dried over 20g dry potassium hydroxide. The solvent was removed and the product distilled 79-85°C/17 torr (lit. 74-75°C/13 torr (169)). The ir spectrum compared well with that published for 2-bromopyridine in the DMS index.

2-Pyridinethiol (170)

Potassium hydrogen sulphide was prepared by passing hydrogen sulphide into 50g potassium hydroxide in 15 ml water, until saturated. The resulting solution was evaporated to dryness, and the white crystalline product dissolved in 125 ml propylene glycol. This solution was heated to 170-175°C while 40g 2-bromopyridine was added at a rate sufficient to promote gentle refluxing. The mixture was heated for 17 hours, with stirring for the last hour. Potassium bromide was filtered off, and washed with ethanol (75 ml). The filtrate and washings were combined and evaporated to dryness under vacuum. The residue was dissolved in 74 ml water, treated with 2.5g charcoal, and the solution, after removing the charcoal, acidified with glacial acetic acid. The product, 2-pyridinethiol, formed as yellow crystals, and was collected, dried, and recrystallized twice from benzene (incurring large losses) m.p. 126-127°C (lit. 128°C (170)). The ir spectrum was identical to that published in D.M.S. Nmr showed the presence of aromatic protons and one other proton, thus indicating that the material was in the form of the thiol, and not the disulphide.

4.1.6.
Aromatic Disulphides

Diphenyl disulphide was purchased (Hopkin & Williams), as was 4,4'-dimethyldiphenyl disulphide (Koch-Light).

Decafluorodiphenyl disulphide was prepared by bromine oxidation of the thiol (Koch-Light) as described in the literature (171). Bromine was added dropwise to a stirred solution of pentafluorothiophenol in glacial acetic acid. When reaction was complete, the acetic acid was removed in vacuum, and the brown gum remaining was triturated with aqueous ethanol, resulting in crystals of the disulphide forming.

4.2. Sample Preparation for Electron Spin Resonance Spectroscopy

4.2.1. Solution in Strongly Acidic Media

In most cases, a few drops of the compound under investigation were added to two to three ml of the concentrated acid. If reaction was vigorous, an ice-salt cooling bath was used. Heating was effected using a direct flame in most cases, but if only gentle warming was required, a water bath was used.

When the solution had been prepared, it was diluted, if necessary, to obtain the desired resolution in the esr spectrum. (Dilution was by addition of concentrated sulphuric acid, not water).

For solutions prepared in inert atmosphere, a nitrogen glove-box was used. Sample tubes having ground glass joints and stoppers were obtained for this work.

4.2.2. uv Photolysis

The source of uv used was a medium intensity mercury vapour lamp.

Irradiation was first attempted via the slots provided in the sample cavity, with the sample in situ in the spectrometer. No esr absorptions were detected after irradiation of diphenyl disulphide (a compound known to give free radicals by photolysis) for two hours, with the sample cooled to liquid nitrogen temperature.

Irradiation of the compound out of the cavity, at room temperature, also failed to give any detectable amount of free radical species.

Successful results were obtained by uv irradiating the sample, outside the cavity, at liquid nitrogen temperature, followed by examination at liquid nitrogen temperature. A diagram of the apparatus used for irradiation is shown in figure 4.2.1. The uv lamp was supplied shielded with a steel case, with a hole in one side to permit the radiation to emerge. This was fitted with a thick glass window, which was found to absorb some uv and so was removed. An identical hole was cut on the opposite side of the case, to extract more uv. Front-aluminised concave mirrors* were positioned in front of each of the holes, at a distance of the radius of curvature from the centre of the source, and set to focus the uv at the side of the source, just outside the lamp case. The sample was placed at this point. Focusing was tested using a piece of filter paper with a spot of a solution of anthracene, which fluoresces in uv light.

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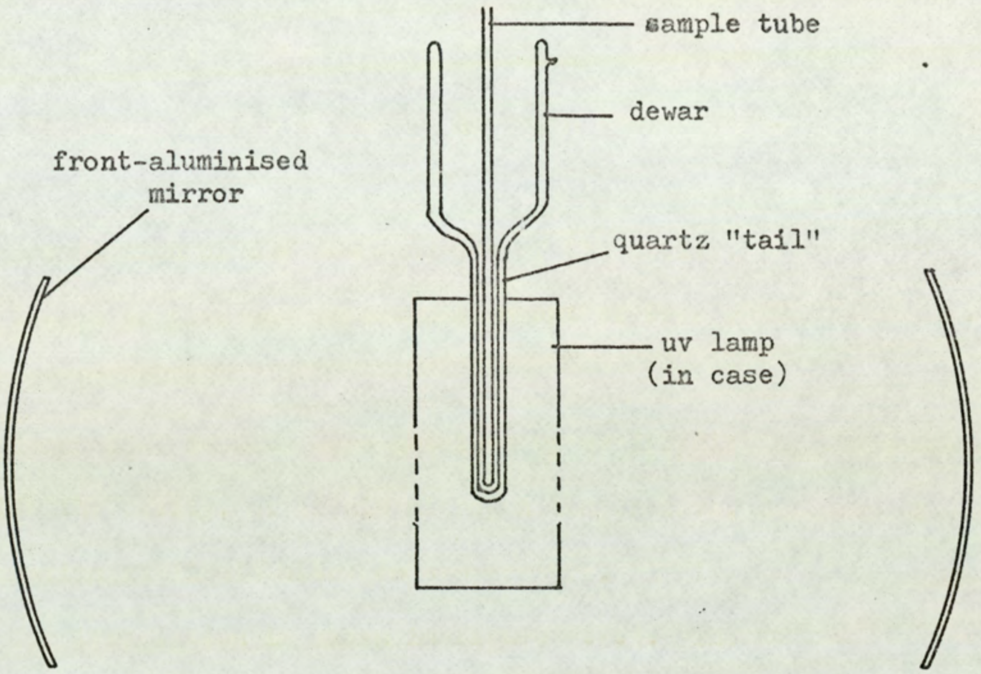
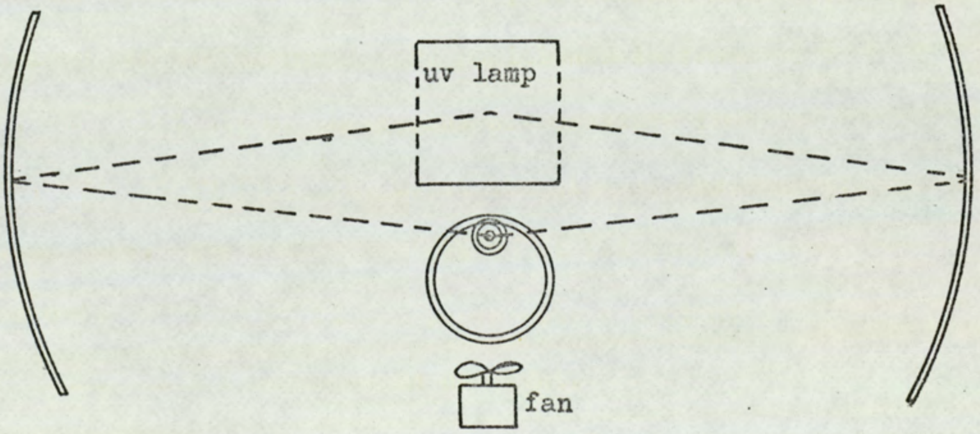
* These mirrors were prepared by evaporating a thin film of aluminium onto watch glasses of suitable curvature. This was carried out by the Department of Physics.



front view without fan



top view

Figure 4.2.1. Ultraviolet photolysis apparatus (enclosure not shown).

The sample was contained in a quartz tube, approximately 3 mm o.d., which was immersed in a dewar containing liquid nitrogen. This dewar, supplied by Hilger and Watts Ltd., had an unsilvered quartz "tail" in which the sample tube rested.

Before irradiation, the compounds were de-gassed to remove dissolved oxygen, which is known to broaden the hyperfine lines and so degrade resolution (172, 173, 174). This was accomplished by connecting the sample tube, containing the material to be irradiated, by its B10 ground glass joint via a tap unit to a simple vacuum manifold, evacuated by a single stage rotary pump. The "freeze-thaw" technique (175) was used to de-gas the material. The sample was frozen by raising a dewar of liquid nitrogen to surround the lower part of the sample tube, and then the tap was opened to the vacuum manifold. After pressure equalization, the sample was isolated from the vacuum system and allowed to thaw, when dissolved gasses could be seen forming bubbles in the liquid before leaving it. The cycle was repeated until no bubbles were observed on thawing, and then twice more. The manifold and sample tube, with the sample frozen, were then filled with oxygen-free nitrogen and the tap between sample tube and manifold closed. The presence of a slight positive pressure of nitrogen in the tube helps to prevent the diffusion of oxygen into the tube.

The sample tube and tap unit were then transferred to the irradiation apparatus, and the uv lamp switched on for the required period - usually 1 hour. During this time, a small fan was used to blow a stream of air at the dewar tail. This prevented moisture accumulating on the quartz surface, and also prevented heat from the lamp being transferred to the dewar.

After irradiation, the sample tube, with the still sealed tap unit, was transferred to an identical dewar, also full of liquid nitrogen. During the transfer, a stream of liquid nitrogen was poured over the sample tube. It has been estimated (176) that a rise of a few degrees at most occurs in the sample temperature. This second dewar was then taken to the esr apparatus and the tail inserted into the sample cavity. The equipment was set-up and tuned, and signals recorded.

The dewar used for irradiation was not used for examination in the spectrometer due to the presence in it of F centres, electrons trapped in negative ion vacancies, caused by the radiation (177). These gave rise to a large absorption in the esr spectrum close to $g = 2$ and overlapped the signal from the sample. These F centres were not detected in the sample tubes themselves, as these were made of very high purity quartz ("spectrosil" grade), which is less susceptible to this effect. The sample tubes were also taken to red heat after cleaning, before re-use, destroying any F centres present.

During examination of the sample in the spectrometer, water was found to condense on the tail of the dewar. Water has a dipole moment (electric) and absorbs microwave energy by interaction with the electric component. This absorption reduces the effective Q value of the cavity and thus reduces the signal size. The accumulation of water also alters the natural resonant frequency of the cavity. This causes the instrument to go "off-tune" and the signal then observed has a component due to the dispersion mode instead of being due to pure absorption, leading to a spectrum of unbalanced appearance, and giving errors in g values. This condensation was prevented by passing a stream of dried nitrogen over the dewar. The gas was admitted at the bottom of the cavity, and allowed to escape through the irradiation slits in the cavity side and also past the dewar out of the top of the cavity.

4.3. The Spectrometer

4.3.1. A Description of the Instrument

The Electron Spin Resonance Spectrometer used in this work was a commercially available one, the "Microspin", manufactured by Hilger & Watts Ltd. This is an instrument using high frequency modulation and phase sensitive detection. This is also known as homodyne detection, and involves modulating the magnetic field at high frequency (usually 100 kHz), with an amplitude small compared with the line width, and then sweeping slowly through the resonant condition.

A block diagram of the apparatus is given in figure 4.3.1.

The spectrometer is shown using a reflection type cavity.

Energy is fed into the hybrid tee bridge from the klystron and is split equally between the side arms. One arm feeds the resonant cavity, the other has components which reflect back a reference wave, adjustable in amplitude and phase. These two reflected waves are detected in the fourth arm of the tee. In the off-resonant condition, the reference wave is adjusted such that it is equal in amplitude but opposite in phase to the reflection from the sample cavity, and therefore cancels, with zero power being transmitted to the crystal detector in

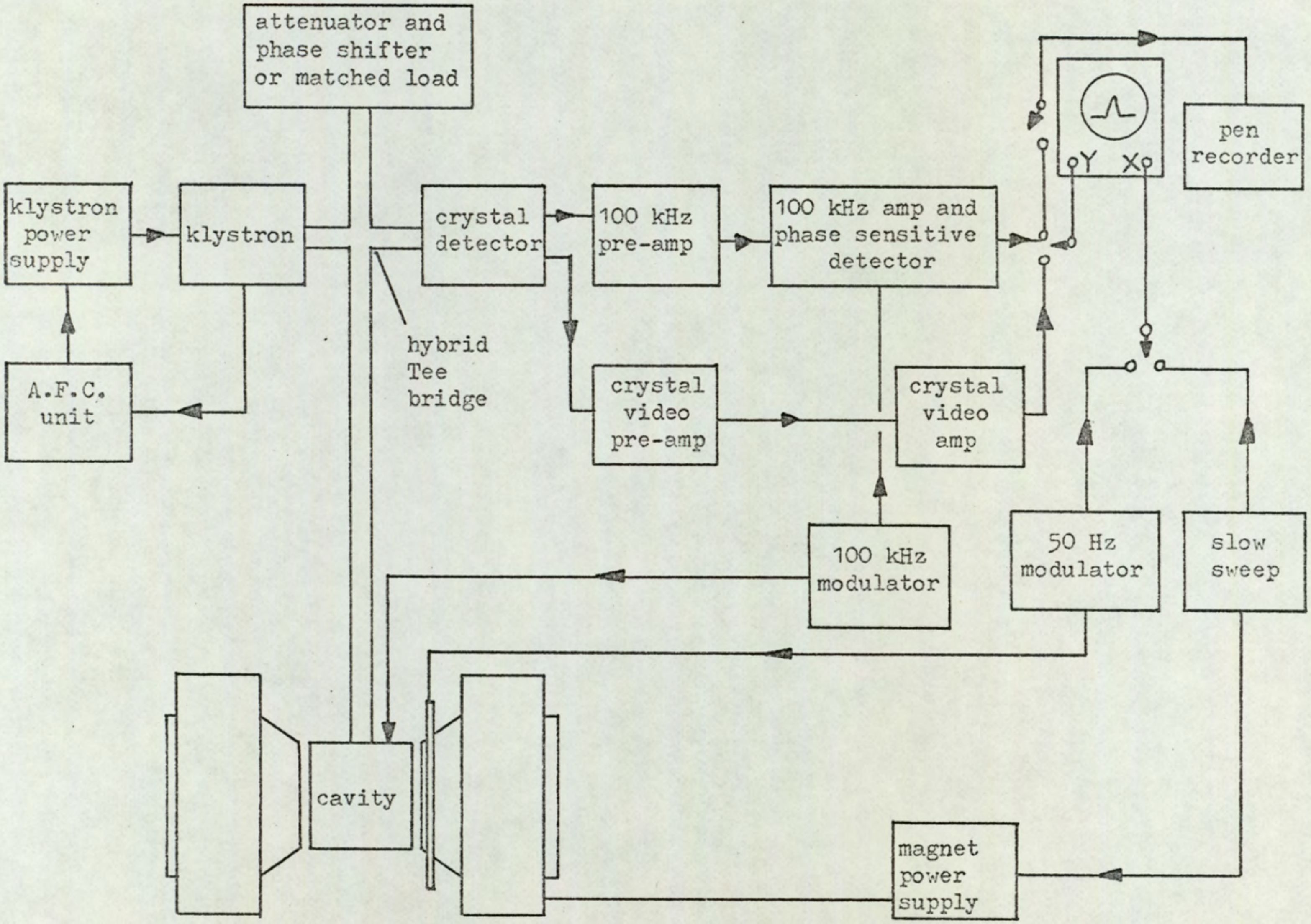


Figure 4.3.1 Block diagram of high frequency modulation spectrometer.

the fourth arm. At resonance, an off-balance signal is detected.

A modulation coil is positioned either inside or outside of the cavity wall. It modulates the steady magnetic field of the sample at the modulation frequency. Any absorption or dispersion due to resonance in the specimen changes the reflection coefficient of the cavity and thus unbalances the bridge. The crystal detects the resulting high frequency signal - 100 kHz - which passes through a low noise pre-amplifier and a narrow band amplifier to the phase sensitive detector, which is also fed with a reference signal of adjustable phase relative to the modulation. The 100 kHz modulator supplies the modulation coils and also a reference output for the phase sensitive detector.

The signal is then displayed on a meter, a crt or by a chart recorder.

In practice, the best signal-to-noise ratio is obtained by working higher up the slope of the crystal characteristic, and the reference arm is allowed, under off-resonance conditions, to reflect back a small amount of signal, so that the crystal works at its optimum point. The slight unbalance also allows absorption and dispersion signals to be separated. A perfectly balanced bridge detects changes in both absorption and dispersion. Unbalance in amplitude allows only absorption changes to be detected, whilst changes in dispersion are detected if the unbalance is only in phase.

For most of the work reported here, an additional piece of equipment was used, the "AFC Accessory", which enabled the klystron frequency to be locked to the sample cavity as reference instead of to the separate reference cavity.

All the work was carried out using X-band radiation, approximately 3cm wavelength, 9GHz frequency.

Cavities

H_{011} mode cylindrical cavity

This cavity was used for most of the work. The magnetic and electric field configuration is shown in figure 4.3.2.

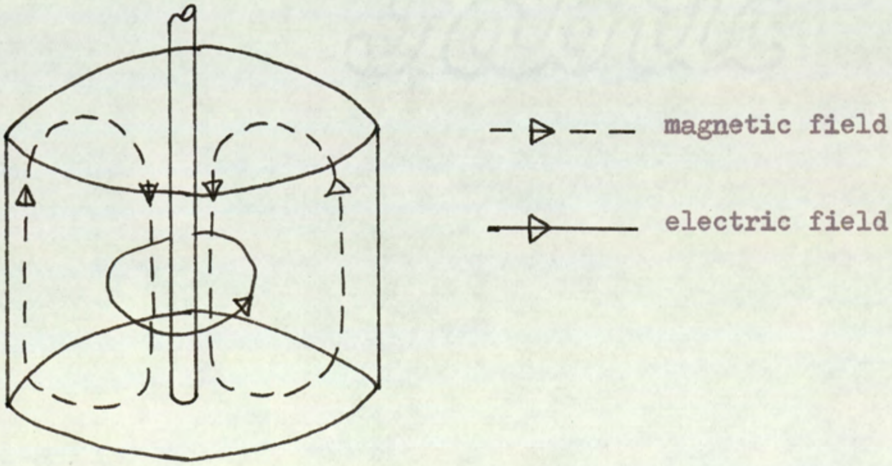


Figure 4.3.2. H_{011} mode cavity showing field configuration

The maximum microwave field is along the central vertical axis. A disadvantage of this cavity is that it must be 4cm in diameter to support the 3.2cm wavelength H_{011} mode. It is, however, very suitable for low temperature work, when a dewar may be inserted down the centre of the cavity.

This cavity has a high Q value, approximately 8000 (loaded), and therefore leads to a sensitive system. If a lossy material such as water, is introduced into the cavity, absorption of the microwave energy occurs by the electric dipole of water, causing a drastic reduction in Q.

This may be minimised by using a very narrow sample tube located accurately along the central axis of the cavity.

$H_{0,1,10}$ mode rectangular cavity

This was designed for use with lossy samples.

The H_{01} mode in a rectangular cavity has the field configuration as in figure 4.3.3.

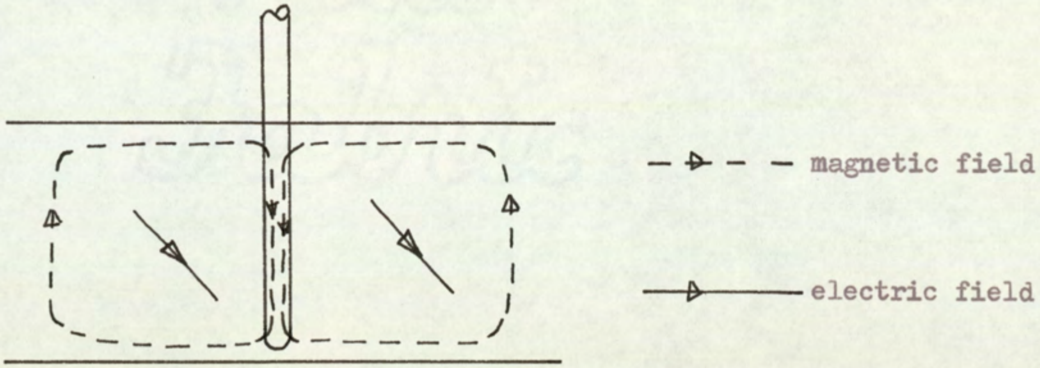


Figure 4.3.3. H_{01} mode rectangular cavity showing field configuration

This shows two complete mode patterns, and would be the H_{012} mode if it completely filled the cavity. Obviously, if the $H_{0,1,10}$ mode is used, there is much less microwave electric field, and thus the effect of the lossy sample is reduced. The filling factor is, however, drastically reduced, and it was found that larger signals could be obtained with a small sample in the cylindrical H_{011} cavity than by using the rectangular $H_{0,1,10}$ cavity. The Q factor for the $H_{0,1,10}$ cavity is about 600 for a water sample.

4.3.2. Spectrometer Operation

The instrument was set up in one of two ways, as instructed by the manufacturers.

A. The natural resonant frequency of the sample cavity and the frequency of the klystron output were adjusted to be the same value. The resonant frequency of the reference cavity built into the klystron generator was then adjusted to coincide with that of the sample cavity. The klystron was then "locked" onto the reference cavity, the automatic frequency control (AFC) unit ensuring that it remained so.

A disadvantage of this method of operation is that the system is only stable until the resonant frequency of the sample cavity changes. If this occurs, the size of the detected signal decreases rapidly, if not totally vanishing, and the spectrometer goes "off-tune", becoming very noisy electronically. The sample cavity may change frequency for several reasons. The sample may increase in temperature by absorbing microwave power, transmitting heat to the cavity. If a dewar is used in the cavity, bubbling of the coolant continually alters the resonant frequency. A large temperature difference between sample and reference cavities also causes instability.

An alternative, and usually preferable method of operation, dispenses with the reference cavity. This is the method used for almost all of the work reported herein:-

B. The frequency of the klystron and the natural resonance frequency of the sample cavity were adjusted to be the same, and the klystron frequency was then locked to the sample cavity frequency by an AFC unit. Changes in sample cavity frequency were then followed by the klystron, the instrument remaining "on tune" (assuming changes in sample cavity frequency were small). This enabled the spectrometer to be used with a dewar in the cavity, and also to be set up and used for several hours without retuning. Samples were often changed without necessitating more than very minor adjustment of the spectrometer, enabling comparisons between different samples to be carried out.

The absorption of microwave energy was detected using phase-sensitive detection with a 100 kHz modulation current, and the first derivative signal thus obtained displayed on an oscilloscope. The magnitude of the modulation current, and thus the amplitude of the modulating field, was made small enough to minimise lack of resolution by modulation current broadening (see section 3.5.5), and the scan speed and amplitude set to display the signal. A permanent recording was made by a chart recorder.

Complete operating instructions are given in Appendix 1.

4.3.3. Use of Derivative of Absorption

The reason why the derivative of the absorption line is used is an experimental one. The amount of the supplied microwave power absorbed by the sample is only a small fraction, necessitating amplification of the signal. If the dc output from the microwave detector were amplified, it would be difficult to detect the small change in the dc level the absorption would make. If, instead, a small oscillating magnetic field is superimposed onto the large applied field, a process referred to as modulation of the applied field, this small field alternately adds to and subtracts from the large field, H_o.

As the resultant $H_o + H_{modulation}$ swings up and down, the dc output also increases and decreases. This therefore supplies an ac signal which may be amplified, and is not a small alteration of a large signal level, but is zero when the sample is not absorbing microwave power. This process is illustrated diagramatically in figure 4.3.4.

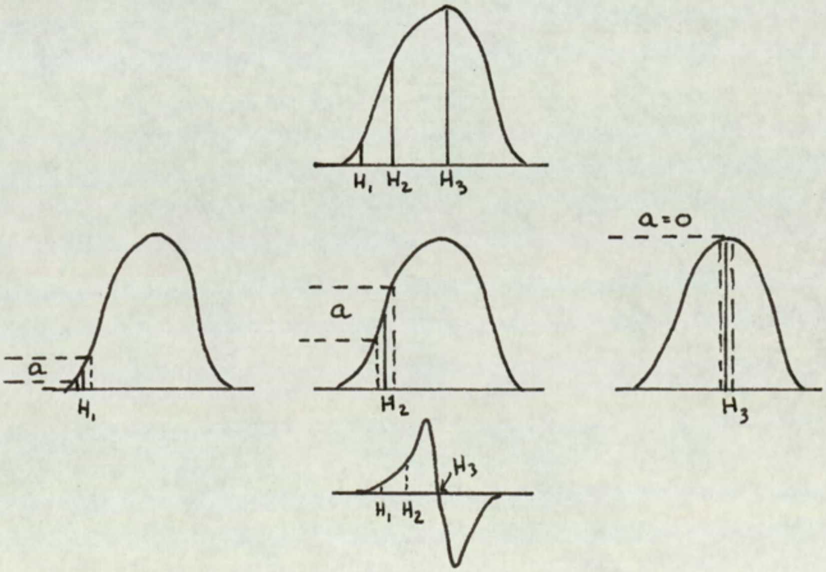


Figure 4.3.4.

4.3.4. Measurement of g values and hyperfine splitting constants

The g value or spectroscopic splitting constant of a paramagnetic species is defined by the equation

$$h\nu = g\beta H$$

where:- h = Plank's constant

ν = frequency of absorbed radiation

β = Bohr magneton (converts angular momentum to magnetic moment)

H = external magnetic field

h and β are known constants, and it is usual for practical reasons, to hold ν constant and sweep the magnetic field over the resonance positions. Thus,

$$gH = \frac{h\nu}{\beta} = \text{constant}$$

Thus, if the frequency ν and the magnetic field H are measured, g may be calculated. It was, however, found that the measurement of frequency was subject to errors. Several determinations using the micrometer-screw frequency meter were needed, the results being averaged. Consistent g values were not obtained from different measurements on the same sample. It was therefore decided to follow the general practice and measure g values relative to a standard.

If two paramagnetic species with differing g values are present in a sample, two resonance absorptions will be found, one for each sample, at different values of magnetic field strength. As h and β are constants, and ν is held constant

$$H_1 g_1 = \frac{h\nu}{\beta} = H_2 g_2$$

(where H_1 and g_1 are the magnetic field at resonance, and the g value for free radical 1).

If the magnetic field strengths H_1 and H_2 are measured, and g_1 is known, g_2 can be calculated.

The standard chosen was diphenylpicrylhydrazyl, DPPH. The g value of this stable free radical has been measured many times, and is accurately known. The value used in this work was 2.0036 (178).

The spectrum of the unknown free radical was recorded, then a small amount of the standard added and the resultant combined spectrum recorded. The magnetic field corresponding to the resonance absorption of the standard was then determined, using the proton resonance method. A probe consisting of a small tube, containing water, and surrounded by a copper coil, was inserted into the magnetic field as close as possible to the sample position. An rf signal was supplied to the coil, the frequency of the rf being adjusted until the nuclear magnetic resonance absorption of the protons occurred at the same magnetic field strength as the electron spin resonance absorption of the DPPH standard, the two absorptions being displayed together on the crt, the spectrometer being used in the crystal video mode. The frequency of the rf was measured (for details see Appendix 2) and converted, using tables* to give the magnetic field strength.

It was necessary to display the absorption signal of the DPPH standard, not the derivative signal usually used. The detection system for the former is much less sensitive than for the latter, putting a lower limit on the amount of DPPH which could be used. Although the absorption of DPPH occurred at a different magnetic field value to that of the unknown, they were usually separated by less than 20 gauss. It was thus necessary to make the DPPH sample small enough to avoid the loss of the unknown signal in the wings of the DPPH line. It was found most satisfactory to use a mixture of finely ground DPPH and talc. Several such mixtures were prepared, containing concentrations of DPPH varying from one part in 10 to one in 10,000 (by weight). The one used was chosen on consideration of the size of the unknown signal.

The DPPH was added to solutions by placing a small amount of DPPH/talc mixture in a melting point tube, and dropping this into

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* The tables in "Introduction to Electron Spin Resonance" H.M. Assenheim, Hilger & Watts Ltd. 1966, were used.

the solution. This was found not to de-tune the spectrometer. For the free radicals produced by photolysis, the standard could not be added by this method as the sample tube was sealed from the atmosphere. Also, the material was frozen, preventing the standard from reaching the bottom of the tube. For these samples, the DPPH/talc mixture was again placed in a melting point tube, but the tube was sealed and broken just above the powder, giving a small glass bead containing the standard. This was dropped into the Dewar, and allowed to fall to the bottom of the inner tube, at the sample position. The very small size and heat capacity of this bead allowed it to be cooled very quickly, and it did not give rise to undue bubbling with resulting instability of the spectrometer.

The magnetic field strength at the resonance position of the unknown free radical was determined from that measured for the DPPH absorption and the separation between the two signals, which was found from a calibration of the recorder chart. This calibration was carried out using Fremy's salt, potassium peroxylamine disulphonate. When dissolved in water, this yellow compound yields the purple paramagnetic ion $O\dot{N}(SO_3)_2^{2-}$ which has three hyperfine components, due to interaction of the odd electron with the nitrogen nucleus. The hyperfine splitting has been accurately measured as 13.07 gauss (179). Solutions in saturated aqueous sodium bicarbonate are more stable than in water, and were used for the calibration. Although water causes large losses when used in the cylindrical-type cavity used for most of this work, it was found to be satisfactory if a very small amount (approximately 0.025 ml) of solution was used. The spectrum was recorded at all combinations of sweep amplitude and rate used for recording the unknown spectra, ranging from 20 gauss/20 minutes to 500 gauss/5 minutes. This calibration was checked periodically, but was found to remain reasonably constant as long as the reference battery in the magnet control unit was performing correctly.

Using this calibration, hyperfine splittings were easily determined from the recorded spectra.

5. RESULTS

5.1. Formation of Free Radicals by Photolysis

The compounds studied were irradiated with uv light as described in section 4.2.2. All irradiations and observations were carried out with samples cooled to liquid nitrogen temperature, unless otherwise indicated.

A series of alkyl mercaptans and disulphides were irradiated to produce free radical species. Most of these gave esr spectra which were interpreted as arising from a species with three asymmetric g values. The g values were measured, according to the method of F.K. Kneubuhl (121) for polycrystalline materials, and are tabulated below (Table 5.1). The spectra are shown (figures 5.1.1. to 5.1.14).

Compounds giving spectra not capable of analysis by this method, and some miscellaneous compounds, are described later.

All compounds developed a yellow colouration on irradiation, except methyl disulphide, which turned pink. On warming, the colour and esr signal were destroyed before the material liquified.

Table 5.1

Alkyl group	Thiol				Disulphide			
	g_1	g_2	g_3	figure	g_1	g_2	g_3	figure
methyl	-	-	-		2.0597	2.0232	1.9990	5.1.10
ethyl	2.0576	2.0248	2.0003	5.1.1	-	see below	-	
n-propyl	2.0546	2.0231	2.0012	5.1.2	2.0655	2.0301	2.0048	5.1.11
isopropyl	2.0596	2.0275	2.0023	5.1.3	-	see below	-	
n-butyl	2.0536	2.0241	2.0022	5.1.4	2.0652	2.0319	2.0062	5.1.12
isobutyl	2.0576	2.0232	2.0022	5.1.5	-	see below	-	
s-butyl	2.0536	2.0234	2.0006	5.1.6	2.0507	2.0168	1.9919	5.1.13
t-butyl	2.0585	2.0250	2.0010	5.1.7	2.0520	2.0148	1.9916	5.1.14
2-propenyl	2.0230	2.0084	1.9940	5.1.8	-	-	-	
cyclohexyl	2.0441	2.0200	2.0012	5.1.9	-	-	-	

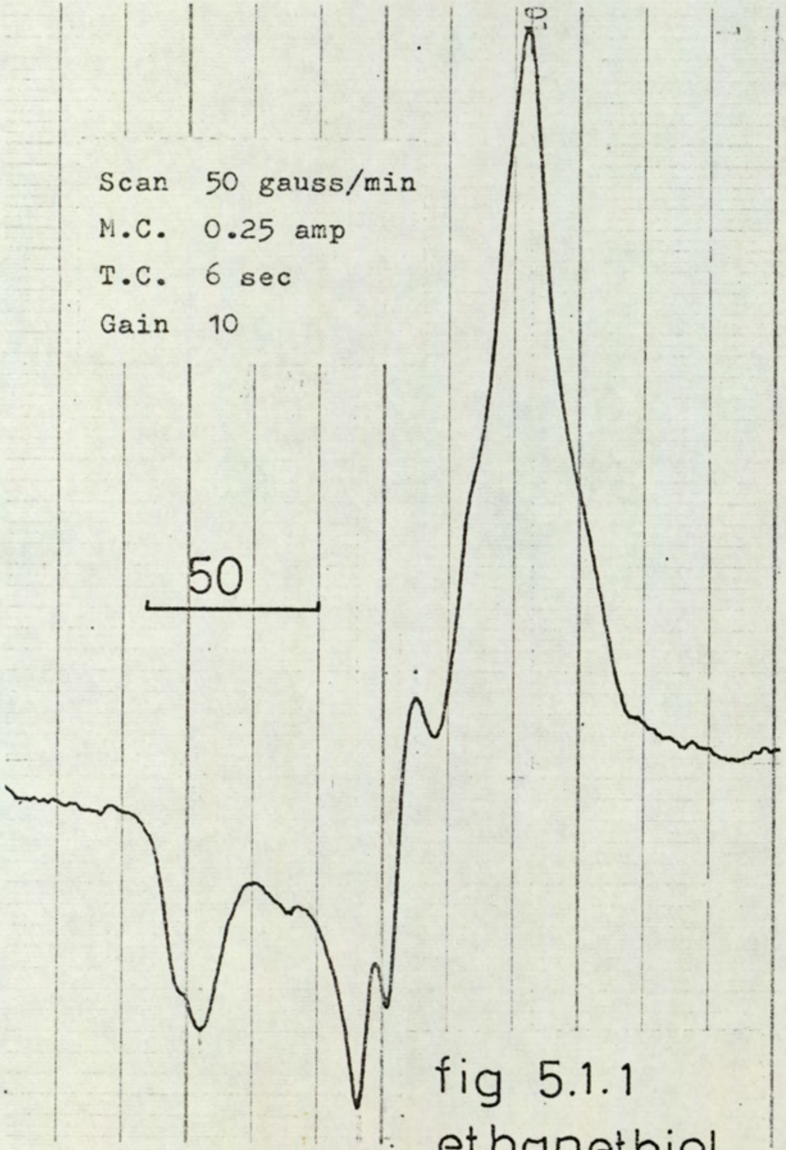


fig 5.1.1
ethanethiol

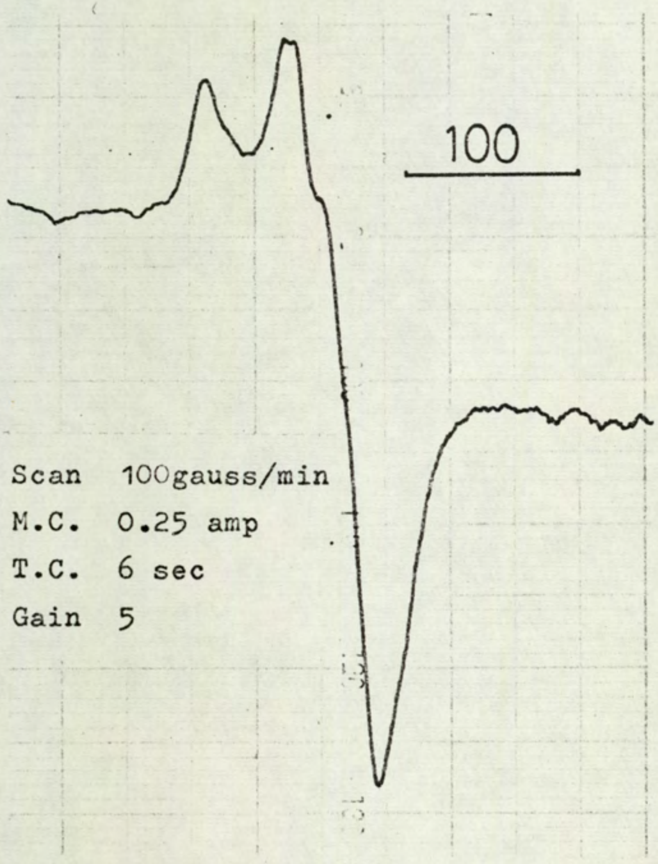


fig 5.1.2
propanethiol

Scan 50 gauss/min
M.C. 0.25 amp
T.C. 3 sec
Gain 1.25

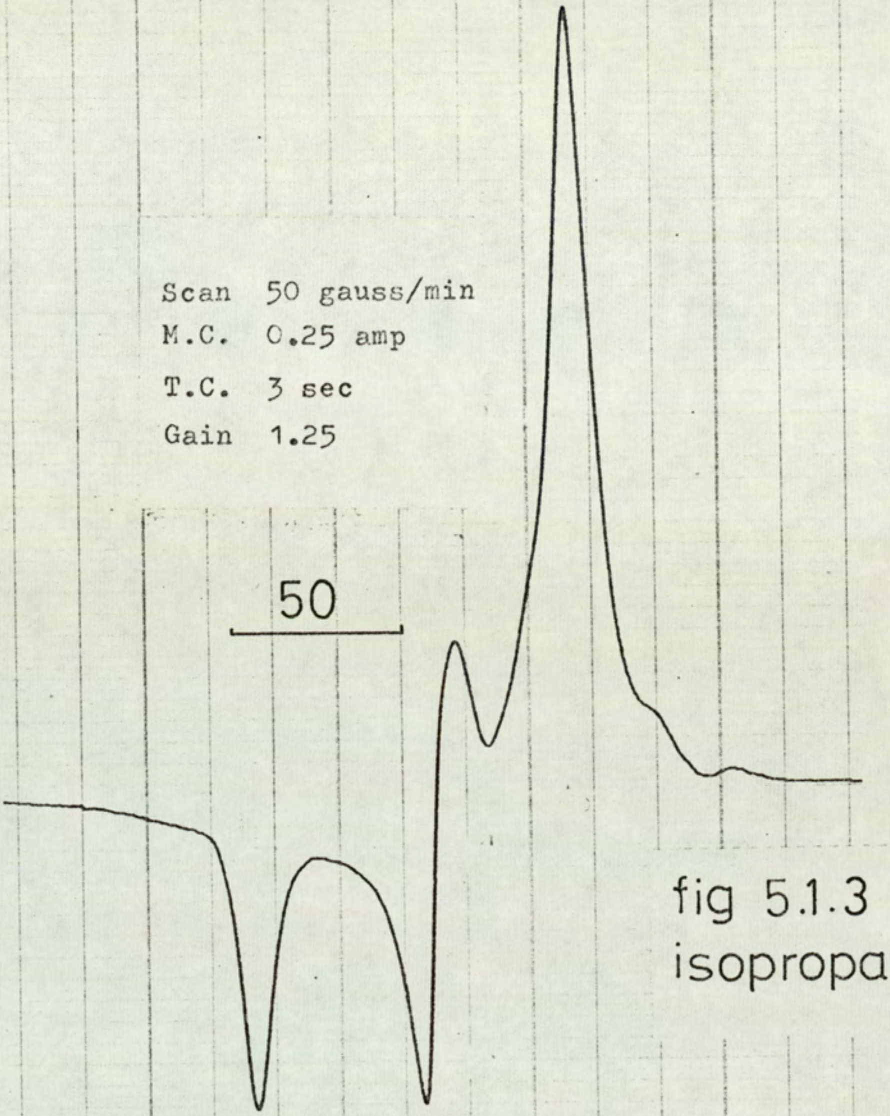
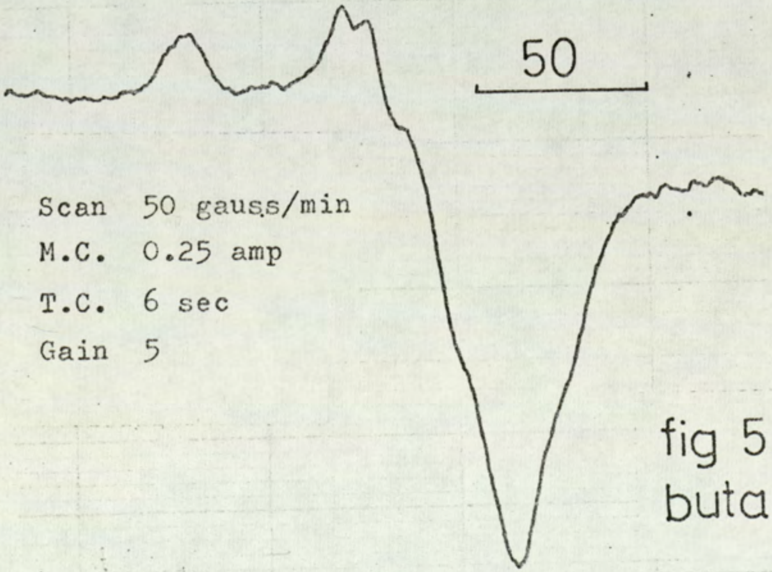


fig 5.1.3
isopropanethiol



Scan 50 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 5

fig 5.1.4
butanethiol

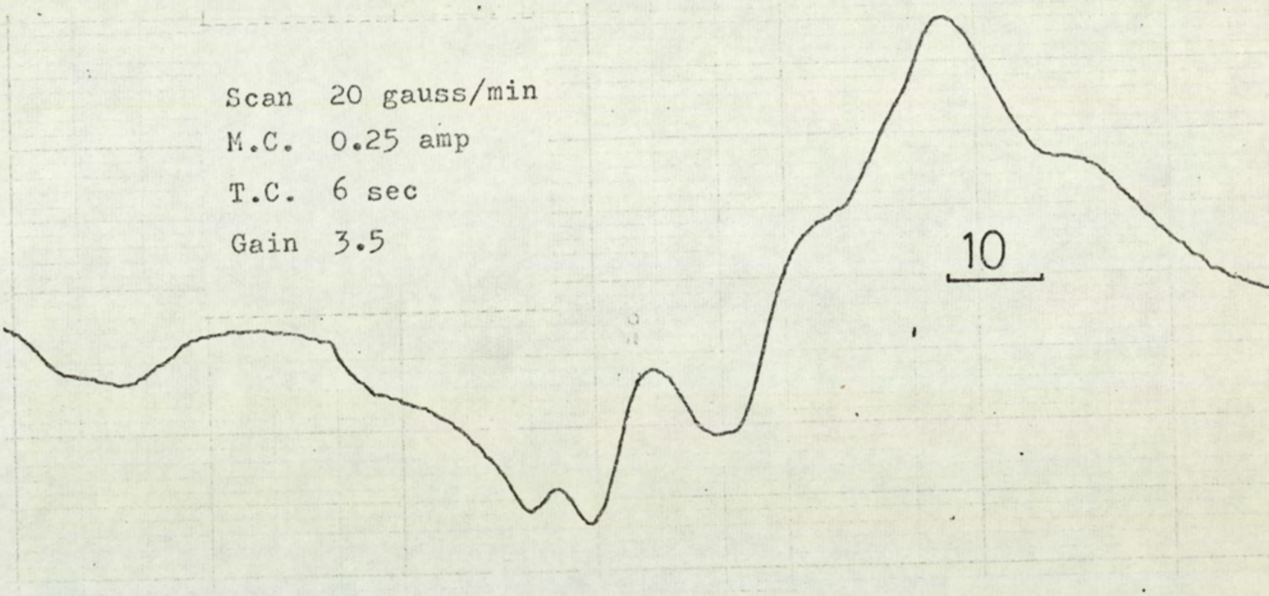


fig 5.1.5
isobutanethiol

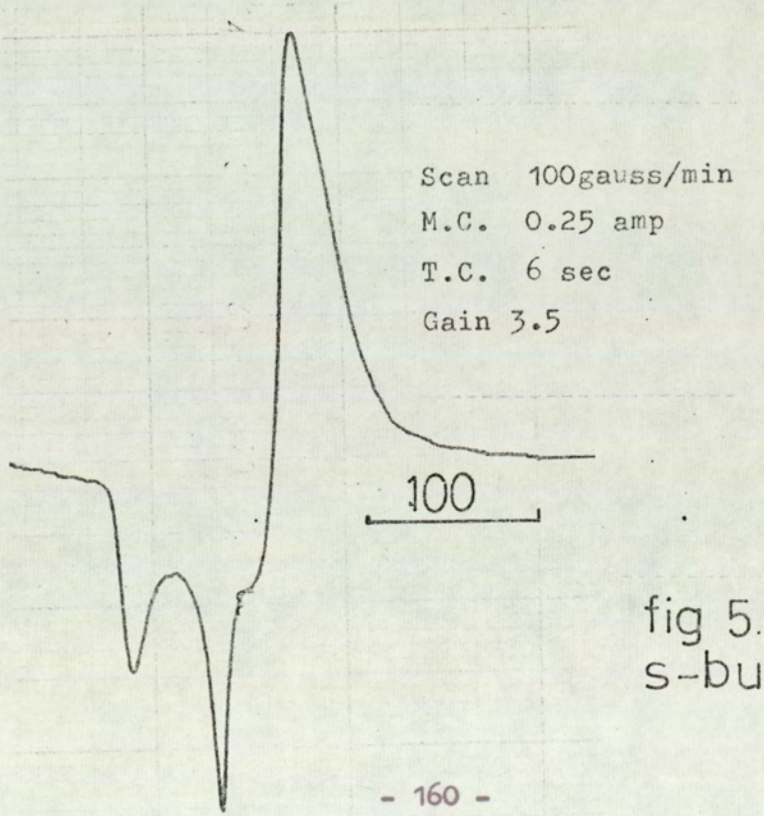
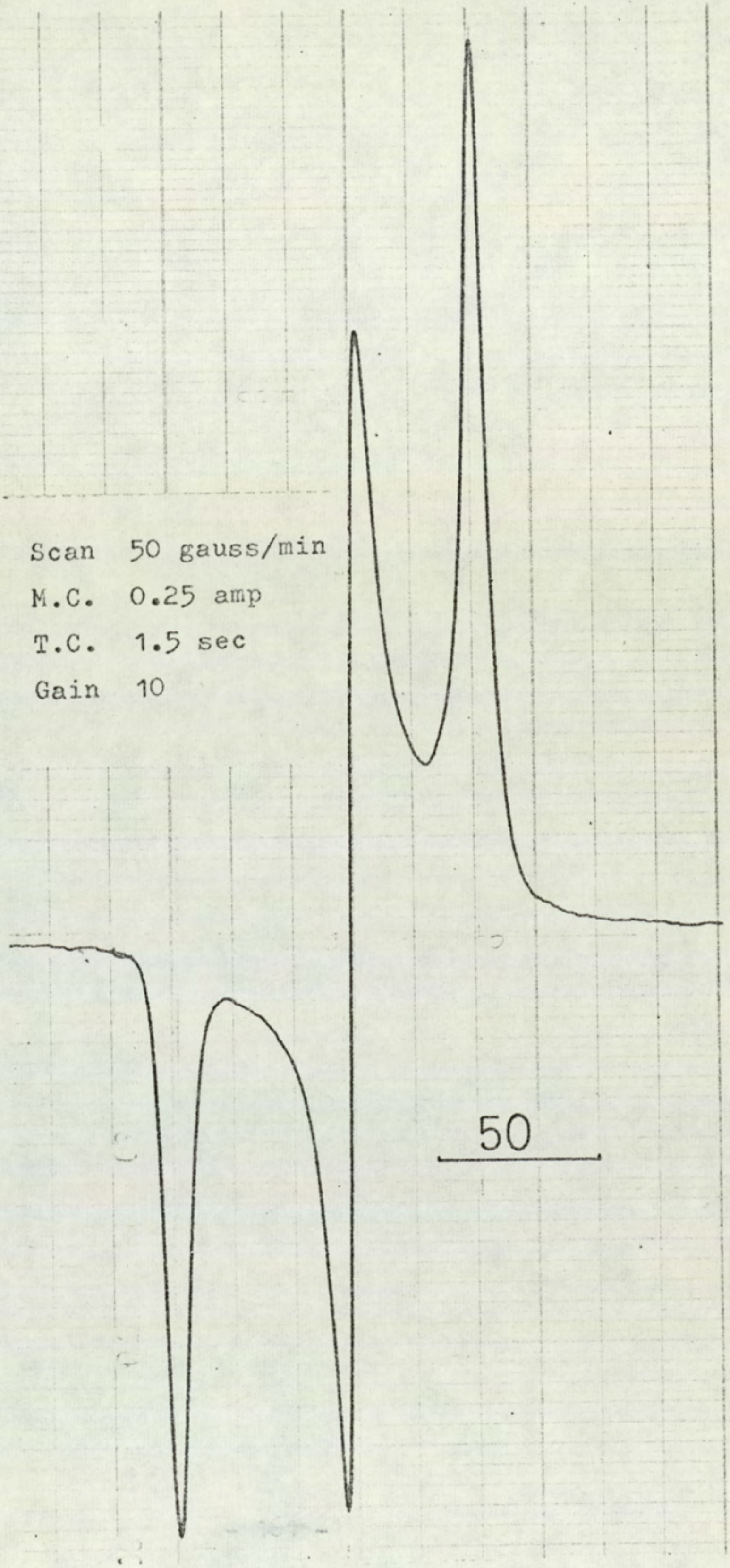
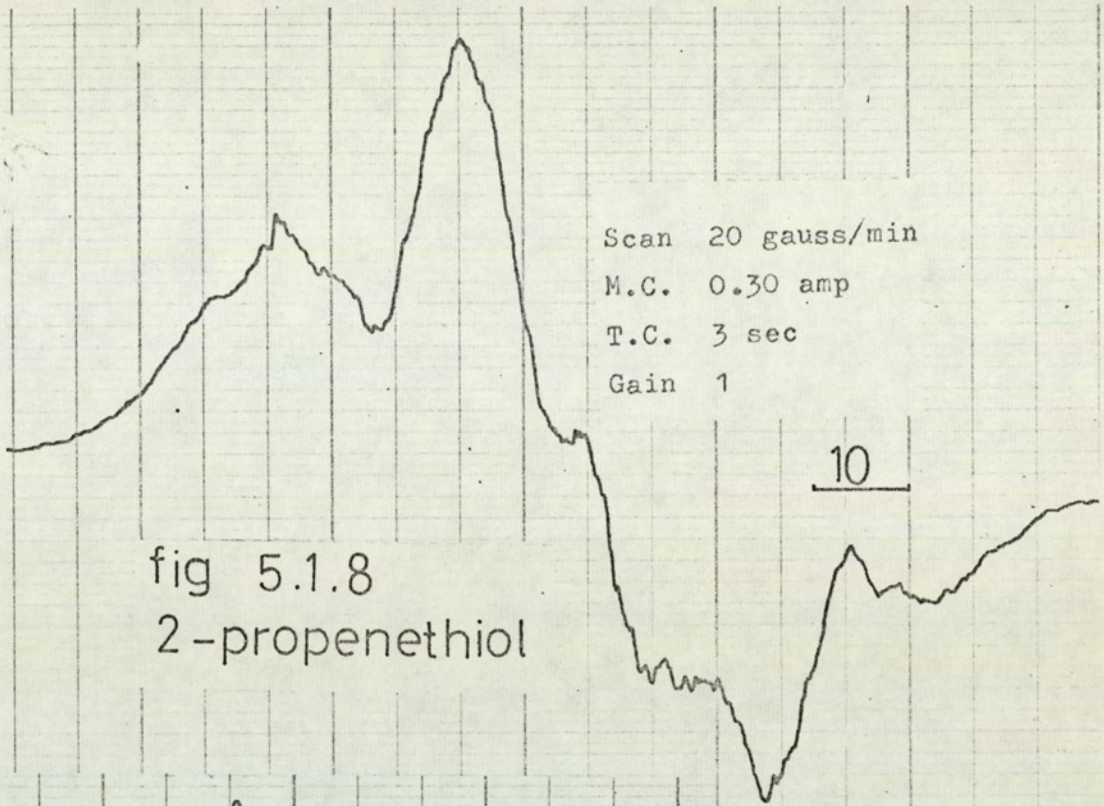


fig 5.1.6
s-butanethiol



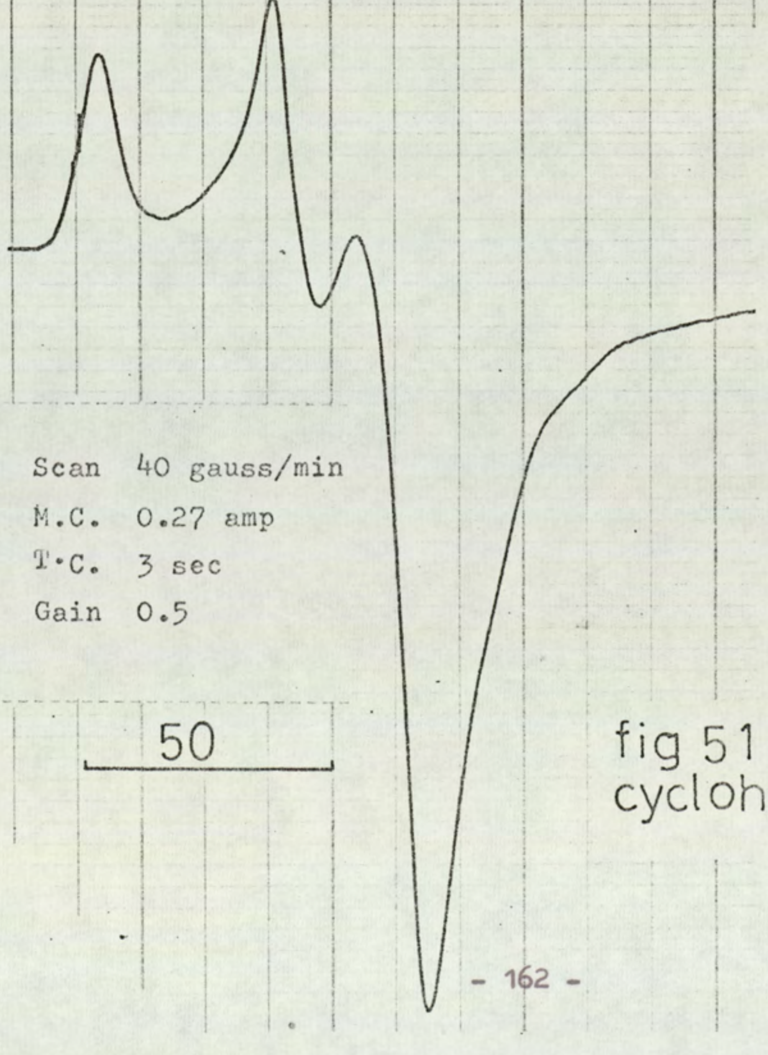
Scan 50 gauss/min
M.C. 0.25 amp
T.C. 1.5 sec
Gain 10

fig 5.1.7
t-butanethiol



Scan 20 gauss/min
M.C. 0.30 amp
T.C. 3 sec
Gain 1

fig 5.1.8
2-propenethiol



Scan 40 gauss/min
M.C. 0.27 amp
T.C. 3 sec
Gain 0.5

fig 51 9
cyclohexanethiol

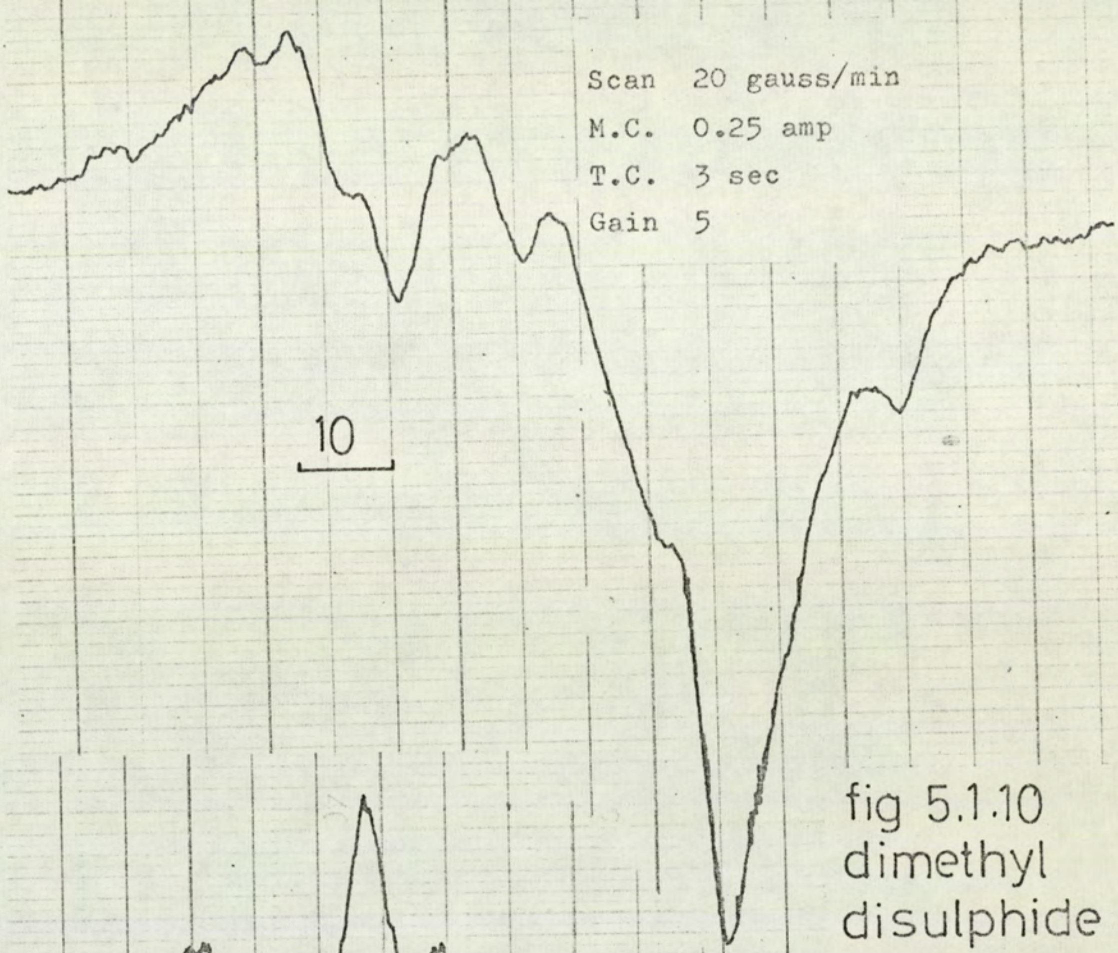


fig 5.1.10
dimethyl
disulphide

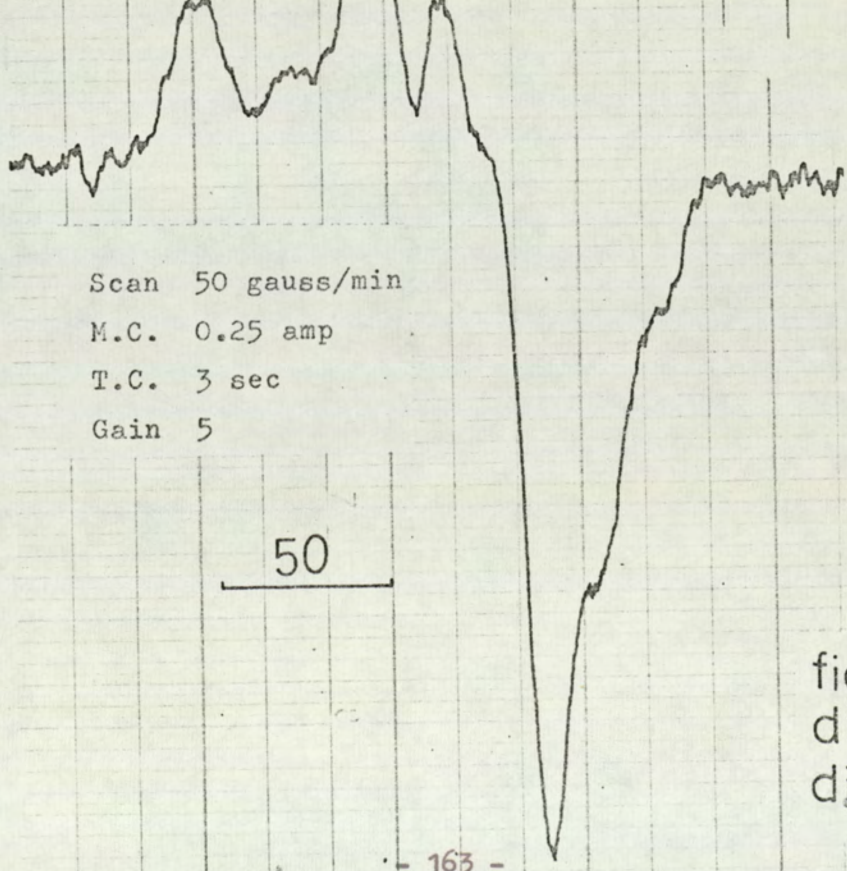
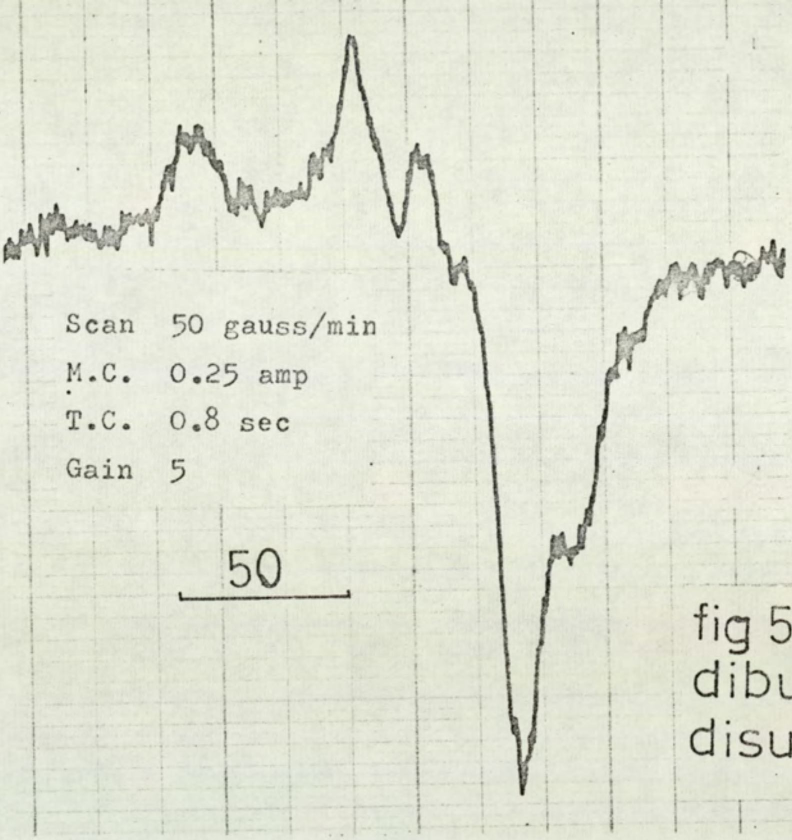
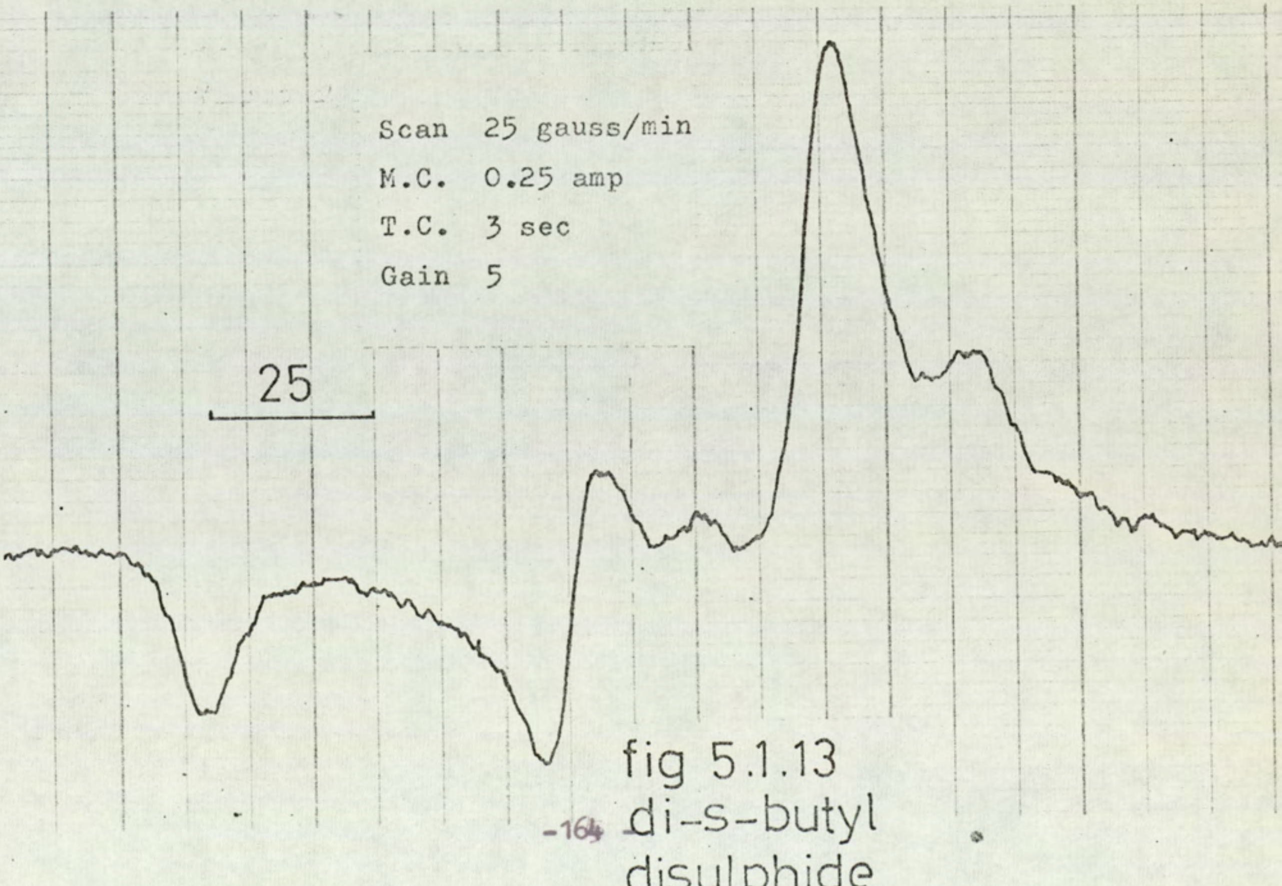


fig 5.1.11
dipropyl
disulphide



Scan 50 gauss/min
M.C. 0.25 amp
T.C. 0.8 sec
Gain 5

fig 5.1.12
dibutyl
disulphide



Scan 25 gauss/min
M.C. 0.25 amp
T.C. 3 sec
Gain 5

fig 5.1.13
di-s-butyl
disulphide

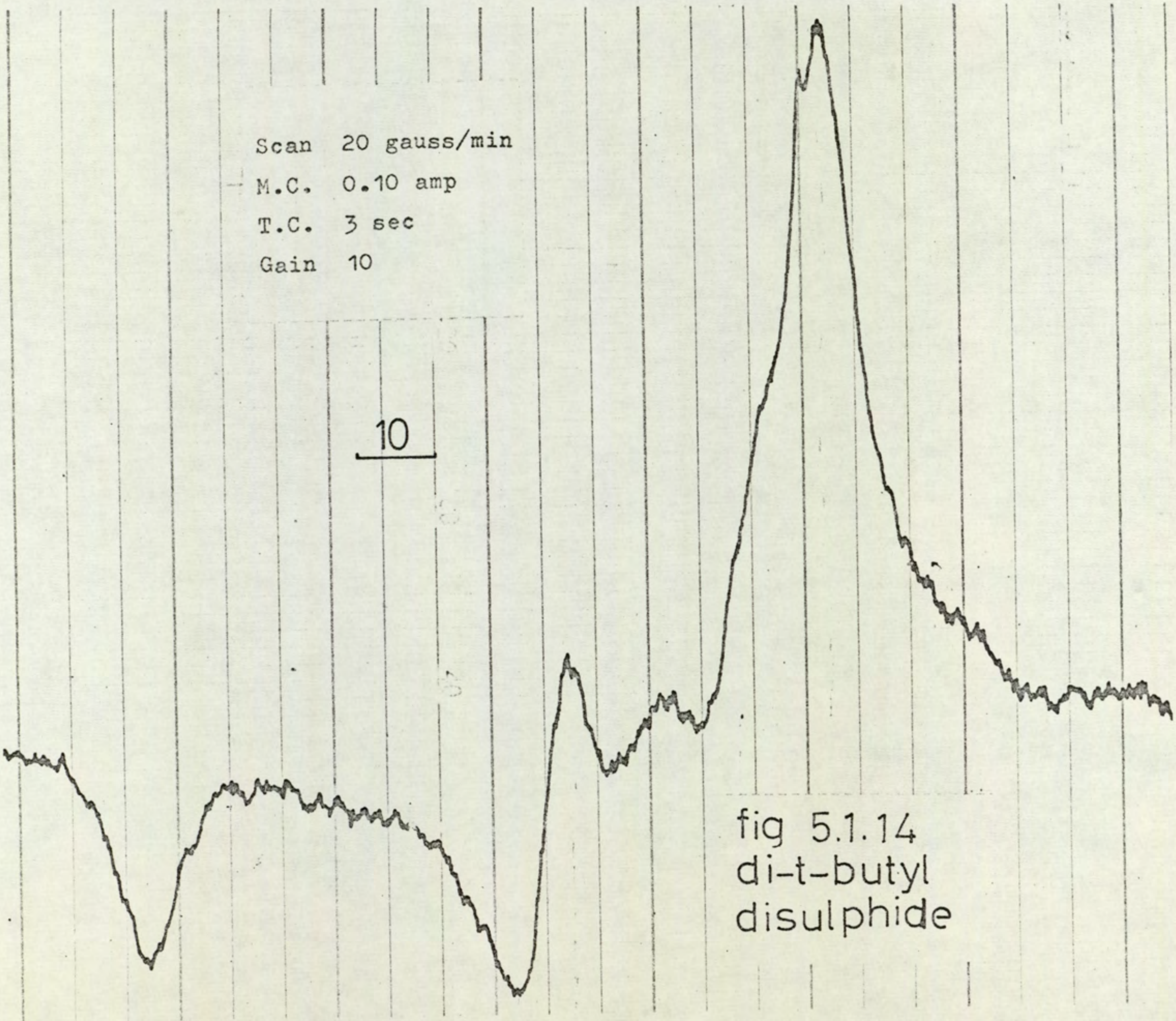


fig 5.1.14
di-t-butyl
disulphide

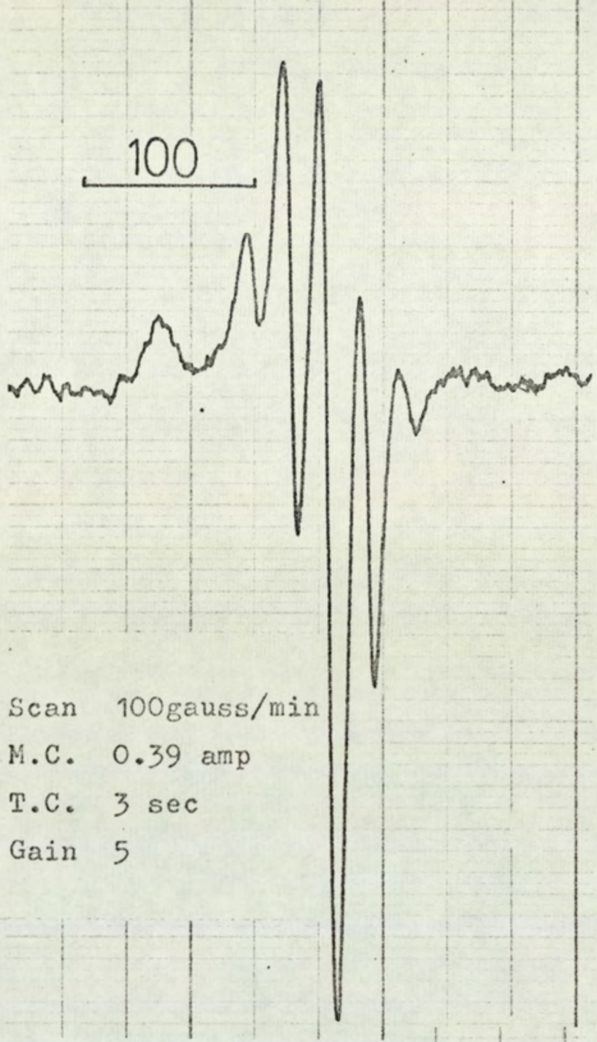
Diethyl disulphide

The spectrum observed from this compound, after irradiation, was interpreted as arising from two species. A small peak was observed at g = 2.0610, followed by a larger signal at g = 2.0036, which was split into five hyperfine components. The intensity distribution was found to be 1.0 : 5.2 : 9.2 : 5.0 : 1.2, and the splitting constant 18.63 gauss. The spectrum is shown in figure 5.1.15, with the low g value line shown under increased resolution in figure 5.1.16.

Di-isopropyl disulphide

This disulphide gave a similar spectrum to that of diethyl disulphide, with a small signal at 2.0617, and a larger one at g = 2.0092. The lower g value signal was split into seven hyperfine components, with the intensities in the ratio 1.0 : 18.3 : 22.6 : 40.0 : 20.0 : 6.5 : 0.9 and splitting constant 18.95 gauss.

The spectrum is shown in figure 5.1.17, the two wing lines are very small. These are more easily seen in figure 5.1.18, where the spectrum is shown under higher gain.



Scan 100gauss/min
M.C. 0.39 amp
T.C. 3 sec
Gain 5

fig 5.1.15
diethyl
disulphide

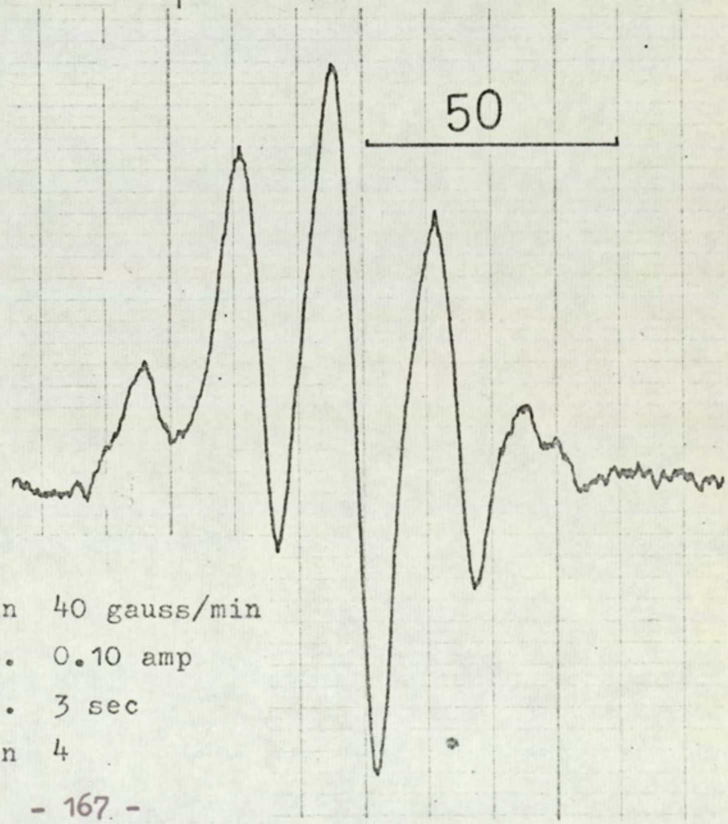
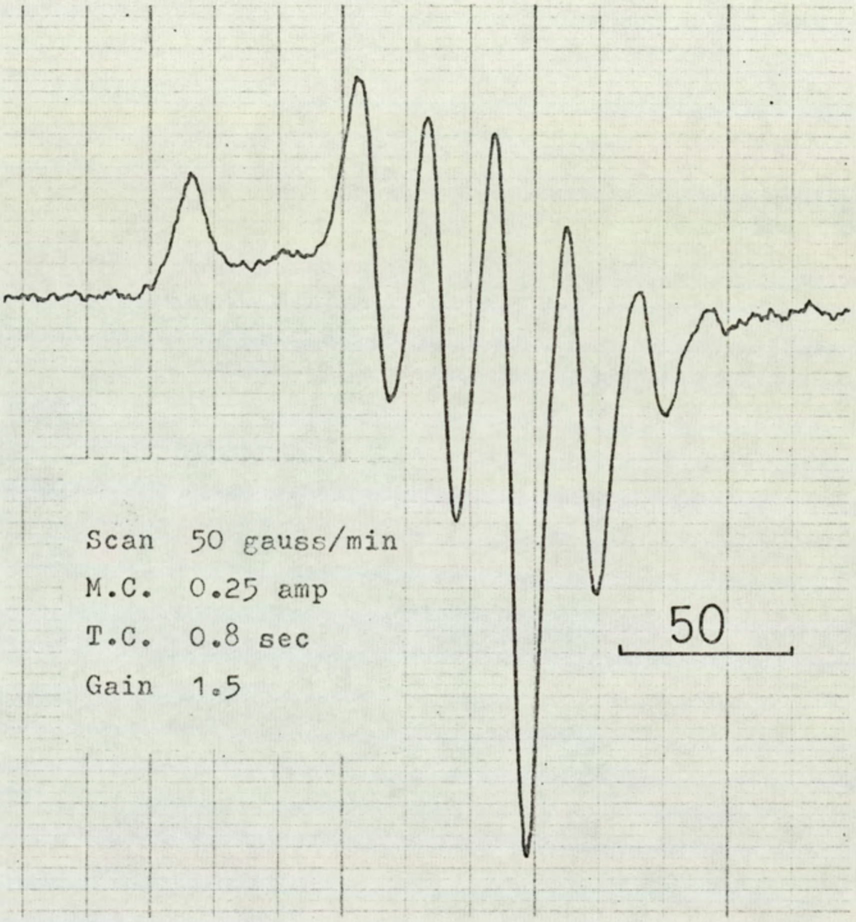


fig 5.1.16
diethyl
disulphide

Scan 40 gauss/min
M.C. 0.10 amp
T.C. 3 sec
Gain 4



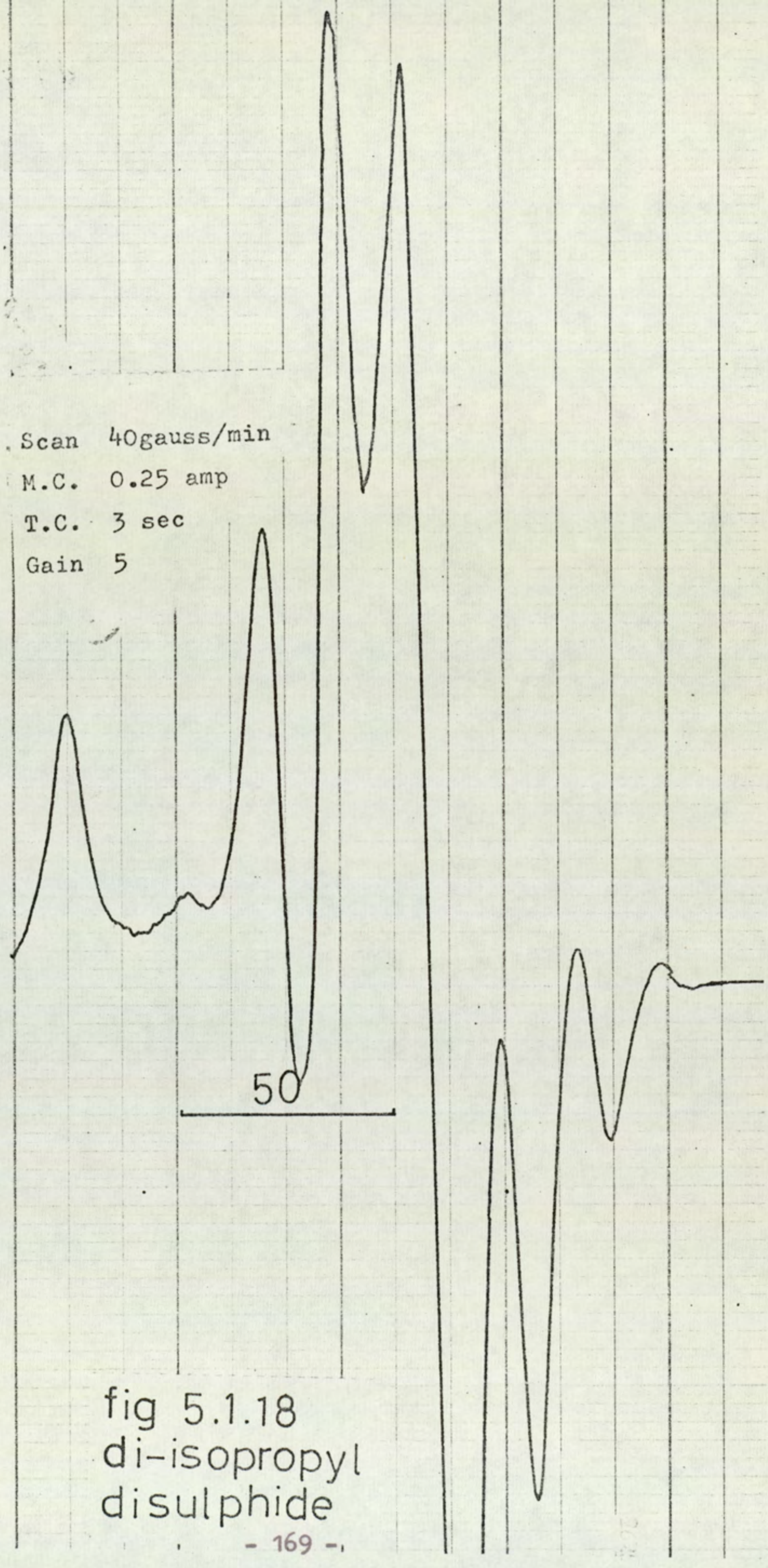
Scan 50 gauss/min

M.C. 0.25 amp

T.C. 0.8 sec

Gain 1.5

fig 5.1.17
di-isopropyl
disulphide



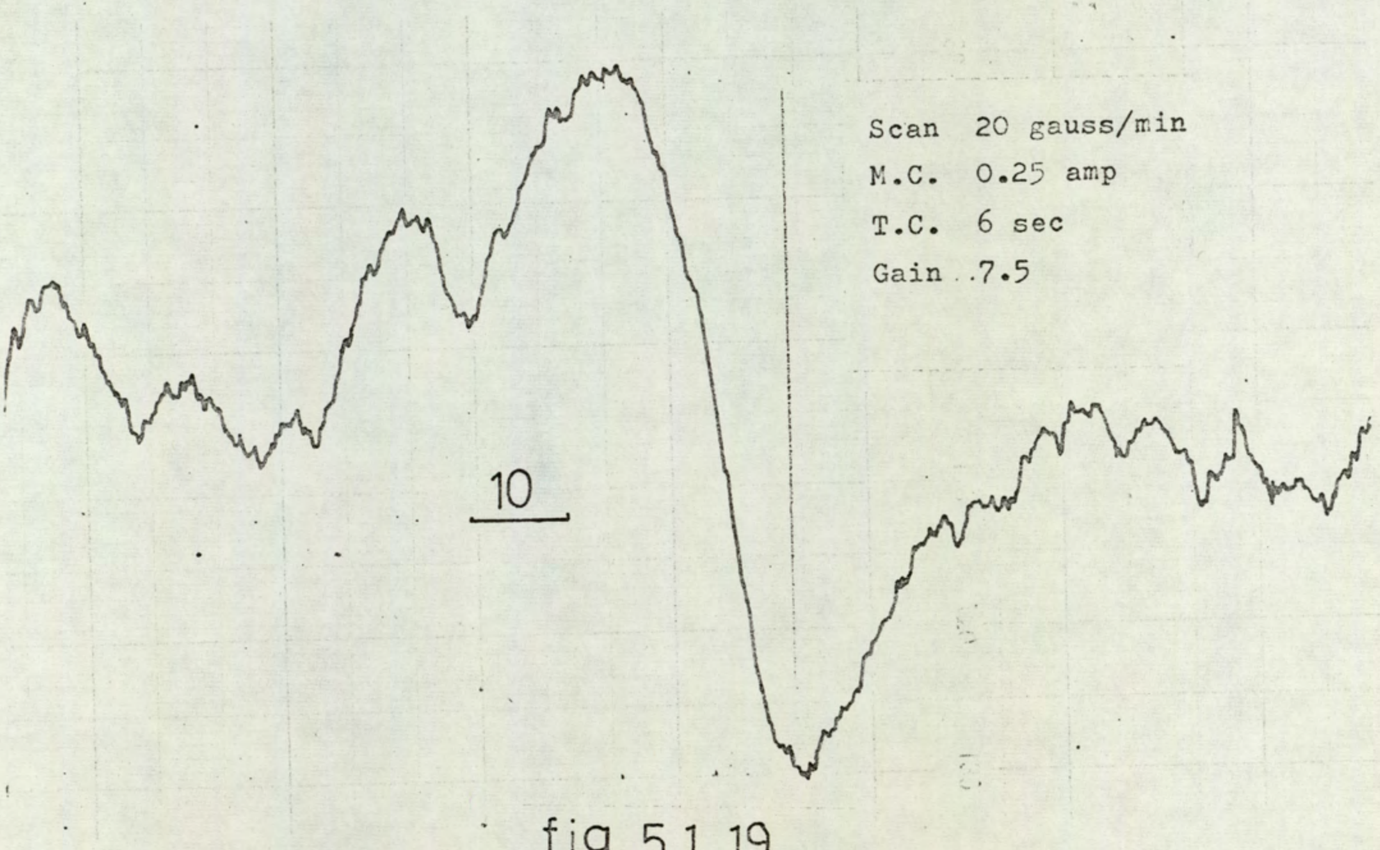
Scan 40gauss/min
M.C. 0.25 amp
T.C. 3 sec
Gain 5

fig 5.1.18
di-isopropyl
disulphide

Di-isobutyl disulphide

This signal was thought to arise from an axially symmetric species, that is, one in which the g values along two molecular axes are the same. The g values measured were 2.0089 and 2.0182.

There appeared to be some background signal also, which extended by at least 200 gauss either side of the main resonance. The spectrum is shown in figure 5.1.19.



Scan 20 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 7.5

fig 5.1.19
di-isobutyl
disulphide

Sulphides

On irradiation for one hour at liquid nitrogen temperature, diethyl sulphide and di-phenyl sulphide did not give a detectable yield of free radicals. Di-n-propyl sulphide gave a very small signal, only slightly greater than the noise level. The spectrum is not shown. The g value was not measured.

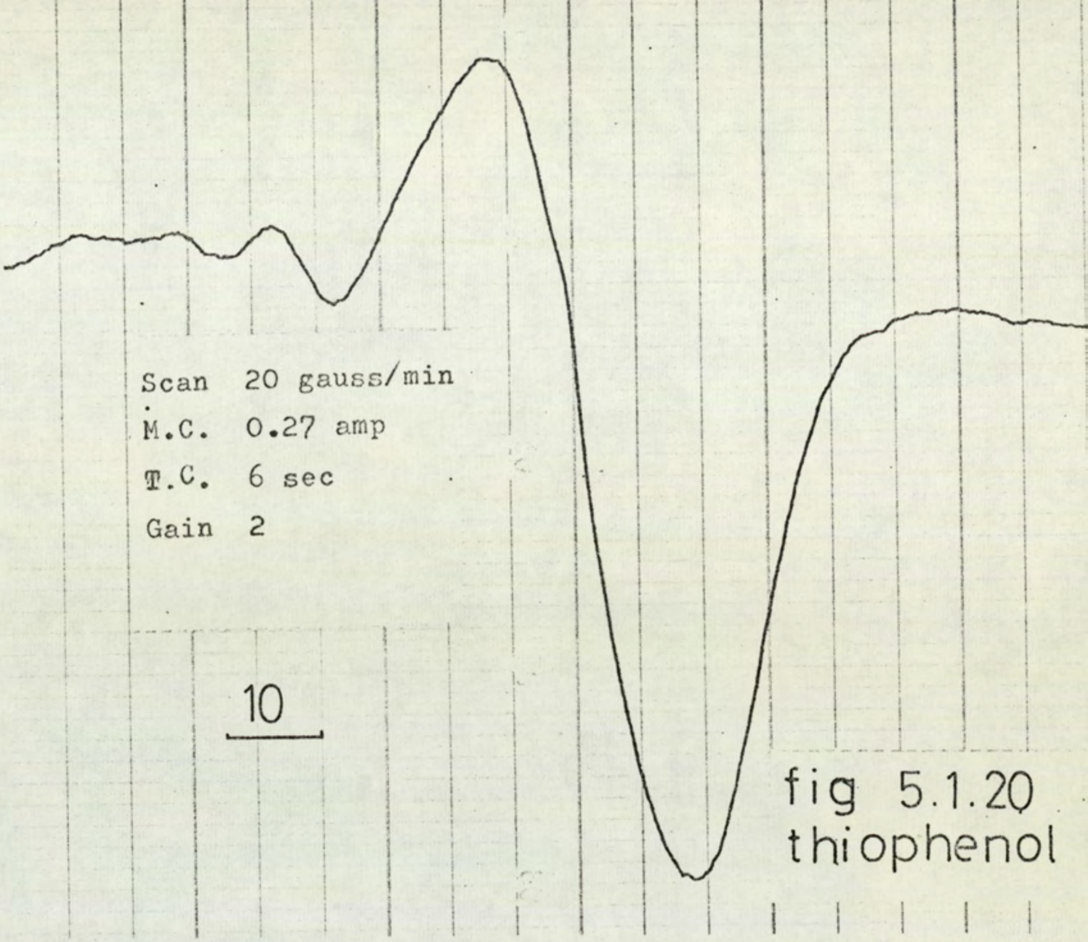
Miscellaneous Compounds

Thiophenol and Diphenyl disulphide

On irradiation of these compounds at liquid nitrogen temperature, identical spectra were obtained, as shown in figures 5.1.20 and 5.1.21. These were thought to arise from a radical species with three different g values, these being 2.0220, 2.0149 and 2.0070.

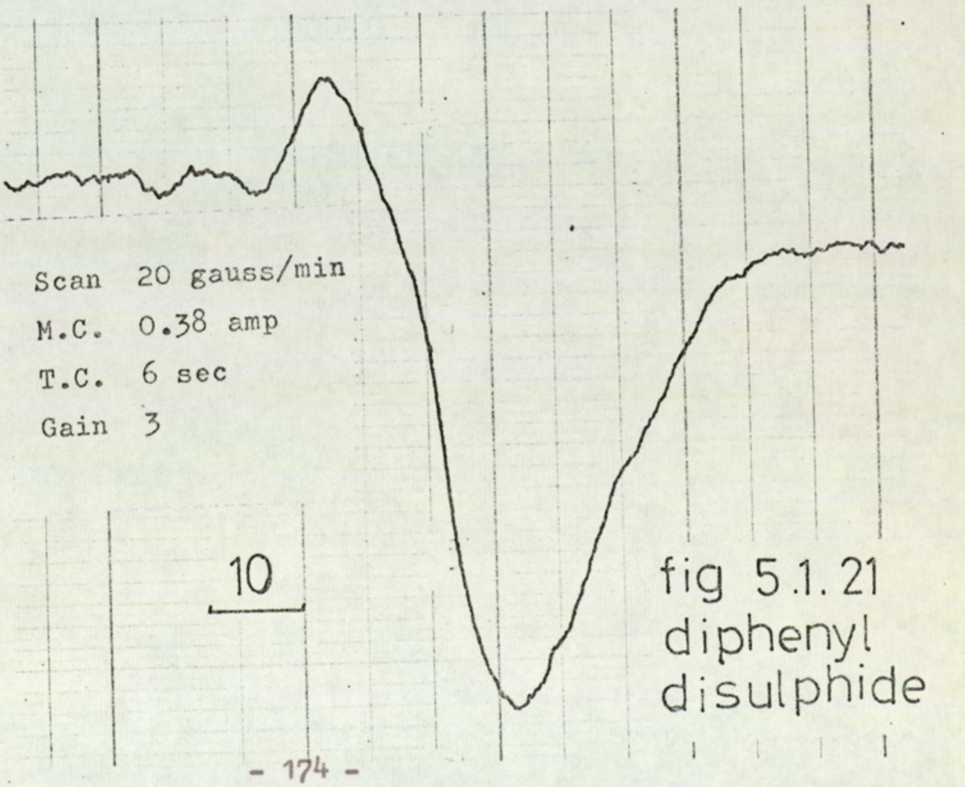
A sample of diphenyl disulphide was melted in the sample tube and then plunged into liquid nitrogen before irradiation. The spectrum was identical to that obtained using the polycrystalline material.

Diphenyl disulphide retained its esr signal when allowed to warm to room temperature, but it decayed when the crystals were warmed near their melting point. The signal from thiophenol decayed before the frozen material melted.



Scan 20 gauss/min
M.C. 0.27 amp
T.C. 6 sec
Gain 2

fig 5.1.20
thiophenol



Scan 20 gauss/min
M.C. 0.38 amp
T.C. 6 sec
Gain 3

fig 5.1.21
diphenyl
disulphide

Compounds containing the -N-S-S-N- Link

N,N'-dithiobis(piperidine)

The spectrum shown in figure 5.1.22, obtained on irradiation of this compound, probably arises from a paramagnetic entity having three different g values, the material being in polycrystalline form. Some additional splitting is also present, although this was not well resolved under the conditions used. The g values were measured as 2.0337, 2.0223, and 2.0003.

N,N'-dithiobis(morpholine)

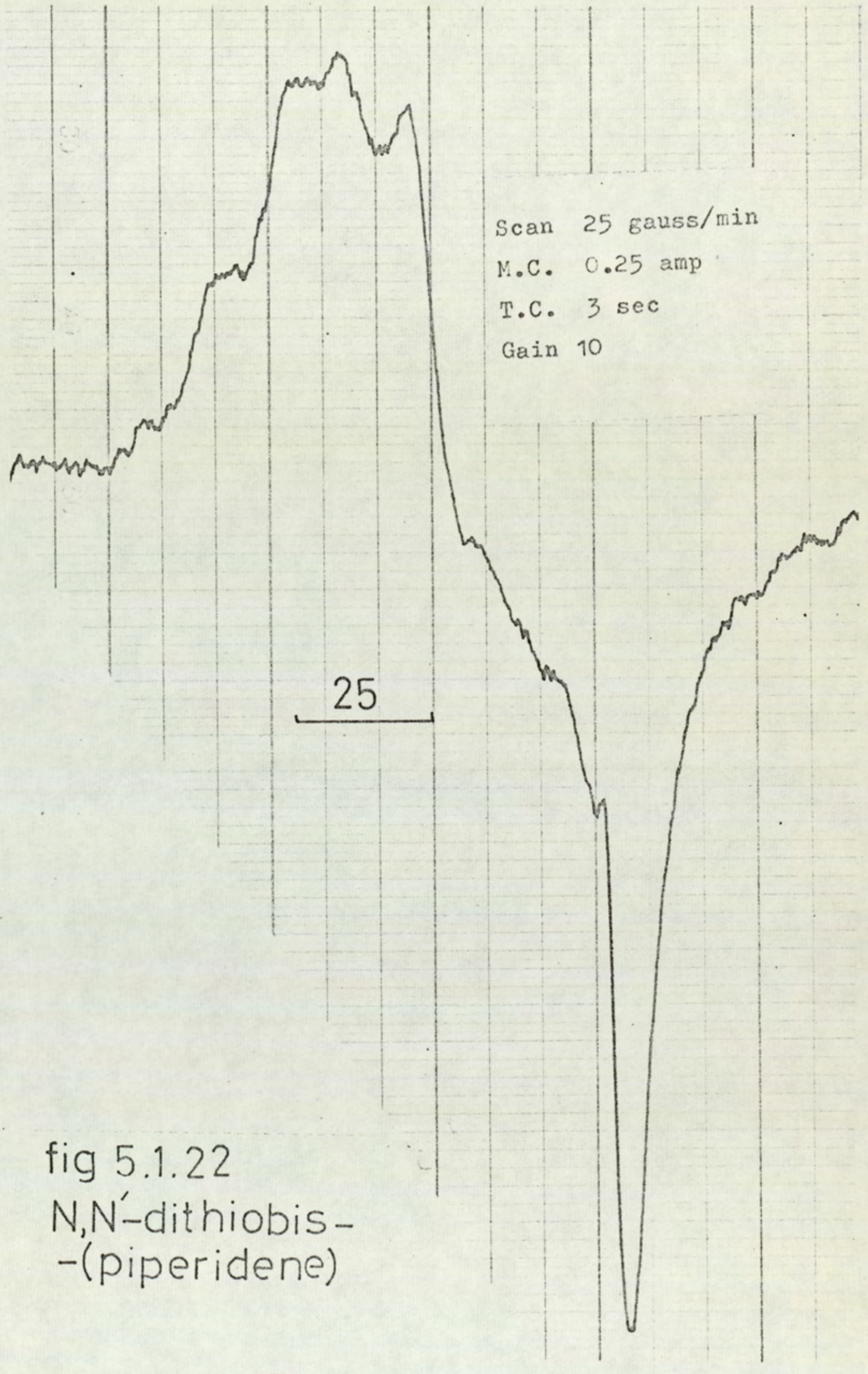
This compound gave rise to a similar spectrum, with less evidence for further splitting. The g values were 2.0325, 2.0180 and 1.9938. The spectrum is shown in figure 5.1.23.

N,N'-dithiobis(dibenzylamine)

This compound yielded the spectrum shown in figure 5.1.24 when irradiated. This was interpreted in terms of three asymmetric g values, with some unresolved splitting causing the complex appearance of the spectrum. The g values were measured as 2.0388, 2.0220, 2.0002.

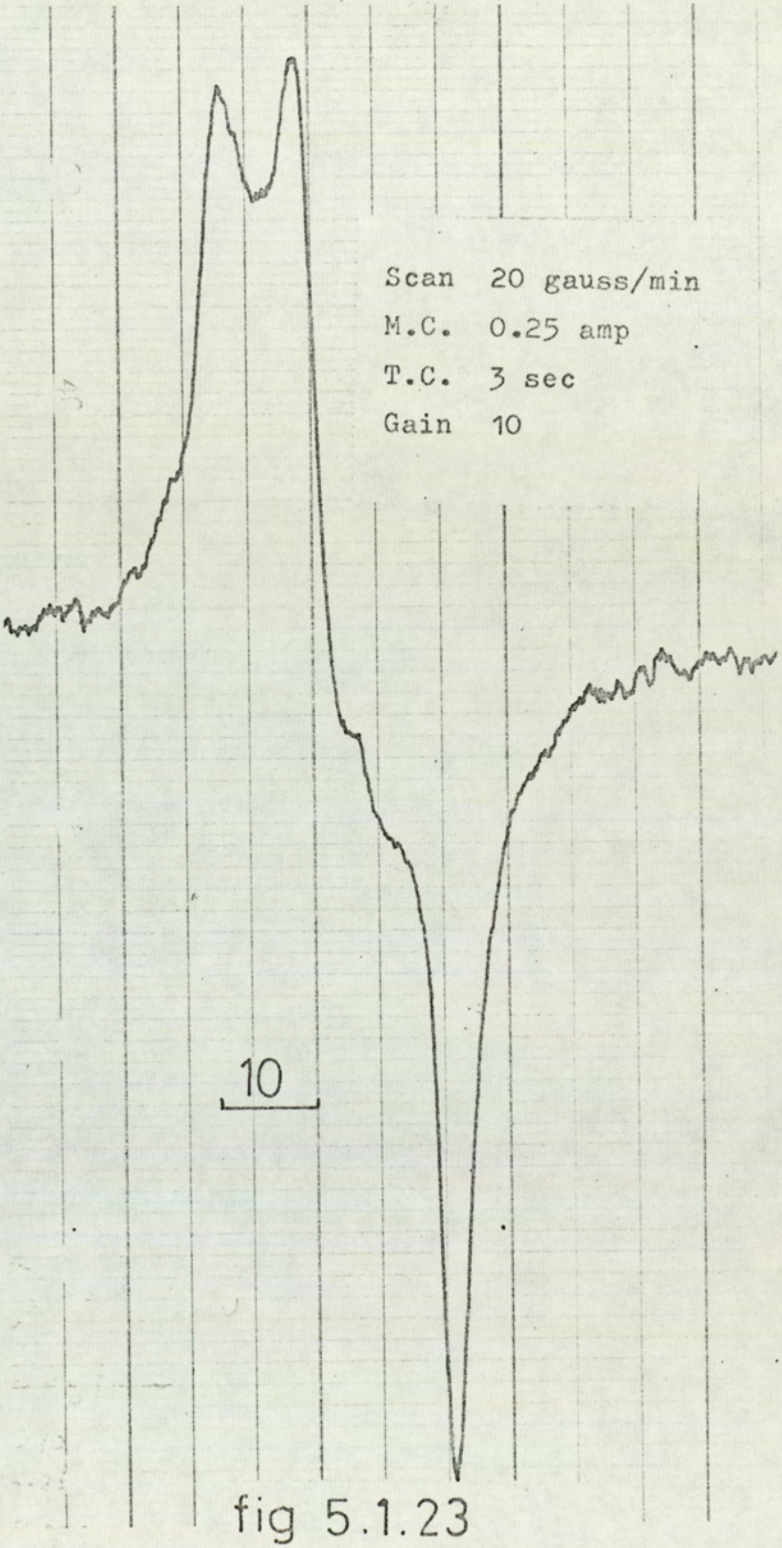
N,N'-dithiobis(phthalimide)

The signal obtained from this compound after irradiation was small. It appeared similar to the signals from the other compounds with the -N-S-S-N- bond, and was thus interpreted in the same way. The g values obtained were 2.0364, 2.0193, 2.0098. The spectrum is shown in figure 5.1.25.



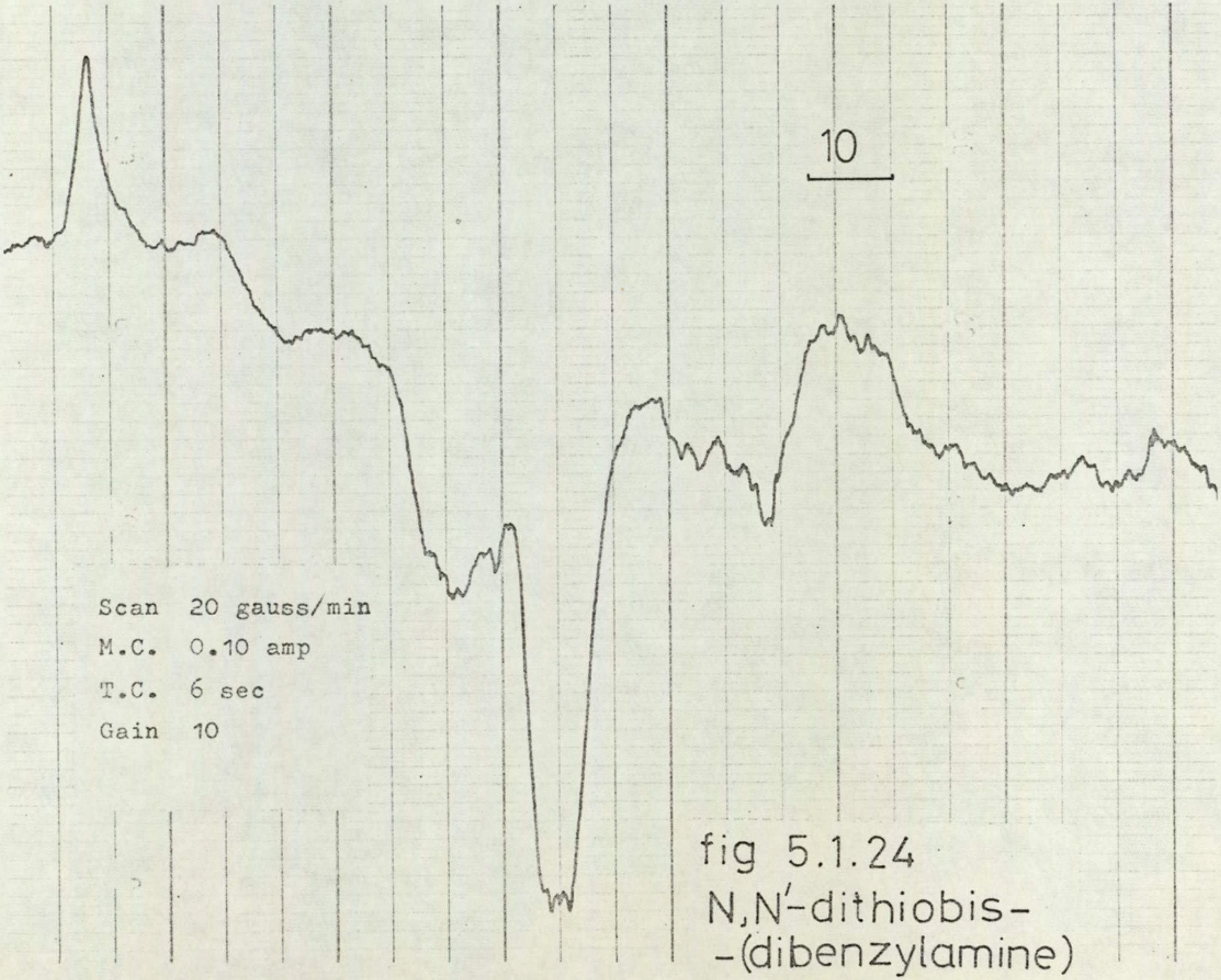
Scan 25 gauss/min
M.C. 0.25 amp
T.C. 3 sec
Gain 10

fig 5.1.22
N,N′-dithiobis-
-(piperidene)



Scan 20 gauss/min
M.C. 0.25 amp
T.C. 3 sec
Gain 10

fig 5.1.23
N,N′-dithiobis-
-(morpholine)



Scan 20 gauss/min
M.C. 0.10 amp
T.C. 6 sec
Gain 10

fig 5.1.24
N,N′-dithiobis-
-(dibenzylamine)

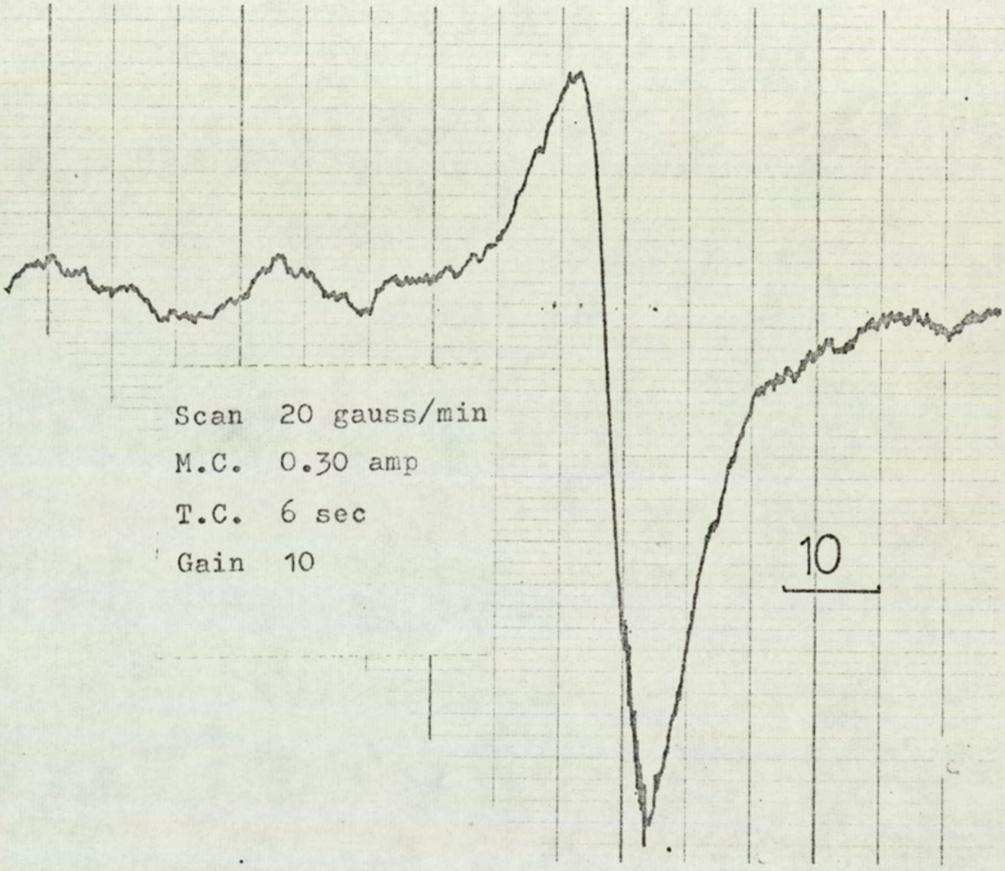
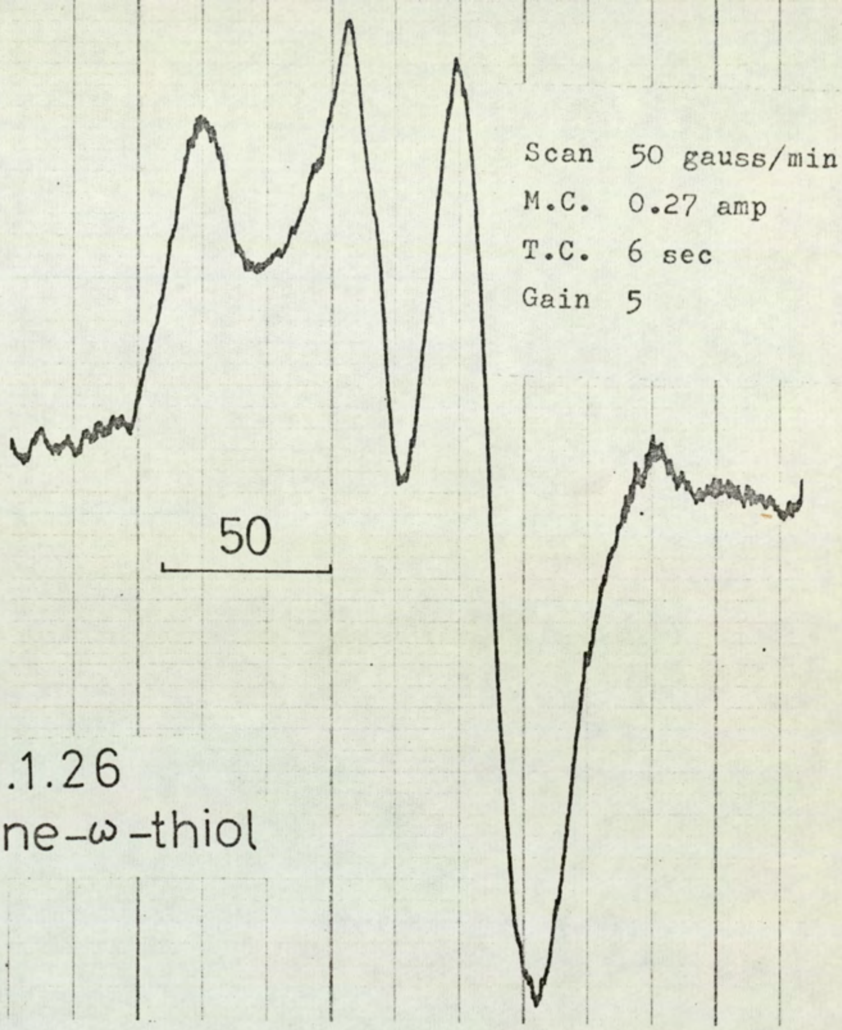


fig 5.1.25
N,N′-dithiobis-
-(phthalimide)

Toluene-ω-thiol and Dibenzyldisulphide

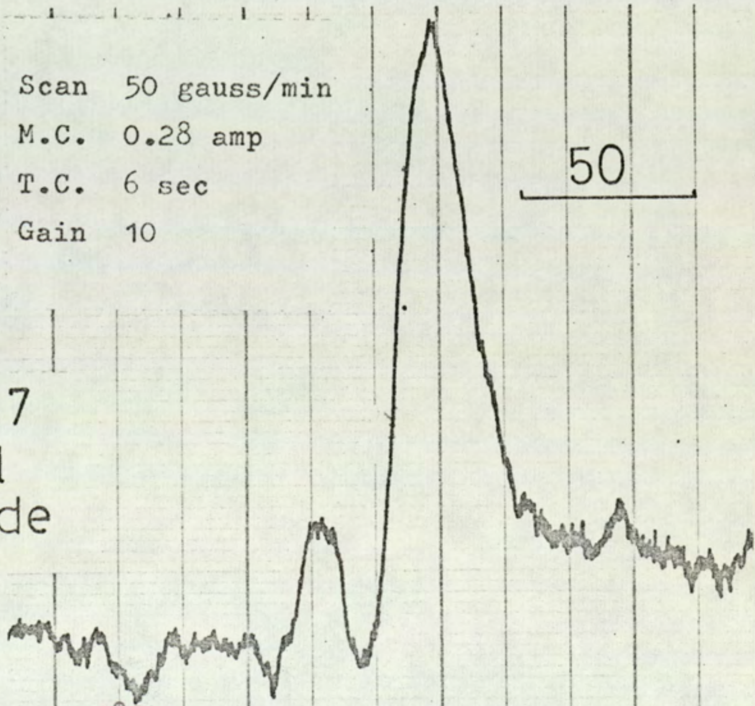
The spectrum from irradiated toluene-ω-thiol, shown in figure 5.1.26, is that of a polycrystalline compound with three asymmetric g values. These were measured as 2.0483, 2.0170 and 1.9905.

The spectrum obtained from similarly treated dibenzyl disulphide is shown in figure 5.1.27. This is of different phase to the spectrum of the thiol, and is not so well resolved. The signal was small in comparison. It is, however, thought to be the same signal.



Scan 50 gauss/min
M.C. 0.27 amp
T.C. 6 sec
Gain 5

fig 5.1.26
toluene-ω-thiol



Scan 50 gauss/min
M.C. 0.28 amp
T.C. 6 sec
Gain 10

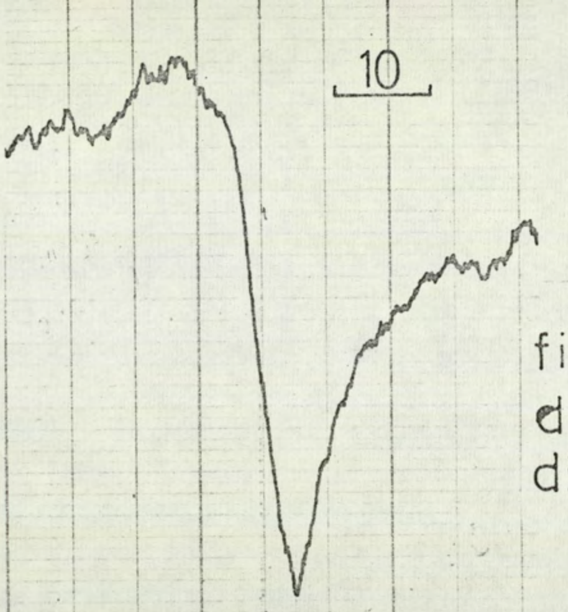
fig 5.1.27
dibenzyl
disulphide

Dibenzothiazolyl disulphide

The esr absorption found for this compound after irradiation was characteristic of the polycrystalline axially symmetric species. The g values were $g_{\parallel} = g_3 = 2.0159$ and $g_{\perp} = 2.0006$. The spectrum is shown in figure 5.1.28.

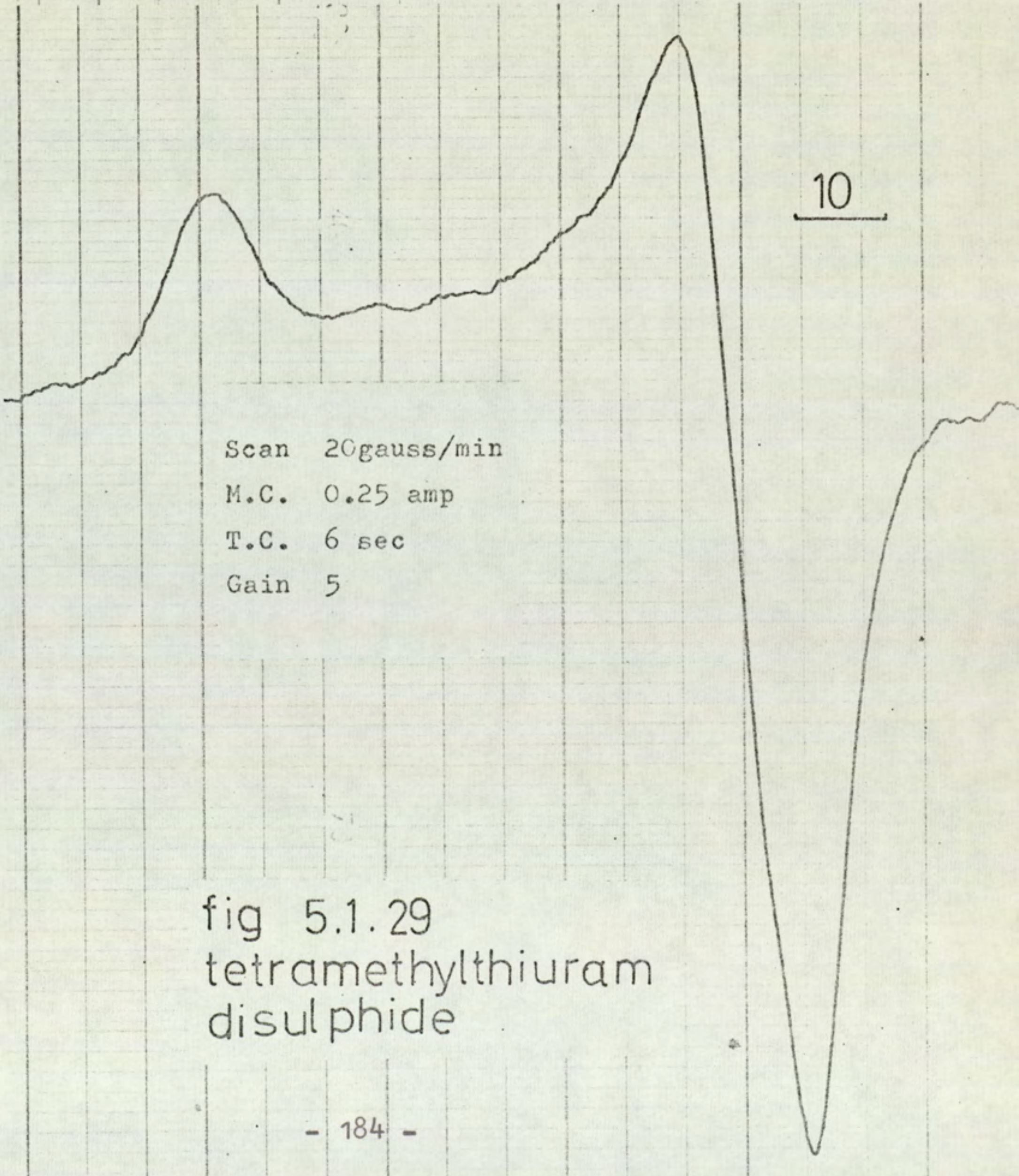
Tetramethylthiuram disulphide

On irradiation, this compound gave an axially symmetric free radical, with the g values $g_{\parallel} = g_3 = 2.0182$ and $g_{\perp} = 2.0052$. The spectrum is shown in figure 5.1.29.



Scan 20 gauss/min
M.C. 0.25 amp
T.C. 3 sec
Gain 10

fig 5.1.28
dibenzothiazolyl
disulphide



Scan 20gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 5

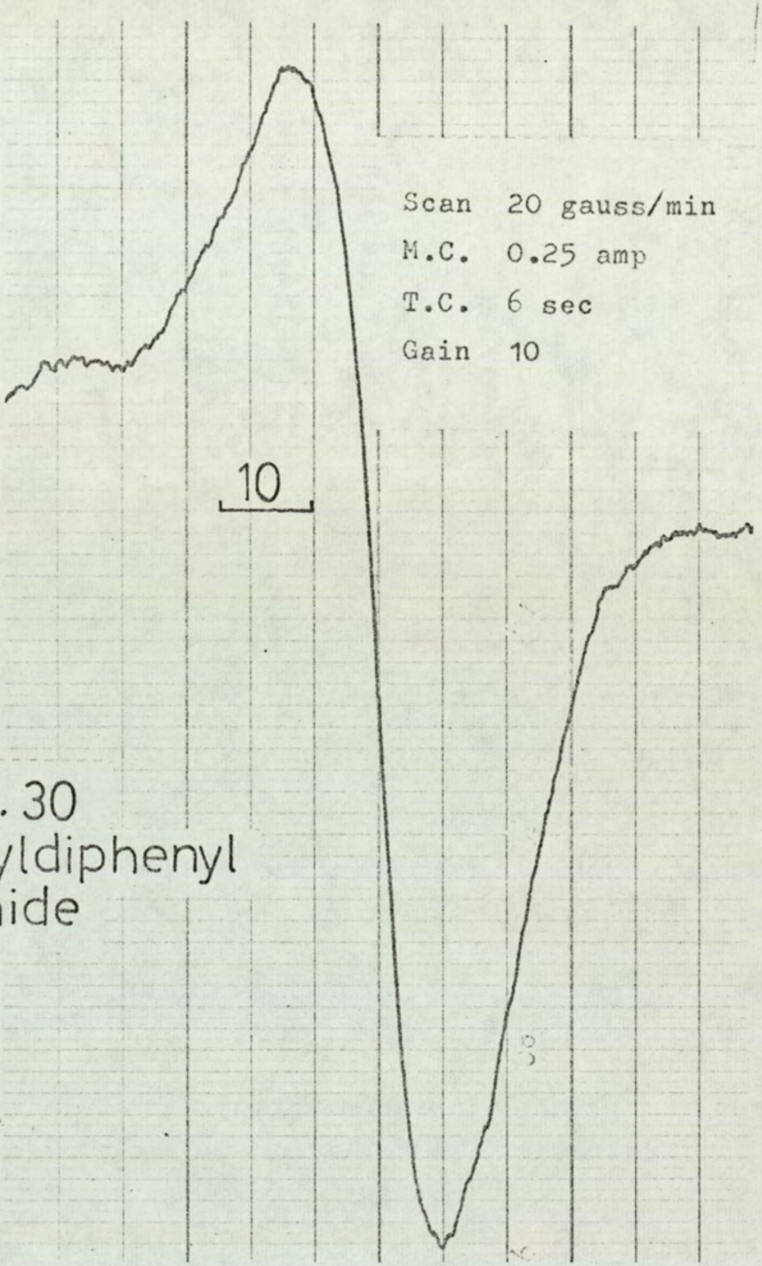
fig 5.1.29
tetramethylthiuram
disulphide

4,4'-dimethyldiphenyl disulphide

This compound, on irradiation yielded a paramagnetic species with an esr absorption consisting of a single broad line at $g = 2.0036$. The spectrum is shown in figure 5.1.30.

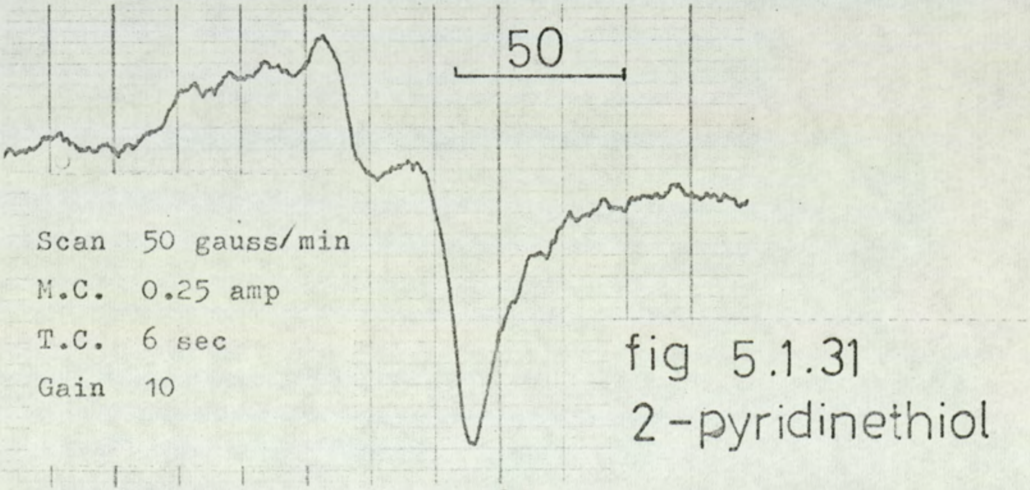
2-Pyridinethiol

On irradiation, a species was obtained having asymmetric g values. The g values were found to be 2.0373, 2.0229, 2.0068. The spectrum is shown in figure 5.1.31. On warming to room temperature, the spectrum decayed to approximately 15% of its size at liquid nitrogen temperature.



Scan 20 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 10

fig 5.1.30
4,4'-dimethyldiphenyl disulphide



Scan 50 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 10

fig 5.1.31
2-pyridinethiol

5.2. Aliphatic Sulphur Compounds in Sulphuric Acid

The acids used were:-

Concentrated sulphuric acid
Oleum (Fuming sulphuric acid) 20% SO_3 and 65% SO_3
Chlorosulphonic acid
Deuterosulphuric acid

The solutions were prepared as described in section 4.2.1.

Sulphur

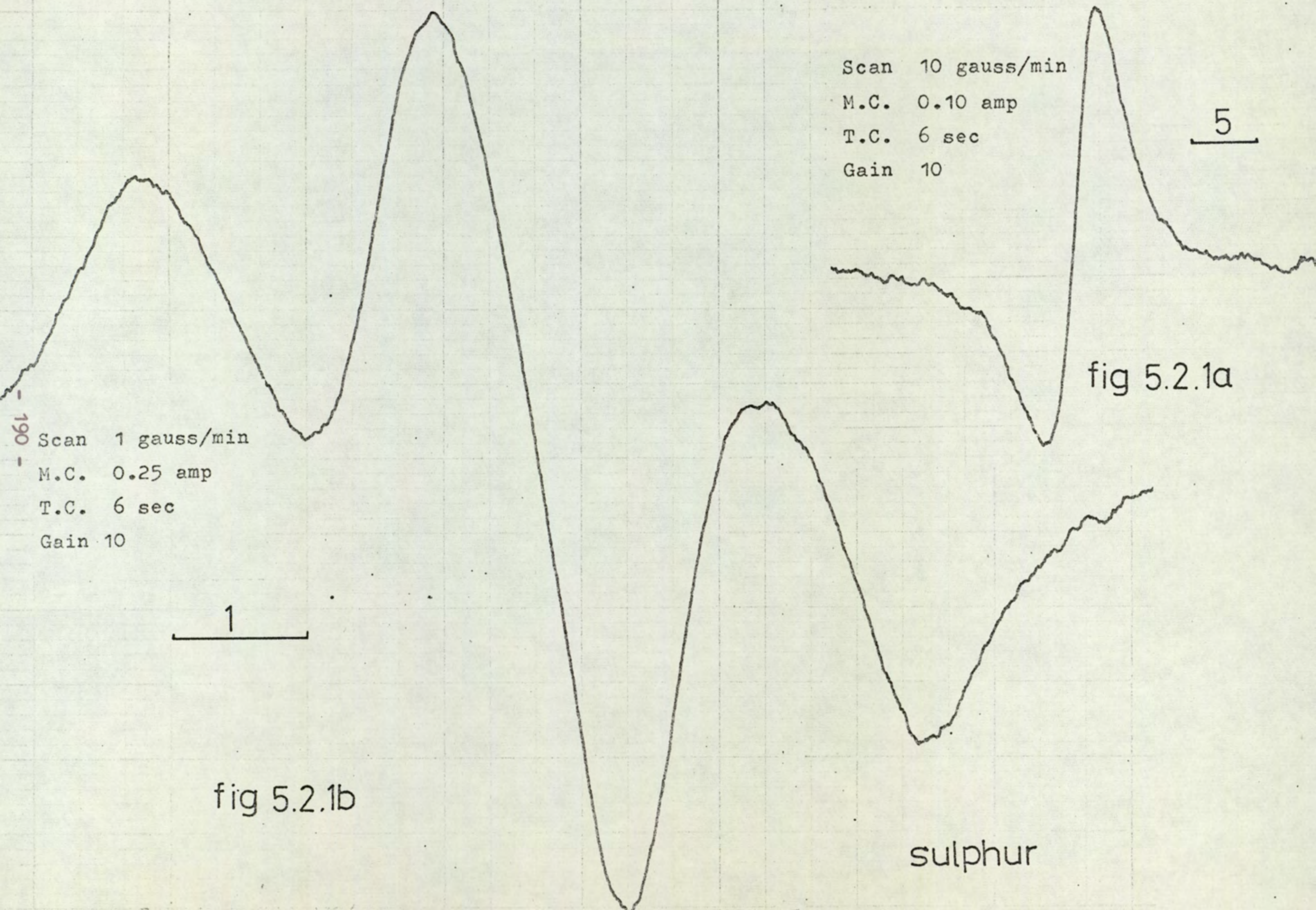
A yellow solution of sulphur in concentrated sulphuric acid at room temperature was found to possess an esr absorption, consisting of a single line at $g = 2.0222$. This is shown in figure 5.2.1a. On warming gently this signal increased in size. On stronger heating, the singlet disappeared, and a second signal developed at $g = 2.0133$. This was a triplet, of splitting constant 2.23 gauss, and intensity ratio 1.00 : 3.45 : 1.31. The spectrum is shown in figure 5.2.1b.

On solution in deuterosulphuric acid, no signal was observed until the solution was heated briefly, when a singlet was obtained, at $g = 2.0135$. The solution was yellow.

When dissolved in 65% oleum, sulphur formed a dark blue solution, which was found to have a strong esr signal, at $g = 2.0117$. The signal was a singlet.

Sulphur dissolved in 20% oleum formed a green solution, slowly turning blue, then brown. The solutions yielded esr spectra with signals from two radical species, as shown in figure 5.2.1c. Both lines were singlets. The larger signal was at $g = 2.0222$, the other at $g = 2.0117$.

Addition of sulphur to chlorosulphonic acid leads to the formation of a yellow solution, containing two radical species, giving singlet absorption lines at g values 2.0224 and 2.0135. The spectrum is shown in figure 5.2.1d. The signal at higher g value was the first to develop, the lower g signal growing relatively larger with time or heating.



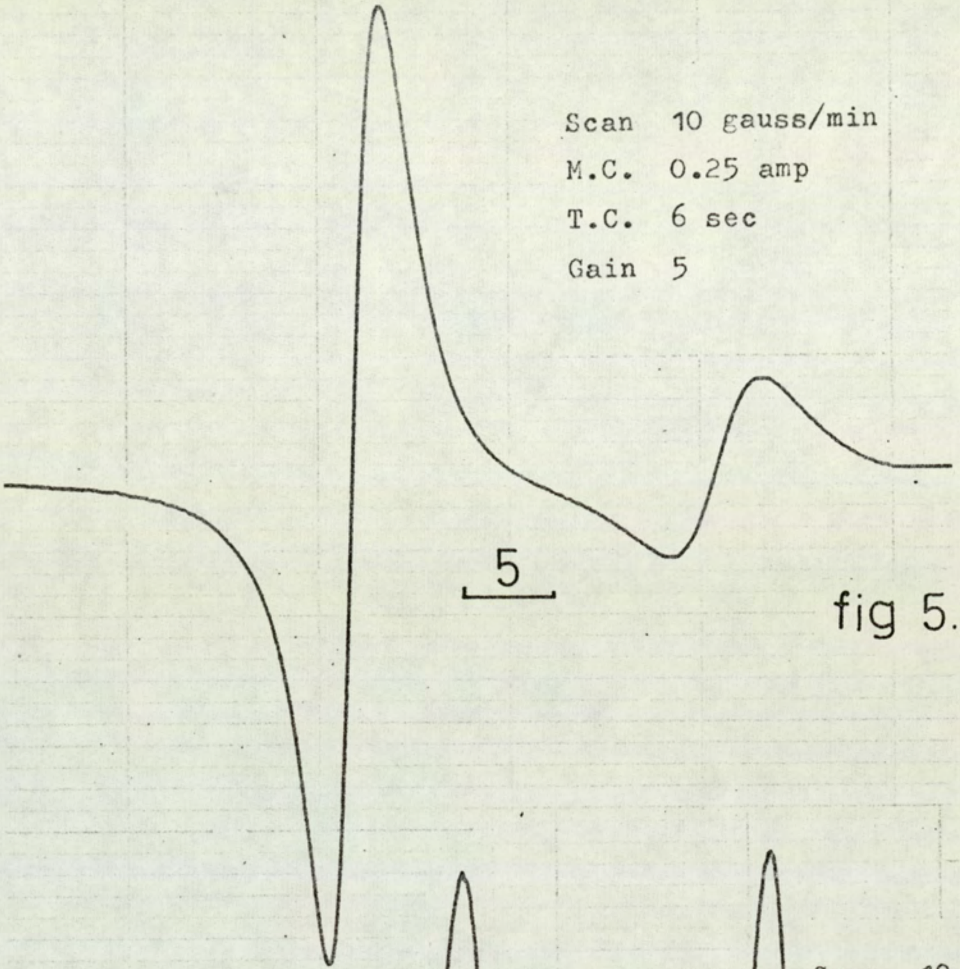
Scan 10 gauss/min
M.C. 0.10 amp
T.C. 6 sec
Gain 10

fig 5.2.1a

Scan 1 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 10

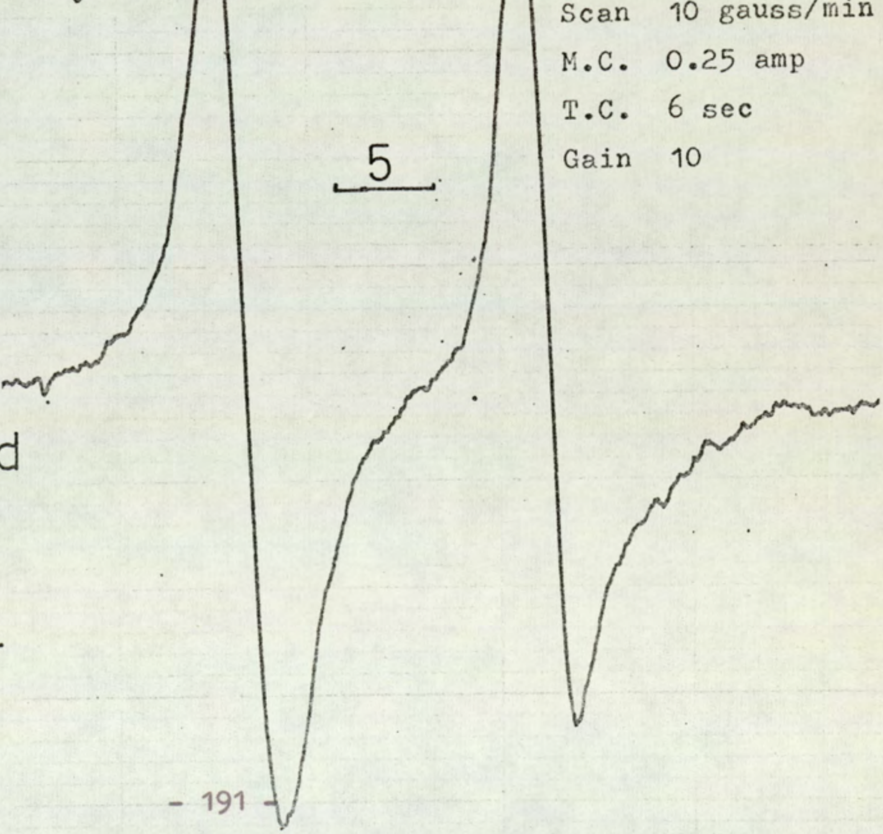
fig 5.2.1b

sulphur



Scan 10 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 5

fig 5.2.1c



Scan 10 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 10

fig 5.2.1d

sulphur

Methanethiol

As this first member of the series of thiols is gaseous at room temperature, it was bubbled through concentrated sulphuric acid. A yellow solution was produced, in which a precipitate formed and subsequently redissolved. No esr signal was found from this solution, even when it was heated before examination.

On bubbling methanethiol into chlorosulphonic acid, a yellow solution was again produced. This had a complex esr signal, consisting of at least six components, shown in figure 5.2.2a. On warming, the signal was converted to a singlet at $g = 2.0133$ and a doublet at 2.0117 shown in figure 5.2.2b. The splitting constant of the doublet was approximately 2.8 gauss.

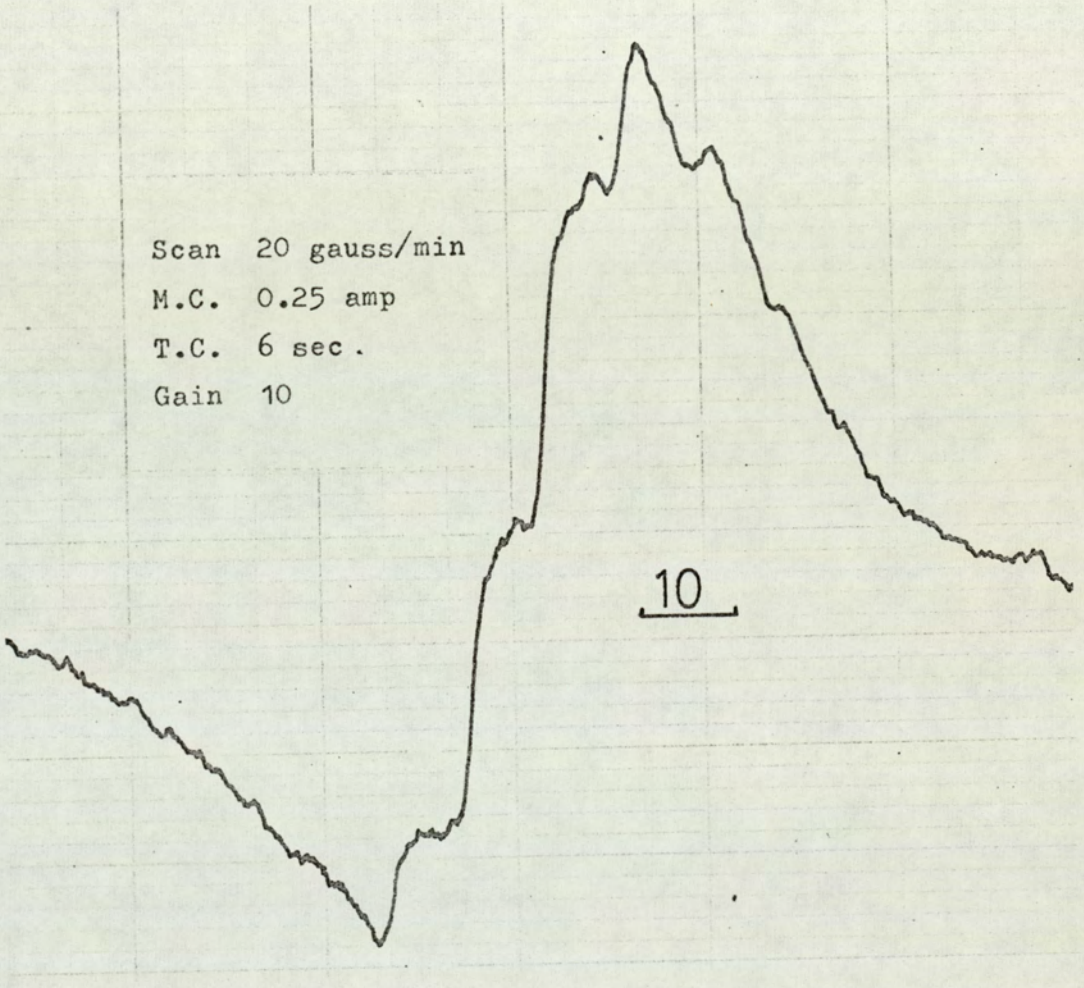
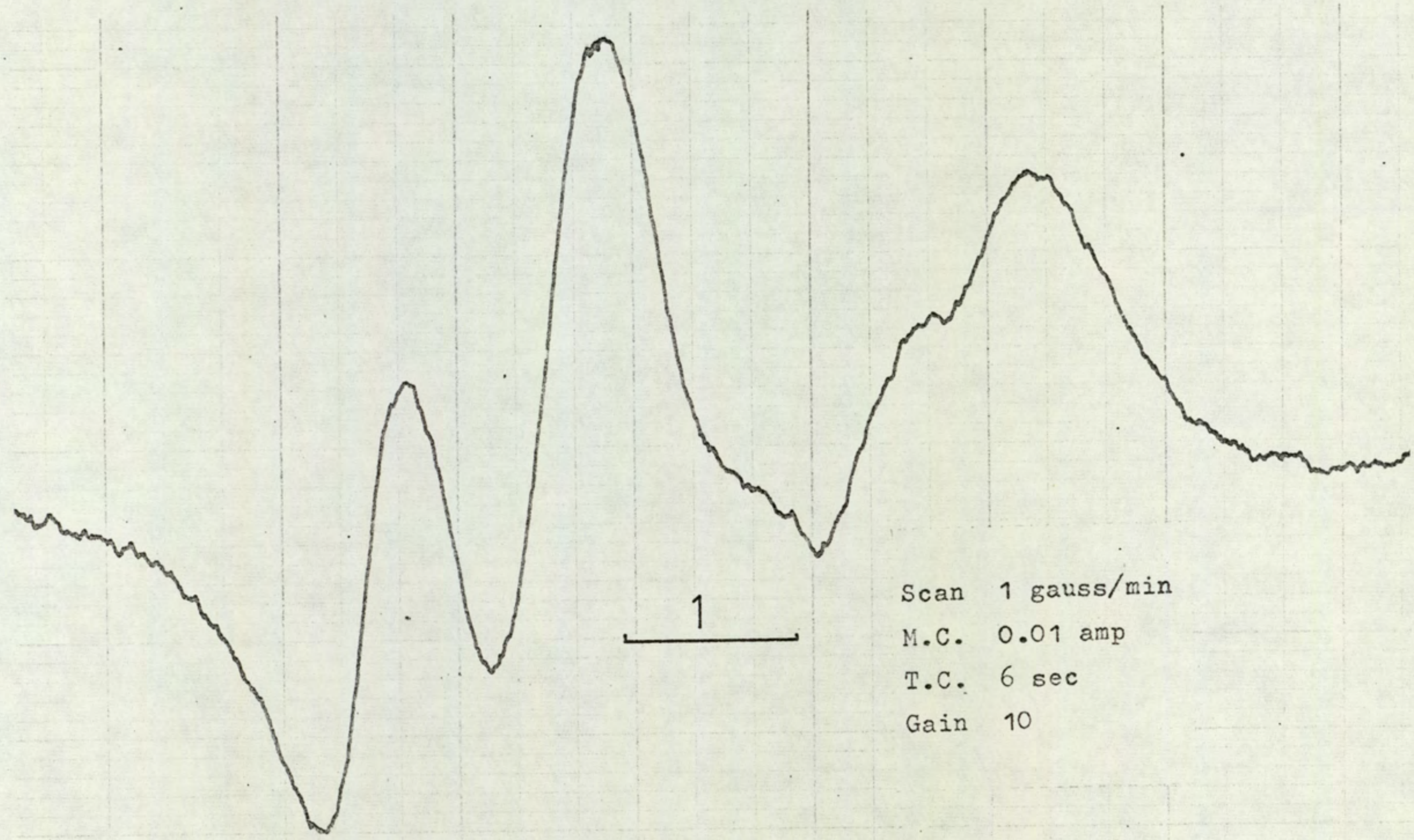


fig 5.2.2a
methanethiol



Scan 1 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 10

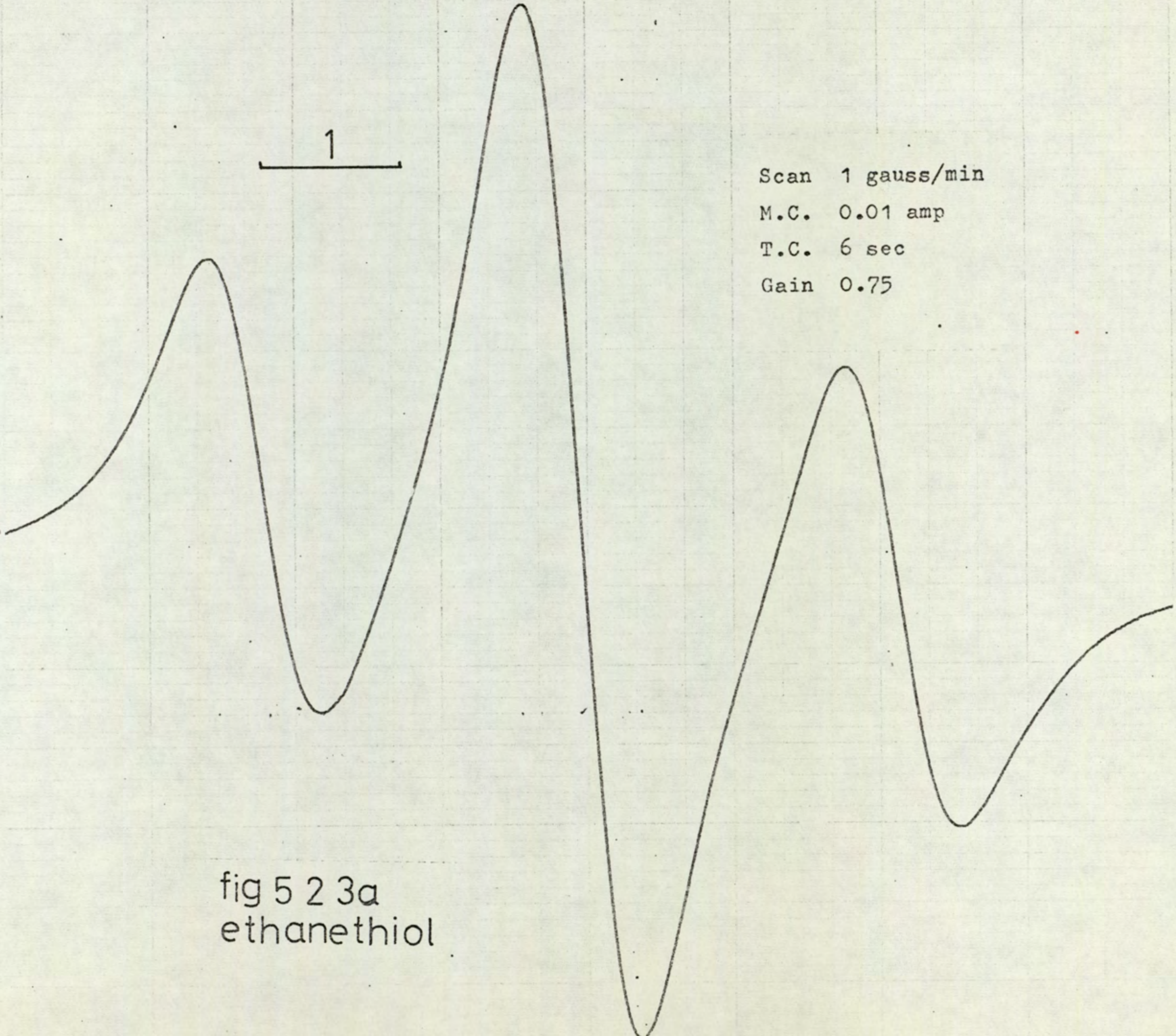
fig 5.2.2b
methanethiol

Ethanethiol

The yellow solution formed by the dissolution of ethanethiol in concentrated sulphuric acid was found to have an esr signal, g value 2.0133, with three hyperfine components. The intensity ratio was 1 : 2.5 : 1 and the splitting constant 2.20 gauss. The signal is shown in figure 5.2.3a.

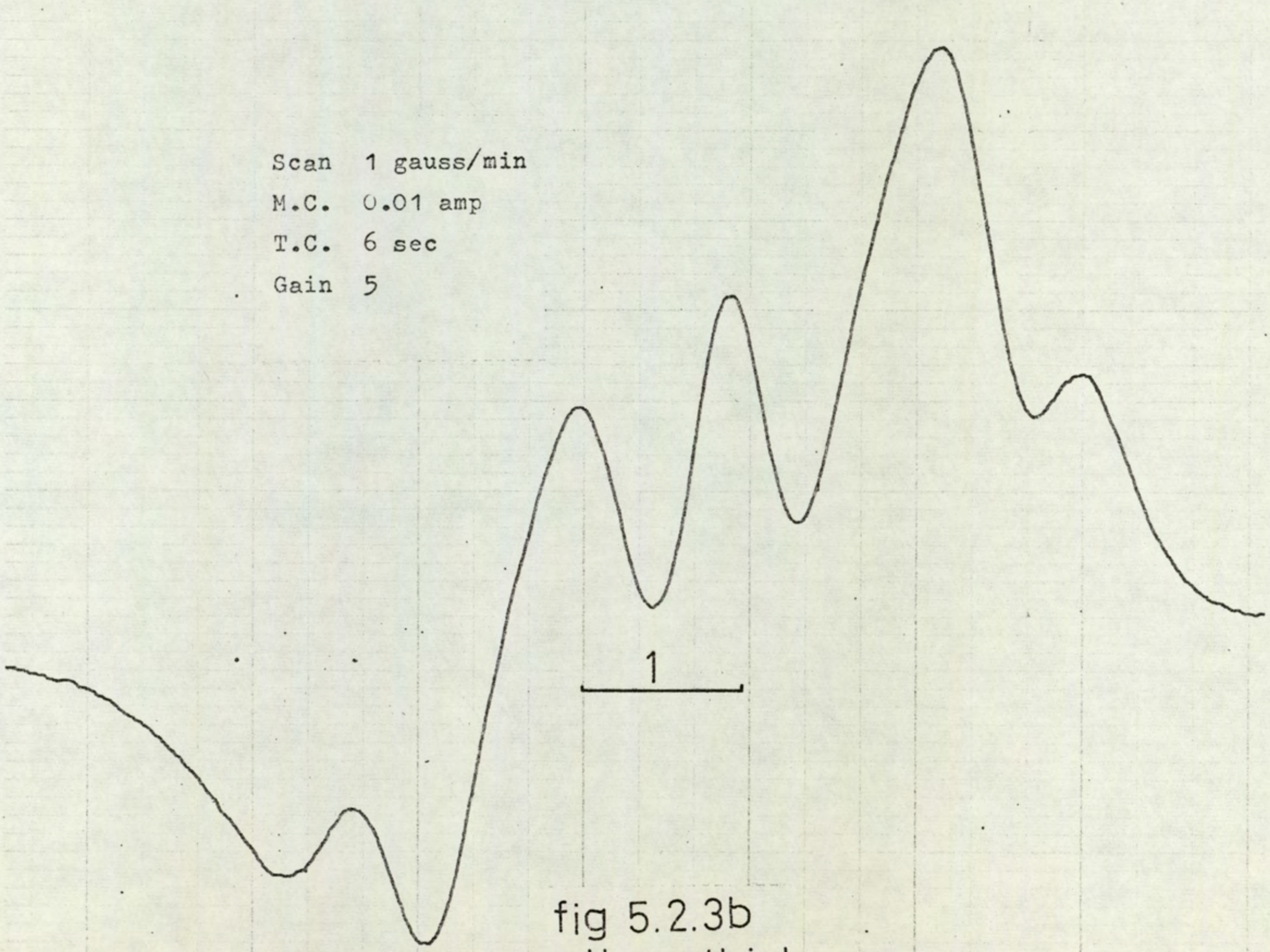
In deuterosulphuric acid, a signal was found at the same g value (2.0133) but having five hyperfine components. The degree of resolution was not great enough to permit the measurement of useful intensity ratios. The splitting constant varied from 0.86 gauss to 1.30 gauss. The resonance is shown in figure 5.2.3b.

In chlorosulphonic acid and in 20% oleum, similar results were obtained. A fairly broad unresolved absorption was first observed from the yellow solutions. This decayed in the course of a few hours, being replaced by a narrower signal which appeared to be a doublet, with slight shoulders on the wings. On standing further and diluting with chloroform or 100% sulphuric acid, a four line signal was observed, as shown in figure 5.2.3c, at g value 2.0132.



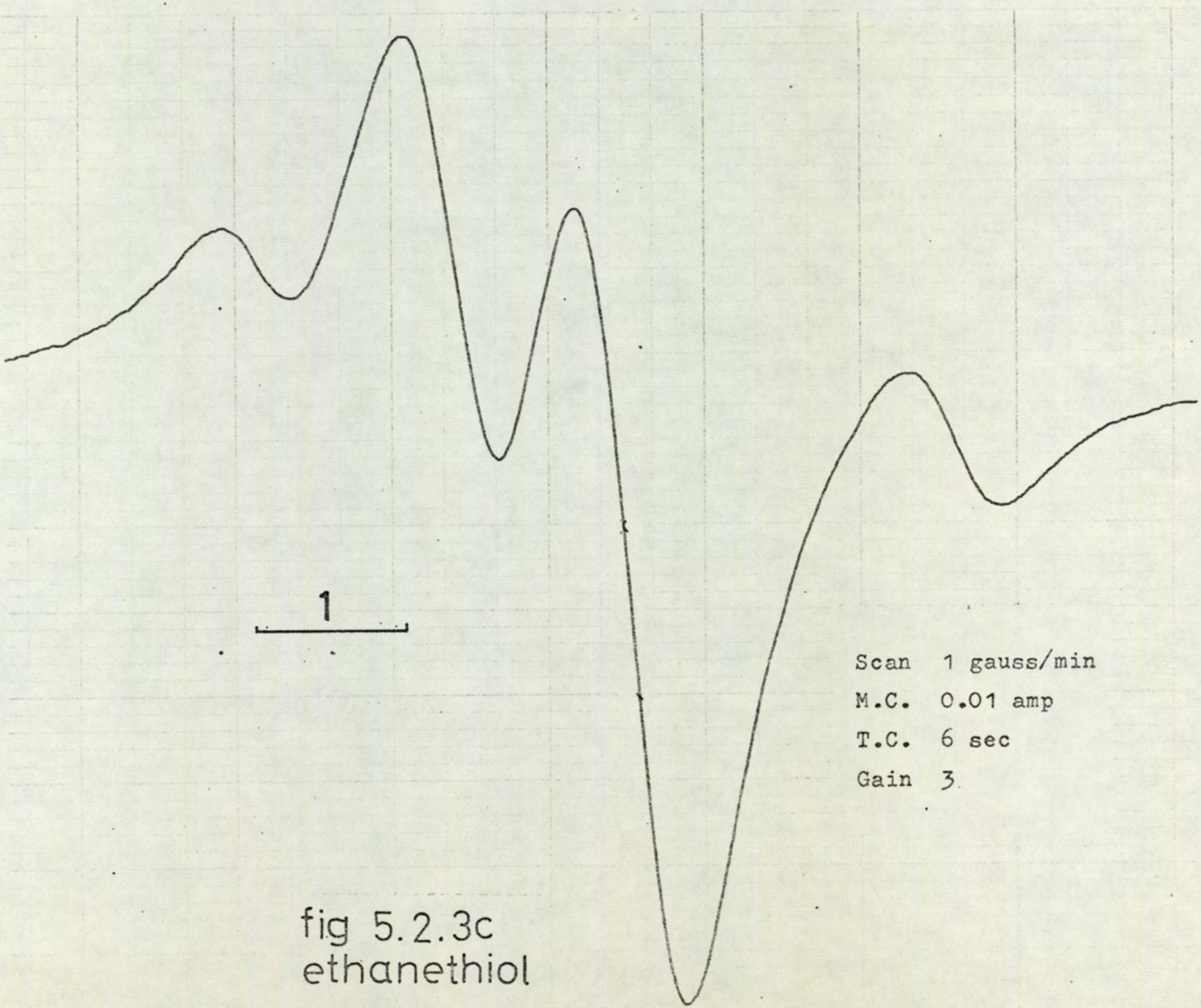
Scan 1 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 0.75

fig 5 2 3a
ethanethiol



Scan 1 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 5

fig 5.2.3b
ethanethiol



Scan 1 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 3

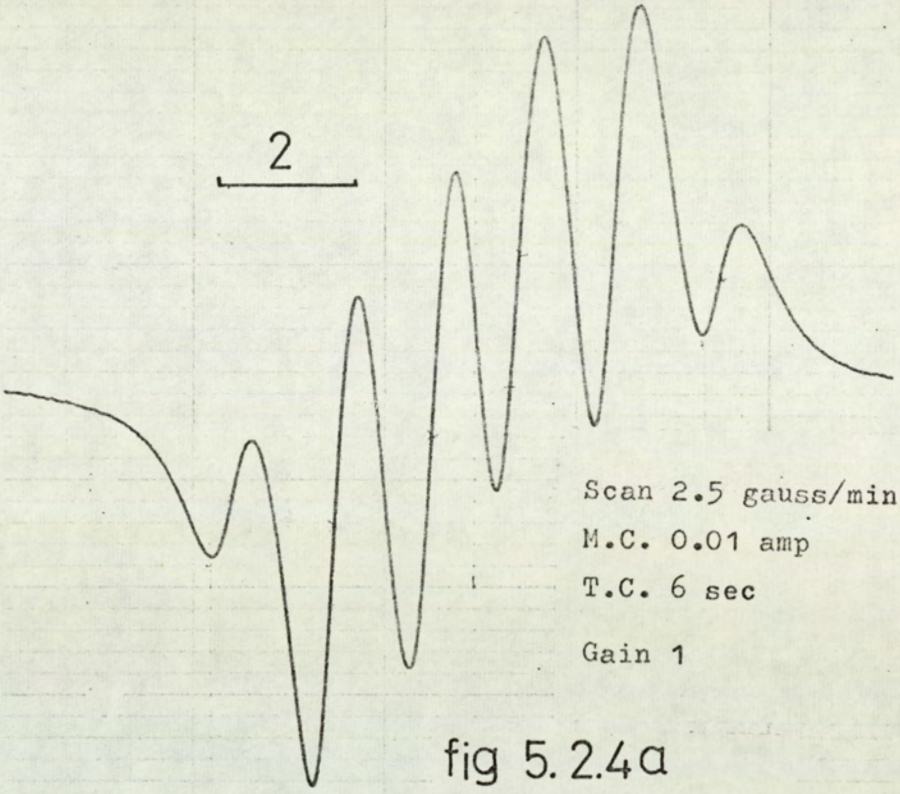
fig 5.2.3c
ethanethiol

n-Propanethiol

A solution of n-propanethiol in 100% sulphuric acid developed a red-brown colour, either slowly on standing, or more rapidly on warming, and was found to contain a paramagnetic species, with a g value of 2.0132. The line was split into six hyperfine components in the intensity ratio 1 : 4.3 : 4.3 : 4.0 : 3.3 : 1 and splitting constant 1.47 gauss. This spectrum is shown in figure 5.2.4a.

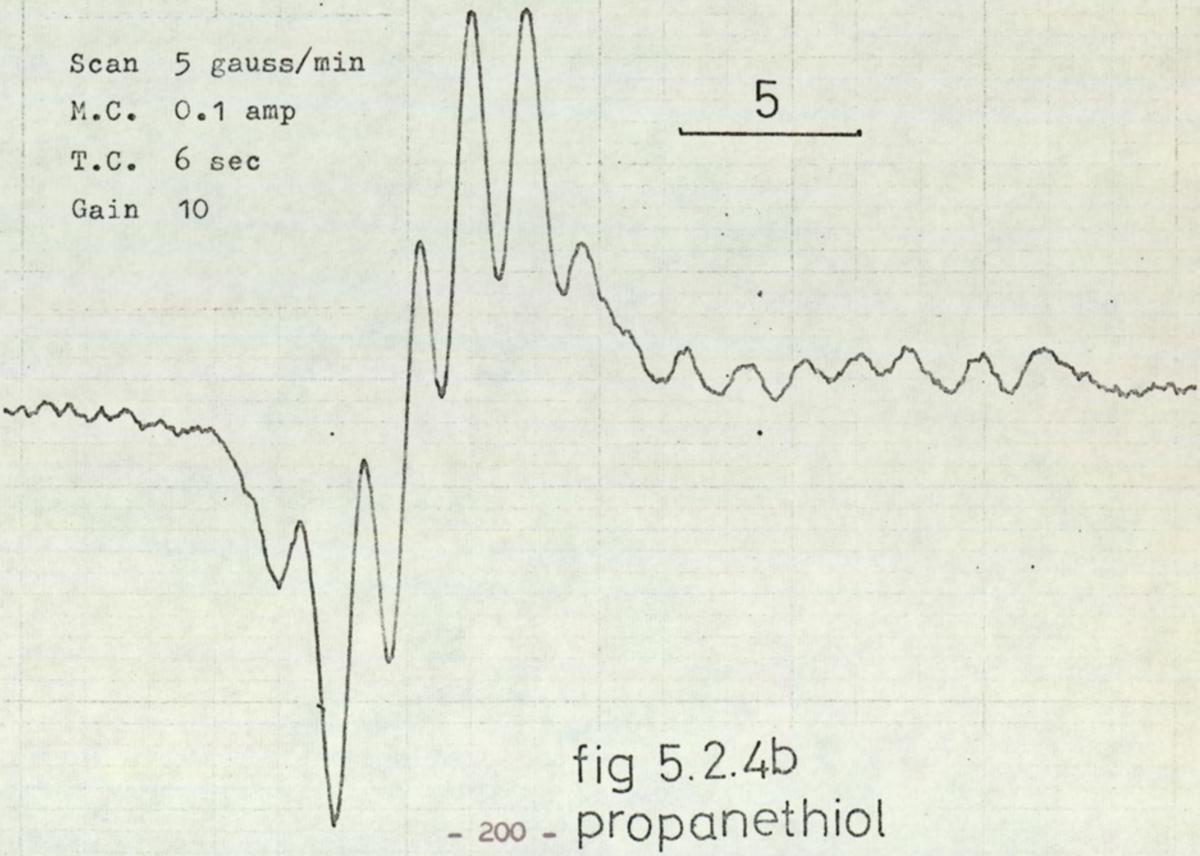
On standing for several hours, another small signal was observed at a lower g value, as shown in figure 5.2.4b. This could not be resolved or obtained any larger than this.

In deuterosulphuric acid, a six line signal was obtained, apparently identical to that found in concentrated sulphuric acid, although resolution was inferior, as shown in figure 5.2.4c.



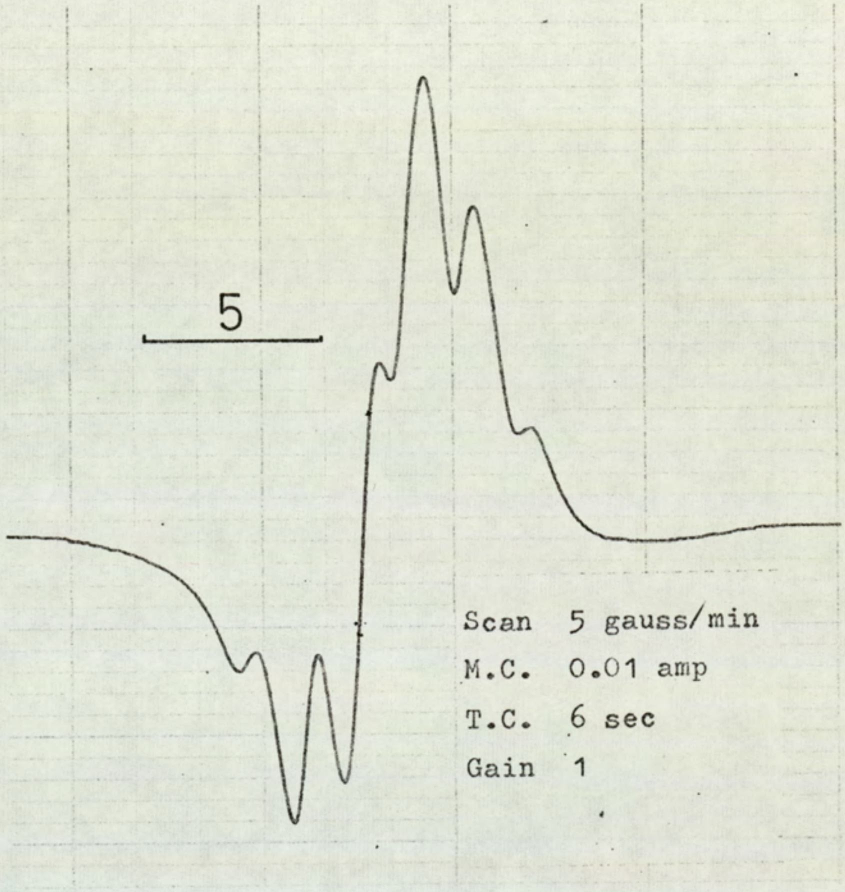
Scan 2.5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 1

fig 5.2.4a
propanethiol



Scan 5 gauss/min
M.C. 0.1 amp
T.C. 6 sec
Gain 10

fig 5.2.4b
propanethiol



Scan 5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 1

fig 5.2.4c
propanethiol

Isopropanethiol

On solution of isopropanethiol in concentrated sulphuric acid, a yellow colour developed, with a small amount of very fine precipitate. The solution gave an esr signal at g value 2.0132, the signal having 6 hyperfine components with intensity ratio 1 : 3.8 : 4.7 : 4.7 : 4.7 : 1.6. The splitting constant was 1.51 gauss. The spectrum is shown in figure 5.2.5a. When the spectrum was recorded using reduced microwave power, different intensity ratios were measured. At 10 dB attenuation, the ratio was 1 : 5.1 : 7.9 : 7.6 : 4.9 : 1.2.

This solution was also examined at different temperatures. At 65°C, an identical spectrum was observed, with no extra splitting, and at liquid nitrogen temperature the signal had broadened to a single line.

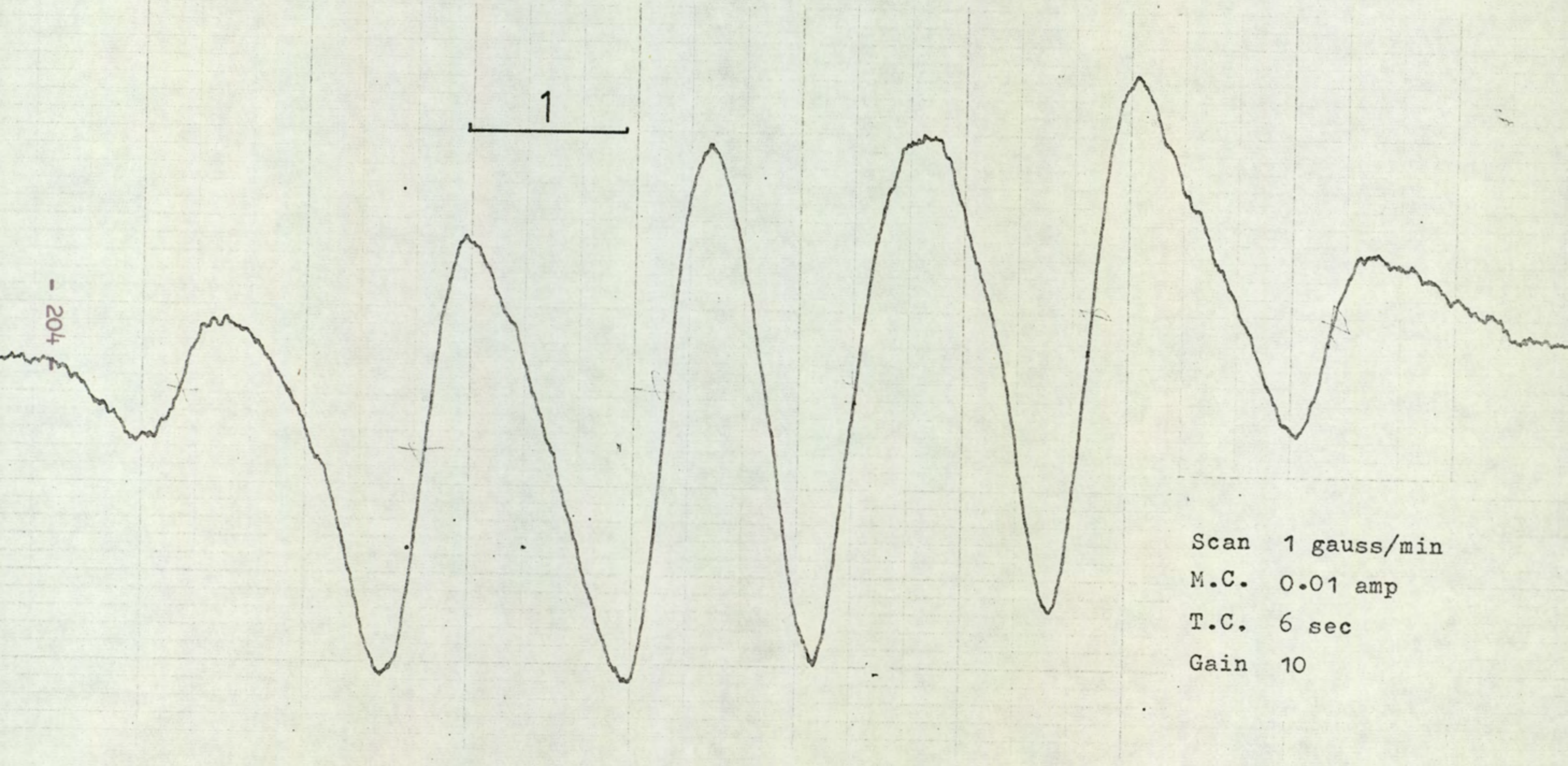
When the solution was warmed, a second resonance appeared at low field, shown in figure 5.2.5b.

Using deuterosulphuric acid, a similar resonance to that in sulphuric acid was observed, again at g = 2.0132. The signal was apparently split into six hyperfine components, although resolution was very poor (see figure 5.2.5c.)

On mixing with chlorosulphonic acid in an ice-salt bath, a green solution was obtained, giving rise to at least two esr signals. The signal at the lower g value was the stronger throughout, and also increased relative to the other signal on standing.

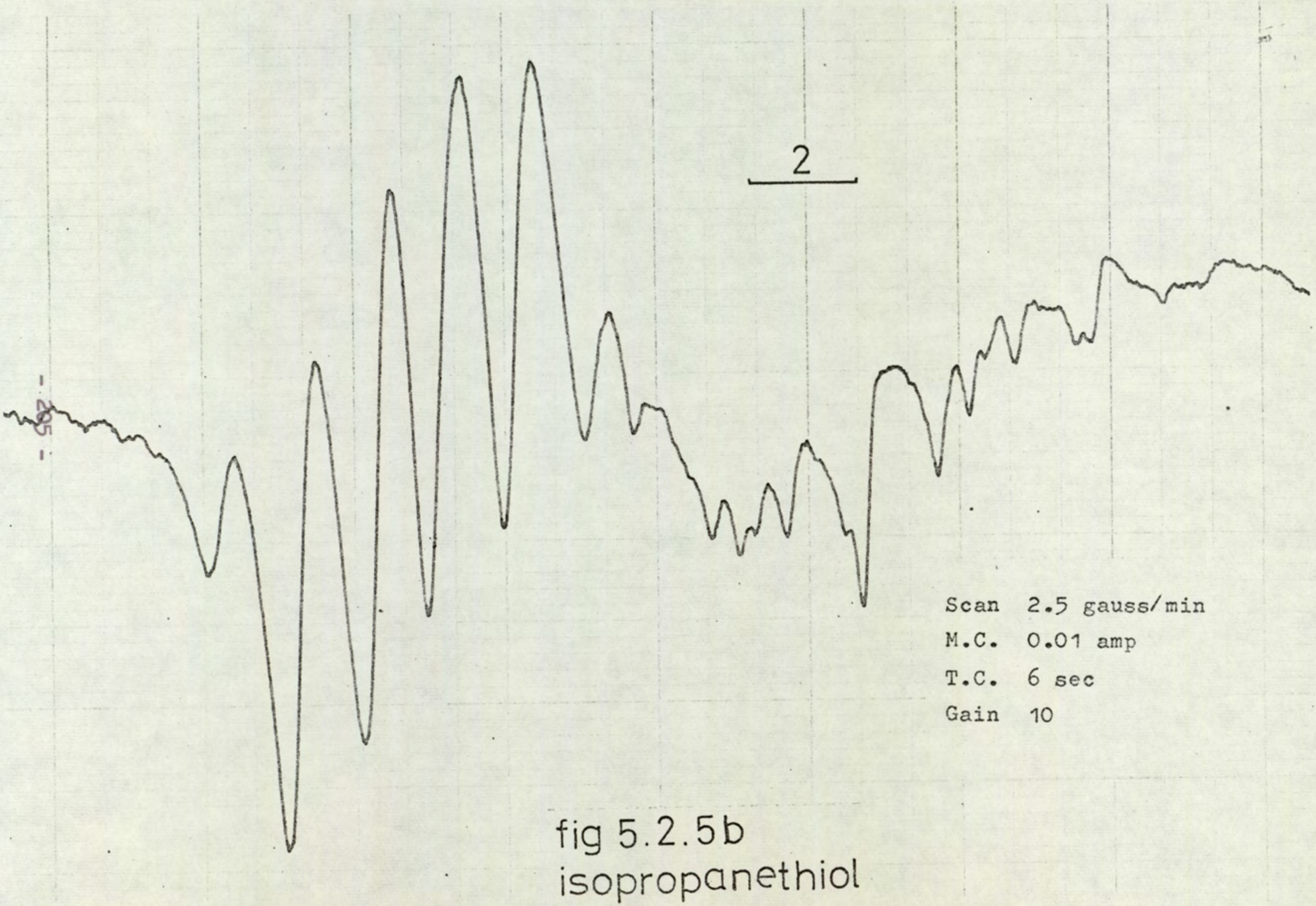
Some indications of hyperfine splitting were observed in the signal at higher g value, but this could not be resolved. The lower g value signal appeared to possess seven hyperfine lines. The resolution of this seven line signal was improved on dilution of the solution with dry chloroform. The g values were found to be 2.0190 and 2.0147. The resonances are shown in figure 5.2.5d.

In 20% oleum, similar signals were found from the resulting green solution, but no structure was resolved.



Scan	1 gauss/min
M.C.	0.01 amp
T.C.	6 sec
Gain	10

fig 5.2.5a
isopropanethiol



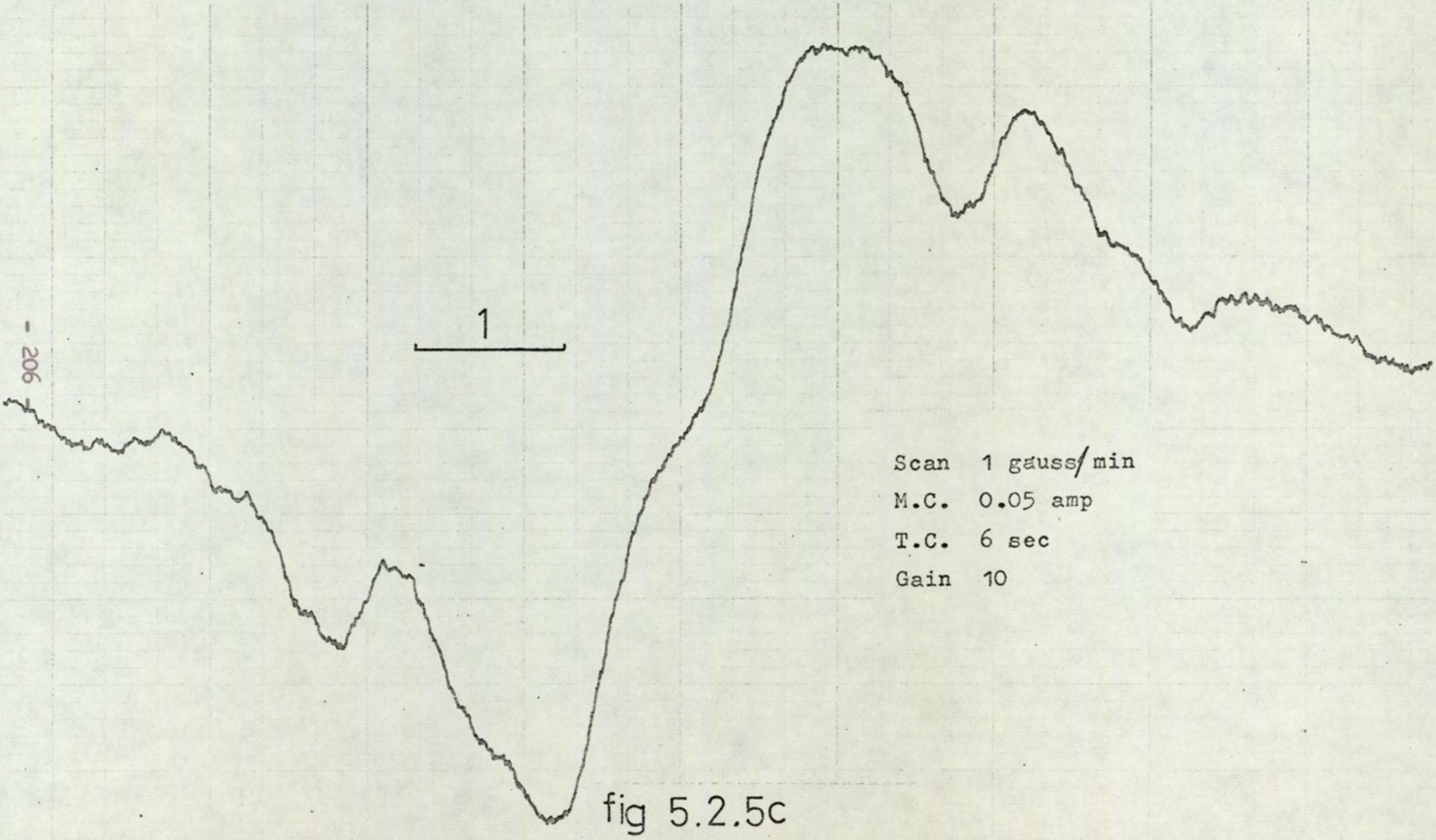
Scan 2.5 gauss/min

M.C. 0.01 amp

T.C. 6 sec

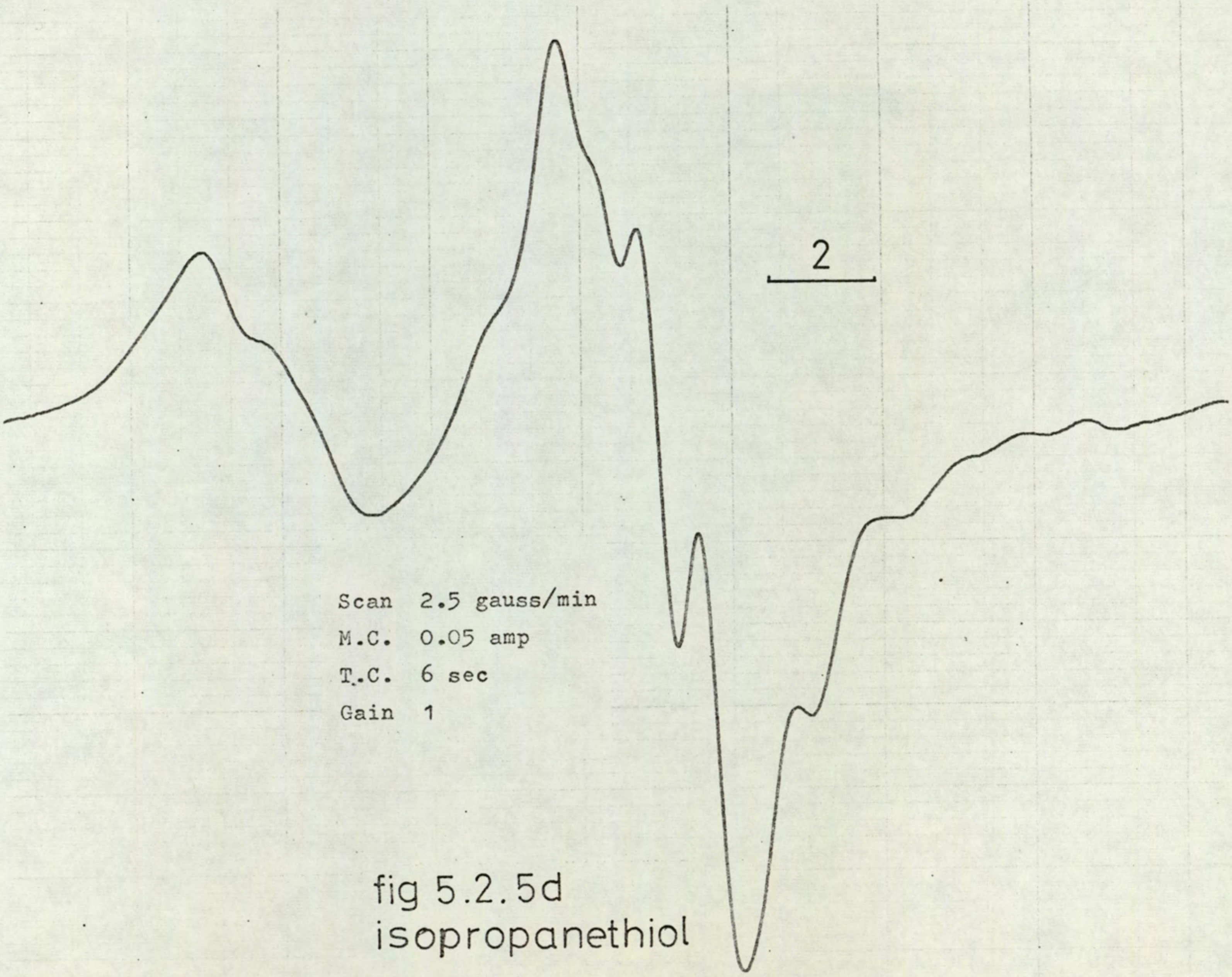
Gain 10

fig 5.2.5b
isopropanethiol



Scan 1 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

fig 5.2.5c
isopropanethiol



Scan 2.5 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 1

fig 5.2.5d
isopropanethiol

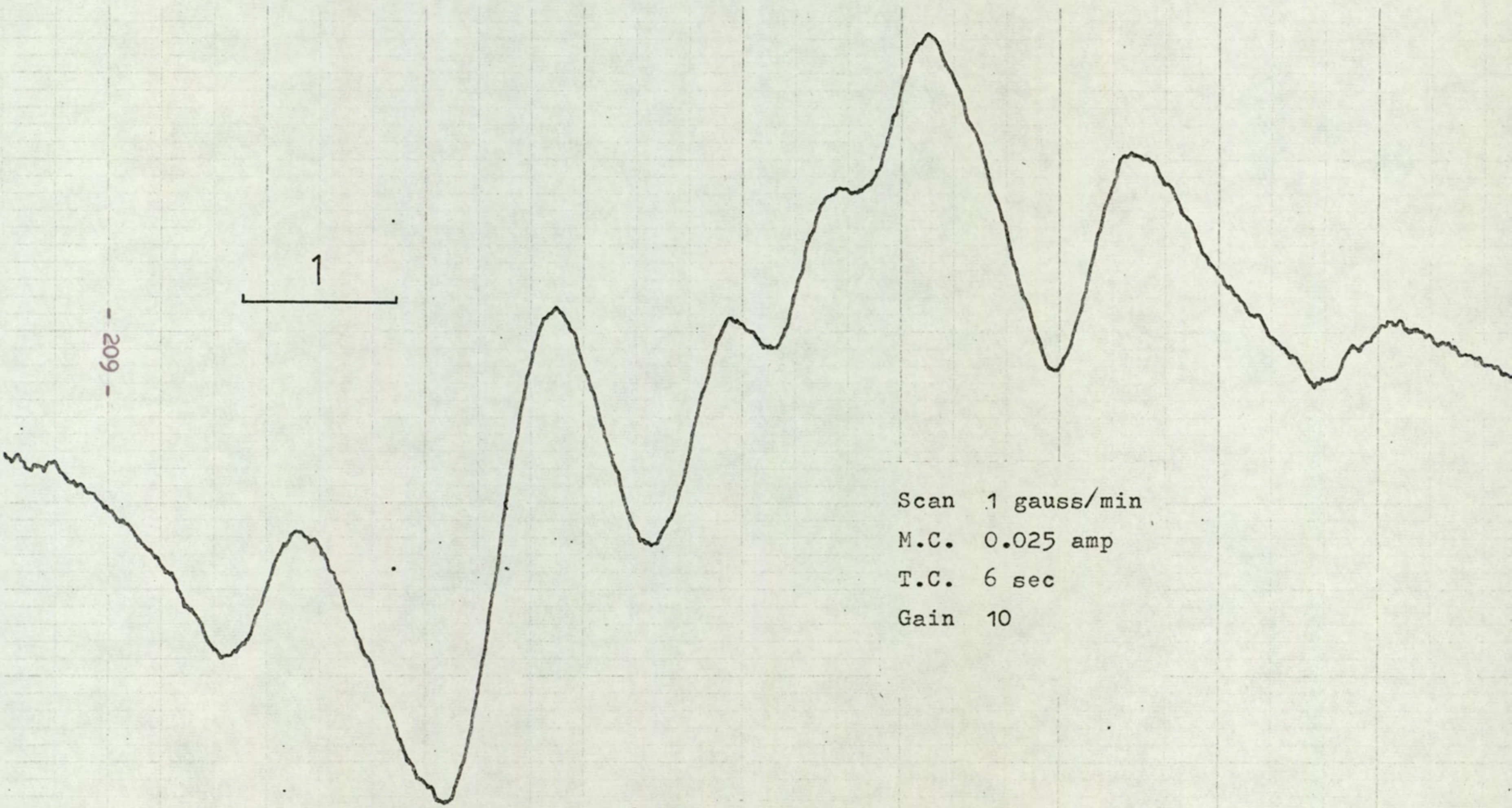
n-Butanethiol

When n-butanethiol was dissolved in 100% sulphuric acid, a yellow solution resulted which gave an esr signal. The absorption was at a g value of 2.0125, and consisted of seven hyperfine components, shown in figure 5.2.6a. On warming, the spectrum changed slightly to that shown in figure 5.2.6b, having intensity ratio

1 : 9.5 : 26.0 : 38.5 : 29.2 : 12.2 : 1.

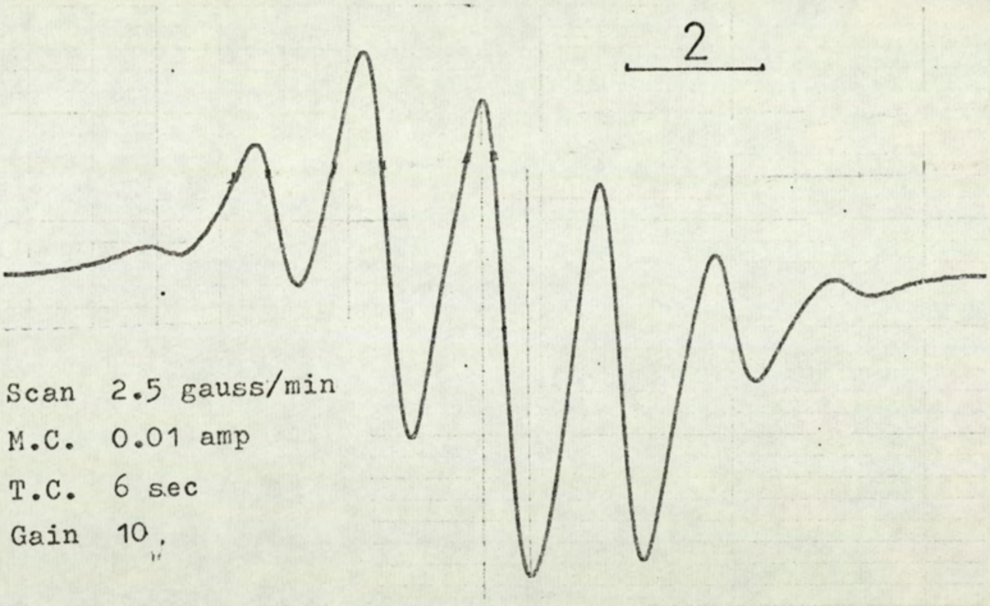
The splitting constant was approximately 1.8 gauss, but varied along the signal.

In deuterosulphuric acid, only five lines were observed, incompletely resolved, at g value 2.0131, figure 5.2.6c.



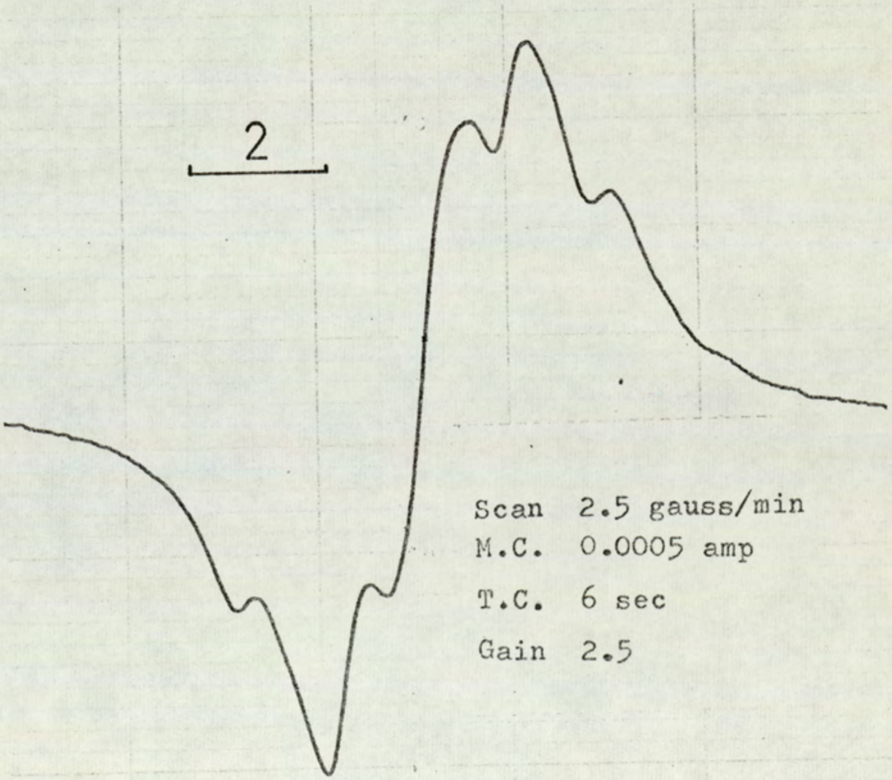
Scan 1 gauss/min
M.C. 0.025 amp
T.C. 6 sec
Gain 10

fig 5.2.6a
butanethiol



Scan 2.5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 10

fig 5.2.6b
butanethiol



Scan 2.5 gauss/min
M.C. 0.0005 amp
T.C. 6 sec
Gain 2.5

fig 5.2.6c
butanethiol

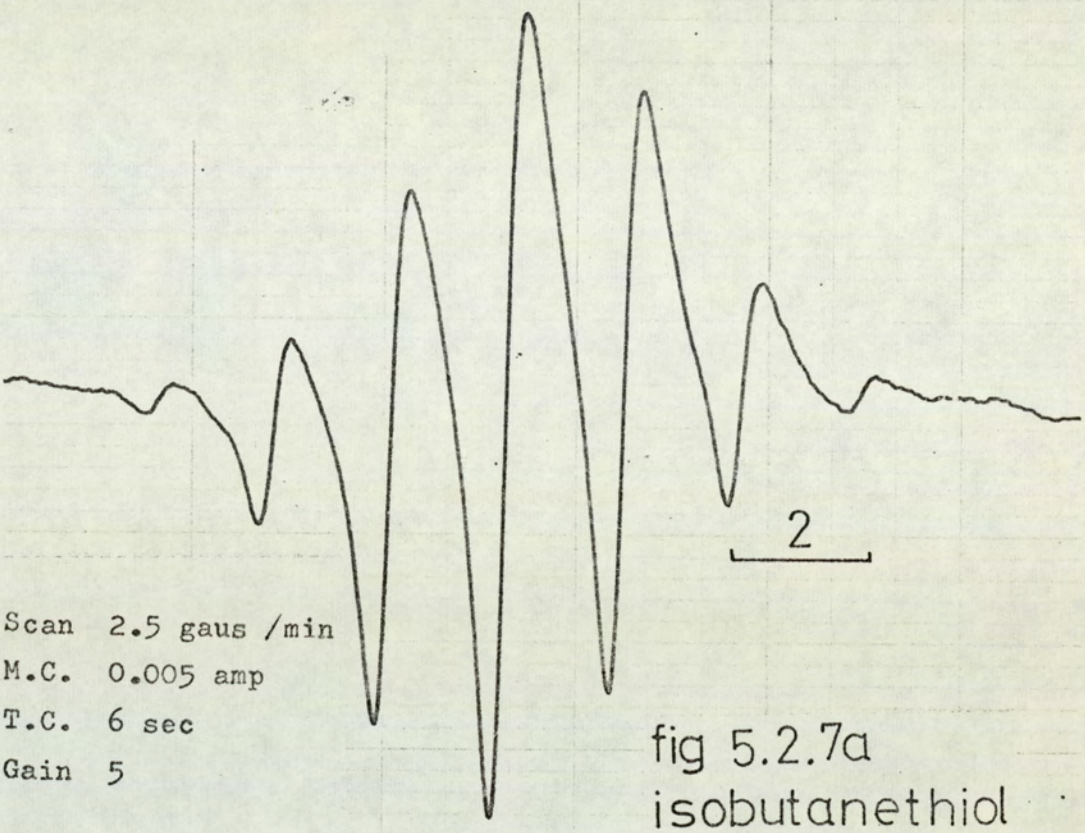
Isobutanethiol

In solution in 100% sulphuric acid, this compound yielded a species having an esr absorption at $g = 2.0125$ consisting of seven hyperfine lines in the intensity ratio

1 : 7.2 : 20.4 : 30.0 : 23.2 : 9.6 : 1.6

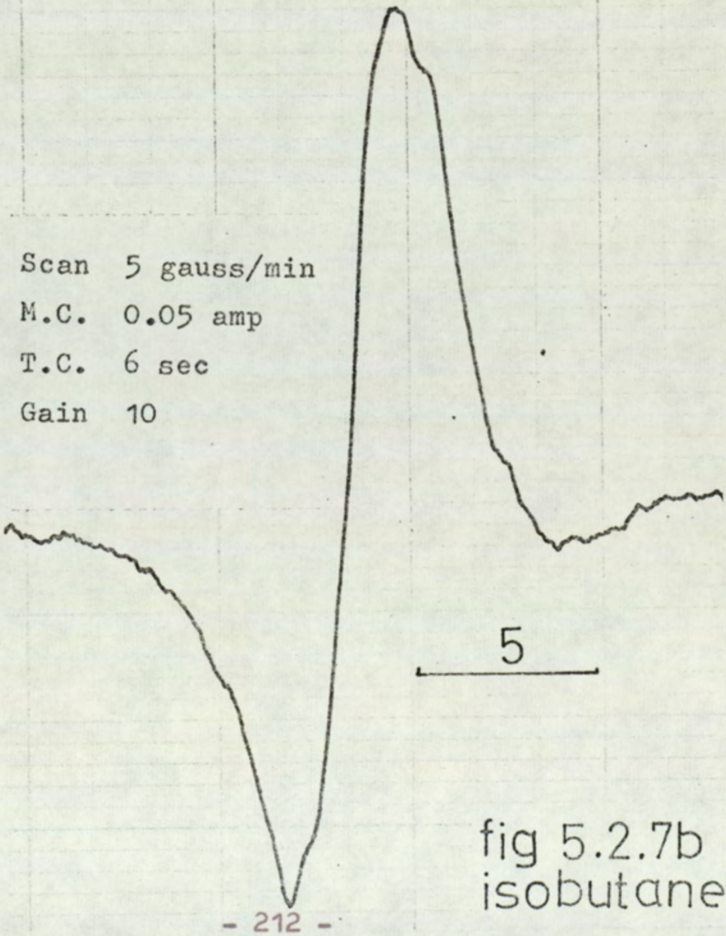
The splitting constant was 1.75 gauss. The resonance is shown in figure 5.2.7a.

In deuterosulphuric acid solution, a signal was obtained having a g value of 2.0127. No hyperfine structure could be resolved, although slight shoulders indicated that splitting existed, but of a degree slightly less than could be resolved under these conditions. The resonance is shown in figure 5.2.7b.



Scan 2.5 gaus /min
M.C. 0.005 amp
T.C. 6 sec
Gain 5

fig 5.2.7a
isobutanethiol



Scan 5 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

fig 5.2.7b
isobutanethiol

t-Butanethiol

When mixed with concentrated sulphuric acid, t-butanethiol gave a yellow solution with some white precipitate. The esr signal obtained from the solution was small, initially growing slowly, then decaying, becoming too small to be detected after nine days. The signal was apparently a doublet, with two other small peaks, one immediately before and one after the doublet.

On warming the solution, the two smaller peaks were found to increase in size relative to the doublet, indicating that they were due to a different species from that giving rise to the doublet.

The g-value of the main doublet was 2.0132, and the splitting constant 2.15 gauss. The spectrum from the solution kept at room temperature is shown in figure 5.2.8a. It can be seen that another small signal is present at higher g value. The signal obtained from the solution after heating is shown in figure 5.2.8b. The small signal at very high g value is still present, and some other signal appears at low g value also.

When dissolved in deuterosulphuric acid, at room temperature, t-butanethiol gave only a very small signal. On warming a larger signal was obtained, g value 2.0131, with more than three hyperfine components, but resolution could not be improved sufficiently to resolve these lines. The spectrum is shown in figure 5.2.8c.

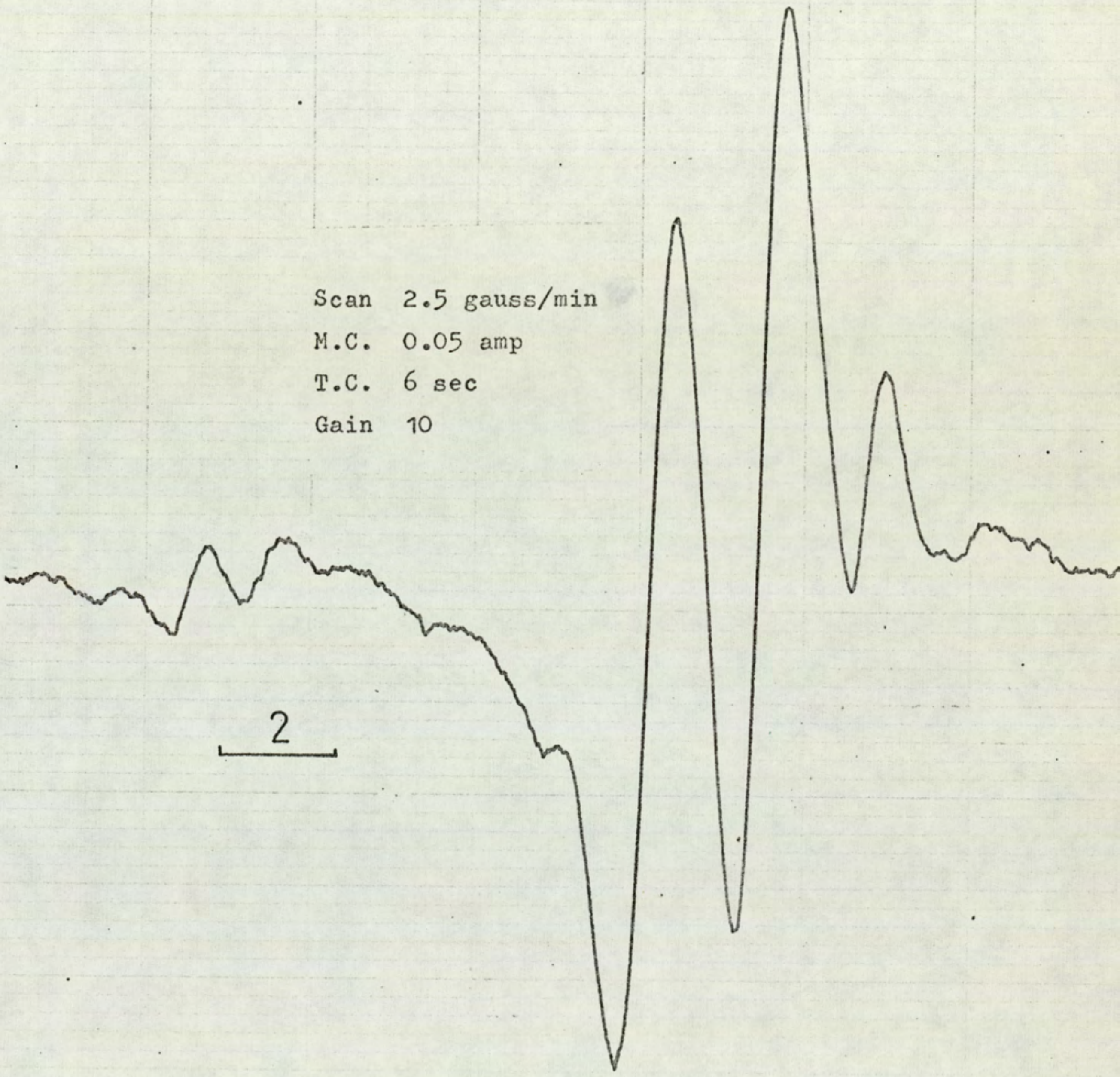
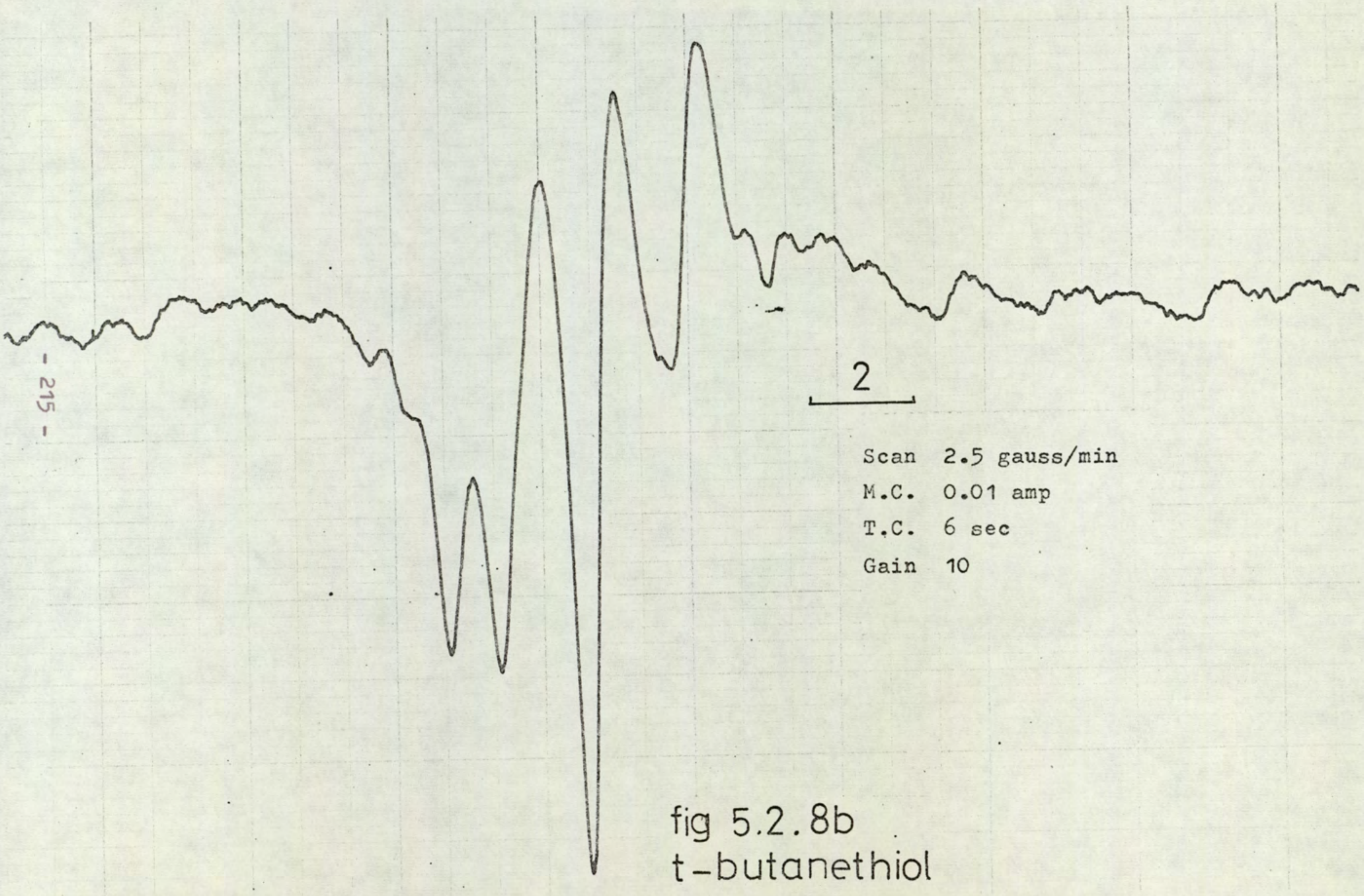
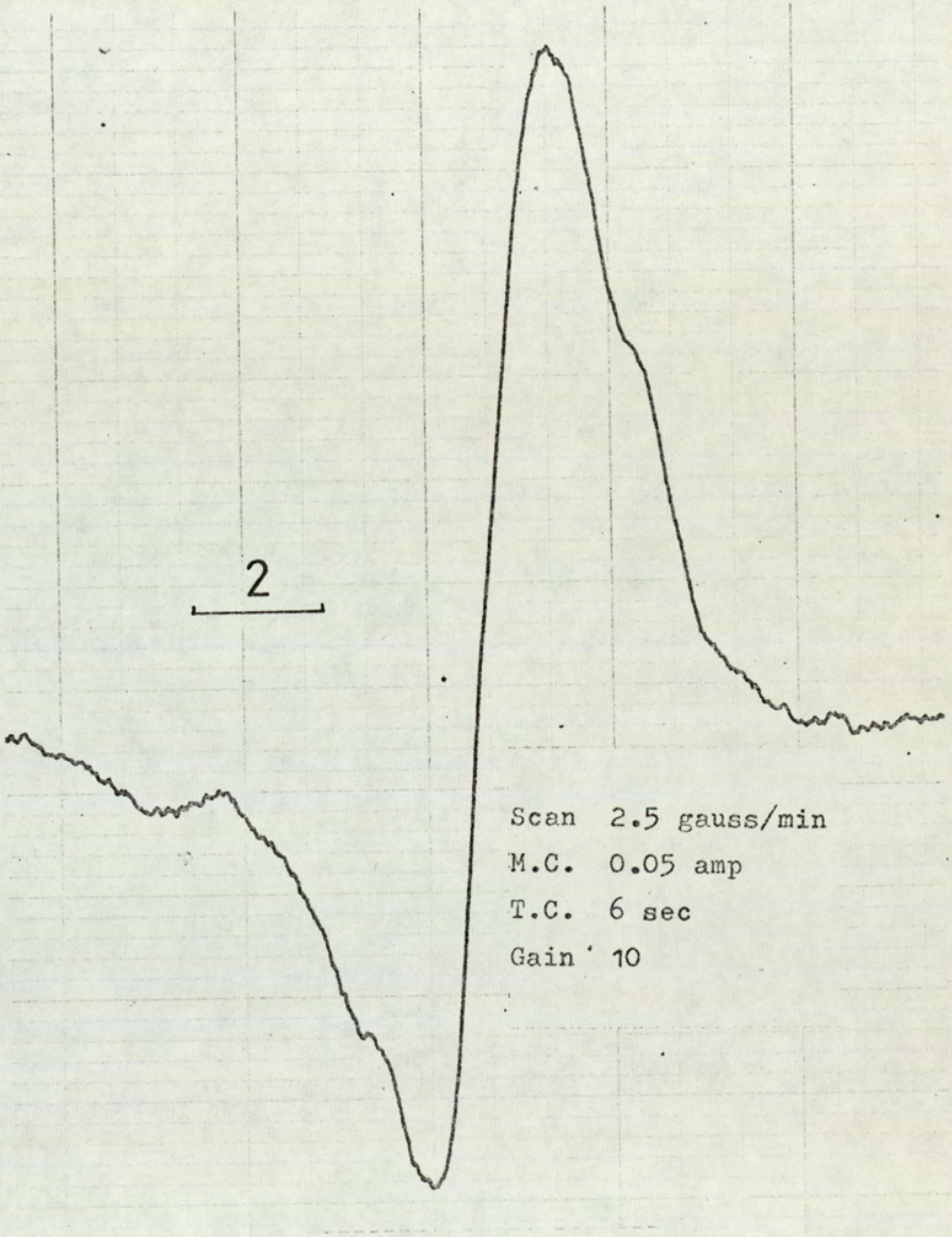


fig 5.2.8a
t-butanethiol



Scan 2.5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 10

fig 5.2.8b
t-butanethiol



Scan 2.5 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

fig 5.2.8c
t-butanethiol

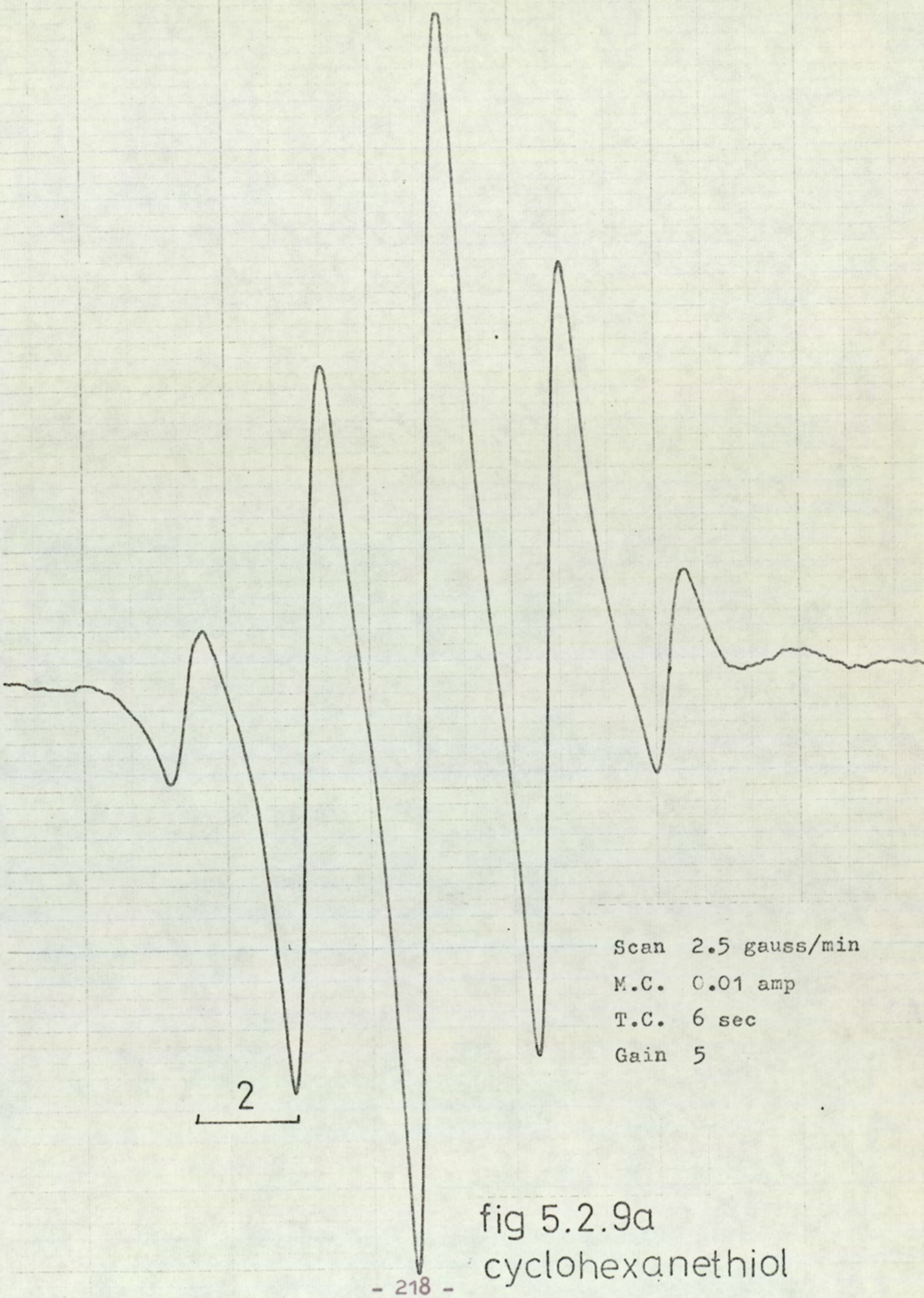
Cyclohexanethiol

When dissolved in 100% sulphuric acid, forming a yellow solution, this compound gave an esr signal, rapidly increasing in size, consisting of a major absorption at a g value of 2.0126, partly overlapped by a minor absorption at the high field side. Seven hyperfine lines were observed in the major absorption (the wing lines at high field,however, hidden by the overlapping minor signal).

The splitting constant was 2.49 gauss. The spectrum is shown in figure 5.2.9a. Figure 5.2.9b shows the spectrum under higher amplification, when the minor signal at the low g value is also visible.

In deuterosulphuric acid solution, a similar spectrum was obtained, the major signal having seven hyperfine components, each split again into three, the splitting constants being 2.49 gauss and approximately half of this value for the smaller one. The g value of the major line was found to be 2.0125.

The spectrum is shown in figure 5.2.9c where some of the structure of the signal with the lower g value can also be seen (the last line is not reproduced).



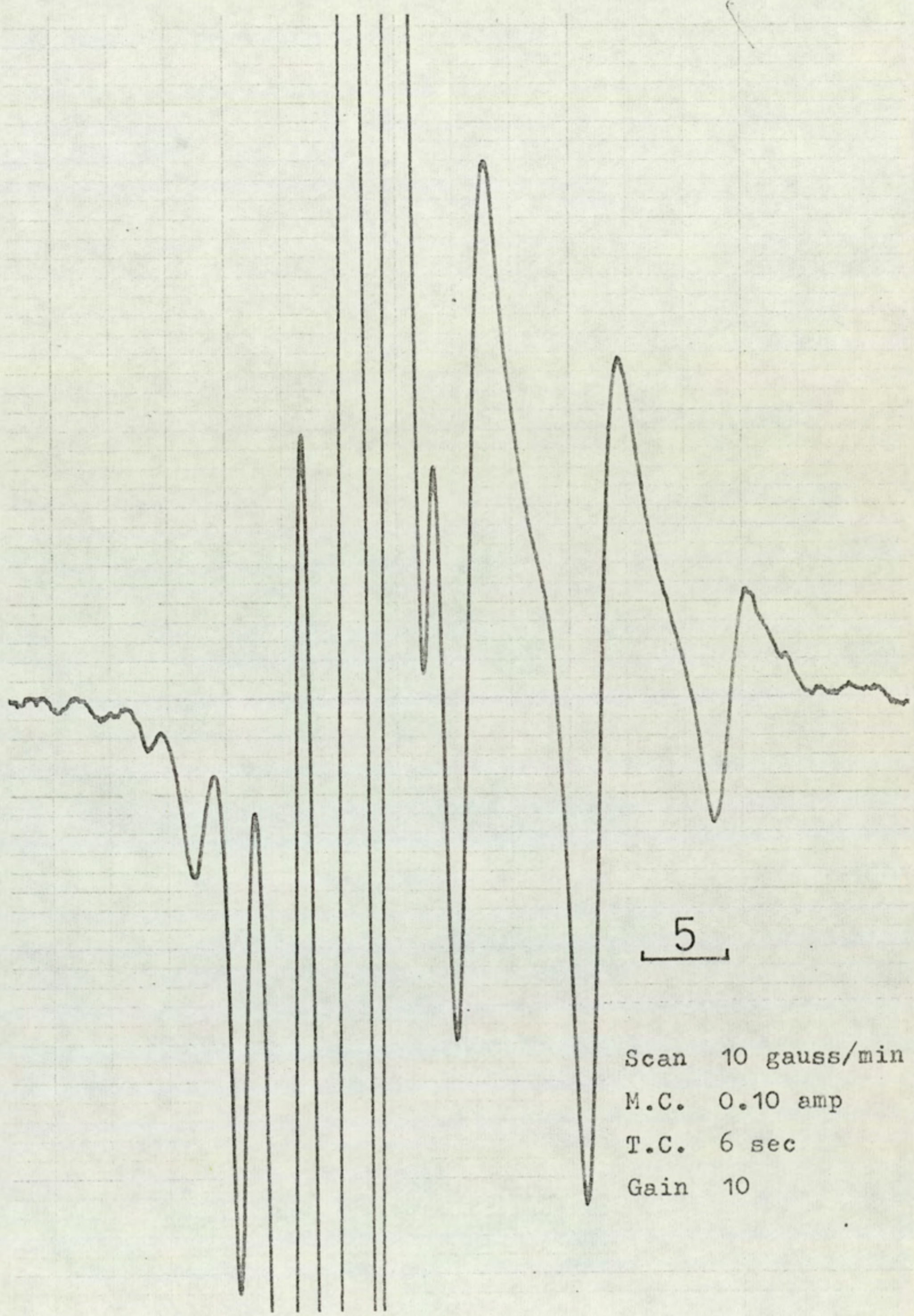
Scan 2.5 gauss/min

M.C. 0.01 amp

T.C. 6 sec

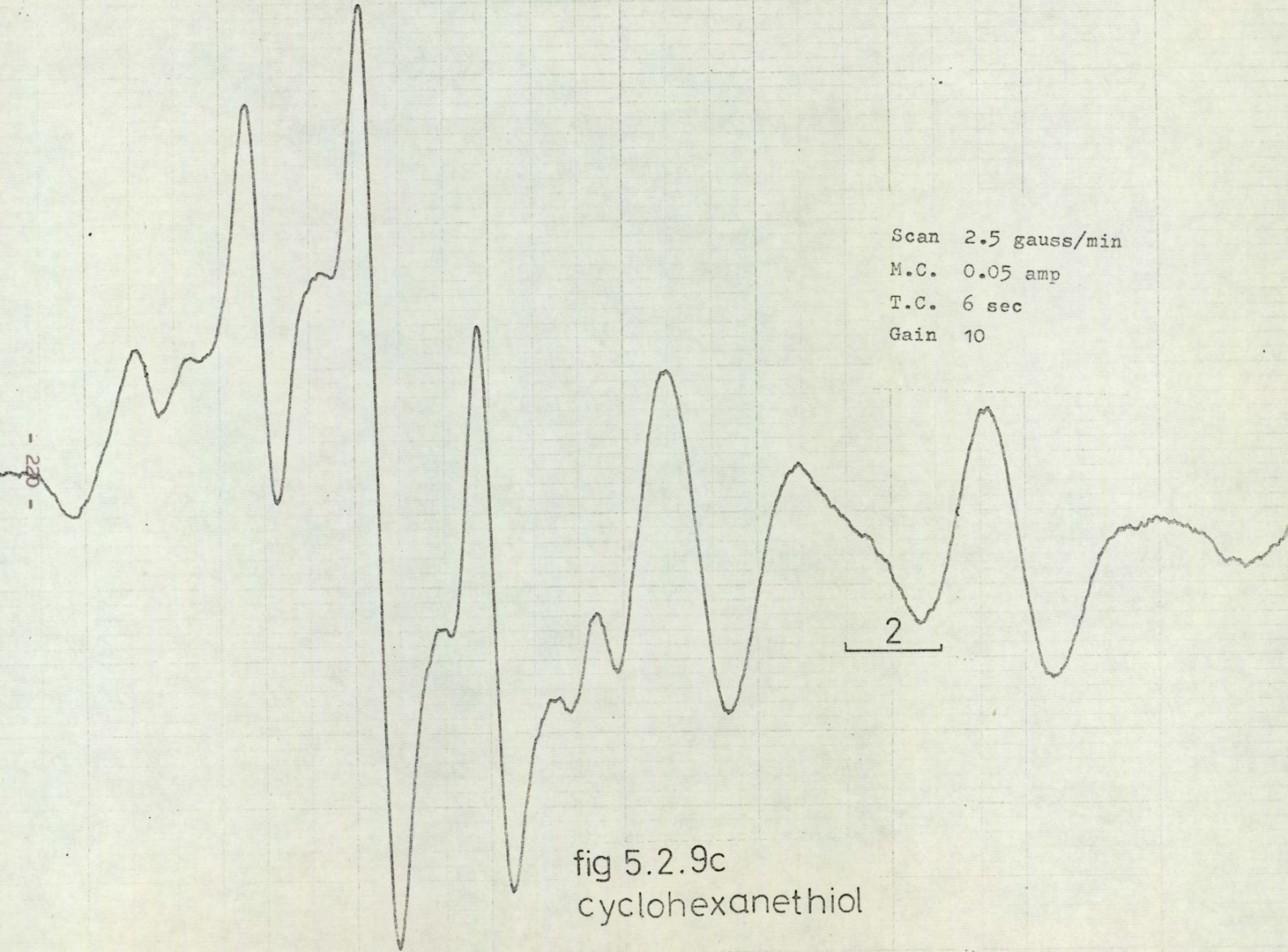
Gain 5

fig 5.2.9a
cyclohexanethiol



Scan 10 gauss/min
M.C. 0.10 amp
T.C. 6 sec
Gain 10

fig 5.2.9b
cyclohexanethiol



Scan 2.5 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

fig 5.2.9c
cyclohexanethiol

2-Propenethiol

A solution of 2-propenethiol in 100% sulphuric acid either a few hours old or on gentle warming developed a yellow-brown colour and yielded an esr spectrum. This spectrum consisted of a major component with a smaller resonance either side.

Under conditions of good resolution, the major component was found to consist of six hyperfine lines, with a splitting of 1.45 gauss and having the intensity ratios 1 : 3.7 : 4.4 : 4.2 : 4.0 : 1.3. It was centred at g = 2.0130. This resonance is shown in figure 5.2.10a.

The two minor resonances are shown in figure 5.2.10b. It was not found possible to resolve any structure in these signals. Under the conditions required to observe these resonances - i.e. a more concentrated solution and a high amplifier gain - the main resonance was not resolved into its components, and was also off-scale.

In deuterosulphuric acid, a similar yellow-brown colour was obtained, the solution giving an esr spectrum. This appeared to consist of a signal with hyperfine structure, at least six lines being present. It was not found possible to resolve this signal completely. The g value was measured as 2.0132. This spectrum is shown in figure 5.2.10c.

Other signals were also found at lower and higher field, as in sulphuric acid. These are shown in figure 5.2.10d.

In chlorosulphonic acid solution, however, a different spectrum was observed. A vigorous reaction occurred when the thiol was added to this acid at room temperature, resulting in tarry products formed with the evolution of heat. If the acid was cooled in an ice-salt bath, and the thiol added dropwise with vigorous stirring, a yellow solution was formed which had an esr spectrum of five hyperfine components, as shown in figure 5.2.10e. This had a g value of 2.016. The intensity ratios were 1.36 : 4.35 : 7.85 : 4.07 : 1.0 and splitting of 9.31 gauss was observed.

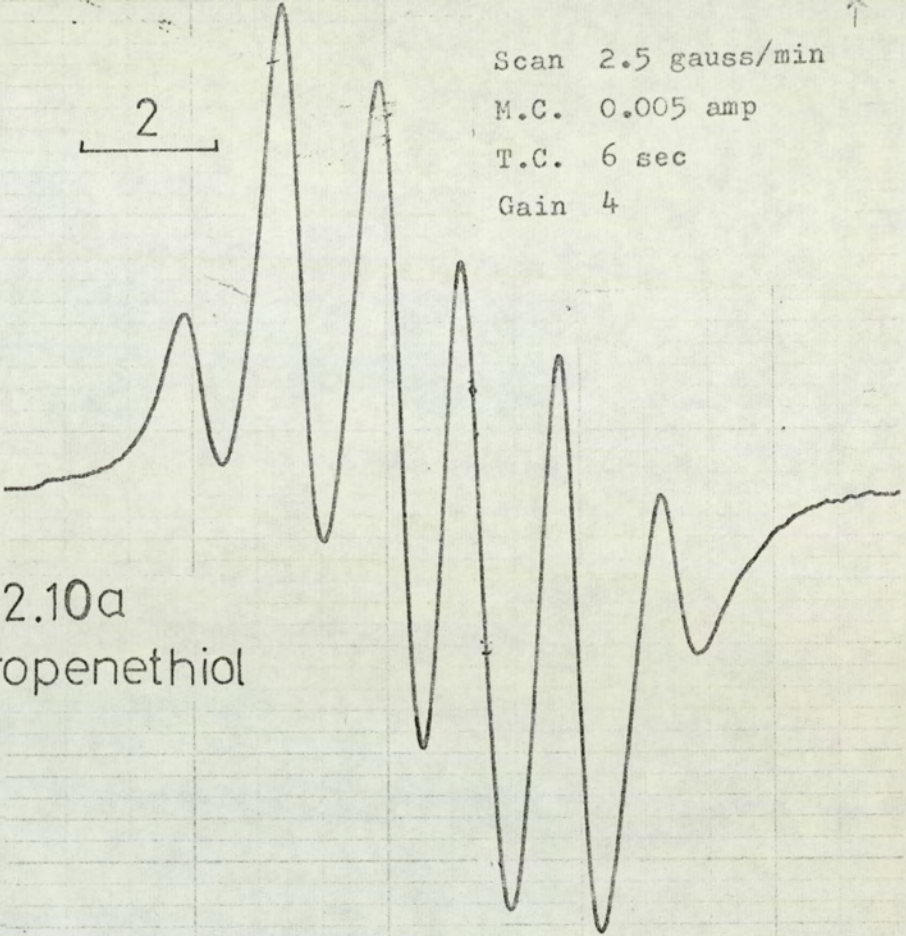
This signal was observed to change with time to a nine line signal, although this was not resolved completely.

The thiol was dissolved in a 1 : 1 mixture of chlorosulphonic acid and chloroform cooled in ice-salt. The six line spectrum was obtained, changing rapidly to a nine line one, shown in figure 5.2.10f. The g value of this signal was 2.015.

Solution in 20% oleum yielded a yellow colour, the solution giving an esr spectrum of basically five lines, as in figure 5.2.10g.

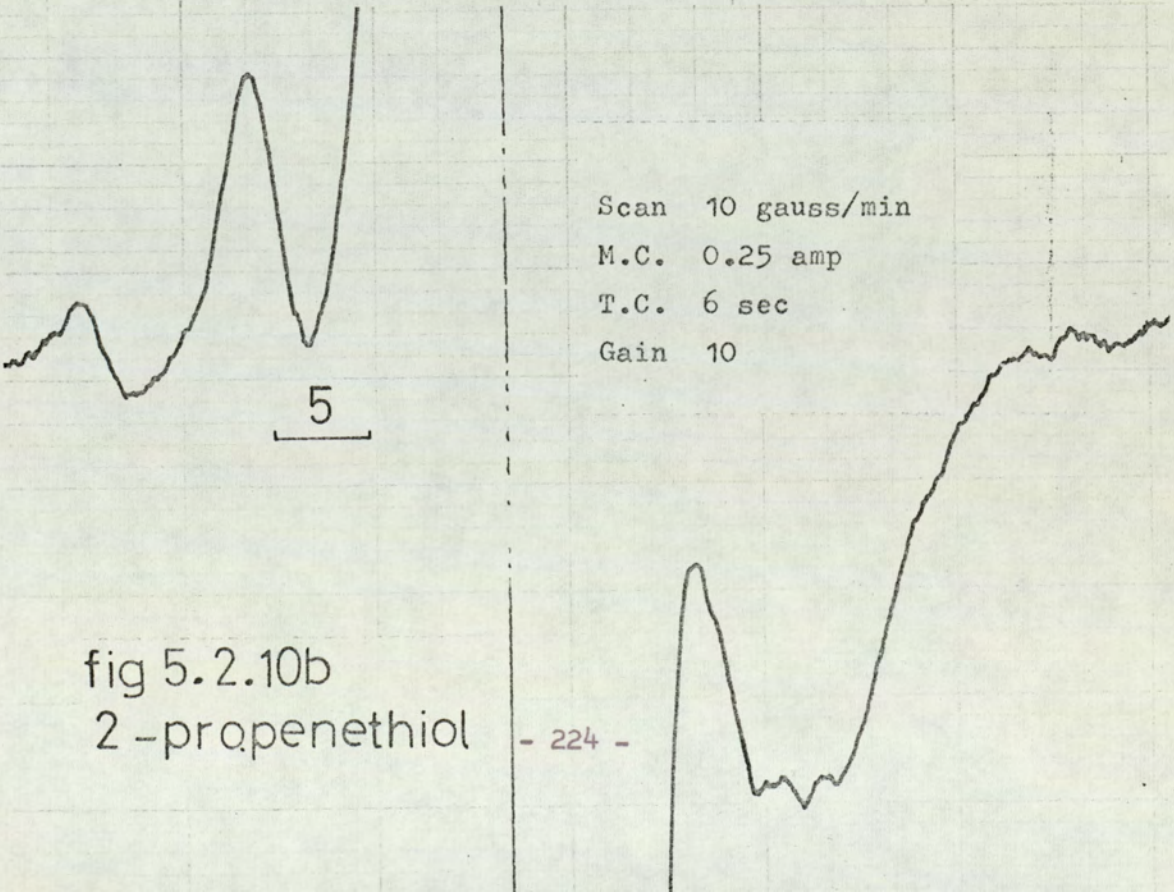
It can be seen that some other splitting is present, although this could not be resolved completely. The major splitting is 8.29 gauss, the secondary splitting is estimated as approximately half this. The g value of this signal was measured as 2.015.

A vigorous reaction was observed between 2-propenethiol and 65% oleum, giving a blackish solution containing a species with an esr spectrum of five hyperfine lines, figure 5.2.10h. This had a g value of 2.016, and a splitting constant of 8.29 gauss. The intensity ratios were approximately 1 : 2.8 : 4.8 : 2.7 : 1.



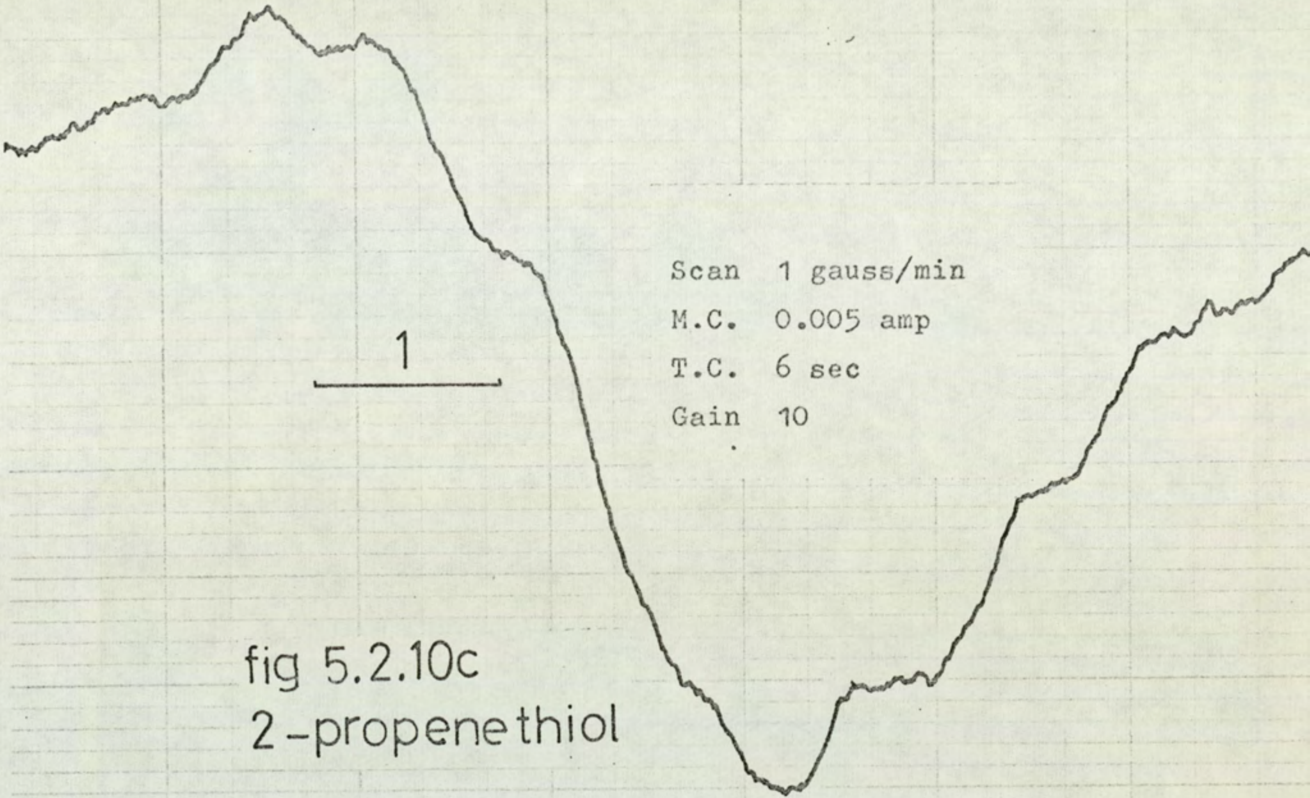
Scan 2.5 gauss/min
M.C. 0.005 amp
T.C. 6 sec
Gain 4

fig 5.2.10a
2-propenethiol



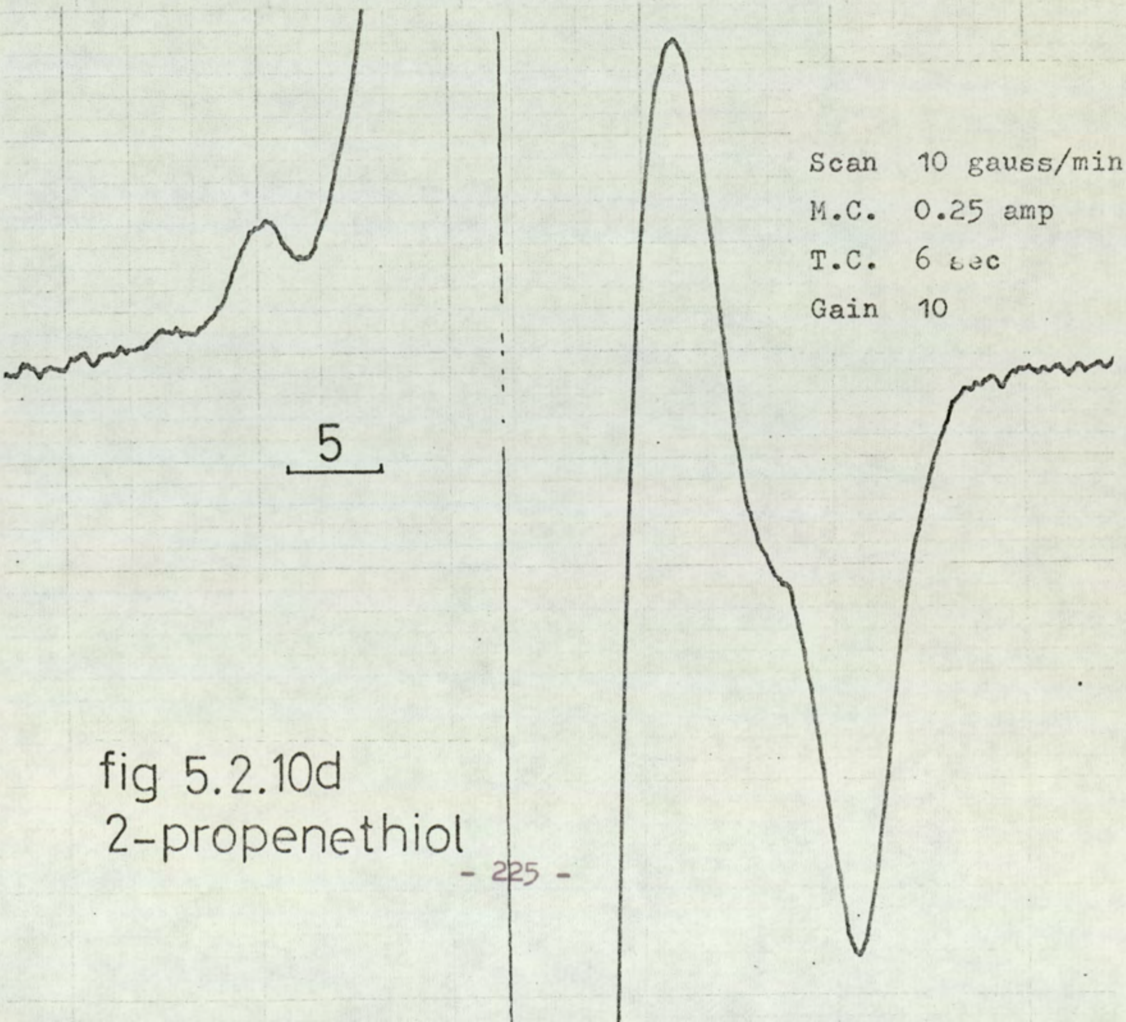
Scan 10 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 10

fig 5.2.10b
2-propenethiol



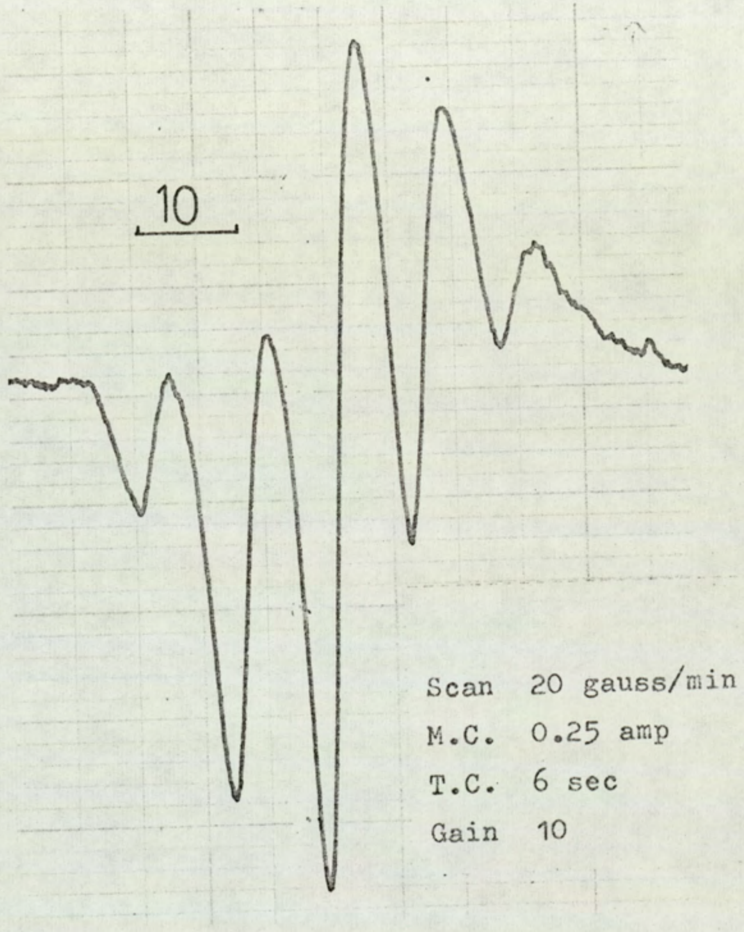
Scan 1 gauss/min
M.C. 0.005 amp
T.C. 6 sec
Gain 10

fig 5.2.10c
2-propenethiol



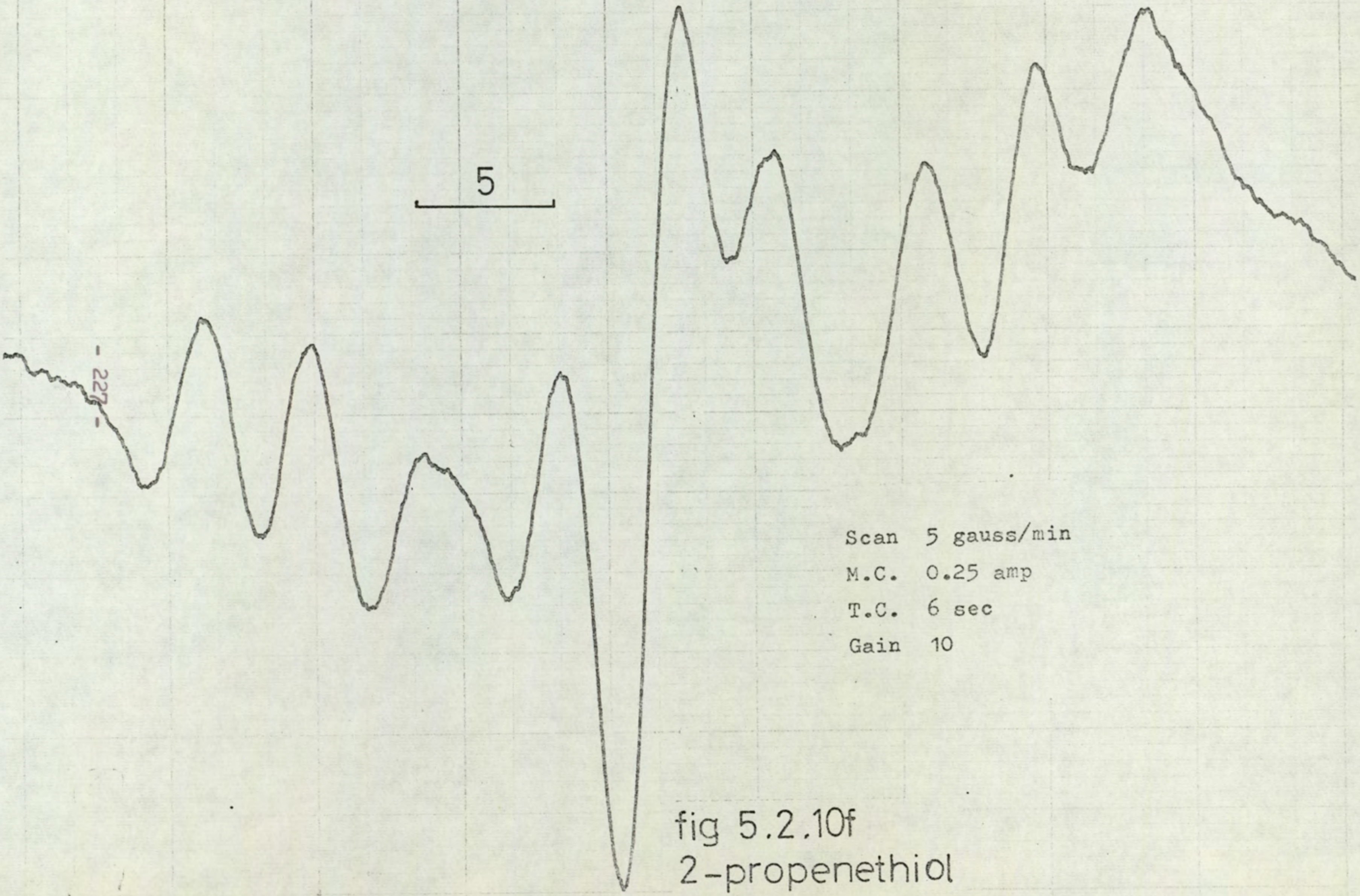
Scan 10 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 10

fig 5.2.10d
2-propenethiol



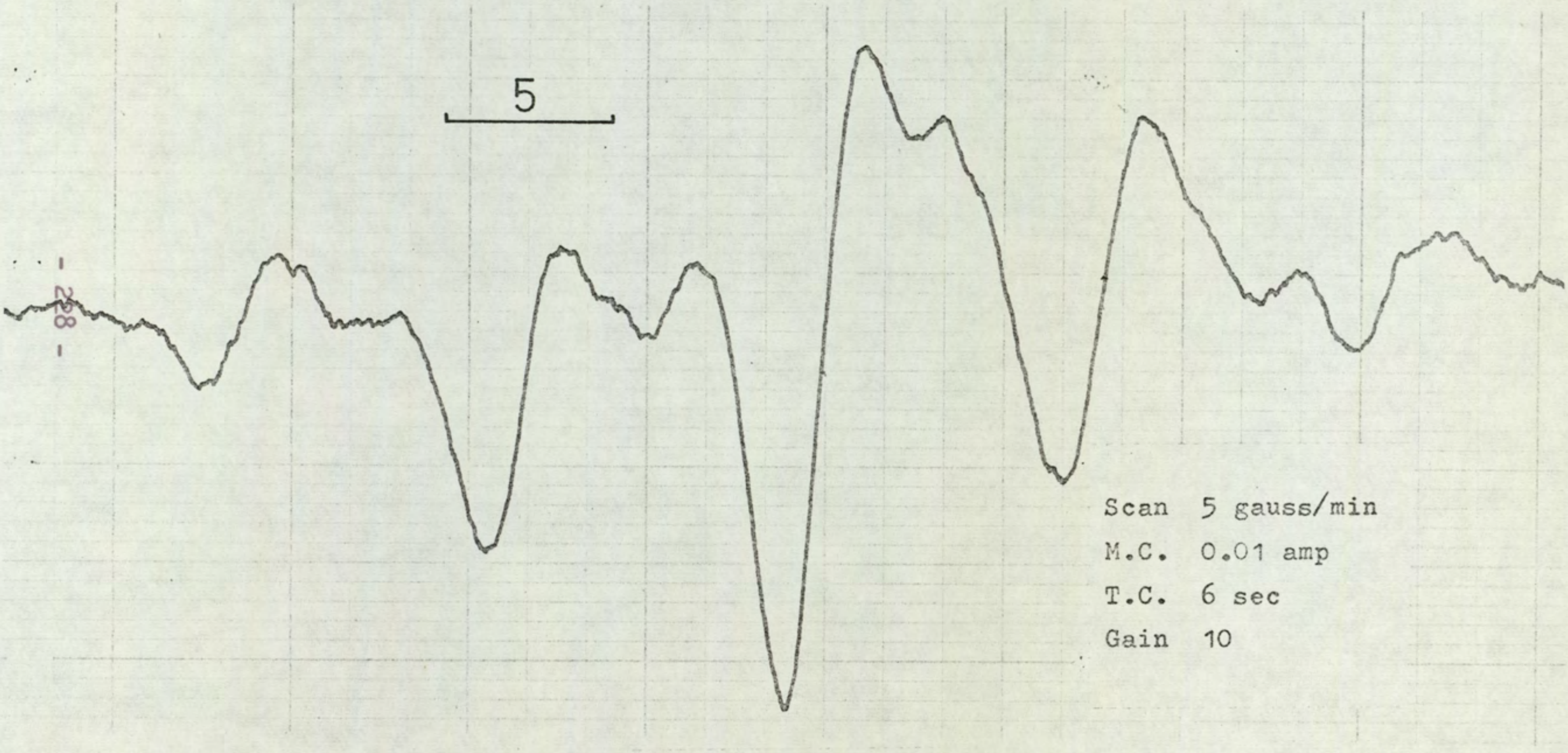
Scan 20 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 10

fig 5.2.10e
2-propenethiol



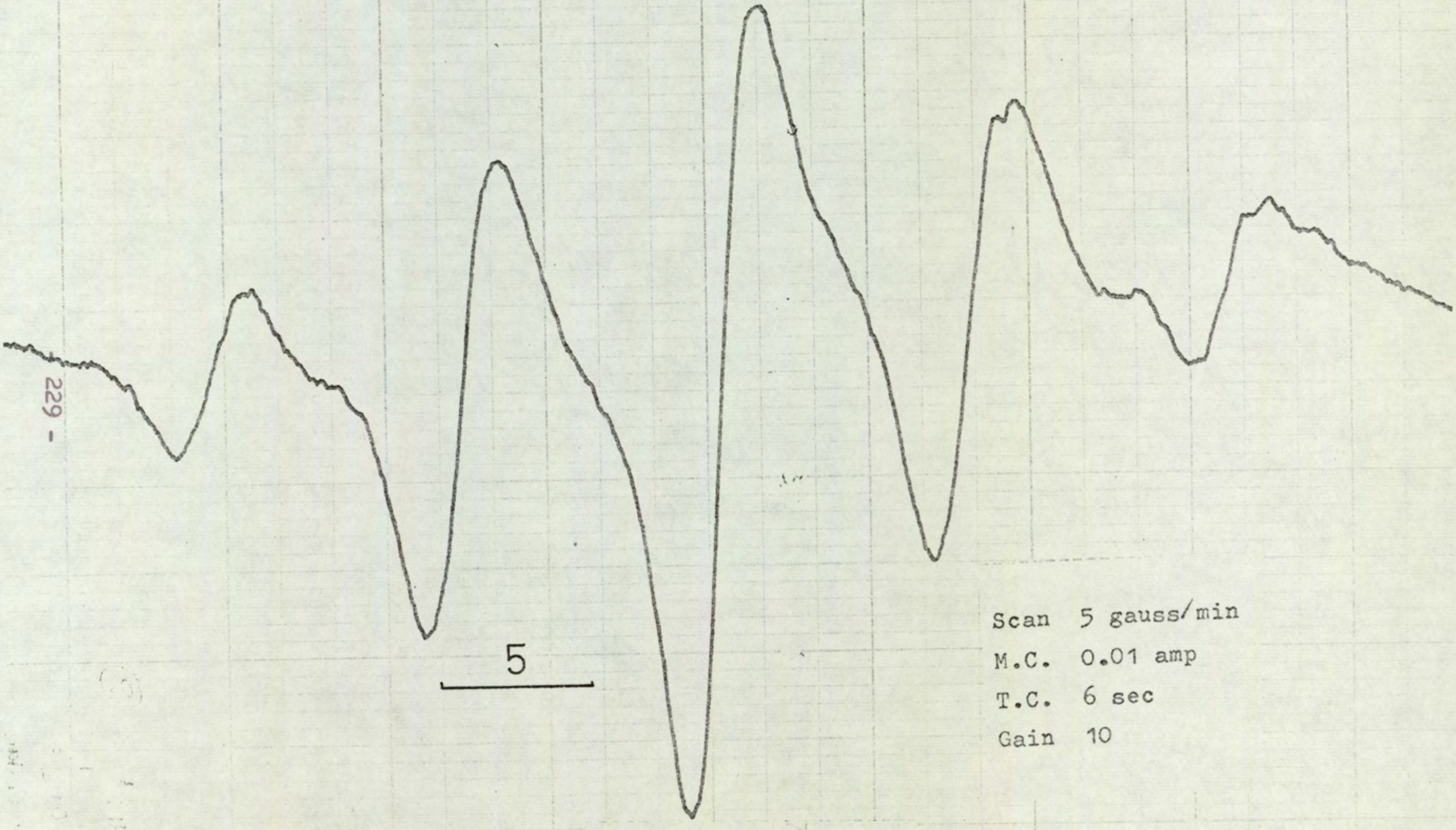
Scan 5 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 10

fig 5.2.10f
2-propenethiol



Scan 5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 10

fig 5.2.10g
2-propenethiol



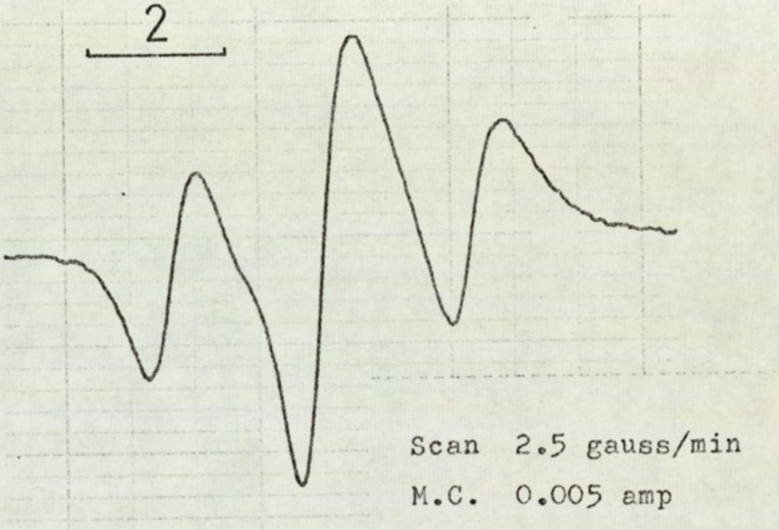
Scan 5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 10

fig 5.2.10h
2-propenethiol

Perchloromethanethiol

At room temperature, a very small signal was obtained from a solution of perchloromethanethiol in 100% sulphuric acid. On warming, however, the initially-formed precipitate redissolved, and a strong signal was found. This had a g value of 2.0135 and intensity ratio 1 : 2.1 : 1. The splitting constant was 2.24 gauss. The spectrum is shown in figure 5.2.11. (The absence of protons in this material was confirmed by nmr spectroscopy).

No hyperfine splitting could be seen in the resonance obtained using a deuterosulphuric acid solution. The resulting singlet had a g value of 2.0134.



Scan 2.5 gauss/min
M.C. 0.005 amp
T.C. 6 sec
Gain 5

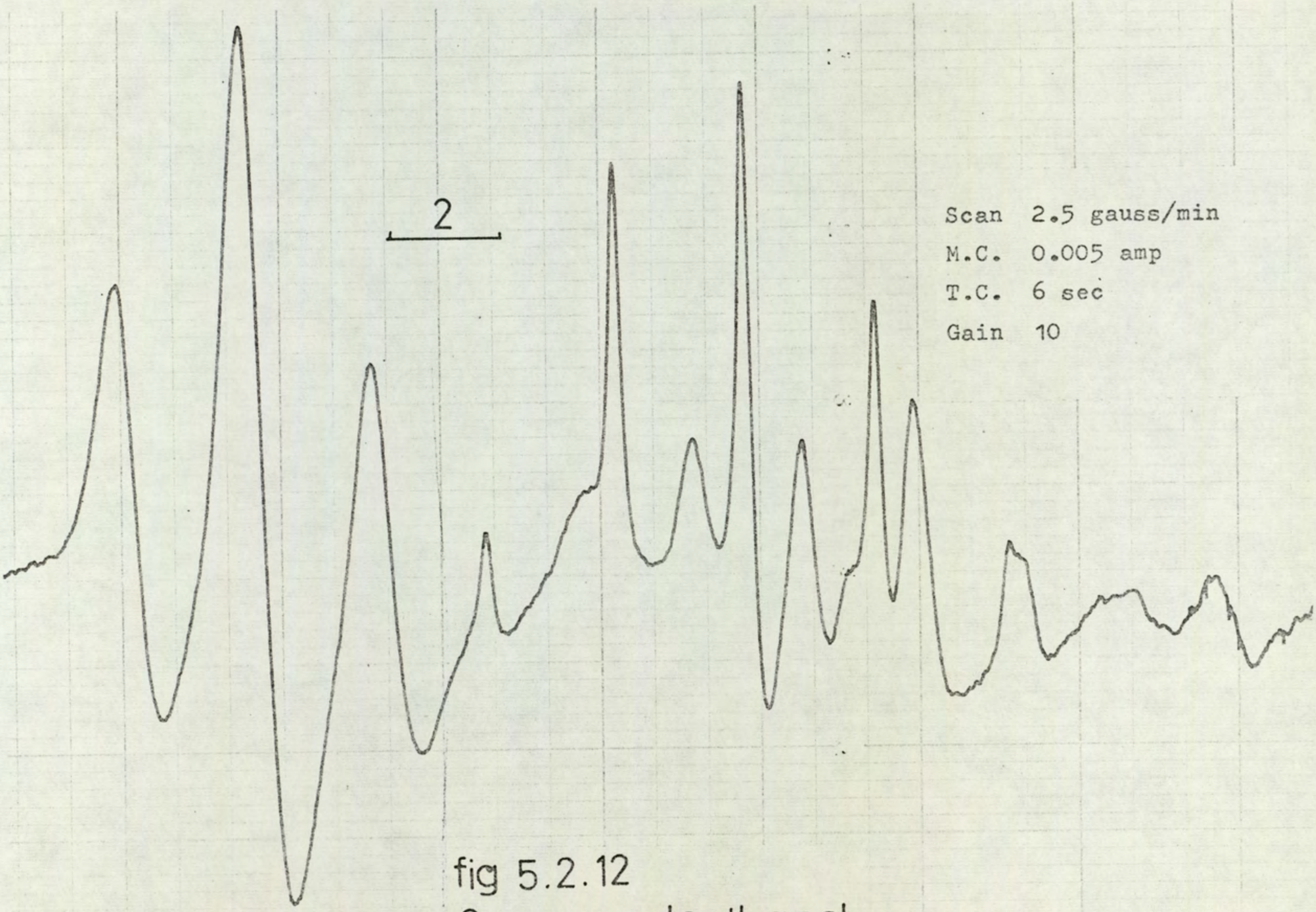
fig 5.2.11
perchloromethanethiol

2-Mercaptoethanol

A vigorous reaction occurred with concentrated sulphuric acid, yielding a crystalline solid, which redissolved to form a yellow solution. A very small esr signal was obtained after several hours, which decayed during a few days. Useful signals were obtained by warming, when the resonance was seen to consist of two absorptions. The absorption at higher g value was a triplet, the lower g value signal was more complex, being basically a quintet, with each line apparently split into three.

The g value of the triplet was 2.0135, the intensity ratios 1.1 : 2.2 : 1.0 and splitting constant 2.26 gauss.

The resonance is shown in figure 5.2.12 where the low g signal can also be seen.



Scan 2.5 gauss/min
M.C. 0.005 amp
T.C. 6 sec
Gain 10

fig 5.2.12
2-mercaptoethanol

2-Methyl-2-(n-octyloxy)propanethiol

On solution in concentrated sulphuric acid, a green colour developed, although no esr signal could be detected, even after two days. On warming, the solution turned brown-red and yielded an esr signal of g value 2.0126. The hyperfine structure observed consisted of seven lines with a splitting constant of 1.81 gauss. The spectrum is shown in figure 5.2.13 where the line indicated at the high field side is thought to be part of a secondary resonance.also observed. The intensity ratio was measured as 1 : 10 : 30 : 44 : 34 : 12 : 2

The spectrum was also recorded using higher gain and modulation current in order to determine whether any more wing lines were present. None were observed, but the signal size could not be increased very much before lack of resolution, brought about by modulation current broadening, made their detection, if present, impossible. Thus this signal could conceivably consist of nine lines, not the seven observed.

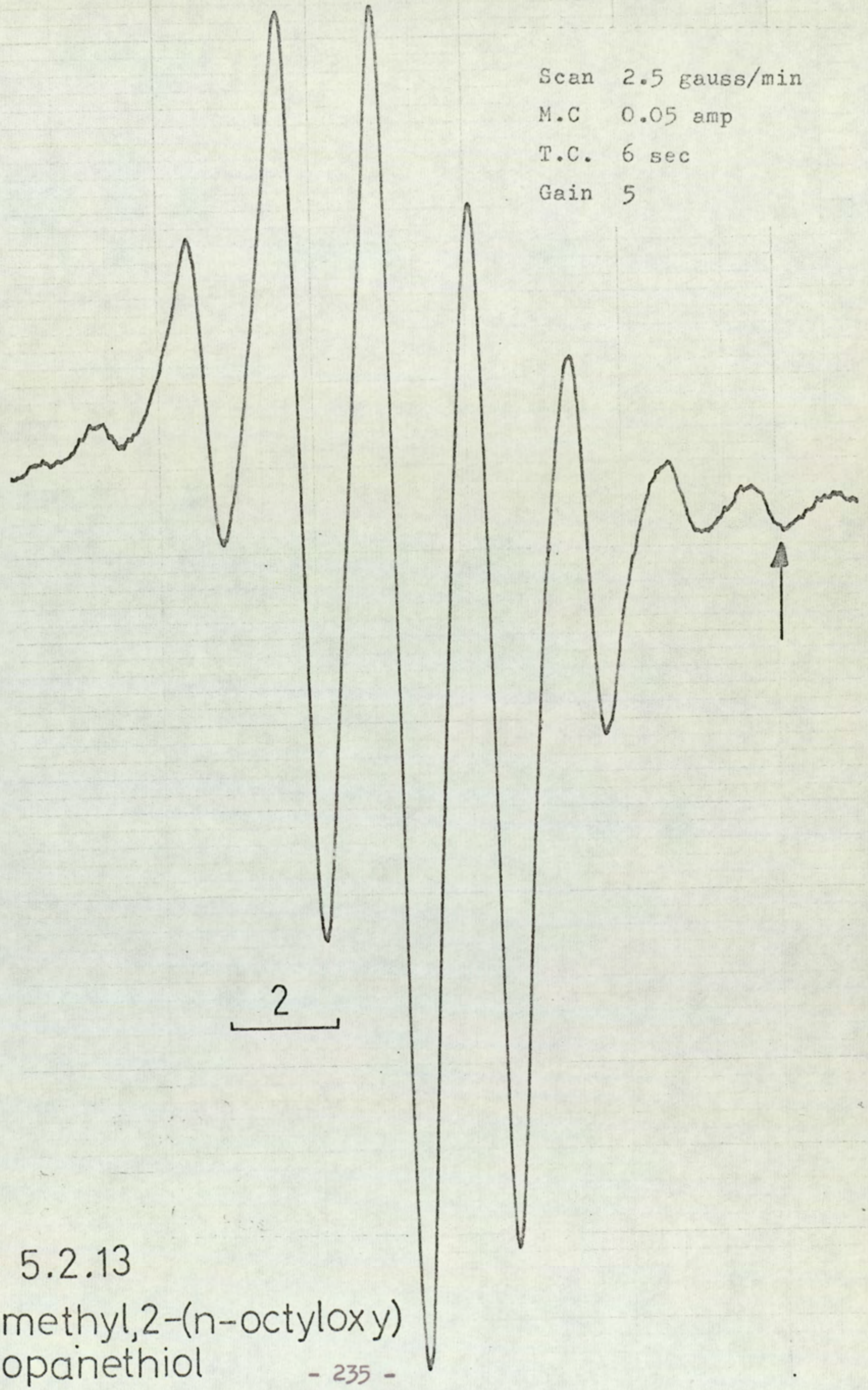


fig 5.2.13
2-methyl,2-(n-octyloxy) propanethiol

Diethyl sulphide

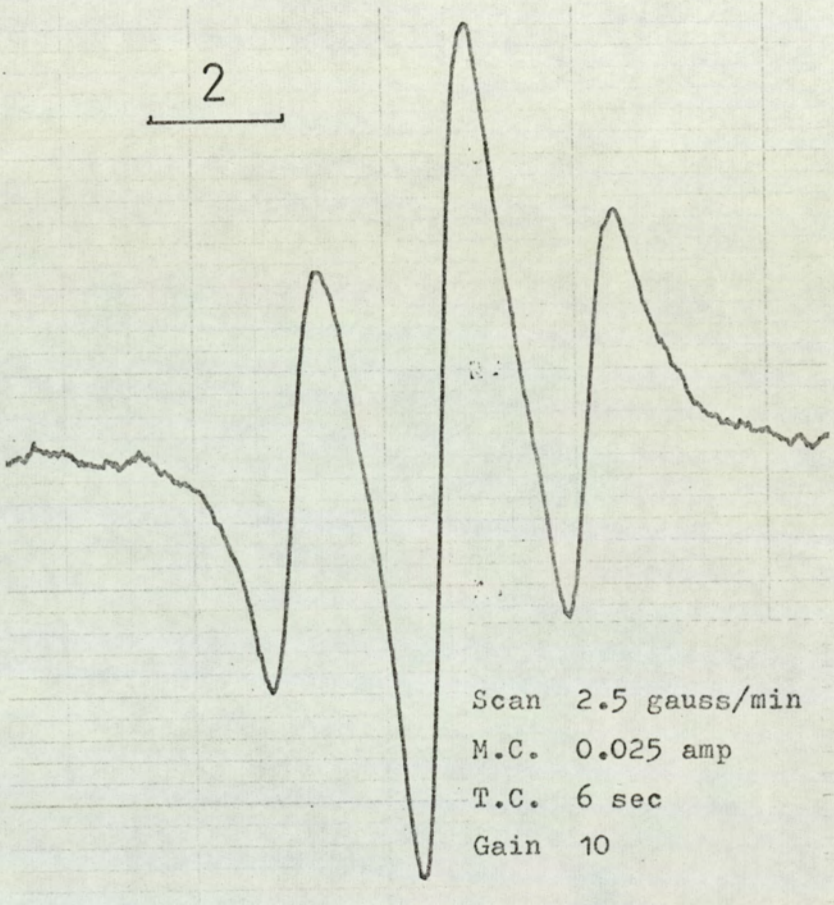
When diethyl sulphide was mixed with concentrated sulphuric acid at room temperature, no reaction was observed to occur even after several days. On warming, however, the solution turned yellow then brown, free radicals being detected only in dark brown solutions.

The esr signal was a triplet at $g = 2.0131$, with splitting constant 2.24 gauss. The intensity ratio was 1.0 : 2.02 : 0.96. The signal is shown in figure 5.2.14.

Ethyl-isopropyl sulphide

When a solution of this mixed sulphide in concentrated sulphuric acid was heated, it developed an esr absorption at $g = 2.0133$, the line being split into a triplet. The splitting constant was 2.46 gauss and intensity ratio 1.0 : 2.9 : 1.3. The spectrum is shown in figure 5.2.15.

On further heating, a small, unresolved resonance was observed at lower g value.



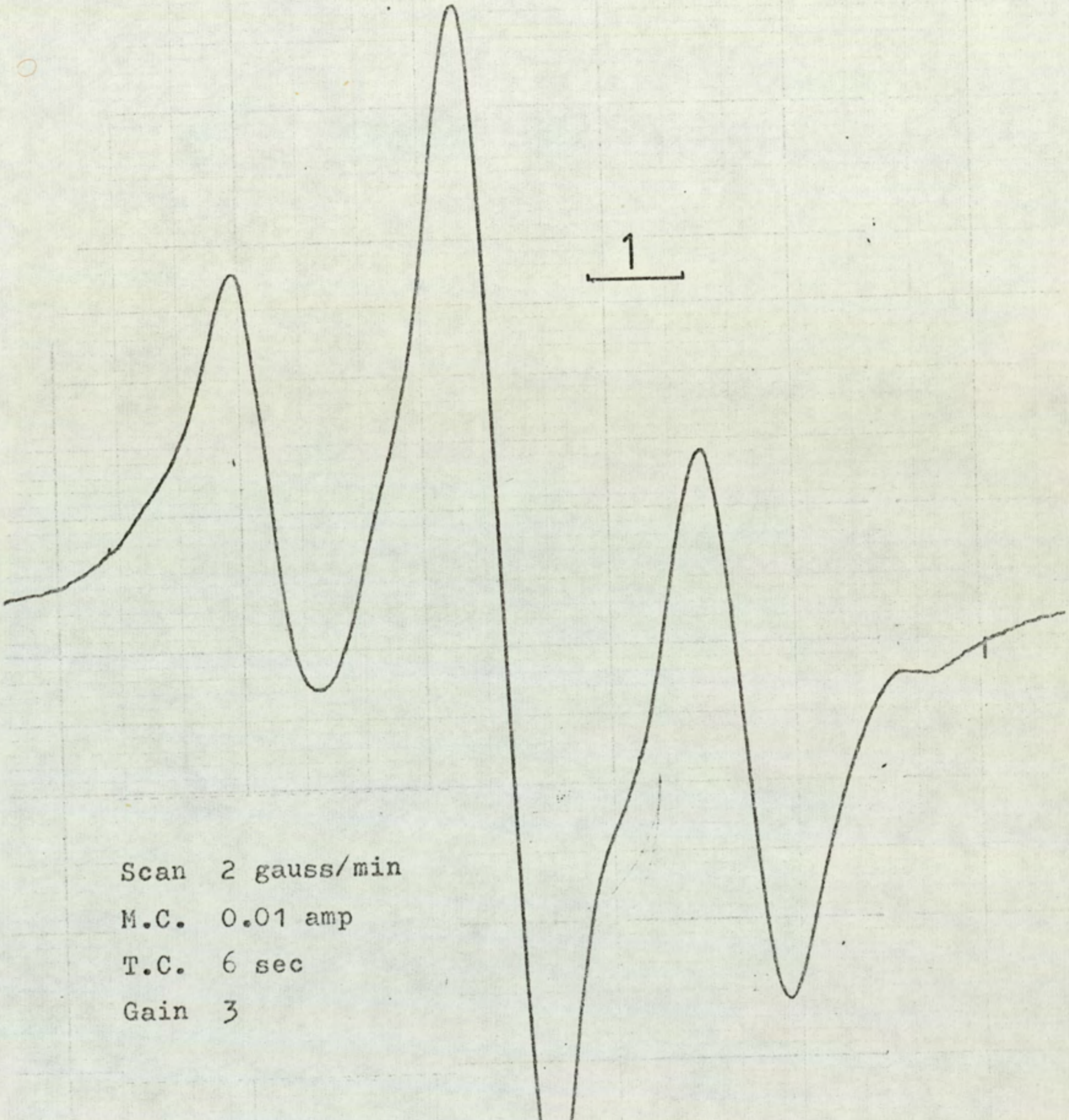
Scan 2.5 gauss/min

M.C. 0.025 amp

T.C. 6 sec

Gain 10

fig 5.2.14
diethyl sulphide



Scan 2 gauss/min

M.C. 0.01 amp

T.C. 6 sec

Gain 3

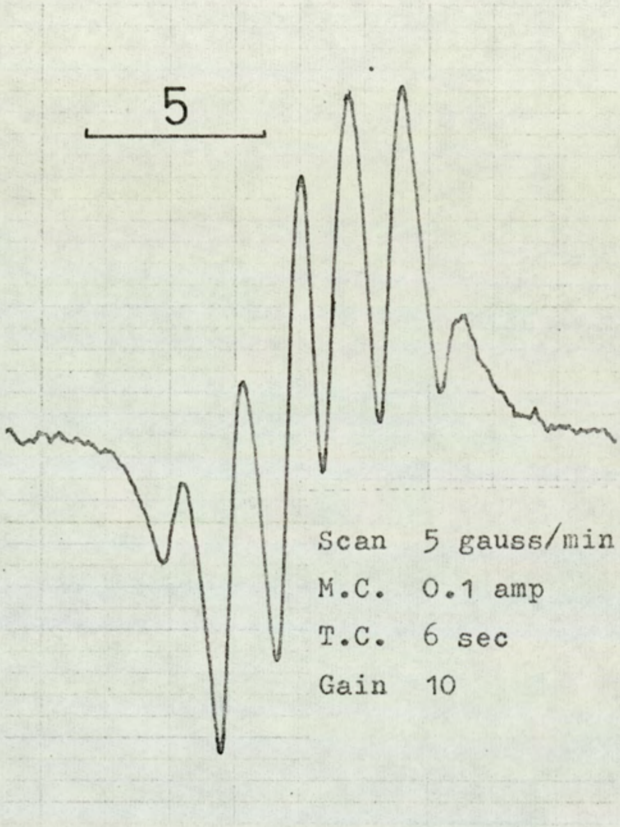
fig 5.2.15
ethyl-isopropyl sulphide

Di-n-propyl sulphide

No signal was obtained from this sulphide in solution in concentrated sulphuric acid at room temperature. On heating, a brown solution was obtained which yielded an esr signal at g = 2.0130. The signal was a sextet, splitting constant 1.48 gauss and intensity distribution 1.0 : 5.0 : 6.5 : 5.0 : 4.5 : 1.0. The spectrum is shown, figure 5.2.16.

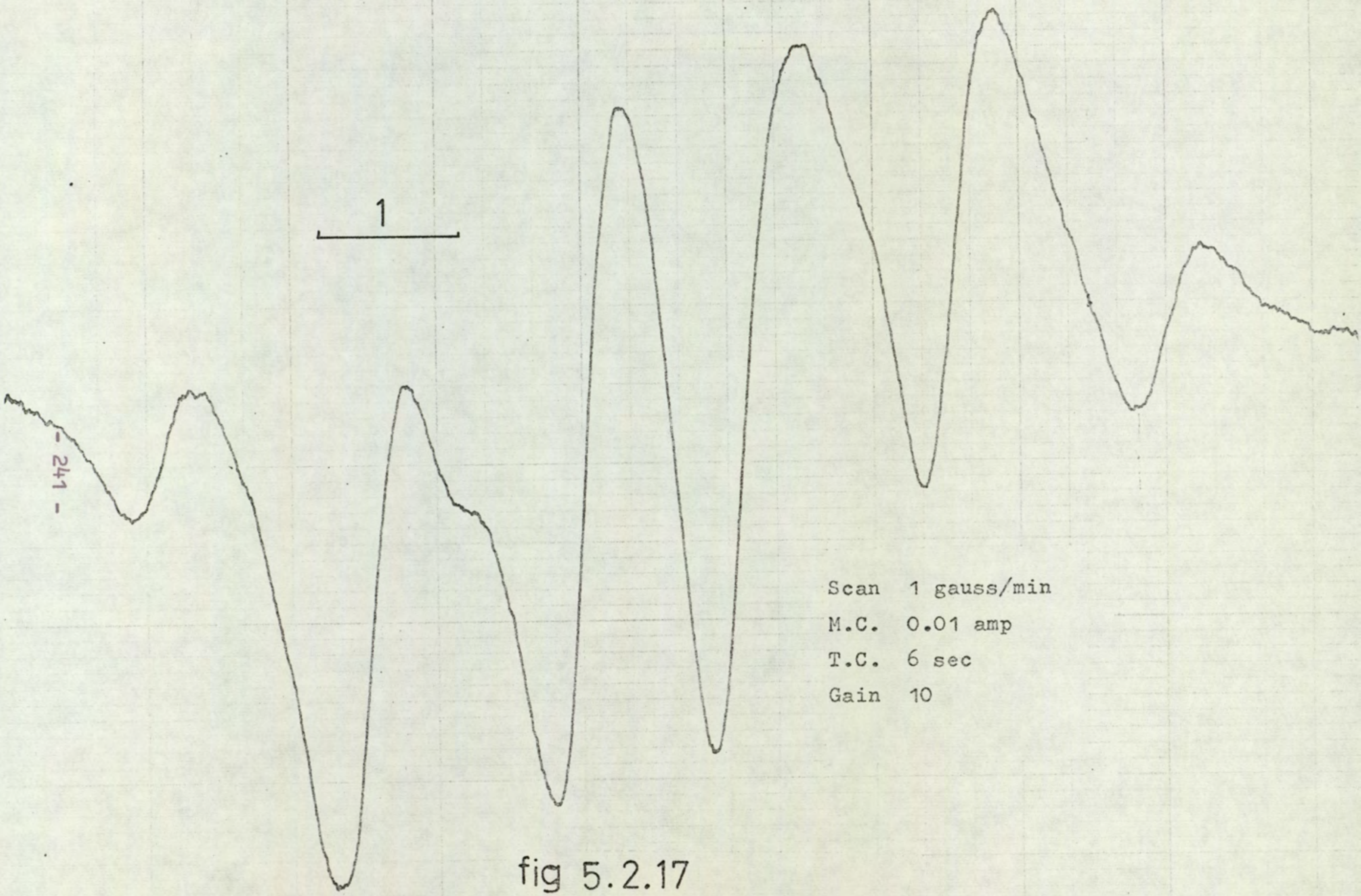
Di-isopropyl sulphide

The brown solution obtained by heating a mixture of di-isopropyl sulphide and concentrated sulphuric acid gave an esr signal at g = 2.0130. The signal was a sextet with splitting constant 1.44 gauss and intensity distribution 1.0 : 4.1 : 5.6 : 5.6 : 3.9 : 1.4. The spectrum is shown in figure 5.2.17.



Scan 5 gauss/min
M.C. 0.1 amp
T.C. 6 sec
Gain 10

fig 5.2.16
dipropyl sulphide



Scan 1 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 10

fig 5.2.17
di-isopropyl sulphide

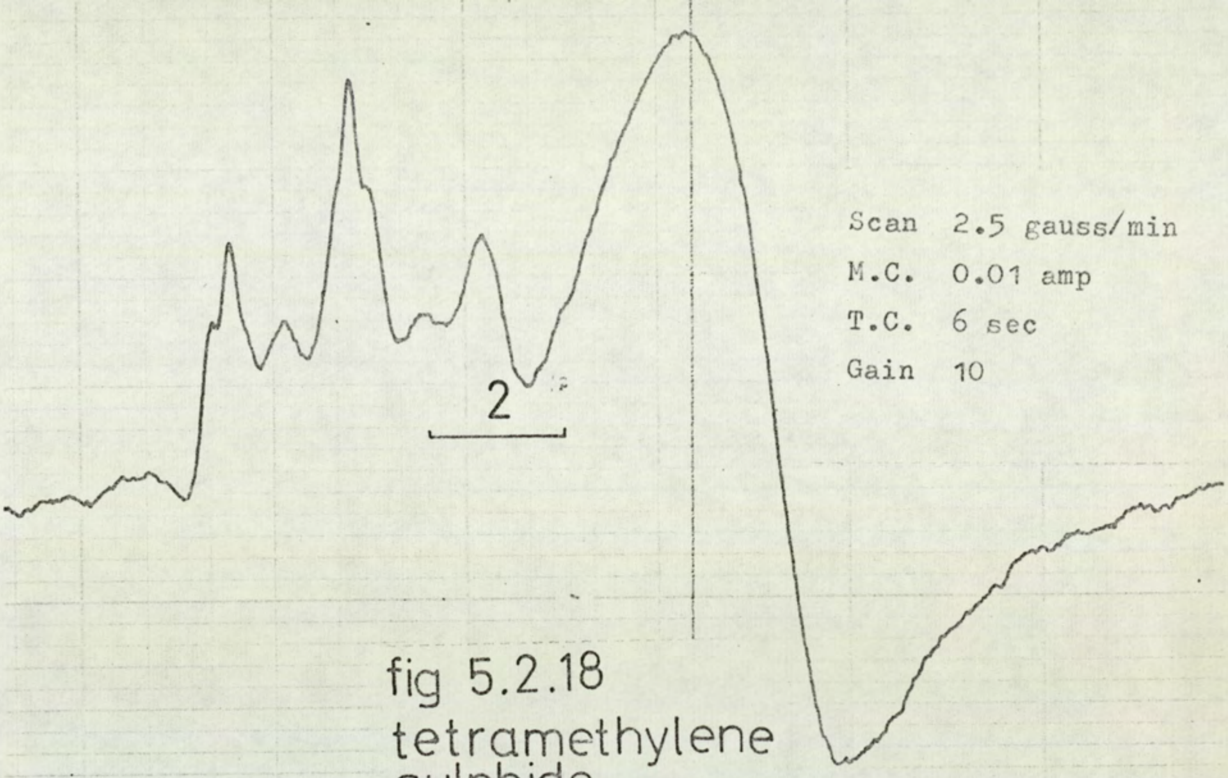
Tetramethylene Sulphide

No detectable absorption was obtained from a solution of this sulphide in concentrated sulphuric acid until it was warmed, when an absorption was obtained from two free radical species as shown in figure 5.2.18. The larger signal was at $g = 2.0029$, and was a single line. The smaller signal, at $g = 2.0070$, was partially resolved, apparently into a triplet, with splitting constant 1.81 gauss, which is further split.

Paradithiane

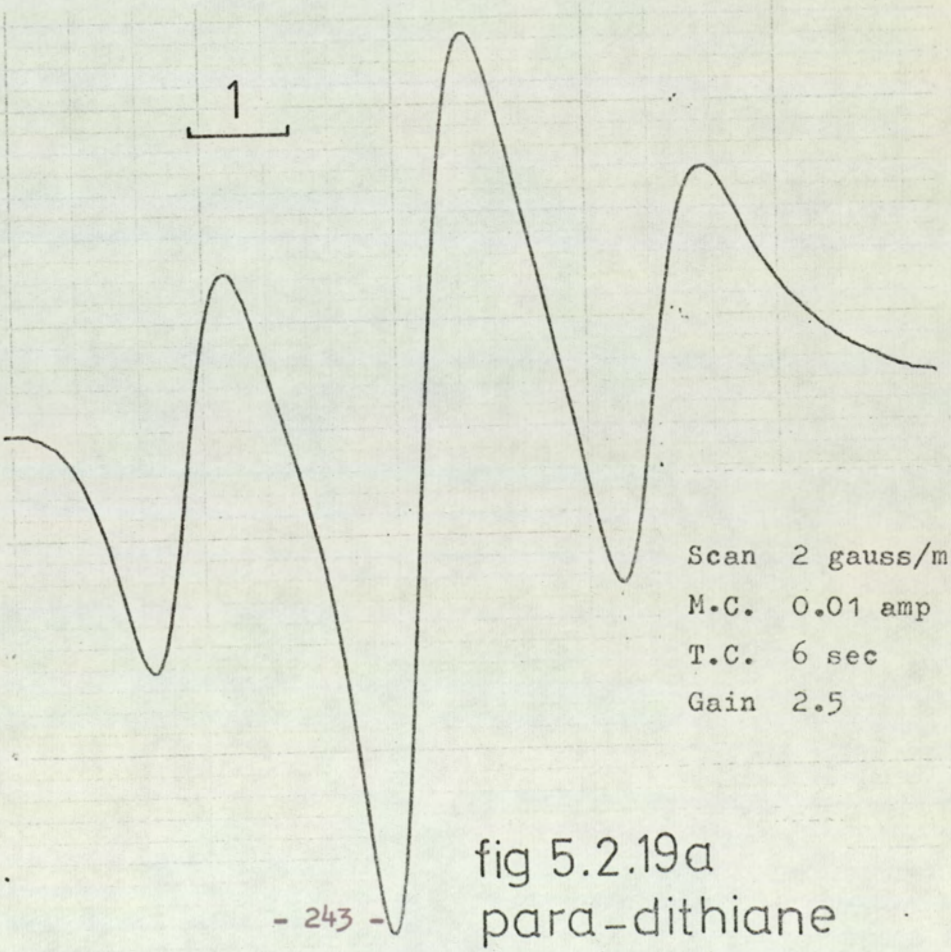
The solution formed by this cyclic sulphide in concentrated sulphuric acid was yellow, but not paramagnetic. On heating, the colour darkened to brown, and esr signals were obtained. The absorption was at $g = 2.0133$, and was a triplet, splitting constant 2.43 gauss and intensity distribution 1.00 : 2.27 : 1.05. It is shown in figure 5.2.19a.

On further heating, another absorption was found at lower g value. This is shown, with part of the triplet, in figure 5.1.19b. As can be seen, it was not fully resolved.



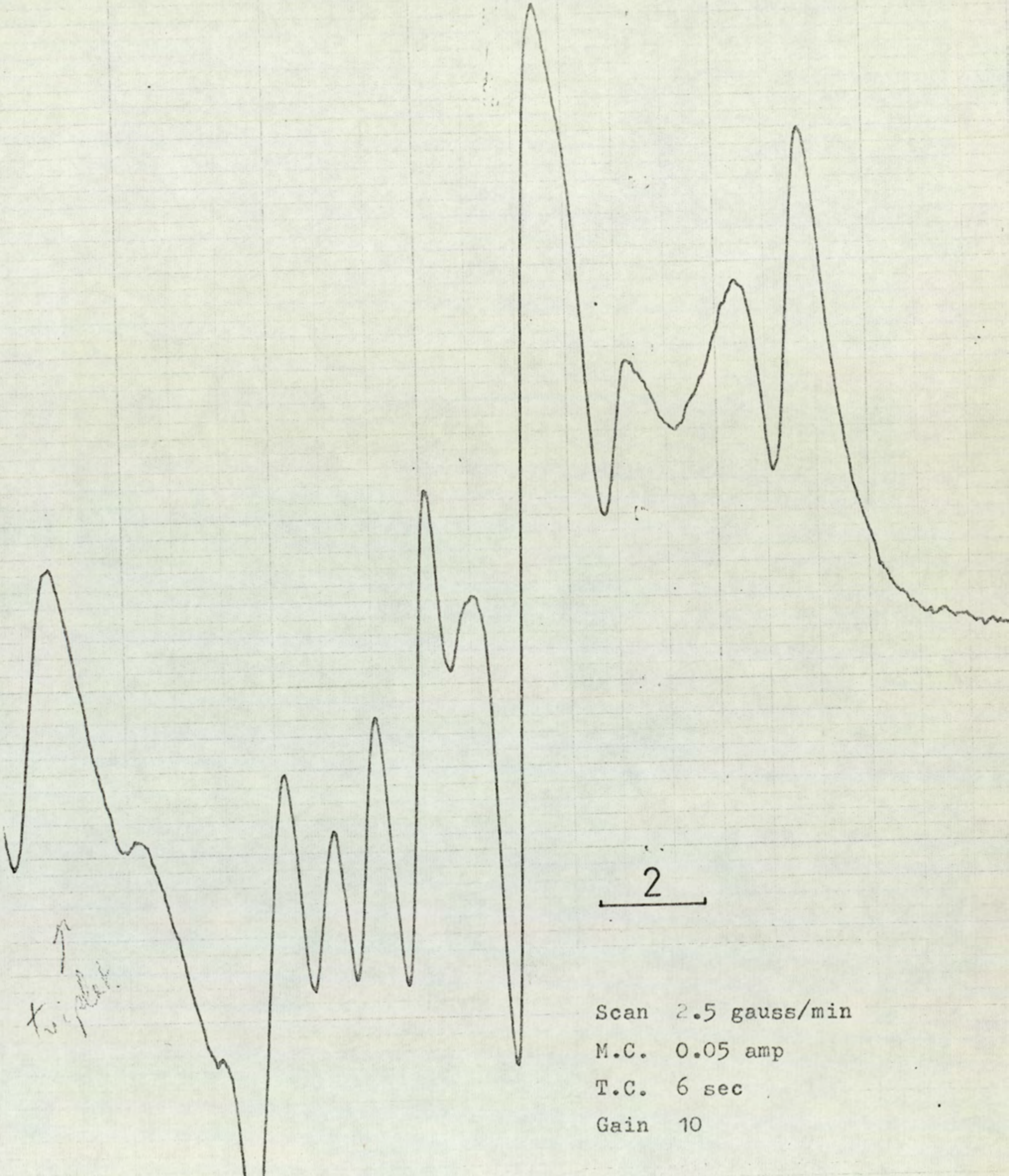
Scan 2.5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 10

fig 5.2.18
tetramethylene sulphide



Scan 2 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 2.5

fig 5.2.19a
para-dithiane



Scan 2.5 gauss/min

M.C. 0.05 amp

T.C. 6 sec

Gain 10

fig 5.2.19b
para-dithiane

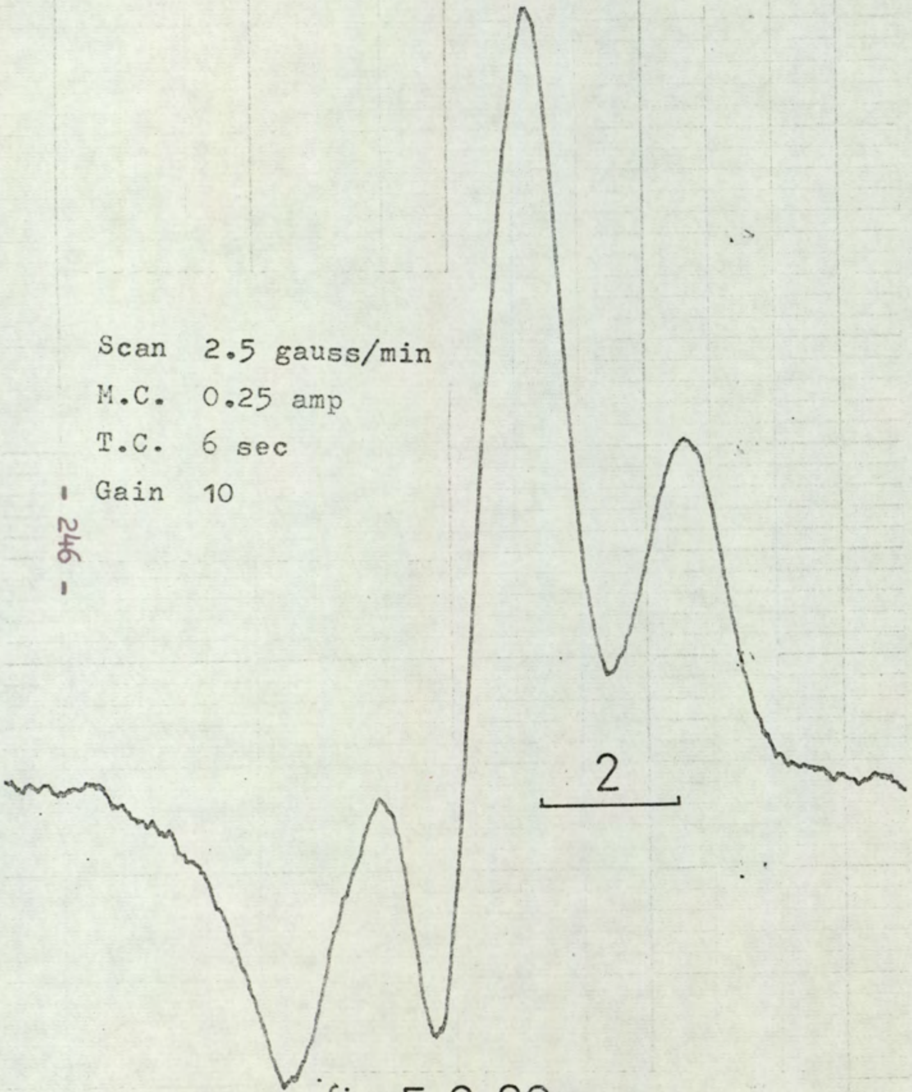
Dimethyl disulphide

On heating a solution of dimethyl disulphide in concentrated sulphuric acid, a weak esr signal could be obtained. This was a triplet, as shown in figure 5.2.20. It is thought that the heating rate or temperature reached was critical as this signal could only be obtained from a few of the many solutions used. The g value was not recorded. The splitting constant was 2.26 gauss.

Diethyl disulphide

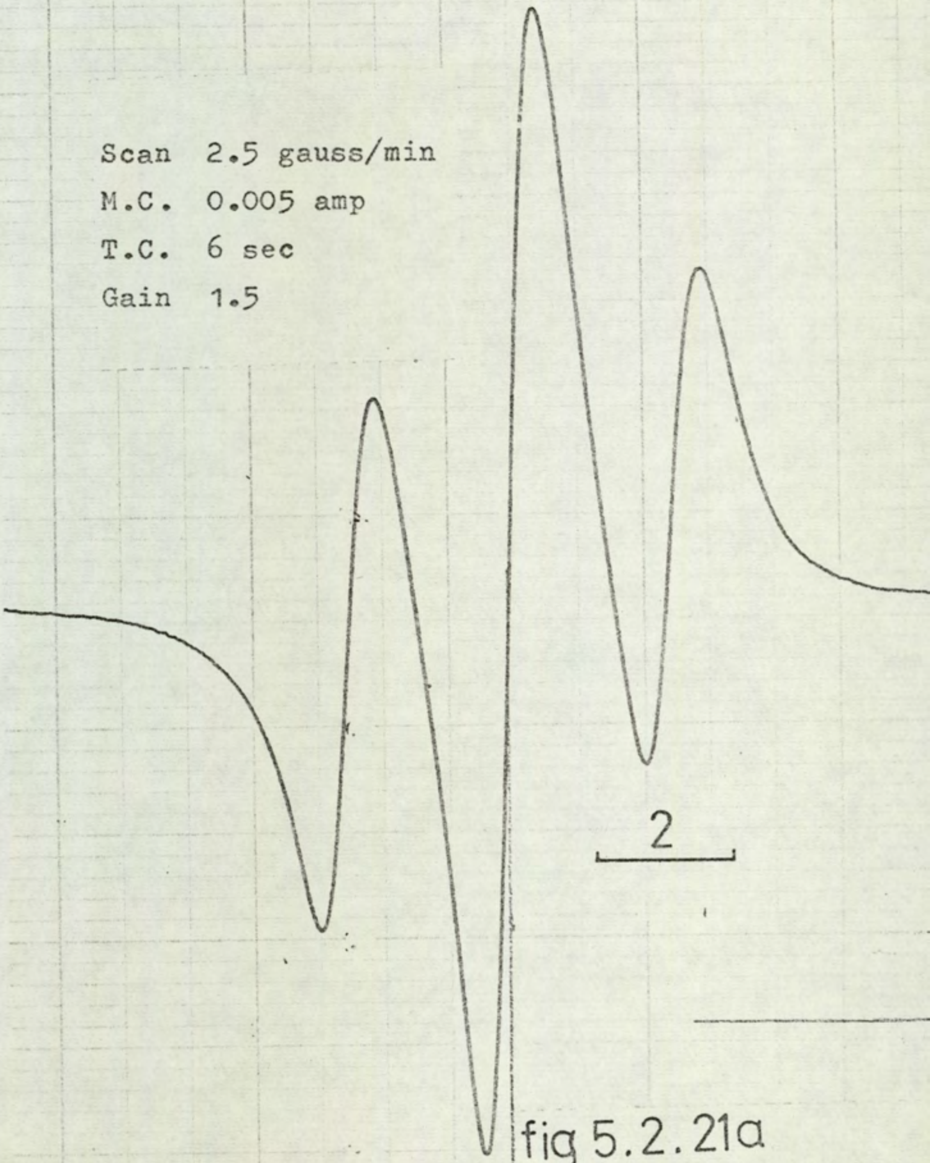
Addition of diethyl disulphide to concentrated sulphuric acid yielded a yellow solution, slowly turning brown with some formation of a brown precipitate. The solution had an esr spectrum with a g value of 2.0139, shown in figure 5.2.21a. The absorption line consisted of three hyperfine lines, with intensity ratio 1.0 : 2.2 : 0.95 and splitting constant 2.37 gauss.

The spectrum of a solution of this compound in deuterosulphuric acid differed from that given by the sulphuric acid solution in that it had five hyperfine lines, as in figure 5.2.21b. The splitting constant was 1.39 gauss and the g value 2.0139. The spectrum was not sufficiently resolved for the intensity ratio to be obtained.



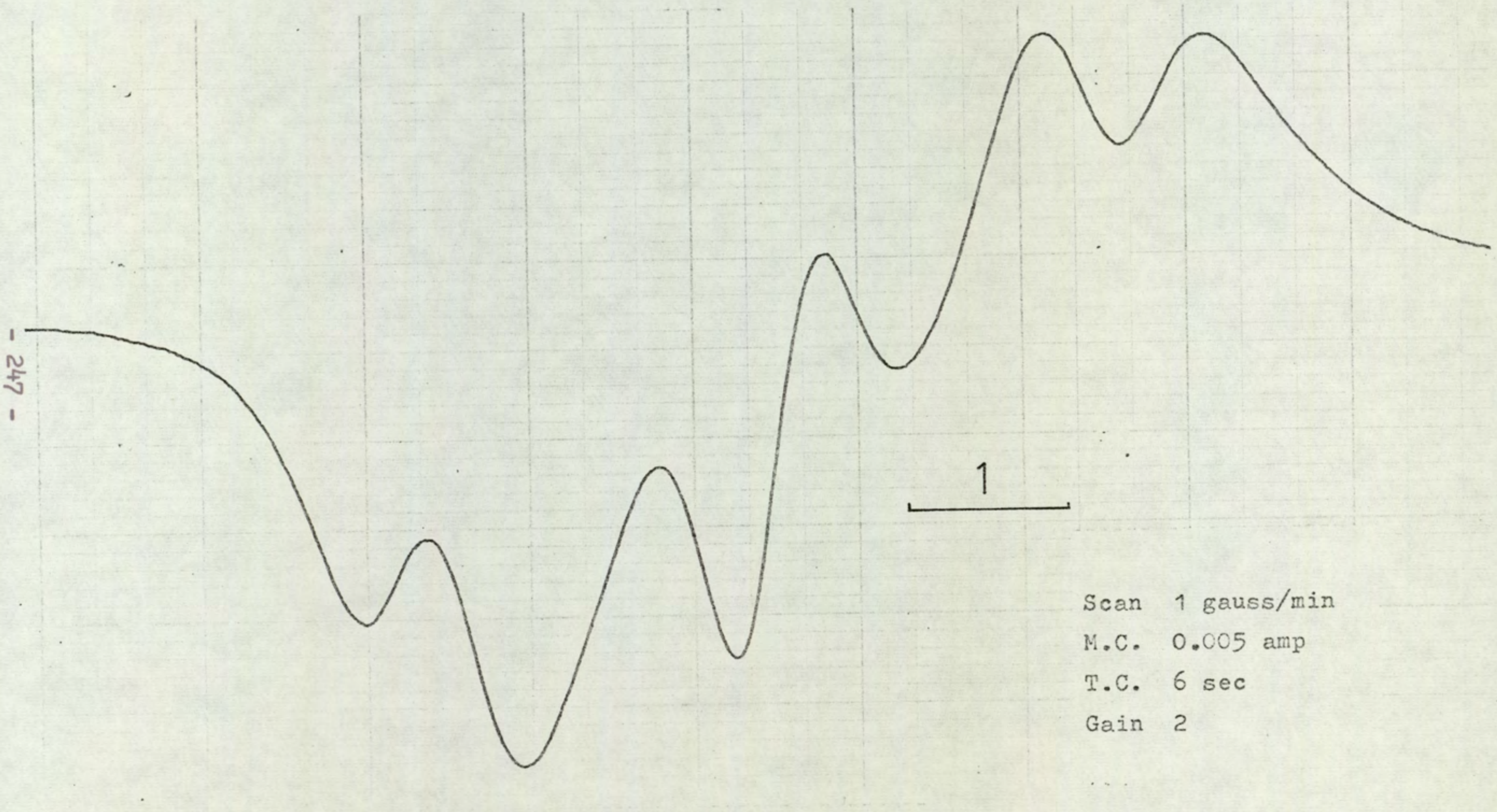
Scan 2.5 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 10

fig 5.2.20
dimethyl disulphide



Scan 2.5 gauss/min
M.C. 0.005 amp
T.C. 6 sec
Gain 1.5

fig 5.2.21a
diethyl disulphid



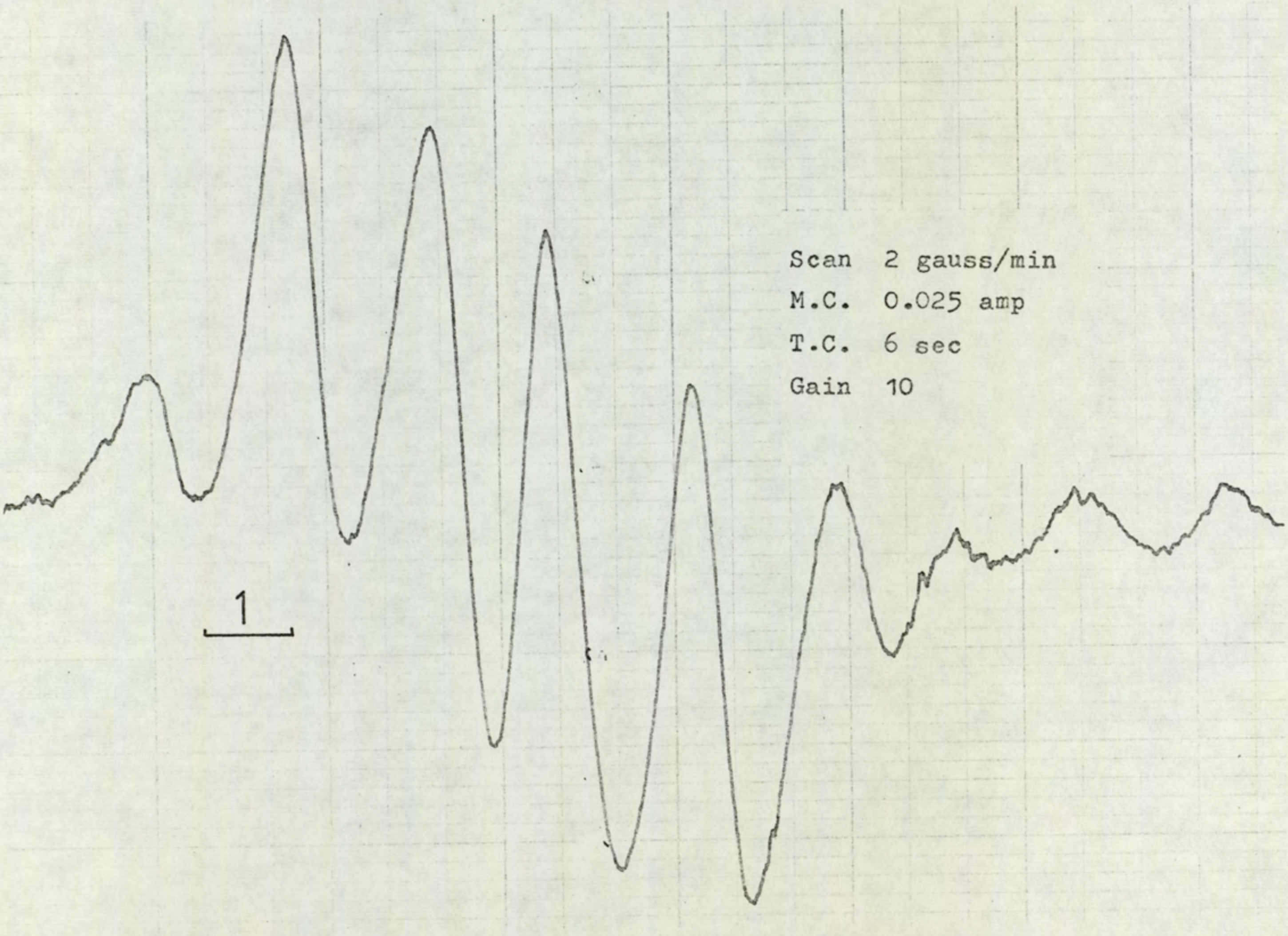
Scan 1 gauss/min
M.C. 0.005 amp
T.C. 6 sec
Gain 2

fig 5.2. 21b
diethyl disulphide

Di-n-propyl disulphide

On standing or warming, the yellow colour of solutions of this compound in concentrated sulphuric acid was observed to deepen to a red-brown. Accompanying this change was the development and growth of an esr signal, consisting of a line at g value 2.009, split into six hyperfine components. The intensity ratio was found to be 1.0 : 4.1 : 5.0 : 5.2 : 3.9 : 1.4 and the splitting constant was 1.67 gauss. The spectrum is shown in figure 5.2.22, which also shows part of the small secondary signal which developed.

The signal obtained from a solution in deuterosulphuric acid was the same except that the splitting constant was smaller, being 1.43 gauss.



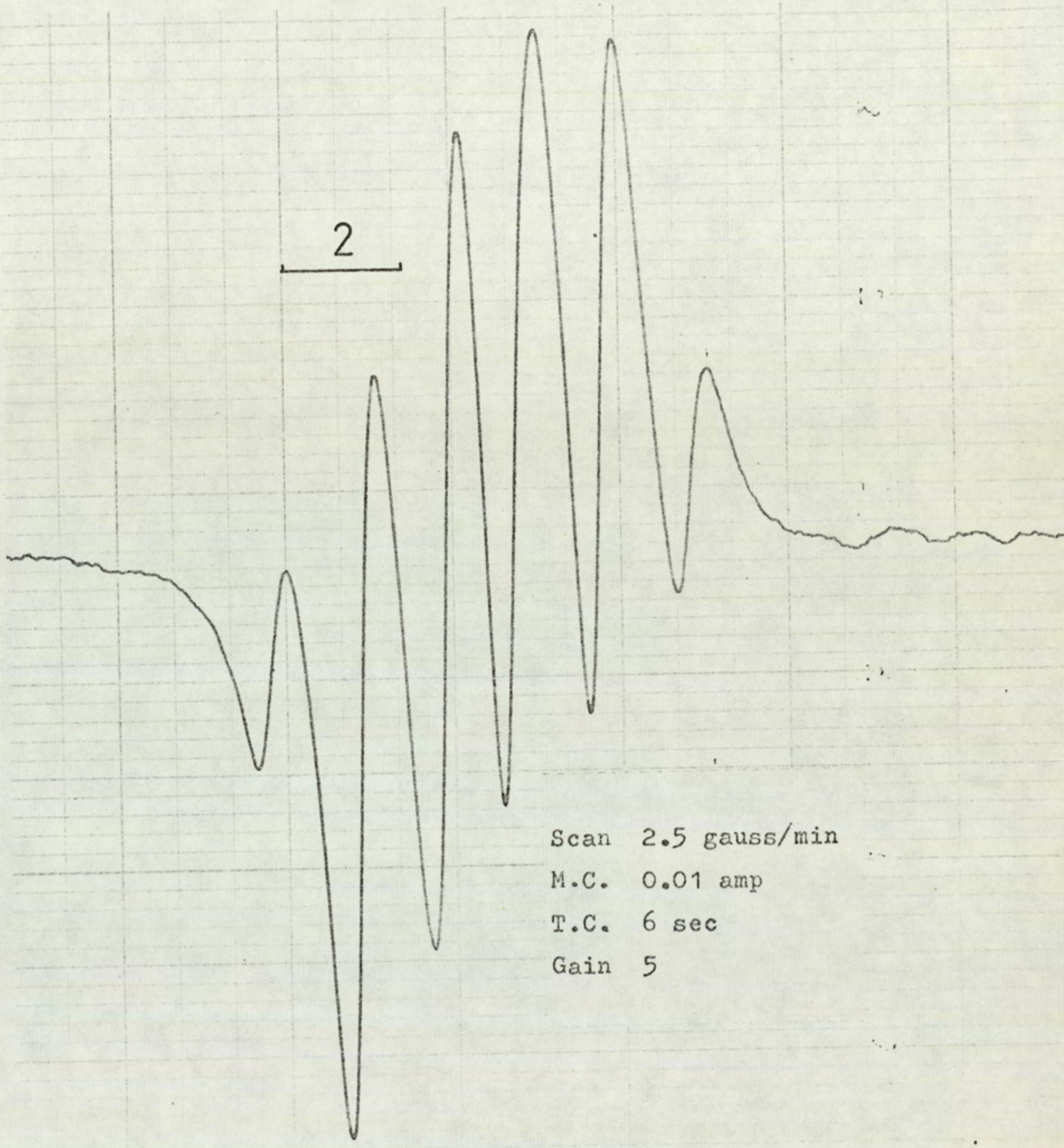
Scan 2 gauss/min
M.C. 0.025 amp
T.C. 6 sec
Gain 10

fig 5.2.22
dipropyl disulphide

Di-isopropyl disulphide

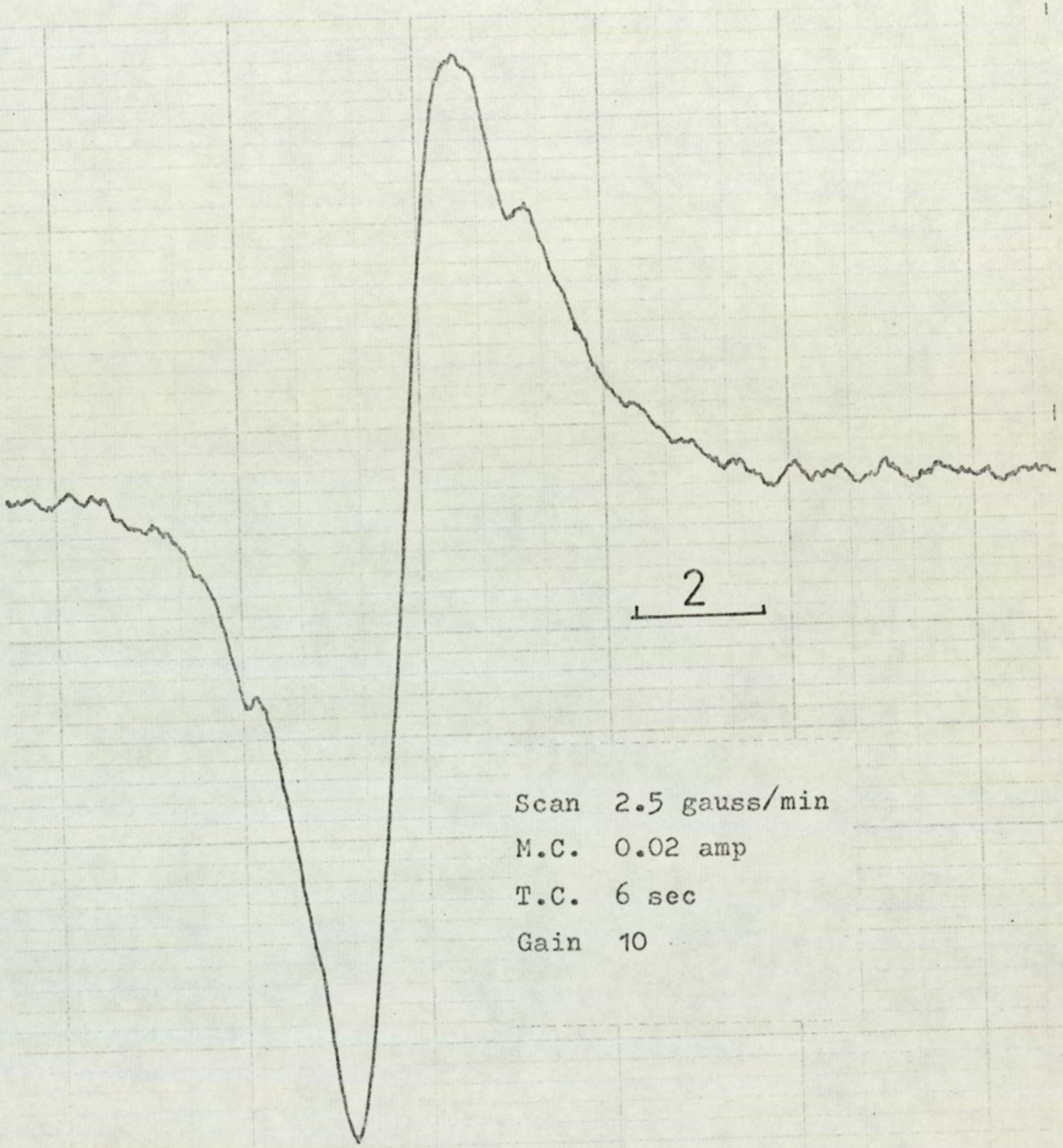
When di-isopropyl disulphide was added to sulphuric acid, a yellow solution slowly formed with some pale yellow precipitate. A very small esr absorption signal was observed at this point, increasing however, with standing or warming. The signal, shown in figure 5.2.23a, had a g value of 2.0130 and was resolved into six hyperfine components, with a splitting constant of 1.36 gauss. The intensity ratio was 1.0 : 3.9 : 4.2 : 4.0 : 3.5 : 1.2. A secondary signal was also observed at high field side of the main signal, but was very small, compared to this main signal, under all conditions, and not resolved.

A signal was obtained from a solution of di-isopropyl disulphide in deuterosulphuric acid, at g value 2.0133. The presence of hyperfine structure was indicated by the shoulders seen on the absorption line (figure 5.2.23b), but this could not be fully resolved.



Scan 2.5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 5

fig 5.2.23a
di-isopropyl disulphide



Scan 2.5 gauss/min

M.C. 0.02 amp

T.C. 6 sec

Gain 10

fig 5.2.23b
di-isopropyl disulphide

Di-n-butyl disulphide

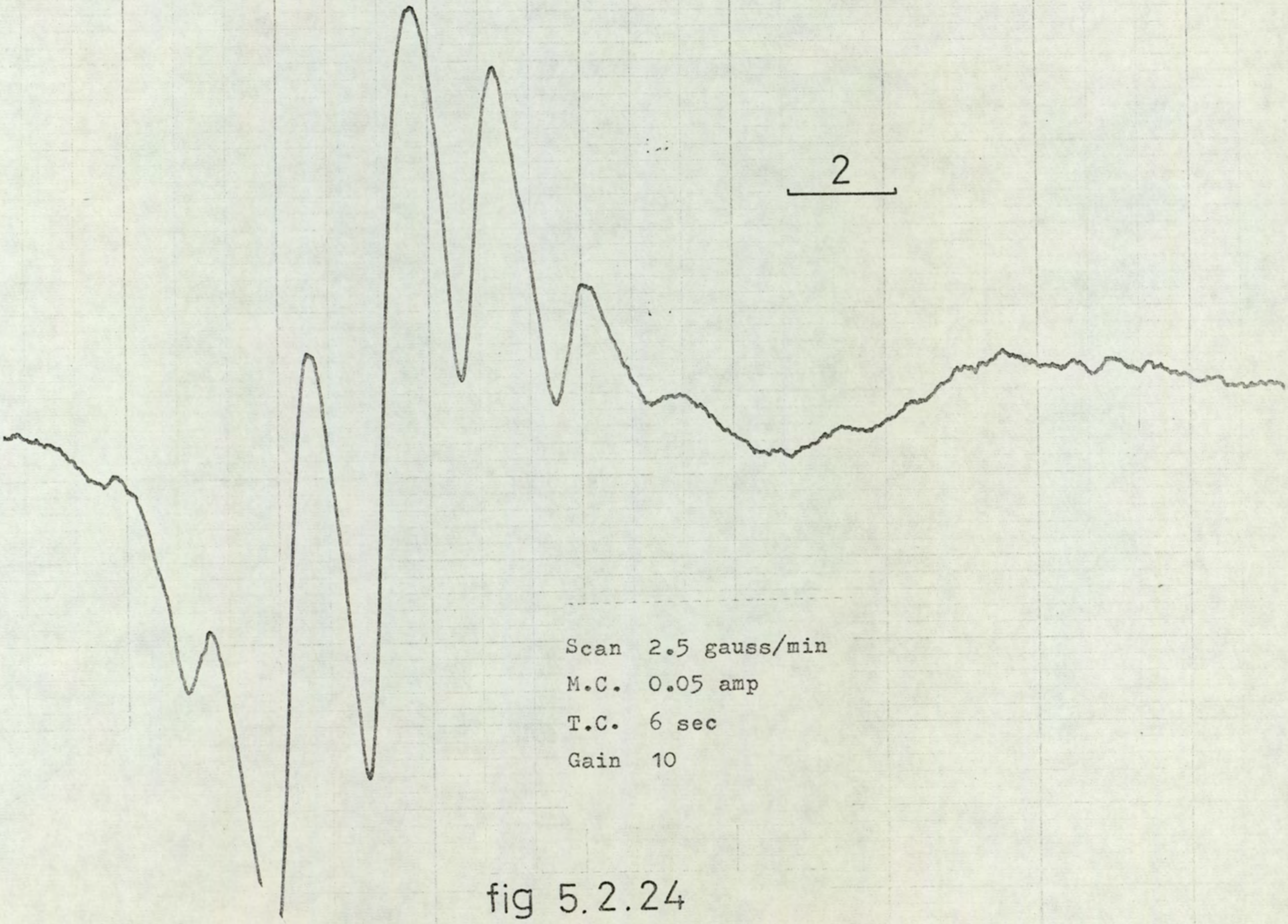
The esr absorption signal obtained from the solutions of di-n-butyl disulphide in concentrated sulphuric acid immediately on mixing was small, but developed over a period of three hours into a large signal at $g = 2.0124$ with a broader, smaller signal at lower g value. After standing overnight the signal was large enough to allow the resolution of 5 lines. After five days, seven lines were resolved, the signal slowly decaying after this time. This seven line spectrum is shown in figure 5.2.24. The broad signal can also be seen at high field. The splitting constant was 1.58 gauss. The intensity ratio of this spectrum is obviously too distorted by the lack of resolution to be meaningful.

Di-isobutyl disulphide

The yellow solution obtained by dissolving di-isobutyl disulphide in concentrated sulphuric acid gave rise to an esr signal, which increased in size with time after mixing. The signal had a g value of 2.0117 and consisted of an absorption with seven hyperfine components in the intensity ratio

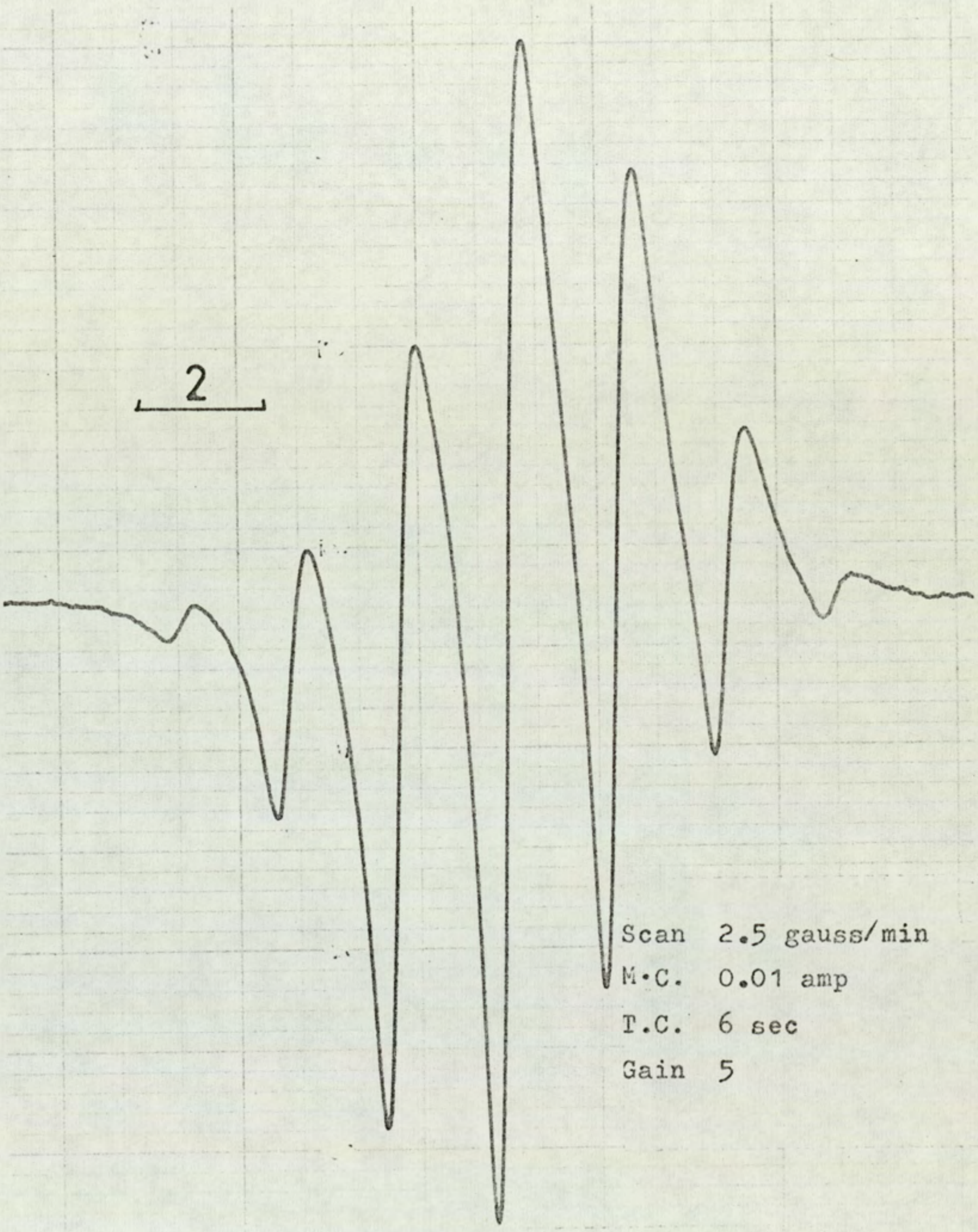
1.0 : 7.4 : 22.0 : 33.2 : 22.8 : 9.0 : 1.4.

The splitting constant was 1.809 gauss. The spectrum is shown in figure 5.2.25.



Scan 2.5 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

fig 5.2.24
dibutyl disulphide



Scan 2.5 gauss/min
M·C. 0.01 amp
T.C. 6 sec
Gain 5

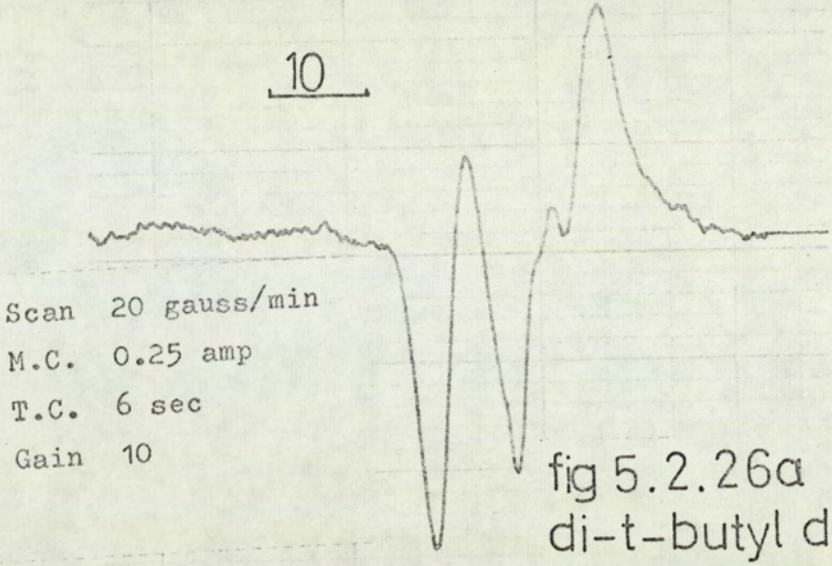
fig 5.2.25
di-isobutyl disulphide

Di-t-butyl disulphide

The yellow solution with white precipitate which resulted from adding this disulphide to concentrated sulphuric acid had the esr spectrum shown in figure 5.2.26a. This was a singlet at high g value with a doublet at lower g. On standing or warming, the signal with the higher g value decayed, the doublet increasing in size. Shoulders could be observed on the wing of the doublet, indicating that further splitting was present, as shown in figure 5.2.26b. The splitting constant in this signal was 1.87 gauss.

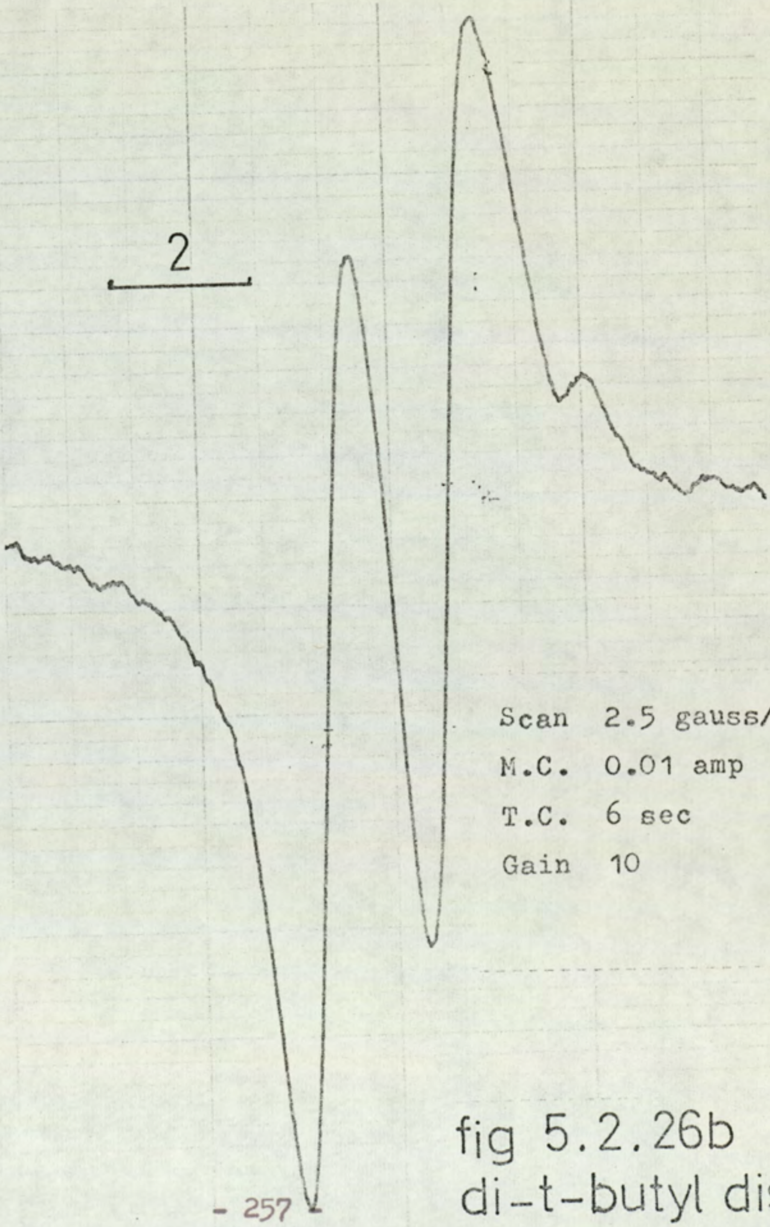
Dicyclohexyl disulphide

On dissolving dicyclohexyl disulphide in concentrated sulphuric acid, a yellow colour was developed. The solution gave an esr signal which was very strong soon after mixing. The resonance, shown in figure 5.2.27, was at g value 2.0126, and consisted of at least seven hyperfine components. The last two lines on the low g value side of this absorption were hidden by an overlapping secondary signal. The first two lines on the high g edge of the signal are shown under higher gain and slower sweep conditions in the inset spectrum.



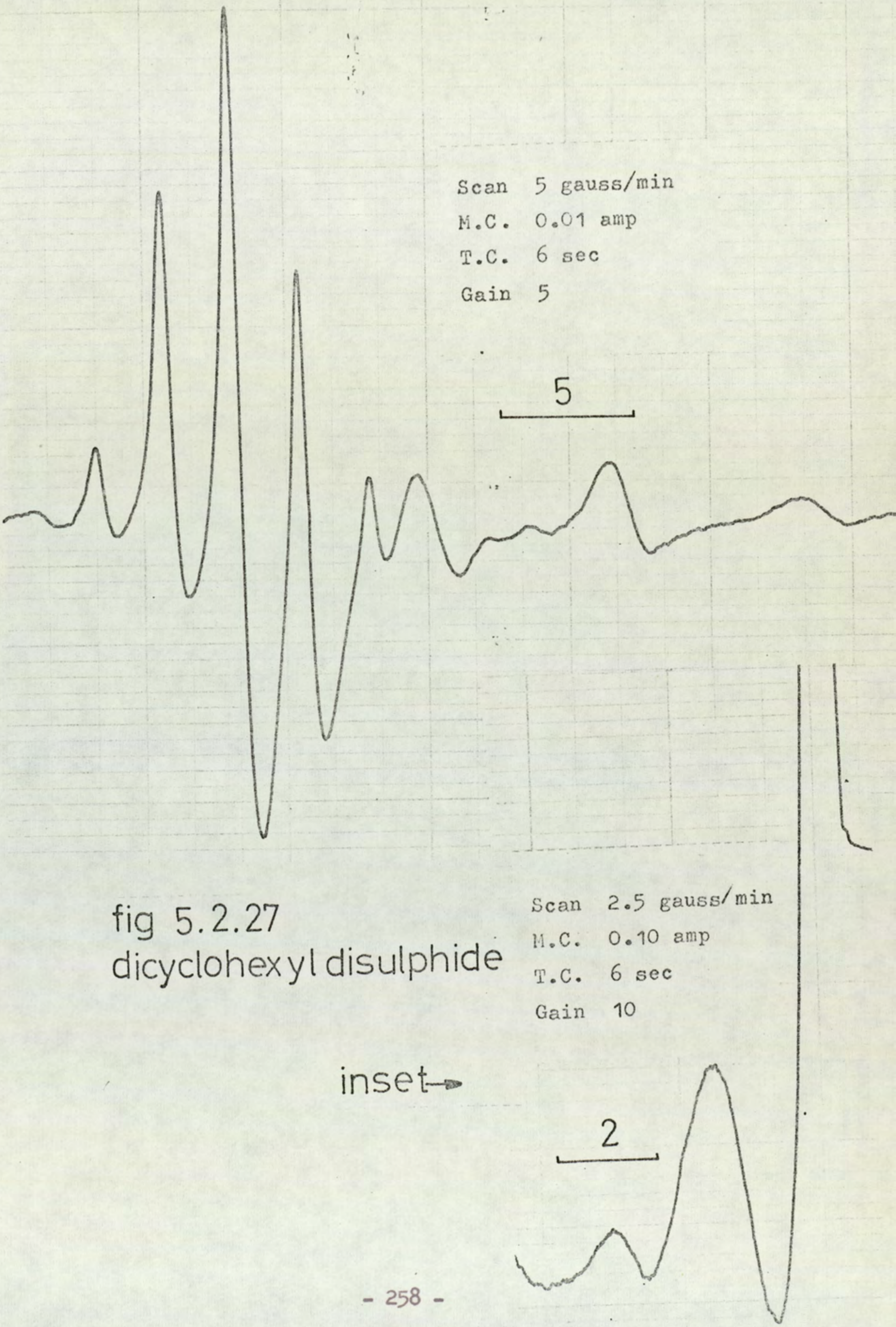
Scan 20 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 10

fig 5.2.26a
di-t-butyl disulphide



Scan 2.5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 10

fig 5.2.26b
di-t-butyl disulphide



Scan 5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 5

fig 5.2.27
dicyclohexyl disulphide

Scan 2.5 gauss/min
M.C. 0.10 amp
T.C. 6 sec
Gain 10

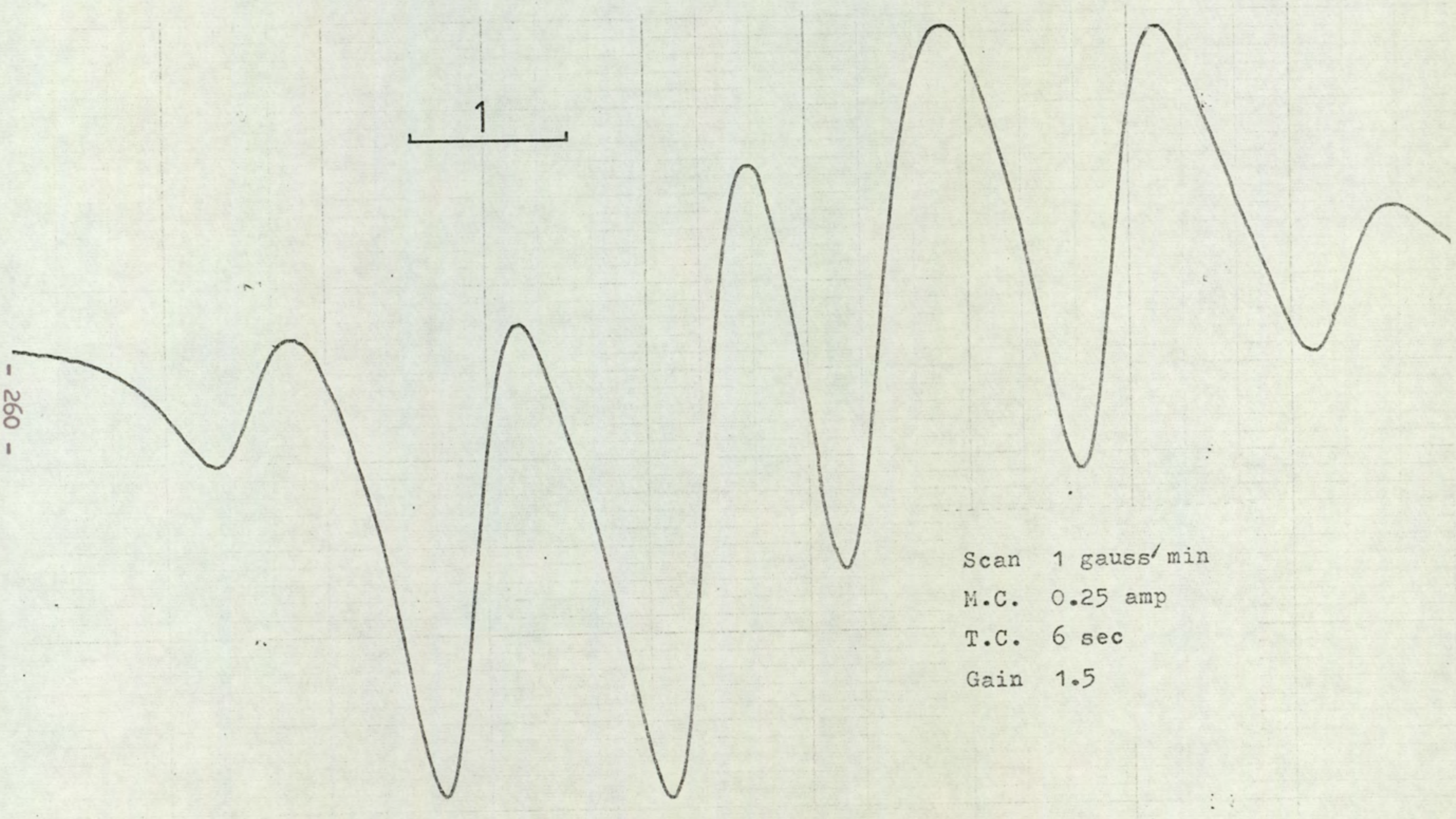
inset→

Diallyl disulphide

The solution of diallyl disulphide in concentrated sulphuric acid either on standing or warming developed an esr absorption at g value 2.0130. The resonance had six hyperfine components, with splitting constant 1.45 gauss. The intensity ratio was

1.0 : 3.6 : 4.8 : 4.1 : 3.3 : 1.1

The spectrum is shown in figure 5.2.28.



Scan 1 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 1.5

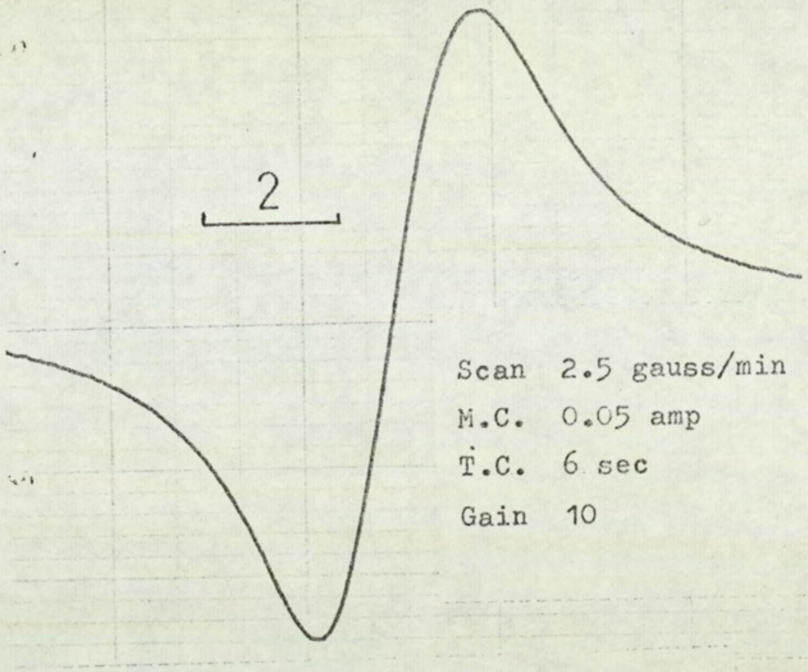
fig 5.2.28
diallyl disulphide

N-N'-dithiobis(dibenzylamine)

On warming the pale orange solution obtained by dissolving this disulphide and potassium persulphate in concentrated sulphuric acid, the colour darkened to brown, and a species was formed having a singlet esr absorption at g value 2.0129, as shown in figure 5.2.29.

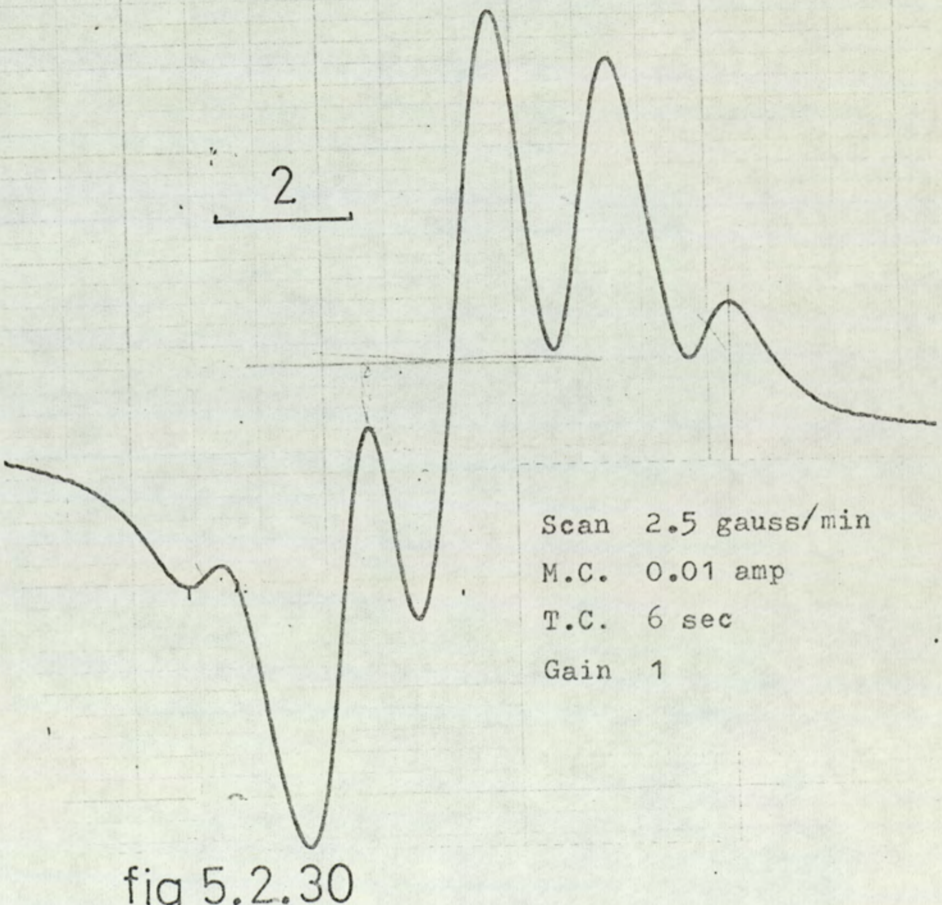
N,N'-dithiobis(piperidine)

On warming a solution of this compound in concentrated sulphuric acid, with a small amount of potassium persulphate, an esr absorption with five hyperfine components was found, figure 5.2.30. The absorption had a g value of 2.0129, and splitting constant of 1.70 gauss. The intensity distribution was measured as 1.0 : 11.0 : 16.0 : 7.8 : 1.4.



Scan 2.5 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

fig 5.2.29
N,N′-dithiobis(dibenzylamine)



Scan 2.5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 1

fig 5.2.30
N,N′-dithiobis(piperidene)

N,N'-dithiobis(morpholine)

On warming a solution of this compound in concentrated sulphuric acid and potassium persulphate, a species was formed which had the esr spectrum shown in figure 5.2.31. As can be seen, this is a triplet, and was centred at $g = 2.0126$. The intensity distribution was found to be 1.00 : 2.37 : 1.00 and the hyperfine splitting 2.24 gauss.

N-N'-dithiobis(phthalimide)

Two esr absorption signals were obtained from a solution of this compound in concentrated sulphuric acid, containing potassium persulphate. The signals developed either on standing for several hours at room temperature or on warming. At first, the signal at high g value was largest, as shown in figure 5.2.32a. The relative sizes reversed on further standing or warming, as shown in figure 5.2.32b. The g values were 2.0134 and 2.0088.

The line at high g value did not contain any hfs that could be resolved, but the low g line was split into three, or possibly five lines, shown in figures 5.2.32c. The splitting constant was approximately 1.9 gauss, but resolution was too poor to allow measurement of the intensity distribution.

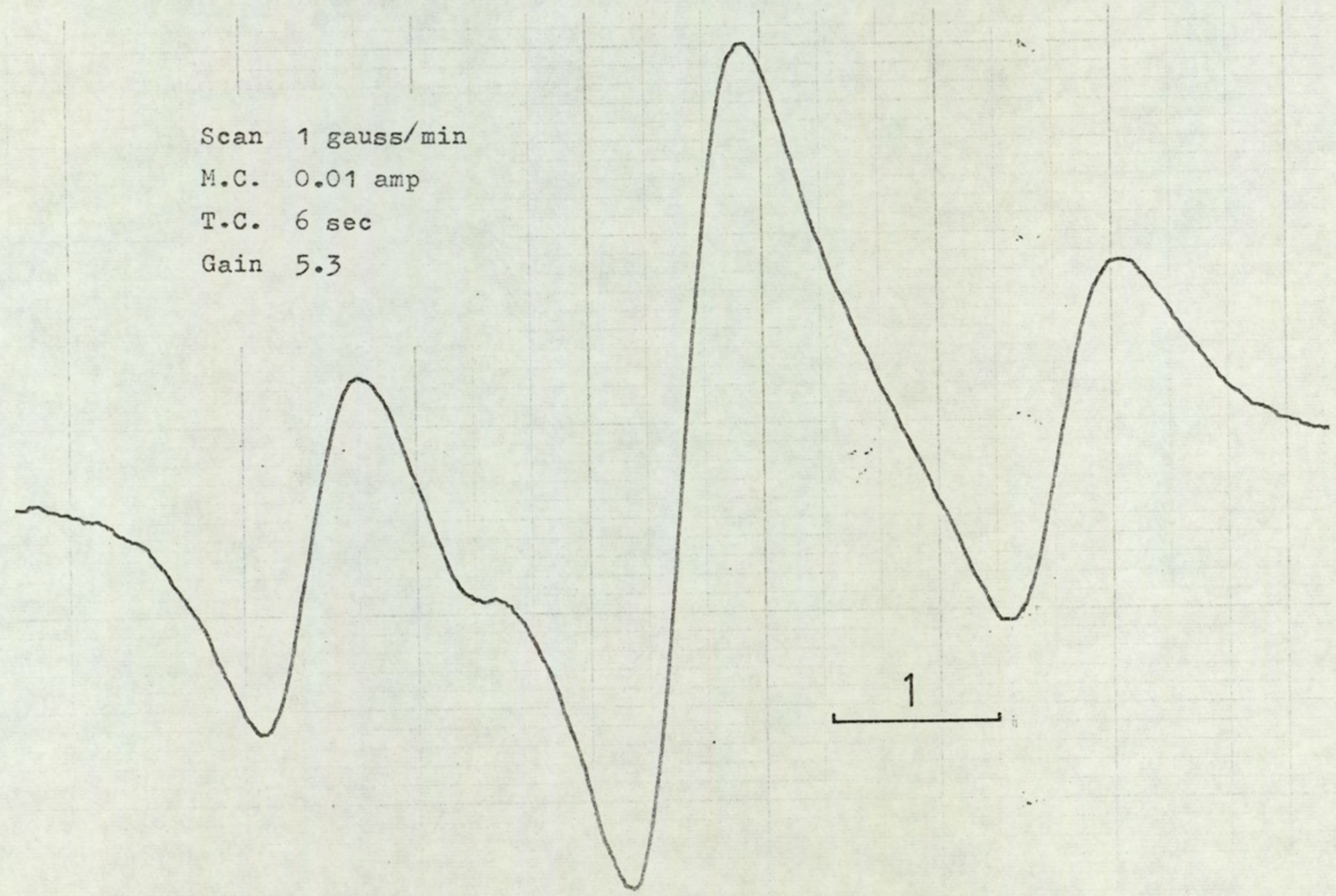


fig 5.2.31
N,N'-dithiobis(morpholine)

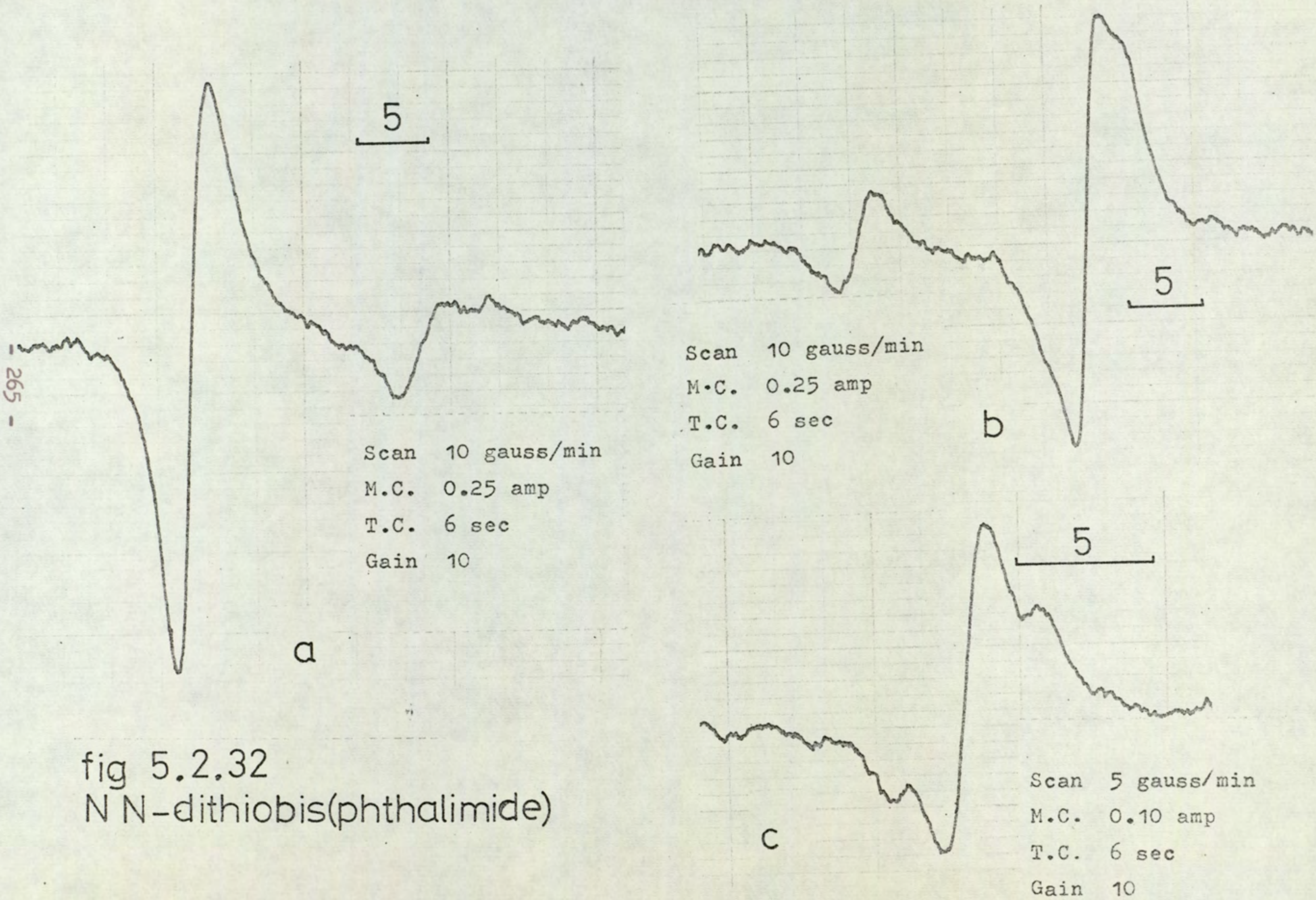


fig 5.2.32
N N-dithiobis(phthalimide)

5.3. Aromatic Sulphur Compounds in Sulphuric Acid

Aromatic thiols, disulphides and monosulphides were found to react with sulphuric acid to yield coloured solutions containing free radical species. In some cases reaction occurred at room temperature - e.g. unsubstituted and alkyl-substituted thiophenols. Other compounds, such as the halogen-substituted thiophenols, required heating to bring about reaction.

Some deuterosulphuric acid solutions were also investigated. Chlorosulphonic acid was used, often as a mixture with sulphuric acid. Reaction of the sulphur compound with chlorosulphonic acid was sometimes vigorous, necessitating preparation of the solution in an ice-salt bath.

Results from disulphides are included with the results from the corresponding thiols, for reasons which will be obvious from the discussion (see section 6.3).

Thiophenol and Diphenyl Disulphide

Solutions of thiophenol in concentrated sulphuric acid were initially a cloudy-yellow. This rapidly (five minutes) turned blue. In the esr absorption, signals were found from two species. Initially the signal at high g value, a triplet, was larger, but reduced in size with time as the quintet at lower g value increased.

The g values and splitting constants were:-

Triplet $g = 2.0139$ Splitting constant = 0.84 gauss
Quintet $g = 2.0076$ Splitting constant = 1.07 gauss

The spectrum is shown, figure 5.3.1a.

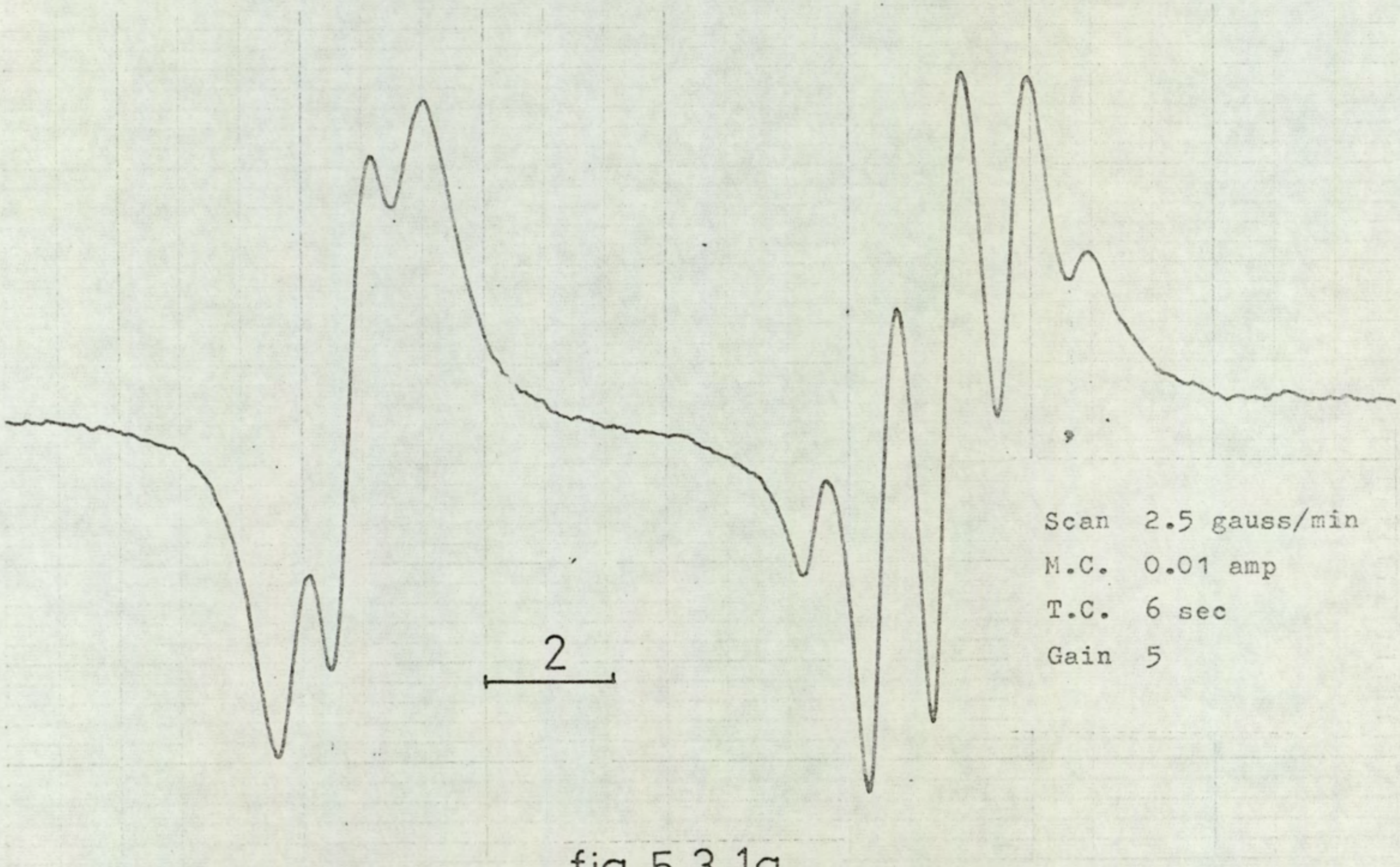
Very similar results were obtained from solution in a 1 : 1 mixture of sulphuric and chlorosulphonic acids, except that resolution was improved. The splitting constant for the triplet was slightly greater at 0.96 gauss. The spectrum is shown in figure 5.3.1b. Intensity ratios were measured on this spectrum and found to be:-

Triplet	1.0 : 2.2 : 0.8
Quintet	1.0 : 4.7 : 7.0 : 4.0 : 0.7

Spectra were also recorded from solutions in sulphuric acid containing potassium persulphate, and from solutions prepared under nitrogen in sulphuric acid from which the dissolved oxygen had been displaced by nitrogen. The spectra obtained were similar to that shown in figure 5.3.1a.

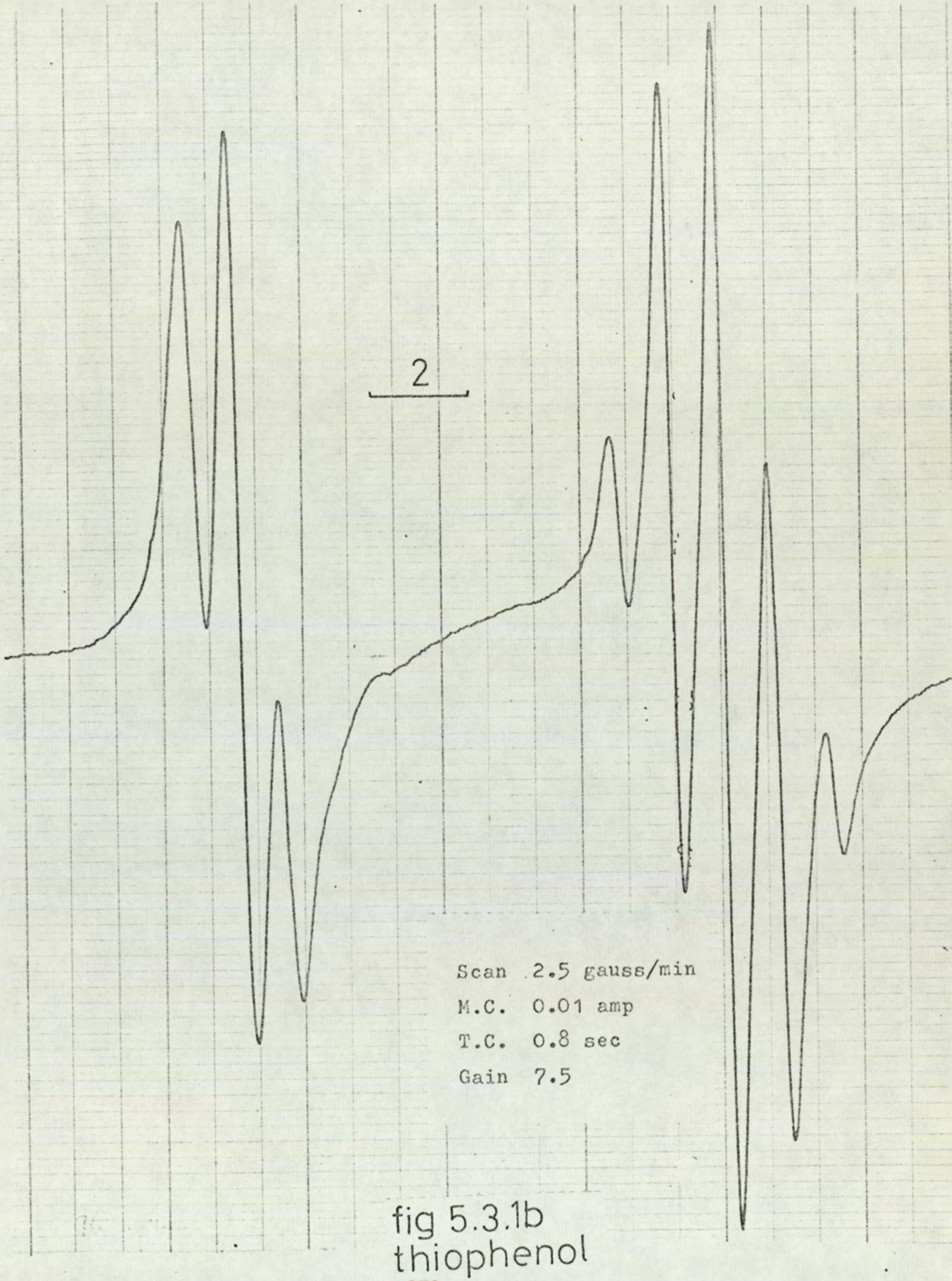
Diphenyl disulphide, when dissolved in concentrated sulphuric acid, formed a paramagnetic species with an esr absorption at g = 2.0076 identical to the quintet at g = 2.0076 obtained from thiophenol. No trace of a signal at higher g value was detected. The spectrum is shown in figure 5.3.2a. However, when dissolved in a 1 : 1 mixture of sulphuric and chlorosulphonic acids, the disulphide gave two free radicals, a triplet (small) and a quintet (very large) identical to the signal from thiophenol. The spectrum is given in figure 5.3.2b under high amplification, to show the triplet. The quintet is off scale and not fully resolved.

The orange/red solution of thiophenol in deuterosulphuric acid gave rise to esr signals of smaller intensity than those obtained from sulphuric acid solutions. The absorption consisted of two lines, apparently a doublet at high g value, and a triplet at lower g value. The triplet was the larger signal, as seen in figure 5.3.2c.



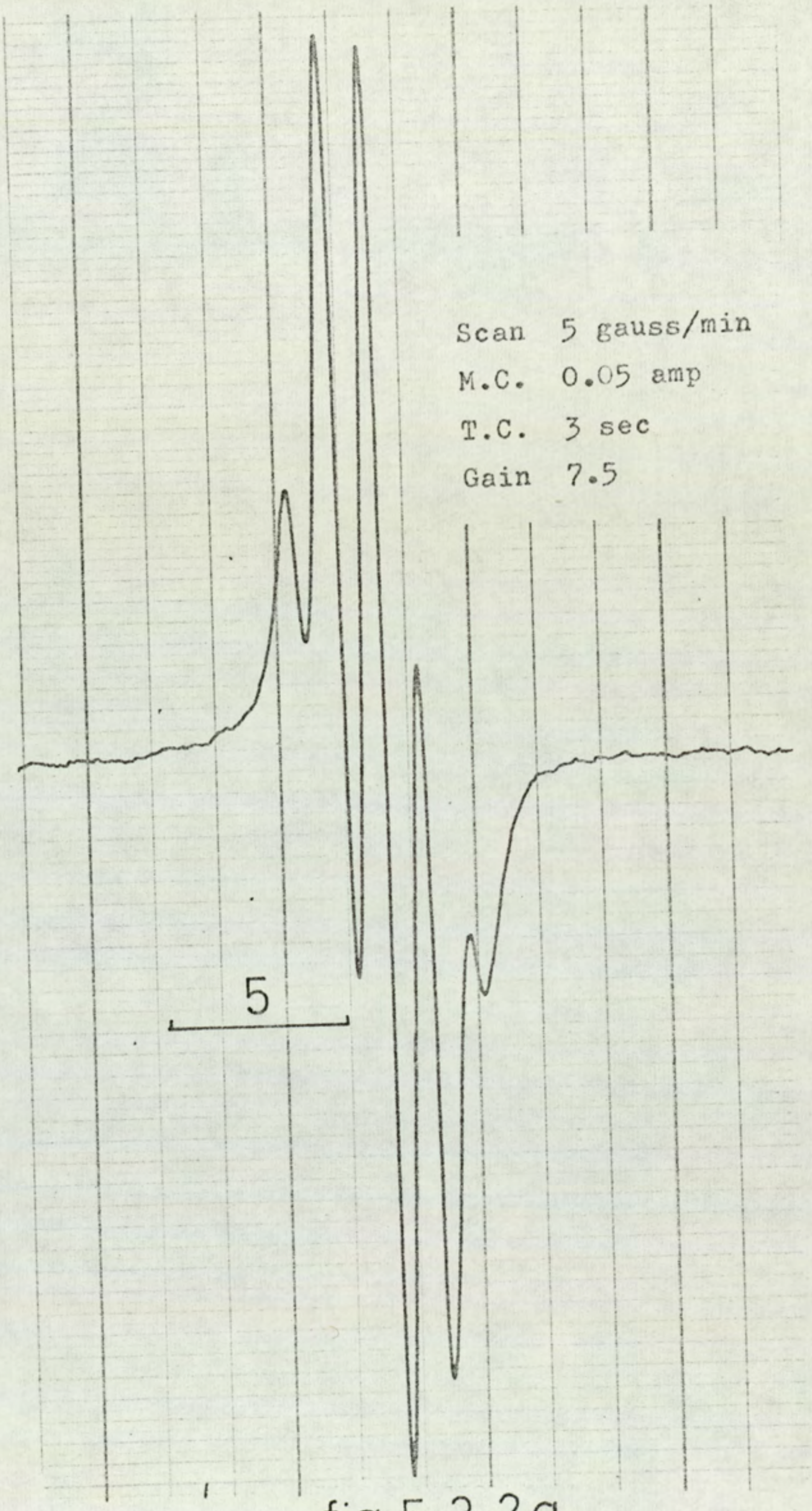
Scan 2.5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 5

fig 5.3.1a
thiophenol



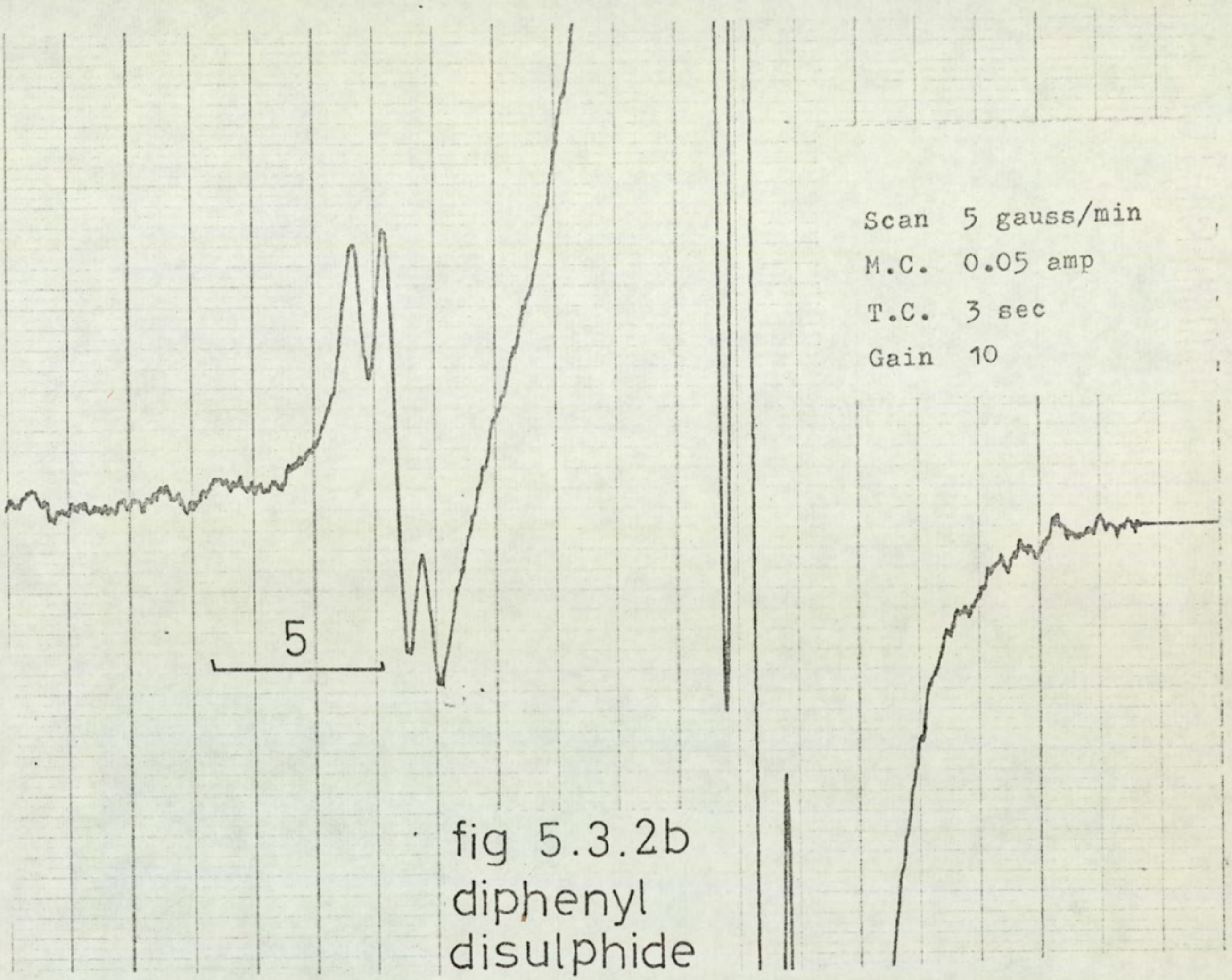
Scan 2.5 gauss/min
M.C. 0.01 amp
T.C. 0.8 sec
Gain 7.5

fig 5.3.1b
thiophenol



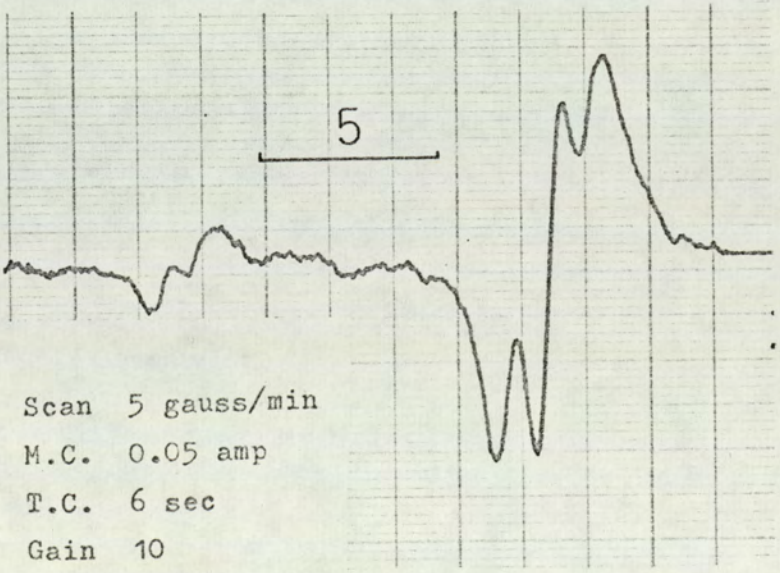
Scan 5 gauss/min
M.C. 0.05 amp
T.C. 3 sec
Gain 7.5

fig 5.3.2a
diphenyl
disulphide



Scan 5 gauss/min
M.C. 0.05 amp
T.C. 3 sec
Gain 10

fig 5.3.2b
diphenyl
disulphide



Scan 5 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

fig 5.3.2c
thiophenol

Alkyl-Substituted Thiophenols and Corresponding Disulphides

2-Methylthiophenol

The green solution in sulphuric acid yielded esr absorption lines at g = 2.0128 and g = 2.0073. The signal at higher g value was resolved into a quintet, of splitting 1.27 gauss. No hfs could be resolved in the lower g value signal. The spectrum is given, figure 5.3.3.

3-Methylthiophenol

The purple sulphuric acid solutions of 3-methylthiophenol had a similar spectrum to that from the 2-substituted compound with five hyperfine lines resolved in the absorption at higher g value, 2.0136. The line at lower g value, 2.0078, was also split. Seven lines were visible, as seen in figure 5.3.4a. In solution in a 1 : 1 mixture of sulphuric and chlorosulphonic acids, the resolution was improved as is shown in figure 5.3.4b. Slight shoulders may be seen (arrowed) indicating that this line has nine components.

The splitting constants from the sulphuric acid solution were found to be approximately 1.3 gauss for the high g signal and 1.38 gauss for the lower g signal.

4-Methylthiophenol

On solution of this thiophenol in sulphuric acid a blue colour developed, and esr absorptions were found for two species, at g values 2.0131 and 2.0072. The signal at 2.0131 was a quintet, splitting 1.38 gauss. The line at lower g value was split into nine components, splitting constant 1.48 gauss. The spectrum is shown in figure 5.3.5a, where the wing lines of the low g value signal are arrowed.

4-Methylthiophenol has also been studied in solution in deuterosulphuric acid. The spectrum obtained is shown in figure 5.3.5b. It is poorly resolved, but appears similar to the one obtained from sulphuric acid solutions.

4,4'-Dimethyldiphenyl Disulphide

Solution of this disulphide in sulphuric acid gave the same esr absorption as the thiophenol. The high g resonance was very small, and is just seen in figure 5.3.6a, which shows the complete spectrum. Figure 5.3.6b is the spectrum recorded under higher gain, where the signal at high g value is more clearly seen. The low g signal is off scale. Figure 5.3.6c shows the spectrum obtained from solution in sulphuric/chlorosulphonic acid mixture, when resolution was greatly improved.

3,5-Dimethylthiophenol

In sulphuric acid solution, this compound gave a blue-green colouration and the esr spectrum shown in figure 5.3.7. The line at higher g value is split into five components, while the other signal overlaps to some extent. This latter signal appears to be split into seven lines, although the two at the low field side are not visible. The wing line at highest field is indicated. There is some evidence for further splitting of these lines, but no structure could be resolved.

4-t-Butylthiophenol

Two esr absorption lines were found for sulphuric acid solutions of 4-t-butylthiophenol, which were initially yellow, turning to purple. The same signals were found when a 1 : 1 mixture of sulphuric and chlorosulphonic acids were used. A doublet of splitting 1.06 gauss was found at $g = 2.0129$, and at $g = 2.0070$, a triplet of splitting 1.48 gauss. The spectra are shown in figures 5.3.8a and 5.38b.

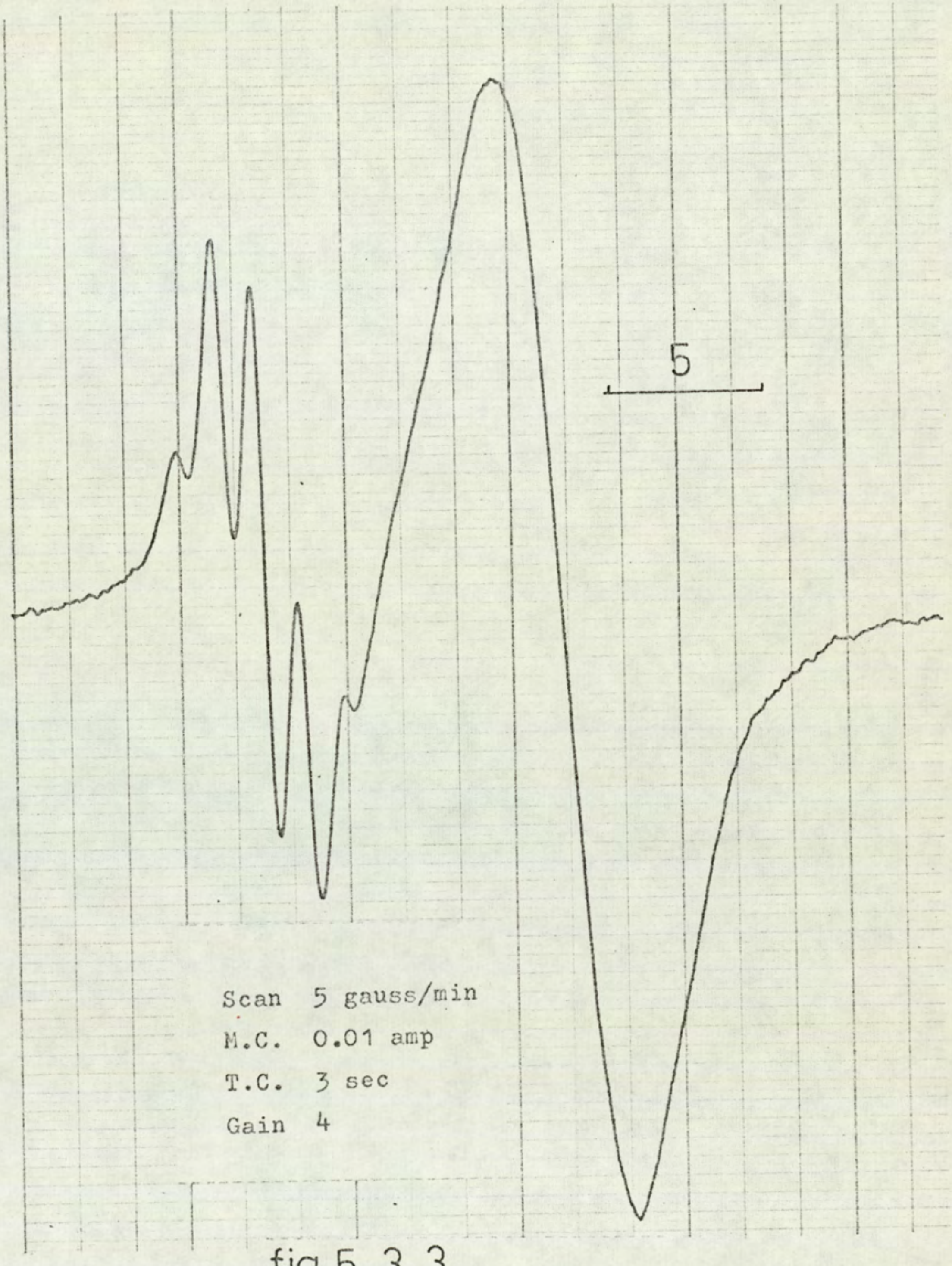
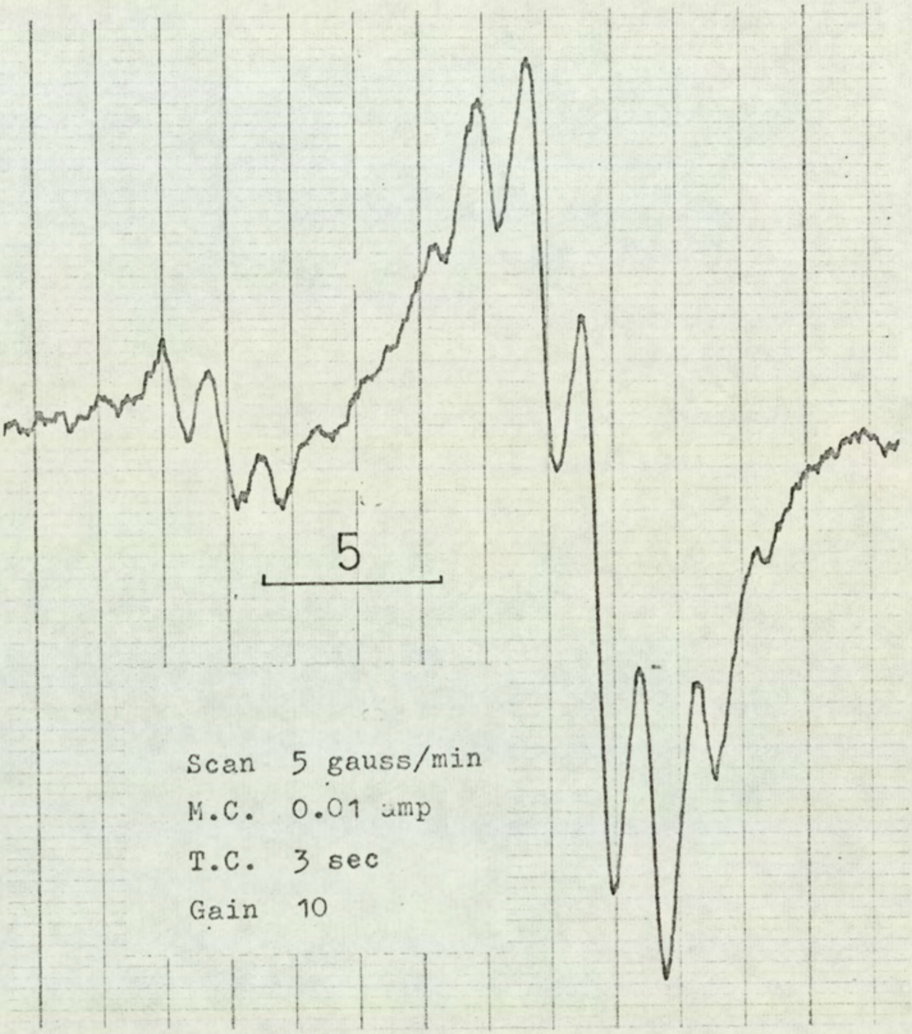
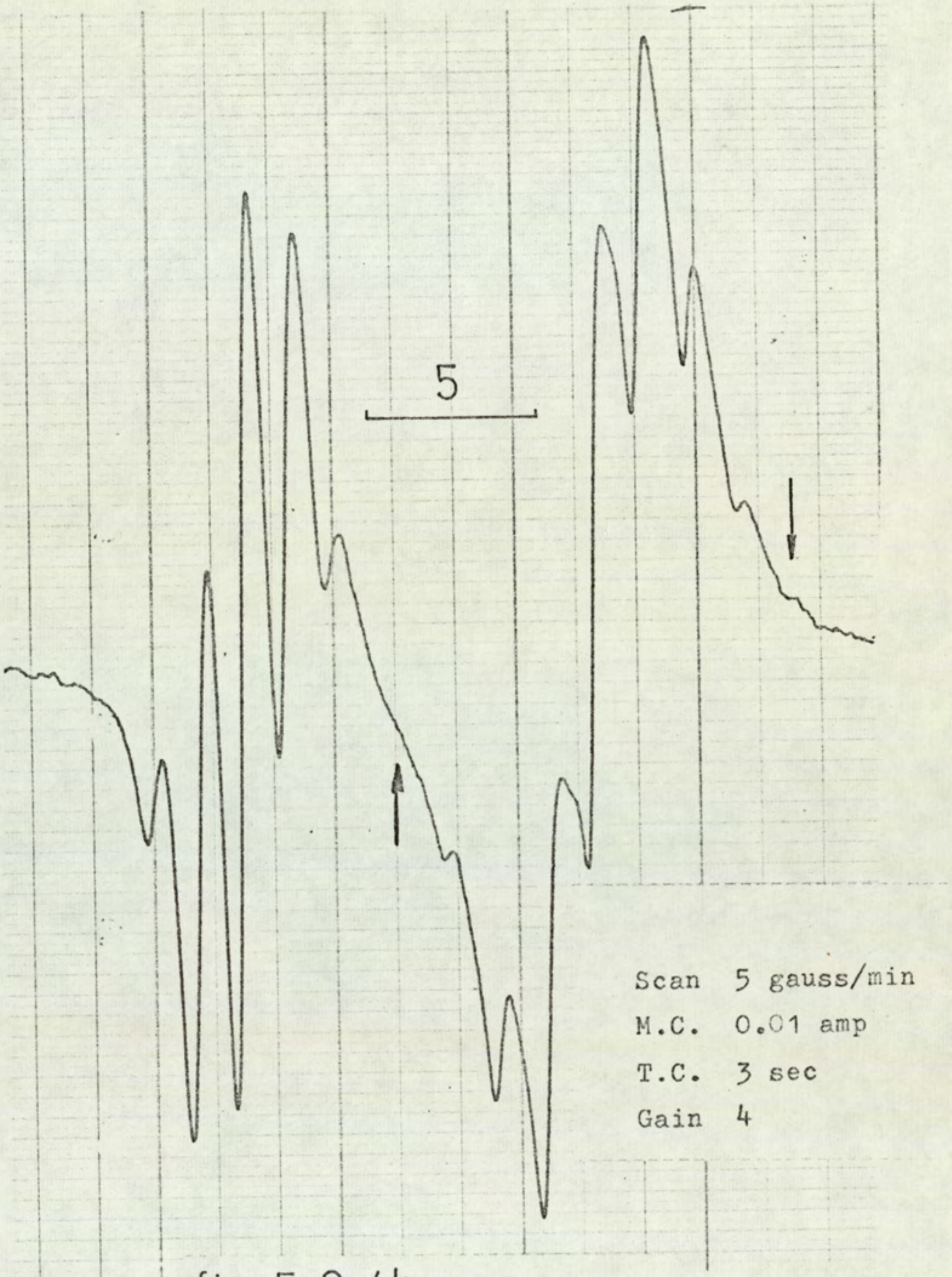


fig 5.3.3
2-methylthiophenol



Scan 5 gauss/min
M.C. 0.01 amp
T.C. 3 sec
Gain 10

fig 5.3.4a
3-methylthiophenol



Scan 5 gauss/min

M.C. 0.01 amp

T.C. 3 sec

Gain 4

fig 5.3.4b
3-methylthiophenol

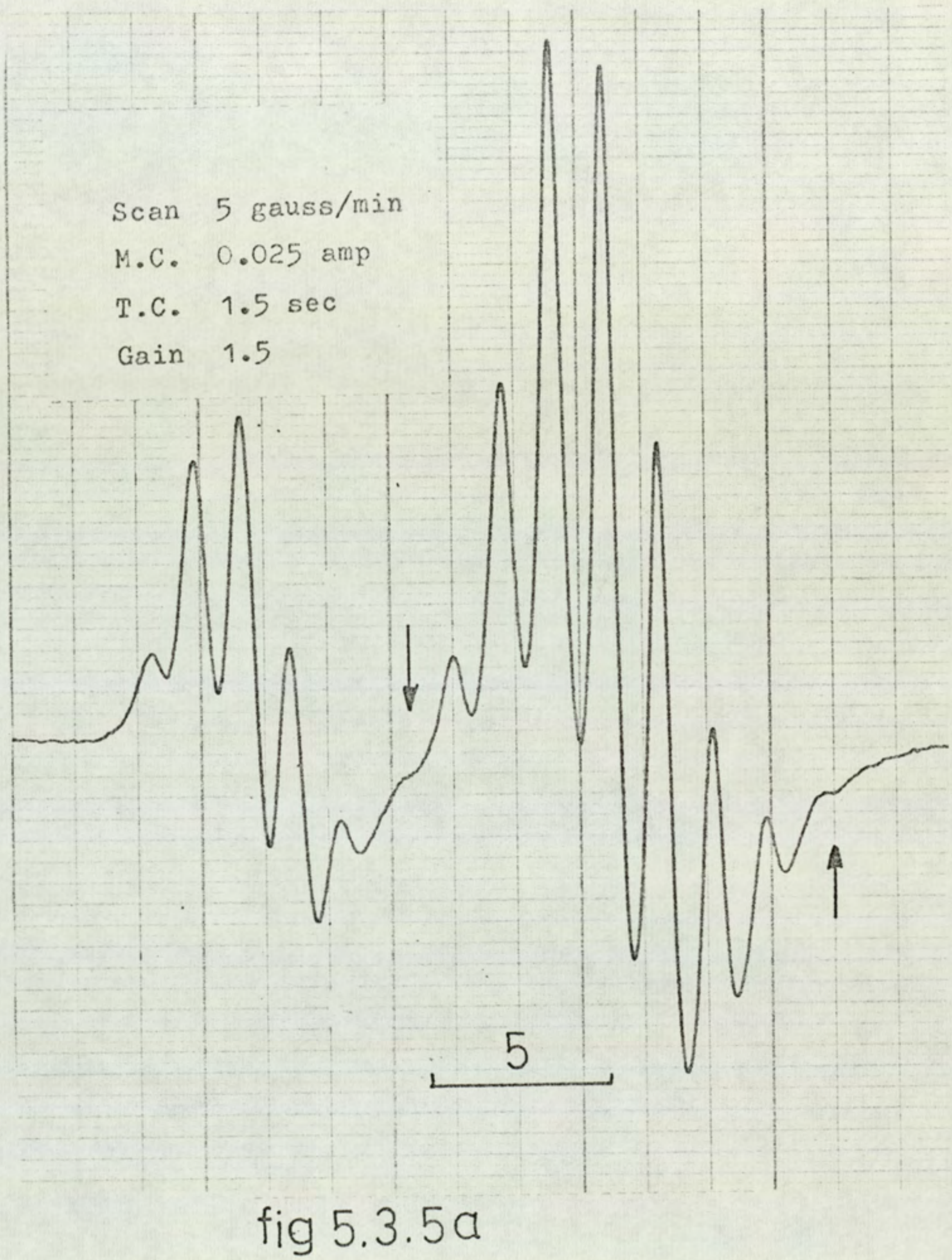
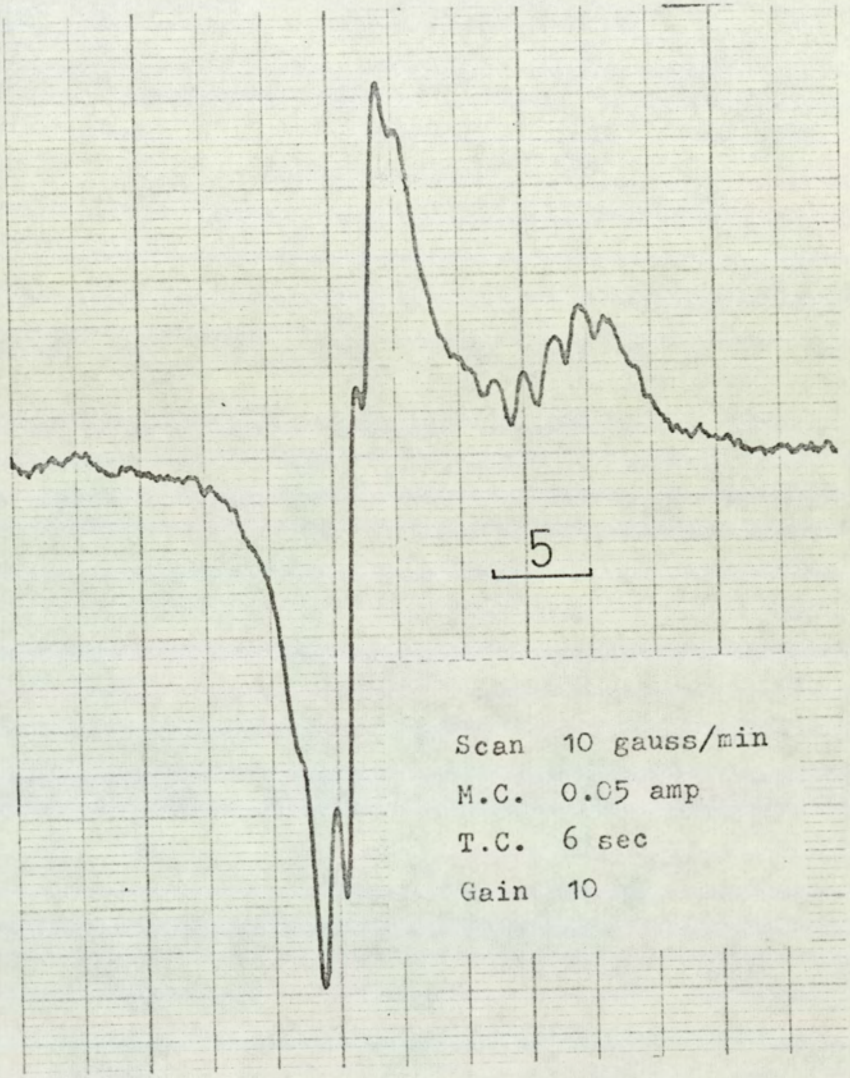


fig 5.3.5a
4-methylthiophenol



Scan 10 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

fig 5.3.5b
4-methylthiophenol

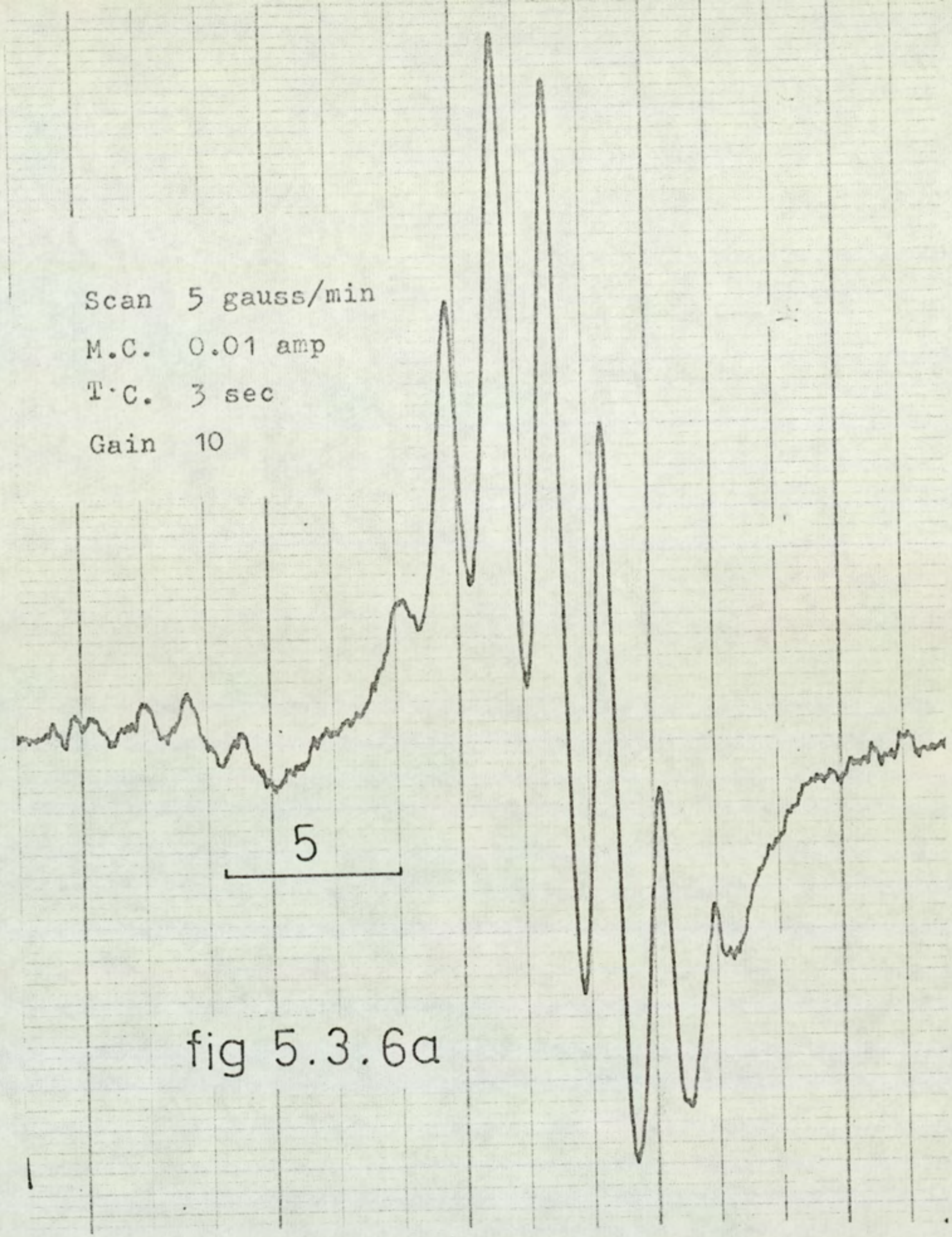


fig 5.3.6a

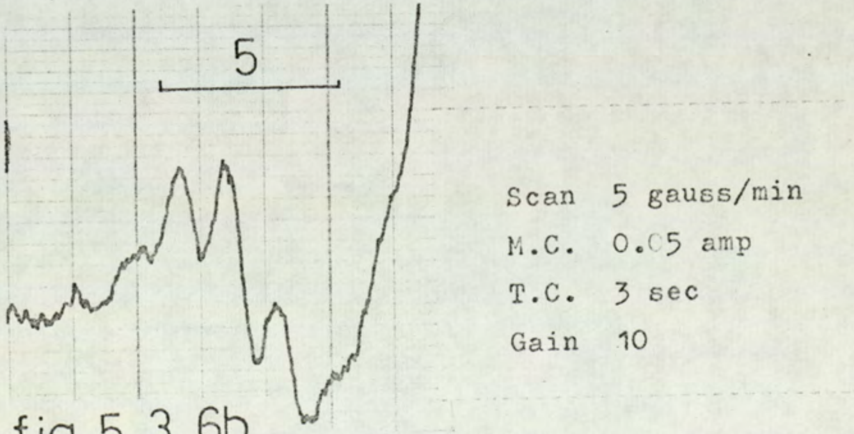
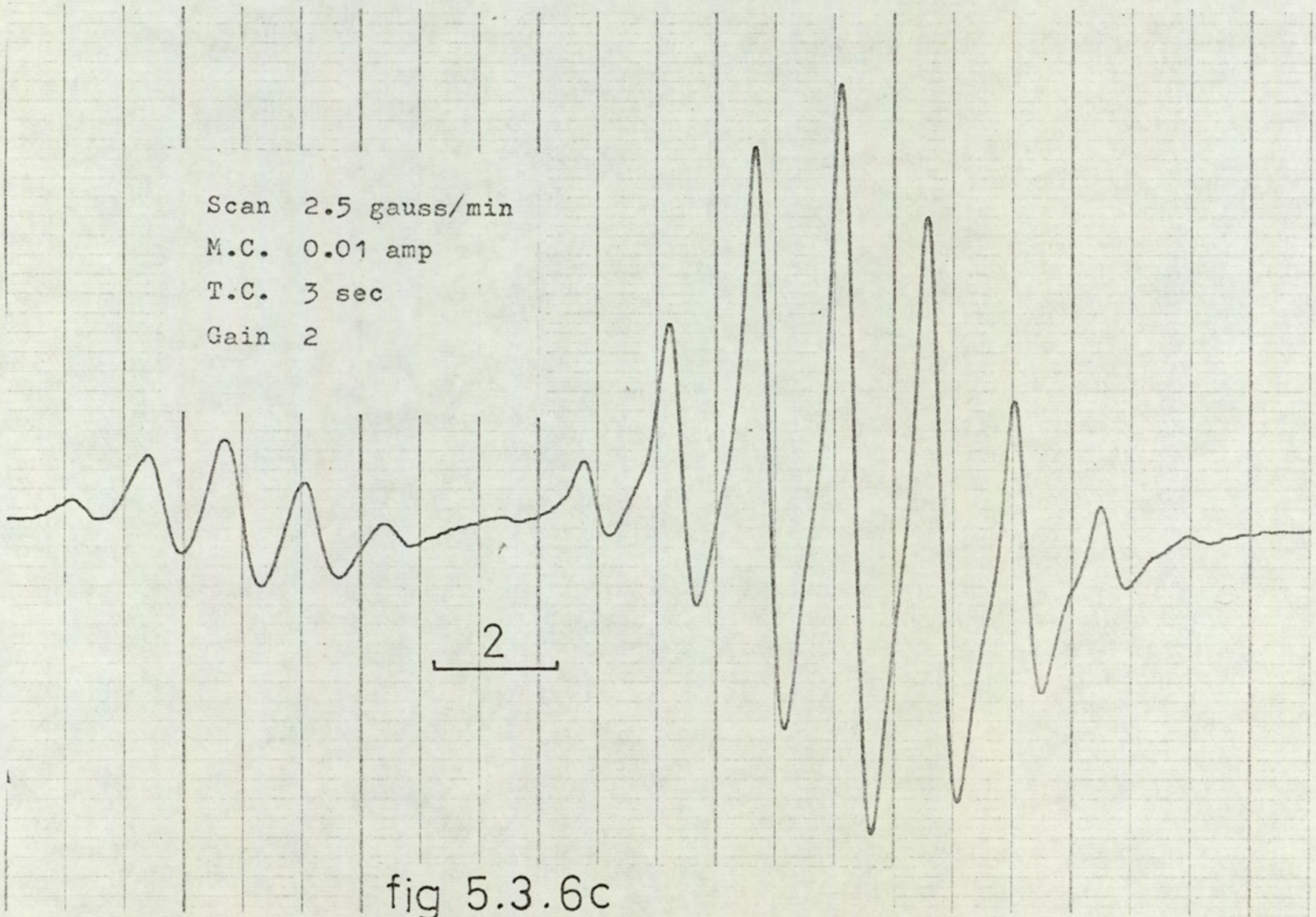


fig 5.3.6b

– 4,4′-dimethyldiphenyl disulphide



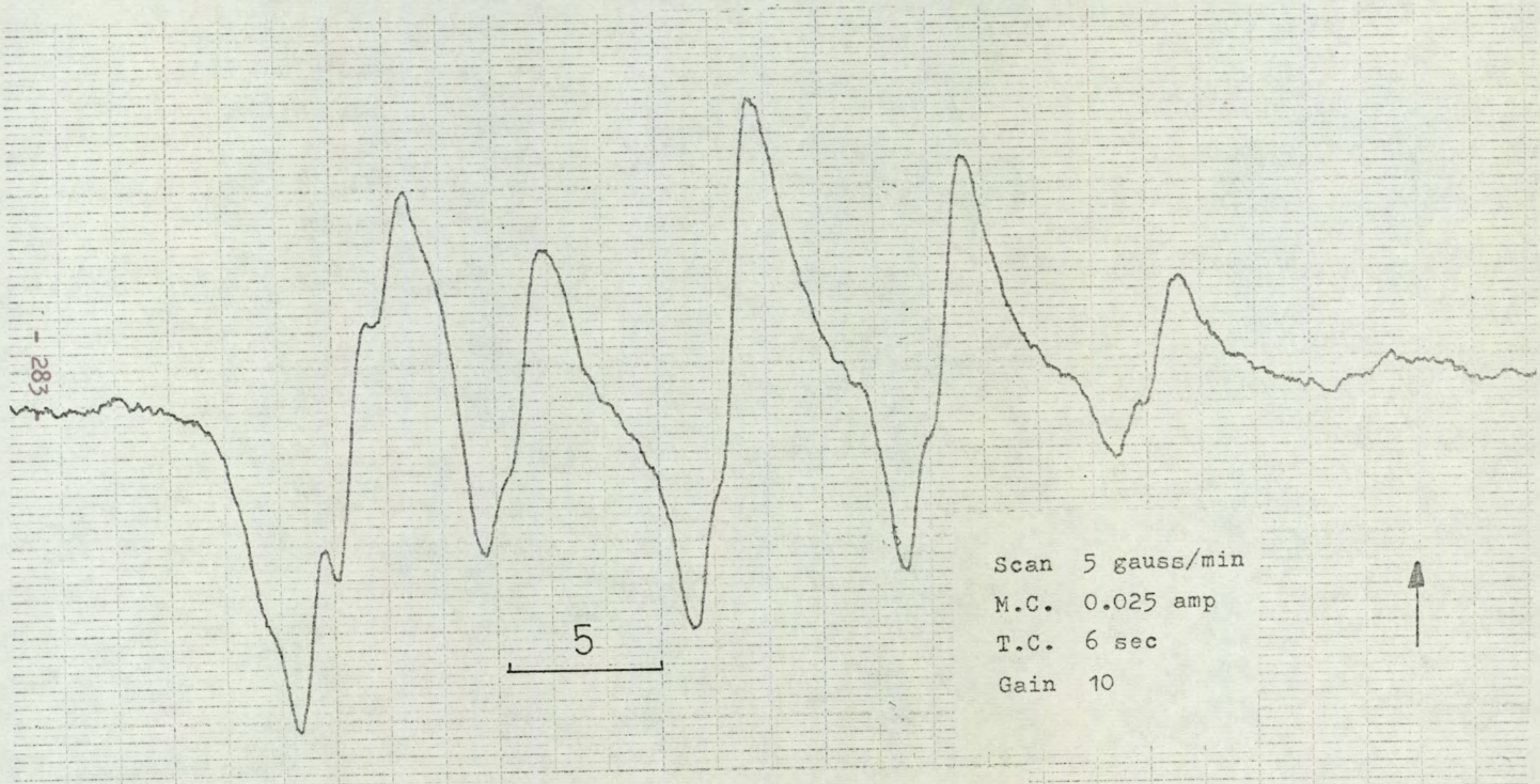
Scan 2.5 gauss/min

M.C. 0.01 amp

T.C. 3 sec

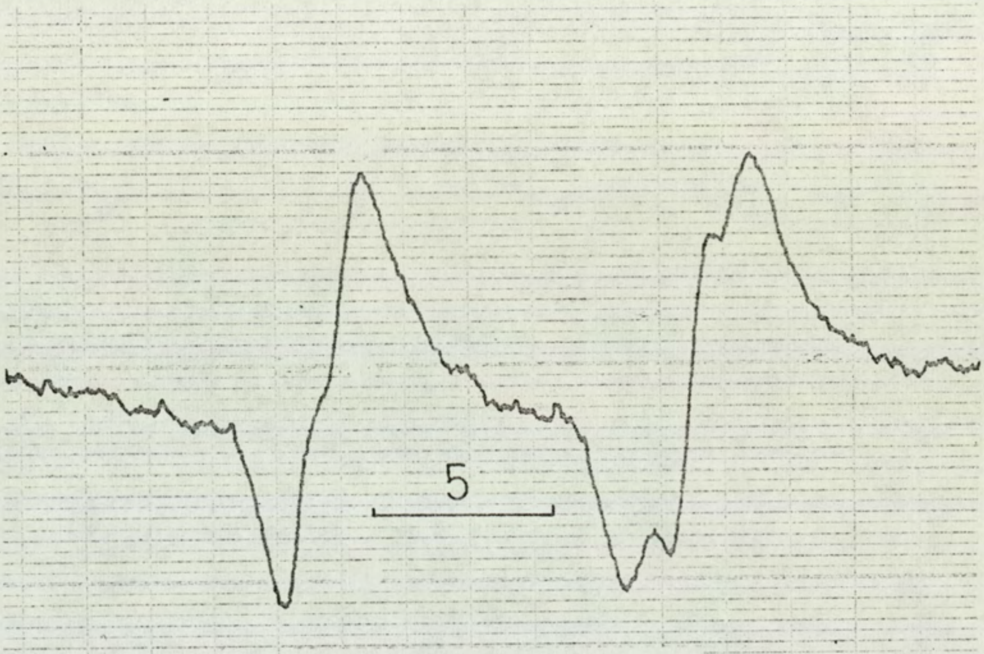
Gain 2

fig 5.3.6c
4,4'-dimethyldiphenyl disulphide



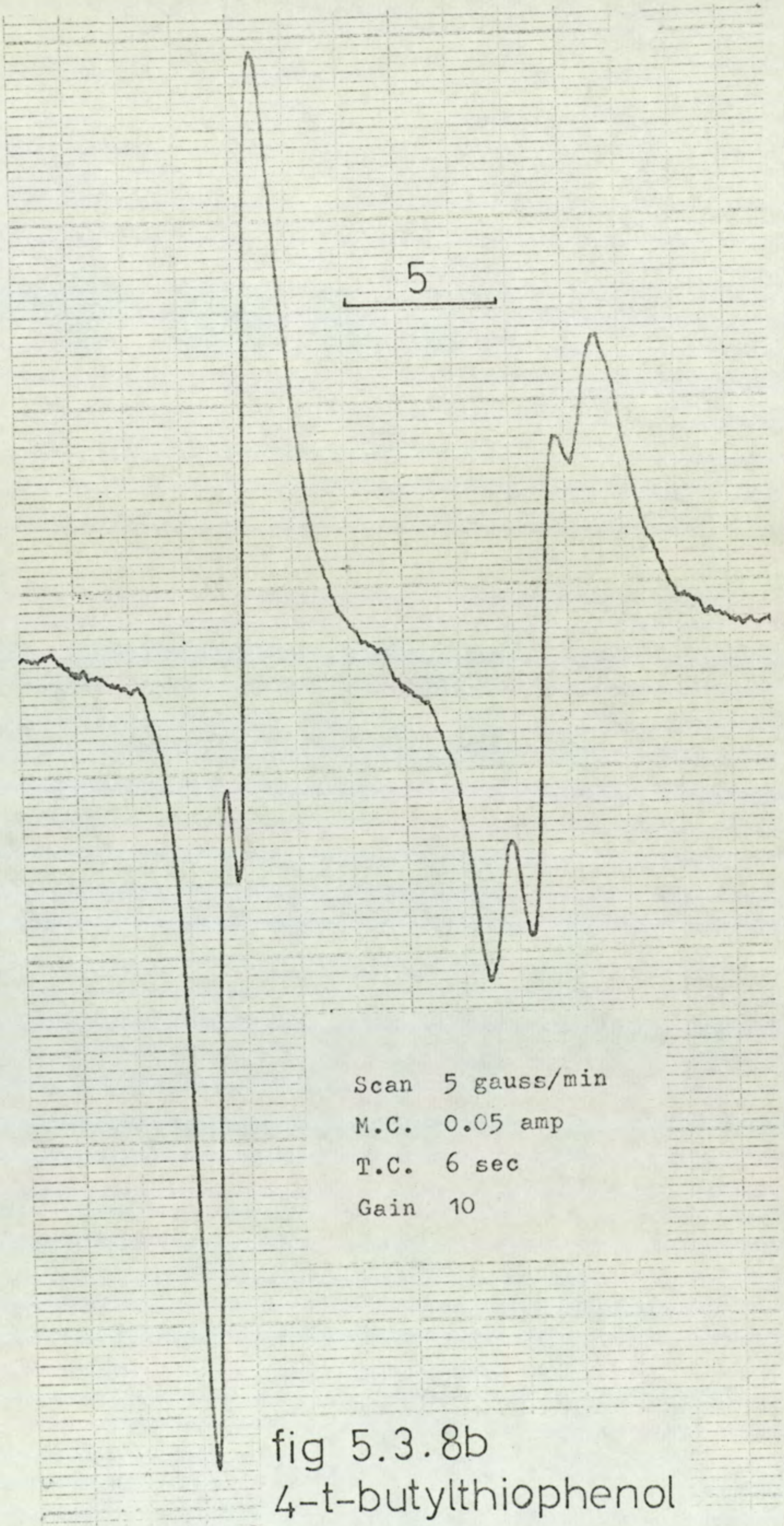
Scan 5 gauss/min
M.C. 0.025 amp
T.C. 6 sec
Gain 10

fig 5.3.7
3,5-dimethylthiophenol



Scan 5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 10

fig 5.3.8a
4-t-butylthiophenol



Scan 5 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

fig 5.3.8b
4-t-butylthiophenol

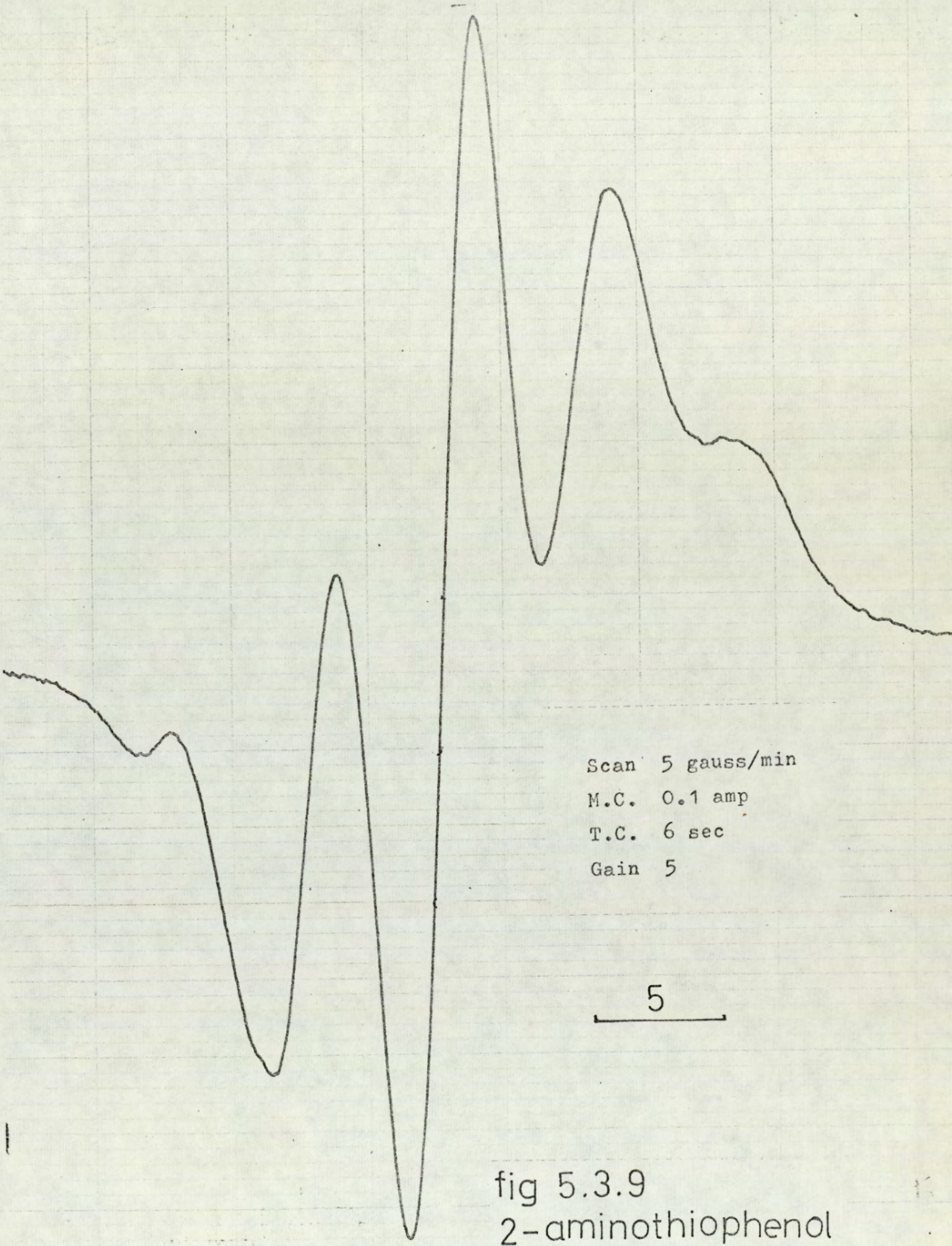
Amine-Substituted Thiophenols

2-Aminothiophenol

On dissolving this amine in sulphuric acid at room temperature, a blue-green solution was obtained, which gave the esr spectrum shown in figure 5.3.9. This was at g value 2.0067. The five hyperfine lines were separated by 5.08 gauss. On heating the solution, very small signals were obtained at both higher and lower fields.

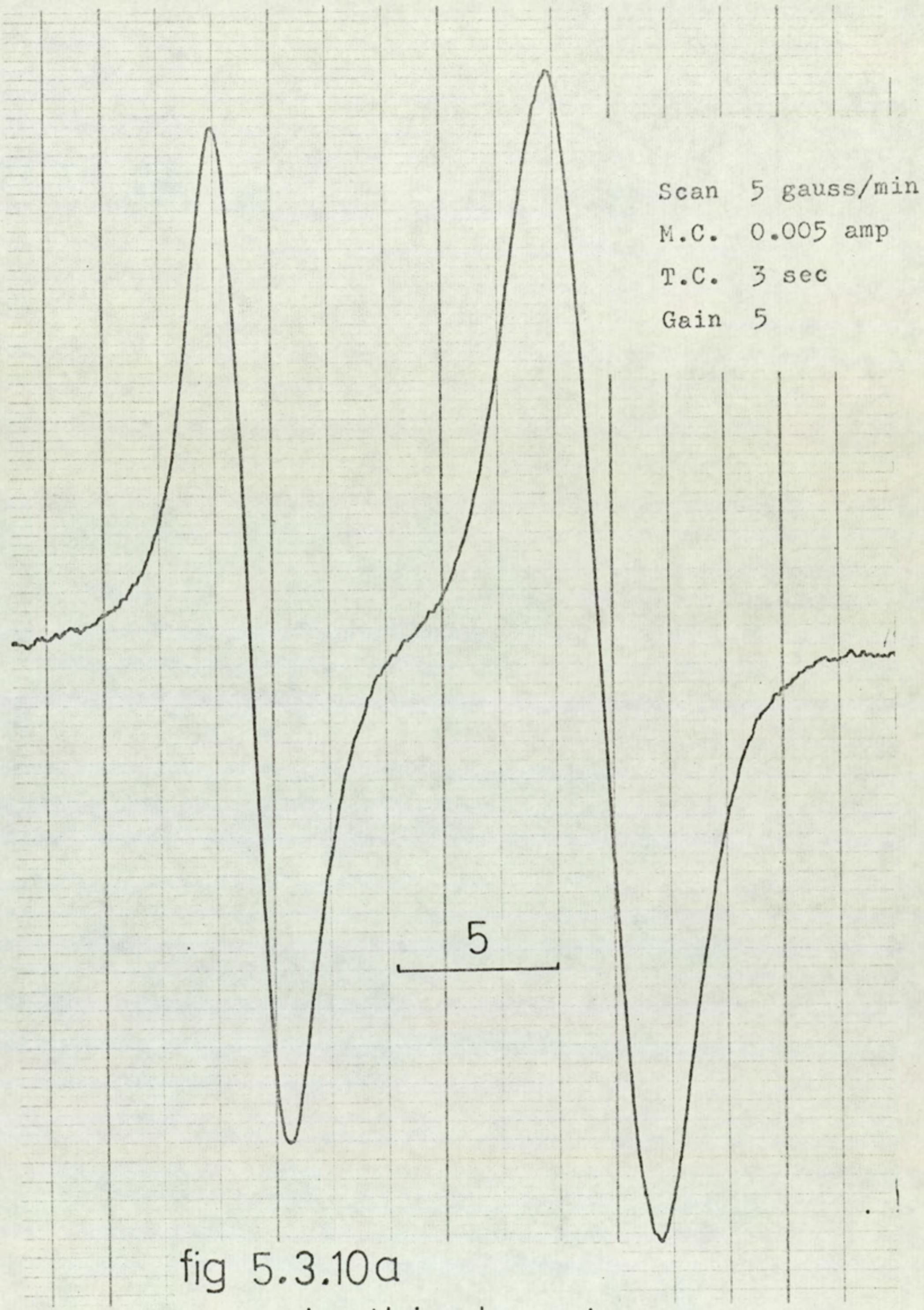
4-Aminothiophenol

The blue-green sulphuric acid solution of this compound gave two lines in the esr spectrum, at g = 2.0144 and g = 2.0078, shown in figure 5.3.10a. Some indications of hyperfine structure were obtained, as shown in figure 5.3.10b, but could not be resolved. From solutions in sulphuric acid - chlorosulphonic acid, the spectrum in figure 5.3.10c was obtained where the signal at higher g value obviously has five components.



Scan 5 gauss/min
M.C. 0.1 amp
T.C. 6 sec
Gain 5

fig 5.3.9
2-aminothiophenol



Scan 5 gauss/min
M.C. 0.005 amp
T.C. 3 sec
Gain 5

fig 5.3.10a
4-aminothiophenol

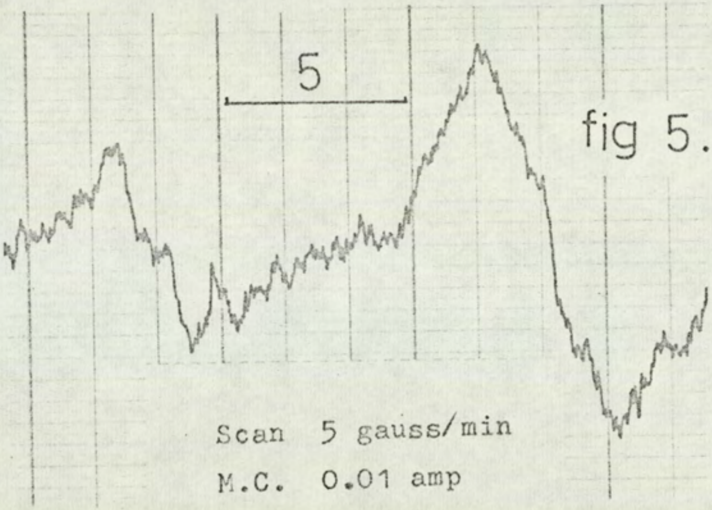
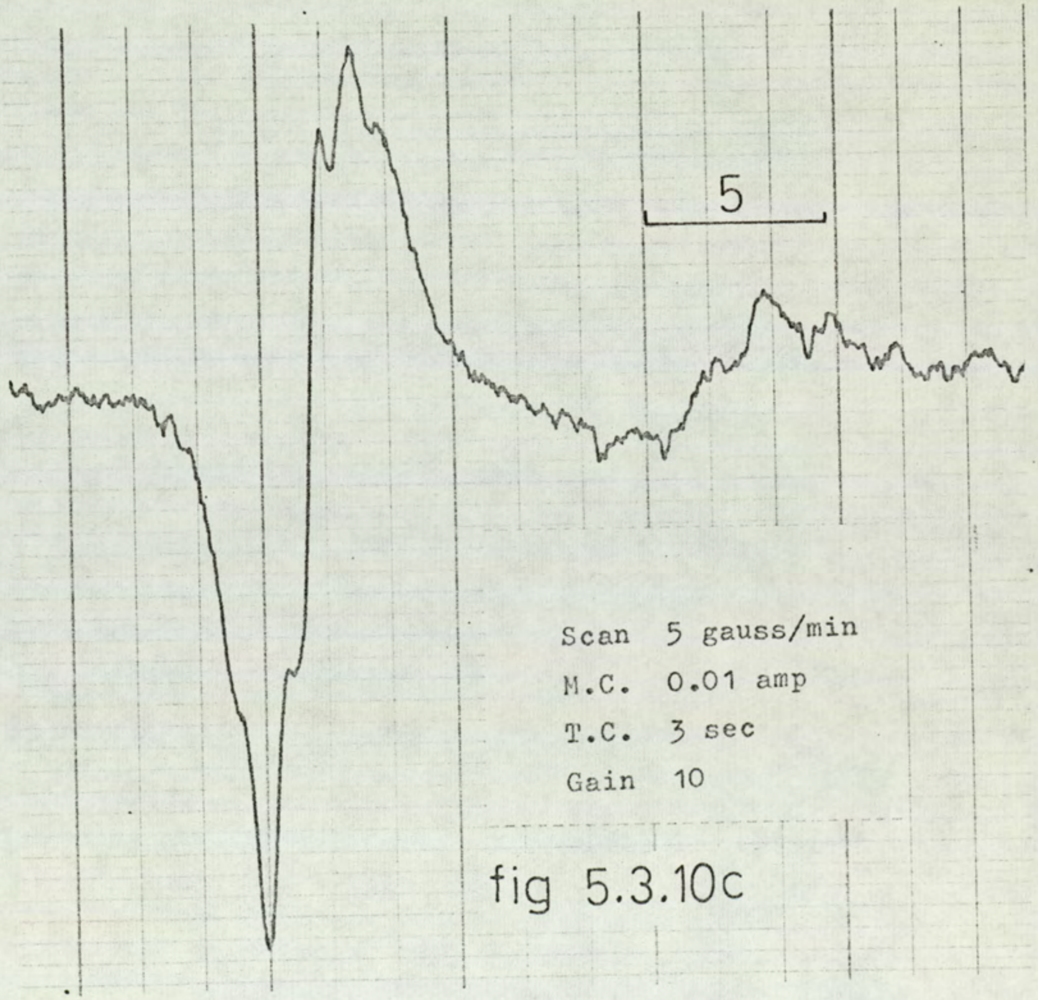


fig 5.3.10b

Scan 5 gauss/min
M.C. 0.01 amp
T.C. 1.5 sec
Gain 10



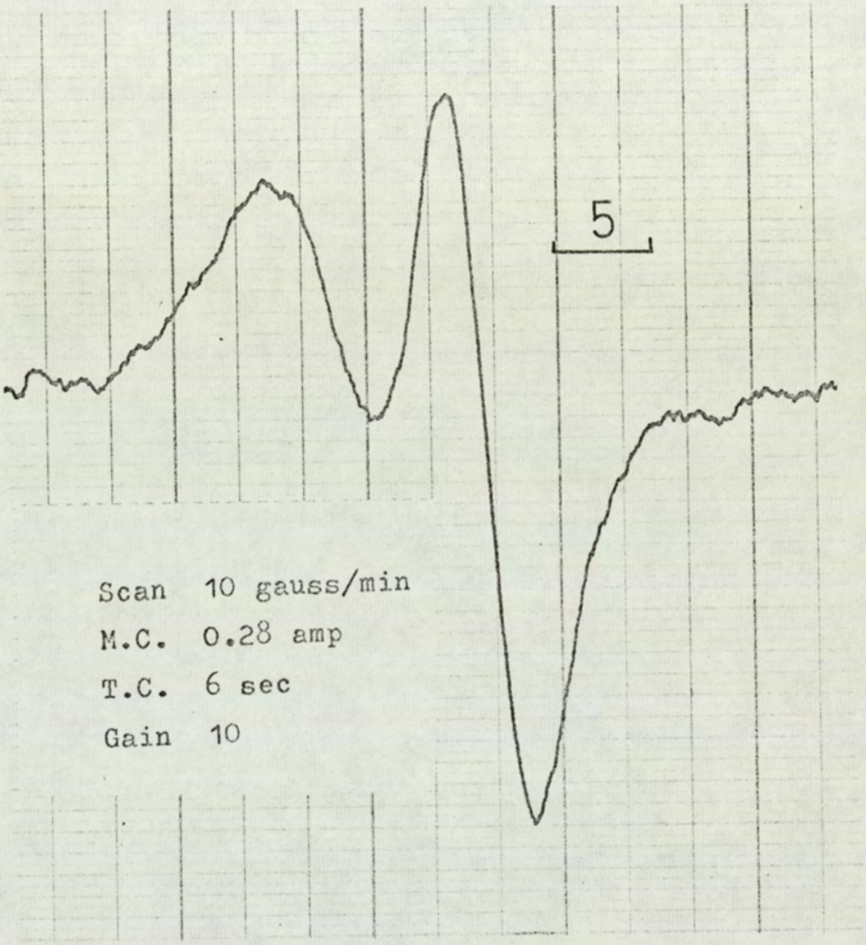
Scan 5 gauss/min
M.C. 0.01 amp
T.C. 3 sec
Gain 10

fig 5.3.10c

4-aminothiophenol

2-Mercaptobenzoic acid

The red sulphuric acid and sulphuric/chlorosulphonic acid solutions of this compound gave the esr spectrum shown in figure 5.3.11. The two lines were at $g = 2.0130$ and 2.0079, no structure could be resolved in either.



Scan 10 gauss/min
M.C. 0.28 amp
T.C. 6 sec
Gain 10

fig 5.3.11
2-mercaptobenzoic acid

Toluene-3,4-dithiol

The purple solutions of this compound in sulphuric acid had two absorption lines in the esr spectrum, at $g = 2.0140$ and $g = 2.0083$. Both resonances had hyperfine splitting, the one at $g = 2.0140$ was a quintet, see figure 5.3.12a, where the partly resolved lower g value signal is also shown. The spectrum is shown under higher resolution in figure 5.3.12b, and the lower g value signal can be seen to have a complicated structure. The splitting in the high g signal is 1.27 gauss.

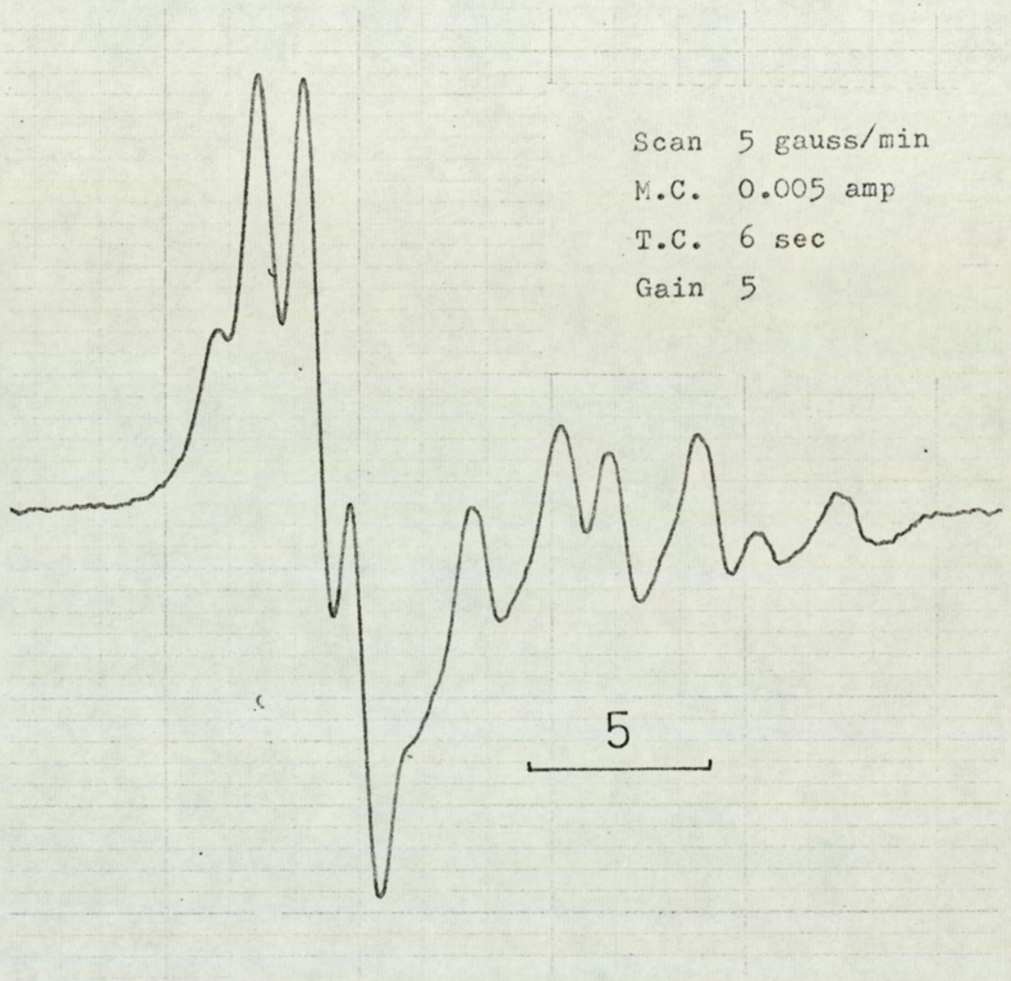
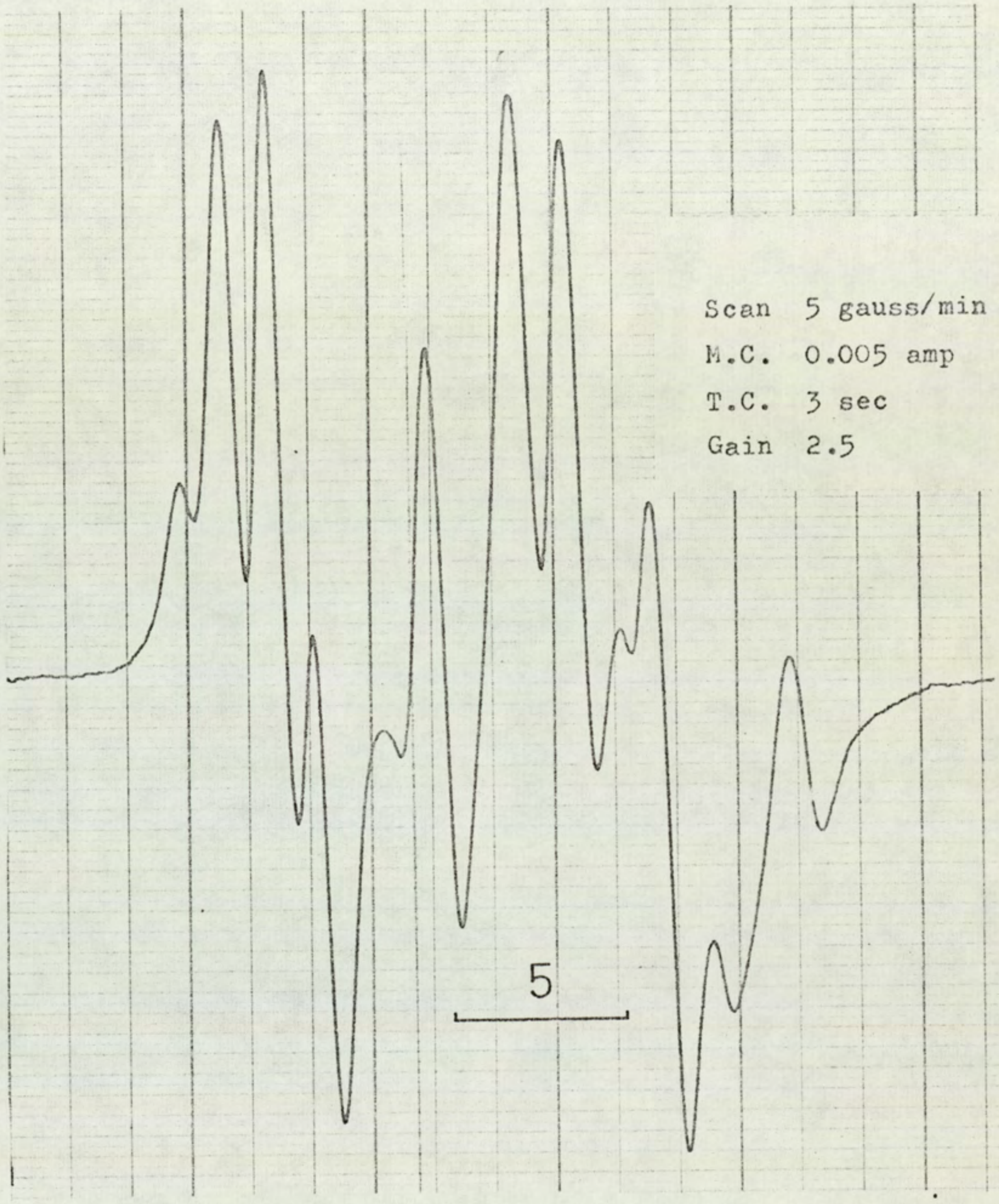


fig 5.3.12a

toluene-3,4-dithiol



Scan 5 gauss/min
M.C. 0.005 amp
T.C. 3 sec
Gain 2.5

fig 5.3.12b
toluene-3,4-dithiol

Halogen-Substituted Thiophenols

2-Chlorothiophenol

The cloudy yellow sulphuric acid solution of 2-chlorothiophenol, later turning green, had an esr spectrum showing two absorptions, both containing hyperfine splitting. The line at higher g value, 2.0126, was partially resolved into five components, with a splitting of approximately 1.3 gauss. The other line, at g = 2.0065 was less well resolved, but was thought to have five components. The spectrum is shown in figure 5.3.13a, and also under conditions of improved resolution but reduced signal : noise ratio in figure 5.3.13b.

4-Chlorothiophenol

The spectrum obtained from the green sulphuric acid solution of this thiophenol is shown in figure 5.3.14a and again in figure 5.3.14b. The two lines are at g = 2.0130 and 2.0075. The line at higher g value is partially resolved into three components. The low g value absorption is also resolved into a triplet, splitting 1.00 gauss.

2-Bromothiophenol

The spectrum from a blue solution of 2-bromothiophenol in sulphuric acid consisted of lines at g = 2.0132 and g = 2.0091. The line at higher g value was partially resolved to show three components, splitting approximately 0.8 gauss, as in figure 5.3.15a. The lower g value line was only very poorly resolved, the best trace recorded is shown in figure 5.3.15b. From this it appears to be a quintet.

4-Bromothiophenol

In sulphuric acid solutions of 4-bromothiophenol, two lines were found. No structure could be resolved in either. The spectrum is shown in figure 5.3.16. The g values are 2.0135 and 2.0088.

2,4,6-Tribromothiophenol

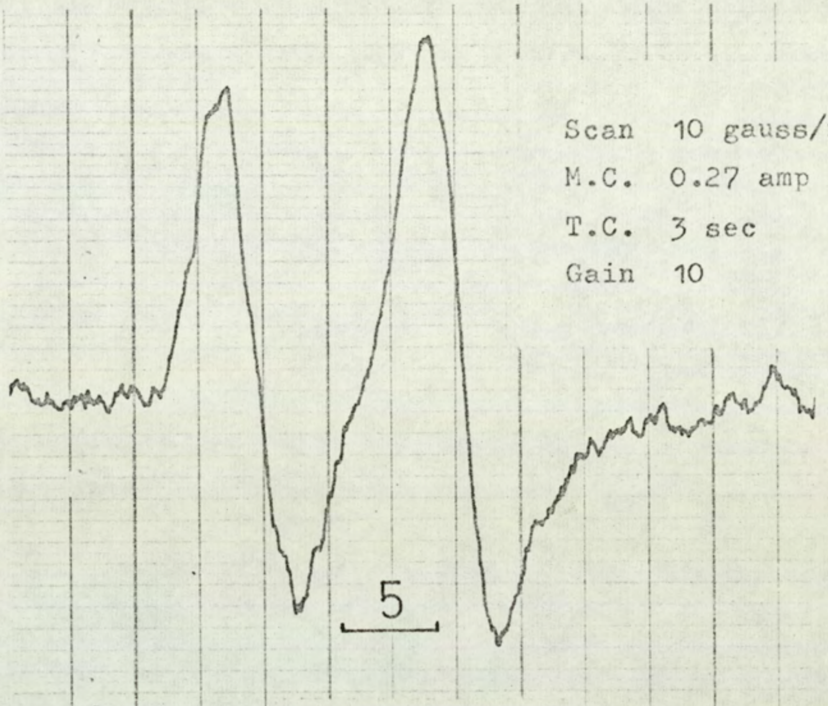
Two resonances were found from green solutions of this compound in sulphuric acid, but no structure was resolved in either. The g values are 2.0139 and 2.0063. The spectrum is shown in figure 5.3.17. There appears to be another signal between these two lines, seen as a "hump". This could not be resolved or obtained any larger.

2,2',4,4',6,6'-Hexabromodiphenyl Disulphide

A spectrum apparently identical to that from the thiol was obtained from solutions of this compound in sulphuric acid. The g values were measured as 2.0131 and 2.0059. The spectrum is shown in figure 5.3.18.

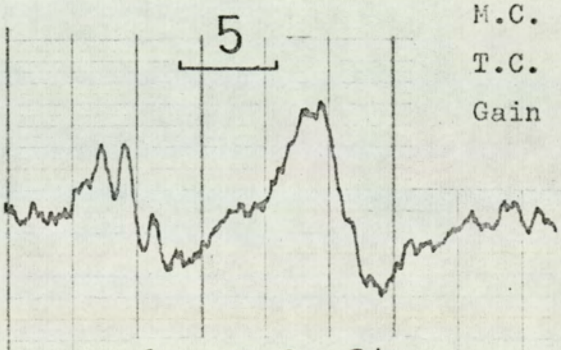
Pentafluorothiophenol

Sulphuric acid solutions of the fully fluorinated thiophenol yielded the esr spectrum shown in figure 5.3.19. The two lines are of g values 2.0126 and 2.0049. The structure, indications of which are just perceptible, could not be resolved any more fully.



Scan 10 gauss/min
M.C. 0.27 amp
T.C. 3 sec
Gain 10

fig 5.3.13a



Scan 10 gauss/min
M.C. 0.05 amp
T.C. 3 sec
Gain 10

fig 5.3.13b

2-chlorothiophenol

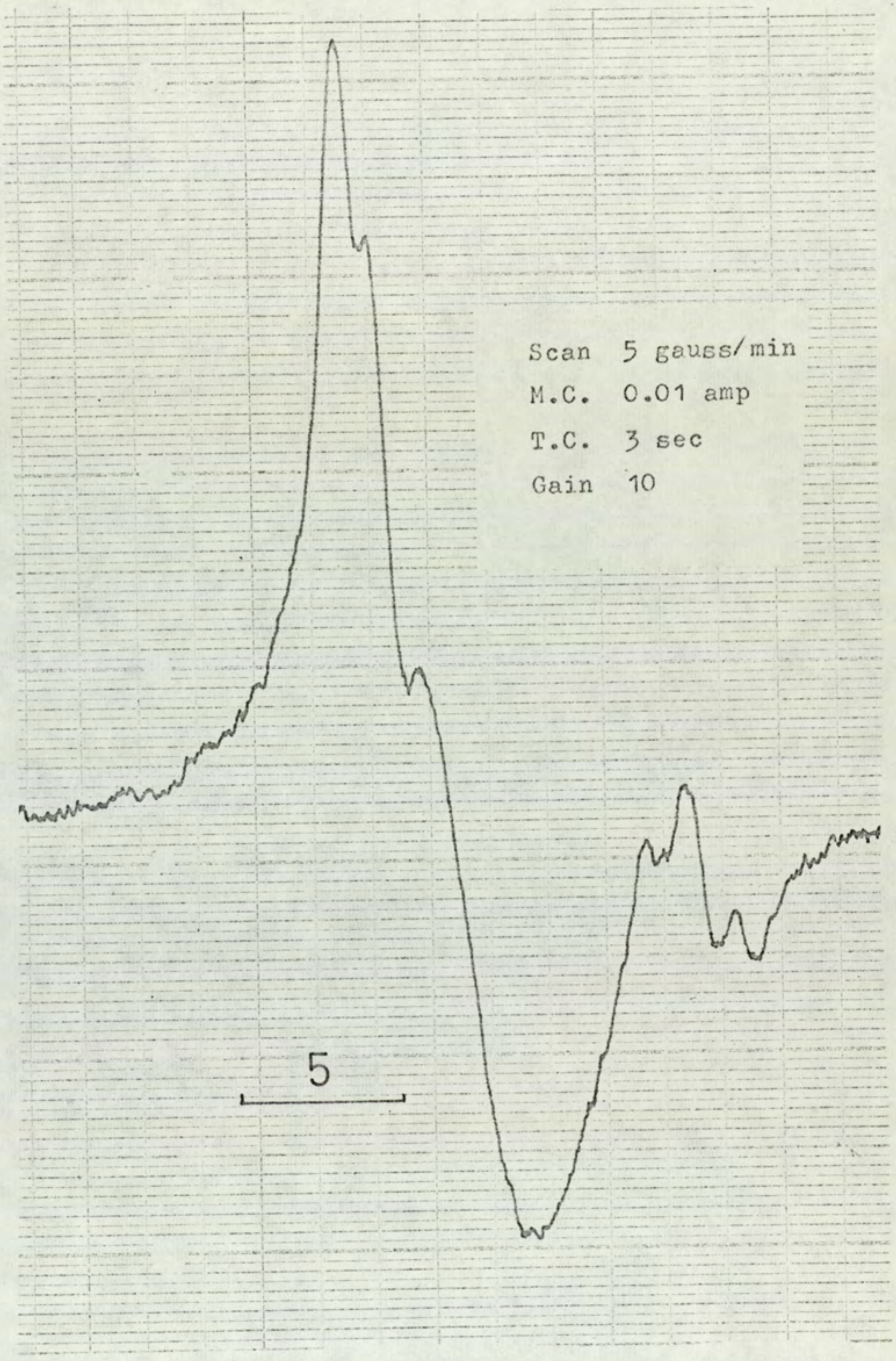
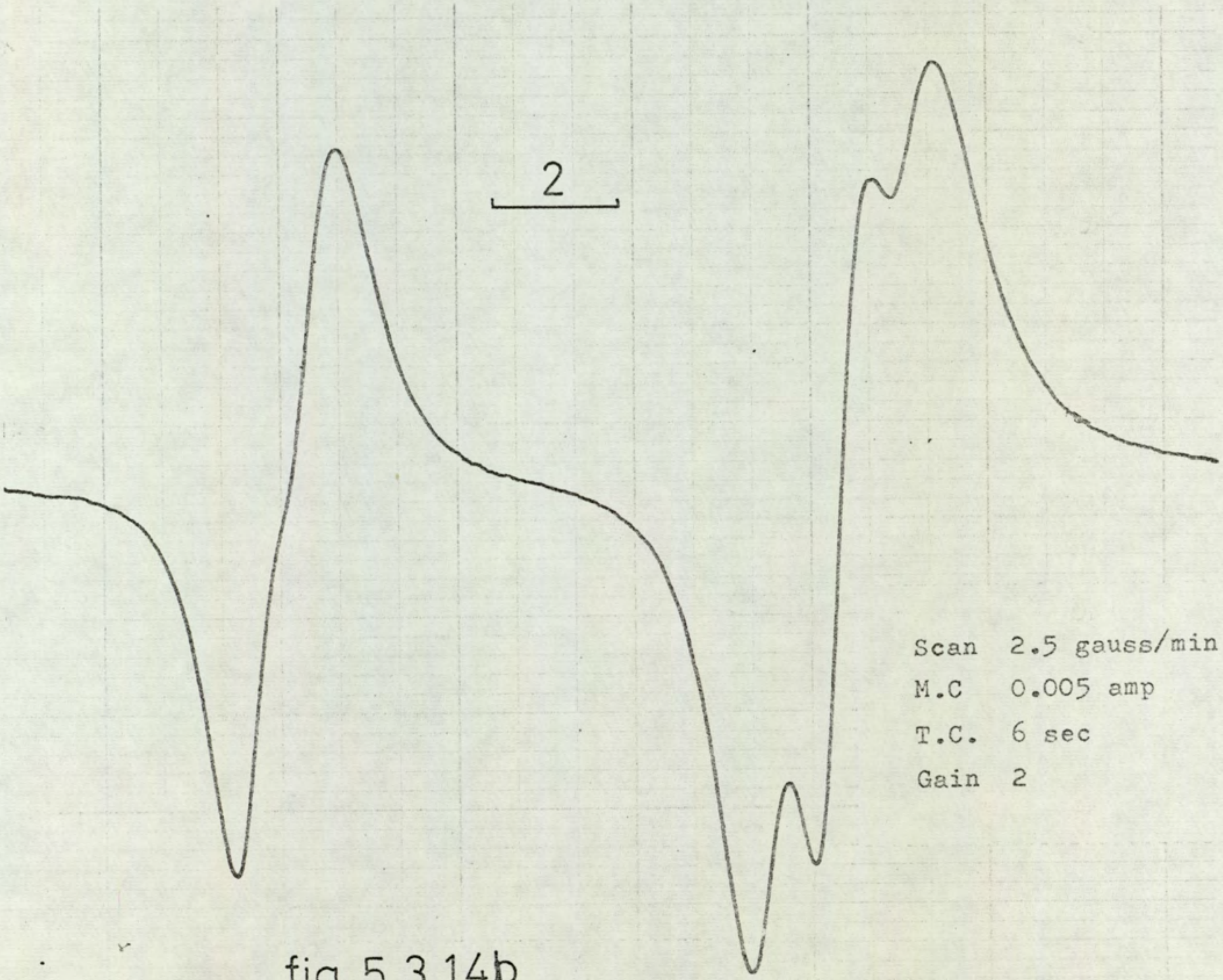
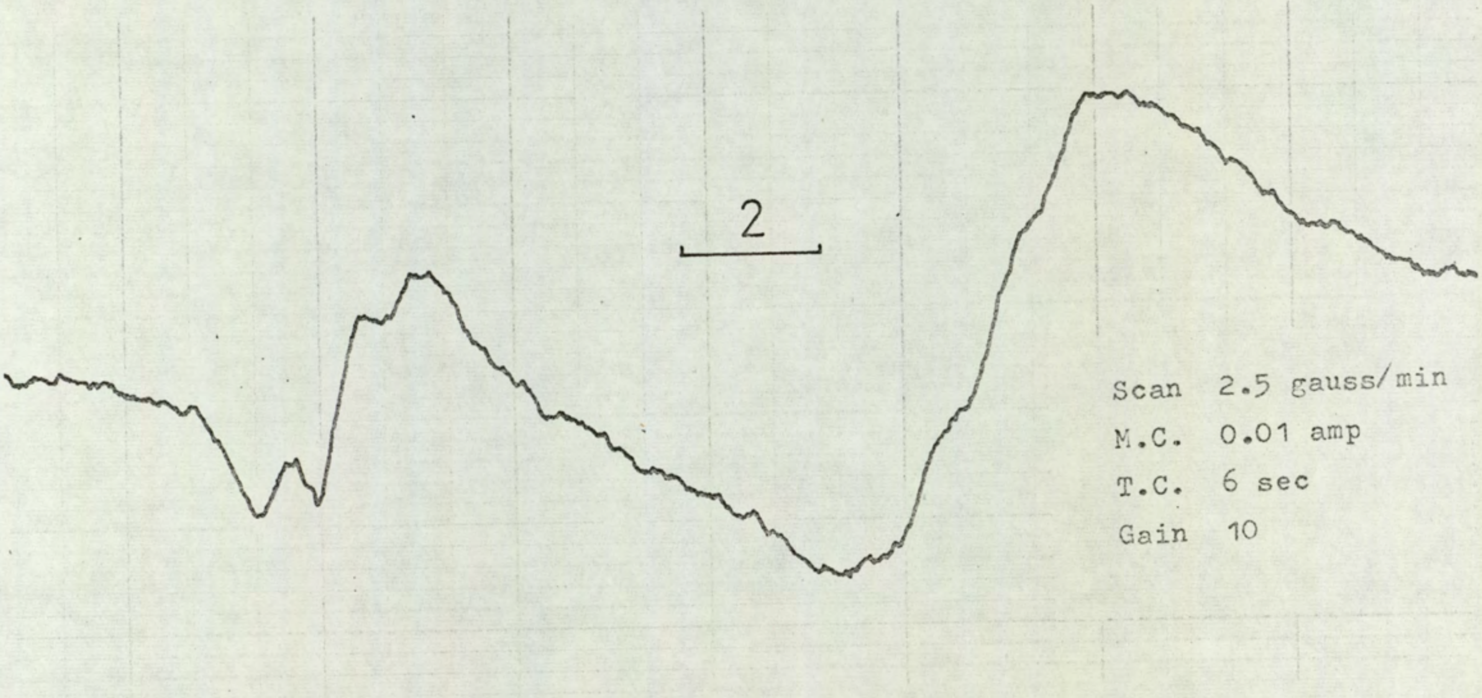


fig 5.3.14a
4-chlorothiophenol



Scan 2.5 gauss/min
M.C 0.005 amp
T.C. 6 sec
Gain 2

fig 5.3.14b
4-chlorothiophenol



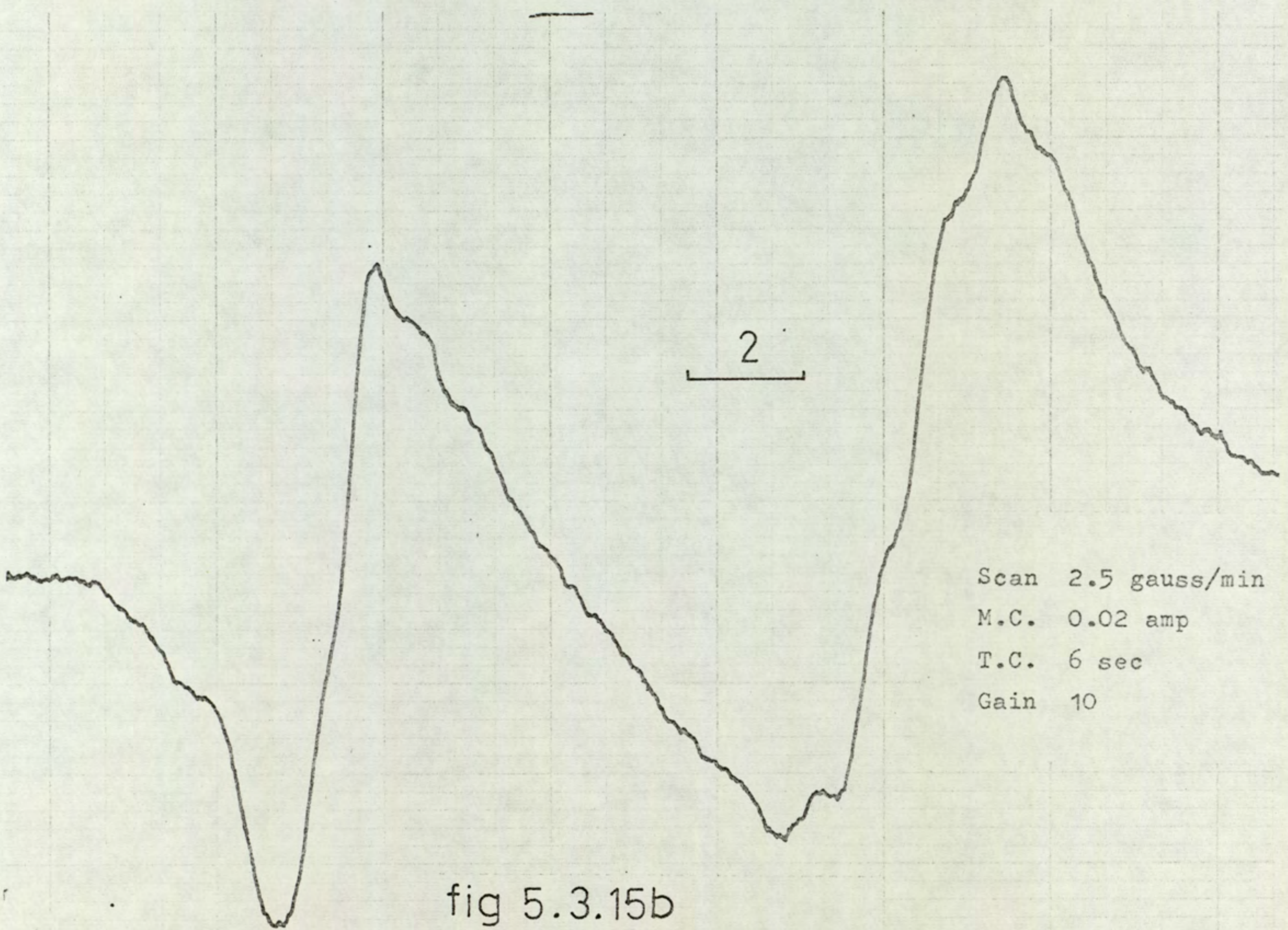
Scan 2.5 gauss/min

M.C. 0.01 amp

T.C. 6 sec

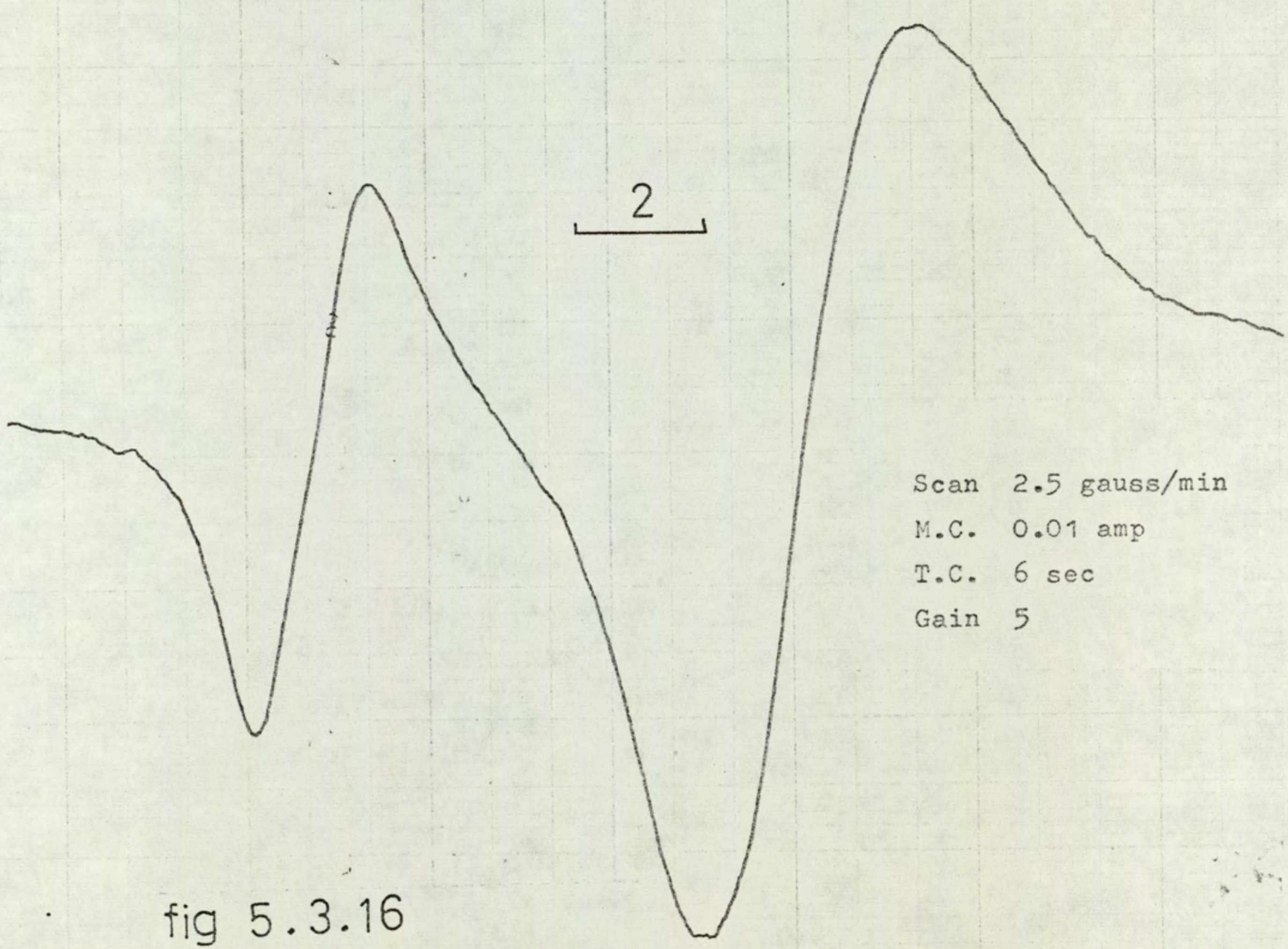
Gain 10

fig 5.3.15a
2-bromothiophenol



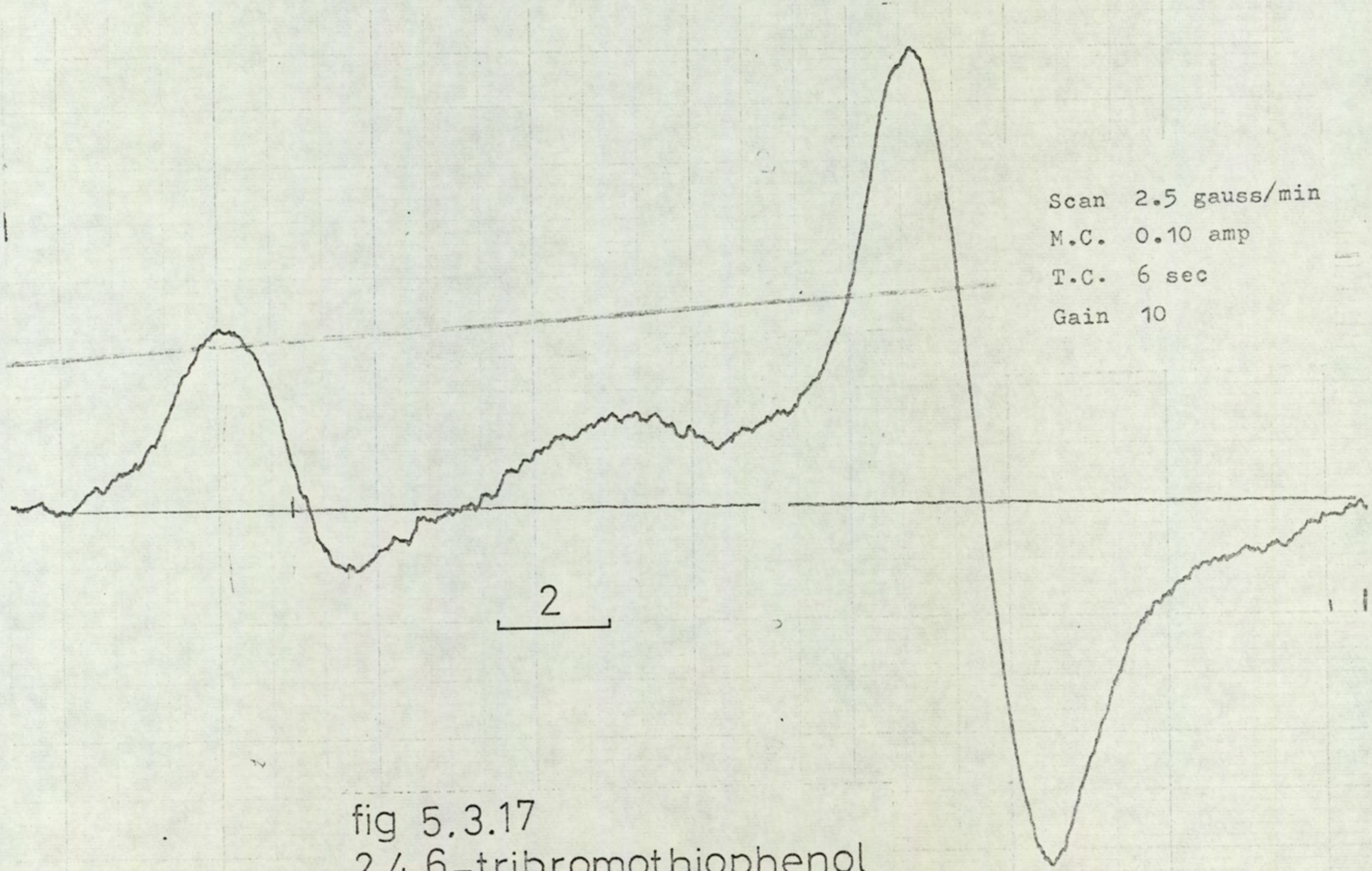
Scan 2.5 gauss/min
M.C. 0.02 amp
T.C. 6 sec
Gain 10

fig 5.3.15b
2-bromothiophenol



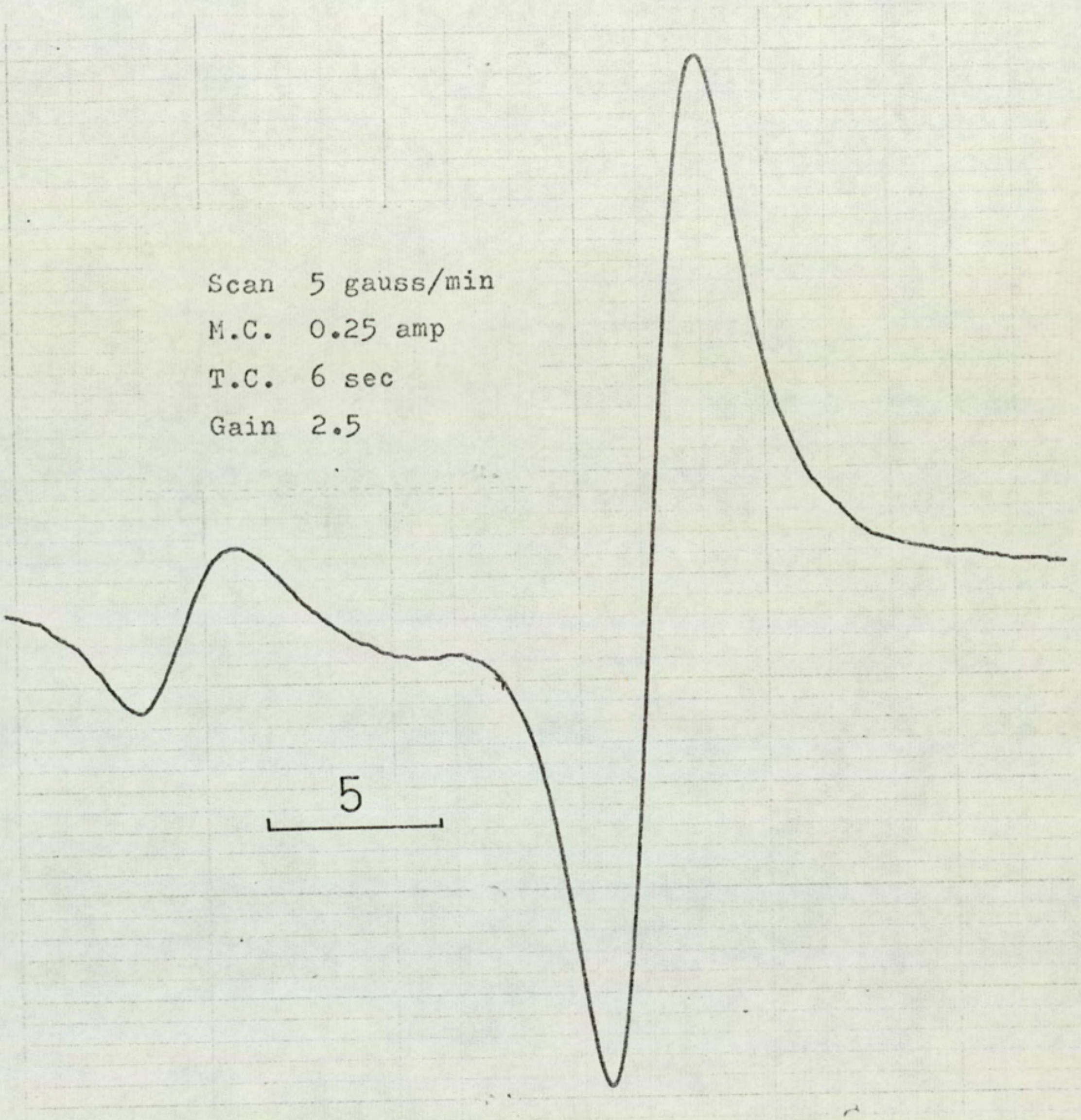
Scan 2.5 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 5

fig 5.3.16
4-bromothiophenol



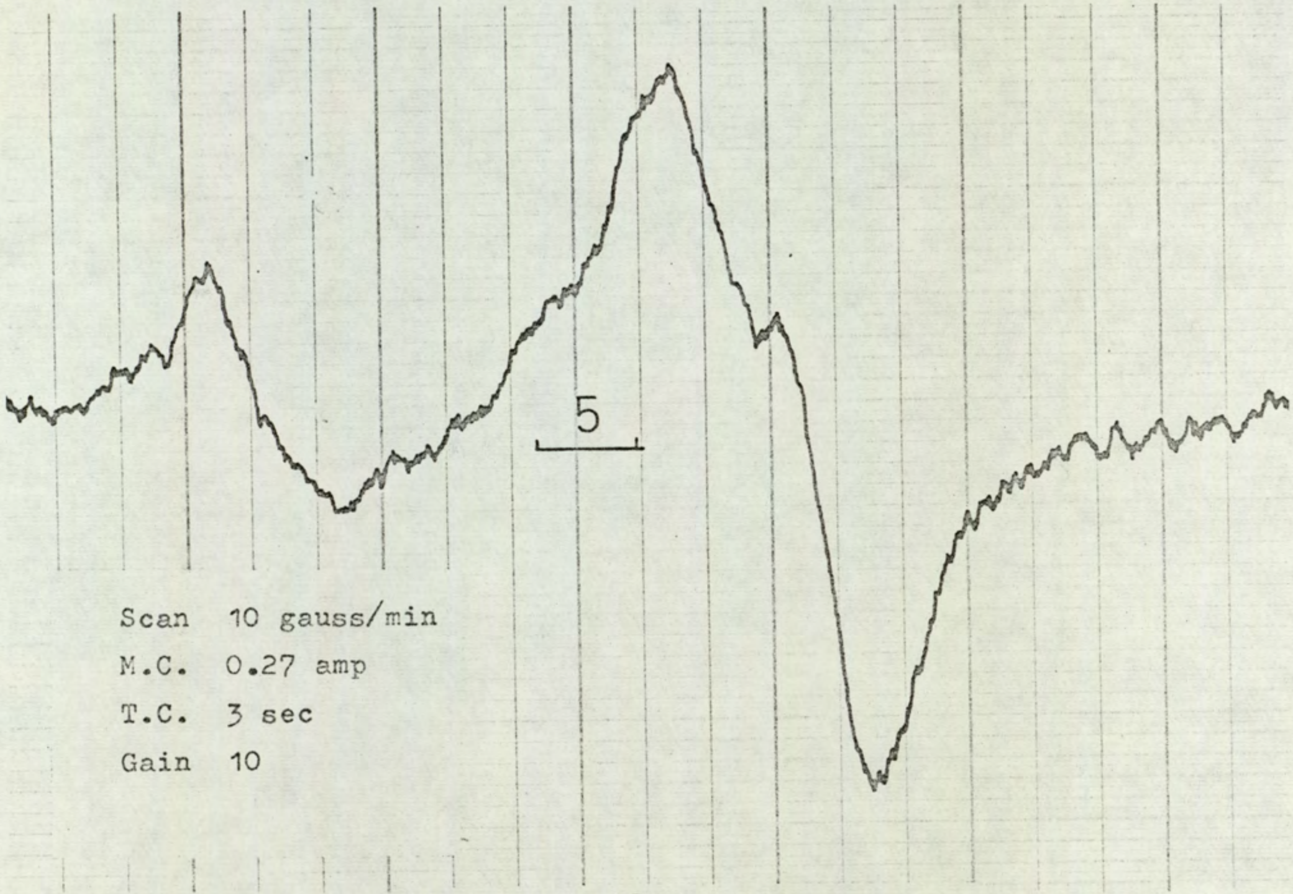
Scan 2.5 gauss/min
M.C. 0.10 amp
T.C. 6 sec
Gain 10

fig 5.3.17
2,4,6-tribromothiophenol



Scan 5 gauss/min
M.C. 0.25 amp
T.C. 6 sec
Gain 2.5

fig 5.3.18
2,2',4,4',6,6'-hexabromodiphenyl disulphide



Scan 10 gauss/min

M.C. 0.27 amp

T.C. 3 sec

Gain 10

fig 5.3.19
pentafluorothiophenol

Monosulphides

Diphenyl Sulphide

The sulphuric acid solution of this sulphide developed a purple colour and had an esr absorption at $g = 2.0069$. The line was resolved into a quintet, of splitting 1.12 gauss, shown in figure 5.3.20a.

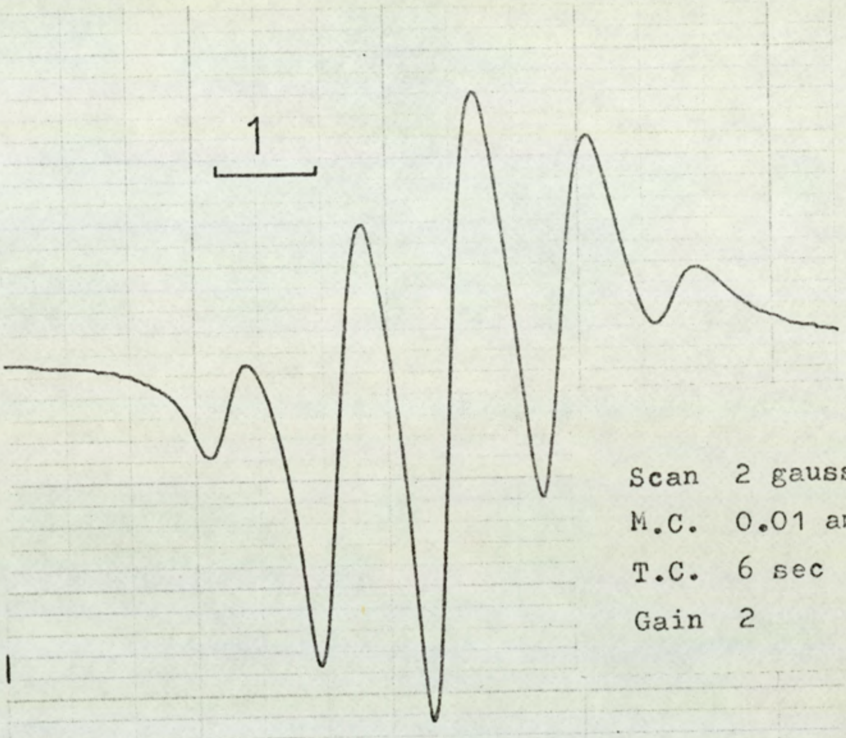
When sulphuric/chlorosulphonic acid mixture was used, another absorption was found at higher g value. This was very much smaller than the main resonance, and also appeared to be a quintet with splitting approximately 1.3 gauss. This resonance is shown in figure 5.3.20b where the main signal is off-scale.

Phenyl Methyl Sulphide

In solution in sulphuric acid, two absorption lines were observed, a small one in which no fine structure could be found, and a larger one, at $g = 2.0070$. The spectrum is shown in figure 5.3.21a. The solution was orange. The larger line was resolved into a quintet, of splitting constant 1.17 gauss, shown in figure 5.3.21b. The g value of the smaller absorption was not accurately measured, but is thought to lie close to that of the high g value signal from thiophenol. Resolution was not improved using chlorosulphonic acid.

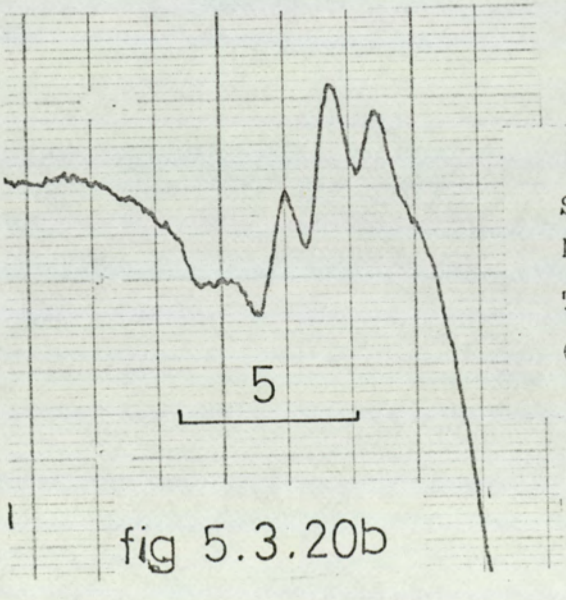
Phenyl Isopropyl Sulphide

Two absorption lines were found for the purple sulphuric acid solution of this sulphide, as shown in figure 5.3.22. The larger line is a quintet, g value 2.0082 and splitting constant 1.07 gauss. The other line, at g = 2.0137, has three components resolved with splitting approximately 0.9 gauss.



Scan 2 gauss/min
M.C. 0.01 amp
T.C. 6 sec
Gain 2

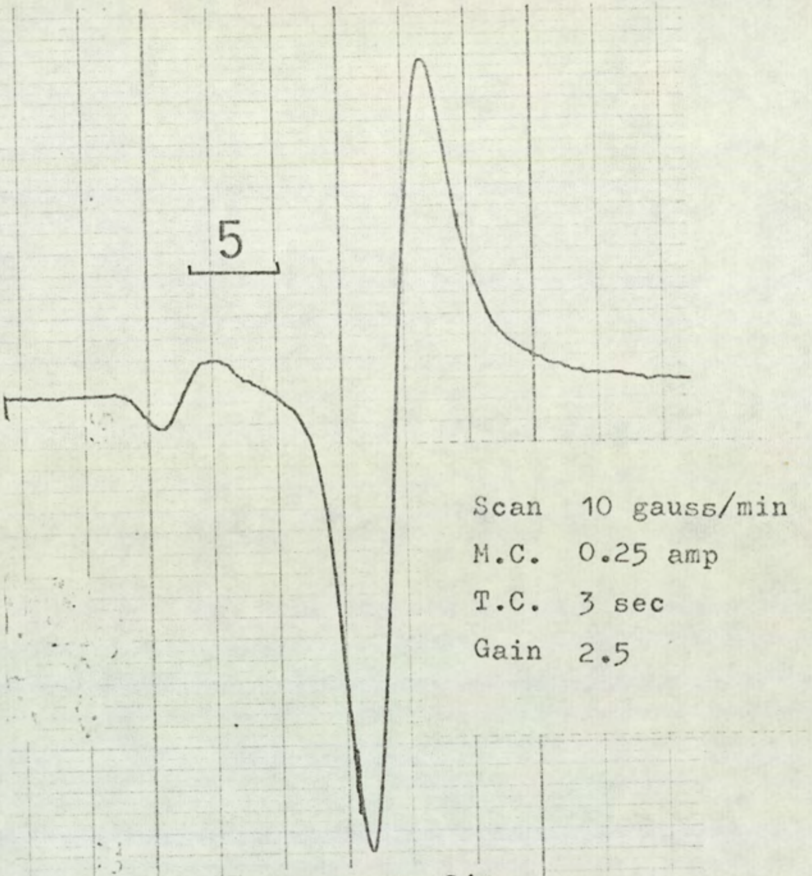
fig 5.3.20a



Scan 5 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

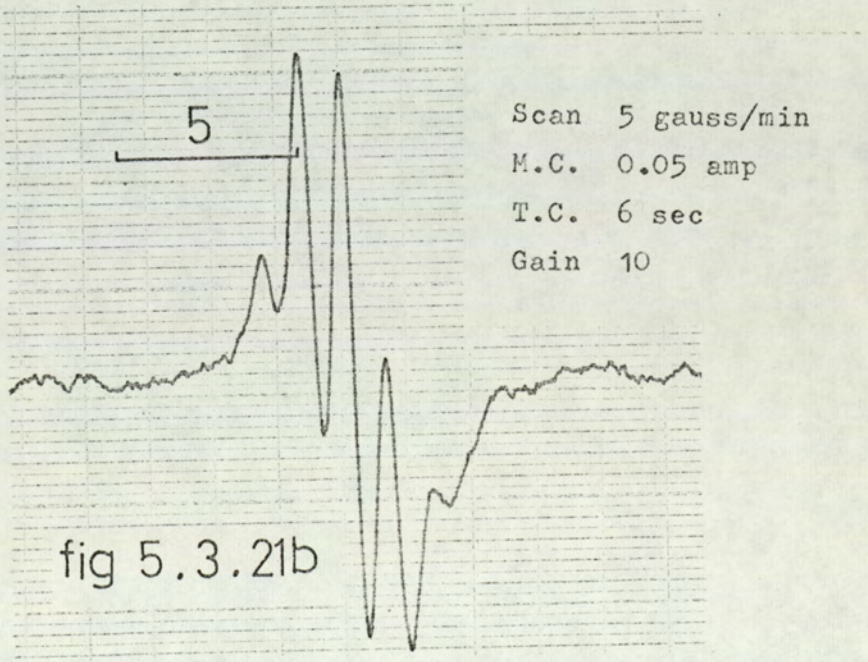
fig 5.3.20b

diphenyl sulphide



Scan 10 gauss/min
M.C. 0.25 amp
T.C. 3 sec
Gain 2.5

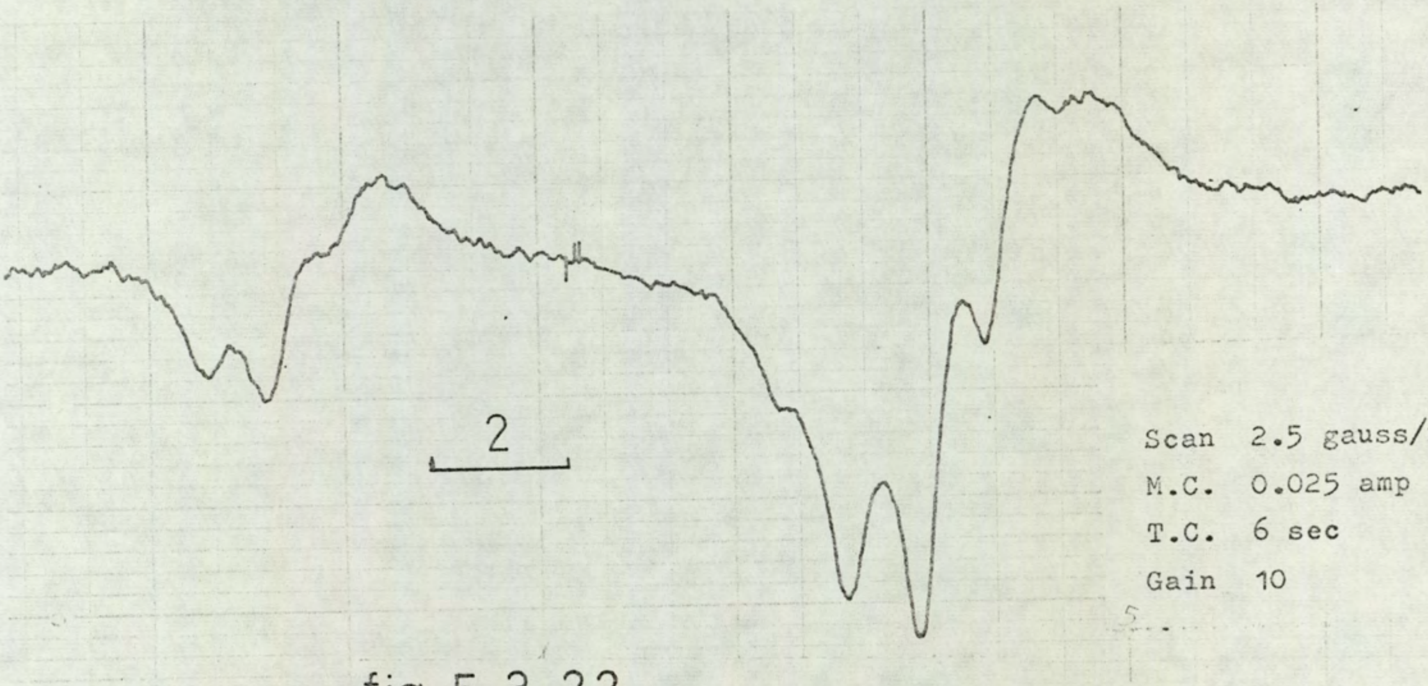
fig 5.3.21a



Scan 5 gauss/min
M.C. 0.05 amp
T.C. 6 sec
Gain 10

fig 5.3.21b

phenyl-methyl sulphide



Scan 2.5 gauss/min
M.C. 0.025 amp
T.C. 6 sec
Gain 10

fig 5.3.22
phenyl-isopropyl sulphide

6. DISCUSSION

6.1. Photolysis Experiments

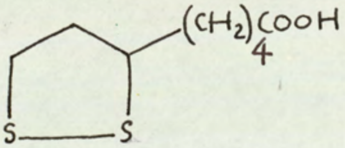
Ultraviolet irradiation has been utilized by other workers to produce free radical species from organic sulphur compounds. Windle, Wierserma and Tappel (101) irradiated (at liquid nitrogen temperatures) sulphur and selenium compounds, including dimethyl, diphenyl, di-n-butyl, and dibenzyl disulphides, and toluene-ω-thiol. From the esr spectra of the irradiated materials, they concluded that the action of uv on disulphide compounds always causes fission of the S-S bond, to form the species $RS^{\bullet}$.

The spectra had the appearance typical of sulphur free radicals - the sulphur pattern earlier described by Gordy for this type of free radical (32, 33, 110, 111, 112, 116) - with 3 asymmetric g values. These were given as:-

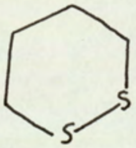
	g_1	g_2	g_3
dimethyl disulphide	1.997	2.025	2.057
diphenyl disulphide		- not measured -	
di-n-butyl disulphide	1.998	2.025	2.058
dibenzyl disulphide	1.995	2.024	2.053

A similar spectrum was obtained for the thiol, although the g values were not reported. It was thought that photolysis cleaved the S-H bond.

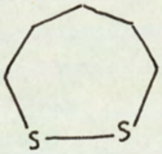
Smissman and Sorenson (102) studied the effect of ultra violet radiation on dimethyl disulphide and three cyclic disulphides, lipoic acid, o-dithiane and 1,2 -dithiepane:-



lipoic acid



o-dithiane



1,2-dithiepane

On the basis of the g values and appearance, the esr spectra were considered to be due entirely to sulphur free radicals, formed by homolytic cleavage of the S-S bond, yielding free radicals of general structure $^{\bullet}S-(CH_2)_n-S^{\bullet}$ - i.e. each free radical having two unpaired electrons, one localized on each sulphur atom. (The free radical from dimethyl disulphide was obviously $CH_3S^{\bullet}$). No evidence for hyperfine splitting or for the species being in a triplet state was observed.

The g values were reported to be:-

dimethyl disulphide	2.0137 at crossover
lipoic acid	2.0128 "
o-dithiane	2.0063 "
1,2-dithiepane	2.0063 "

Truby et al. have investigated the effect of high energy ionising radiation on alkyl disulphides and thiols (96, 98, 99, 100). The compounds were studied in two forms - rapidly frozen, amorphous material, and poly-crystalline material. It was shown that for symmetrical n-alkyl disulphides with more than three carbon atoms in the alkyl groups, the polycrystalline material gave rise to more free radicals by C-H breakage than by S-S fission. For compounds with 3 or less carbon atoms, this did not hold, only 10% of the total number of free radicals present in irradiated n-propyl disulphide were formed by C-H breakage. For the amorphous form, no hyperfine splitting was observed for disulphides with less than 3 carbon atoms in the alkyl groups. Compounds with large alkyl groups showed some additional resonance at lower g value, with hyperfine splitting, resulting from a free radical formed by C-H breakage, of the form $-CH_2-{}^{\bullet}CH-CH_2-$ For amorphous octadecyl disulphide, it was estimated that 30% of the total number of free radicals were of this alkyl type.

Truby et al. also suggested the formation of positive and negative ion species in the amorphous materials to account for some of their observations. These were thought to be strongly localized at the disulphide bond, but to be different to the R-S$^\bullet$ species also present, in smaller amount. The g values of these charged species in octadecyl disulphide were given as:

positive ion species $g_1 = 2.003$
$g_2 = 2.018$
$g_3 = 2.035$

negative ion species (axially symmetric) $g_{\parallel} = 2.003$
$g_{\perp} = 2.022$

The g value at crossover for the radical from dimethyl disulphide was reported as 2.016. Esr spectra were examined for the species formed from methyl, ethyl, propyl, amyl, octyl, and eicosyl disulphides. These were all similar to each other, and of the type associated with sulphur free radicals.

Most of the esr spectra recorded in the course of the photolysis work reported in this thesis are in agreement with the published results described above. The series of alkane thiols all gave spectra consistent with those expected for species having 3 asymmetric g values, as did the corresponding disulphides, except diethyl disulphide and di-isopropyl disulphide, which will be discussed later, and di-isobutyl disulphide, which apparently gave rise to an axially symmetric species, although the very high background signal observed in this sample may have obscured some of the main signal.

Thiophenol and diphenyl disulphide were found to give rise to identical esr spectra after irradiation, these also being typical "sulphur patterns". Diphenyl disulphide was irradiated in two forms, the normal polycrystalline form, and also in rapidly frozen form, (prepared by melting in the sample tube and then plunging into liquid nitrogen). Identical esr spectra were obtained from the two forms after irradiation.

A sulphur pattern was obtained from toluene-ω-thiol, and an identical spectrum was found for the disulphide, although this was small and not well resolved.

2-Pyridinethiol gave rise to a sulphur pattern. Dibenzothiazolyl disulphide and tetramethylthiuram disulphide both gave esr spectra, after irradiation, characteristic of axially symmetric species.

The dithiobisamines all gave esr spectra typical of 3 asymmetric g values.

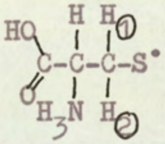
Of the monosulphides irradiated, diethyl monosulphide gave no detectable signal, neither did diphenyl monosulphide. Di-n-propyl monosulphide gave an extremely small signal, very little larger than the noise level.

On the basis of the work published by Windle, Wiersema and Tappel, Swissman and Sorenson, Truby et al., and Gordy et al. (outlined earlier), it seems that the most likely effect of the ultra violet radiation is to form free radicals of type $R\text{-}S^{\bullet}$, with the odd electron localized on sulphur. This species is produced by cleavage of the S-H bond in thiols and cleavage of the S-S bond in disulphide compounds. The g values measured for the series of alkane thiols are all similar, with g_1 falling in the range 2.000 to 2.002, g_2 in the range 2.023 to 2.028, and g_3 lying between 2.054 and 2.060. These values are of the order expected for free radicals with the odd electron localized on the sulphur atom, and considered jointly, are too high to allow the possibility of the free radical being based on carbon.

The g values measured for the disulphides differ slightly from those for the species derived from the corresponding thiols. This may be attributable to the difference in matrix, e.g. tendency to hydrogen bonding.

In almost all the spectra there is evidence for hyperfine splitting by one proton. The splitting is of the order of a few gauss - e.g. 9 gauss for ethanethiol, 7 gauss for isobutanethiol.

In studies on L-cystine dihydrochloride single crystal, γ-irradiated, Kurita and Gordy (32) found evidence for the coupling of the unpaired electron with one proton, with a splitting of 9 gauss. The structure of the free radical was thought to be:-



and the splitting was caused by one of the protons H① or H②. Calculations had shown that the orbital containing the unpaired spin density did not rotate about the C-S bond, in the crystal form, so one proton might be situated closer to the orbital of the unpaired electron than is the other proton, assuming non-rotation of the methylene group. The spin density on this second proton is therefore too small to give resolvable splitting. This is thought to apply in the present case.

The magnitude of the splitting gives a measure of the spin density on the proton. If the unpaired spin were entirely in a proton 1s orbital, a splitting of approximately 500 gauss would be expected (180). The unpaired spin is therefore $\frac{9}{500}$ or $\simeq 2\%$ in the 1s orbital of the proton.

The other thiols and disulphides examined are all thought to have yielded R-S$^\bullet$ type species under the conditions employed. The interpretation of the signal from 4,4'-dimethyldiphenyl disulphide as a single line is probably in error, the other part of the signal being hidden in the electronic noise on the recording. The splitting observed of the order of a few gauss but poorly resolved, in the spectra from the dithiobisamines, particularly marked in the case of N,N'-dithiobis(dibenzylamine) is probably due to interaction with the nitrogen nucleus.

Diethyl disulphide and di-isopropyl disulphide gave esr spectra, after irradiation, which were of different form to the spectra observed for the other compounds examined. They consisted of a peak at low field (high g value), and a signal at higher field with well resolved hyperfine splitting. The g values and splitting constants measured were:-

	g value of low field signal	g value of high field signal	splitting constant
diethyl disulphide	2.061	2.004	18.6 gauss
di-isopropyl disulphide	2.062	2.009	19.0 gauss

A similar spectrum was obtained by Truby et al. (96) from γ-irradiated octadecyl disulphide, and by investigating the decay at various temperatures, these workers were able to assign it to two paramagnetic species, a sulphur radical and an alkyl radical. The sulphur radical was thought to have been formed either by direct action of the ionising radiation on the S-S bond or by migration of the radiation damage along the carbon chain to the sulphur group. The alkyl radical was formed by C-H cleavage by the radiation.

In the work reported here, the peak at low field probably arises from the sulphur radical $R\text{-}S^{\bullet}$, being due to the g_3 component of the signal from this species. The other parts of the spectrum of this species would be obscured by the superimposed high field signal. No facilities were available for variable temperature work or low temperature work at other microwave frequencies, so this could not be tested.

The g values of the high field signals are lower than the g values normally found for aliphatic sulphur free-radicals, although they are higher than the g values normally found for pure carbon free radicals, which are usually close to the free spin value of 2.0023. This may be explained by some slight contribution from the sulphur atom, the unpaired spin density on sulphur being non-zero but small. The hyperfine splitting is of the order of that found for alkyl free radicals, approximately 20 gauss.

The intensity ratios are not, however, binomial. For diethyl disulphide the ratio was found to be 1 : 5.2 : 9.2 : 5.0 : 1.2; the binomial intensity distribution for five lines is 1 : 4 : 6 : 4 : 1.

For di-isopropyl disulphide the respective values are

1 : 18.3 : 22.6 : 40.0 : 20.2 : 6.5 : 0.9

and 1 : 6 : 11 : 20 : 11 : 6 : 1

Some of this divergence from the expected values may be explained by the additive effect of the signal from the sulphur radical species.

A small signal added (with due regard for sign) to the hyperfine pattern will obviously have a much more marked effect on the intensities of the small outside lines than on the larger centre ones.

In the spectrum from diethyl disulphide, the intensities of the centre lines of the high field pattern are not very far removed from the binomial 4 : 6 : 4, being 3.4 : 6 : 3.3

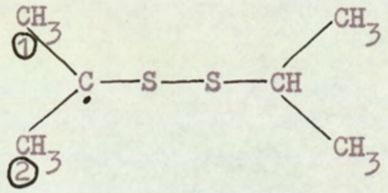
On examination of the spectrum from di-isopropyl disulphide, it can be seen that the three centre lines are almost exactly in the ratio 11 : 20 : 11 predicted from the binomial distribution.

It is thought that the species giving rise to the signals at high field in irradiated diethyl disulphide has the structure:

$$\underset{②}{\mathrm{CH_3}}\text{-}\underset{①}{\dot{\mathrm{C}}\mathrm{H}}\text{-}\mathrm{S}\text{-}\mathrm{S}\text{-}\mathrm{CH_2}\text{-}\mathrm{CH_3}$$

The five line spectrum then arises from equivalent interaction with the methylene proton and the three methyl protons, on carbon atoms 1 and 2.

Di-isopropyl disulphide would yield a free radical of structure



With the coupling to the six methyl protons on carbon atoms 1 and 2 causing the observed splitting into seven lines.

In alkyl radicals, it has been found that approximately equal splitting arises from coupling with α and β protons, for example in the ethyl radical the methylene proton hfs constant is 22.38 gauss, and that due to the methyl proton is 26.87 gauss (181). The same source records the α and β proton splittings in the isopropyl free radical as 22.11 and 24.68 gauss respectively.

These alkyl radical hfs constants are a little larger than the ones measured for the radicals formed from the disulphides. This may be accounted for by the presence of some unpaired spin density on the sulphur atoms, as already suggested to explain the g values, which would result in a slight decrease in the spin density on the protons, and hence a smaller interaction and splitting.

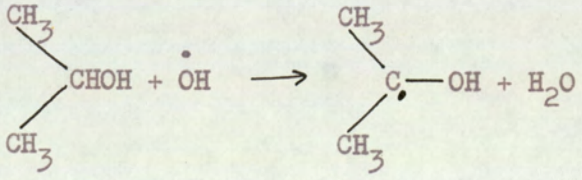
The radical structures suggested are thought to be formed by hydrogen abstraction by the sulphur free radical formed first. The reaction sequence for diethyl disulphide may be represented as:

$$CH_3-CH_2-S-S-CH_2-CH_3 \xrightarrow{h\nu} 2CH_3-CH_2-\dot{S}$$

$$CH_3-CH_2-S-S-CH_2-CH_3 + CH_3-CH_2-S^{\bullet} \longrightarrow CH_3-\dot{C}H-S-S-CH_2-CH_3 + CH_3-CH_2-SH$$

A similar reaction has been reported for the uv irradiation of a solution of hydrogen peroxide in isopropanol (182). The primary radical formed was hydroxyl, which then reacted, by hydrogen abstraction, with the solvent molecules:-

$$H_2O_2 \xrightarrow{h\nu} 2\,\dot{O}H$$



The esr spectrum observed consisted of 7 lines, with a binomial intensity distribution.

The suggested reaction sequence does not explain why the secondary free radicals are only observed in these two disulphides. An explanation may lie in the viscosity of the frozen liquids, it possibly being low enough to allow the necessary diffusion in these two materials, but not in the others studied. Some diffusion is, however, necessary in all cases if the free radicals are not to immediately recombine.

An alternative but less likely process is the direct cleavage of a C-H bond by the uv radiation. This again should apply equally to all the compounds studied. It should be noted that Truby et al. found that γ-irradiation did not yield radicals by C-H cleavage in disulphides with alkyl groups such as ethyl having less than three carbon atoms. The yield in n-propyl disulphide by this process was small. It is thought that uv would be even less likely to cause fission of a C-H bond than the higher energy γ-radiation, making the hydrogen abstraction route the more probable one.

6.2. Aliphatic Compounds

The literature contains several references to the detection by esr spectroscopy of free radicals in solutions of sulphur in oleum (105, 106, 107). Freshly prepared solutions were thought to contain diamagnetic S_8^{2+} and paramagnetic S_4^{+}, the latter giving the solution its deep blue colour. The g value was measured as 2.0131 at room temperature, although when the solution was cooled to 90K, the g value was seen to be axially symmetric, with $g_{\parallel} = 2.0004$ and $g_{\perp} = 2.0192$.

Over a period of time, the esr signal decayed, the formation of the diamagnetic ion S_4^{2+} being thought to occur.

Solutions of less than 40% oleum, concentrations were characterised by another esr signal, this having a g value of 2.0260 at room temperature, and being resolved, at 90K, into three components, $g_1 = 2.0024$, $g_2 = 2.0311$, and $g_3 = 2.0421$. The radical in these solutions was thought to be an open S_n^{+} chain.

No hyperfine splitting was reported by any of the authors.

It is now reported that free radicals are formed when sulphur, aliphatic thiols, monosulphides, and disulphides, and N,N'-dithiobisamines are dissolved in concentrated sulphuric acid, oleum, or chlorosulphonic acid. The spectra all show hyperfine splitting.

The observations made on the solutions in sulphuric acid of the aliphatic thiols and disulphides are summarised in table 6.2.1.

The g values lie in the range 2.012 to 2.014, and are thus much greater than the g values found for free radicals with the odd electron localized on carbon, when the g value is always very close to the free-spin value of 2.0023.

The hyperfine splitting constants lie between 1.36 and 2.49 gauss, and are very small compared to those found for alkyl free radicals in solution, which are of the order of 20 gauss.

The free radicals formed must, therefore, have sulphur present in the structure, the localization of the unpaired electron on this atom giving rise to the high g value by spin-orbit interaction. This localization also reduces the unpaired spin density on the protons, thus reducing the hyperfine splitting by these nuclei.(For a fuller discussion of this, see sections 2 and 6.1)

As the spectra are not all identical, they cannot be due to sulphur itself, liberated by cleavage of the C-S bonds, or to a common species derived from it.

On consideration of the g values, hyperfine splitting constants, and behaviour in deuterosulphuric acid, the compounds are seen to fall

Table 6.2.1.

Thiols

Alkyl Group	g value		Number of Hyperfine Components		Hyperfine Splitting Constant (H_2SO_4) gauss	Intensity Distribution (H_2SO_4)
	H_2SO_4	D_2SO_4	H_2SO_4	D_2SO_4		
Methyl	Signals in chlorosulphonic acid only					
Ethyl	2.0133	2.0133	3	5	2.20	1.0 : 2.5 : 1.0
n-Propyl	2.0132	2.0132	6	6	1.47	1.0 : 4.3 : 4.3 : 4.0 : 3.3 : 1.0
Isopropyl	2.0132	2.0132	6	6	1.51	1.0 : 3.8 : 4.7 : 4.7 : 4.7 : 1.6
n-Butyl	2.0125	2.0131	7	5	1.80	1.0 : 9.5 : 26.0 : 38.5 : 29.2 : 12.2 : 1.0
Isobutyl	2.0125	2.0127	7	*	1.75	1.0 : 7.2 : 20.4 : 30.0 : 27.2 : 9.6 : 1.6
t-Butyl	2.0132	2.0131	2	>3	2.15	
Cyclohexyl	2.0126	2.0125	7	7	2.49	
2-Propenyl	2.0130	2.0132	6	6	1.45	1.0 : 3.7 : 4.4 : 4.2 : 4.0 : 1.3
Perchloromethyl	2.0135	2.0134	3	*	2.24	1.0 : 2.1 : 1.0
2-Hydroxyethyl	2.0135		3		2.26	1.1 : 2.2 : 1.0
2-Methyl-2-(n-octyloxy)propyl	2.0126		7		1.81	1 : 10 : 30 : 44 : 34 : 12 : 2

* unresolved

Table 6.2.1. (Continued)

Disulphides

Alkyl Group	g value		Number of Hyperfine Components		Hyperfine Splitting Constant (H_2SO_4) gauss	Intensity Distribution (H_2SO_4)
	H_2SO_4	D_2SO_4	H_2SO_4	D_2SO_4		
Methyl			3		2.26	
Ethyl	2.0139	2.0139	3	5	2.37	1.0 : 2.2 : 0.95
n-Propyl	2.009		6	6	1.67	1.0 : 4.1 : 5.0 : 5.2 : 3.9 : 1.4
Isopropyl	2.0130	2.0133	6	6	1.36	1.0 : 3.9 : 4.2 : 4.0 : 3.5 : 1.2
n-Butyl	2.0124		7		1.58	
Isobutyl	2.0117		7		1.81	1.0 : 7.4 : 22.0 : 33.2 : 22.8 : 9.0 : 1.4
t-Butyl			singlet at high g doublet at low g		1.87	
Cyclohexyl	2.0126		7			
2-Propenyl	2.0130		6		1.45	1.0 : 3.6 : 4.8 : 4.1 : 3.3 : 1.1

Sulphur itself dissolved in sulphuric acid with the development of a yellow colour. The solution had an esr absorption, g value 2.022, with no hyperfine splitting. On warming the solution, this signal decayed, being replaced by a triplet, of splitting constant 2.23 gauss, and g value 2.0133.

into three distinct classes:-

(a) "Simple Compounds

This group comprises:-

sulphur

methanethiol

ethanethiol

t-butanethiol

perchloromethanethiol

2-mercaptoethanol

and the corresponding disulphides.

The free radicals formed from these compounds all had g values in the range 2.0132 to 2.0135, and hyperfine splitting constants between 2.15 and 2.37. The signals are all triplets of approximately 1 : 2 : 1 intensity ratio, except that from t-butanethiol, which is a doublet.

Ethanethiol, diethyl disulphide, and t-butanethiol were also dissolved in deuterosulphuric acid. The spectra observed from these solutions were found to be different from those from the sulphuric acid solution, in that they showed more fine structure.

(b) "Propyl-Type" Compounds

This group contains n-propanethiol, isopropanethiol and 2-propenethiol, and the corresponding disulphides. Very similar spectra were obtained from these compounds, characterised by a six-line signal at g = 2.0130-2.0132, with splitting constant approximately 1.5 gauss.

The intensity distribution was found to be approximately 1 : 4 : 4 : 4 : 4 : 1, but tended slightly towards the binomial distribution at reduced microwave power. The spectra were found to possess the same number of hyperfine components when deuterosulphuric acid was used.

(c) "Butyl-type" Compounds

The members of this group are:-

n-butanethiol

isobutanethiol

2-methyl-2-(n-octyloxy)propanethiol

cyclohexanethiol

and the corresponding disulphides, (where examined).

The g values measured for this group were 2.0125-2.0126. The spectra all had seven hyperfine components, which appeared to have a binomial distribution of intensities. The splitting constant for the first three members was found to be approximately 1.8 gauss. That for cyclohexanethiol (and disulphide) was 2.49 gauss. This may indicate that the cyclohexyl compounds should be included in the "simple" compounds group.

The hyperfine pattern observed from solution in deuterosulphuric acid was different to that from sulphuric acid solutions, but this may be due to poor resolution, reducing the number of hyperfine components seen in the deuterated acid.

The following main points must therefore be explained:-

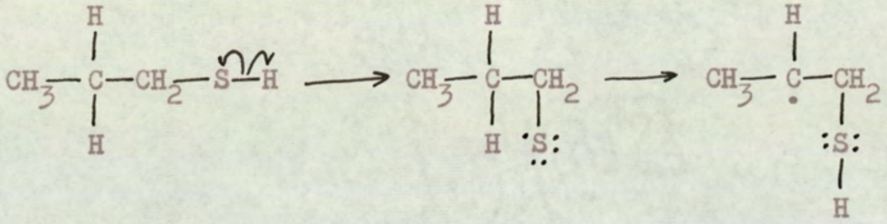
1) Exchange of protons for deuterium changes the esr spectra of some species but not others.
2) The free radicals formed from _n_-propanethiol, isopropanethiol and 2-propenethiol have the same esr spectrum.
3) The free radicals formed from n-butanethiol, isobutanethiol and the alkoxy substituted thiol have the same esr spectrum, although this is different to that of the propyl group compounds.

The simplest mechanism for the formation of a free radical from a thiol or disulphide is the homolysis of the S-H or S-S bond:-

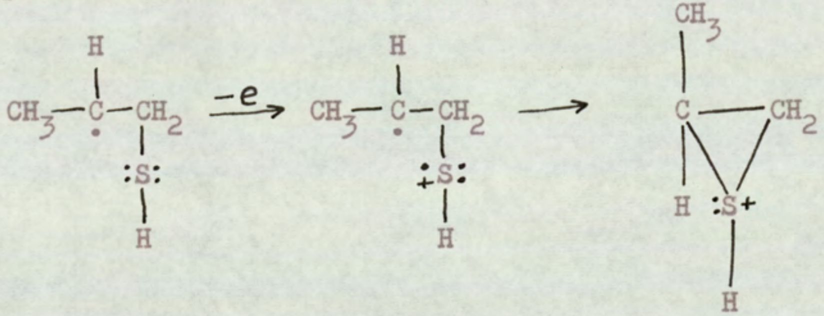
$$R\text{-}S\text{-}H \longrightarrow RS^{\bullet} + H^{\bullet}$$
$$R\text{-}S\text{-}S\text{-}R \longrightarrow 2RS^{\bullet}$$

Hyperfine splitting might be expected from the protons on the α and possibly the β carbon atoms of the alkyl group. The hyperfine patterns from _n_-propanethiol and _n_-butanethiol would be expected to be the same even if the β carbon protons were involved. If only the α carbon protons caused splitting, then the same spectrum would be expected from ethanethiol and the alkoxy compound also.

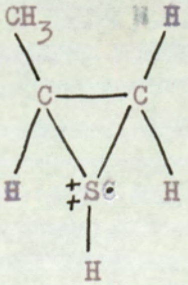
It is thought that the RS$^\bullet$ radical is formed, but reacts further by intramolecular hydrogen abstraction, transferring the radical centre of the β carbon. The mechanism is represented, using n-propanethiol, by:-



One-electron oxidation then removes an electron from one of the sulphur lone pairs, forming a di-radical which cyclises:-

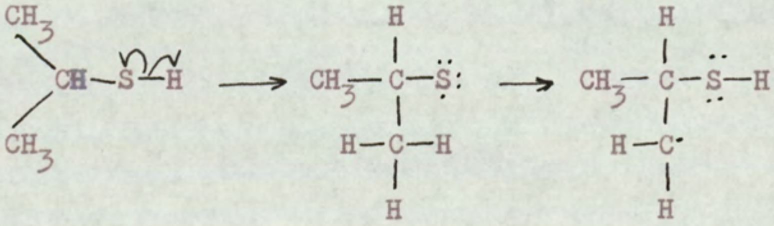


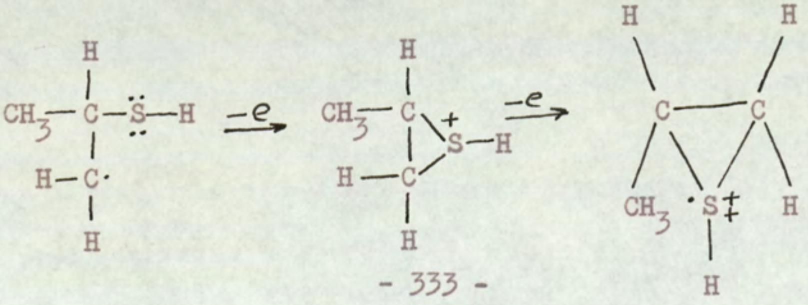
A further one-electron oxidation converts this to a free radical dication, of the form:



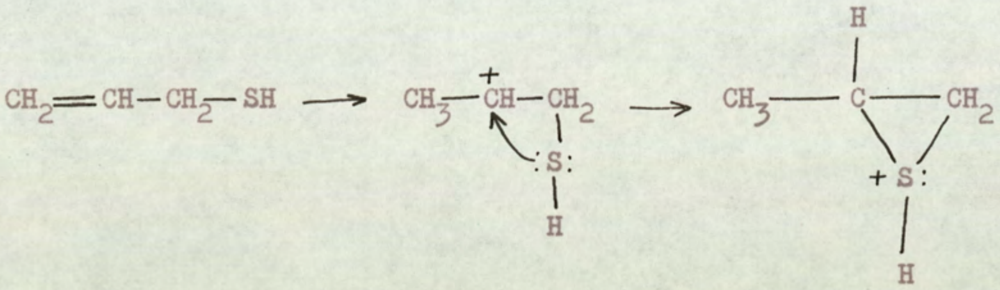
The hyperfine splitting pattern observed was of six lines. The same pattern was observed from deuterosulphuric acid solutions, indicating that the interacting protons are not exchangeable. The splitting is thought to arise by interaction of the methyl group protons with the unpaired electron, made possible by overlap of the methyl group orbitals with the sulphur orbital occupied by the unpaired electron. Spin density on the methyl group would also be shared by the proton on the same ring carbon. If the interaction of the methyl protons are equivalent, and cause splitting equal to half that due to the ring proton, a six-line pattern with the intensity distribution 1 : 3 : 4 : 4 : 3 : 1 would result. This is close to that found.

The same free radical would be formed from isopropanethiol by this mechanism, but with hydrogen abstraction from a methyl group:-



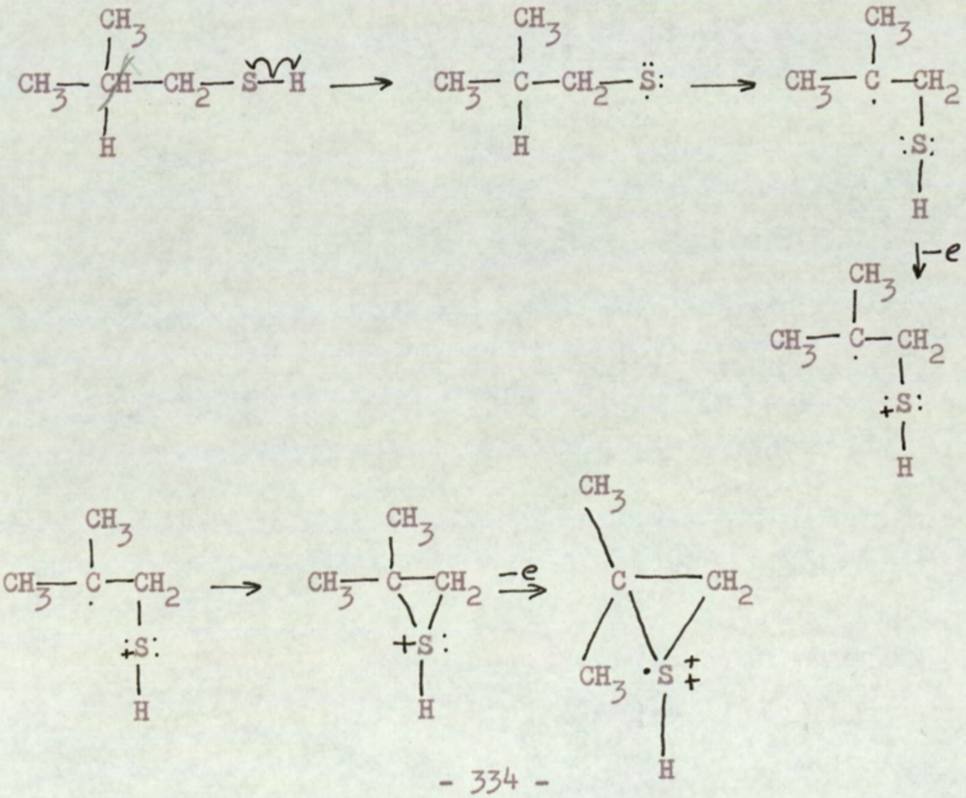


The other member of the propyl group, 2-propenethiol, is thought to form the same species by a different mechanism. The molecule is first protonated, and nucleophilic attack by sulphur follows:



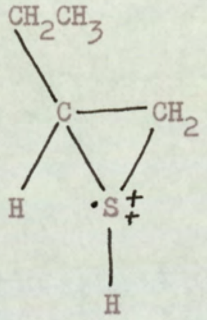
The cyclic species thus formed then undergoes one-electron oxidation, forming the radical dication.

Isobutanethiol should react by the mechanism suggested for the propanethiols to form a similar species:-



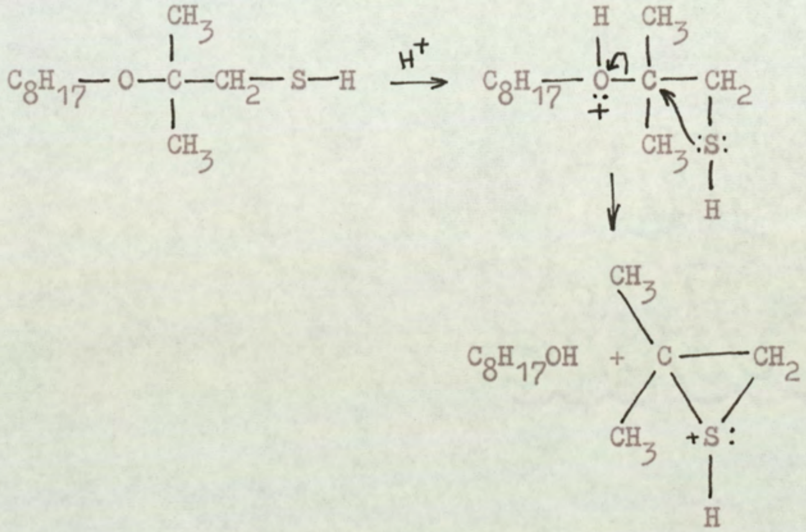
Equivalent splitting would be expected from the 6 methyl protons, giving seven hyperfine components with a binomial intensity distribution. This is in full agreement with observations.

n-Butanethiol would be expected to yield the radical of structure



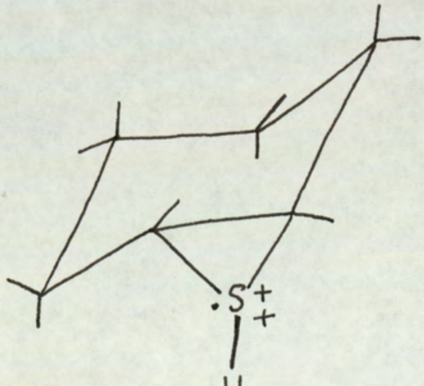
Now, it was found that sulphuric acid solutions of n-butanethiol gave a signal which had seven components, but which was slightly different to the signal from isobutanethiol. On warming, however, the signal changed to one identical with the isobutanethiol signal. It is thought that the ethyl substituted radical cation forms initially, and on warming, undergoes an unusual type of rearrangement to form the dimethyl substituted radical as formed from isobutanethiol. It is considered more probable that the rearrangement occurs post-cyclisation than pre-cyclisation, as no other spectra of pre-cyclised radicals were found.

2-Methyl-2-(n-octyloxy)propanethiol was found to give an esr signal the same, within experimental error, as obtained from n- and isobutanethiols. The reaction sequence leading to the formation of the radical is thought to be represented by:



when one-electron oxidation would form the dimethyl substituted radical dication.

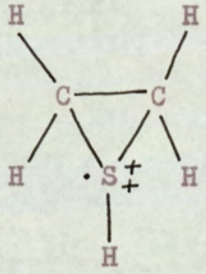
Cyclohexanethiol gave a spectrum which was very similar to the others of the butyl group, except that the splitting constant was considerably larger. A radical of the type:



may be postulated, but it is difficult to account for the splitting pattern observed.

t-Butanethiol would be expected to form the same free radical as isobutanethiol, the reaction proceeding via hydrogen abstraction from one of the methyl groups. That this is not the case is shown by the completely different spectrum obtained from this compound, consisting of a doublet, with another doublet of greater splitting superimposed.

Ethanethiol should react by the mechanism suggested, to form the radical



2-Mercaptoethanol was found to give the same spectrum. This compound may react by the route proposed for the alkoxy-propanethiol to form the same species as is formed from ethanethiol. The same spectrum is also observed from sulphur itself, perchloromethanethiol, and dimethyl disulphide.

The spectrum was found to be a 1 : 2 : 1 triplet, indicating that splitting was caused by two equivalent protons. The spectrum of ethanethiol in deuterosulphuric acid was more complicated, and is best explained as the triplet, as found from sulphuric acid solutions, with a doublet, of splitting 2.1 gauss, superimposed.

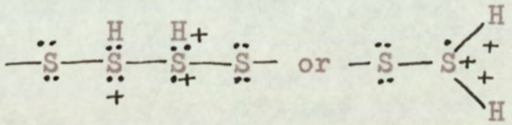
One of the two protons must therefore be exchangeable, and is probably the one bonded to the sulphur atom. (The hyperfine splitting of deuterium is usually found to be about 1/6 that of hydrogen, and would not be resolved here). The other proton must be one of the ring protons, although it is not clear why one of the four ring protons should interact in a different way to the others.

Splitting by the sulphur hydrogen was not observed for the propyl and butyl group compounds. It is likely, however, that the interaction of the unpaired electron with the methyl group orbitals in these compounds would alter the spin density on the sulphur proton sufficiently to make the splitting by this nucleus too small to be resolved.

The absence of esr absorption in solutions of methanethiol in sulphuric acid is thought to be due to low solubility of this gaseous thiol in the acid. Dimethyl disulphide was found to react to give a triplet absorption.

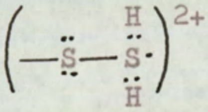
Sulphur, dimethyl disulphide, and perchloromethanethiol cannot form the cyclic radical.

The paramagnetic species present in solutions of sulphur in oleum were thought to be S_4^+ or open S_n^+ chains. It is possible that this type of radical may be protonated, yielding species of the type



when equal interaction from the two protons would give rise to the 1 : 2 : 1 hyperfine pattern.

Sulphur near its melting point (118°C) consists of puckered eight membered rings. As the temperature is raised, these rings open, and the resulting biradicals join together to form long chains, which cause the viscosity of the melt to increase. The viscosity increase is less if impurities such as sulphuric acid are present, presumably because the end groups of the biradicals are modified (183). This suggests that the radical may be of the form

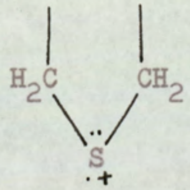


Perchloromethanethiol was observed to form a precipitate in sulphuric acid, the esr signal developing as this dissolved. It is probable that the precipitate was sulphur, formed by the cleavage of the C-S bond.

The results obtained for the other compounds used are summarised in table 6.2.2.

Diethyl, di-n-propyl and di-isopropyl monosulphides gave the same esr spectra as the corresponding thiols and disulphides. Ethyl-isopropyl monosulphide gave a spectrum the same as that from ethanethiol. It is thought that the homolysis of a C-S bond occurred in these compounds forming an alkyl radical, which would not be stable and would react, probably by dimerisation, and an RS$^{\bullet}$ species which would react to form the cyclic radical as before.

The two cyclic sulphides would be expected to form species very similar to that suggested for ethanethiol. One electron oxidation would yield the radical cation



which might be protonated to form the radical dication

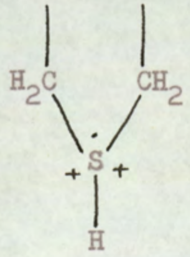


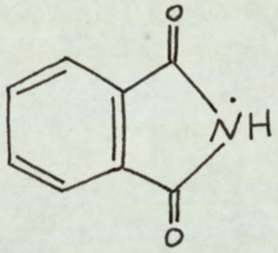
TABLE 6.2.2.

Compound		g value	Number of Hyperfine Components	Hyperfine Splitting Constant gauss	Intensity Distribution
Dimethyl monosulphide		2.0131	3	2.24	1.0 : 2.0 : 1.0
Ethyl-isopropyl monosulphide		2.0133	3	2.46	1.0 : 2.9 : 1.3
Di-n-propyl monosulphide		2.0130	6	1.48	1.0 : 5.0 : 6.5 : 5.0 : 4.5 : 1.0
Di-isopropyl monosulphide		2.0130	6	1.44	1.0 : 4.1 : 5.6 : 5.6 : 3.9 : 1.4
Tetramethylene sulphide		This compound had two absorptions:-			
	1)	2.0029	1	-	
	2)	2.0070	3	1.81	
p-Dithiane		2.0133	3	2.43	1.0 : 2.7 : 1.1
N,N'-dithiobis-(dibenyzlamine)		2.0129	1	-	
N,N'-dithiobis-(piperidine)		2.0129	5	1.7	1.0 : 11.0 : 16.0 : 7.8 : 1.4
N,N'-dithiobis-(morpholine)		2.0126	3	2.24	1.0 : 2.4 : 1.0
N,N'-dithiobis-(phthalimide)		This compound had two absorptions:-			
	1)	2.0134	1	-	
	2)	2.0088	3	1.9	

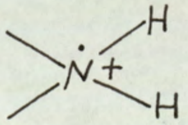
p-Dithiane has an esr absorption similar to that of ethanethiol. Tetramethylene sulphide, however, appears to form two separate radical species, with g values of 2.0029 and 2.0070. Although the signal of g value 2.0070 is a triplet with a 1 : 2 : 1 ratio of intensities, the g values are both lower than are normally associated with sulphur radicals.

The dithiobisamines dissolve in sulphuric acid to form free radicals with g values in the range accepted for sulphur radicals.

N,N'-dithiobis(phthalimide) also forms another free radical, of g value 2.0088. This is probably not a sulphur radical, but may be of the form

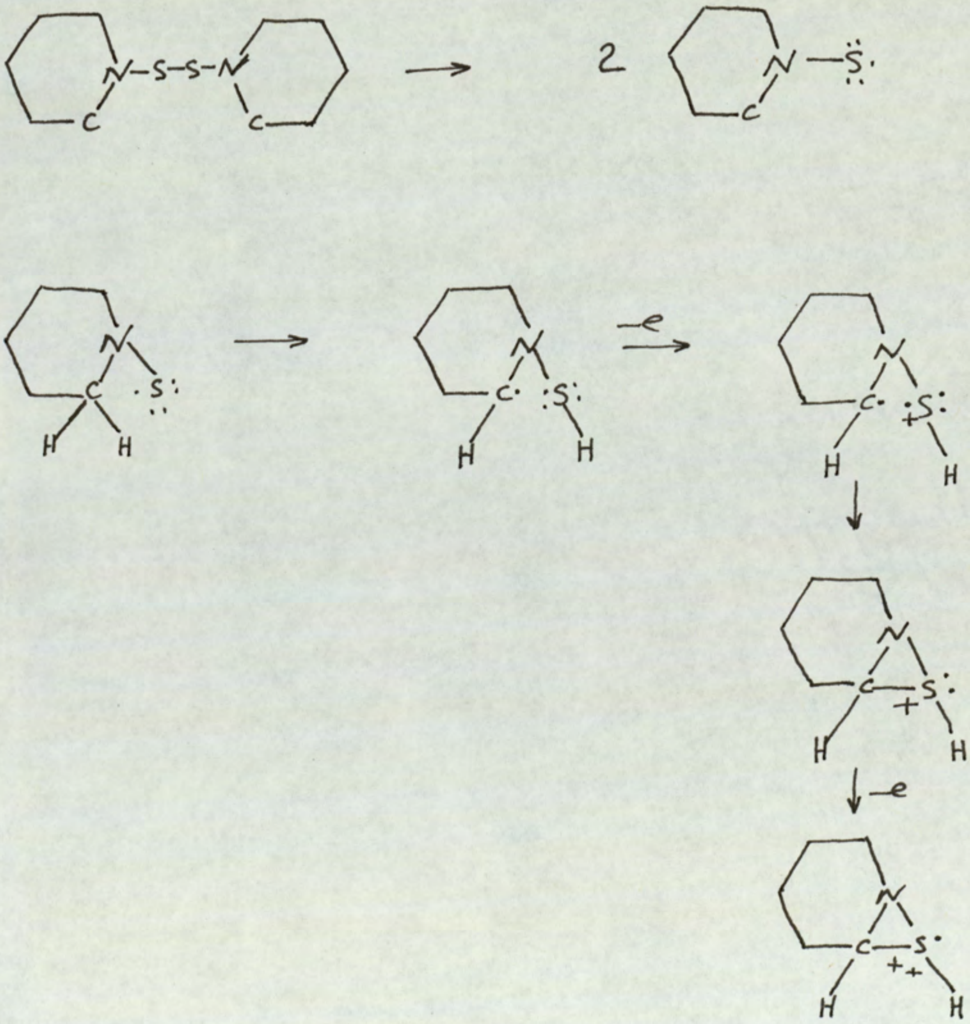


although it is difficult to explain the observed triplet splitting, which is not due to nitrogen. The radical may be protonated, and be of the form



Of the high g value signals found for these compounds, those from N,N'-dithiobis(dibenzylamine) and N,N'-dithiobis(phthalimide) do not show any hyperfine splitting making structural assignment difficult.

N,N'-dithiobis(piperidine) gave a signal with five hyperfine components. The measured intensity ratios were 1 : 11 : 16 : 7.8 : 1.4, which can be compared to the 1 : 3 : 4 : 3 : 1 distribution predicted for equivalent splitting by one nitrogen nucleus and two protons. This could be the situation in the radical formed by a reaction such as suggested for the alkanethiols and disulphides:-



The two protons indicated would be the two causing splitting. N,N'-dithiobis(morpholine), however, gives a spectrum with three hyperfine components. These are in the ratio 1 : 2.4 : 1, and are not therefore due to interaction with a nitrogen nucleus, but probably with two equivalent protons.

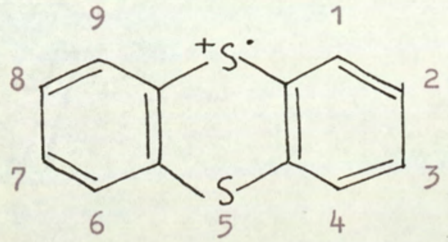
6.3. Aromatic Compounds

In 1953, it was reported (46) that the coloured solutions of certain compounds, among them thiophenol, p-thiocresol, thio-β-naphthol, diphenyl disulphide, and thianthrene, in concentrated sulphuric acid were paramagnetic. The similarities observed between the colours of these solutions and also between the esr spectra were thought to indicate that similar species were present in the solutions. It was noted that it had previously been reported that thiophenol was oxidized by sulphuric acid to diphenyl disulphide (48) and thianthrene (47).

It was later shown (42) that the esr spectra from the acidic solutions of thiophenol, diphenyl disulphide, p-thiocresol, and α and β thionaphthols, were due to two separate species. Hyperfine splitting was observed in both parts of the spectra. The line found at lower g value was thought to be due to the same species as present in solutions of thianthrene in sulphuric acid.

The g value of the thianthrene absorption was given as 2.0078, the absorption having 5 hyperfine components. The g values measured for the species formed from p-thiocresol were given as 2.0151 and 2.0081. It was suggested that the species giving rise to the absorption at high g value was a radical of the type $(C_6H_5S^\bullet)H^+$, a type of species already postulated by Mulliken (184).

The paramagnetic species formed from thianthrene has been the subject of extensive investigation (49, 52, 53, 54, 57 and 50), and is thought to be the simple cation radical,



The major splitting arises from equal interaction of the odd electron with the protons on carbon atoms 2, 3, 7, and 8. (Splitting from all the protons has been resolved (50) in the esr spectrum of the species formed by reaction of thianthrene with aluminium chloride in nitromethane. This is thought to be at least very similar to the radical formed by solution in sulphuric acid).

The esr spectra of the free radicals formed from several substituted thianthrenes have been reported. Rundel and Scheffler's (53) results are given in table 6.3.1.

Table 6.3.1.

substituent	no. of hyperfine components	hyperfine splitting
2,7-dimethyl	9	1.55 gauss
2,7-dimethoxy	3	2.1
2,7-di-t-butyl	3	1.52
1,6-di-t-butyl	5	1.25
1,3,6,8-tetra-t-butyl	3	1.53
2,3,7,8-tetrabromo	-	-

The results reported by Shine et al. (54, 57) are summarised in table 6.3.2.

Table 6.3.2.

substituent	no. of hyperfine components	hyperfine splitting	g value
unsubstituted	5	1.32 gauss	2.0081
monoxide	5	1.32	2.0081
1-amino	5	1.31	2.0081
2-amino	5	1.27	2.0080
1-bromo	5	1.40	2.0081
2-bromo	4	**	2.0091
1-chloro	5	1.35	2.0081
2-chloro	3	**	2.0079
1-hydroxy	5	1.27	2.0081
2-hydroxy	3	1.91	2.0077

Table 6.3.2.
(continued)

substituent	no. of hyperfine components	hyperfine splitting	g value
1-carboxylic acid	*	**	2.0082
2-carboxylic acid	3	**	2.0082
2,7-dimethyl	9	1.65	2.0088
2,7-dihydroxy	3	1.90	2.0076
2,7-dichloro	3	1.49	2.0083
2,7-dibromo	1	**	2.0101
2,7-di-t-butyl	3	1.60	2.0078

* - Poorly resolved

** - Not measurable

Alkyl group substituents in the 2,3,7,8 positions alter the hyperfine splitting pattern. The protons of methyl group substituents interact to give splitting equivalent to that from the ring protons, thus, 2,7-dimethylthianthrene has a splitting pattern of 9 lines with a binomial intensity distribution, resulting from equal interaction with 8 protons - 2 ring protons and 6 methyl protons. t-Butyl groups do not give resolvable splitting, and like the halogen substituents reduce the number of lines in the hyperfine pattern.

Substituents in the 1 position do not interact with the odd electron strongly enough to produce resolvable splittings under these conditions. It is interesting to note that with an amino substituent in the 2 position, five hyperfine components are still observed.

The work reported in this thesis on solutions of thiophenols and disulphides in sulphuric acid was carried out in order to attempt to identify the species giving rise to the esr absorption observed at high g value. The observations made are given in table 6.3.3.

Table 6.3.3.

Compound	High g value signal			Low g value signal		
	no. of hyperfine components	hyperfine splitting (gauss)	g value	no. of hyperfine components	hyperfine splitting (gauss)	g value
thiophenol	3	0.84	2.0139	5	1.07	2.0076
thiophenol in D_2SO_4	2			3		
diphenyl disulphide	No signal in H_2SO_4, but triplet in $H_2SO_4/ClSO_3H$ mixture			5	1.07	2.0076
2-methyl-thiophenol	5	1.27	2.0128	1		2.0073
3-methyl-thiophenol	5	1.30	2.0136	7 9 under improved resolution in $H_2SO_4/ClSO_3H$	1.38	2.0078
4-methyl-thiophenol	5	1.38	2.0131	9	1.48	2.0072
4,4'-dimethyl-diphenyl disulphide	signal identical to that from 4-methylthiophenol					

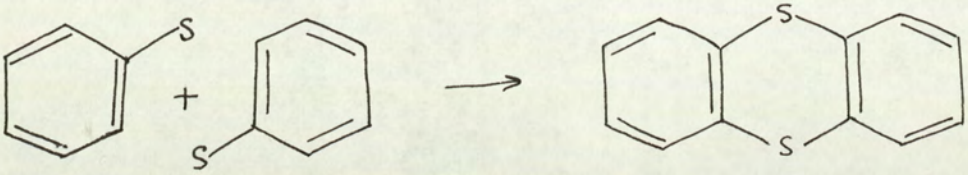
Table 6.3.3.
(continued)

	High g value signal			Low g value signal		
Compound	no. of hyperfine components	hyperfine splitting (gauss)	g value	no. of hyperfine components	hyperfine splitting (gauss)	g value
3,5-dimethyl-thiophenol	5			7		
4-t-butyl-thiophenol	2	1.06	2.0129	3	1.48	2.0070
2-amino-thiophenol	not observed			5	5.08	2.0067
4-amino-thiophenol	5		2.0144	1		2.0078
2-mercapto-benzoic acid	1		2.0130	1		2.0079
toluene-3,4-dithiol	5	1.27	2.0140			2.0083
2-chloro-thiophenol	5	1.3	2.0126	3 or 5 poor resolution		2.0065
4-chloro-thiophenol	3 or 5 poor resolution		2.0130	3	1.00	2.0075
2-bromo-thiophenol	3 or 5 poor resolution		2.0132	5	0.8	2.0091

Table 6.3.3.
(continued)

Compound	High g value signal			Low g value signal		
	no. of hyperfine components	hyperfine splitting (gauss)	g value	no. of hyperfine components	hyperfine splitting (gauss)	g value
4-bromo-thiophenol	1		2.0135	1		2.0088
2,4,6-tribromo-thiophenol	1		2.0139	1		2.0063
2,2',4,4',6,6'-hexabromo-diphenyl disulphide	1		2.0131	1		2.0059
Pentafluoro-thiophenol	1		2.0126	2		2.0049
diphenyl sulphide	No signal observed in H_2SO_4. In $H_2SO_4/ClSO_3H$, a quintet of 1.3 gauss splitting was observed.			5	1.12	2.0069
phenylmethyl sulphide	1	g value close to that for thiophenol		5	1.17	2.0070
phenylisopropyl sulphide	3	0.90	2.0137	5	1.07	2.0082

If the absorptions at low g value are considered first, these are mostly seen to be consistent with those expected from the corresponding substituted thianthrenes. The formation of thianthrene from thiophenol may be represented* by:-



Substituted thiophenols thus lead to di-substituted thianthrenes, the products possible from several substituted thiophenols are shown in Table 6.3.4.

Table 6.3.4.

substitution position in thiophenol	substitution positions in thianthrene	no. of hyperfine components if methyl substituent	no. of hyperfine components if non-interacting substituent
2	4,9 (equivalent to 1,6)	5	5
3	1,6	5	5
	3,6 (equivalent to 1,8)	7	4
	1,8	7	4
	3,8 (equivalent to 2,7)	9	3
4	2,7	9	3
3,5-di	1,3,6,8	9	3

Not covered by the above are (a) toluene-3, 4-dithiol, which would be expected to yield

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* This is only intended to show the relationship between substitution positions in the thiophenol and thianthrene molecules. It does not represent the reaction mechanism.

1,6-dimethyl-4,9-dimercaptothianthrene, 5 hyperfine components

1,7-dimethyl-4,9-dimercaptothianthrene, 7 hyperfine components

2,7-dimethyl-4,9-dimercaptothianthrene, 9 hyperfine components

b) 2,4,6-tribromothiophenol and

c) Pentafluorothiophenol. At least one halogen atom per molecule must be removed by reaction with the sulphuric acid if these last two compounds are to form the thianthrenes.

The spectra of these lower g value species will now be discussed.

Thiophenol itself was found to yield the 5-line thianthrene spectrum.

Alkyl substituted thiophenols.

2-Methylthiophenol is interesting as no hyperfine structure could be resolved in this part of the spectrum. The thianthrene expected to be formed is 1,6-dimethylthianthrene, with both methyl substituents in non-interacting positions with respect to the unpaired electron. The esr spectrum should therefore have five hyperfine components.

3-Methylthiophenol could possibly form three substituted thianthrenes, with substituents on the 1,6-, 1,8-, or 2,7- positions, giving 5, 7 or 9 hyperfine components respectively. 7 lines were found from the sulphuric acid solution, but the signal was not very large, and it is highly probable that if 2 more wing lines were present, they would have been lost in the general noise level. When this compound was dissolved in a mixture of sulphuric and chlorosulphonic acids, a similar spectrum was obtained, except that there were two slight changes of curvature, one on each of the outside lines of the 7 line absorption. These may be due to wing lines, in which case the spectrum is a 9 line one, as expected from the symmetrical 2,7-dimethylthianthrene. It should be noted, however, that these apparent shoulders are very small.

4-Methylthiophenol gave a spectrum having 9 lines, due to 2,7-dimethylthianthrene. As the g value and hyperfine splitting constant of this differed from the values found for 3-methylthiophenol it is thought that the 3-substituted compound yields 1,8-dimethylthianthrene, possibly with traces of the 2,7-disubstituted material giving rise to the shoulders.

The spectrum of 3,5-dimethylthiophenol is complicated by the apparent overlap of the signals due to the two species. The lower g value species has a spectrum with 3 lines clearly visible, and one other of identical shape at the high field side. It is assumed that the corresponding low field partner of this is obscured by the high g value signal. There is also a very small line at higher field, at the correct position considering splitting constant for a component of this signal, its partner at low field would again be hidden. This would therefore appear to be a 7 line signal. From the intensity ratios, it is obvious that the signal has an odd number of components. The intensity ratios of the central line and the ones to high field may be compared to those predicted from the binomial theory for 5,7 and 9 hyperfine components. (For five components, the small line at high field must be neglected.)

Table 6.3.5.

No. of components		Intensity ratios*
5	measured	6.0 : 4.7 : 2.1
	binomial	6.0 : 4.0 : 1.0
7	measured	20.0 : 15.8 : 7.0 : 1.2
	binomial	20.0 : 15.0 : 6.0 : 1.0
9	measured	70.0 : 54.8 : 24.1 : 5.0 : -
	binomial	70.0 : 56.0 : 28.0 : 8.0 : 1.0

It can be seen that approximately the same measure of agreement is found for 7 lines and 9 lines.

3,5-Dimethylthiophenol would be expected to form 1,3,6,8-tetramethylthianthrene, assuming that no rearrangement occurs. This has two methyl groups in interacting positions, and the other two in non-interacting

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* The measured ratios have been adjusted to make the largest value numerically the same as that from the binomial distribution.

positions, and would therefore be expected to have a 9 line spectrum, resulting from splitting by 8 equivalent protons. It is thought most likely that the spectrum is a 9 line one, with the extreme line not seen.

4-t-Butylthiophenol yields the triplet expected for 2,7-di-t-butylthianthrene. The protons of thet-butyl groups do not interact strongly enough with the odd electron to contribute to the splitting. It is, however, worth noting that the resolution in this spectrum is not as great as in those from, e.g. thiophenol, or 4-methylthiophenol, suggesting some broadening caused by a small and unresolved interaction with the alkyl protons.

Amine substituted thiophenols

2-Aminothiophenol, which should form 1,6-diaminothianthrene, gives a 5 line spectrum, as predicted. The splitting constant measured, however, is of the order of 5 gauss, which is much larger than those measured for any other of these compounds. Shine found a splitting constant of 1.31 gauss for 1-aminothianthrene (p.347)

4-Aminothiophenol gave a spectrum showing some very slightly resolved splitting. The formation of 2,7-diaminothianthrene would by expected. It is interesting to note that Shine observed a quintet when 2-aminothianthrene was examined, possibly indicating that some rearrangement or elimination had occurred to remove the amino-group from the interacting 2-position.

2-Mercaptobenzoic acid gave an esr spectrum with no hfs in the high field signal, although the COOH groups should be in the 1 and 6 positions in the thianthrene and therefore not interact with the odd electron. Shine found a poorly resolved single line for thianthrene-1-carboxylic acid (p.348)

Toluene-3,4-dithiol. As already stated, this compound can be considered as possibly forming three thianthrenes, with methyl groups in the 1,6 positions, the 1,7 positions, or the 2,7 positions, leading to 5, 7, or 9 hyperfine components respectively (assuming equivalent protons). The spectrum observed is, however, not a simple one. It has two separate splittings, and appears to overlap the low field signal.

It may be explained as a quintet, with splitting 4 gauss, with each line split into a triplet, but not fully resolved. This indicates that the product formed is the 1,6-dimethyl-4,9-dimercapto-thianthrene, which gives a quintet by interaction involving the 2,3,7,8- protons, which is then further split. If this is so, however, it is difficult to acoant for the magnitude of the major hyperfine splitting.

Halogenated thiophenols

2-Chlorothiophenol gave a spectrum with poor resolution. Some splitting was evident, and the absorption was thought to have 9 components, consistent with that expected for 1,6-dichlorothianthrene.

2-bromothiophenol gave a similar spectrum to the chlorine analogue, although the resolution was a little better.

4-chlorothiophenol. The spectrum of this compound showed the three hyperfine components expected for 2,7-dichlorothiophenol.

4-bromothiophenol. No hfs was observed in the spectrum of this compound, in agreement with Shine's findings (p.348) for 2,7-dibromothianthrene.

2,4,6-tribromothianthrene also gave a single line. It is assumed that whatever causes the lack of resolvable hfs in the dibromothianthrene is also present in the 2,4,7,9-terabromo-compound thought to be formed here.

Pentafluorathiophenol. The absorption appears to have some structure, although not resolved. Until further evidence becomes available, this must be attributed to interaction of the unpaired electron with fluorine nuclei.

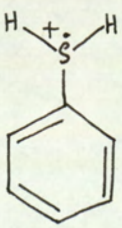
Disulphides. The disulphides examined gave the same signal at high field as the corresponding thiols.

Sulphides

The sulphides used were of the type Ph-S-R. The high field signals were all quintets, similar to that from thiophenol, but differing slightly in g value and splitting constant. This is taken to indicate that some re-arrangenent has occurred such that alkyl substituted thianthrenes are obtained (substituted in non-interacting positions).

The low field, or high g-value signals will now be considered. The magnitude of the g values of these signals, and the small hyperfine splitting constants observed suggest that the unpaired electron has a high density on the sulphur atom (see also section 6.1).

The high g value part of the esr spectrum of solutions of thiophenol in sulphuric acid has 3 hyperfine components, with the intensity ratio 1 : 2 : 1. These therefore arise from interaction of the unpaired electron with two equivalent protons. It is usually considered that compounds dissolved in sulphuric acid are protonated, thus species of the type:-



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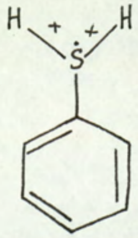


might be expected to be responsible, with the splitting arising from the two hydrogen atoms indicated. If this were the case, however, all the thiophenols should give the same spectrum, which they do not.

If solutions of thiophenol in deuterosulphuric acid are examined, a 1 : 1 doublet is found. This indicates that only one of the protons is exchanging and thus that the sulphur atom carried only one proton. The splitting may therefore arise by equal interaction of the unpaired electron with a proton attached to the sulphur atom, and one ring proton.

The spectrum from 4-t-butylthiophenol in sulphuric acid is a doublet, suggesting that the ring proton is in the 4-position.

Five hyperfine components were observed for 4-aminothiophenol. These may arise from coupling with the proton on the sulphur atom to give a doublet, and splitting of this by the amino-nitrogen atom, with a splitting constant half the size of that for the proton. This would lead to a 1 : 1 : 2 : 1 : 1 ratio of intensities. Unfortunately, resolution was very poor for this species and precluded measurement of the intensity distribution.

4-Methythiophenol also fits into this scheme, giving rise to five hyperfine components. These would arise from equal coupling of the methyl and sulphur protons.

2-Mercaptobenzoic acid shows no hyperfine splitting. Shine found a single line for the spectrum of thianthrene with a COOH group in a non-interacting position (p.348)

4-Bromo, 2,4,6-tribromo-, and pentafluorothiophenol all gave a single line, when on the above theory, a doublet would be expected. As in the case of the brominated thianthrenes, it is thought that the spin-orbit coupling of the halogen atom broadens the hyperfine structure out of detection.

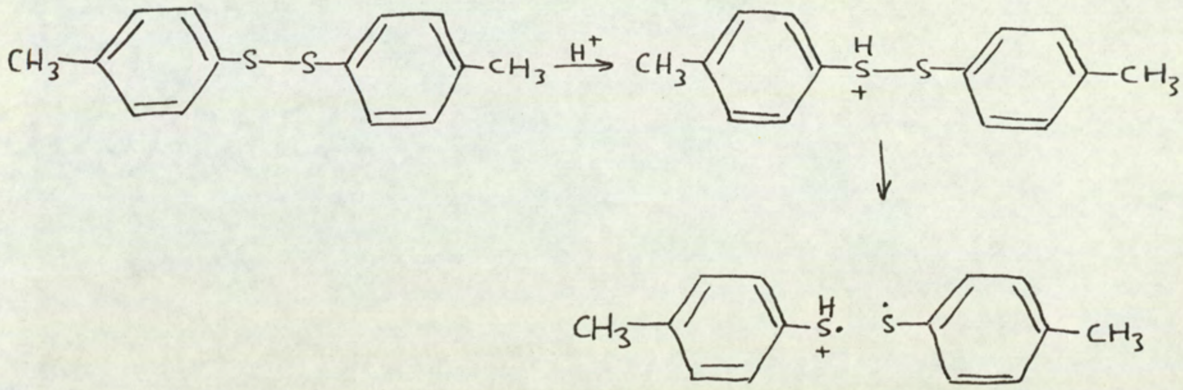
2-Methyl- and 3-methylthiophenol do not give spectra consistent with this theory. They both give signals with 5 hyperfine components where three would be predicted. It may be thought that a rearrangement might occur to form 4-methylthiophenol, which would then give a quintet, but this is not so as the g values and splitting constants of the signals are not the same for the three compounds. It should also be noted that the low g value signal from 2-methylthianthrene has no hfs, indicating that this is not formed from the 4-methylthiophenol, which yields a low g signal having 9 components.

3,5-Dimethylthiophenol, and the 2-halogenothiophenols and 4-chlorothiophenol are similarly not explained.

The high g value signals must be due to a precursor of thianthrene or to a species formed by some alternative reaction to that of formation of thianthrene, as they have never been reported as being observed when thianthrene and its derivaties have been examined. Thianthrene does not, therefore, undergo fission in solution in sulphuric acid. The disulphides are precursors of thianthrene. However, the triplet found at high g value for thiophenol in sulphuric acid could not be detected under these conditions for diphenyl disulphide. When a mixture of concentrated sulphuric acid and concentrated chlorosulphonic acid was used, the triplet was observed. This shows that to form the radical species from the disulphide, more vigorous conditions than solution in sulphuric acid are required, suggesting that fission of the disulphide molecule must be brought about, and that the free radical is not likely to be, for example, a protonated disulphide molecule.

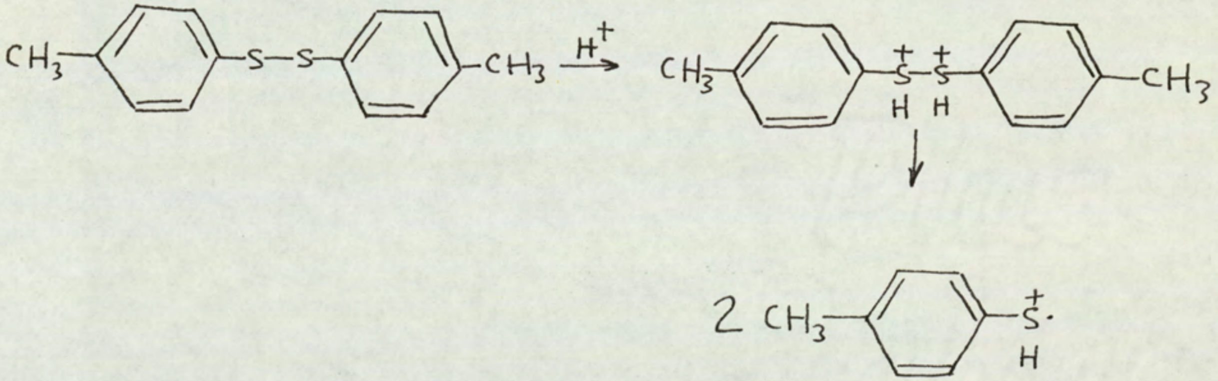
4,4'-Dimethyldiphenyl disulphide yields a free radical species in sulphuric acid alone, unlike diphenyl disulphide (see above). Hyperconjugation by the methyl groups would be expected to increase the electron density in the ring, and therefore on the sulphur atoms, so leading to easier fission of the S-S bond in the substituted case. The increased electron density on the sulphur atom would also increase the stability of positively charged species formed by the cleavage of the S-S bond in singly or doubly protonated disulphide molecules,

(a) singly protonated

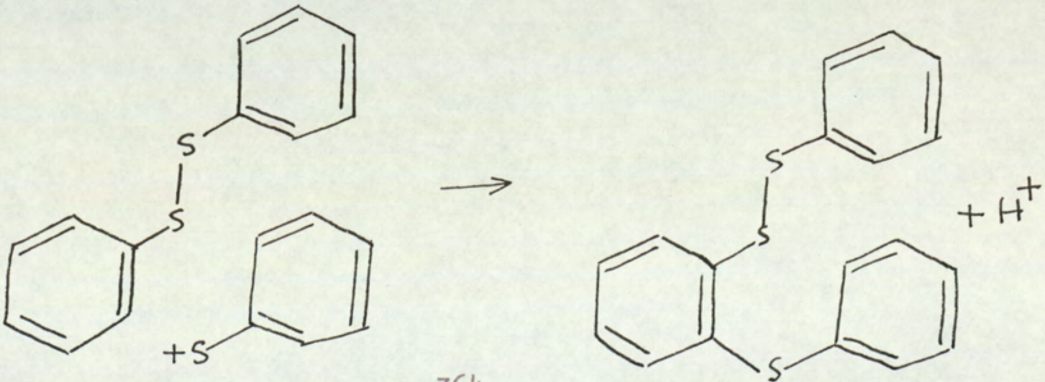


Dimerisation of the neutral radical would probably then occur, to form disulphide molecules.

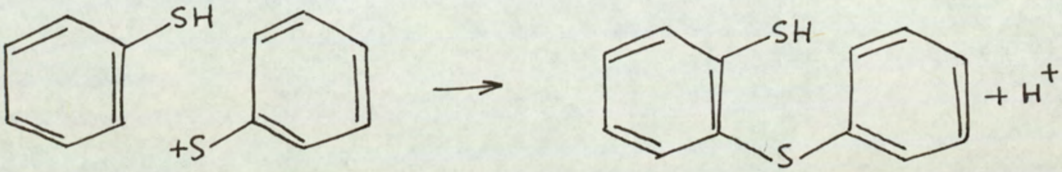
(b) doubly protonated



The positive ion radical could then react by the mechanism suggested by Fava, Sogo and Calvin (49).

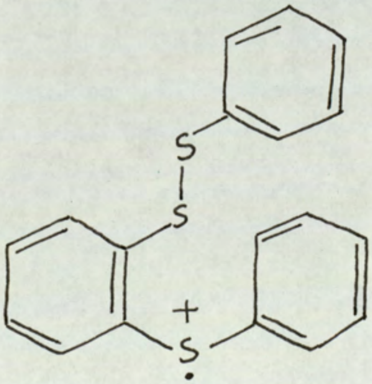


A similar reaction can be written starting from the thiol:-

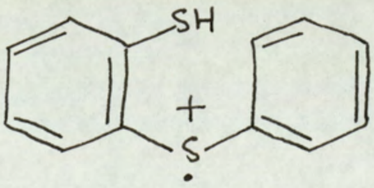


Now, it has been shown that aromatic sulphides are oxidized to free radical species in sulphuric acid, the species being thought to be Ar-$\overset{\bullet}{\underset{+}{S}}$-AR (185). It was considered that these would be more stable than the Ar-S$^\bullet$ type of free radical as the positive charge would tend to prevent the association to form diamagnetic dimers or polymers. The presence of two aromatic rings also gives greater resonance stabilization than one.

In the present case, the free radical would have the structure



from the disulphide



from the thiol

Cyclization would then yield the thianthrene cation radical directly.

7. CONCLUSIONS

Free radical species have been produced from aliphatic and aromatic thiols, monosulphides, and disulphides by uv irradiation at liquid nitrogen temperatures and by solution in concentrated sulphuric acid and in other strongly acid media.

The uv-photolysis work confirmed the results of other workers on dimethyl-, di-n-butyl-, diphenyl-, and dibenzyl disulphides and toluene- -thiol, and extended this field to include all other alkane thiols in the range C_1 to C_4, and the corresponding disulphides, some sulphides, aromatic thiols and disulphides and N,N'-dithiobisamines.

All the compounds yielded radicals having esr spectra consistent with the $RS^{\bullet}$ "sulphur radicals" thought to be formed by photolytic cleavage of the -S-S or-S-H bond. Most of the radicals had anisotropic g values, in the range (for the thiols) of

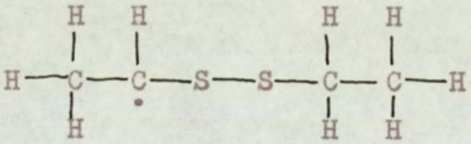
$$g_1 = 2.000 - 2.002$$

$$g_2 = 2.023 - 2.028$$

$$g_3 = 2.054 - 2.060$$

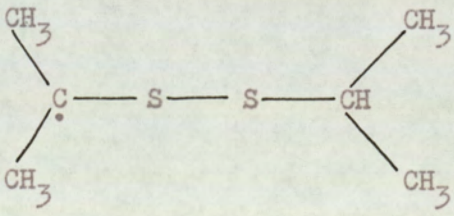
Di-isobutyl disulphide, dibenzothiazolyl disulphide and tetramethylthiuram disulphide gave spectra typical of axially symmetric species. No signals were detected from the monosulphides irradiated. Most of the spectra showed evidence for hyperfine splitting by one proton, of a magnitude comparable to that reported in the literature for the radical formed by γ-irradiation of L-cystine dihydrochloride single crystal, and arising by interaction with a proton on the α carbon.

The spectra of irradiated diethyl disulphide and di-isopropyl disulphide contained absorptions due to a second species. These had g values slightly lower than those of the $RS^{\bullet}$ radicals, and also showed hyperfine splitting, of the order of 20 gauss. The species responsible for these signals are thought to be



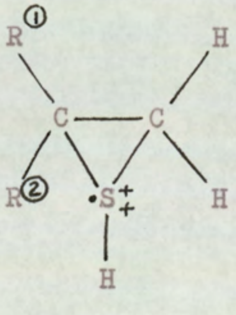
$$H_3C-\dot{C}H-S-S-CH_2-CH_3$$

in diethyl disulphide, and



in di-isopropyl disulphide, formed by hydrogen abstraction by the initially formed RS$^{\bullet}$ species. This reaction is similar to that reported in the literature for the uv irradiation of solutions of hydrogen peroxide in alcohols.

Free radicals are formed by the solution of aliphatic thiols, monosulphides, and disulphides, and N,N'-dithiobisamines in concentrated sulphuric acid. All the spectra show hyperfine splitting. The literature contains reports of radicals in solutions of sulphur in oleum, no hyperfine splitting being reported. It is believed that this is the first report of the detection of stable aliphatic organo-sulphur free radicals in solution at room temperature. The species are thought to be radical dications, with structures based on a three-membered sulphur-containing ring, having the form

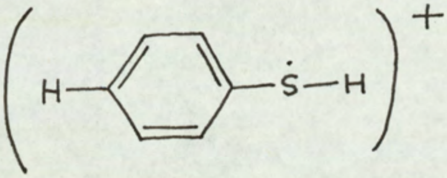


A possible mechanism has been suggested for the formation of this species. Hyperfine splitting is caused by interaction of the unpaired electron with the protons in the R groups where one or both of these are methyl, occuring by overlap of the methyl group orbitals with the sulphur orbital occupied by the unpaired electron.

Aromatic thiols and disulphides in solution in sulphuric acid were found to form free radicals. This has been reported in the literature for thiophenol and 4-methylthiophenol, the spectra being due to two radicals. The lower g value signal is derived from thianthrene, a product of the oxidation of thiophenol. The structure of the other radical was tentatively suggested as being of the type $(C_6H_5S^{\bullet})H^+$. The esr spectra of a range of substituted thiophenols in sulphuric acid are presented in this thesis, two radicals being present in all cases. Of the thianthrenes formed, the esr spectra have not previously been reported for the following:-

1,6-dimethylthianthrene
1,8-dimethylthianthrene
1,6-diaminothianthrene
2,7-diaminothianthrene
1,6-thianthrenedicarboxylic acid
1,6-dichlorothianthrene
1,6-dibromothianthrene
1,3,6,8-tetrabromothianthrene
1,6-dimethyl-1,4-dimercaptothianthrene

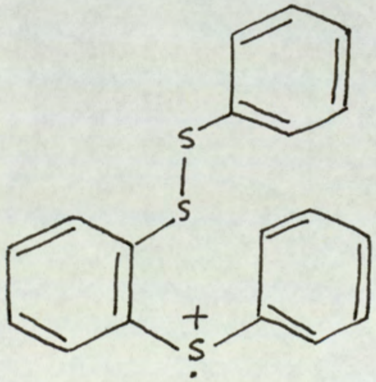
The esr spectra of the higher g value signal from thiophenol, and thiophenol substituted in the 4-position with methyl-, t-butyl-, amino-, and bromo-groups, 2,4,6-tribromothiophenol, and pentafluorothiophenol are consistent with a radical structure such as



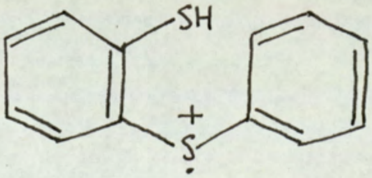
formed by one-electron oxidation of the thiol, with hyperfine splitting caused by the protons shown.

The other compounds used, 2-methyl-, 3-methyl-, 3,5-dimethyl- and the 2-halogeno-thiophenols did not give esr signals consistent with this structure.

The high g value signal is not due to species formed by fission of the thianthrene molecule, nor are they due to, for example, protonated disulphide molecules. It is thought that some species such as



from the disulphides



from the thiols

may be involved.

APPENDIX 1

"Microspin" ESR Spectrometer

X-Band, with W956 AFC Accessory

Setting-up Procedure

1. Switch on by main switch on waveguide console.

   Check:-

Heater volts	6.1 - 6.3V.	Adjust if necessary
Reflector volts	~150V.	
Resonator volts	290V.	
Resonator current	15-25 mV.	

   Allow to warm up for 15 minutes

2. Microwave generator W903 Bridge Balance Arm Amplitude to minimum (clockwise) RF Power and Klystron output max (counter clockwise). Klystron Power unit FA 909, Modulation Switch to Auto AFC unit FA 912 to Klystron Monitor. Monitor-Gain Control to mid position.

3. Using Reflector Voltage (FA 909) and Klystron Frequency (W903) obtain Klystron mode response on oscilloscope wave form.

Centralise (Reflector voltage), vary Klystron Frequency until cavity response is seen as a sharp dip in Klystron mode. Centralize.

4. Insert sample tube. Readjust Klystron Frequency to centralize dip on mode curve and readjust reflector voltage to set curve central. Ensure that AFC Frequency (W903) is <u>out</u> of range and maximise cavity dip with cavity matching screw.

5. W956 AFC Accessory - StabCavity to ESR

   Reverse Waveform - either position

   RF Bias - minimum

   Discriminator - any position

   Signal amplitude - minimum

   Switch Function Switch (FA 912) to Discriminator.

   <u>W.956</u> - Switch Meter to crystal Bias, apply 10 μamp RF Bias. Switch meter to monitor, and adjust balance crystals (FA 912) until wave form height is not more than 1 cm. with central portion of trace on or crossing the base line. Increase signal amplitude (W956) until trace nearly fills screen and adjust Discriminator (W956) to give desired symmetrical shape with central portion rising from left to right. If correct wave form is not obtainable, operate Reverse Waveform switch (956) and repeat this paragraph (paragraph 5).

6. Switch function switch (FA912) to Automatic. If trace is not in

central portion of screen but is near top or bottom, RF Power attenuator (W903) should be turned clockwise then anticlockwise, during which operation the trace will be seen to remain near the centre.

7. Switch meter to crystal current (W903). With max. sensitivity pressed, zero reading with small adjustments of Reflector voltage (FA 909) and cavity matching screw. Apply 50μamp (with max. sensitivity button pressed) with Bridge Balance Arm Amplitude.

8. FA206. Switch meter to RF, Gain Controls to maximum. Use phase control on W903 to minimise reading on FA206 meter. Should reduce to 3μamp. Readjust Bridge Balance Arm Amplitude to give 50μamp if necessary.

9. Switch on water supply to magnet console, switch on magnet and adjust to value required (270 for $g \simeq 2$) allow a few minutes to settle, or cycle twice over a few hundred gauss about value required.

10. Select Modulation current (FA210), Sweep Amplitude and Time (FA204), Gain and Time Constant (FA206).

Instrument now operates when "Start Sweep" button pressed.

APPENDIX 2

Measurement of Magnetic Field

The magnetic field strength is measured by determining the frequency of radiation required by a proton in that magnetic field to undergo nuclear magnetic resonance transitions.

The equipment comprises:-

1. Proton Head Probe - a tube containing water and surrounded by a coil of copper wire. This coil is supplied with RF power by
2. Proton Head Oscillator

   The frequency of this R.F. signal is measured by
3. Proton Head Frequency Meter. This covers the range 8 MHz to 22 MHz in five ranges. It has two built-in crystal controlled harmonic generators, operating at 250 kHz and 25 kHz.

The equipment is used in the following manner:-

1. Modulate external field at 50 Hz, with a modulation amplitude greater than 2 gauss, peak to peak.
2. Insert proton head probe into the field as close as possible to

the sample cavity. Adjust frequency of RF supplied by Proton Head oscillator until a proton resonance is observed on the spectrometer display unit, switched to 50 Hz (crystal video) sweep. Centralize the proton peak under the electron resonance absorption signal.

3. Note approximate frequency from the dial on the oscillator, and select appropriate range on the Frequency meter.
4. The frequency of the frequency meter is then adjusted until a beat note is heard via the loudspeaker, and also seen on the oscilloscope display. The frequency is adjusted forzero beat.
5. The 250 kHz crystal generator is then switched in, and the frequency control on the frequency meter adjusted to the nearest 0.25MHz calibration mark, and then tuned, for zero beat on the speaker to the 250 kHz harmonic closest to the calibration mark. This scale reading is noted.
6. The 25 kHz generator is switched in, and the frequency of the meter adjusted to move the dial pointer in the direction of the original setting. The number of 25 kHz harmonics passed through, heard on the speaker, before this position is reached is noted. The original position is recognised as the beat note is observed displayed on the oscilloscope of the display unit.
7. Addition or subtraction of the number of 25 kHz harmonic beat notes to or from the frequency noted from the frequency meter dial then gives the required frequency.

8. Greater accuracy is given by interpolating between the 25 kHz harmonics.

9. Conversion of the frequency to corresponding magnetic field is then carried out using tables.

BIBLIOGRAPHY

1. C. Wallin, "Free Radicals in Solution," Wiley, New York, 1953, p.335.
2. As (1), pp.156, 319.
3. W. A. Pryor, "Mechanisms of Sulphur Reactions," McGraw-Hill, New York, 1962, p.46.
4. W. Gordy and H. Shields, Radiation Res., 1958, 9, 611.
5. N. P. Skerrett and N. W. Thompson, Trans. Faraday Soc., 1941, 37, 81.
6. W. E. Haines, G. L. Cook and J. S. Ball, J. Amer. Chem. Soc., 1956, 78, 5213
7. Y. Schaafsma, Chem. Weekblad, 1958, 54, 61.
8. Y. Schaafsma, A. F. Bickel, and E. C. Kooyman, Tetrahedron, 1960, 10, 76.
9. K. J. Rosengren, Acta Chem. Scand., 1962, 16, 1401.
10. K. J. Rosengren, Acta Chem. Scand., 1962, 16, 1418.
11. A. Schonberg and A. Mustafa, J. Chem. Soc., 1949, 889.
12. A. H. Sehon and B. de Be Darwent, J. Amer. Chem. Soc., 1954, 76, 4806.

13. J. A. R. Coope and W. A. Bryce, Canad. J. Chem., 1954, 32, 768.

14. A. Schonberg, A. Stephenson, H. Kaltschmitt, E. Pettersen and H. Schulter, Ber., 1933, 66, 237.

15. H. Hauptman and B. Wladislaw, J. Amer. Chem. Soc., 1950, 72, 710.

16. R. M. Pierson, A. J. Costaze and A. H. Weinstein, J. Polymer Sci., 1955, 17, 221.

17. C. F. Birch, T. V. Collum and R. A. Dean, J. Inst. Petroleum, 1953, 39, 206.

18. T. E. Ferrington and A. V. Tobolsky, J. Amer. Chem. Soc., 1955, 77, 4510.

19. M. S. Kharash, W. Nudenberg and T. H. Meltzer, J. Org. Chem., 1953, 18, 1233.

20. W. B. Reynolds and E. W. Cotton, Ind. Eng. Chem., 1950, 42, 1905.

21. C. Walling and R. Rabinowitz, J. Amer. Chem. Soc., 1957, 79, 5326.

22. C. Walling and R. Rabinowitz, J. Amer. Chem. Soc., 1959, 81, 1243.

23. W. A. Pryor and P. K. Platt, J. Amer. Chem. Soc., 1963, 85, 1496.

24. W. A. Pryor and H. Guard, J. Amer. Chem. Soc., 1964, 86, 1150.

25. U. Schmidt, Angew. Chem. (International Edition), 1964, 3, 602.

26. F. W. Stacey and J. F. Harris, "Organic Reactions," Wiley, New York, 1963, Vol. XIII, p.164 et seq.

27. F. O. Rice, J. Chem. Phys., 1956, 24, 1259.

28. M. S. Blois, H. W. Brown, R. M. Lemmon, R. O. Lindblom, and M. Weissbluth, Eds., "Free Radicals in Biological Systems," Academic Press, New York, 1961, p.117.

29. M. Bersohn and J. C. Baird, "An Introduction to Electron Paramagnetic Resonance," Benjamin, New York, 1966, p.69.

30. K. Akasaka, J. Chem. Phys., 1965, 43, 1182.

31. M. Kinoshita and H. Akamatu, Bull. Chem. Soc. Japan, 1962, 35, 1040.

32. Y. Kurita and W. Gordy, J. Chem. Phys., 1961, 34, 282.

33. Y. Kurita and W. Gordy, J. Chem. Phys., 1961, 34, 1285.

34. H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, J. Amer. Chem. Soc., 1960, 82, 766.

35. As (29), p.239.

36. T. R. Tuttle, Jr. and S. I. Weissman, J. Amer. Chem. Soc., 1958, 80, 5342.

37. J. R. Bolton, A. Carrington, A. Foreman and L. E. Orgel, Mol. Phys., 1962, 5, 43.

38. J. R. Bolton, A. Carrington and A. D McLachlan, Mol. Phys., 1962, 5, 31.

39. E. A. C. Lucken, Theoret. Chim. Acta., 1963, 1, 397.

40. G. Vincow, J. Chem. Phys., 1962, 37, 2484.

41. Y. H. Hahn and H. N. Rexroad, J. Chem. Phys., 1963, 38, 1599.

42. J. E. Wertz and J. L. Vivo, J. Chem. Phys., 1955, 23, 2193.

43. B. C. Gilbert, P. Hanson, R.O.C. Norman and B. T. Sutcliffe, Chem. Communications, 1966, 161.

44. G. Feher and A. F. Kip, Phys. Rev., 1955, 98, 337.

45. W. R. Datars, Phys. Rev., 1968, 126, 975.

46. J. M. Hirshon, D. M. Gardner, and G. K. Fraenkel, J. Amer. Chem. Soc., 1953, 75, 4115.

47. K. Fries and W. Volk, Ber., 1909, 42, 1107.

48. J. Stenhouse, Annalen, 1869, 149, 247.

49. A. Fava, P. B. Sogo and M. Calvin, J. Amer. Chem. Soc., 1957, 79, 1078.

50. H. J. Shine and P. D. Sullivan, J. Phys. Chem., 1968, 72, 1390.

51. M. Kinoshita, Bull. Chem. Soc. Japan, 1962, 35, 1137.

52. H. J. Shine and L. Piette, J. Amer. Chem. Soc., 1962, 84, 4798.

53. W. Rundel and K. Scheffler, Tetrahedron Letters, 1963, 993.

54. H. J. Shine, C. F. Dias and R. J. Small, J. Chem. Phys., 1963, 38, 569.

55. H. J. Shine and T. A. Robinson, J. Org. Chem., 1963, 28, 2828.

56. H. J. Shine and D. R. Thompson, Tetrahedron Letters, 1966, 1591.

57. H. J. Shine, C. F. Dias and R. J. Small, J. Org. Chem., 1964, 29, 21.

58. E. T. Kaiser and D. H. Eargle, J. Amer. Chem. Soc., 1963, 85, 1821.

59. R. Gerdil and E. A. C. Lucken, Proc. Chem. Soc., 1963, 144.

60. E. T. Kaiser and D. H. Eargle, Jr., J. Chem. Phys., 1963, 39, 1353.

61. E. T. Kaiser and D. H. Eargle, Jr., J. Phys. Chem., 1965, 69, 2108.

62. W. Moffit, Proc. Roy. Soc. (London), 1950, A200, 409.

63. M. M. Urberg and E. T. Kaiser, J. Amer. Chem. Soc., 1967, 89, 5179.

64. D. H. Eargle Jr. and E. T. Kaiser, Proc. Chem. Soc., 1964, 22.

65. E. T. Kaiser, M. M. Urberg, and D. H. Eargle Jr., J. Amer. Chem. Soc., 1966, 88, 1037.

66. J-P. Billon, G. Cauquis, J. Combrisson and A-M. Li, Bull. Soc. chim. France, 1960, 2062.

67. L. D. Tuck and D. W. Schieser, J. Phys. Chem., 1962, 66, 937.

68. D. Gagnaire, H. Lemaire, A. Rassat and P. Servoz-Gavin, Compt. rend., 1962, 255, 1441.

69. M. Kinoshita, Bull. Chem. Soc. Japan, 1963, 36, 307.

70. M. Bruin, F. Bruin, and F. W. Heineken, J. Org. Chem., 1964, 29, 507.

71. J-P. Billon, G. Cauquis, and J. Combrisson, J. Chim. phys., 1964, 61, 374.

72. S. Odiot and F. Tonnard, J. Chim. phys., 1964, 61, 382.

73. C. Bodea and I. Silberg, Rev. Chim. (Roumania), 1965, 10, 887.

74. T. N. Tozer and L. D. Tuck, J. Pharm. Sci., 1965, 54, 1169.

75. H. J. Shine and E. E. Mach, J. Org. Chem., 1965, 30, 2130.

76. D. W. Schieser and L. D. Tuck, J. Pharm. Sci., 1962, 51, 694.

77. L. H. Piette and I. S. Forrest, Biochim. Biophys. Acta, 1962, 57, 419.

78. J. C. Baird and J. R. Thomas, J. Chem. Phys., 1961, 35, 1507.

79. B. Lamotte, A. Rassat and P. Servoz-Gavin, Compt. rend., 1962, 255, 1508.

80. B. Lamotte, Proc. Colloq. AMPERE (Atomes Mol. Etudes Radio Elec.) 1963, 12, 282.

81. M. Tomita, S. Ueda, Y. Nakai, Y. Deguchi and H. Takaki, Tetrahedron Letters, 1963, 1189.

82. U. Schmidt, K. Kabitzke and K. Markau, Ber., 1964, 97, 498.

83. H. J. Shine and R. J. Small, J. Org. Chem., 1964, 30, 2140.

84. F. W. Heineken, M. Bruin and F. Bruin, J. Chem. Phys., 1962, 37, 452.

85. B. Eda, R. J. Cook and D. H. Whiffen, Trans. Faraday Soc., 1964, 60, 1497.

86. P. Cavalieri d'Ore, A. Mangini, G. F. Pedulli, P. Spagnolo and M. Tiecco, Tetrahedron Letters, 1969, 48, 4179.

87. A. Zweig and A. K. Hoffmann, J. Org. Chem., 1965, 30, 3997.

88. E. T. Strom and G. A. Russell, J. Amer. Chem. Soc., 1965, 87, 3326.

89. H. J. Shine, M. Rahman, H. Nicholson and R. K. Gupta, Tetrahedron Letters, 1968, 50, 5255.

90. Y. Yokozawa and I. Miyashita, J. Phys. Soc. Japan, 1957, 12, 107.

91. P. J. Zandstra and J. D. Michaelson, J. Chem. Phys., 1963, 39, 933.

92. A. Zweig, W. G. Hodgson, W. J. Jura and D. L. Maricle, Tetrahedron Letters, 1963, 1821.

93. A. Zweig and W. G. Hodgson. Proc. Chem. Soc., 1964, 417.

94. E. A. C. Lucken, J. Chem. Soc., 1964, 4240.

95. M. McMillan and W. A. Waters, J. Chem. Soc., (B), 1966, 422.

96. F. K. Truby, J. Chem. Phys., 1962, 36, 2227.

97. F. Patten and W. Gordy, Proc. Nat. Acad. Sci., U.S.A., 1960, 46, 1137.

98. F. K. Truby, C. McCallum and J. E. Hesse, J. Chem. Phys., 1962, 37, 2777.

99. F. K. Truby, J. Chem. Phys., 1964, 40, 2768.

100. F. K. Truby, D. C. Wallace, and J. E. Hesse, J. Chem. Phys., 1965, 42, 3845.

101. J. J. Windle, A. K. Wiersema, and A. L. Tappel. J. Chem. Phys., 1964, 41, 1996.

102. E. S. Smissman and J. R. J. Sorensen, J. Org. Chem., 1965, 30, 4008.

103. P. B. Ayscough, K. J. Ivin, and J. H. O'Donnell, Trans. Faraday Soc., 1965, 61, 1110.

104. U. Schmidt, A. Meuller and K. Markau, Ber., 1964, 97, 405.

105. D. M. Gardner, and G. K. Fraenkel, J. Amer. Chem. Soc., 1956, 78, 3279.

106. D. J. E. Ingram and M. C. R. Symons, J. Chem. Soc., 1957, 2437.

107. W. F. Giggenbach, J. Chem. Soc. D, 1970, 852.

108. W. G. Hodgson, S. A. Buckler and G. Peters, J. Amer. Chem. Soc., 1963, 85, 543.

109. D. G. Redman, D. W. E. Axford, G. A. H. Elton and J. A. Brivati, Chem. and Ind., 1966, 1298.

110. W. Gordy, W. B. Ard, and H. Shields, Proc. Nat. Acad. Sci., U.S.A. 1955, 41, 983.

111. G. McCormick and W. Gordy, J. Phys. Chem. 1958, 62, 783.

112. H. Shields and W. Gordy, J. Phys. Chem. 1958, 62, 789.

113. T. Henriksen and A. Pihl. Nature, 1960, 185, 307.

114. T. Henriksen and A. Pihl. Internat. J. Radiation Biol., 1961, 3, 351.

115. R. Koch and K. Markau, Z. Naturforsch, 1961, 166, 586.

116. F. Patten and W. Gordy, Radiation Res. 1961, 14, 573.

117. T. Henriksen, J. Chem. Phys., 1962, 36, 1258.

118. T. Henriksen, J. Chem. Phys., 1962, 37, 2189.

119. T. Henriksen, J. Chem. Phys., 1963, 38, 1926.

120. H. Monig and R. Koch, Nature, 1964, 202, 289.

121. F. K. Kneubuhl, J. Chem. Phys., 1960, 33, 1074.

122. H. C. Box and H. G. Freund, J. Chem. Phys., 1964, 40, 817.

123. K. Akasaka, S-I. Ohnishi, T. Suita and I. Nitta, J. Chem. Phys. 1964, 40, 3110.

124. H. C. Box and H. G. Freund, J. Chem. Phys., 1964, 41, 2571.

125. E. Cipollini and W. Gordy, J. Chem. Phys., 1962, 37, 13.

126. D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworths, London, 1958, p.18.

127. As (29), p.44.

128. As (29), p.78.

129. H. M. McConnell, J. Chem. Phys., 1956, 24, 764.

130. R. Bersohn, J. Chem. Phys., 1956, 24, 1066.

131. S. I. Weissman, J. Chem. Phys., 1956, 25, 890.

132. H. S. Jarrett, J. Chem. Phys., 1956, 25, 1289.

133. As (29), p.64.

134. J. H. Van Vleck, Phys. Rev., 1948, 74, 1168.

135. M. H. L. Pryce and K. W. H. Stevens, Proc. Phys. Soc., 1950, A63, 36.

136. R. de L. Kronig, Physica, 1939, 6, 33.

137. P. W. Anderson and P. R. Weiss, Rev. Mod. Phys., 1953, 25, 269.

138. D. Kivelson, J. Chem. Phys., 1957, 27, 1087.

139. As (126), p.129.

140. H. M. Assenheim, "Introduction to Electron Spin Resonance," Hilger & Watts Ltd., London, 1966, p.58.

141. J. Burgin, G. Hearne and F. Rust, Ind. Eng. Chem., 1941, 33, 385.

142. C. E. Wilson and H. J. Lucas, J. Amer. Chem. Soc., 1936, 58, 2396.

143. H. R. Snyder, J. M. Stewart and J. B. Ziegler, J. Amer. Chem. Soc., 1947, 69, 2672.

144. H. R. Snyder, J. M. Stewart and J. B. Ziegler, J. Amer. Chem. Soc., 1947, 69, 2675.

145. "Dictionary of Organic Compounds," Eyre & Spottiswode, London, 1965, vol 2, p.1016.

146. D. T. McAllan, T. V. Cullum, R. A. Dean and F. A. Fidler, J. Amer. Chem. Soc., 1951, 73, 3627.

147. As (145), 5th. Cumulative Supplement, p.318.

148. As 145, vol 2, p.952.

149. S. F. Birch and W. S. G. P. Norris, J. Chem. Soc., 1925, 127, 858.

150. J. Kenyon, H. Phillips, V. P. Puttman, R. B. Shackelton, D. E. Kahn, F. H. Yortson and N. E. Cochinaras, J. Chem. Soc., 1935, 1072.

151. As 145, vol 2, p.953.

152. A. Mailhe and M. Murat, Bull. Soc. Chim., 1910, 70, 288.

153. As 145, vol 2, p.904.

154. A. G. Wheway, Undergraduate Project Report, University of Aston in Birmingham. 1967.

155. V. N. Ipatieff, H. Pines and B. S. Friedman, J. Amer. Chem. Soc., 1938, 60, 2731.

156. "Organic Chemistry of Bivalent Sulphur" Reid, E. E., Chemical Publishing Co., Inc., New York, Vol II, p.113.

157. H. Gilman and N. J. Beaber, J. Amer. Chem. Soc., 1925, 47, 1449

158. E. V. Whitehead, R. A. Dean and F. A. Fidler, J. Amer. Chem. Soc., 1951, 73, 3632.

159. "Inorganic Syntheses" McGraw-Hill, New York and London, 1939, vol 1. p.151.

160. C. B. J. Pearce, Undergraduate Project Report, University of Aston in Birmingham, 1969.

161. "Elementary Practical Organic Chemistry," A.I. Vogel, Longmans, 1957, Part 1, p.169.

162. G. H. Stillson, D.W. Sawyer, and C. K. Hunt, J. Amer. Chem. Soc., 1945, 67, 303.

163. I. Brown, G. Eglinton and M. Martin-Smith, Spectrochim. Acta, 1962, 18, 1593

164. "Organic Syntheses Collective Volume IV" Wiley, New York, 1963, p.130.

165. M. S. Newman and H. A. Karnes, J. Org. Chem. 1966, 31, 3980.

166. "Experiments in Organic Chemistry" L. F. Fieser, D. C. Heath & Co., New York, and London, 1941, p.306.

167. J. B. Cohen, F. W. Skirrow, J. Chem. Soc., 1899, 75, 887.

168. H. R. Hirst and J. B. Cohen, J. Chem. Soc., 1895, 826.

169. "Organic Syntheses" Collective Volume III, Chapman & Hall, 1965, p.136.

170. J. R. Thirtle, J. Amer. Chem. Soc., 1946, 68, 342.

171. P. Robinson, M. Stacey, R. Stephens & J. C. Tatlow, J. Chem. Soc., 1960, 4754.

172. "Electron Spin Resonance" C. P. Poole Jr., Interscience, New York, 1967, p.601.

173. Y. Deguchi, J. Chem. Phys., 1960, 32, 1584.

174. H. Ueda, Z. Kuri and S. Shida, J. Chem. Phys., 1962, 36, 1676.

175. As 172, p.629.

176. As 126, p.174.

177. As 172, p.686.

178. As 126, p.136.

179. G. E. Pake, "Paramagnetic Resonance", W. A. Benjamin, New York, 1962, p.109

180. As 125, p.24.

181. R. W. Fessenden & R. H. Schuler, J. Chem. Phys. 1963, 39, 2147.

182. J. F. Gibson, D. J. E. Ingram, M.C. R. Symons and M. G. Townsend, Trans. Faraday Soc., 1957, 53, 914.

183. E. de Barry Barnet and C. L. Wilson, "Inorganic Chemistry," Longmans, London, 1959, p.480.

184. R. S. Mulliken, J. Phys. Chem., 1952, 56, 801.

185. M. J. Janssen, Ed., "Organo-Sulphur Chemistry", Wiley, New York, London and Sydney, 1967, p.80.

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