SYNTHESIS AND STUDIES OF
NEW ORGANOTELLURIUM COMPOUNDS

by

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ABSTRACT

The syntheses of a new range of compounds in which azobenzene is metallated with tellurium (IV) or tellurium (II) are reported. The compounds include $(C_{12}H_9N_2)$ $TeXY_2$ (X = Y = Cl ; X = Y = Br; X = Cl, Y = Br) and the tellurium (II) compounds $(C_{12}H_9N_2)TeCl$ (phenylazophenyl-2C, N')tellurenyl chloride and $(C_{12}H_9N_2)Te$-$(C_6H_4$-OEt-p). The reaction of $(C_{12}H_9N_2)TeCl$ with sodium borohydride affords di(o-aminophenyl)ditelluride which is shown to form co-ordination compounds with copper (I) and copper (II).

Physical data, including infra-red spectra, are presented and discussed. It is concluded that the new tellurium (IV) derivatives are five co-ordinate monomers.

The synthesis of the first diorganotellurium diisothiocyanates is reported. It is argued that the tellurium interacts more strongly with the nitrogen than with the sulphur atom of the NCS group. Two structural classes are noted : (a) $R_2Te(NCS)_2$ (R = Ph, p-$CH_3O.C_6H_4$) in which the interaction of tellurium with the two NCS groups is equal and in which intermolecular association via long Te-S bonds probably occurs, and (b) $R_2Te(NCS)^+(NCS)^-$ (R = p-$C_2H_5OC_6H_4$) in which the tellurium interacts unequally with the two NCS groups to give a structure with some telluronium salt character.

The chemistry of $MePh_2Te(NCS)$ is studied. In solvents of reasonable polarity (e.g. DMSO), and probably in the solid state, it behaves as an essentially ionic telluronium salt $MePh_2\overset{+}{Te}(NC\overset{-}{S})$. However, in a $CDCl_3$ solution it exists in a covalent form, $MePh_2$-$Te(NCS)$, from which reductive elimination of exclusively methyl thiocyanate occurs. The mechanism of the decomposition is not simple. Initially it is probable that a free radical pathway dominates, but after approximately 100 min., the rate of decomposition increases and there is evidence that the second rate process is catalysed by diphenyl telluride. Other salts, $MePh_2TeX$, $X = BF_4, PF_6$, are reported for comparison.

Tellurium tetrachloride and $(p\text{-}C_2H_5OPh)TeCl_3$ both reacted with 2-vinylpyridine in benzene or in toluene, and gave $(C_7H_7NH)_2^+ (Cl_4Te{-}O{-}TeCl_4)^-$, $(C_7H_7NH)^+ (p\text{-}EtOPhTeCl_4)^-$ consequently.

The Ph-Sn bond was cleaved in preference to the Bu-Sn bond; Bu_3PhSn with tellurium tetrachloride or $p\text{-}EtOPhTeCl_3$ produced phenyltellurium trichloride or $Ph(p\text{-}EtOPh)TeCl_2$ and Bu_3SnCl in each case.

The uv-spectra of Ph_2TeX_2, $X = Cl, Br, I$ in CH_2Cl_2 were studied. Charge transfer transitions are believed to dominate the longer wave length region.

Keywords

Tellurium
Organotellurium
Azobenzene
Thiocyanate
Structure
Synthesis

The work described in this thesis was carried out between 1975 and 1978 at the University of Aston in Birmingham.

It has been done independently, and has not been submitted for any other degree.

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CHAPTER I

INTRODUCTION

Tellurium was discovered in 1782 by F. J. Müller von Reichenstein and named tellurium by M. H. Klaproth, from the Latin tellus meaning earth.[1]

As a member of group VIB of the periodic table, with the electronic structure of (Kr) $4d^{10}$ $5s^{2}$ $5p^{4}$, it displays a number of similarities to selenium and sulphur in many of its properties. The increasing metallic nature of the elements with increasing atomic weight is seen by the fact that oxygen and sulphur are insulators, selenium and tellurium, semiconductors, and polonium more positively metallic.

Since its discovery, numerous commercial applications for tellurium have been found : e.g. as an additive element, it is added to steel and copper for improving machinability, in fuses for explosives, in rubber as a vulcanizing agent, in glass and ceramics for colouring, in lead as a strengthening agent, and in chemical reactions as a catalyst.

One of our group, Davies [2] reported the synthesis of a range copper (1) halide ditelluride complexes. He suggested that these complexes have possible potential as catalysts, especially for the hydrocyanation of butadiene.

The solid-state thermoelectric devices produced from bismuth, cadmium and lead tellurides have important implication in many fields.

Tellurium and its compounds appear to be less toxic than selenium, with the exception of hydrogentelluride which produces toxic symptoms very similar to those of hydrogen selenide.

Tellurium has not presented any serious hazards in its industrial applications, the metabolism of tellurium in the animal body is by no means understood, and in contrast to selenium, no essential nutrient role for tellurium has been found.

The aim of this project is to synthesise new classes of Organotellurium compounds, then investigate them by different techniques : e.g. i.r., 'H n.m.r., u.v., and mass spectroscopy.

The organic chemistry of tellurium has been covered in several reviews ; Petragnani and de Moura Campos[3] have discussed the significant developments which have taken place in this field up to 1967. "Tellurium" (C. W. Cooper, 1971)[1] is a book dealing with all aspects of tellurium and its chemistry. "The Organic Chemistry of Tellurium",[4] a book in which all aspects of the chemistry of compounds containing at least one tellurium-carbon bond have been reviewed, has been published in 1974.

The publications, which have appeared from 1840, when Wöhler[6] reported the preparation of the first organic tellurium compound, through 1971 and papers abstracted in Chemical Abstracts, volume 76, No. 1 to 11 have been considered in Irgolic's book.[4]

The survey by Irgolic which appeared in 1975 covering the years 1972-1974 is based mainly on the literature,[5] which became available since 1971 and has been abstracted in Chemical Abstracts volume 76, No. 12 through volume 81, No. 26.

Tellurium is located between selenium and polonium in group VIB in the series oxygen, sulphur, selenium tellurium and polonium. Its atomic number is 52. The outer electron shell of tellurium is $5s^2\ 5p^4$, and its inner shell (2, 8, 18, 18) is completely filled. It is markedly similar to selenium in its chemistry. In both cases the most common oxidation states are (II), (IV) and (VI). The higher co-ordination numbers are not known. Tellurium can also exhibit oxidation states of (-II) by accepting two electrons, producing Te^{2-} ions to complete the inert gas configuration, of which it lacks two electrons, e.g. H_2Te. This is an example of the more metallic behaviour of tellurium, and it is not observed in organotellurium compounds.

During the course of our investigations, we discovered new organotellurium (II, IV) compounds which ultimately became the major theme of the investigation, hence a brief review of the chemistry of tellurium (II) and (IV) is now given.

Te^{II} :-

The compounds treated in this section include symmetrical, unsymmetrical tellurides, tellurenylhalide derivatives and diarylditelluride ; e.g. R_2Te or $RR'Te^{II}$ RTeX and R_2Te_2.

R_2Te^{II}, $RR'Te^{II}$

The literature which describes the aromatictellurides is considerably more extensive than that which is concerned with aliphatic derivatives. The first organotellurium compound, diethyltelluride, was prepared by Wöhler in 1840 by reacting potassiumtelluride with ethylsuphate.[6] Diphenyltelluride was prepared first in 1894 by the reaction between diphenylmercury and elemental tellurium.[7]

There are many methods used to prepare tellurides, including here the methods which gave good yields :

1. The reduction of tetravalent diorganotellurium compounds, Ar_2TeX_2 was investigated by Bergman [8]. He introduced hydrazine as a reducing agent for diaryltellurium dihalides. The tellurides were obtained in 80% yields ;

$$2\,R_2TeX_2 + N_2H_4 \longrightarrow 2R_2Te + N_2 + 4HX$$

2. Another method was reported by Sadekov [9] by refluxing diarylditellurides in dioxane for eight hours in the presence of activated copper powder and isolating the diaryltellurides in good yields.

3. McWhinnie, et. al.[10] studied the alkylation of tellurium tetrachloride by aromatic Grignard reagents they synthesised diphenyl, dibenzyl and bis(pentafluorophenyl)telluride by reacting tellurium tetrachloride with an appropriate Grignard reagent and produced diaryltellurides, (the separation of tellurium reported [11] to occur in these reactions was not observed, using the new condition)

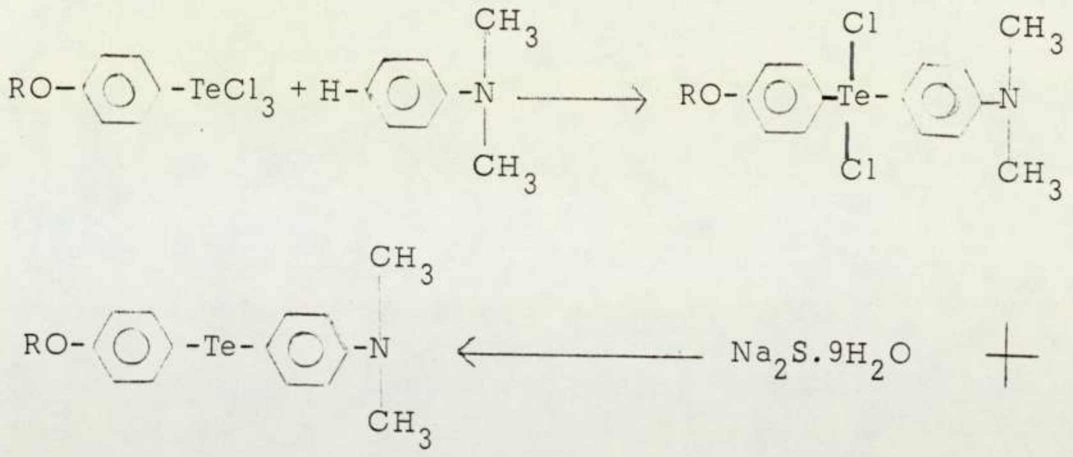
$$4RMgX + TeCl_4 \longrightarrow R_2Te + R_2 + 4MgX.Cl.$$

4. The reaction between aryltellurium trihalides with arylmercuric-chloride in boiling dioxan , that resulted in unsymmetric diaryltellurium dichloride [12] which was reduced with sodium sulphide nonahydrate at 100°C to the unsymmetrical diaryltelluride ;

$$ArTeCl_3 + ClHgAr' \xrightarrow{1,4\text{-dioxane}} HgCl_2,1,4 \text{ dioxane} + ArAr'TeCl_2$$

$$ArAr'Te^{II} \xleftarrow[100^{\circ}C]{Na_2S.9H_2O}$$

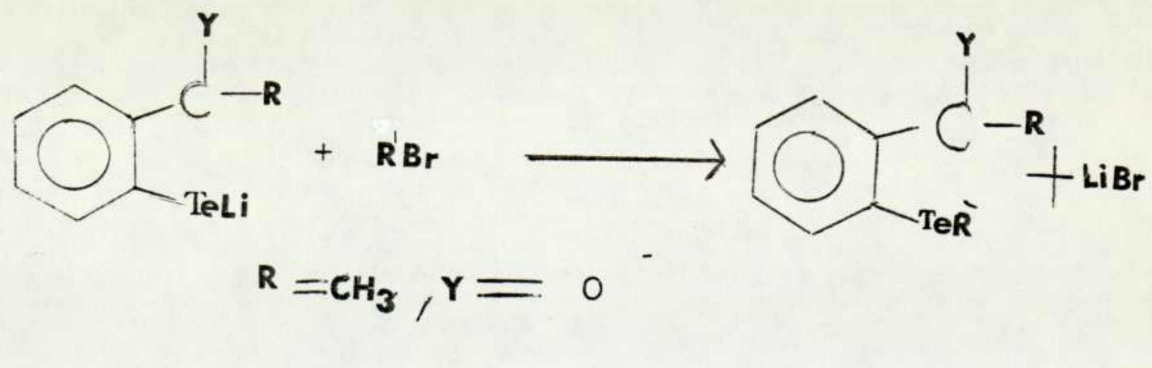
5. Petragnani [13] prepared various unsymmetric diaryltellurides by condensation of aryltellurium trihalides with dimethylaniline, followed by reduction of the halides with $Na_2S.9H_20$;



6. Lederer[14] treated bis(p-methoxyphenyl)tellurium dibromide with a five fold molar excess of phenylmagnesiumbromide and isolated the unsymmetric compound. After the addition of bromine, as dibromide, the dibromide was reduced by $NaHSO_3$.

7. The synthesis of unsymmetric diaryltellurides[15] has also been successfully carried out by cleavage of the Te-Te bond in diarylditellurides with an excess, from three fold to five fold of an aromatic Grignard reagent or with only two fold of phenyllithium.

8. Methods developed earlier[16] have been extensively applied to synthesis new unsymmetric diorganyltellurides ; Piette and Renson[16a] synthesised tellurides, which contain a functional group in the ortho position :



Piette[16] prepared 2-formylphenyl and 2-cinnamoylphenylmethyltellurides[17] from the respective phenyltellurium monobromide, and dimethyl cadmium. The 2-formylphenylmethyltellurides assumed according to 'H n.m.r.result in a conformation which allows the tellurium atom to interact with the carbonyloxygen atom[18].

R_2Te_2II

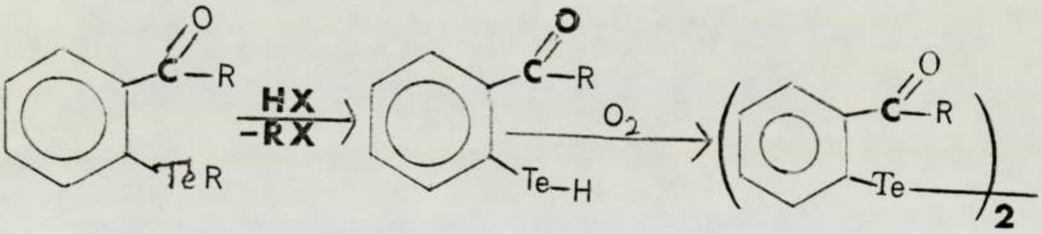
Ditellurides have the general formula R-Te-Te-R,(R is in the organic group). They are red or orange colour. The recrystallization of di-p-ethoxyphenylditelluride gave golden yellow or orange crystals. No structural studies have been done on these crystals. We may suggest that some intermolecular bonding system involving heavy atoms (tellurium) causing different crystals colour as observed in diaryltellurium diiodide ; The structural studies of di-p-chlorophenyltellurium diiodide (violet),[19] 1-thia-4-telluracyclohexane 4,4 diiodide (metallic luster)[20] and 1-oxa-4-telluracylclohexane 4,4 diiodide (bright red)[21] have shown that the intermolecular bonding in the first two compounds (violet, metallic cluster) consist mainly of a nearly linear chain of the type ......I-Te-I...I-Te-I with secondary I....I bonds. In contrast, the third compound is bright red and the intermolecular bonds have been found to consist of the Te...I interaction only.

The volume of literature concerned with chemistry of the diarlditellurides is considerably more extensive than that which deals with dialkylderivatives. This may be due to greater stability of the diarylditellurides and that they are odourless.

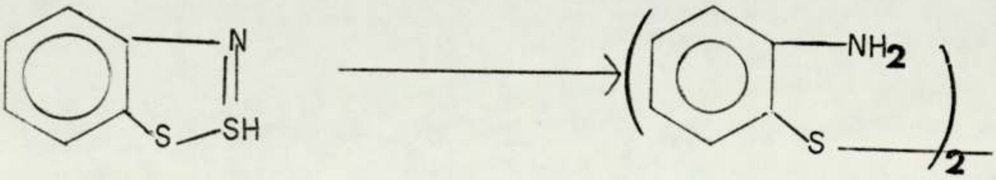
It was not possible to prepare asymmetric diarylditellurides by reducing a mixture of two different aryltelluriumtrichloride or irradiating a benzene solution containing diphenyl and bis(4-methoxypheny)ditelluride[22]. More recently Dance[23] has provided the first evidence for the existence of unsymmetric diarylditellurides, R-Te-Te-R' by the examination of the mixture of two ditellurides by mass and 'H n.m.r. spectroscopies.

The reduction of aryltellurium trichlorides by sodium sulphide has been extensively employed to produce diarylditellurides, Bergman[8] found that aryltellurium trichlorides were reduced to ditellurides by hydrazine in ethanolic medium and gave a lower yield than with other reduction methods.

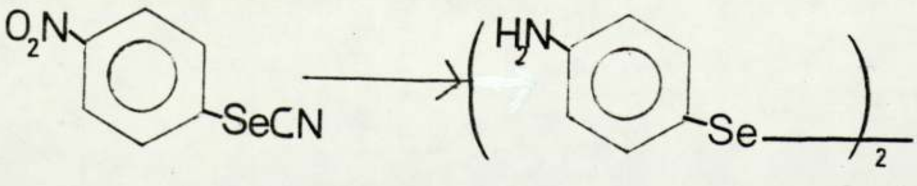
In the present work new diarylditellurides with an amino-group in the ortho position are reported. Several diarylditellurides with carbonyl or acetal groups in ortho position were prepared from alkyltellurides by cleavage of the alkyl group and air oxidation of the tellurol intermediate in acidic medium[16a] as follows :



In the field of organo sulphur or selenium compounds, there are several diaryldisulphides or diselenides with a functional group in the ortho position, e.g. 2-mercapto benzothiazole was readily cleaved by nickel to yield o-aminophenyldisulphide[24] .



Or the reduction of p-nitrophenylselenocyanate with $Na_2S_2O_5$, followed by oxidation with H_2O_2, gave bis(p-amino phenyl)-diselenide.[25]



Dithiodipyridine exists in the isomeric forms, 2,2' dithiodipyridine and 4,4'-dithiodipyridine which are available for bonding to metal as $CoCl_2$ and $CoBr_2$ [26].

2,2-dipyridiyl diselenide was prepared by oxidation of 2-selenopyridine by peroxide and gave yellow needles[27]. No pyridyl-derivatives of tellurium have been reported.

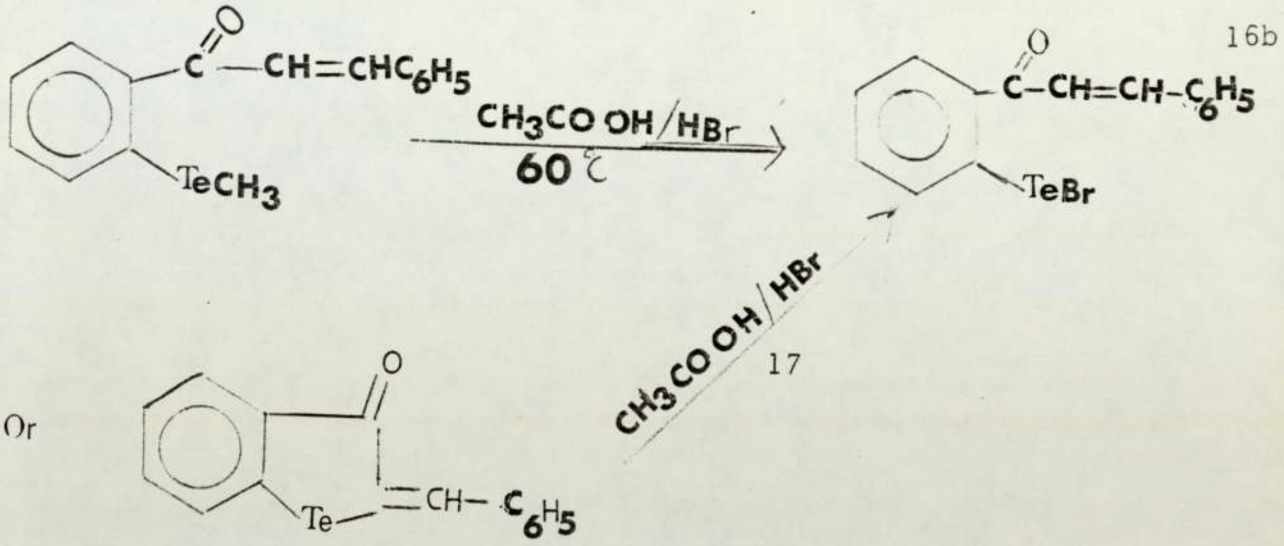
Diorgano ditellurides often undergo tellurium-tellurium bond cleavage when reacted with transition metal compounds to afford material in which RTe groups bridge metal centers [4] but two elements have been reported to give simple complexes with R_2Te_2 ; e.g. ($((C_6H_5)_2 Te_2)HgCl_2$[28], $(p\text{-}MeOC_6H_4)_2Te_2HgI_2$,[29] and uranium $((C_6H_5)_2Te_2)UCl_5$ [30]. More recently Davies[31] reported syntheses simple complex ditellurides with copper (1) halides ; e.g. R_2Te_2CuX where R is ethyl, butyl, pentyl, phenyl and phenetyl, X is Cl or Br.

RTeCl :-

With the exception of the 2-naphthyltellurium iodide, it has not been possible to isolate other aryltellurium halides, which do not have in the ring a stabilising carbonyl group in ortho-position to the tellurium atom. Aliphatic tellurium halides, RTeX, are still unknown. However, aromatic derivatives can be prepared in a solution from diaryl ditellurides and equimolar amount of elementary halogen in the presence of thiourea, selenourea or a phosphine selenide [32].

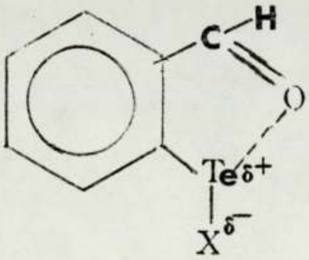
$$C_6H_5Te\text{-}Te\text{-}H_5C_6 + X_2 + 2L \longrightarrow 2C_6H_5TeLX$$

Organotelluriummonohalides were prepared by Piette and Co-workers described as follows :



The successful preparation of 2-formylphenyltellurium derivatives RTeX (X = Cl, Br, CN, SCN^-) has been claimed [18] . Chlorine with 2-formylphenyltellurium chloride gave trichloride [16a] .

The 'H n.m.r. investigation employing carbon disulphide solution of the 2-formylphenyltellurium derivatives, RTeX (X = Cl, Br, CN SCN) [18] showed the existence of the molecule in the conformation



which permits the tellurium atom to interact with the carbonyl group. This interaction sufficiently stabilizes the tellurium halides which is now co-ordinatively less unsaturated to allow the isolation of these compounds.

The crystal and molecular structure of 2-formylphenyltellurium bromide has been determined by Piette, [33] . The molecule has a planar cis configuration. The co-ordination of the Te(II) atom is bonded to an oxygen, a carbon and a bromine with all four atoms in one plane. Figure (A) gives more details about these compounds.

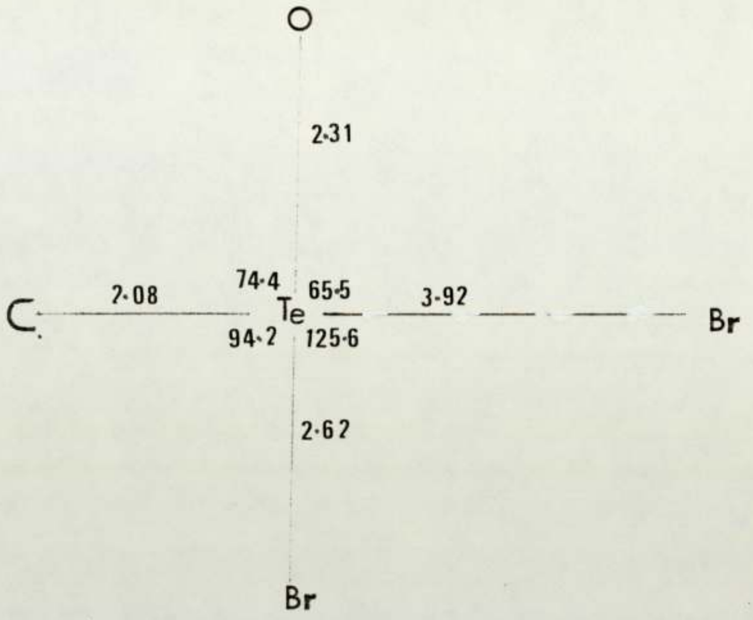
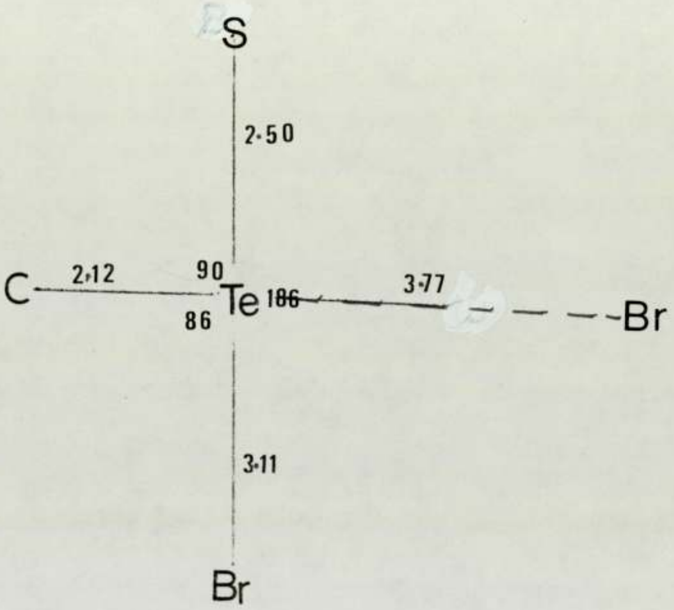


Fig. (A)

The structure described above with the model proposed by Foss

The crystal structures of the phenyltelluruium halide thiourea adducts were determined by Foss and Coworkers[34, 35]. The tellurium atom in the compounds $C_6H_5TeX.SC(NH_2)_2$ (X = Cl, Br) is bonded to a sulphur, a carbon and a halogen atom with all four atoms in one plane. The chlorine or bromine atoms from the next molecule approach within 3.71A° and 3.77A° respectively. These long distances indicate weak bonding . This presumably results from the removal of electron density from the 5p orbital by the group <u>trans</u> to the weakened bond. The angle between the directions of the tellurium-carbon and tellurium-halogen bond is 164° in both cases .

The arrangement of the ligands around the divalent tellurium atom can be regarded as squre planar with a vacant position trans to the phenyl group.



The structure of phenylthiourentelluriumbromide

Organo-Tellurium IV Compounds :-

The compounds treated in this section included R_2TeX_2, $RTeX_3$ and R_3TeX.

R_2TeX_2 :-

The reaction of diorganyltellurides with the elemental halogen which is a widley used method for the synthesis of diorganyl-tellurium dihalides, was used to prepare a number of new derivatives[36] :

$$R_2Te^{II} + X_2 \longrightarrow R_2Te^{IV}X_2$$

Several diaryltellurium dicarboxylates have been prepared, either by the reaction between the corresponding telluriumdichlorides with metal carboxylates [37b]:

$$Ar_2TeCl_2 + 2\ AgCCOR \longrightarrow Ar_2Te(OCOR)_2 + 2\ AgCl$$

or via the lead tetracetate oxidation of tellurides [37a] :

$$Ar_2Te + Ph(OAC)_4 \longrightarrow Ar_2Te(OAC)_2 + Pb(OAC)_2$$

McWhinnie [38] has reported that the sodium salt of <u>ortho</u>-phthalic acid reacts with diaryltellurium dichlorides to give dimeric tellurium phthalates. Quite recently Tamagaki, Hatanaka and Kozuka [39] have reported a facile method for the preparation of a number of tellurium dicarboxylates from diphenyltelluroxide with an equivalent of acetic acid [39].

$$Ph_2TeO + 2HOAC \longrightarrow Ph_2Te(OAC)_2$$

Meanwhile the diphenyltellurium diformate was attained in a quantitiative yield by the reaction of telluroxide with a slight excess of formic acid :

$$Ph_2TeO + HCOOH \longrightarrow Ph_2Te(OCOH)_2$$

or by ligand exchange reaction of the corresponding diacetate with a large excess of formic acid ;

$$Ph_2Te(OAC)_2 + 2HCOOH \longrightarrow Ph_2Te(OCOH)_2$$

Reaction of dialkyl or diaryltellurium-dihalides with sodium alkoxides gave open chain diorganodialkoxytellurium compounds[40]

$$R_2TeCl_2 + 2\ NaOMe \longrightarrow R_2Te(OMe)_2 + NaCl.$$

It has now been established that one chlorine atom in 4-ethoxyphenyltelluriumtrichloride was replaced at room temperature by a phenyl group in a reaction with triphenyl lead chloride[41].

$$Ph_3PbCl + p\text{-}C_2H_5OC_6H_4TeCl_3 \longrightarrow Ph_2PbCl_2 + Ph(p\text{-}C_2H_5OC_6H_5)TeCl_2$$

Paul[42] has synthesised diphenyltellurium dichloride from organotin compounds with telluriumtetrachloride or with phenyltellurium trichloride.

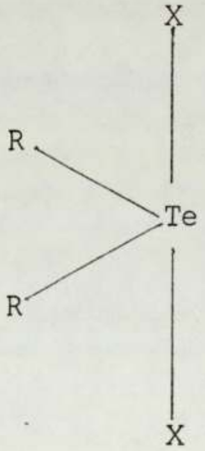
$$(C_6H_5)_4Sn + TeCl_4 \xrightarrow[\text{reflux}]{\text{Toluene}} (C_6H_5)_2TeCl_2 + (C_6H_5)_2SnCl_2$$

$$(C_6H_5)_3SnCl + PhTeCl_3 \longrightarrow (C_6H_5)_2SnCl_2 + (C_6H_5)_2TeCl_2.$$

The recently reported synthesis of triphenyltellurium-pseudohalides [43a] together with crystallographic data[43b] and the crystal and molecular structure of $(Ph_3Te)\ (NCS)$[44] relate to new results, communicated in this thesis, on the compounds ; $R_2Te(NCS)_2$ where R = Ph, $p\text{-}CH_3O\text{-}C_6H_4$ and $p\text{-}C_2H_5OC_6H_4$.

The complexes of thiocyanate ions are known with most of the complex-forming metal ions. One aspect of these compounds which has been of interest is the mode of bonding of this ligand, either the nitrogen or the sulphur may be bonded to the metal ion (isothiocyanate and thiocyanate) to be designated $NC\bar{S}$ or SCN^- respectively.[45a] According to the concepts of Pearson[45b] the nitrogen end of this ion is hard, and the sulphur end is a soft base. Consequently, N-bonding is expected with hard (class a) metal ions while S-bonding should take place with those of soft (class b). Further, bridging of two metal ions in form M-NCS-M' is well known[45a].

It is known that diorganyltelluriumdihalides have a ψ-trigonal bipyramidal structure[19,46]. The axial positions are occupied by the halide (more electronegativity) and the equatorial positions are occupied by the two remaining organic groups and the non-bonding electron pairs.



The structure of R_2TeX_2

Hence, it is of interest to know for the reaction :

$$R_2Te + (NCS)_2 \longrightarrow R_2Te(CNS)_2$$

whether the soft nature of tellurium will favour S bonding in the product or whether the greater electronegativity of nitrogen will be required to accommodate the electron density associated with the non-bonding molecular orbital in the axial bond system.

Triorganotellurium salts ; R_3TeX

This category includes a large variety of compounds. (R_3) may be triaryl, diarylalkyl, aryldialky., and trialkyl. The anion X may include almost any anionic species. The following equations illustrate the various methods which have been used for the preparation of these compounds :

(1) Reaction of tellurides with organic halide e.g.[47]

$$Ph_2Te + CH_3I \longrightarrow Ph_2CH_3TeI$$

(2) Reaction of various tellurium compounds with organometallic compounds :[48, 49]

$$TeCl_4 + 3RMgX \longrightarrow R_3TeCl + 3MgClX$$

(3) Exchange of the anion ;[47]

$$R_3TeI + AgX\ (X=Br, Cl) \longrightarrow R_3TeX + AgI$$

Triphenyltelluronium pseudohalides $(C_6H_5)_3TeX$ (X = CN, N_3, NCO NCS, NCSe), are synthesised by reaction of triphenyltelluronium-chloride and excess alkali pseudohalides[43a].

The triphenyltelluronium pseudohalides decompose to form diphenyltelluride and phenyl pseudohalides as shown below :

$$Ph_3TeX \longrightarrow Ph_2Te + PhX$$

which is supported by T G A and mass spectra data[34a].

There are no crystallographic studies on the structures of trialkyltelluronium halide, but recently Titus and Ziolo[44] have reported the crystallographic study of the structure of triphenyltelluronium-isothiocyanate, and observed that the crystals of triphenyltelluroniumisothiocyanate contain oligomers in the solid state. Three crystallographically indpendent $(C_6H_5)_3Te(NCS)$ units form discrete centrosymmetric dimers and tetramers separated by Van der Waals distances. The dimer has a chair configuration with dihedral angle 93.2°. The (NCS) group is nearly linear and therefore, nearly parallel to other groups in the dimer. The two dimeric sub-units are joined by a long Te-S interaction 3.616A° to give an overall step configuration to the tetramer with dihedral angle 99.9°.

The oligomers are predominantly ionic with tellurium-nitrogen and tellurium-sulphur distances significantly shorter than respective Van der Waal's distances. The mean Te.....N distance is 3.1A° and Te----S distance is 3.43 Å. The C-Te----X (X = S, N) interaction are approximately linear and range from 169.1° to 179.1°.

The three crystallographically independent cations have the expected trigonal-pyramidal shape but possess no symmetry due to the conformation adopted by the phenyl ring. Figures A, and B give more details of this compound.

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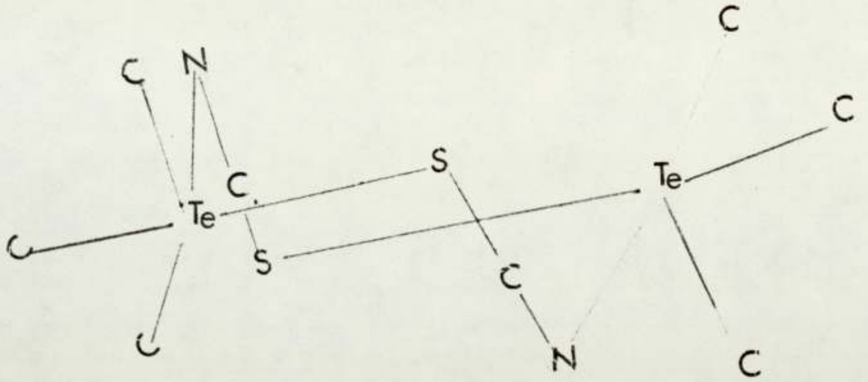

Fig. (A) The $(C_6H_5)_3$ Te(NCS) dimer

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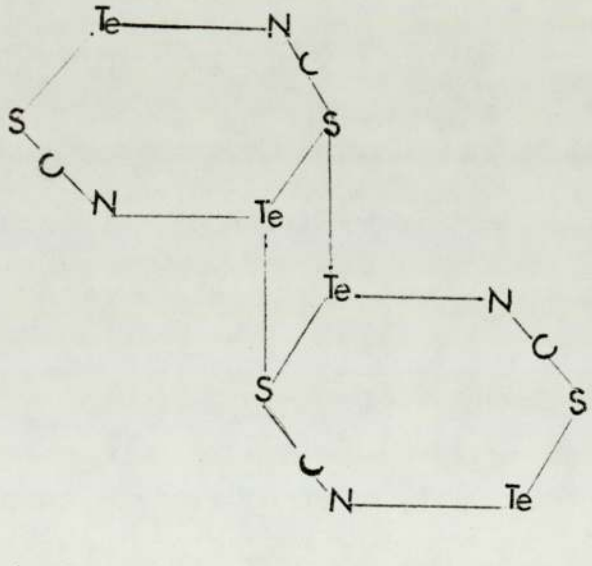
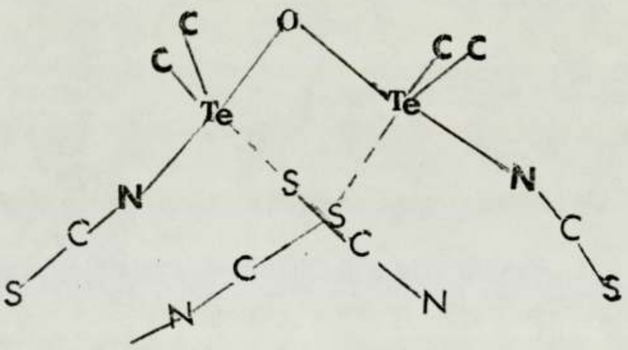


Fig (B)$C_6H_5)_3$ Te (NCS) Tetramer

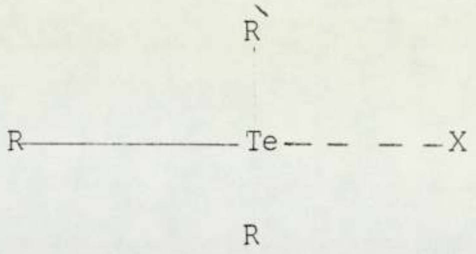
In earlier literature the bis(isothiocyanatodiphenyltellurium(iv) oxide was synthesised by mixing aqueous solution of diphenyl tellurium(iv)-dichloride (near boiling) and excess sodiumthiocyanate [50].

The crystal structures of $(Ph_2TeNCS)_2O$ has been reported by Mancinelli, Titus and Ziolo [51]. Three-dimensional X-ray crystal structure analysis shows that $(Ph_2TeNCS)_2O$ is molecular in the solid state. The molecule has two-fold symmetry, with the rotation axis passing through the oxygen atom and bisecting the Te-o-Te angle. The ether-like Te-o-Te moiety is bent, 121.7°, with a Te-O distance of 1.985 A°. An intermolecular Te-S contact at 3.416 A° completes a square-pyramidal geometry around the tellurium atom, and links the molecule into chains running parallel to the C axis. The N-Te-O axis is non-linear at 172.2° and is nearly coplaner with the Te-O-Te plane at 8.5°. - The Te-N bond distance, 2.4 A°, is considerably longer than the sum of covalent radii, indicating a tendency toward ionic character in the bond.



The Structure of $(Ph_2TeNCS)_2O$

Another interesting phenomenon observed by Dance [52], was the behaviour of Ph_2MeTeX (Where X is Cl, Br, I) in chloroform solutions. The conductivity of these telluronium salts in dimethylformamide (DMF) and in dimethylsulphoxide (DMSO)solutions indicatates that considerable ion pairing occurs in solutions :-



The 'Hn.m.r. spectra were recorded for these telluronium salts whichare soluble in deuterio chloroform, and gave singlets with satellite peaks (caused by coupling between 'H and ^{125}Te (spin $\frac{1}{2}$) due to methyl group which is still attached to the tellurium atom). But these singlets are in different positions and decrease with time at different rates while growing other singlets in different positions due to methyl halides (table below).

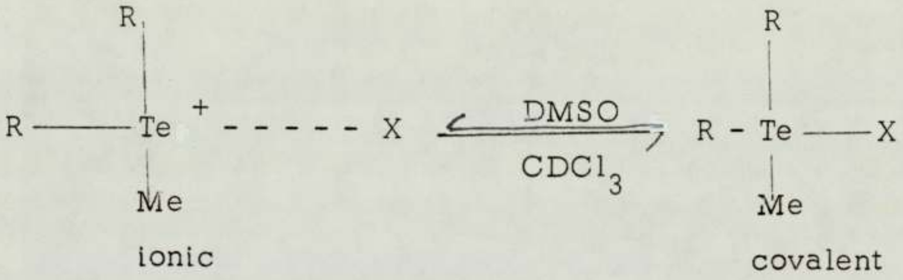
Compound	Solvent	Resonance 1 (ppm)	Resonance 2 (ppm)
$Ph_2MeTe^+I^-$	$CDCl_3$	3.04	2.15
$Ph_2MeTeBr$		2.90	2.61
$Ph_2MeTeCl$		2.76	2.96
Ph_2MeTeI	DMSO	2.69	2.15

The positions of the methyl resonances occurring in the PMR specra of Diphenylmethyltelluronium salts (Dance thesis).

The difference in the positions of the methyl resonances for telluronium salts due to the change in anion has produced a change in the electronic environment at the tellurium atom.

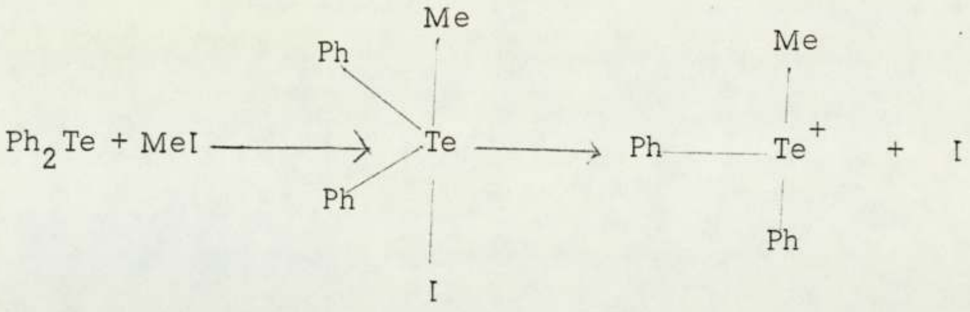
The n.m.r. spectrum of Ph_2MeTeI in deuterio DMSO contain a methyl singlet at 2.69 ppm. This singlet has a satellite. The low δ value of the resonance is attributed to the methyl group attached to tellurium.

Hence, Dance concluded that the telluronium salts in chloroform formed a covalent form which decomposed to give diphenyltelluride and methylhalides and in DMSO solutions where the ionic form is present, little decomposition took place.


$$R-\overset{R}{\underset{Me}{Te}}{}^{+}\,-\,-\,-\,-\,-\,X \;\underset{CDCl_3}{\overset{DMSO}{\rightleftharpoons}}\; R-\overset{R}{\underset{Me}{Te}}-X$$

A simple kinetic investigation of the reaction between methyliodide and diphenyltelluride was attempted using n.m.r. spectroscopy. The first product observed was the covalent form of diphenylmethyltelluronium iodide.[52] Subsequently, the ionic form was also formed which is considered to have exclusively axial methyl and halide groups within a pseudo-trigonal bipyramidal arrangement about tellurium atom.

The plot of concentration against time for the ionic form is sigmodial, indicating that it has been formed from an intermediate. The covalent form was initially formed more rapidly than the ionic form, but finally, the rates are reversed.



Mass spectroscopy data for Ph_2MeTeX show the thermolysis pathway is

$$Ph_2RTeX \longrightarrow Ph_2Te + RX.$$

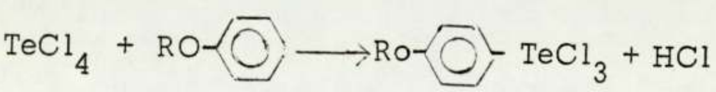
$RTeCl_3$:-

A fair number of new organyltelluriumtrihalides have been prepared by established methods such as :- [53, 54]

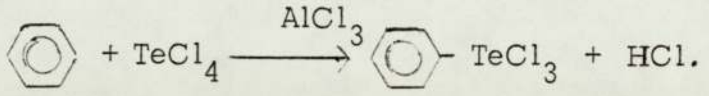
Diarylditellurides were converted to aryltellurium trichloride by halogen e.g.

$$R_2Te_2 + X_2 \longrightarrow RTeX_3$$

or by the condensation of telluriumtetrachloride with aromatic compounds containing activating substituent such as alkoxy group has been known for long time [55] :



Guenther[56] found that the trichlorotelluro group can be introduced into benzene by refluxing it with a 1:2 molar mixture of telluriumtetrachloride and aluminium chloride until an amount of hydrogenchloride equimolar to the telluriumtetrachloride had been generated.



The arylation of telluriumtetrachloride to phenyltellurium trichloride was carried out in 98% yield with triphenyl lead chloride and with triphenyl tin chloride[42].

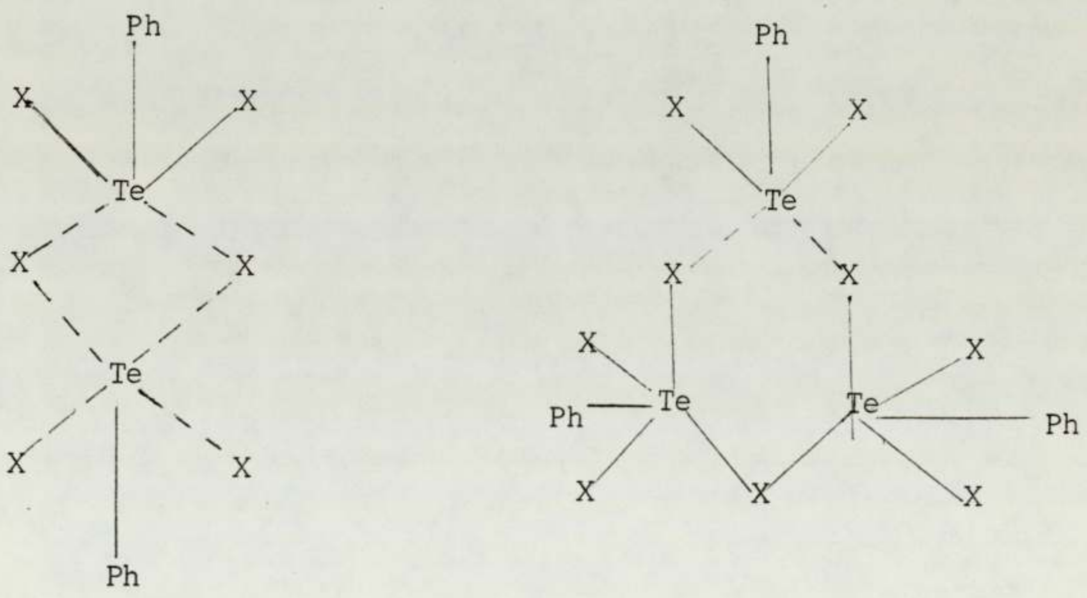
$$Ph_3PbCl + TeCl_4 \longrightarrow PhTeCl_3 + Ph_2PbCl_2$$

$$Ph_3SnCl + TeCl_4 \longrightarrow PhTeCl_3 + Ph_2SnCl_2$$

The reaction of organomercuric chloride with tellurium tetrachloride in boiling dioxane gave aryltelluriumtrichloride in good yields use of dioxane has the advantage of precipitating mercuric chloride as dioxane adduct[57].

$$R\,HgX + TeCl_4 \xrightarrow{\text{dioxane}} RTeCl_3 + HgCl_2\ \text{dioxane}$$

There are many works on the structural investigation of dialkyl and diaryltellurium dihalides, and trialkyl and triaryl-tellurium monohalides. The structures of these compounds are now well established and understood. The structure of aryltelluriumtrichlorides were investigated by Thavornyutikarn[58]. He established assignments of tellurium-halogen modes, and gave possible structures built up from the donor acceptor interactions of $PhTeX_2^+$ and X^- units which agree with the theory of Wynne and Pearson[59]. The structures have five- co-ordinate tellurium atoms and an absence of bonds to halogens in positions *trans* to the phenyl groups. This process of building up the structures also accounts for the differing degrees of association of the molecules Thus if $PhTeCl_3$ and $PhTeI_3$ are dimers, $PhTeBr_3$ may be a trimer as illustrated below :-



Dimer

trimer

The structure of $RTeX_3$

CHAPTER TWO

EXPERIMENTAL

Chemicals :-

All chemicals were obtained from commercial sources and "Analar" grade reagents were used when necessary. Tellurium tetrachloride ($TeCl_4$) which is the important starting material, was supplied by British Drug House (B.D.H.) in a sealed ampoule. Azobenzene was supplied by(B.D.H.).

Solvents :-

All solvents were obtained from commercial sources. If pure solvents were needed, they were purified according to literature methods, [60] i.e. benzene[60a], toluene [60b] methanol [60c] and dioxane [60d]

Elemental Analysis :-

Micro-analysis for carbon, hydrogen, halogen, nitrogen, and sulphur were carried out by the micro analytical laboratories of the Chemistry Department of Aston University.

Physical Measurements :-

(a) Infrared spectra :-

Spectra in the range 4000-250 cm^{-1} were recorded on a Perkin-Elmer 457 Spectrophotometer. Solid state specimens were prepared as Nujol mulls supported between KBr plates, CsI plates or polythene plates, or examined as KBr discs, prepared by pressing a mixture of sample and powdered KBr. Solution spectra were obtained from 10% solutions in chloroform, using a standard liquid cell, with chloroform as reference.

(b) 400-200 cm^{-1} :-

Spectra in this range were recorded on a Perkin-Elmer Spectrophotometer model 225. Solid state samples were prepared as Nujol mulls supported between CsI plates or between two sheets of polythene, if the compounds attacked CsI plates.

The spectra were recorded on slit programme 5.0, speed 0.1 (fast) and pen traverse time 10 sec.

Nuclear Magnetic Resonance (n.m.r.) spectra :-

All proton magnetic resonance spectra at 60 MHZ were recorded on Perkin-Elmer R 14 spectrometer. Tetramethyl-silane (TMS) was used as internal reference.

Mass spectra :-

The mass spectra of all compounds were recorded on AEI MS9 Spectrometer at 70 eV.

Electronic spectra :-

Electronic absorption spectra in the ultra violet and visible regions were obtained using a Unicam SP800 spectrometer using matched silica cells.

Conductivity Measurements :-

Molar conductivities were measured with a Mullard conductivity bridge, using a standard conductivity cell type E 7591/B with a cell constant of 1.36 and with bright platinum electrodes.

Melting Points :-

These were determined using a Gallenkamp electrically heated melting point apparatus.

CHAPTER THREE

SOME NEW ORGANOTELLURIUM COMPOUNDS DERIVED FROM AZOBENZENE

INTRODUCTION

Organotellurium (IV) compounds have previously been prepared by established methods such as the halogenolysis of ditellurides in an organic medium[53,54] the condensation of tellurium tetrachloride with aromatic hydrocarbons containing an activating substituent, (e.g. OR, NH_2),[29], and reaction of arylmercuric chlorides with tellurium tetrachloride[57].

$RTeX_3$($R = CH_3$, Aromatic) have associated structures[61,58]. In addition, X-ray crystallographic investigation of the structure of 2-chloroethyltellurium (IV) trichloride has clearly shown a polymeric structure containing penta co-ordinate tellurium[62]. Thavornyutikarn considered a series of Raman and infra-red spectra of aryltellurium (IV)trihalides ; tellurium-halogen vibrations were assigned and it was suggested that the molecules are associated to give five co-ordinate tellurium atoms[58].

The aryltellurenyl compounds, ArTeX, where Ar is phenyl, and X represents Cl, Br, ClO_4, NO_3 and CNS, have been isolated only as complexes with donor molecules; Foss and Co-workers[34,35] found the addition of phenyltellurium-trichloride in methanol to thiourea in warm water yielded $(C_6H_5)Te\left[SC(NH_2)_2\right]Cl$. These investigators have carried out complete crystallographic studies of these molecules which show that the sulphur atom is co-ordinated directly to the tellurium atom (introduction). However, co-ordination is not essential for stabilisation of RTeX since Renson[16a] has shown that a bulky substituent ortho to tellurium in the aromatic nucleus may lead to the isolation of $\overset{II}{RTeX}$.

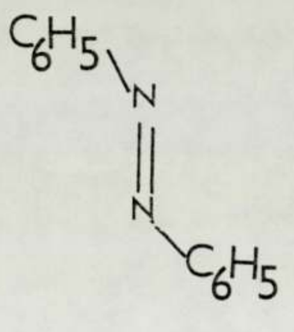
Controlled halogenolysis of a ditelluride was used to prepare 2-naphthyltellurium(II)iodide ; [54] .

$$R_2Te_2 + I_2 \longrightarrow RTeI, \text{ R is naphthyl only.}$$

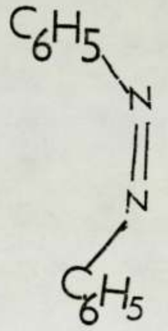
Recently, Klar, has reported another controlled reaction of ditellurides, R_2Te_2 with the halogen X_2 in nonpolar solvents to afford simple tellurenyl halides [63] .

$$R_2Te_2 + X_2 \longrightarrow RTeX$$

Azobenzene (orange-red crystals) exist as geometrical isomers, the trans - form being the ordinary commercial variety. Azobenzene has a zero dipole moment and melts at 68°C, the cis - form is a bright red crystalline material with a dipole moment of 3.0D. The unstable cis form passed rapidly into the stable trans form.



trans, μ = 0

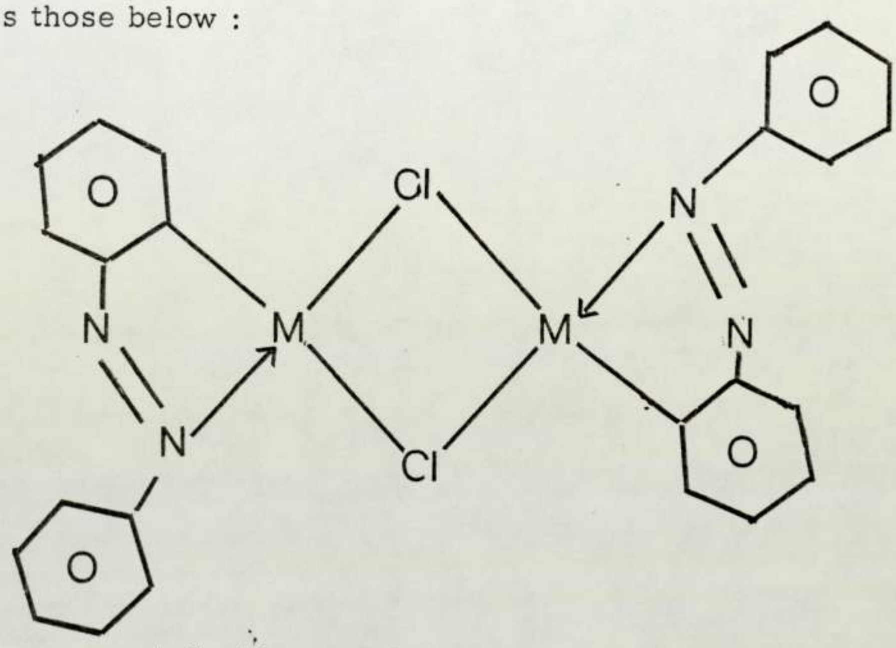


Cis, μ = 3.0 D

X-ray crystal analysis of solid trans azobenzene by Brown [64] showed that two non-equivalent molecules in the unit cell have slightly different geometrical configurations.

Few organotellurium compounds are known which contain tellurium to nitrogen bonds, apart from examples containing the thiocyanato group [43a] .

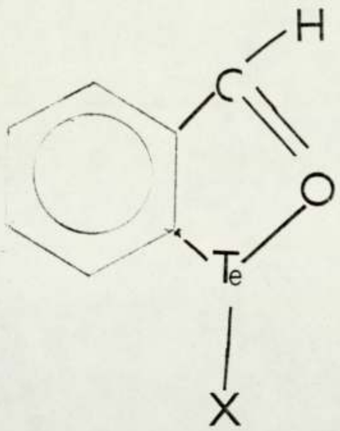
The ready metallation of azobenzene by both transition metals and non-transition metals[65,66] is well known . The reaction has been found between aromatic azo compounds and potassium tetrachloro platinate (II) or palladium(II)dichloride producing species such as those below :



Azobenzene reacted with mercuric acetate in methanol formed (phenylazophenyl 2C,N')mercury(II)acetate, the latter with lithium chloride gave (phenylazophenyl 2C,N')mercuric(II)chloride.[67, 68.]

The structure of an azobenzene complex of Pd(II) was studied by Siekman and Weaver[69] . Perhaps the most interesting aspect of this structure is that the potentially bidentate ligand, azobenzene forms a stable complex single σ-bond to the metal and thus maintains a square planar configuration around the Pd atom.

The preparation of 2-formylphenyltellurium halides has been claimed[18a] and the n.m.r. investigations using a carbondisulphide solution of 2-formylphenyltellurium derivatives showed that the molecule exists in conformation.



which seeing the availability of a potential donor group (CO) occupying ortho positions of an aromatic ring bound to tellurium, permits the isolation of monomeric organotellurium (II) halide or organotellurium(IV)trihalide .

The observation by Cope and Siekman[65,69] that azobenzene reacts with platinium (II), palladium (II)chlorides and Piette[18a] on 2-formylphenyltellurium (II) halides has led us to search for similar reactions including that of azobenzene with tellurium tetrachloride or of (phenyl azophenyl 2C, N')mercury(II)chloride with tellurium tetrachloride.[70]

The availability of a potentially co-ordinating nitrogen atom in the azo-group introduces the possibility that monomeric organotellurium-trihalides may be formed as well, since it is known that the association normal to $RTeX_3$ (X = halogen) may be broken down by a reaction with Lewis bases such as tetramethylthiourea[70].

It was, therefore, likely that reduction of the azobenzene derivatives of tellurium (IV) with mild reducing agents would give tellurenyl compounds, and it was also possible that use of stronger reducing agents would lead to an attack of the azo group and give a convenient route to aryltellurium compounds with ortho- amino-group.

This would be a new variety of ditelluride which should be soluble in dilute aqueous acid and which might, therefore, be of interest to other workers in our laboratory who wish to investigate the reaction of R_2Te_2 with Cr (II) in aqueous media.

EXPERIMENTAL

PREPARATION OF THE NEW ORGANOTELLURIUM COMPOUNDS DERIVED FROM AZOBENZENE AND THEIR COPPER DERIVATIVES

Preparative Work :-

The direct reaction of azobenzene with tellurium tetrachloride gave no sign of proceeding to any significant degree after several hours, consequently, the following transmetallation method was adopted based on (phenylazophenyl-2C,N') mercury (II) chloride prepared following Roling [68] .

The Modification of Roling's Synthesis to Produce $(C_{12}H_9N_2)HgCl$

In a round-bottomed flask equipped with a reflux condenser surmounted with a calcium chloride drying tube, were placed equal molecular amounts of the azobenzene (10gm) and mercuric acetate (18gm) in methanol (125ml.) (dried over anhydrous magnesium sulphate and distilled). The mixture was stirred by means of a magnetic stirrer and refluxed for 6 hours. (Roling's method reported 22 hours refluxing). At the end of the reflux period, the reaction mixture was allowed to cool to room temperature and then lithium chloride (5 gm) dissolved in hot methanol was added and the resulting thick mixture stirred for about 10 mins, whereupon it was poured into water ($\frac{1}{2}$l.). The resulting precipitate was filtered, and contained mercurials and the starting azobenzene.

Azobenzene was then extracted with hot petrolium ether until the extracts were colourless. The residue $(C_{12}H_9N_2)HgCl$ was recrystallised from hot benzene. Yield 40% (Roling separated azobenzene and $(C_{12}H_9N_2)$-HgCl by chromatography). The $(C_{12}H_9N_2)HgCl$ melted at 202°C lit[68] 202-204°C lit[68], yield 40%.

Found C, 34.41, H 2.25 N = 6.65

Required 34.65, 2.17 =6.73

(Phenylazophenyl-2C,N')tellurium (IV) trichloride.

(Phenylazophenyl-2C,N') mercury (II) chloride (3.2g) and tellurium (IV) chloride (2.0g) were refluxed in sodium dried dioxan (20 cm^3) for 6h under dry nitrogen. On cooling the 2:1 addition compound of dioxan and mercury (II) chloride separated as white plates which were removed by filtration. The filtrate was concentrated on a rotatory film evaporator and nitromethane (20 cm^3) added. Evaporation was taken to dryness and the residue was recrystallised from nitromethane to give an almost quantitative yield of orange crystals melting at 235°C. The crystals were soluble in methanol, chloroform, ether, nitromethane and acetonitrile. Solutions in acetonitrile are non-conducting.

The reduction of $(C_{12}H_9N_2)TeCl_3$ to $(C_{12}H_9N_2)\overset{II}{Te}Cl$ was carried out by two methods ;

1. (Phenylazophenyl-2C,N')tellurium (II) chloride :-

(Phenylazophenyl-2C, N')tellurium (IV)trichloride (0.2)gm. was suspended in water (20 ml.). The mixture was reduced by the solution of potassium metabisulphite (0.15)gm. in water (10 ml.). The solution was slowly added at 0°C with continuous stirring. The orange precipitate appeared, after the solution was used up, stirring was continued for another hour. An ether extraction was carried out to afford, after recrystallisation from ether, red crystals of the product of mp 80°C, yield 90%.

2. (Phenylazophenyl-2C,N')tellurium (II) chloride.

The above compound (3.5g) was dissolved in methanol (50 cm^3) and heated under reflux. A solution of hydrazine hydrate (0.5g) in methanol (50 cm^3) was added slowly to the refluxing solution. The solution was filtered and cooled to afford brown crystals of the product of m p 80°C and showing solubility in a wide range of organic solvents. (Yield, 80%).

Di-(o-aminophenyl)ditelluride:-

Sodium borohydride was added to a boiling methanolic solution of (phenylazophenyl-2C,N')tellurium (II) chloride until the deep red colour had disappeared. The solution was filtered, during this time the deep red colour returned and was then poured into water. An ether extraction was carried out to afford, after recrystallisation from ether red crystals of the product of m p 100°C.

(Phenylazophenyl-2C,N')tellurium (IV) chloridedibromide :-

(Phenylazophenyl-2C,N')tellurium (II) chloride (0.2g) in boiling carbon tetrachloride (25 cm^3) was treated with a solution of bromine (0.2g) in carbon tetrachloride (10 cm^3). Heating was continued for 10 min. after which the solution was filtered and cooled. Orange crystals formed which were recrystallised from benzene to m p 145°C.

Reduction of (phenylazophenyl-2C) (p-ethoxyphenyl)tellurium (IV) dichloride :-

(Phenylazophenyl2C,N')mercury (II) chloride (2.0g) and (p-ethoxyphenyl) tellurium (IV) trichloride were mixed in 1.4-dioxane (20 cm^3). The mixture was stirred and refluxed for 2h. On cooling, crystals of $HgCl_2 \cdot 2$ dioxan separated and were removed. Concentration of the solution, followed by the addition of n-hexane (10 cm^3) gave the crude dichloride.

The crude material was dissolved in refluxing ethanol (50 cm^3) and treated dropwise with an ethanolic solution of hydrazine. Addition of hydrazine was discontinued when evolution of dinitrogen ceased. Cooling the solution afforded orange crystals which were recrystallised from benzene to m.p 120°C. The material analysed as <u>(Phenylazophenyl-2C) (p-ethoxyphenyl)telluride</u>.

(Phenylazophenyl-2C,N')tellurium (IV) tribromide.

The above telluride (0.2g) in carbon tetrachloride (25 cm^3) was treated with bromine (0.1g) in carbon tetrachloride (10 ml) and refluxed for 10 min. The solution was filtered and cooled to afford orange <u>crystals</u> which were recrystallised from benzene to m.p 245°C.

Copper (I) halide :-

Copper (I) chloride was prepared as follows :
Copper (II) chloride (24 gm) was dissolved in degassed water (60 ml.), stirred under a nitrogen atmosphere, and an aqueous solution of sodium sulphite (48 gm) was added dropwise over a period of half an hour. The solution slowly changes colour from green to pale yellow. The solution was decanted from the white precipitate of copper (I) chloride. The precipitate was washed with distilled water, absolute alcohol, and dry diethylether (3 x 50 ml). The solvents were all degassed prior to use a nitrogen blanket was kept over the solution at all times.

The copper (I) chloride was vacuum dried and stored under nitrogen.

Di-o-aminophenylditelluride copper (I) chloride.

Copper (I) chloride (0.07g) was dissolved in acentonitrile under dry nitrogen and mixed with an etherial solution of di-o-aminophenylditelluride (0.3g). The solution was briefly warmed after which the dark brown <u>product</u> was separated and recrystallised from acetonitrile to m.p. 140°C.

Di-o-aminophenylditelluride copper (II) dichloride.

Anhydrous copper (II) chloride (0.05g) in acetonitrile (25 cm^3) was treated with an etherial solution ofdi-o-aminophenylditelluride (0.25g) under dry nitrogen. The mixture was stirred for 30 min, filtered, and treated with a further quantity of ether to induce precipitation of the product. The material decomposed at 90°C. The 1:1 stoichiometry was confirmed by quantitative recovery of the ditelluride after treatment of the complex with standard EDTA.

Regeneration of di-(o-aminophenyl)ditelluride

Di-(o-aminophenyl)ditelluride copper (II) dichloride (0.0329) gm was suspended in water (10ml.). The solution of EDTA (0.022)gm was added with continuous stirring and heating for ½h. The red precipitate appeared. An ether extraction was carried out to afford, after recrystallisation from ether, red crystals of the di-(o-aminophenyl)ditelluride of mp 100°C. The same method was used to generate di(o-aminophenyl)ditelluride from di-(o-aminophenyl)ditelluride copper (I) halide.

RESULTS

Analytical data for the new compounds are presented in (Table 1). All compounds were shown to be non-electrolytes in weakly polar solvents. The mass spectrum of (phenylazophenyl-2C, N') tellurium (IV)trichloride showed a parent ion peak at $^{m}/_{e} = 416$ ($^{12}C_{12}\ ^{1}H_{9}\ ^{35}Cl_{3}\ ^{14}N_{2}\ ^{130}Te$) together with other high mass peaks at $^{m}/_{e} = 381$, 346 and 311 corresponding to the stepwise loss of ^{35}Cl. The mass spectroscopic data is listed in table (2). Infra-red data are given in table (3), and are shown in figures 1, 2, 3, 4, 5, 6, 7, 8. The u.v.- data are given in table (5). The proton n.m.r. spectrum of $(C_{12}H_{9}N_{2})Te-(C_{6}H_{4}OC_{2}H_{5}-p)$ in carbontetrachloride was recorded. The centre of resonance of the triplet methyl of ratio 1:2:1, J = 15 Hz is at $\delta = 1.4$ ppm. Methylene shows a quartet of ratio 1:2:2:1, J = 25 Hz at $\delta = 4$ ppm. Aromatic protons absorb at $\delta = -(8-6.7)$ ppm. The ratio of aromatic (azobenzene + phenyl) peaks : $C_{2}H_{5}$ peak = 13:5 confirms the metallation of azobenzene and the presence of the p-ethoxyphenyl group. The n.m.r. spectrum of di(o-aminophenyl)ditelluride was recorded, showing correct integration (2:1), with a broad band resonance at $\delta = 4.20$ ppm attributed to the $-NH_{2}$ group.

TABLE 1

	Colour	m p	Found				Calculated			
			%C	%H	%N	%X	% C	%H	%N	%X
$(C_{12}H_9N_2)\overset{IV}{Te}Cl_3$	Orange	235°	34.7	2.18	6.74	25.6	35.5	2.17	7.08	25.1
$(C_{12}H_9N_2)TeCl$	Deep red	80°	40.1	2.67	8.20	11.0	41.7	2.61	8.1	10.3
$(O\text{-}NH_2.C_6H_4)_2Te_2$	Deep red	100°	32.3	2.78	6.22	-	32.8	2.80	6.37	-
$(C_{12}H_9N_2)TeClBr_2$	Orange	145°	28.8	1.74	5.24	-	28.5	1.78	5.50	-
$(p\text{-}C_2H_5O.C_6H_4)(C_{12}H_9N_2)Te$	Orange	120°	54.6	4.24	6.51	-	55.8	4.66	6.50	-

ANALYTICAL DATA FOR NEW AZOBENZENE DERIVATIVES OF TELLURIUM

TABLE 1 (continued)

		Colour	m p	Found				Calculated			
				% C	% H	% N	% X	% C	% H	% N	% X
	$(C_{12}H_9N_2)TeBr_3$	Orange	245°	27.1	1.72	4.45	-	26.2	1.64	5.1	- -
(A)	$((O\text{-}NH_2.C_6H_4)_2Te_2).CuCl$	Dark brown	140°	24.9	2.44	5.46	-	26.8	2.22	5.20	-
(B)	$((O\text{-}NH_2.C_6H_4)_2Te_2).CuCl_2$	Dark brown	90°	23.5	2.57	4.88	-	25.1	2.00	4.88	-

ANALYTICAL DATA FOR NEW COMPLEXES A, B AND FOR $(C_{12}H_9N_2)TeBr_3$

TABLE 2

Species	$^{m}/_{e}$	Rel. Int.
$(C_{12}H_9N_2)TeCl_3^+$	416 p^+	10
$(C_{12}H_9N_2)TeCl_2^+$	381	15
$(C_{12}H_9N_2)TeCl^+$	346	50
$(C_{12}H_9N_2)Te^+$	311	98
$C_6H_5Te^+$	207	50
$(C_6H_5)_2^+$	154	90
$(C_{12}H_8N_2)^+$	182	100
$(C_6H_5)^+$	77	100

Mass spectral data for (phenylazophenyl 2C,N^-)tellurium trichloride
Relative to ^{130}Te, ^{14}N, ^{12}C, ^{1}H, ^{35}Cl

TABLE 3 (Continued)

$(C_{12}H_9N_2)TeCl_3$	$(C_2H_9N_2)TeCl$	$(C_{12}H_9N_2)TeClBr_2$	$(C_{12}H_9N_2)(p\text{-}C_2H_5o\text{-}C_6H_4)Te$	$(C_{12}H_9N_2)TeBr_3$	Assignment
		264s			ν (TeBr) +
		259s			azobenzene mode
	247s				ν(TeCl)
		205s			ν (TeBr)
361m	364m	258w		355w	other bands below 400 cm^{-1}
319sh	312sh				
	270sh				
	259m				
225	218m	225			

Selected infra-red absorptions (to 200 cm^{-1}) for azobenzene derivatives of tellurium

TABLE 3

$(C_{12}H_9N_2)TeCl_3$	$(C_2H_9N_2)TeCl$	$(C_{12}H_9N_2)TeClBr_2$	$(C_{12}H_9N_2)(p\text{-}C_2H_5o\text{-}C_6H_4)Te$	$(C_{12}H_9N_2)TeBr_3$	Assignment
781	770	776	771	775;	
770	760	768	760	768	
709	709	705	712	705	ν(CH)
675	676	672	690	674	
	670 sh	670			
353					(TeCl)
	300			295	(TeN)
307s, br		303			(TeCl) + (Te N)
285 sh.		290 sh			
				260 sbr	(TeBr) + azobenzene modes
266 s, vbs					(TeCl) + azobenzene modes

Cont/d..

TABLE 4

Compound	cm^{-1}	Assignment
$(O\text{-}NH_2\text{-}C_6H_4)_2Te_2$	ν_{as} 3410	NH_2
	ν_s 3320	
	1600 deformation mode	NH_2
$NH_2\text{-}C_6H_5$ [A]	ν_{as} 3509	NH_2
	ν_s 3460	
	1600 deformation mode	NH_2
$(O\text{-}NH_2\text{-}C_6H_5)_2Te_2)$ $CuCl_2$	3350	NH
	3270	
	3205	
	3120	
$(O\text{-}NH_2\text{-}C_6H_5)_2Te_2$ CuCl	3240, v.br	NH

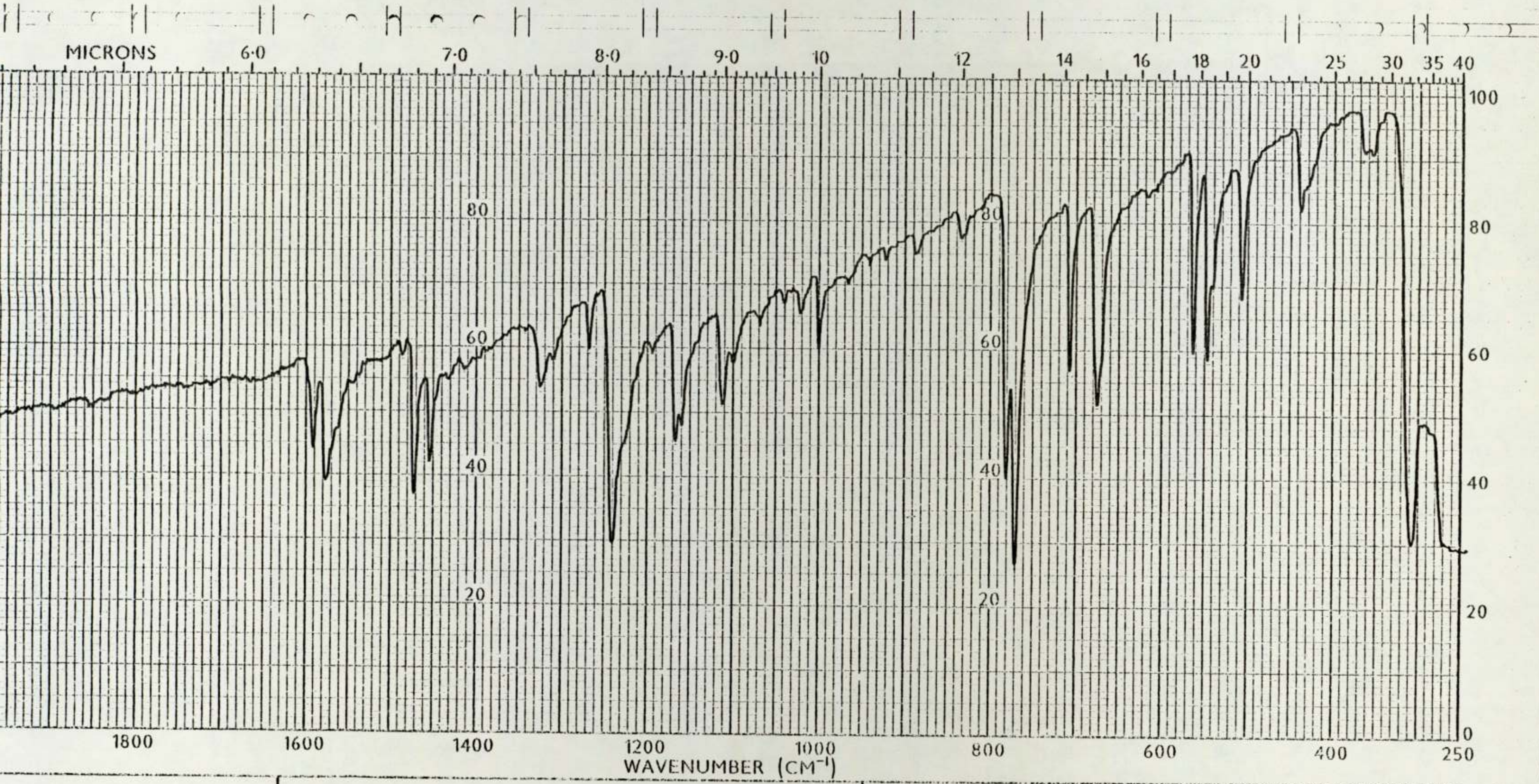
(A)

Infra-red data for New (o-aminophenyl)ditelluride and their Complexes

TABLE 5

COMPOUND	nm
$(C_{12}H_9N_2)TeCl_3$	230 360
$(C_{12}H_9N_2)TeCl$	230 347
$(C_{12}H_9N_2)TeClBr_2$	268 358
$(C_{12}H_9N_2)TeBr_3$	265 360
$(O\text{-}NH_2\text{-}C_6H_4)_2Te_2$	225 342 480

Ultra-violet data for new azobenzene derivatives of tellurium



.1·0%

/m. dia. disc.

REMARKS Infra-red spectra of $(C_{12}H_9N_2)TeCl_3$

Fig. (1)

SCAN SPEED Medium.

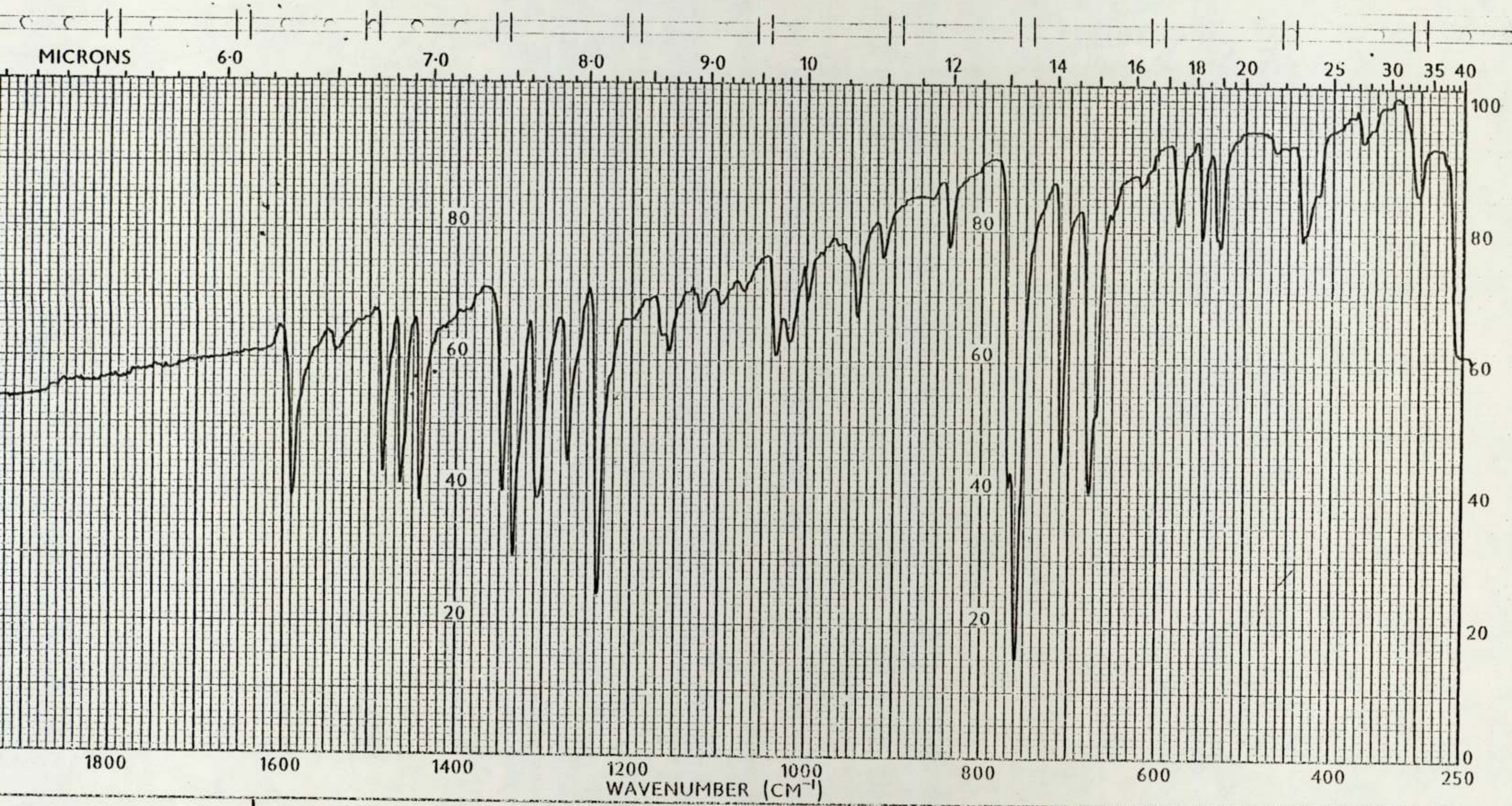
SLIT Standard.

RPK/215/1002 457-5001
Intek

OPERATOR V.M. Clenton.

DATE 22nd. March 1977.

REF. No. 9610.



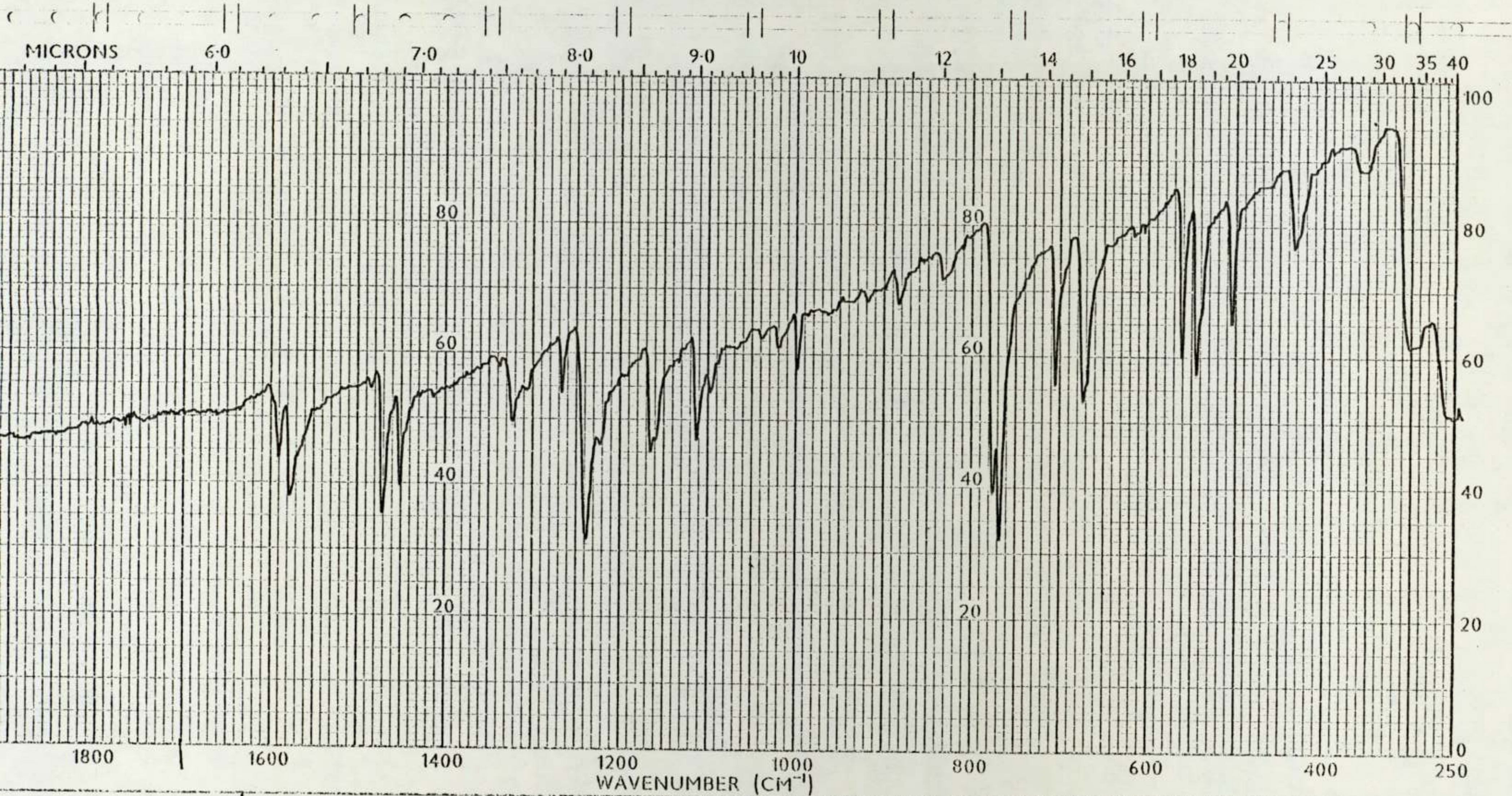
-o%
. dia : disc

REMARKS Infra-red spectra of ($C_{12}H_9N_2$)TeCl

Fig. (2)

SCAN SPEED Medium.
SLIT Standard
RPK/219/1002 457-5001
Intek

OPERATOR V.H. Clenton.
DATE 13th. December 1976
REF. No. 9211.

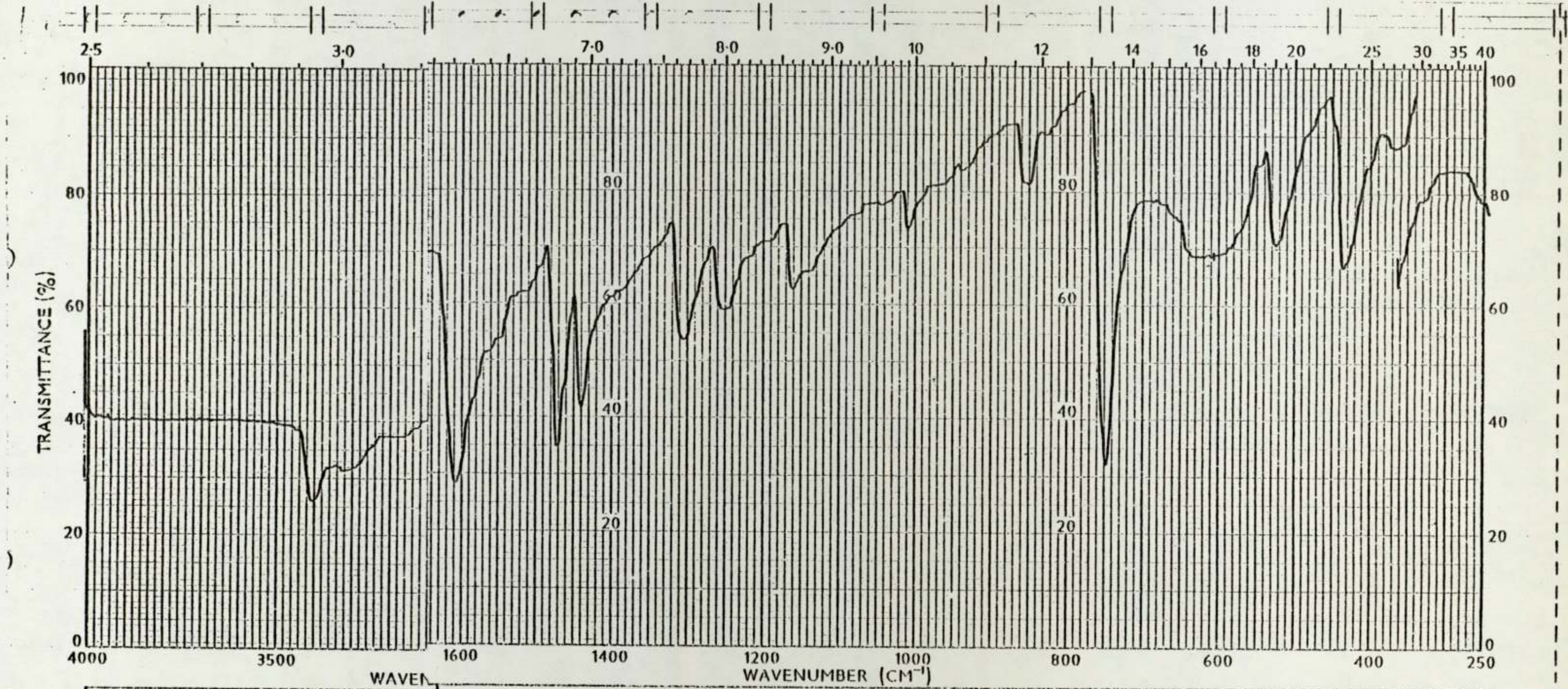


REMARKS Infra-red spectra of $(C_{12}H_9N_2)TeClBr_2$

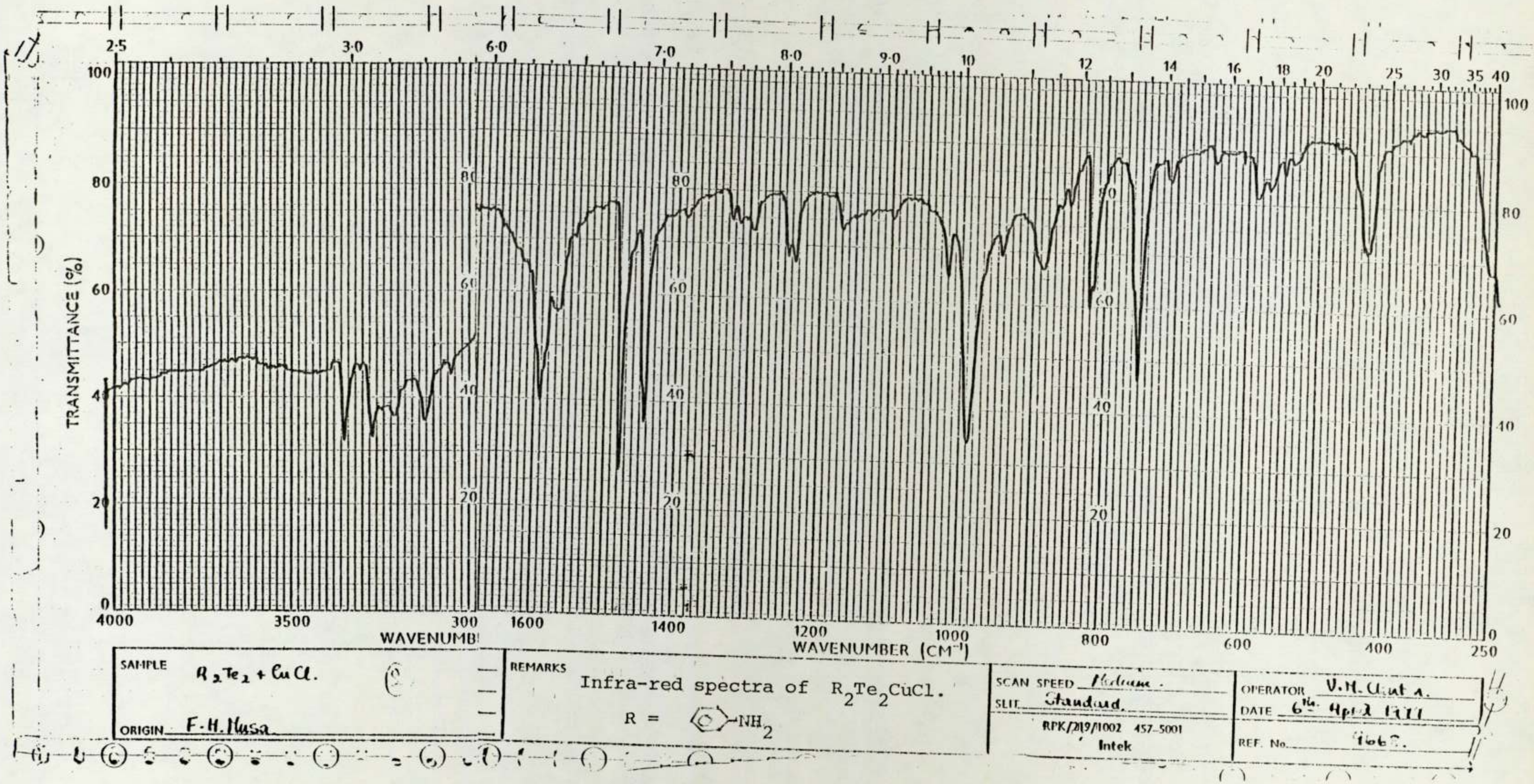
Fig. (3)

SCAN SPEED Medium.
SLIT Standard.
RPK/215/1002 457-5001
Intek

OPERATOR V.H. Clenton.
DATE 14th. December 1976
REF. No. 7250.

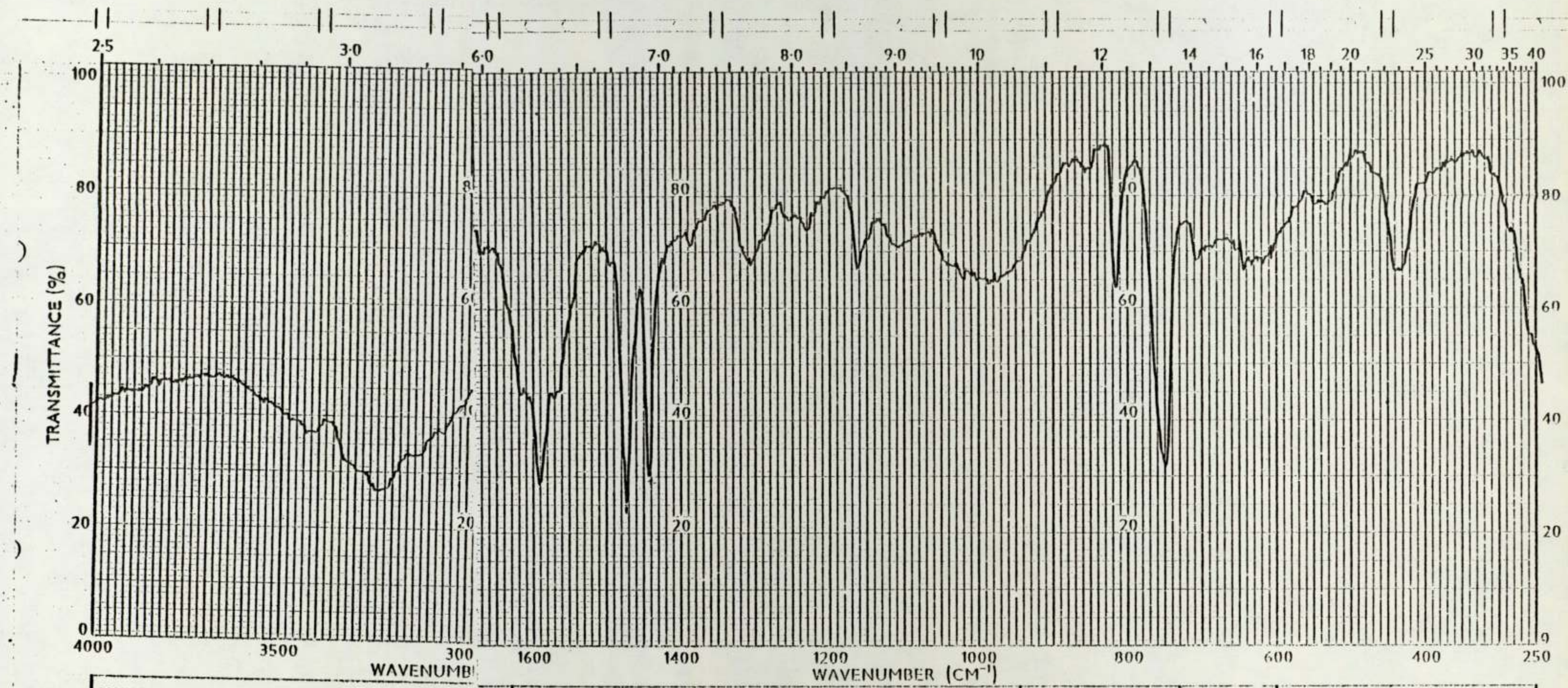


SAMPLE R_2Te_2, $\bigcirc$-NH_2	REMARKS Infra-red spectra of R_2Te_2	SCAN SPEED Medium.	OPERATOR V.H. Glenton.
		SLIT Standard.	DATE 8th March 1976
ORIGIN E. Hus[illegible]	R = $\bigcirc$-NH_2 Fig. (4)	RPK/219/1002 457-5001 Intek	REF. No. 9524



Infra-red spectra of R_2Te_2CuCl.

Fig. (5)



SAMPLE $R_2Te_2CuCl_2$

ORIGIN F. H. Musa.

REMARKS Infra-red spectra of $R_2Te_2CuCl_2$

R = o-amino-phenyl Fig. (6)

SCAN SPEED Medium

SLIT Standard

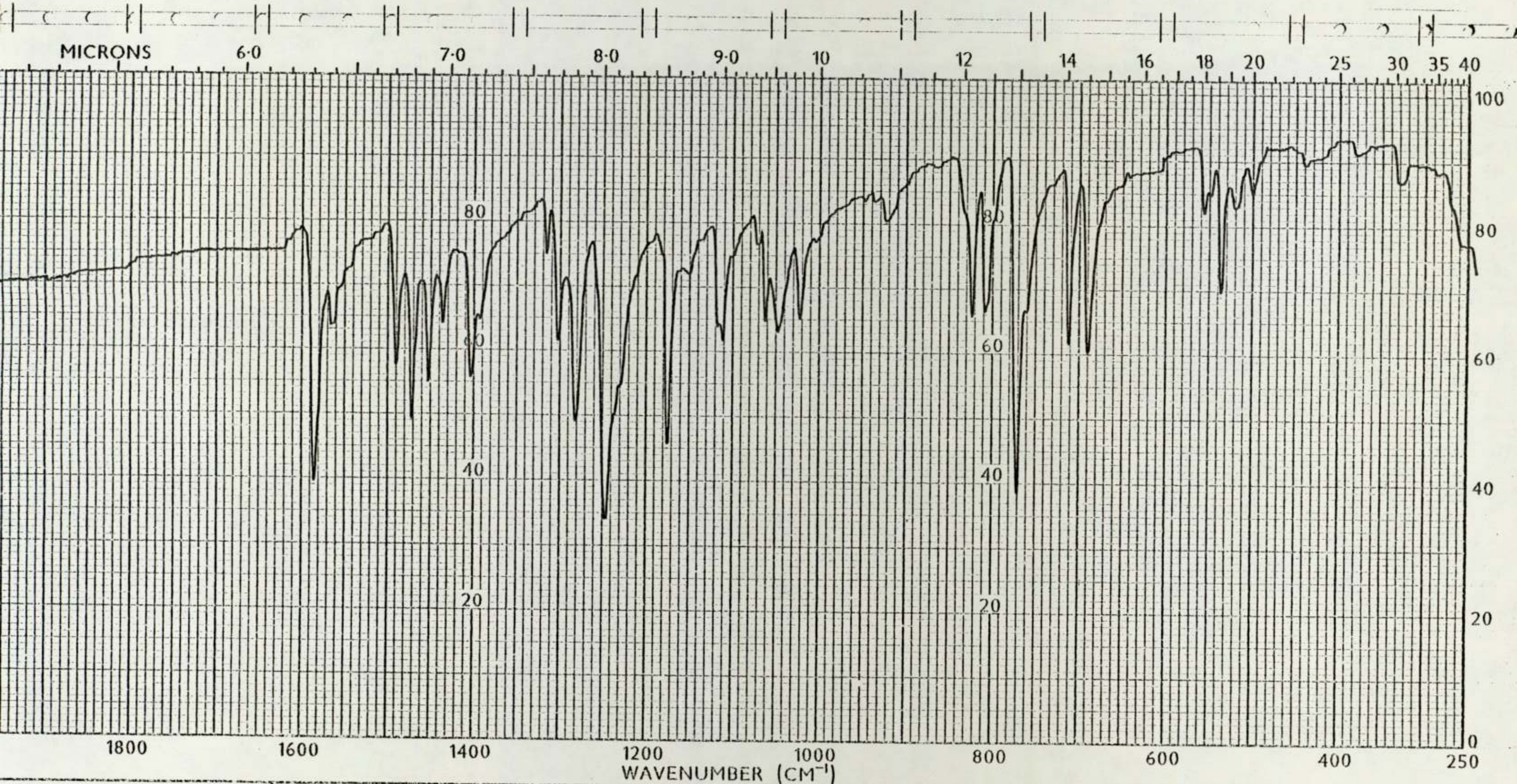
RPK/219/1002 457-5001

Intek

OPERATOR [illegible]

DATE 15th April [illegible]

REF. No 1630



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n. dia.dioc

REMARKS

Infra-red spectra of

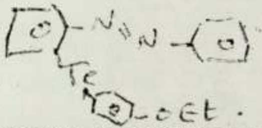
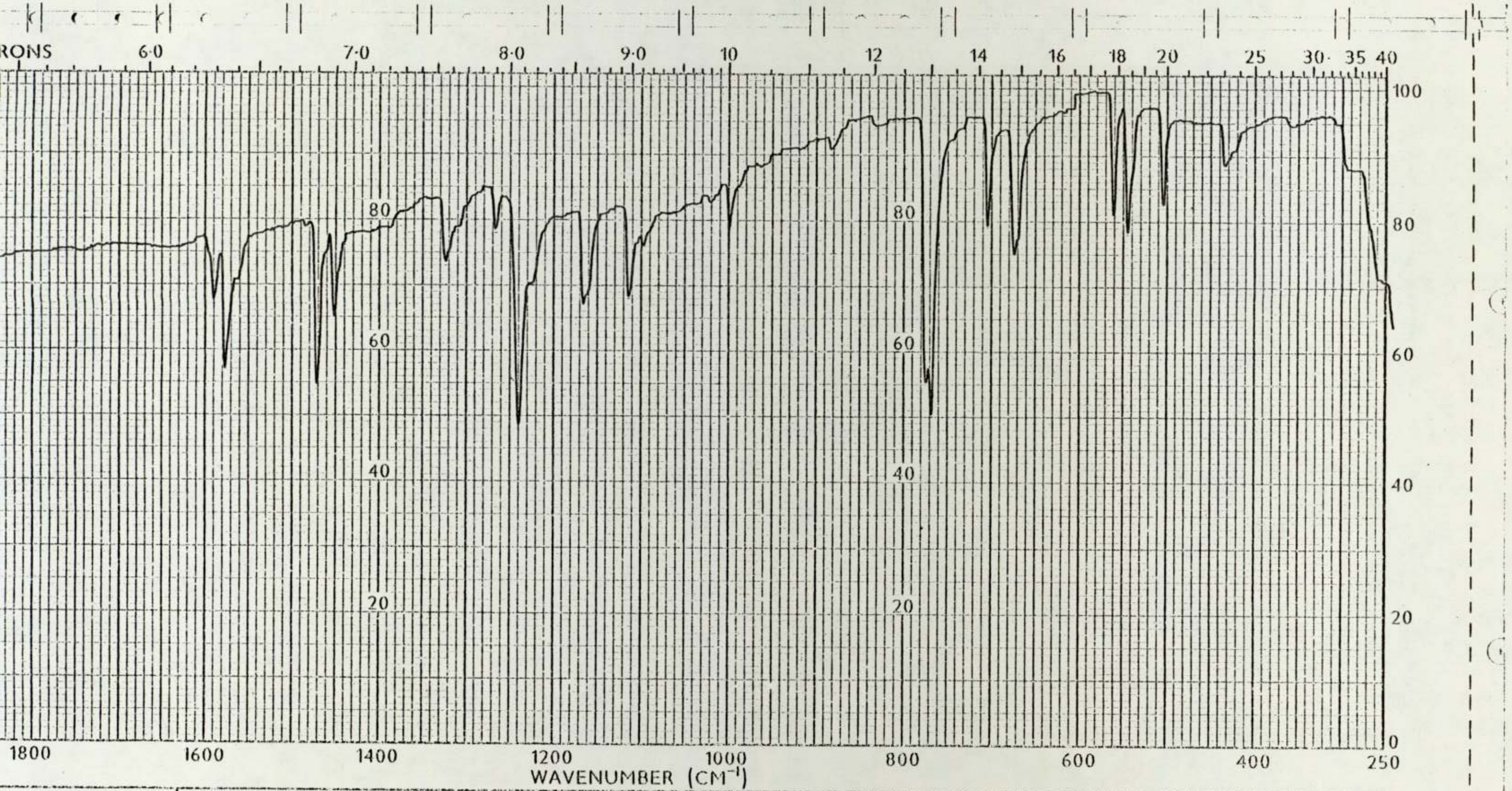


Fig. (7)

SCAN SPEED Medium.
SLIT Standard.
RPK/219/1002 457-5001
Intek

OPERATOR V.H. Clenton.
DATE 13th December 1976
REF. No 9214.



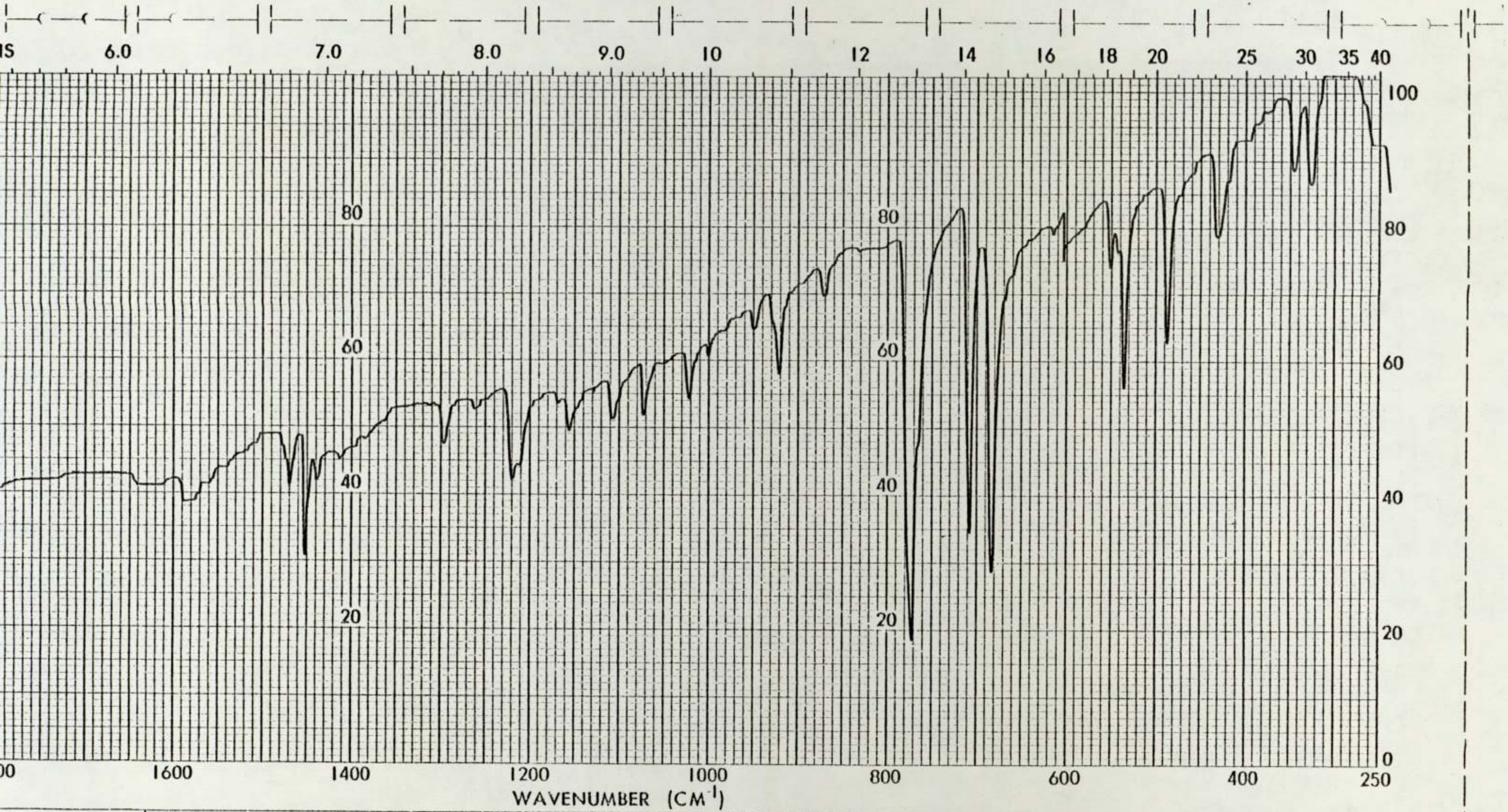
REMARKS

Infra-red Spectra of $(C_{12}H_9N_2)TeBr_3$

Fig (8)

SCAN SPEED Medium.
SLIT Standard.
RPK/215/1002 457-5001
Intek

OPERATOR V.H. Clinton.
DATE 4th. January 1977
REF. No. 92 64.



REMARKS Infra-red Spectra of $(C_{12}H_9N_2)HgCl$

Fig. (9)

SCAN SPEED Medium.

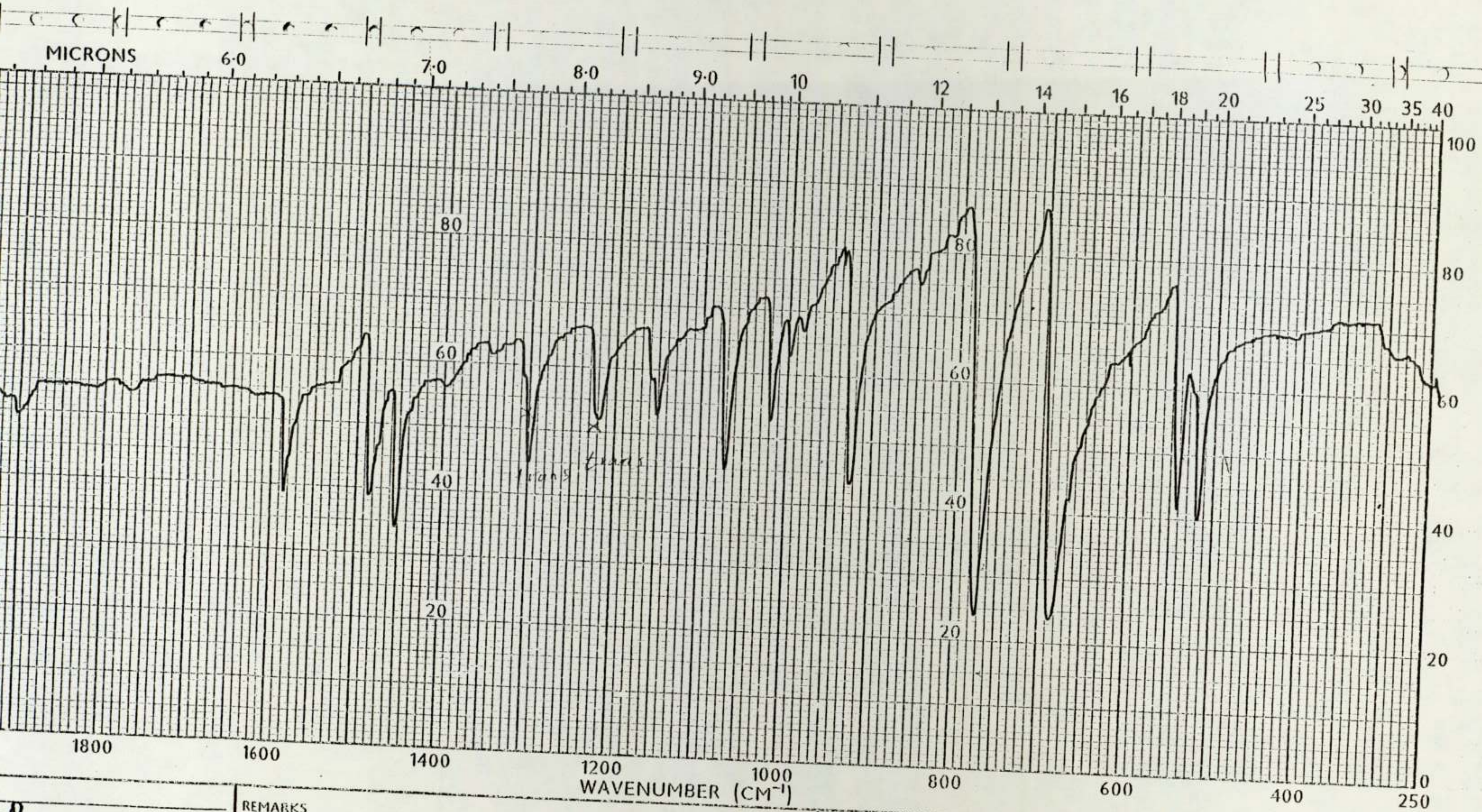
SLIT Standard.

No 457 - 5001

OPERATOR V.H. Clenton.

DATE 3rd. August 1977

REF. No 9875.



%

ia. disc.

REMARKS

Infra-red Spectra of azo-benzene

(Fig. 10)

SCAN SPEED Medium.

SLIT Standard.

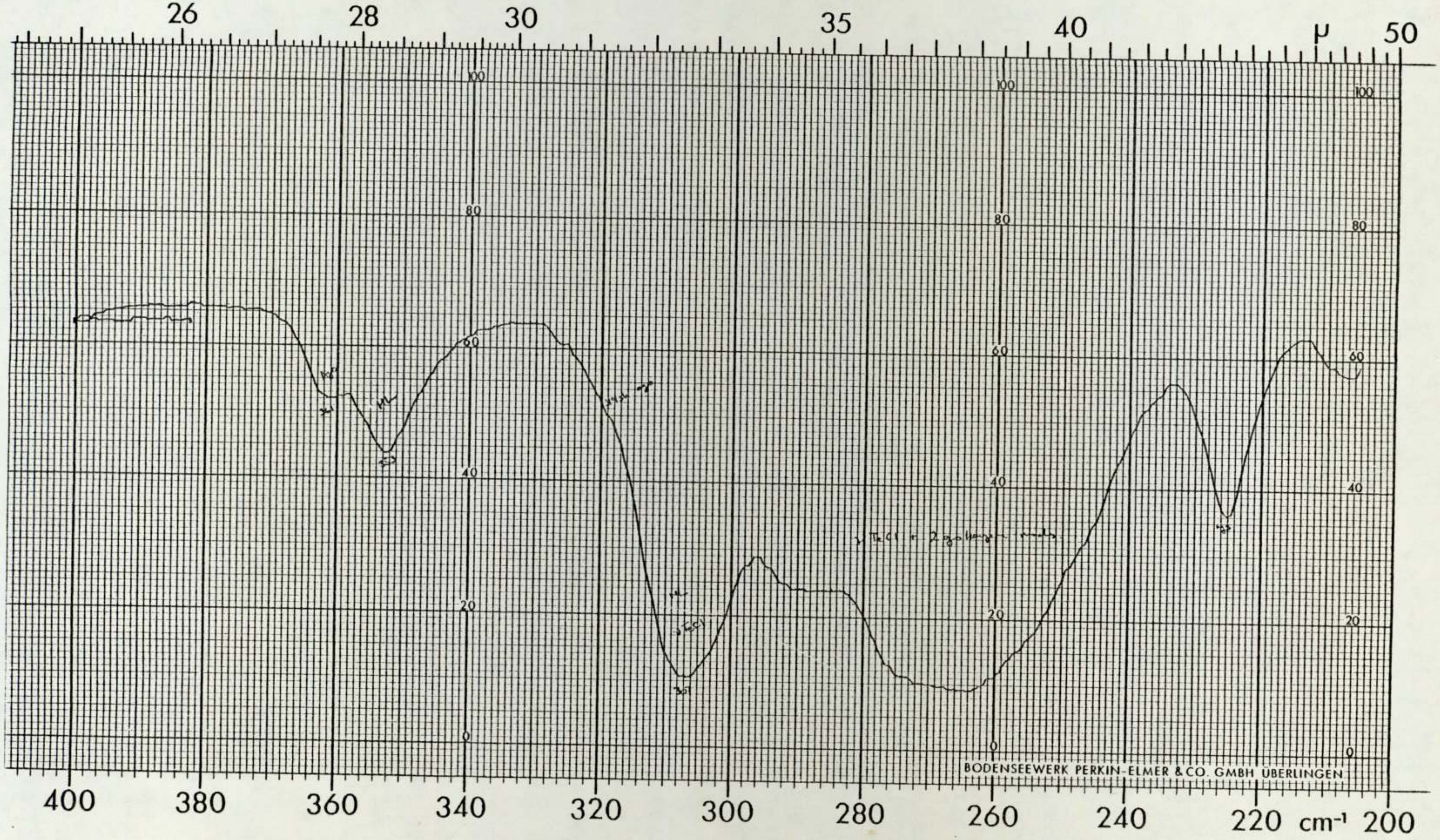
RPK/219/1002 457-5001

Intek

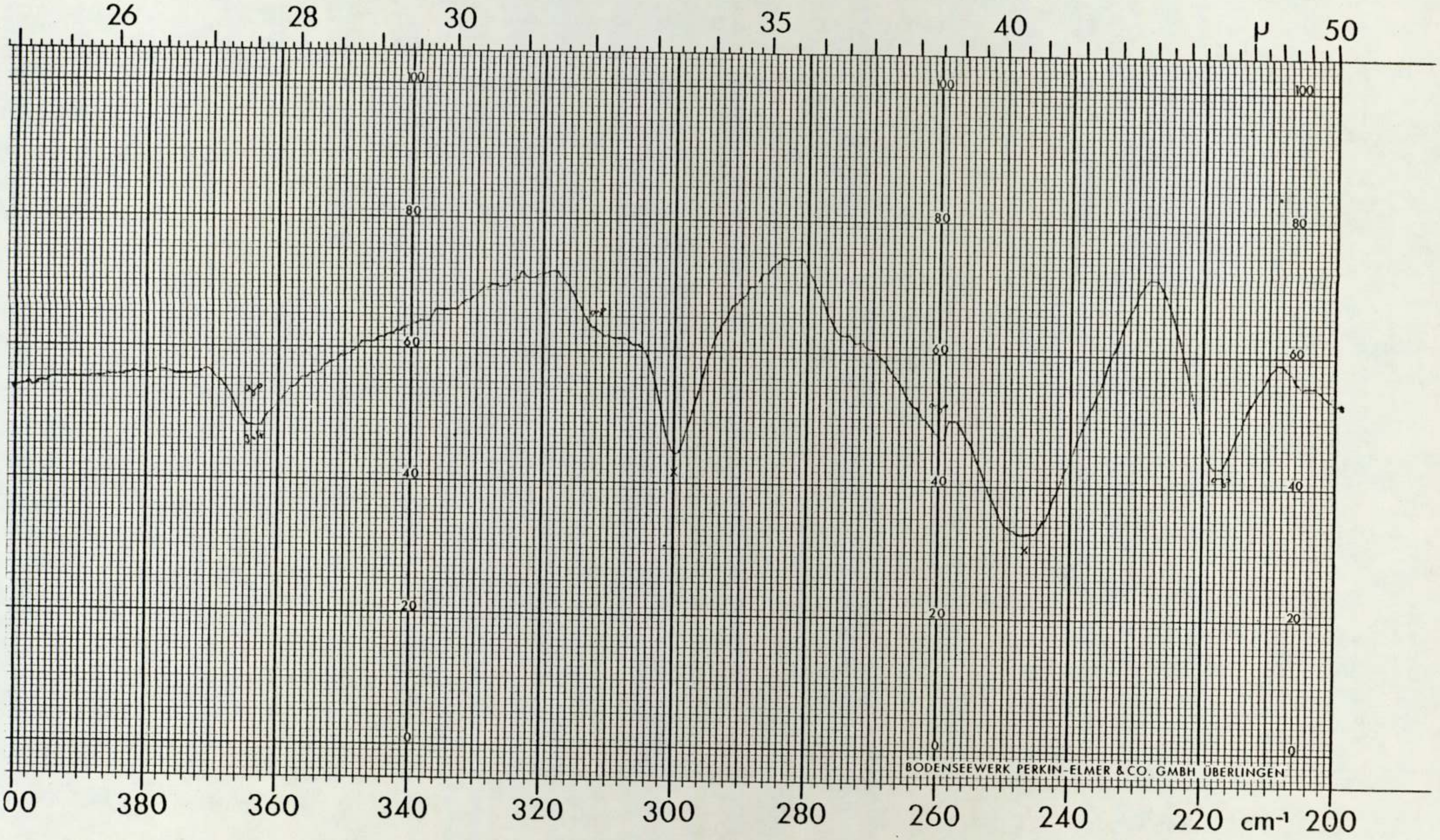
OPERATOR V.M. Clenton.

DATE 2A^th^ September 1976

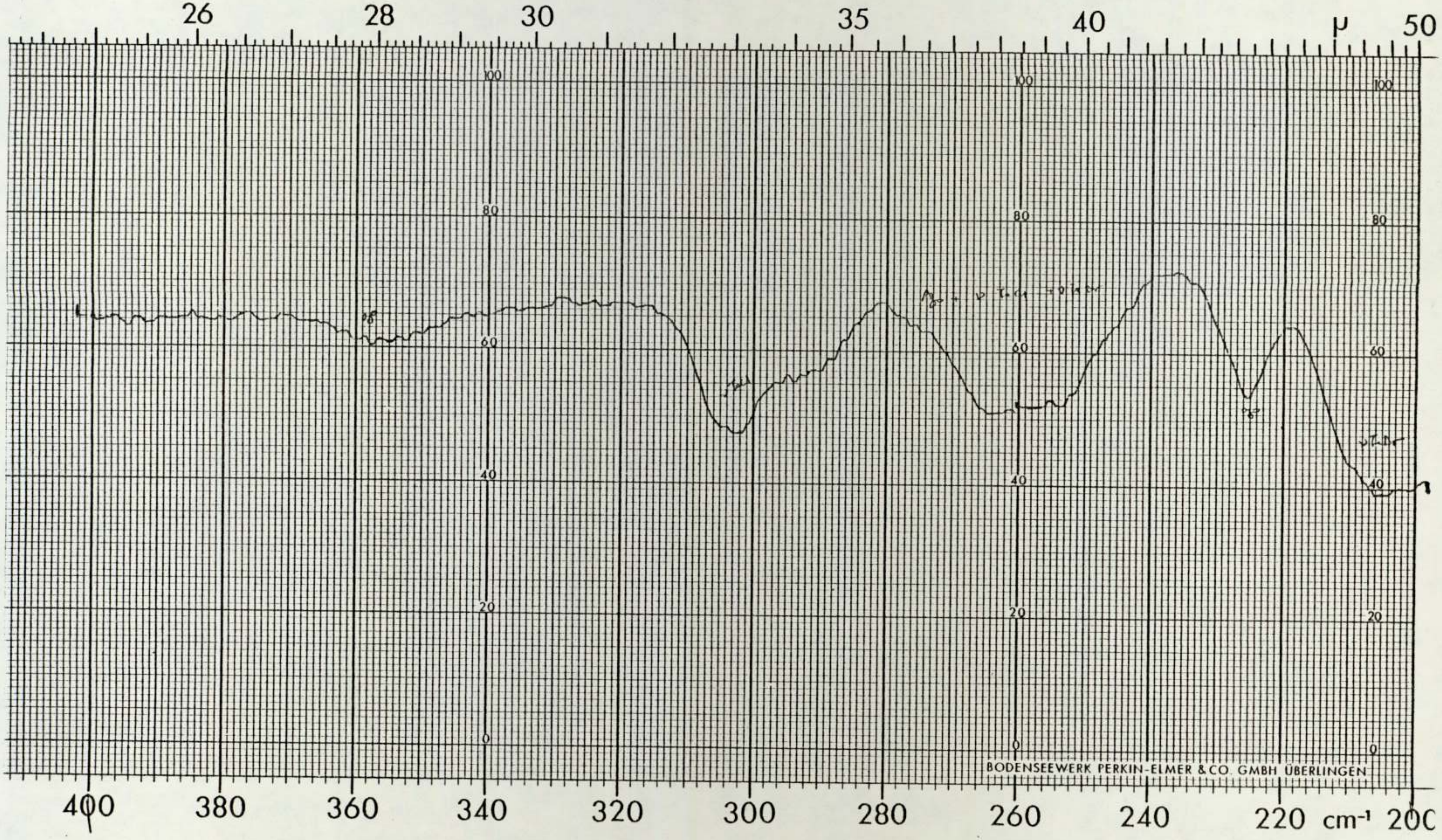
REF. No. 8959



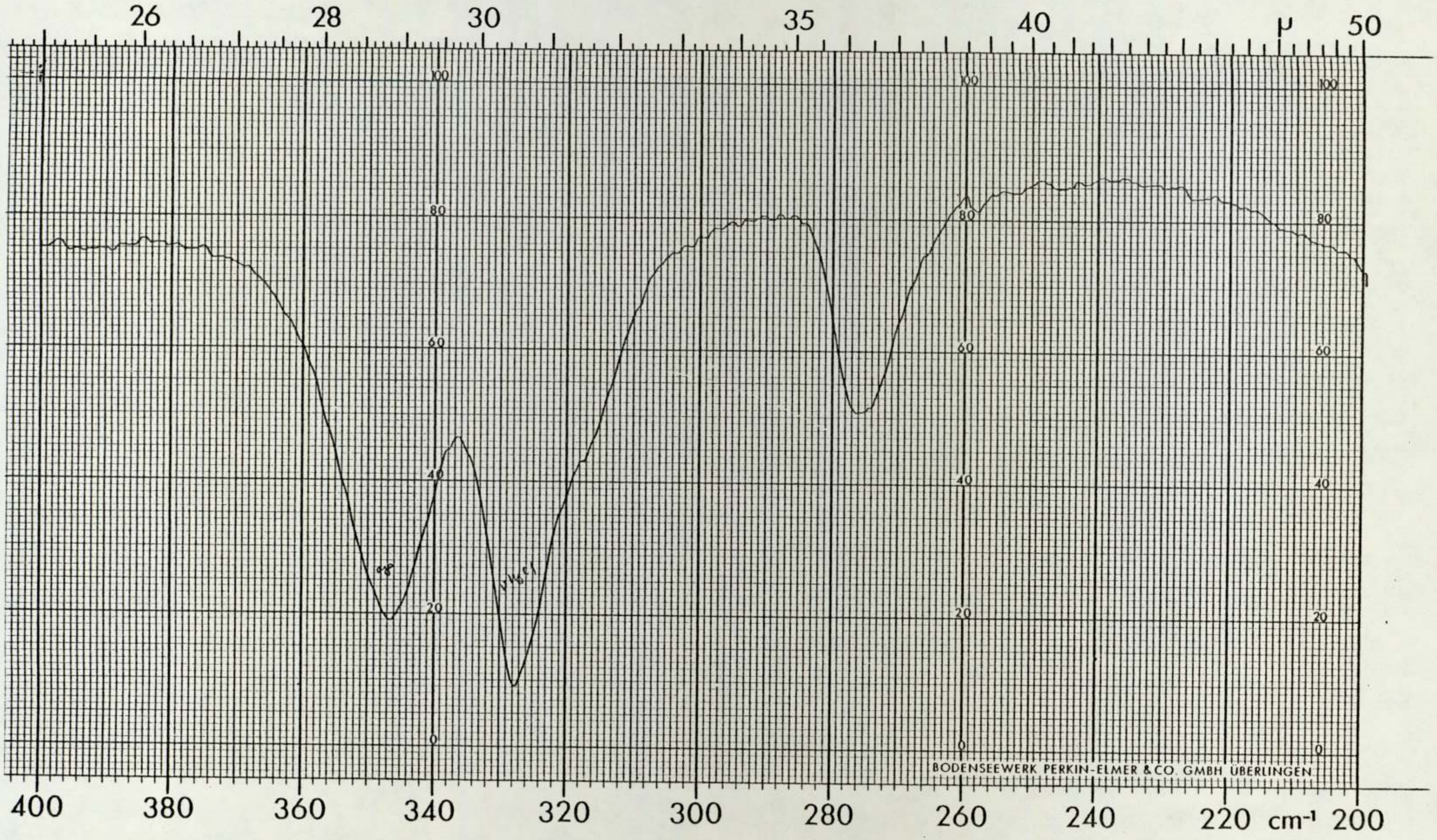
Far-Infra-red of $(C_{12}H_9N_2)TeCl_3$ Fig. (11)



Far-Infra-red $(C_{12}H_9N_2)TeCl$ Fig. (12)



Far- Infra-red of $(C_{12}H_9N_2)TeClBr_2$ Fig. (13)



Far Infra-red of $(C_{12}H_9N_2)HgCl$ Fig. (14)

REMARKS Infra-red spectra of R_2Te_2,CuCl

R is $(C_6H_4NH_2)$ Fig. (15)

SCAN SPEED Medium.

SLIT Standard.

RPK/219/1002 457-5001

Intek

OPERATOR V.M. Cleut a.

DATE 6th. April 1977

REF. No. 9668.

DISCUSSION

Mass Spectra :-

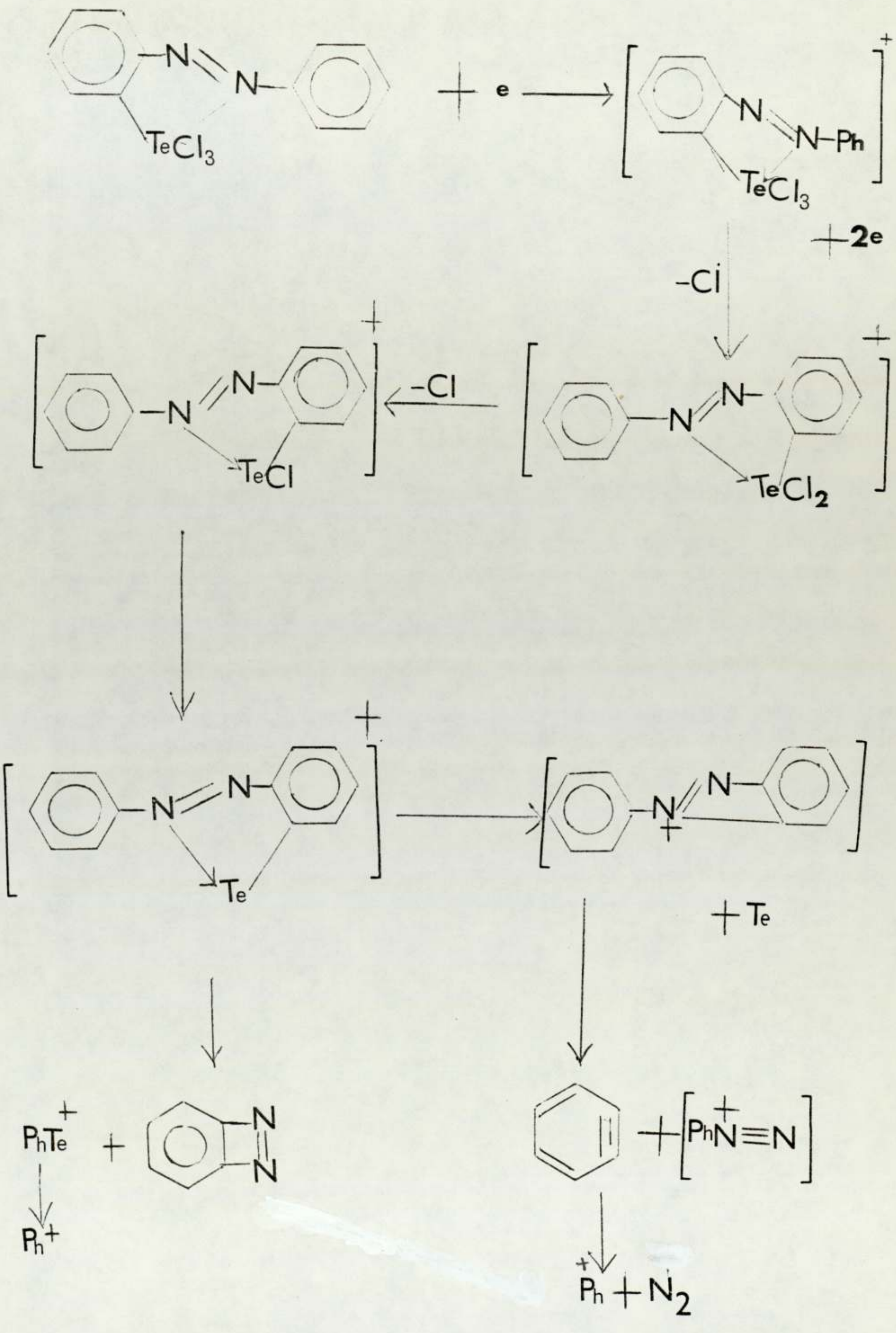
A few mass spectroscopic investigations of organotellurium compounds have been carried out. Many organotellurium compounds gave major peaks corresponding to the molecular ion, and subsequent ion-decomposition products.

Thavornyutikarn[71] reported the mass spectra of some aryltellurium trihalides, and observed the formation of the $R_2Te_2^+$ ion. This was interpreted as an indication that these compounds are at least dimeric or trimeric in the mass spectrometer.

The mass spectral data (table 2) for (phenylazophenyl 2C,N') trichloride showed a parent ion at $^m/_e$ = 416 ($^{12}C_{12}\,^{1}H_9\,^{35}Cl_3\,^{14}N_2\,^{130}Te$) together with other high mass peaks at $^m/_e$ = 381, 346. (The 346 peak is due to (phenylazophenyl 2C,N')tellurium(II)chloride which was isolated and the crystal and molecular structure has been determined) the 311 peak corresponds to a stepwise loss of ^{35}Cl.

Excess energy of P^+ causes fragmentation. We are in the gas phase with very low concentrations, hence bimolecular processes are very improbable. The following is a more likely scheme :

The Scheme :-


TeCl₃
+ e
N
N–Ph
TeCl₃
+2e
-Cl
TeCl₂
-Cl
TeCl
Te
+ Te
PhTe
+
N
N
Ph⁺
PhN≡N
Ph + N₂

The most important evidence from mass spectra is that (phenylazophenyl-2C,N')tellurium (IV)trichloride must be a monomer. There were two main reasons ; the first was that the parent ion peak at $^{m}/_{e}$ 416 was observed, and the second was that there was no observation o a ditelluride ion. This ion could not occur from a monomer molecule, but , according to Thavornyutikarn's work, was expected froma dimer or a polymer .

Vibrational Spectroscopy :-

Infra-red spectroscopy provides some useful information on the metallated azobenzene compounds with tellurium (IV) or tellurium (II). The compounds include $(C_{12}H_9N_2)TeXY_2$ (X = Y = Cl; X = Y = Br ; X = Cl, Y = Br) and tellurium (II) compounds include $(C_{12}H_9N_2)TeCl$, $(C_{12}H_9N_2)Te-(C_6H_4.O-C_2H_5-p)$ and di-(o-aminophenyl)ditelluride, with their complexes with copper (I) and copper (II).

It is convenient to discuss the tellurium-organic group and tellurium halide assignments separately. The many azo compounds show cis - trans isomerism, the trans form is generally the more stable. The spectra of the cis and trans compounds show certain differences [72] . There has been some controversy on the position of frequencies of azo-group in the infra-red spectra of azo compounds. A survey [72] of the observations on azo-compounds reveals that there are common frequencies in the usual double bond region around (1400) and (1585) cm^{-1}. The spectra published by Barnes, Liddel and Williams [73] show a weak absorption for azobenzene at (1400) cm^{-1} and astronger one at (1590) cm^{-1}, but it is possible that two absorptions under attention do not arise from the $-N_2-$group. In the infra-red spectra of PhX where X = F, Cl, Br, I, were investigated by Whiffen [74]. A band was shown around 1600 cm^{-1} which attributed to (C-X) stretching frequencies, since this motion involves some admixture of (νC-C) in benzene as well, but this has been resolved by some elegant work by Luttke. Using ^{15}N-substitution, they have been able to show that in aromatic azo compounds in the trans configuration, the (N=N) band occurs between (1440) and (1410) cm^{-1}. The higher value is that of trans-azobenzene, and the frequency falls when electron donors are substituted in the ring[75].

The infra-red spectrum of azobenzene shows bands at 1450 cm^{-1}, (phenylazophenyl-2C,N') mercury (II) chloride and azobenzene derivatives of tellurium (IV) and tellurium (II) show bands at 1450 cm^{-1} as shown on pages (53, 52, 44). We have assigned that vibration to (N=N) following on Luttke's work.

Ortho-Metallation :-

Since the original discovery [76, 66] of direct metallation of an aromatic ring, there have been numerous other examples discovered. [77]

Several complexes have been the subject of X-ray crystallographic determinations [78] and the formation of a transition metal to carbon bond by direct metallation is now a very well authenticated process for many types of organic substrate, including, for example, derivatives of nitrogen such as azo-compounds,[76,66] oximes,[79] amines[80] Several examples from phosphorus chemistry are known [81], as are some derivatives of organosulphur compounds,[82]

It is well known that mono and 1,2 di substituted benzenes have characteristic spectra in the γ(CH) region of the spectrum [83].
Ortho-metallation of azobenzene by derivatives of tellurium (IV) or

tellurium (II) will generate a 1,2 disubstituted benzene and should lead to characteristic changes in the 680-800 cm^{-1} region. This criterion has also been used by other workers [66, 84, 85, 86].

The spectra of ortho substituted azo compounds show intense absorption between (850-600) cm^{-1} and are in good agreement with those we measured for (phenylazophenyl-2C,N')mercury (II)chloride (page 52) and for tellurium compounds derived from azobenzene. In the infra-red spectrum of phenylazophenyl-2CN') tellurium(IV) trichloride is shown on(page 44) . The characteristic δ(C-H) deformation mode of a trans azobenzene at 1225, 1300 cm^{-1} (fig. 10) are absent but an intense band at 710 cm^{-1} and other bands which are shown in(page 44) can be assigned to the C-H deformation mode of an ortho disubstituted benzene. This behaviour is anologous to that of the spectra of the rest of the organotellurium derived from azobenzene as are shown on pages; (44, 45, 46, 50, 51).

The ortho-metallation reaction is generally accompanied by the formation of a chelate ring, and preferably a five-membered ring [65]., Renson and Piette [87] studied the infra-red spectra of o-formylphenyltellurenyl and seleneyl derivatives : Te-X, Se-X, X = Cl, Br, I, SCN. They have shown that the infra-red vibration frequency of the carbonyl group decreases in these compounds with the charge carried by the ortho substituent group. This was attributed to a field-effect between the selenium or tellurium positively polarized by induction through the electronegative substituent it is carrying, and the oxygen of the carbonyl. This effect stabilizes the cis - form, usually still more stable by steric effect. The X-ray structure analysis of o-formylphenyltellurenylbromide has confirmed the presence of a (Te-O) bond as well.[33]

Inspection of azobenzene derivatives of tellurium (IV) or (II) compound $RTeX_3$ or RTeCl indicates that planar five member chelate rings could be formed by co-ordination through the azo-group lone pair of electrons on nitrogen donated to tellurium substituted in the ortho position. This effect should stabilize the (phenylazophenyl 2C,N')tellurenyl(II)chloride and (phenylazophenyl 2C,N')tellurium trihalides; indeed, they are stable and not sensitive to the moisture. They introduce the possibility that monomeric azobenzene derivates of tellurium (IV) or tellurium (II) may be formed. Mass spectrum of (phenylazophenyl-2C,N')tellurium trichloride (page 59) confirmed that this compound is monomeric.

The following discussion is mainly concerned with the tellurium-halogen (halogen = Cl, Br) and tellurium-nitrogen stretching frequencies. We have used the far-infra-red 600-200 cm^{-1} for this analytical purpose.

The assignments of the tellurium-halogen makes (table 3 page 40) for azobenzene derivatives of tellurium compounds do agree with Thavornyutikarn[58] and Patel[10].

The infra-red spectra of azobenzene derivatives below 600-200 cm^{-1} are relatively rich for metallated azobenzene species, as compared with previous work[88].

The i.r. spectrum of the (phenylazophenyl-2C,N')tellurium(IV) trichloride is less complex than that of (phenylazophenyl-2C,N') tellurium(II)chloride, a fact which may relate to the identification of two discrete molecules in the asymmetric unit of the latter compound. However, for $(C_{12}H_9N_2)TeCl_3$ (table 3 page 42) three vibrations are seen : 353, 307, 266 cm^{-1}. These are assignable as ν (Te-Cl) in comparison with $(C_{12}H_9N_2)TeClBr_2$.

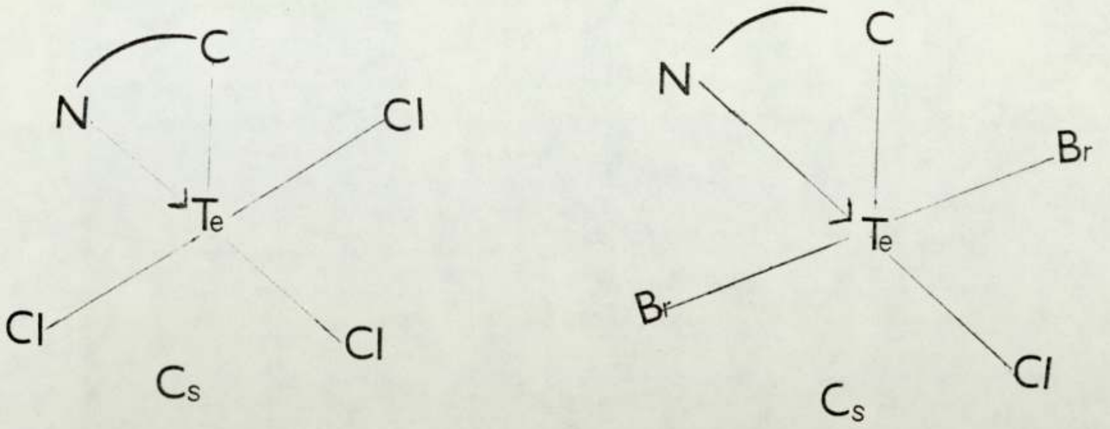
Thavornyutikarn[58] has considered a series of aromatic tellurium trihalides, assigned for ν (Te-Cl) at (337), 317 306 cm^{-1} and reported bands at 220, 213 and 198 cm^{-1} for ν (Te-Br).

An interesting comparison is between $(C_{12}H_9N_2)TeCl_3$ and $(C_{12}H_9N_2)TeClBr_2$ where bands are reasonably assigned to both ν (Te-Cl) and ν (Te-Br) (table 3 page 42).

In the case of $(C_{12}H_9N_2)TeClBr_2$, the assignment of ν (Te-Cl) is at 303 cm^{-1}, ν (Te-Br) at 264 and 205 cm^{-1}.

The band at 353 cm^{-1} in $(C_{12}H_9N_2)TeCl_3$ has shifted, probably to 260 cm^{-1} whereas the band at 300 cm^{-1} is unshifted between $(C_{12}H_9N_2)TeCl_3$ and $(C_{12}H_9N_2)TeClBr_2$. It is tempting to conclude that the ν (Te-Cl) mode close to 300 cm^{-1} is the unique chlorine (trans to nitrogen) in $(C_{12}H_9N_2)TeCl_3$ and that the more electronegative chlorine retains its position trans to nitrogen in $(C_{12}H_9N_2)TeClBr_2$.

The structures envisaged are best described as square-pyramidal of C_s symmetry.

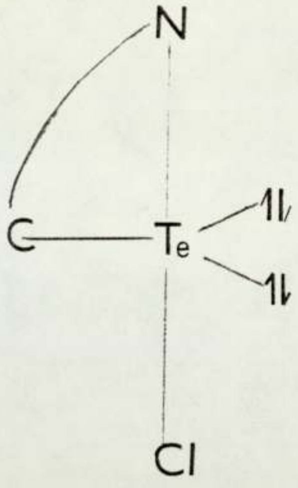


Schematic structures envisaged for compounds $(C_{12}H_9N_2)TeCl_3$ and $(C_{12}H_9N_2)TeClBr_2$.

Data available for compound (phenylazophenyl2C,N')tellurium(IV) tribromide (table 3 page 42) do not conflict with the above hypothesis and further establish regions close to 260 cm^{-1} and 200 cm^{-1} as those in which tellurium-bromine stretching modes are located. The positions of tellurium-bromine modes (i.e. ν (Te-Br), 226 and 202 cm^{-1}, reported by Thavornyutikarn for phenyltelluriumtribromide and by Chen and George[61] for $MeTeBr_3$ are in good agreement with those assinged for (phenylazophenyl-2C,N')telluriumtribromide as well.

Of course the possibility of longer tellurium halogen inter molecular contacts giving distorted six co-ordinate environments may not be eliminated.

The spectrum below 400 cm^{-1} of $(C_{12}H_9N_2)TeCl$ (page 55 table 3) shows two bands not immediately assignable to the azobenzene group of these, that at (247) cm^{-1} is most reasonably assigned to ν(Te-Cl). The structure of the compound may be interpreted (vide infra) as a pseudotrigonal bipyramid with nitrogen and chlorine in axial positions.



McWhinnie and Patel [10] have made assignments for ν (Te-X), X = Cl, Br, I) for R_2TeX_2 (R = p-tolyl, o-tolyl, p-Meo.C_6H_4, C_6H_5) using i.r.: ν (Te-Cl) is located around 260-280 cm^{-1}. They concluded that all these compounds have Ψ trigonal-bipyramidal structures with axial halogen atoms regardless of the nature of the substituents in the aryl ring.

It is known that the ν (Te-Cl) bands are shifted towards lower wave numbers in the order ;

$$Te^{IV} - Cl > Te^{II} - Cl$$

So it is reasonable that this tellurium (II) derivative should show ν (Te-Cl) at lower frequency ν (247) cm^{-1}. The other new vibration at 300 cm^{-1} is then tentatively assigned to ν (Te-N) and it is noted that the strong ν (Te-Cl) vibrations for the tellurium (IV) compounds probably overlap this mode.

<u>(Phenylazophenyl-2C)(p-ethoxyphenyl)telluride</u> :-

The infra-red spectra of (phenylazophenyl 2C)(p-ethoxyphenyl) telluride is shown on (page 50) .

Additional absorption in 709 cm^{-1} indicates the metallation of azobenzene. The spectrum confirmed the presence of p-ethoxyphenyl group as well.

The ^{1}H n.m.r. spectrum of $(p\text{-}C_2H_5O.C_6H_4)(C_{12}H_9N_2)Te$ in carbontetrachloride was recorded (page 36). The spectrum shows the expected chemical shifts for triplet methyl and quartet methylene and confirmed the presence of aromatic protons. The integrated ratio of aliphatic to aromatic protons was correct for the metallated structure (i.e. 5:13).

The oxidation of (phenylazophenyl 2C) (p-ethoxyphenyl)telluride with bromine gave (phenylazophenyl-2C,N')tellurium (IV)tribromide. This reaction must proceed with the breaking of a tellurium -to-carbon bond.

Di(o-amino-phenyl)ditelluride, R_2Te_2, and complexes

The i.r. and raman spectra of a series of diaryl ditellurides, R_2Te_2(R = Ph, $p\text{-}CH_3C_6H_4$, 2-naphthyl, $p\text{-}MeO.C_6H_4$, $pEtO.C_6H_4$ and $p\text{-}PhOC_6H_4$) have been assigned.[22] In particular bands in the far infra-red have been found to be characteristic of ν(Te-Te) between 187 and 167 cm^{-1}, and it was suggested that the ditellurides have structures of C_2 symmetry with a relatively large dihedral angle.

Di-(o-aminophenyl)ditelluride shows ν (NH) at (3410) cm^{-1} and (3320) cm^{-1}, (page 47), the first being due to the asymmetric stretching mode and the second, to the corresponding symmetrical mode.

Aniline[89] gave two bands ν_{as} (3509) and ν_s (3460)cm^{-1}. The frequency shifts can be attributed to the electron donating or withdrawing properties of the ring substituents.[90] The higher frequencies corresponding to electron withdrawing substituents and the lower to electron donors. Indeed, the fact that the $-NH_2$ frequencies in di-(-o-aminophenyl)ditelluride have shifted is a lower position might suggest that the NH_2 group co-ordinates to tellurium by donating the lone pair.

The di-(o-aminophenyl ditelluride gave a band at (1600) cm^{-1} which was assigned to the internal deformation mode of ν (NH_2). This band has appeared in aniline [89] and amine compounds at 1600 cm^{-1}.[90]

The ^1H n.m.r. spectrum of di(o-aminophenyl)ditelluride in deuteriochloroform was recorded (page 36). The ^1H n.m.r - spectrum of aniline is known [91]. The aromatic amines absorb in the region δ = (6.0 - 7.2) ppm and a broad band at about 3.7 ppm was assigned to NH_2 group. The aromatic amine in di-(o-aminophenyl)ditelluride absorbs between δ = (6.4 - 8) ppm and a broad band at δ = 4.2 ppm. The ^1H n.m.r. spectra of this ligand showed a correctly integrating ^1H n.m.r. spectrum 2:1, that would confirm the metallation of aniline. The broad band resonance at δ = 4.20 ppm, attributed to the NH_2 group, might arise from spin-spin coupling of ^1H with ^{14}N nucleus and the effect of quadrupole relaxation of this nucleus as demonstrated in aniline [91]. No spin-spin coupling of these protons with tellurium was observed.

According to the concept of Pearson [45b] the N-end of this ligand is hard, and tellurium issoft. Consequently N-bonding is expected with the hard (class a) metal ions while Te-bonding should take place with soft (class b). This ditelluride should, potentially, function as abidentate ligand, including a hard donor - NH_2 group and soft tellurium. We therefore, carried out two experiments, one with copper (I) and the other with copper (II). In both cases new complexes were isolated.

The chemistry of copper (II) and copper (I) complexes has been extensively studied [92].

Copper (I) is a soft or class (b) metal. Copper (II) is a somewhat borderline case, and has shown previously no great affinity for tellurium ligands [93]. Presumably the presence in the ligand molecule of a hard donor centre to complement the soft tellurium is the reason for success of preparation of $R_2TeCu^{II}Cl_2$.

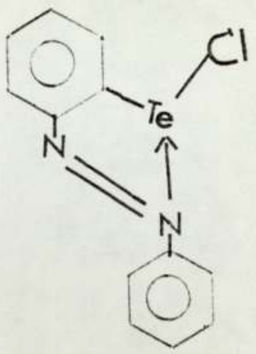
Copper (I) has shown affinity for tellurium bases, e.g. Davies [31] prepared a series of diaryl and dialkyl ditelluride complexes of copper (I) halides of formulae : R_2Te_2CuX. The complex with copper (I) chloride has stoicheiometry $\left[R_2Te_2\cdot\right]\left[CuCl\right]$; $(R = o\text{-}NH_2.C_6H_4)$. The single concentration $(10^{-3}M)$ conductivity study of this complex in acetonitrile gives the value of the molar conductivity (Λ_m) (60.75 mhos cm^2 mol^{-1}). This represents an appreciable conductivity but is well below the value expected for a 1:1 electrolyte in this solvent (120-160 mhos cm^2 mol^{-1}). However, doubling the emirical formula will bring the experimental value within (1:1) range and formula is taken to be $\left[(R_2Te_2)Cu\right]\left[CuCl_2\right]$. The infra-red spectrum shows four cleanly resolved NH stretching vibrations ; 3350, 3270, 3205, 3120 cm^{-1} (page 48), as compared with the free ligand which shows (NH) at (3410) and 3320 cm^{-1} page (47).

The lower frequency pair of which may be taken to arise from a co-ordinated- NH_2 group. Thus, a reasonable proposition would be that the cation contains tetrahedrally co-ordinated copper (I), each ligand being bidentate via one amino-group and one tellurium atom.

The interpretation of the data for the copper (II) complex is less straightforward. The ν (NH) region of the infra-red spectrum is poorly resolved and consists of a very broad band peaking at 3240 cm^{-1} (page 49). The material gives conducting solutions in acetonitrile. (Λ_m = 95 mhos cm^2 mol^{-1}) based on $R_2Te_2.CuCl_2$.

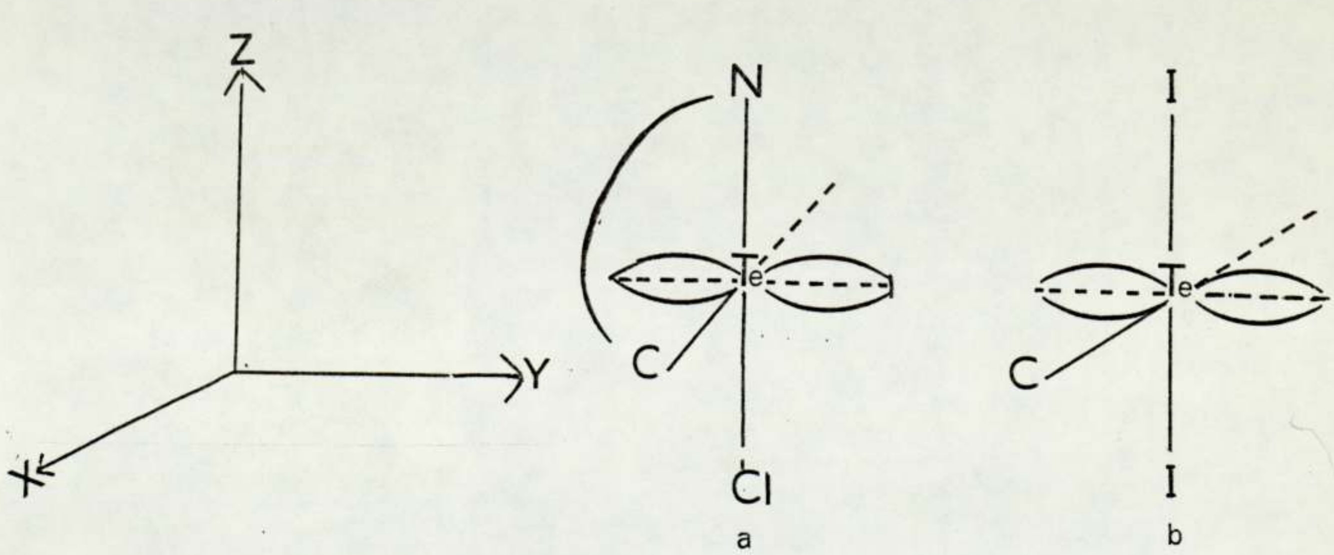
The development of the co-ordination chemistry of ditellurides was not one of the major objectives of this study, thus no further complex forming reactions were carried out. However, the two examples quoted do confirm the ability of the new ditelluride to function as a bidentate ligand with solubility in solvents of a wide range of polarity.

Mössbauer data

	δ (mm sec^{-1})	Δ (mm sec^{-1})	$\Gamma_{\frac{1}{2}}$
	0.63	11.76	6.6
$EtO.C_6H_4TeI_2^-$ (For comparison)	0.46	13.93	7.1

Discussion

(a) The Chemical Isomer Shift (δ) The value, 0.63 mm sec^{-1}, is relatively large compared with other tellurium (II) compounds, e.g. R_2Te_2 and R_2Te. It is also larger than the value of 0.46 mm sec^{-1} obtained for a salt of the di-iodo(p-ethoxyphenyl)tellurate(II)anion. In part, this difference may be attributable to the greater electronegativity of Cl and N compared with I. Thus more effective withdrawal of p-electron density should occur along the indicated z- axis (figure below) for the azobenzene derivative :



This will lead to less shielding of the s electrons in (a) than in (b) and a greater isomer shift. Even allowing for this, the value of O.63 is rather large and not consistent with a significant sp hybidisation to accommodate the lone pairs of electrons. Thus, although, as explained later, the VSEPR model provides a useful background to the discussion of the observed molecular parameters, it probably over simplifies the electronic picture of the molecule.

(b) The Quadrupole Coupling (Δ) Previously, a simple additive model has been developed to account for the observed quadrupole splitting of a wide variety of organotellurium compounds (Jones, Schultz, McWhinnie and Dance, Can. J. Chem. 1976). This model works well despite its crudity and for a tellurium (II) compound of the type considered here a quadrupole splitting of ~ 14 mm sec^{-1} is predicted. The value for $(p\text{-EtOC}_6H_4)TeI_2^{(-)}$ is in excellent accord with this figure and gives continued credibility to the approach. Hence an explanation of the unexpectedly low value of 11.76 for our azobenzene derivative must be sought.

In simple terms the value of 11.76 mm sec^{-1} means that there is another mechanism for withdrawing p-electron density - probably from Py as defined in the figure. Unfortunately, the carbon atom bonded to tellurium in molecule B within the unit cell behaved poorly on refinement of the structure. It has been stated that no chemical significance can be read into the values of 2.04 and 2.20 for molecules A and B. The latter figure (2.20) is definitely on the high side and probably unreliable. The value of 2.04 Å for Te-C in molecule A is however, to our knowledge, the shortest Te-C bond yet recorded for an organotellurium compound.

It is at least possible that the tellurium py orbital could interact with π-orbitals associated with the chelate ring. Such delocalization would decrease the p-orbital imbalance (and hence lower in comparison with a situation where the mechanism for delocalisation does not exist, e.g. $p\text{-}EtO.C_6H_4TeI_2^-$) ; also the delocalisation of p electron density onto the chelate ring would further deshield the tellurium s electron and hence enhance δ . It is therefore, proposed that the Mössbauer data support the view that there is a positive π- interaction between tellurium and the chelate ring.

Structure Determination and Refinement

The tellurium atoms were located from a three-dimensional Patterson synthesis and the remaining non-hydrogen atoms were obtained from a subsequent Tower synthesis assuming the space group to be $p\bar{1}$. The structure was refined using isotopic thermal parameters to a conventional R value of 0.112. A difference synthesis indicated anisotropic motion of the tellurium and chlorine atoms. Introduction of anisotropic parameters for these atoms in the full-matrix least-squares refinement reduced R to 0.06. Inclusion of hydrogen atoms in fixed calculated positions (assuming a C-H distance of 1.00 Å gave a final R factor of 0.059. In the later stages of refinement the weighting selene used was $w = 1/\sigma F_o^2$. Scattering factors were taken from International Tables for X-ray crystallography including anomalous scattering factors for the Te and Cl atoms. On the final cycle of refinement, the largest parameter shift was 0.06σ. Final positional and thermal parameters are listed in Tables 2 and 3 respectively.

Carbon atoms C(2) and C(3) of molecule B behaved poorly during the refinement and periodic attempts to obtain more chemically reasonable parameters were unsuccessful.

Structural determination and refinement for (phenylazophenyl-2C,N')tellurium (II) chloride.[+]

Small crystals were obtained by slow evaporation from a solution in chloroform. Weissenberg and precession photographs (Cu Ka radiation) gave approximate lattice constants and showed the reddish-purple crystal to be triclinic. Accurate cell dimensions were obtained by the method of least-squares from the setting angles of 11 reflexions ($2\theta > 25^{o}$) centred on a Picker FACS-I automatic four circle diffractometer (Mo Ka_1 radiation). Crystal data are given in Table 1. 1502 intensities with $2\theta \leqslant 35^{o}$ were collected with the diffractometer using a graphite monochromator and a scintillation counter with pulse-height discrimination. A θ -2θ scan was used with a scan speed of 2^{o}/min. in 2θ . The scan base width was 1.5^{o} with an increment to allow for dispersion Background measurements of 20 second duration were made at either side of the reflexions. The intensities of two standard reflexions were measured every 50 reflexions and no decay in their intensities was observed during the data collection. 972 of the 1502 unique reflexions with $I \quad 2.30\sigma(I)$ were classed as observed where $\sigma(I) = \; S + (t_5/t_6)B + (0.03I)^{2} \; ^{\frac{1}{2}}$ and S is the total scan count, B the total background count and t_5 and t_6 are the scan and background count times respectively.

The intensities were corrected for Lorentz and polarization effects. No correction was applied for absorption.

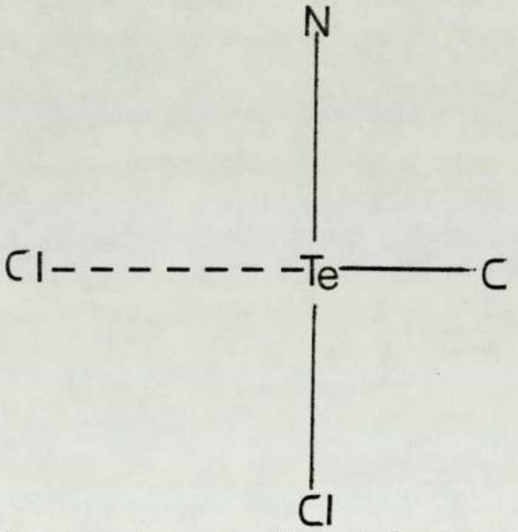
[+] This determination was carried out at Simon Fraser University. The details are those obtained from Professor F. I. Einstein.

The Crystal and Molecular Structure of (Phenylazophenyl-2C,N') tellurium (II) Chloride.

The asymmetric unit consists of two discrete molecules (A and B) with similar stereochemistry. Fig.2 . shows molecule A with the atom numbering. Bond lengths and angles are given in Tables 3 and 4 respectively. If the two tellurium lone pairs are taken into consideration the geometry around Te atom can be considered to be distorted trigonalbipyramidal. The phenylazophenyl ligand is bidentate and its co-ordination via an ortho-metallating carbon atom of one of the phenyl rings and a nitrogen atoms forms a five-membered chelate ring. The carbon atom and the lone pairs are in the equatorial plane and the more electronegative nitrogen and chlorine atoms occupy the axial position. This trigonal-bipyramidal stereochemistry is in agreement with that predicted by Valence Shell Electron Pair Repulsion Theory[94] , for a molecule with three bonding and two non-bonding electron pairs in the valence shell of the central atom. The theory also predicts the lengthening of axial bond lengths and the distortion of bond angles from ideal values as a result of the differing repulsive forces between bonding and lone pairs of electrons. The Te-Cl distances of 2.552 (8) and 2.549 (8) Å (increased to 2.562 and 2.556 if riding motion of the Cl atom on the Te atom is assumed) and the Te-N distances of 2.23 (2) and 2.19 (2) Å in the two molecules are equivalent within the limits of the experimental errors. These axial distances are significantly longer than the sums of the appropriate single covalent bond radii (Te = 1.37, Cl = 0.99, N = 0.70 Å)[95] but the Te-Cl distances are comparable with axial Te-Cl bonds in other trigonal-bipyramidal structures[96] . For the Te-N distances, no comparison can be made since this is the first reported structure with a tellurium-nitrogen bond. However, although the Te-C distances of 2.04 (2) and

2.20 (3) Å are statistically non-equivalent we do not consider the differences to be chemically real. The carbon atom involved in molecule B behaved poorly during refinement and other bond lengths and angles involving C (2) are abnormal.

Additionally, atom C (3) of the same molecule has an unreasonably low isotropic parameter. The axial atoms are displaced away from the lone pairs reducing the Cl-Te-N (1) angles to 167.6 (6) and 165.7 (6)° from an ideal vlaue of 180°. The N(1)-Te-C(2) angles of 72.8 (9) and 76.8 (9)° are greatly distorted from the ideal value of 90° while the Cl-Te-C(2) angles of 94.8 (7) and 89.0° are probably so large because of constraints arising from the five membered chelate ring. The bonding can be formulated as in form (I). A similar arrangement can be considered to occur in the structure of o-formylphenyltellurenyl bromide [33] where the axial Te-Br bond (2.618(3)Å) is trans to an oxygen atom of the bidentate o-formylphenyl ligand (Te-O=2.31Å) and the ortho metallating Te-C distance is 2.08 (2) Å.



The N=N distances of 1.25(2) and 1.28(2) Å are similar to values observed in other ortho - metallating azo compounds (e.g. 1.27 (1) and 1.29 (1) Å in acetatobis (phenylazophenyl-2C, N') rhodium) [97] and only slightly longer than the value of 1.24(3) Å found in free azobenzene[66]. The phenylazophenyl ligand is in the trans configuration.

The main difference between the two crystallographically distinct molecules in this structure is the degree of tilt of the non-bonded phenyl ring. In molecule A, this ring makes an angle of 13.6° with the least-squares plane through the five-membered chelating ring defined by atoms Te, N(1), N(2), C(1) and C(2), whereas in molecule B the angle is 28.4°. Equations of relevant least-square planes are the deviations of atoms from them are given in Table 5. The molecules are approximately planar and the maximum displacements from best least-squares planes through them are 0.3 and 0.6 Å respectively for molecules A and B.

Closest intermolecular contacts are given in Table 6. The structure consists of parallel sheets of molecules and within each sheet pairs of molecules are in close association in such a way that the Te atom of each molecule is involved in a contact with a Cl atom of the other molecule giving pseudo square planar geometry about the Te atoms. Each pair consists of an A and a B molecule and there is an approximate non-crystallographic centre of symmetry relating the two molcules. Thus the Cl atom of one molecule lies close to the equatorial plane of the other molecule and between the Te lone pairs. The closest contacts are Te(A)---Cl(B)=3.66, and Te(B)---Cl(A)=3.67Å, and the relevant angles are C(2)-Te(A)---Cl(B) = 171.2, Cl-Te(A)---Cl(B) = 88.5, C(2)-Te(B)---Cl(A) = 173.6, Cl-Te(B)---Cl(A) = 88.4°. Between the sheets there is a close contact between Te atoms with Te(A)---Te(B) = 4.17Å. These distances are shorter than the sum of the appropriate van der Waal's radii[95] taking Te=2.20 and Cl=1.80Å. However, if the value of 1.9Å given by Briegleb[98] for Te (c.f. 1.91 Å suggested by Foss[99]) is used the distances are not unusual.

TABLE 1

Atomic Fractional Co-ordinates ($X\ 10^4$) with estimated standard deviations in parentheses. Isotropic U values are in ($\AA^2 \times 10^3$)

MOLECULE A

Atom	x	y	z	u
Te	69(2)	8270(2)	2157(2)	-
Cl	1062(9)	10805(7)	2873(6)	-
N(1)	-1113(24)	6102(19)	1275(17)	37(7)
N(2)	-2138(25)	5724(20)	520(18)	48(8)
C(1)	-2319(30)	6812(26)	305(21)	37(8)
C(2)	-1382(27)	8068(23)	927(19)	23(8)
C(3)	-1602(30)	9169(25)	706(21)	38(8)
C(4)	-2619(30)	8909(25)	-153(22)	41(8)
C(5)	-3485(31)	7594(29)	-781(22)	57(9)
C(6)	-3363(33)	6544(27)	-559(24)	53(9)
C(7)	-860(37)	5034(31)	1506(25)	53(10)
C(8)	464(31)	5492(24)	2212(21)	46(8)
C(9)	785(33)	4549(29	2531(22)	55(9)
C(10)	-245(36)	3194(30)	2088(24)	62(10)
C(11)	-1492(38)	2790(29)	1410(26)	65(11)
C(12)	-1927(33)	3705(30)	1108(23)	54(9)

TABLE 1 - (continued)

MOLECULE B

Atom	x	y	z	u
Te	2807(2)	822(2)	5395(2)	-
Cl	2121(9)	-1651(7)	-4556(7)	-
N(1)	3742(24)	2899(20)	6416(17)	43(7)
N(2)	4626(23)	3231(19)	7276(16)	37(6)
C(1)	4760(27)	2176(24)	7459(19)	21(7)
C(2)	4060(29)	792(27)	6788(21)	41(9)
C(3)	4242(26)	-133(22)	6901(18)	1(7)
C(4)	5023(32)	2 7(26)	7783(23)	50(9)
C(5)	5815(29)	1284(25)	8558(21)	42(8)
C(6)	5713(30)	2391(26)	8363(22)	43(9)
C(7)	3513(33)	3947(28)	6138(23)	37(8)
C(8)	2130(29)	3554(23)	5548(20)	37(8)
C(9)	1940(32)	4596(29)	5308(22)	57(9)
C(10)	3011(38)	5913(30)	5639(25)	67(11)
C(11)	4357(34)	6223(27)	6221(23)	51(9)
C(12)	4612(32)	5256(28)	6499(22)	49(9)

TABLE 2

Anisotropic Thermal Parameters $(\mathring{A}^2 \times 10^4)$ in the form :

$$\exp\,(-2\ ^2(h^2\ a^{*2}\ U_{11} + k^2\ b^{*2}\ U_{22} + e^2\ C^{*2}\ U_{33}$$

$$+ 2\ hka^*\ 6^*\ U_{12} + 2hl\ a^*\ C^*\ U_{13} + 2klb^*C^*U_{23}))$$

With estimated standard deviations in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
MOLECULE A						
Te	441 (17)	296 (16)	576 (19)	113 (14)	-207 (14)	9 (13)
Cl	802 (64)	227 (47)	672 (64)	122 (44)	-372 (50)	-27(43)
MOLECULE B						
Te	480 (18)	281 (16)	544 (19)	130 (14)	-221 (14)	1 (13)
Cl	607 (61)	342 (51)	670 (65)	111 (44)	-315 (50)	-116 (45)

TABLE 3

BOND ANGLES (°)

	MOLECULE A	MOLECULE B
Cl - Te - N	167.6 (6)	165.7 (6)
Cl - Te - C	94.8 (7)	89.0 (8)
N(1) - Te - C	72.8 (9)	76.8 (9)
Te - N(1) -N (2)	119 (2)	119 (2)
Te - N(1) -C (7)	127 (2)	124 (2)
N(2) - N(1) -C (7)	5 (2)	118 (2)
N(1) - N(2) -C (1)	113 (2)	112 (2)
N(2) - C(1) -C (2)	117 (2)	127 (2)
N(2) - C(1) -C (6)	119 (3)	119 (2)
C(2) - C(1) -C (6)	124 (3)	114 (2)
Te - C(2) -C (1)	118 (2)	105 (2)
Te - C(2) -C (3)	125 (2)	127 (2)
C(1) - C(2) -C (3)	116 (2)	128 (3)
C(2) - C(3) -C (4)	120 (2)	119 (3)
C(3) - C(4) -C (5)	120 (3)	123 (3)
C(4) - C(5) -C (6)	122 (3)	118 (3)
C(1) - C(6) -C (5)	118 (3)	119 (3)
N(1) - C(7) -C (8)	114 (3)	116 (3)
N(1) - C(7) -C(12)	121 (3)	120 (3)
C(8) - C(7) -C(12)	125 (3)	124 (3)
C(7) - C(8) -C (9)	119 (3)	115 (3)
C(8) - C(9) -C(10)	117 (3)	124 (3)
C(9) - C(10)-C(11)	123 (3)	118 (3)
C(10)- C(11)-C(12)	123 (3)	121 (3)
C(7) - C(12)-C(11)	114 (3)	119 (3)

TABLE 4

BOND LENGTHS (Å)

	MOLECULE A		MOLECULE B	
Te - Cl	2.552(8)	2.562[+]	2.549 (8)	2.556[+]
Te - N(1)	2.23 (2)		2.19 (2)	
Te - C(2)	2.04 (2)		2.20 (3)	
N(1) - N(2)	1.25 (2)		1.28 (2)	
N(1) - C(7)	1.45 (3)		1.45 (3)	
N(2) - C(1)	1.43 (3)		1.35 (3)	
C(1) - C(2)	1.36 (3)		1.46 (3)	
C(1) - C(6)	1.40 (3)		1.40 (3)	
C(2) - C(3)	1.47 (3)		1.20 (3)	
C(3) - C(4)	1.38 (3)		1.30 (3)	
C(4) - C(5)	1.40 (3)		1.41 (3)	
C(5) - C(6)	1.36 (3)		1.40 (3)	
C(7) - C(8)	1.40 (3)		1.37 (3)	
C(7) - C(12)	1.38 (4)		1.37 (3)	
C(8) - C(9)	1.40 (3)		1.39 (3)	
C(9) - C(10)	1.40 (3)		1.37 (3)	
C(10) - C(11)	1.33 (4)		1.36 (4)	
C(11) - C(12)	1.43 (4)		1.37 (3)	

[+] Distance averaged over thermal motion, assuming the second atom is riding on the first.

TABLE 5

EQUATIONS OF LEAST - SQUARES PLANES AND DEVIATIONS (Å) OF ATOMS FROM THE PLANES

(a) Plane defined by C(1), C(2), C(3), C(4), C(5), and C(6)

$0.7170x + 0.2792y - 0.6387z + 2.2647 = 0$ (A)

$0.7641x + 0.3587y - 0.5362z + 1.8280 = 0$ (B)

	Molecule A	Molecule B
C(1)	-0.02(3)	-0.01(3)
C(2)	0.03(3)	-0.03(3)
C(3)	-0.02(3)	0.04(3)
C(4)	0.00(3)	-0.03(3)
C(5)	0.02(3)	-0.02(3)
C(6)	-0.01(3)	0.04(3)
Te	0.000(2)	0.050(2)
N(1)	0.07(2)	-0.02(2)
N(2)	0.01(2)	0.01(2)
C(7)	0.12(3)	0.00(3)
	X^2=2.31	X^2=5.50

(b) Plane defined by C(7), C(8), C(9), C(10), C(11) and C(12)

$0.5836x + 0.1713y - 0.7938z + 2.5229 = 0$ (A)

$0.5168x + 0.1125y - 0.8487z + 5.1277 = 0$ (B)

	Molecule A	Molecule B
C(7)	0.02(3)	0.01(3)
C(8)	0.01(3)	0.00(3)
C(9)	-0.02(3)	0.00(3)
C(10)	0.00(3)	-0.01(3)
C(11)	0.02(3)	0.01(3)
C(12)	-0.03(3)	-0.01(3)

Continued...

	Molecule A	Molecule B
Te	-0.475(2)	0.870(2)
N(1)	-0.02(2)	-0.01(2)
N(2)	0.19(2)	-0.51(2)
C(1)	0.18(3)	-0.48(2)
	$X^2 = 1.98$	$X^2 = 0.42$

TABLE 5 (continued)

(c) Plane defined by Te, N(1), N(2), C(1) and C(2).

$0.7104x + 0.2964\,y - 0.6383\,z + 2.1023 = 0$ (A)

$0.7754x + 0.3642\,y - 0.5158\,z + 1.6194 = 0$ (B)

	Molecule A	Molecule B
Te	0.000(2)	0.000(2)
N(1)	0.03(2)	-0.03(2)
N(2)	-0.02(2)	0.02(2)
C(1)	-0.02(3)	0.01(3)
C(2)	0.04(3)	-0.03(3)
Cl	-0.042(9)	0.097(9)
C(7)	0.07(3)	-0.02(3)
	$X^2 = 5.51$	$X^2 = 4.39$

(d) Angles between normals to planes.

		A	B
Plane	Plane	Angle (°)	Angle (°)
a	b	13.3	27.1
a	c	1.1	1.4
b	c	13.6	28.4

Equations of the planes are of the form $l\,x + m\,y + n\,z \quad p = 0$ referred to an orthogonal set of axes with x parallel to the a axis z parallel to the $\overset{*}{c}$ axis and y in the a b plane.

TABLE 6

INTERMOLECULAR CONTACTS
(Å)

Te^{i}	(A)	.....	Cl^{ii}	(B)	3.66
Te^{i}	(A)	.....	Te^{ii}	(B)	4.51
Te^{i}	(A)	.....	Te^{iii}	(B)	4.17
Te^{i}	(B)	.....	Cl^{iv}	(A)	3. 67
C(5)^{i}	(B)	.....	C(4)^{iii}	(A)	3.45
C(11)^{i}	(B)	.....	C(7)^{v}	(B)	3.48
C(3)^{i}	(A)	.....	C(3)^{vi}	(A)	3.46
Te^{i}	(A)	.....	C(5)^{v}	(B)	3.74
Te^{i}	(A)	.....	N(1)^{iii}	(B)	3.74

Superscript	Symmetry Position		
i	x,	y,	z
ii	x,	1+y,	z
iii	x,	1-y,	1-z
iv	x,	-1+y,	z
v	1-x,	1-y,	1-z
vi	x,	2-y,	z

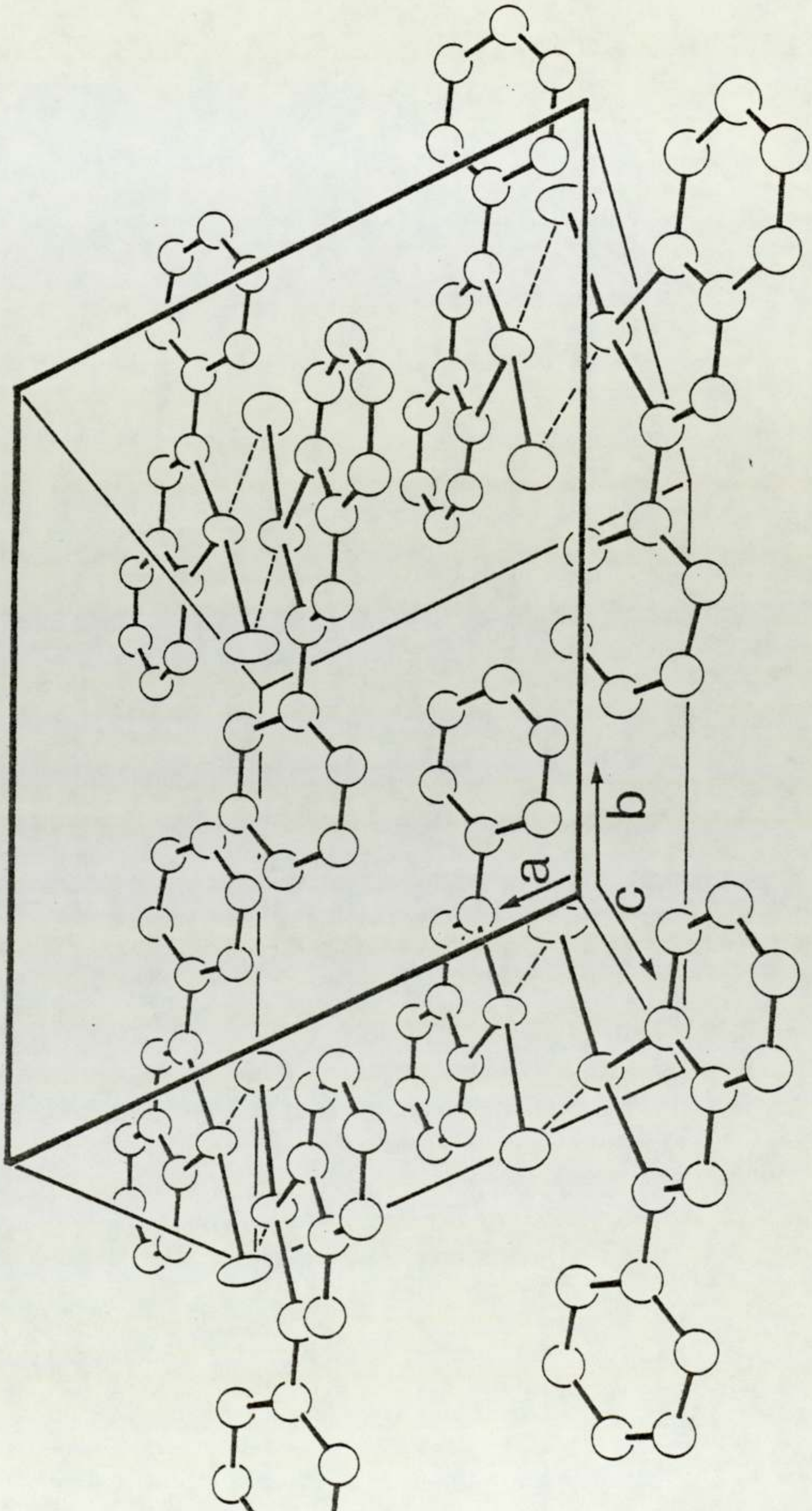


FIG. 1.

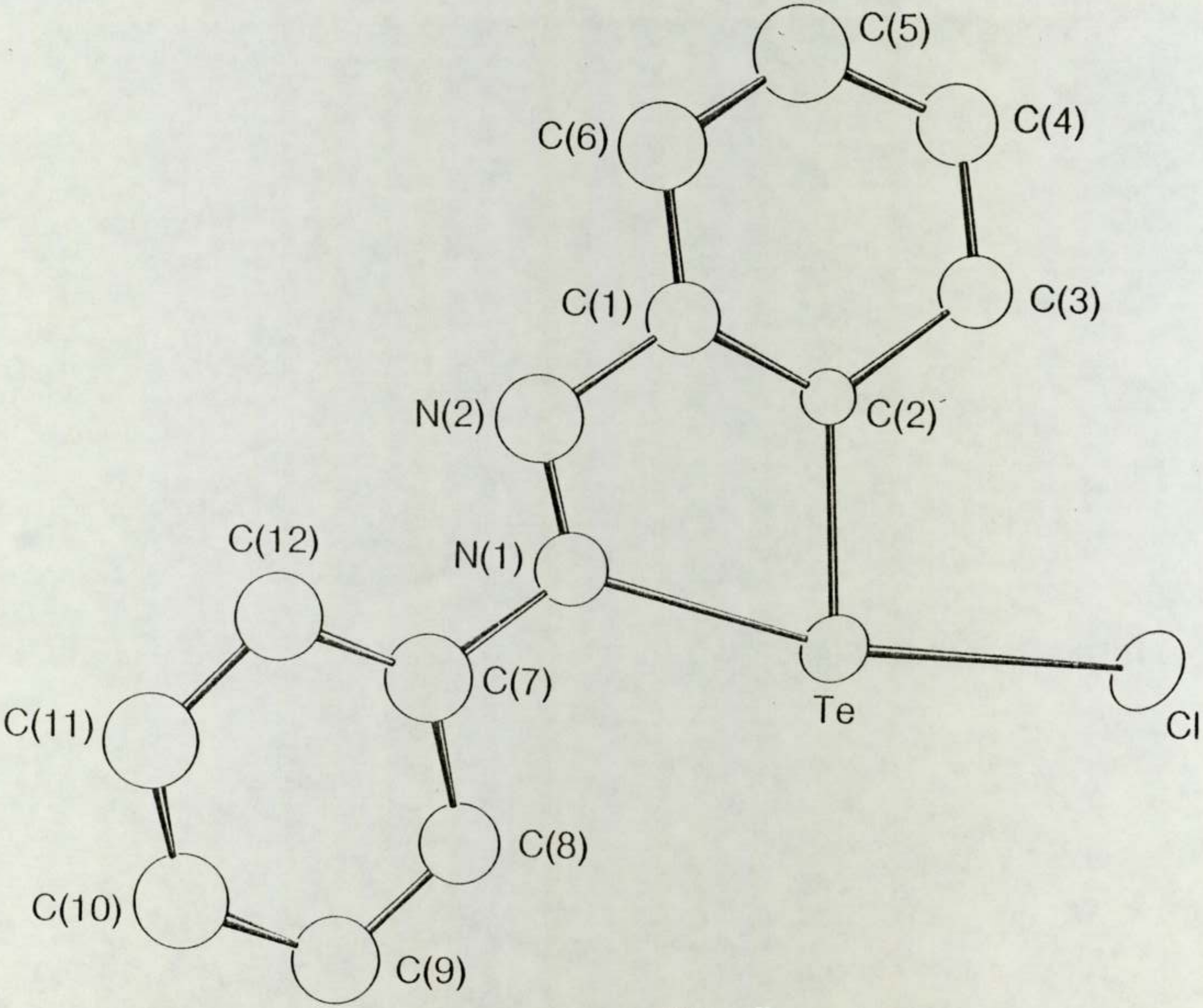


FIG.2

CHAPTER V

STUDIES OF DIORGANOTELLURIUMDIISOTHIOCYANATES AND OF A TRIORGANOTELLURIUM ISOTHIOCYANATE IN SOLID STATE AND IN SOLUTION.

INTRODUCTION

Diorganotellurium dihalides, R_2TeX_2 (X = Cl, Br, I ,) are crystalline solids. A large number of chlorides, bromides and iodides have been prepared, e.g. as follows ;

$$R_2Te + X_2 \longrightarrow R_2TeX_2$$

The structures of some of these diorganotellurium dihalides have been determined by X-ray methods[19, 40, 100,] . The groups bonded to the tellurium atom expand its electronic shell to ten electrons with four bonding electron pairs and one stereochemically active lone electron pair. These molecules possess as expected a trigonal bipyramidal shape with the lone electron pair and two organic groups occupying the equatorial positions. The halogen atoms take up the axial positions [100,101]

Thiocyanogen $(SCN)_2$ resembles the halogens in many of its reactions and has been called a pseudohalogen[102] . The reagent is used to synthesise a new series of R_2TeX_2 where X_2 is $(SCN)_2$ in essentially the same way as the halogens, with the exception that certain precautions must be observed owing to the instability of thiocyanogen, to moisture and heat ;

$$R_2Te + (NCS)_2 \longrightarrow R_2Te(NCS)_2$$

In this work, R is phenyl, $p\text{-}CH_3OC_6H_4\text{-}$ and $p\text{-}C_2H_5OC_6H_4\text{-}$.

Thiocyanogen can add to a triaryl derivative; such as triphenylantimony[103] and triphenylbismuth[104]; e.g.

$$(C_6H_5)_3\,Sb + (SCN)_2 \longrightarrow (C_6H_5)_3\,Sb\,(SCN)_2$$

and

$$(C_6H_5)_3Bi + (SCN)_2 \longrightarrow (C_6H_5)_3\,Bi\,(SCN)_2$$

The thiocyanate ion $(:N\equiv C-S)^-$, presents itself as the most logical candidate for examples of linkage isomerism. It is known to form both thiocyanato-(M-SCN) and isothiocyanato-(M-NCS) complexes, depending on the central metal atom employed as well as bridged[45a] (M-SCN-M) species

Pearson [45] suggests that S in SCN is soft and will prefer to co-ordinate with soft acids (class b metals) whereas N in SCN is hard and co-ordinates with hard acids (class a metals). The terms soft and hard are used to designate substances which are polarizable and non polarizable, respectively.

Further interesting and significant observation were made by Turco and Pecile [105]. They found that, for palladium (II) and platinum (II) complexes, co-ordinated thiocyanate ion is either S - or N - bonded, depending upon the nature of the other ligands present, thus, the systems $M(SCN)_4^{2-}$ and $M(NH_3)_2(SCN)_2$ are S - bonded, whereas $M(PR_3)_2\,(NCS)_2$ is N-bonded.

Turco and Pecile [105] pointed out that there are two sets of anti - bonding π - orbitals localized on the sulphur atom, which, along with the sulphur atoms vacant d- orbitals, can accept electron density from the metal's filled non-bonding d-orbitals, resulting in additional stability of the M-S bond. The importance of this additional stability will depend on the availability of the electrons of the metal and their relative energy as compared with that of the orbitals of the thiocyanate. Strong π - electron acceptors, as trialkylphosphine are believed to make the metal d-orbital electrons less available for donation to the thiocyanate, removing the source of additional stability for the M-S bond.

Another way of saying about the same thing is that π - bonding in these systems tends to reduce the electron density on the metal and thereby change class b, or soft metals, to class a, or hard metals. This is accompanied by a change in M-SCN bonding to M-NCS, respectively.

It has been shown that the steric factors can alter the nature of SCN^- bonding in these systems. In most comparisons, such as $\left[Pt(NH_3)_2(SCN)_2\right]$ and $\left[Pt(PR_3)_2\text{-}(NCS)_2\right]$ both electronic and steric factors change with changes in the ligands.

Many triorganyl tellurium salts $\left[R_3Te\right]^+X^-$, have been described in the introduction (page 15).

Once a telluronium salt has been formed, the anion can be exchanged easily. The solubility of the telluronium halides decreases in the order chloride > bromide > iodide. The chlorides can therefore be converted into the bromides and iodides, and the bromides into the iodides upon treatment of the aqueous solutions of the telluronium halides with the appropriate potassium halides.

The recent literature [43a, 52,] contains several papers which indicate a growing interest in organotellurium pseudohalides and the solution behaviour of diphenylmethyltelluronium halides. (X = Cl, Br, I).

Dance [52] has investigated the solution behaviour of Ph_2MeTeX (X = Cl, Br, I) in deuteriochloroform and DMSO (d_6) using 'H n.m.r. spectroscopy and it was noted that the chemical shift of methyl group attached to tellurium (identified by 'H -^{125}Te satellites) was significantly dependent on the anion (page 19).

The results of the measurements in DMSO and $CDCl_3$(page 19).

$$\underset{\text{ionic}}{Ph_2MeTe^{+}\ \text{-------}\ X^{-}} \longrightarrow \underset{\text{covalent}}{Ph_2MeTeX} \longrightarrow Ph_2Te + MeX$$

The equilibrium lies to the left in more polar DMSO and well to, or entirely to, the right in $CDCl_3$ depending upon X (More details on introduction(page 19) .

Ziolo has prepared a range of triphenyl telluronium pseudohalides ;
$(C_6H_5)_3TeX$, X = CN, N_3, NCO, NCS, NCSe [43a], by the reaction of triphenyl telluronium chloride and excess alkali-pseudohalides. The crystal and molecular structures of $(Ph_3Te)(NCO).\frac{1}{2}CHCl_3$ [43b], and of $(Ph_3Te)(NCS)$ [44], have shown an association to tetramers in the isocyanate and to both dimers and tetramers in the thiocyanate. The association within the oligomers seems to be predominantly ionic. - A further interesting structure is that of $(Ph_2TeNCS)_2O$ in which the tellurium is located on a distorted square based pyramidal environment (more detail in introduction).[51]

The observations by Dance [52] of the behaviour of Ph_2MeTeX X = Cl, Br, I in solutions has led us to prepare Ph_2MeTeX X = SCN, BF_4^- and PF_6 to study the behaviour of Ph_2MeTeX (X = SCN) in solutions and to compare them with other new organotelluronium salts; Ph_2CH_3TeX, X = BF_4 and PF_6.

The mode of bonding of thiocyanate to tellurium is of particular interest since it has been known that the more electronegative halogen atoms occupied the axial - positions in the ψ -trigonal pyramidal. The nitrogen in $(NCS)^-$ is more electronegative than sulphur, hence it is possible that it will occupy the axial positions forming Te-N bond; on the other hand, the soft nature of tellurium may favour S- bonding in $R_2Te(SCN)_2$.

EXPERIMENTAL

PREPARATION OF DIARYLTELLURIDE

All the tellurides prepared are known compounds. The methods employed are according to the literature sources.

Diphenyl telluride

Diphenyl telluride was synthesised by a modification [10] of the method of Rheinboldt and Petragnani [11]. To an etheral solution (100 ml) of a Grignard reagent synthesised from bromo benzene (39.3 g) and magnesium (6.1 g) was added benzene (100 ml). The temperature of the solution was lowered to 0° and vigorous stirring was commenced. Tellurium tetrachloride (13.5 g) in benzene (200 ml) was added slowly to the stirred solution, after which the reaction mixture was heated under reflux for 2h. The cooled solution was treated with saturated ammonium chloride solution (300 ml) and the separated organic layer was washed three times with distilled water and dried ; the solvent removed in a rotatory evaporator to afford crude diphenyl telluride (18.5 g) this method gave no free tellurium which was reported to be a side product by Rheinboldt [11].

Bromine oxidation of the crude telluride [14] gave diphenyltelluriumdibromide (20 g). A portion (10 g) of the dibromide was reduced with sodium sulphide [3] to give pure diphenyltelluridewhich is pale yellow, identified by i.r. spectra.

Di-p-methoxyphenyltelluride :-

Di-p-methoxyphenyl telluride [8] was prepared by reducing di-p-methoxy phenyltellurium dichloride [29] by sodium metabisulphite ; to a stirred benzene (50 ml) solution of di-p-methoxyphenyl tellurium dichloride (10 g) was added a saturated aqueous solution (60 ml) of sodium metabisulphite. The mixture was stirred for 4h. after which organic layer was separated and washed with distilled water. Removal of benzene afforded the crude telluride which was recrystallised from aqueous ethanol m.p 54° (lit.[8] 54°).

Di-p-ethoxyphenyl telluride :-

Di-p-ethoxyphenyltellurium dichloride was prepared following Morgan and Burstall's method[106] ;

Tellurium tetrachloride (10 g) and phenetol (23 g) were heated for 6 hr. at 170° , the solution was allowed to cool at lab. temperature. After cooling, (20 ml) of petrolium ether was added, followed by another 20 ml of ethanol. On cooling, it yielded dichloride. By crystallization from methanol colourless crystals were obtained m.p. 108° (lit[106] 108°).

The di-p-ethoxyphenyltellurium dichloride was reduced following Bergman's method[8] ;

Hydrazine (3.2 g) in ethanol (20 ml) was added slowly to a refluxing mixture of bis(4-ethoxyphenyl)tellurium dichloride (8.3 g) in ethanol (150 ml) and water (20 ml.).

In the beginning every addition resulted in vigorous evolution of N_2 and the dichloride dissolved gradually. The reaction was considered completed when an addition of hydrazine no longer caused evolution of N_2. The mixture was poured into water (200 ml) and extracted with ether after washing by water, and dried. The solvent was removed in a rotatory evaporator to afford di-p-ethoxyphenyl telluride, recrystallised from methanol, m.p. 54°C. (lit[8] 54°).

Thiocyanogen solution $(SCN)_2$:-

The action of bromine upon various metallic thiocyanates gives thiocyanogen in better yield, following Gardner and Weinberger's method[107] :-

Plumbous thiocyanate :-

Two solutions are prepared, one containing (25 gm) of purified sodium thiocyanate; the other, (65 gm) of the purified lead-nitrate, each in 100 ml. of distilled water. Both solutions are cooled to 0 to 5°C., and the solution of the sodium salt added to that containing the lead nitrate. The precipitate plumbous thiocyanate is filtered, washed with ice water, and allowed to dry over a suitable desiccant in the dark.

Acetic Acid-Acetic Anhydride solution

To the glacial acetic acid (99.5 per cent) 10 per cent acetic anhydride is added. This solution should be kept in a stoppered container protected from moisture.

Bromide :-

The commercial product may be dried (and partially purified) by shaking with an equal volume of concentrated sulphuric acid, and then separating the acid, the bromine is fractionated.

Bromine solution

The (8.4 gm) of pure bromine is dissolved in 200 ml of re-distilled, water-free carbon tetrachloride. To this is added 300 ml. of the specially prepared acetic acid solution.

Preparation of thiocyanogen solutions :-

To a suspension of (30 gm) of plumbous thiocyanate in 300 ml. of the acetic acid is added 5 ml. of the bromine solution. The mixture is agitated vigorously on a shaking machine until it is practically colourless, and another portion of the bromine solution is added. This procedure is continued until all of the bromine solution has been added. The mixture is then rapidly filtered through a dry fluted filter paper. This method gives an approximately O.1 N solution.

Diorganotellurium diisothiocyanates

Two methods of preparation were developed. (a) The appropriate telluride (5×10^{-3} mole) was dissolved in carbon tetrachloride (25 cm^3) and cooled to $0^{\circ}C$. A solution of thiocyanogen (20 cm^3, 0.1M) was added to the telluride solution under dry dinitrogen. Crystals were deposited overnight which were filtered and washed with carbon tetrachloride.

(b) e.g. Di(p-ethoxyphenyl)tellurium dichloride (2g) and ammonium thiocyanate (0.5g) were refluxed in methanol (25 cm^3) for 4 h. Ether (10 cm^3) was added to the cooled solution to precipitate ammonium chloride (i.r) which was removed by filtration. Water (50 cm^3) was then added to concentrate the tellurium compound in the ether layer The ether layer was separated and dried, after which removal of the solvent afforded the product.

An attempted reaction between dibutyltin diisothiocyanate and the diaryltellurium dichloride afforded only unreacted starting materials.

RESULTS :-

The analytical data for the $R_2Te(NCS)_2$, R is Ph, p-MeOPh, p-EtOPh are given in (table 1). Relevant i.r. data are given in (table 2) and are shown in (figures 3, 4, 5, 6).

The results of conductivity measurements are included in (table 1), the value of the molar conductivity in each case being consistent with the presence of 1:1 electrolyte. Conductivities were also measured as a function of concentration, hence two examples are shown on pages, (102, and 103).

The mass spectra of the three diisothiocyanates were tabulated on (page 101).

TABLE (1)

Compounds	Found			Calculated			Molar Conductivity
	%C	%H	%N	%C	%H	%N	($\Lambda_m = 10^{-3}$M Soln)
$Ph_2Te(NCS)_2$	42.7	2.05		42.3	2.53	7.04	Insouluble
$(p\text{-}MeOPh)_2Te(NCS)_2$	41.6	3.30		42.0	3.08	6.12	61($MeNO_2$)
$(p\text{-}EtOPh)_2Te(NCS)_2$	44.27	3.48	5.62	44.5	3.73	5.76	102($MeNO_2$)

Analytical and conductivity data for $R_2Te(NCS)_2$

TABLE (2)

Compounds	Solid state - ν(CN) thiocyanate and anion bands
$Ph_2Te(NCS)_2$	2060 s, 2050 s
$(p\text{-}MeOPh)_2Te(NCS)_2$	2060 sh, 2040 s
$(p\text{-}EtOPh)_2Te(NCS)_2$	2040 s, (sharp) 1980 s (U.br)

Infra-red data (frequencies in wave numbers) for $R_2Te(NCS)_2$

TABLE (3)

Mass Spectra of $R_2Te(NCS)_2$ Relative to ^{130}Te, ^{14}N, ^{32}S

$Ph_2Te(NCS)_2$			$(p\text{-MeOPh})_2Te(NCS)_2$		
m/e	R.I%	Species	m/e	R.I%	Species
400	0.05	$Ph_2Te(NCS)_2^{+\cdot}$	346	100	$(p.MeOPh)_2Te^+$
342	1	$Ph_2Te(NCS)^+$	284	100	Ph_2Te^+
284	100	Ph_2Te^+	207	100	$PhTe^+$
207	100	$PhTe^+$	164	100	$Ph_2{}^+$
164	100	$(C_6H_5)_2{}^+$	77	100	Ph^+
77	100	$(C_6H_5{}^2)^+$	116	100	$(SCN)_2{}^+$
116	100	$(SCN)_2{}^+$	106	70	$MeOPh^+$

$(p\text{-EtOPh})_2Te(NCS)_2$

m/e	R.I%	Species
488	1	$(p\text{-EtOPh})_2Te(NCS)^+$
372	2	$(p.EtOPh)_2Te^+$
252	50	$p\text{-EtOPhT}_e{}^+$
207	20	$PhTe^+$
164	100	$Ph_2{}^+$
121	100	$p\text{-EtOPh}^+$
77	100	Ph^+
116	100	$(SCN)_2{}^+$

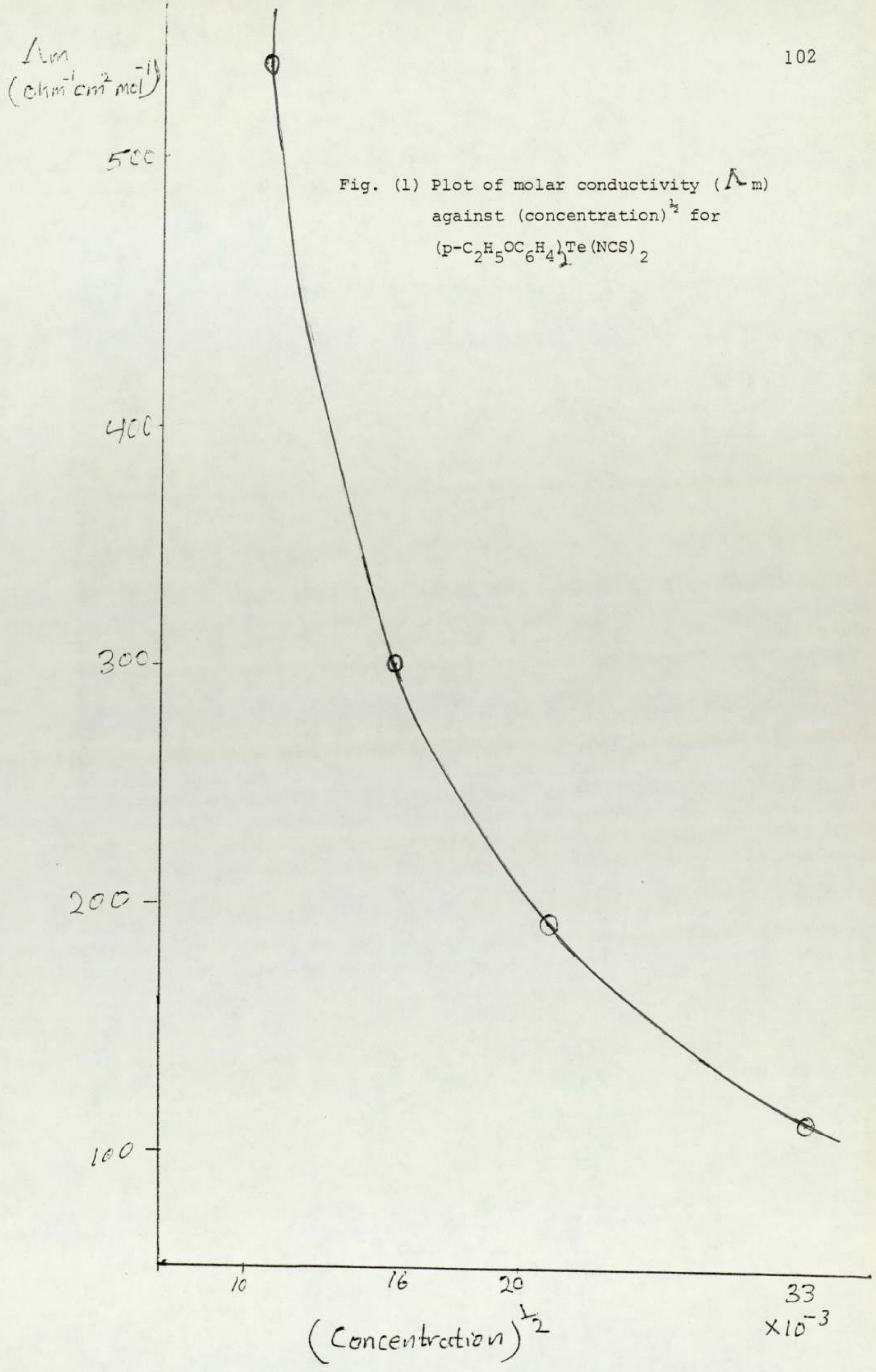
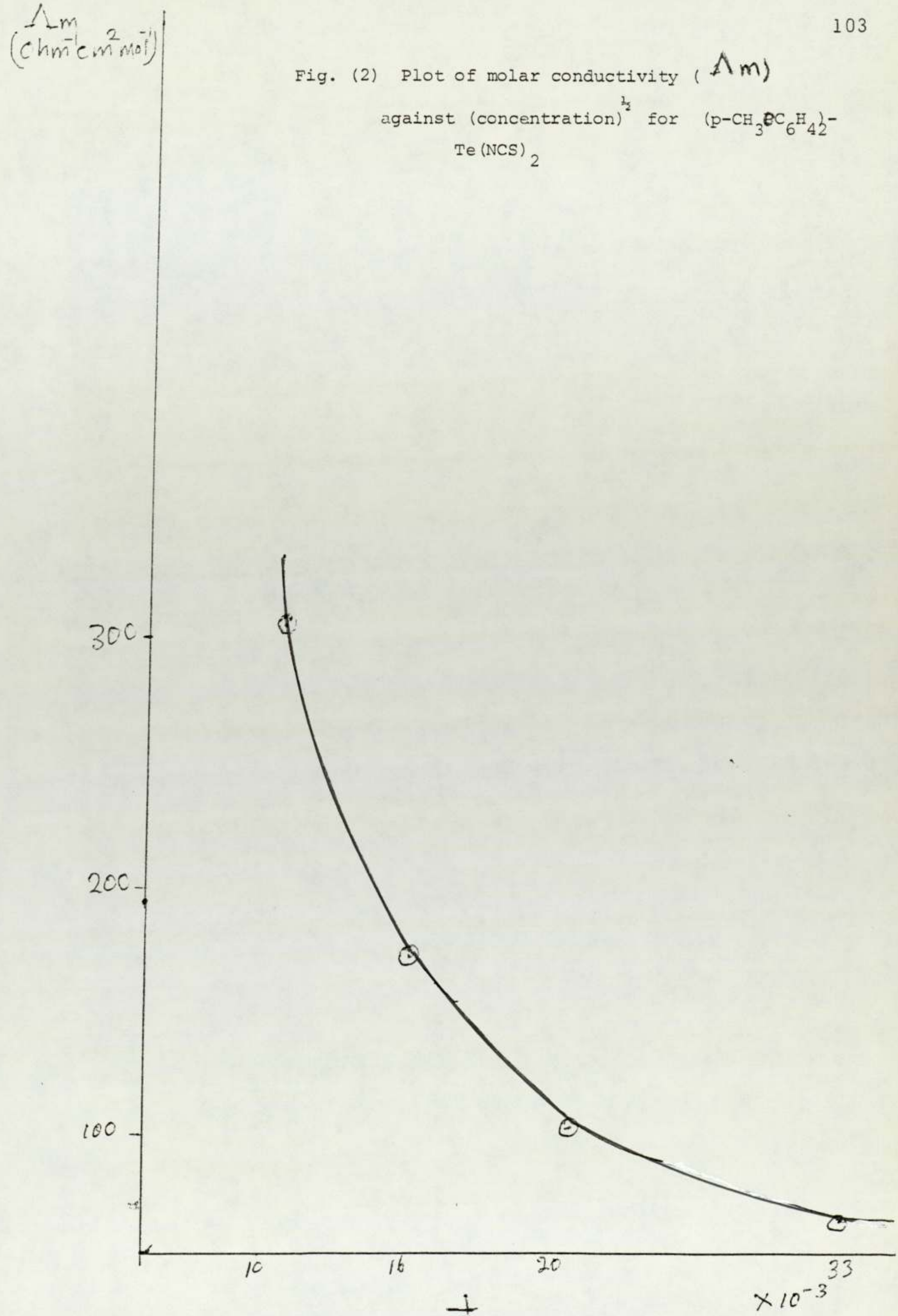
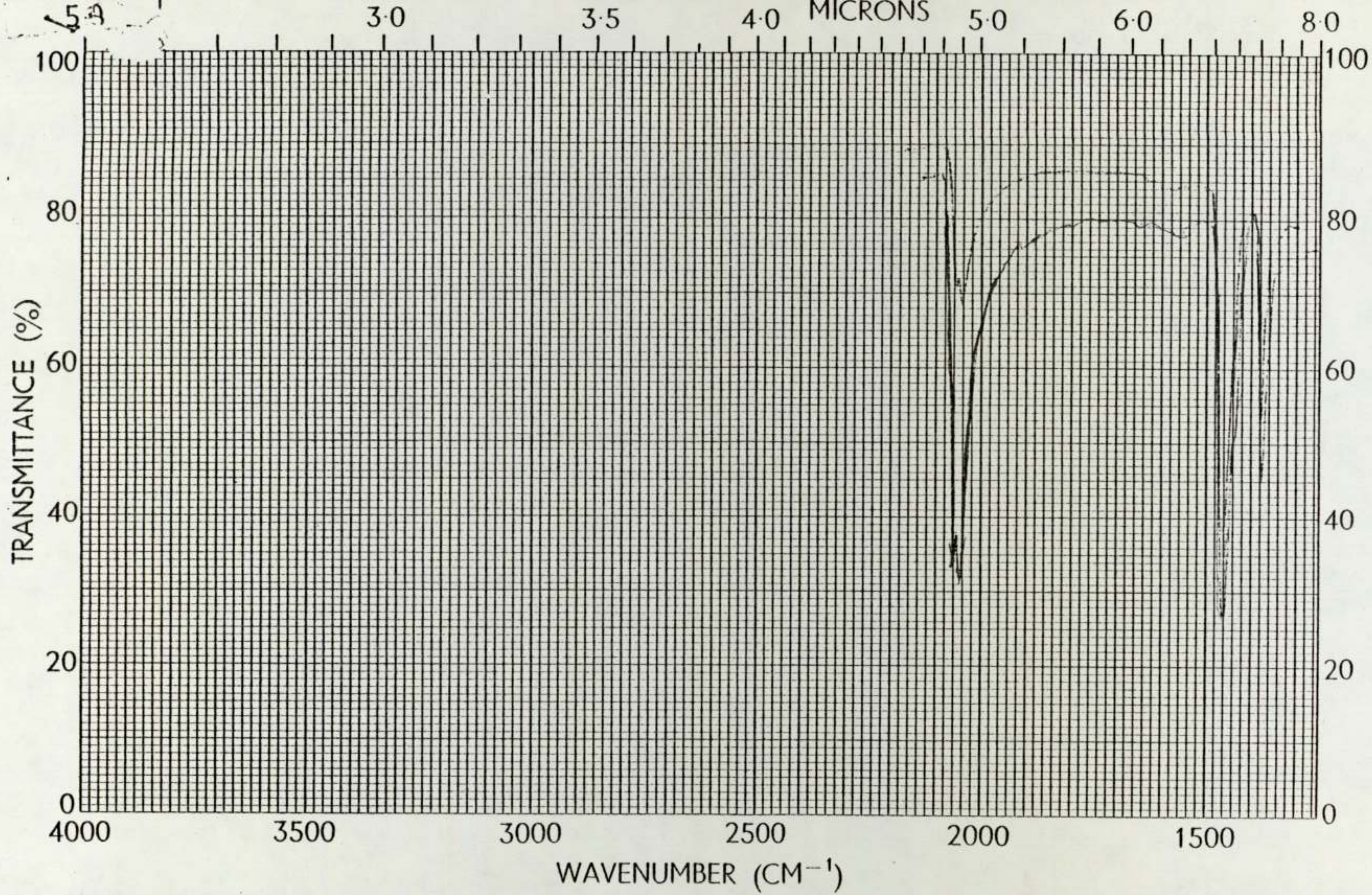


Fig. (1) Plot of molar conductivity (Λm) against (concentration)$^{\frac{1}{2}}$ for $(p\text{-}C_2H_5OC_6H_4)_2Te(NCS)_2$

Fig. (2) Plot of molar conductivity (Λm) against (concentration)$^{\frac{1}{2}}$ for (p-CH$_3$OC$_6$H$_4$)$_2$-Te(NCS)$_2$





SAMPLE

Infra-red spectra of $Ph_2Tl(NCS)_2$

Fig. (3)

ORIGIN

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CONC.

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REFERENCE

SCAN SPEED

SLIT

OPERATOR

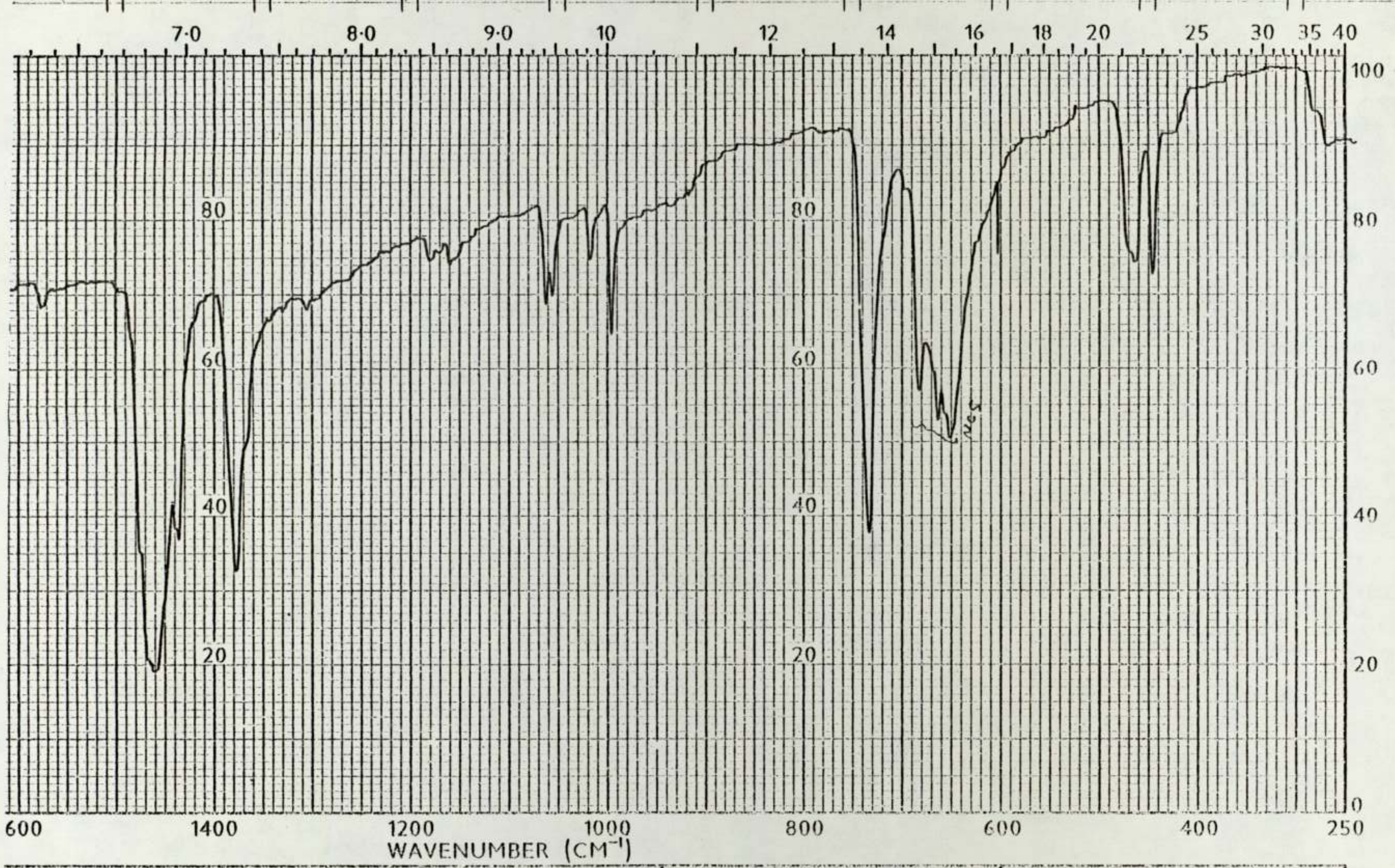
DATE

REMARKS

No.

PART No. 237E - 1034/C2

SENSITISED COATINGS LTD., COULSDON, SURREY 4/82



REMARKS Infra-red spectra of $ph_2Te(NCS)_2$ (KBr)

Continued....

SCAN SPEED Medium.

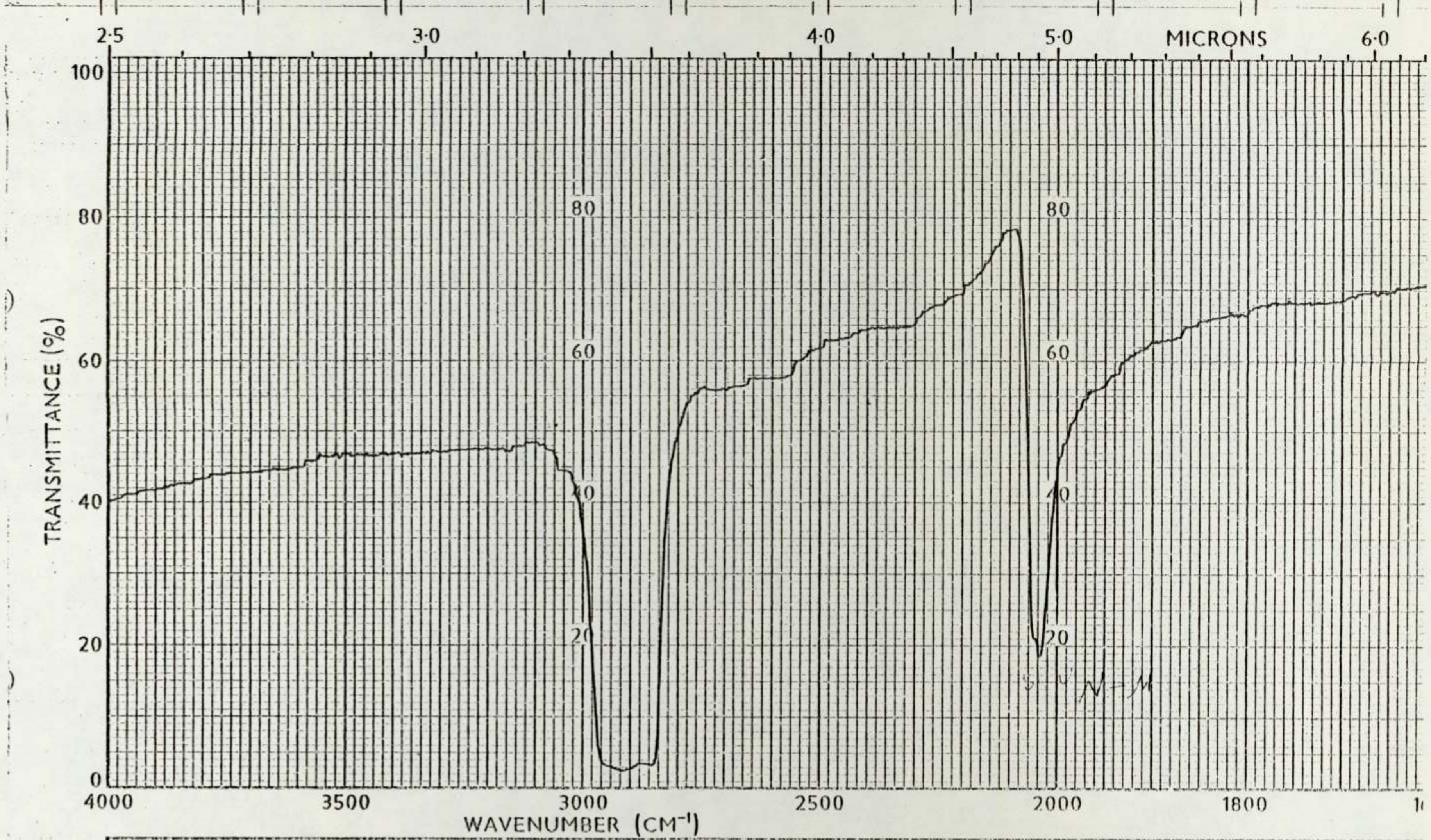
SLIT Standard.

RPK/219/1002 457-5001
Intek

OPERATOR V.H. Clenton

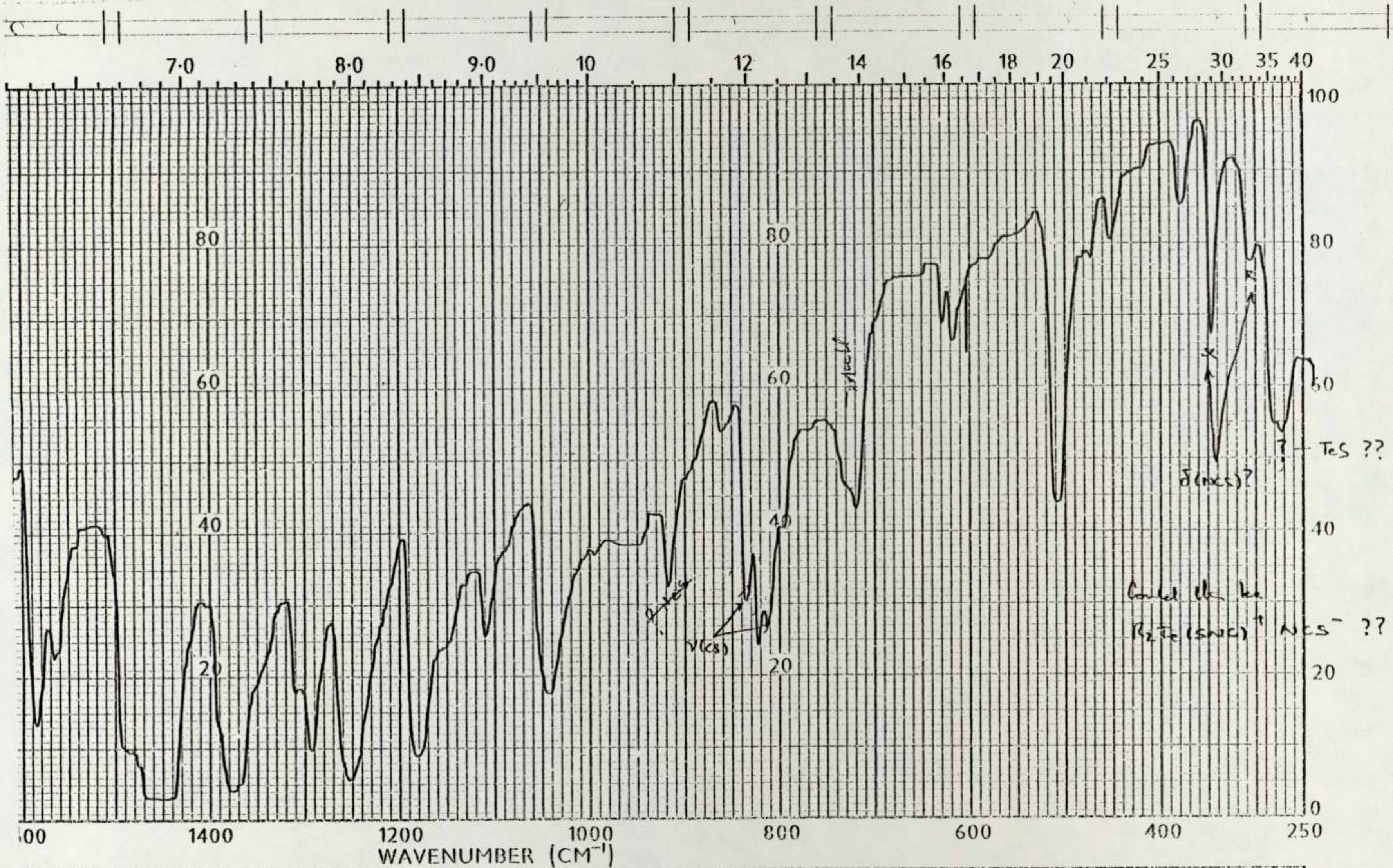
DATE 20th. January 1977

REF. No. 9310



SAMPLE
Infra-red spectra of $Ph_2Te(NCS)_2$
Fig. (4)
ORIGIN F. H. Musa.

SOLVENT Nujol
CONCENTRATION Mull
CELL PATH CsI plates
REFERENCE Air.



EMARKS

Infra-red spectra of p-EtOPh)$_2$Te(NCS)$_2$

Fig. (5)

SCAN SPEED Medium

SLIT standard

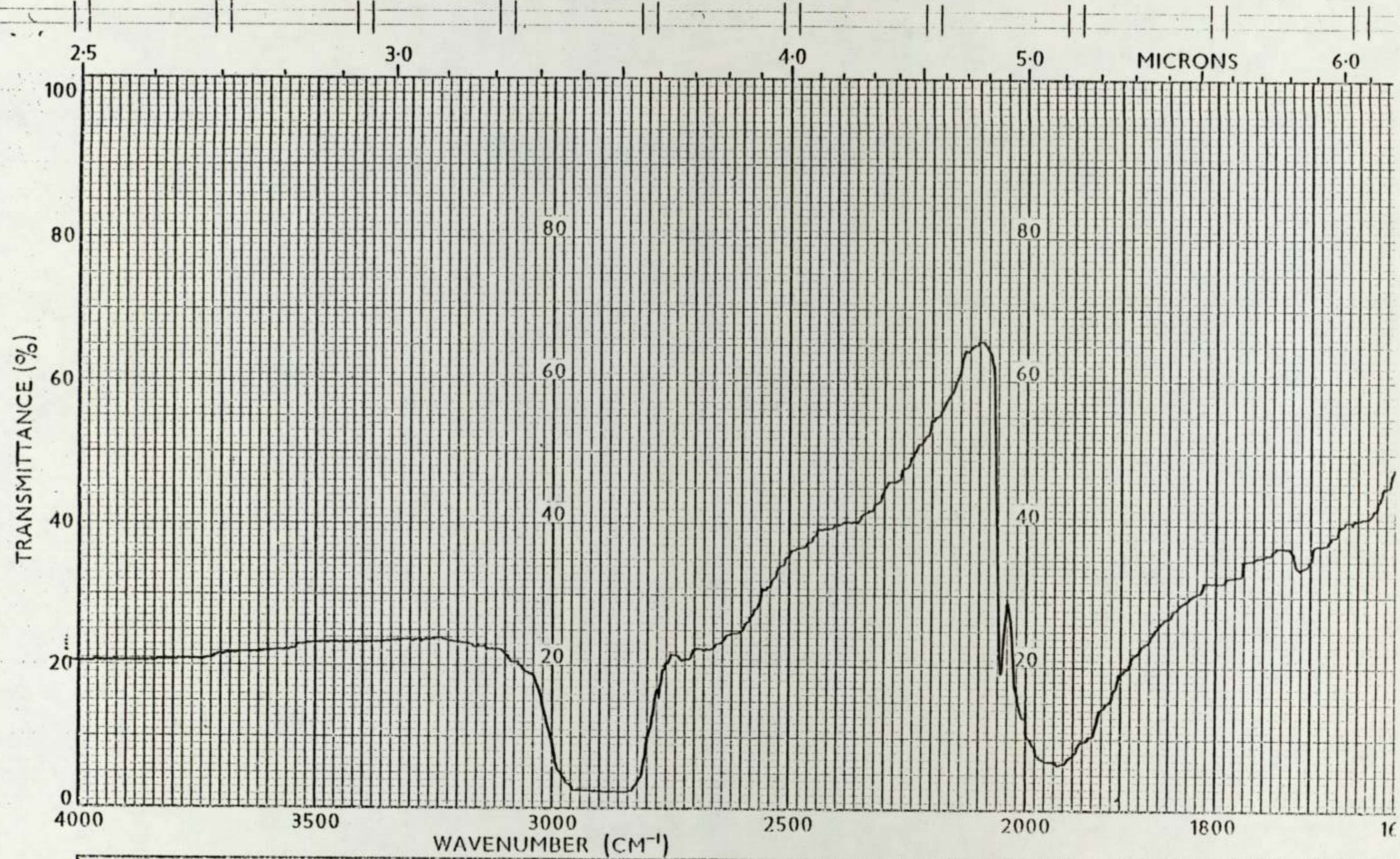
RPK/2I9/1002 457-5001

Intek

OPERATOR V. M Clenton

DATE 20th Jan. 1977

REF. No. 9302.



SAMPLE (p-EtOph)$_2$Te(NCS)$_2$

cont. Fig. (5)

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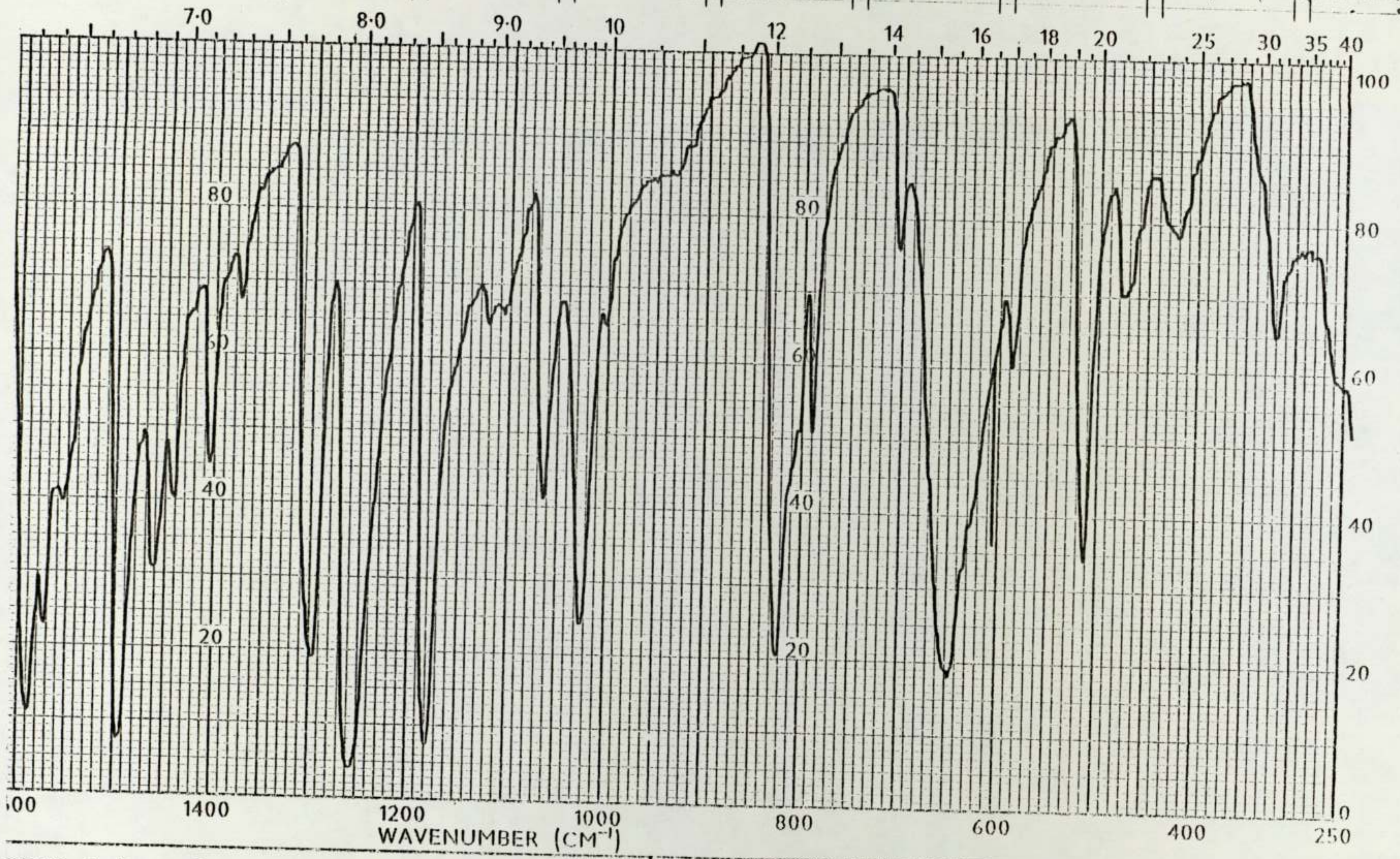
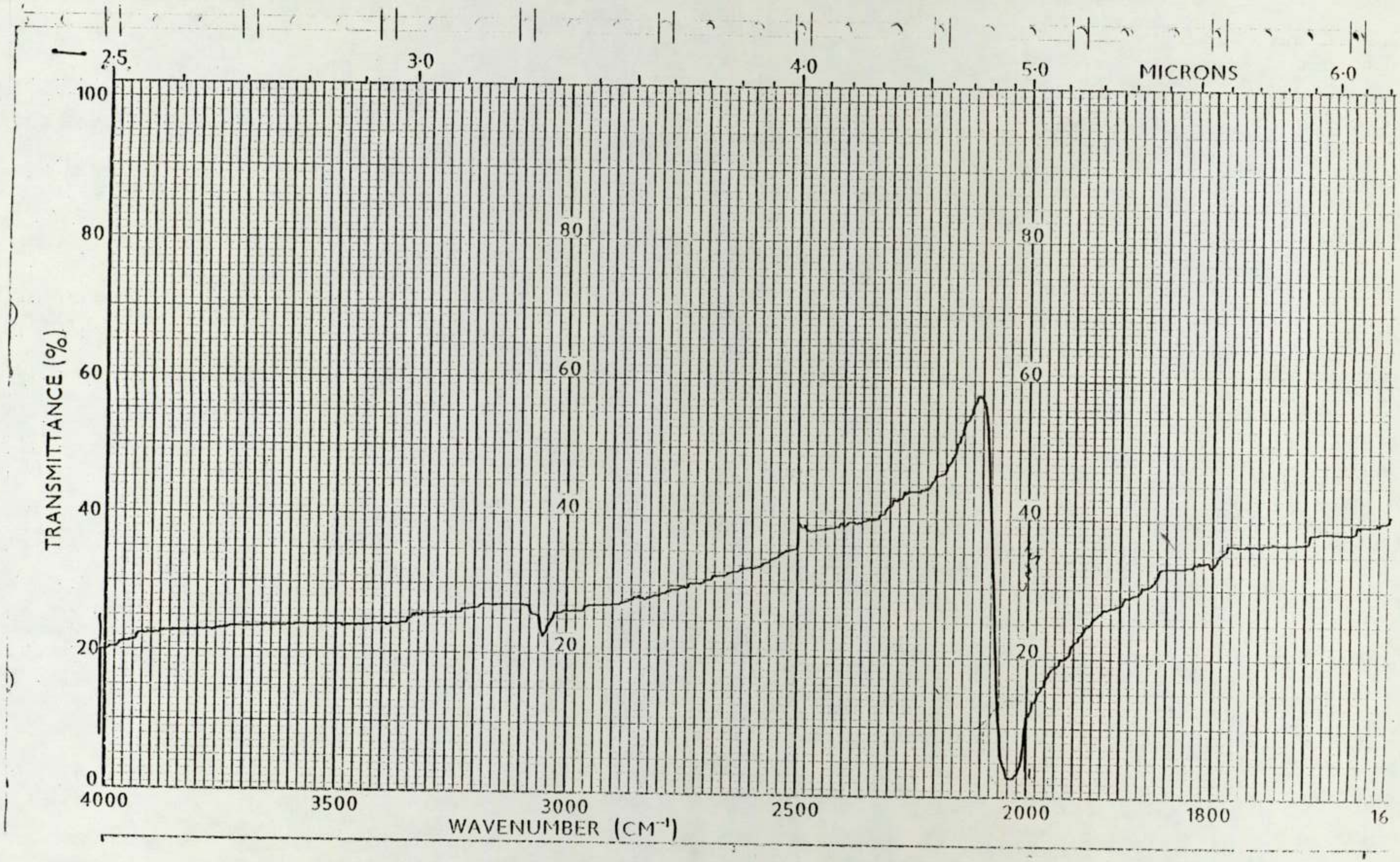


EMARKS Infra-red spectra of $(p\text{-}MeOph)_2Te(NCS)_2$

Fig. 6

SCAN SPEED Medium.
SLIT standard.
RPK/219/1002 457-5001
Intek

OPERATOR Q. M. Clenton.
DATE 14th April 1977
REF. No. 7622.



Infra-red spectra of (p-MeOph)$_2$Te(NCS)$_2$ (KBr)

Fig. (6) continued.

DISCUSSION OF $R_2Te(NCS)_2$

Conductivity :-

The solution behaviour of these materials is also of interest, $Ph_2Te(NCS)_2$ is insoluble in solvents suitable for conductivity measurements, but p-methoxy and p-ethoxyphenyl derivatives dissolve in nitromethane to give colourless conducting solutions. Single concentration (10^{-3} M) conductivity studies of the (p-$MeOC_6H_4)_2Te(NCS)_2$ and $(p\text{-}C_2H_5OC_6H_4)_2Te(NCS)_2$ in nitromethane give values of the molar conductivity (Λm) 61, 106 mhos cm^{2} mol^{-1}. This represents an appreciable conductivity with a 1:1 electrolyte. Investigation of the conductivity over a range of concentration for both compounds gives non-linear plots of Λm against (concentration)$^{\frac{1}{2}}$ (Fig. 1, 2), hence we are probably dealing with the following equilibria :

$$R_2Te(NCS)_2 \rightleftharpoons R_2Te(NCS)^{+} + NCS^{-}$$

$$R_2Te(NCS)^{+} \rightleftharpoons R_2Te^{+} + NCS^{-}$$

$$R = p\text{-}CH_3OC_6H_4, \quad p\text{-}C_2H_5OC_6H_4.$$

This provides an interesting parallel with the infrared spectra of these compounds and comparable with mass spectra which confirm the decomposition of these compounds led to diphenyl telluride and thiocyanogen. Thus the p-methoxy-compound shows properties intermediatebetween those of the phenyl and p-ethoxyphenyl compounds, resembling the former in the solid state and the latter in solution.

Vibrational spectroscopy :-

There has been a rapid growth of interest in the study of the thiocyanate ion in inorganic and organic compounds and co-ordination complexes. The recently reported synthesis of a range of triphenyltellurium pseudohalides [43a] together with crystallographic data [43b] and the crystal and molecular structures of $(Ph_3Te)(NCO)\frac{1}{2}CHCl_3$ and $(Ph_3Te)(NCS)$ [44] together with the work of Dance [52] on Ph_2MeTeX (X = Cl.Br.I) have led to attempts to synthesise new thiocyanate derivatives.

Three new compounds ($R_2Te(NCS)_2$ R = Ph, p-$CH_3OC_6H_4$, p-EtO.C_6H_4) which are the first examples of di-organo tellurium dipseudohalides are conveniently prepared from the reaction of thiocyanogen [107] with the appropriate telluride. Alternatively, the compounds may also be prepared by the reaction of ammonium thiocyanate and the diorgano tellurium dichloride in methanolic solution.

Unfortunately, all attempts made by ourselves and others [108] to grow crystals of $(p\text{-}C_2H_5OC_6H_4)_2Te(NCS)_2$ suitable for structural investigation have failed, thus it is not possible to establish whether it is nitrogen or sulphur which is bound to tellurium. But we have been able to obtain information by other physical methods. The fact that the bonding extremes are M-N=C=S and M-S-C≡N, on conventional formulation, suggested that it should be possible to distinguish between the two forms by studying the CN and CS frequencies in the infrared spectrum.

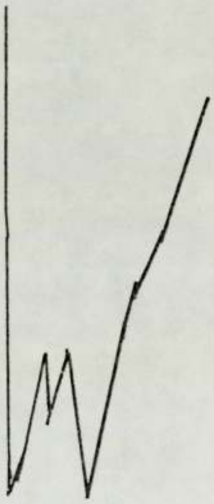
Turco and Pecile [105] have investigated the vibrational behaviour of the thiocyanate group in several inorganic compounds (as have Chamberlain and Bailar [109], Kinel and Strandberg, [110] and Mitchell and Williams [111]). However, the last two authors have limited their work to the CN stretching vibrations. There are three ways in which the di-functional thiocyanate ion can be attached to a metal cation, namely, M-SCN, M-SCN-M' and M-NCS. They can be differentiated by the frequencies assigned to the fundamental stretching modes of the triatomic group, approximating to CN and CS stretching. In fact the CS-stretching frequency is more diagnostic, particularly in the absence of M-SCN-M' bridges. Analysis of the CS-stretching frequencies in S-bonded compounds; $Hg(SCN)_2$, $K_2Hg(SCN)_4$, $K_2Pd(SCN)_4$ showed that ν (CS) occurs between 690 and 720 cm^{-1}, and is in the range 780 - 860 cm^{-1} for the $M \leftarrow NCS$ compounds $Ni(PR_3)_2(NCS)_2$, <u>trans</u> $(Pt(PEt_3)_2)(NCS)_2$, $Zn(N_2H_4)(NCS)$

Unfortunately, in the infrared spectra of $R_2Te(NCS)_2$ where R is phenyl, $p\text{-}CH_3OC_6H_4$ and $p\text{-}C_2H_5OC_6H_4$, these regions are obscured by the rich contribution to the spectrum of the aromatic groups. Thus, we will concentrate on the region 2100 - 2000 cm^{-1}.

The criterion adopted until now is to establish the band type. Thus, the thiocyanato-complexes exhibit very sharp well formed N-C stretching bands above 2100 cm^{-1}, whereas the isothiocyanato-complexes exhibit relatively broad more intense, bands around or below 2100 cm^{-1}. The infrared absorption spectra of KNCS in the solid is 2053 cm^{-1} due to ν(CN)[112]. Thus, for complexes of palladium (II), ν(CN) is said to be sharp and above 2100 cm^{-1} for thiocyanato complex, but below 2100 cm^{-1} and broad for N-bonded case[113]. The complex of $(RuCl_3)(AsPh_3)_3$ with thiocyanate[114] shows that bands in 2100 cm^{-1} region suggested that SCN groups are linked in the complexes, possibly in two different ways. The band at 2080 cm^{-1} may be assigned to ν (CN) of the N-bonded terminal thiocyanato-group while the band at 2140 cm^{-1} arises from the bridged SCN group. The organic thiocyanates showed a sharp strong peak due to the nitrile (CN) stretching vibration around 2140 cm^{-1}. Methylthiocyanate showed band at

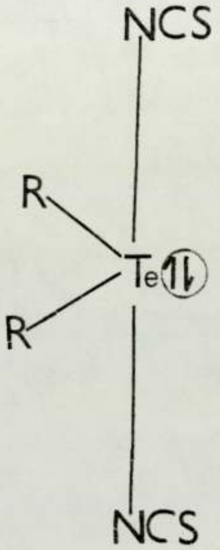
2140 cm^{-1} which can be ascribed to the (SCN) . The organic isothiocyanates exhibit abroad and very strong band centred around 2080 - 2105 cm^{-1} due to the isothiocyanate group [115] . However, the frequencies of these ; R NCS cannot be compared directly with organo-metallic thiocyanate because of the mass effect of the metal.

The recently reported synthesis of triphenyltellurium-isothiocyante [43a] together with crystallographic data [43b] studied infra-red spectrum. The infrared of the triphenyl telluronium isothiocyanate showed three infrared ν (CN) stretching vibrations around 2062 cm^{-1} due to three bridging crystallographically independent (NCS) groups, as illustrated below.



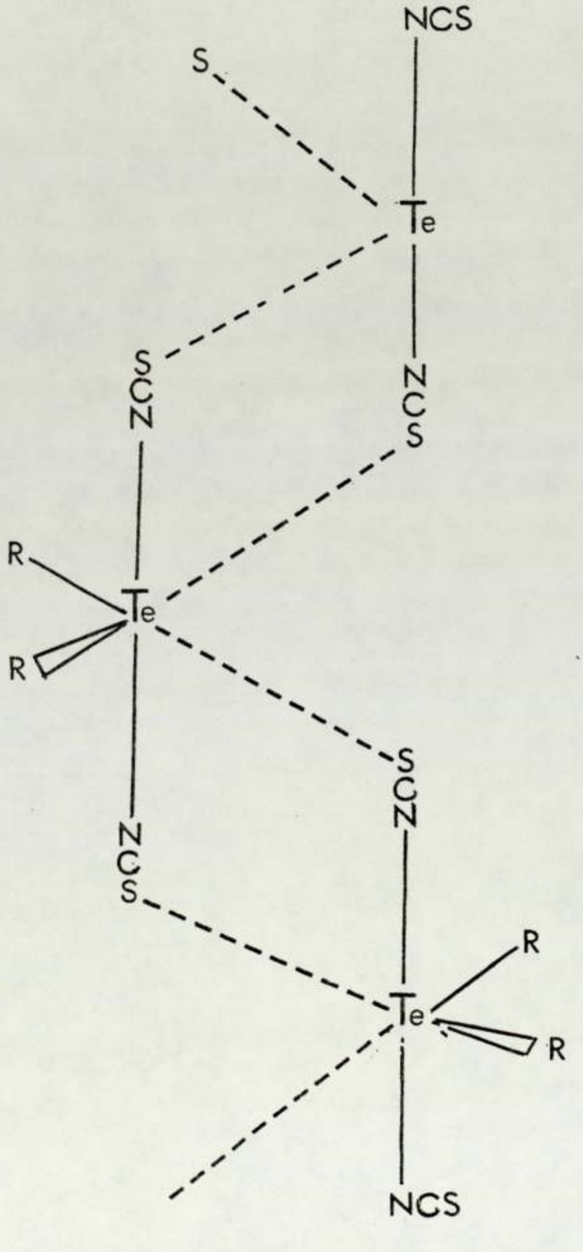
i.r. spectrum (KBr) (1900-2200 cm^{-1}, of Ph_3TeNCS

The data on the high-frequency stretching vibration of $R_2Te(NCS)_2$ where R is Ph, MeOPh, EtOPh are assembled in table 2 . The ν (CN) vibration is split in $R_2Te(NCS)_2$ for both R = Ph and R = p-MeOC$_6$H$_4$. The infrared spectrum of $(p\text{-EtO.}C_6H_4)_2Te(NCS)_2$ is rather different in the ν (CN) region and is characterised by a broad band at 1980 cm^{-1} and a sharp one at 2040 cm^{-1}. In the light of this data, and the argument made above, we might conclude that the (NCS) groups are bonded via nitrogen to tellurium (IV) in the case of the phenyl and p-methoxyphenyl compounds. This would be expected if we take the usual view that in the compounds, R_2TeX_2, the more electronegative X will take an axial position in the pseudotrigonal bipyramid and will thereby be better able to accommodate the electron density within the non-bonding molecular orbital associated with axial bonds. Clearly this is a role more suited to nitrogen than to sulphur as indicated schematically.



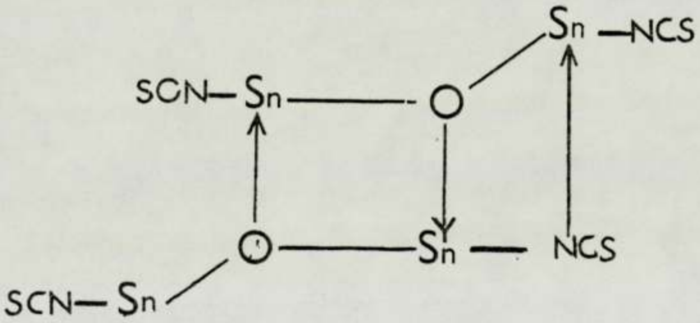
R = Ph, $MeOC_6H_4$, p-$EtOC_6H_4$

However, the above structure is probably not well described by the term "pseudo trigonal bipyramidal". Furthermore, substantial differences are noted in the solid state i.r. spectra. The infrared spectra of diphenyl or di p-methoxy phenyl tellurium diisothiocyanates are shown on page 104, 109. The absorption due to ν (CN) is a doublet with components above 2000 cm^{-1}. The dialkyltin diisothiocyanate $R_2Sn(NCS)_2$(where R is methyl ethyl, propyl and butyl,) which were investigated by WADA[116] showed marked high frequency bands for NC - stretching vibration as follows ; 2088 VS, 2062 VS for $(CH_3)_2Sn(NCS)_2$. $(C_2H_5)_2Sn(NCS)_2$ absorbed at 2079 VS, $(^nC_3H_7)_2Sn(NCS)_2$ showed band at 2075 VS, 2066 VS and $(^nC_4H_9)_2Sn(NCS)_2$ showed a band at 2081 VS. It might result from the bridging of NCS groups to adjacent tin atoms as interpreted for the spectra of triphenyl telluronium isothiocyante. Thus in the infrared spectra of the diphenyl tellurium diisothiocyanate, the components are at 2060, 2050 cm^{-1} and for di p-methoxypheny tellurium diisothiocyanate, the components are at 2060 and 2040 cm^{-1}. Which may imply a non-linear SCN-Te-NCS system with relatively weak tellurium-nitrogen bonds, but more probably hints at some molecular association via weakly bridging thiocyanate groups in which the sulphur atoms form long bonds to tellurium in a neighbouring molecule, thus giving the tellurium a distorted six-coordinate environment, as indicated schematically below :

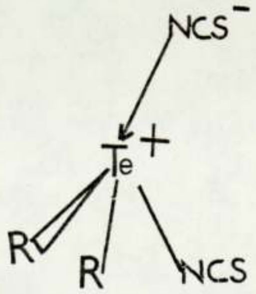


Schematic structures envisaged for $R_2Te(NCS)_2$ R = Ph, p-$CH_3OC_6H_4$

The infra-red spectrum of di-p-ethoxyphenyl tellurium diisothiocyanate is shown on page 107 . The NCS stretching band at 1980 cm^{-1} for $(p\text{-}EtOC_6H_4)_2Te(NCS)_2$ is unique, since such a low frequency band has never been observed in the spectra of other triphenyltelluronium isothiocyanate and in $R_2Te(NCS)_2$(where R is phenyl or p-methoxyphenyl) and in dialkyltindiisothiocyanate. But the N-C stretching band at 1960 cm^{-1} for the (SCN) $R_2SnOSnR_2$-(NCS) was observed. The lowering of this ν (NC) stretching band frequency was interpreted as being caused by the bridging to another tin atom by the nitrogen atom, and such a bridging was expected for the NCS group attached to the oxygen-co-ordinated in the atom in the dimeric distannoxanes as shown below .



The infrared spectrum of $(p\text{-}EtOC_6H_4)_2Te(NCS)_2$ gives the ν (CN) region which is characterised by a broad band at 1980 cm^{-1} and implies a much stronger covalent bond interaction of one group than of the other ν (CN) = 2040 cm^{-1}. A reasonable interpretation is that a telluronium compound, $\left[(p\text{-}EtO.C_6H_4)_2TeNCS\right]^+$ $(NCS)^-$, provides a better model as shown below ;



This proposition receives excellent support from conductivity measurements on $(p\text{-EtO.Ph})_2Te(NCS)_2$ in acetonitrile which suggested a 1:1 electrolyte (more details on page 111) ;

$$R_2Te(NCS)_2 \longrightarrow (R_2Te.NCS)^+ + NCS^-$$

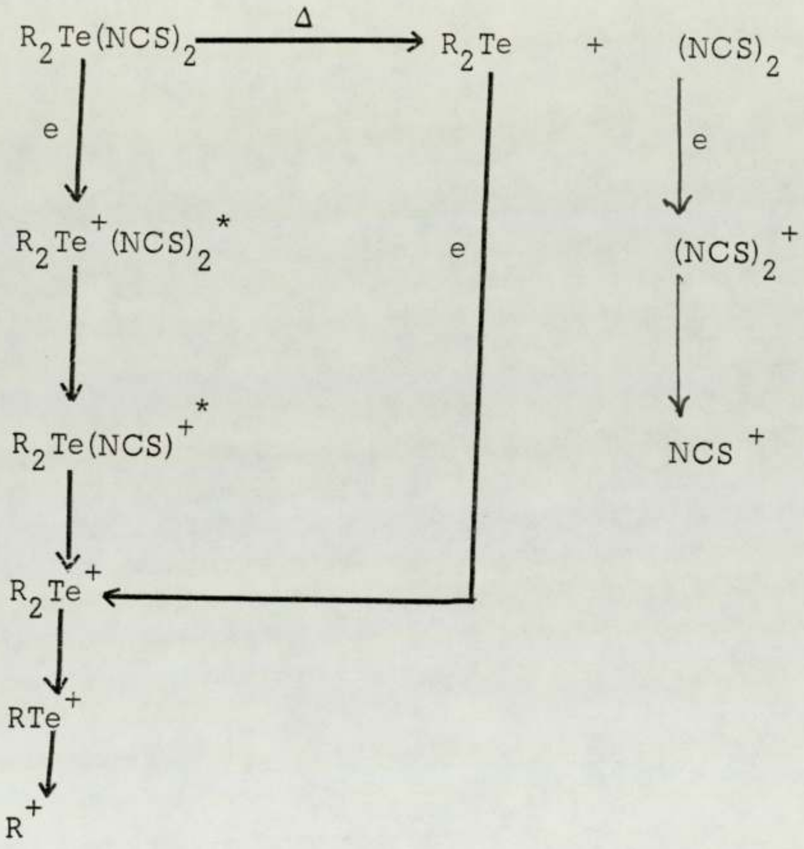
Even in this case it is likely that some degree of oligomerisation occurs within the solid. But the tellurium does not interact symmetrically with two NCS groups. The energy balance between the two structural classes that appear to exist is probably delicate. Thus we argue that the change occurs as a result of the influence of the para - substituent (H, MeO or EtO) on the relative lattice energies of the two structures, rather than as a consequence of any electronic effect at the tellurium.

Mass Spectra :-

Mass spectra of $R_2Te(NCS)_2$(where R is Ph, p-MeOPh, p-EtOPh) were tabulated in table 3 . The $Ph_2Te(NCS)_2$ is shows a weak parent ion at m/e = 400 ($^{12}C_{14}\,^{1}H_{10}\,^{32}S_2\,^{130}Te$) together with fragments showing stepwise loss of NCS , i.e. $Ph_2Te(NCS)^+$ m/e = 342 and Ph_2Te^+ m/e = 284. The $(p\text{-MeOPh})_2Te(NCS)_2$ showed no peak due to the parent ion but the major peak m/e = 346 due to $(p\text{-MeOPh})_2Te$ and thiocyanogen m/e = 116. The $(p\text{-EtOPh})_2Te(NCS)_2$ gave a weak parent ion at m/e = 488 and a major peak at m/e = 372 due to $(p\text{-EtOPh})_2Te$.

Thus, some differences are observed in the behaviour of these materials in the mass spectrometer. As is often the case with such organometallic compounds, the fragmentation pattern observed probably arises from a combination of thermolysis (reductive elimination of thiocyanogen), which dominates in the case of $(p\text{-MeOPh})_2Te(NCS)_2$, and volatilisation to monomeric species in the vapour phase. We may usefully conclude that the spectra do confirm that the structures building blocks for the solids are indeed $R_2Te(NCS)_2$. The fragmentation patterns of these diisothiocyanates are as follows :

General Scheme



* These could give $R_2Te(NCS) + NCS^+$

$R_2Te + NCS^+$

R is Ph, p-MeOPh, p-EtOPh.

Preparation of Triorganotelluronium Salts :-

The modification of Lederer's method to produce Ph_2MeTeI

The concial flask was dried and flushed with dry nitrogen were placed a freshly distilled methyliodide (10-15 ml.) and diphenyltelluride (5 gm). The mixture was left for 2 hrs. (Lederer's method reported 48 hrs.), gave glistening needles, which were recrystallised from water to m.p. 123-124 °C (lit.[47] 123-124°C).

Methyldiphenyltelluronium isothiocyanate

An aqueous solution of silver nitrate (1.5 g) was added to an aqueous solution of potassium thiocyanate (1.5 g) to afford a curdy white precipitate of silver thiocyanate. To this mixture was added an aqueous solution (200 cm^3) of methyldiphenyltelluronium iodide (1.5 g). The mixture was stirred for 1 h. at room temperature, then heated under reflux for 4 h. The reaction mixture was then concentrated and the precipitate of silver iodide removed. On further concentration and cooling white crystals of the product appeared, m.p. 125°C.

Methyldiphenyltelluronium tetrafluroborate

Silver tetrafluroborate was obtained by crystallising the solution resulting from the neutralization of tetrafluroboric acid with silver oxide. The above method was then followed using Ph_2MeTeI (0.5g) and $AgBF_4$ (0.23g). The product was obtained as white crystals, m.p. 135°C.

Methyldiphenyltelluronium hexafluorophosphate

IRA 400 resin (30 g), exchanged with PF_6^-, was added to an aqueous solution (200 ml) of methyldiphenyltelluronium iodide (0.2 g). The mixture was gently warmed and stirred for 4 h.

The resin was removed and the solution concentrated to afford white crystals of m.p. 135°C.

RESULTS :-

Analytical data for the tellurium salts : ie. Ph_2MeTeX, X = BF_4, PF_6, (SCN) are listed in table (2).

Conductivity Measurements :-

The molar conductivity of each telluronium was determined in dimethylsulphoxide or in dimethylformamide for Ph_2MeTe (NCS) as well. The value of the molar conductivity the value of the molar conductivity being within the ratio 1:1. The results are tabulated on (page 124). Conductivities were also measured as a function of concentration. 3- examples are described on (pages 148 - 150).

Solubility :-

The telluronium salts are soluble in DMSO, but, with the exception of $Ph_2MeTeNCS$, they are not soluble in chloroform.

Infra-red spectra :-

The infra-red spectra, 4000-250 cm^{-1} of telluronium salts in a KBr matrix and in a nujol mull, 4000-650 cm^{-1} are presented on (pages 132, 136, 139).

The infra-red spectrum of $Ph_2MeTe(NCS)$ in chloroform solution is shown on page 135. The initial spectrum consists of a broad band due to ν (CN) centred on 2059 cm^{-1} this decays with time,(about 3h.) to be replaced by extremely sharp band at 2161 cm^{-1} due to methyl thiocyanate in chloroform is given on (page 136).

^{1}H.n.m.r. Spectra

The ^{1}H.n.m.r. spectra obtained for Ph_2MeTeX, X = NCS, BF_4, PF_6, which were readily soluble in DMSO (d_6), are shown on pages (145, 146), and recorded in table 8 . A single methyl resonance in the range δ = 2.72-2.68 ppm. (relative to TMS) with satellites due to coupling of ^{125}Te($J\,^{125}Te-{}^1H$ = 24 Hz) is seen. The 'H n.m.r.

spectra of $Ph_2MeTeNCS$ in $CDCl_3$ is shown on (page 142) and recorded in table 8 . The methyl resonance is initially located at $\delta = 2.90$ ($J^{125}Te-{}^{1}H = 25$ Hz) as time passes, the initial methyl resonance decays to be replaced by a new resonance at $\delta = 2.56$ ppm, reasonably assigned to methyl thiocyanate, e.g reasonably assigned to methyl thiocyanate in view of the complementary i.r. data and of the fact that ethanolic solution of MeSCN give $\delta = 2.60$, table 8.

The plot of concentration of growing methyl thiocyanate against time, and the plots of log (a-x) versus time are shown on (pages 152, 153), and recorded in table 6, 7 . a is initial concentration of Ph_2-MeTe(NCS), after a time t , x of a has decomposed to MeSCN, the remaining concentration of a is (a-x).

The first order rate plot was constructed from the data fig 20 The reductive elimination of, exlusively methyl thiocyanate occurs. The mechanism of the decompsotion is not simple, since after approximately 100 min. the rate of decomposition increases. In the presence of excess Ph_2Te, this increase in rate occurs earlier. The studies of $Ph_2MeTePF_6$ in DMSO/$CDCl_3$ indicated the slow production of methyl chloride, (fig 11).

TABLE (1)

COMPOUND	Solvent/molar conductivity (ohm^{-1} cm^{-1} mol^{-1})	
	DMF	DMSO
$Ph_2MeTe(NCS)$	95	27
$Ph_2MeTeBF_4$	39-	34
$Ph_2MeTePF_6$	39-	36

Conductivity Measurements on Solutions of some New telluronium salts.

Solution was 10^{-3} Molar.

TABLE (2)

COMPOUNDS	FOUND			CALCULATED		
	%C	%H	%X	%C	%H	%X
$Ph_2MeTe(NCS)$	47.2	3.70	3.54	47.4	3.69	3.95^a
$Ph_2MeTeBF_4$	40.4	3.67	9.0^b	40.7	3.42	9.2^b
Ph_2MePF_6	35.3	2.93	6.38	35.3	2.97	7.01^c

Analytical data for some new organotelluronium salts

a% N, b% S %C P

TABLE 3

Compound	Solid state ν (CN) thiocyanate and anion bands	Solution - $CHCl_3$	(Te - Me) solid
$Ph_2MeTe(NCS)$	2078s (assymm. to low wave number	Time = 0 2059 s, br. Time 0 2059 (assym. to low wave number - diminishing, 216 (sharp, growing).	536.W
MeSCN		2161 s, sharp	-
$Ph_2MeTeBF_4$	1088 1060 $\nu_3(BF_4)$ 1038	Insoluble	520.W
$Ph_2MeTePF_6$	880 860 $\nu_3\ (PF_6)^-$ 840		
	556 $\nu_4\ (PF_6)^-$	Insoluble	Masked

Infra-red data (frequencies in wave numbers) for some new telluronium salts.

TABLE 4

$Ph_2MeTe(NCS)$			$Ph_2MeTePF_6$		
m/e	Rel. Intensity	Species	m/e	Rel. Intensity	Species
357	22.2	$Ph_2MeTe(NCS)^+$	299	100	Ph_2MeTe^+
299	5.52	Ph_2MeTe^+	284	100	Ph_2Te^+
284	100	Ph_2Te^+	222	22.2	$PhTeMe^+$
222	11.1	$PhTe^+Me$	207	100	$PhTe^+$
207	100	$PhTe^+$	145	100	PF_6^+
154	100	$(C_6H_5)_2^+$	107	100	PF_4^+
			88	22.2	PF_3
73	100	$(CH_3SCN)^+$	34	11.1	CH_3F
58	50	$(SCN)^+$			
77	100	$C_6H_5^+$	154	100	$(C_6H_5^+)_2$
51	100	$C_4H_3^+$	77	22.2	$C_6H_5^+$
29	-	$C_2H_5^+$	-	-	

33.8 metastable for :

$C_6H_5^+ \longrightarrow C_4H_3^+$

84.0 metastable for:

$(C_6H_5)_2Te^+ \longrightarrow (C_6H_5)_2^+$

Mass spectra data for $Ph_2MeTe(NCS)$, $Ph_2MeTePF_6$.

TABLE (5)

m/e	Rel. Intensity	Species
367	5.55	$Ph_2MeTeBF_3^+$
329	5.55	$Ph_2MeTeBF^+$
299	100	Ph_2MeTe^+
284	100	Ph_2Te^+
222	100	$PhTe^+Me$
207	100	$PhTe^+$
154	100	$(C_6H_5)_2^+$
91	92	$C_7H_7^+$
77	100	$C_6H_5^+$
68	66.6	$^{11}BF_3^+$
67	22.2	$^{10}BF_3^+$
49	100	BF_2^+
34	100	CH_3F^+

33.8 metastable for :

$C_6H_5^+$ $C_4H_3^+$

84.0 metastable for :

$(C_6H_5)_2Te$ $(C_6H_5)_2^+$

Mass spectrum for $Ph_2MeTeBF_4$

TABLE 6

RUN 2

(a-x)	x	time(min/sec)		log (a-x)
30.0	0			1.477
28	2.0	5	300	1.447
26	4.0	10	600	1.415
24	5.5	13	780	1.380
24.5	5.5	16	960	1.389
23.0	6.0	19	1140	1.362
23	7.5	22	1320	1.362
22	8.0	31	1860	1.342
21	10.0	42	2520	1.322
19	12.0	56	3360	1.279
18	12.5	64	3840	1.255
17	14.0	76	4560	1.230
15	16.5	88	5280	1.217
14	17	100	6000	1.146
12	19	110	6600	1.079
11	19	122	7320	1.041
8	22	135	8100	0.903
7.5	22.5	145	8700	0.875
7.0	24	153	9180	0.845
4.5	24	165	9900	0.653
3.0	25.5	188	11280	0.477
2.0	29.0	210	12600	0.301
-	30	00		

'H n.m.r. spectra, a = initial concentration, x = concentration at time t. for MePh$_2$Te(NCS) : Ph$_2$Te = 1 : 1·5

TABLE 7

RUN 1

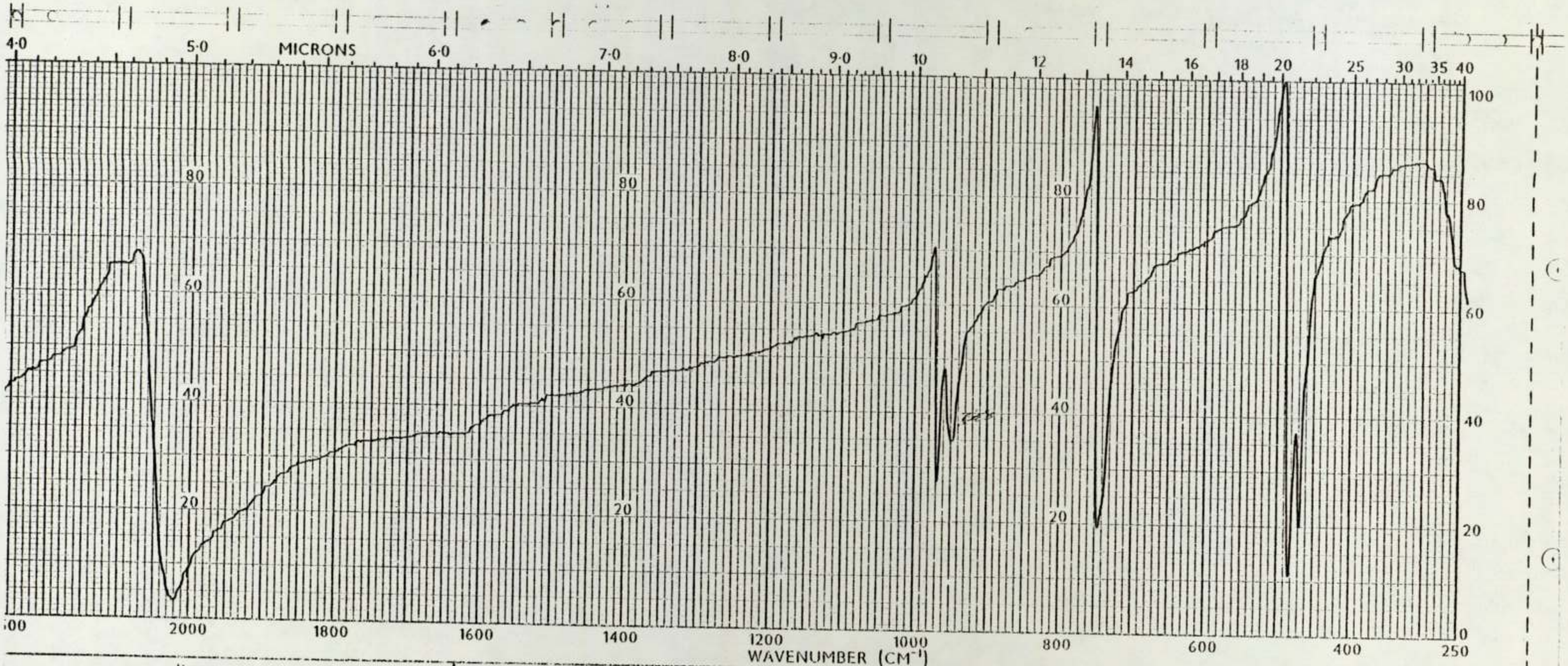
(a-x)	x	time (min)/sec		log (a-x)	log x
23.5	0	0	0	1.371	
22	1.5	7	420	1.342	0.176
21	3.0	9	540	1.322	0.544
21	3.0	11	660	1.322	0.477
20	3.0	12	720	1.301	0.477
21	4.0	13	780	1.322	0.602
18.5	5.0	16	960	1.267	0.699
17	6.5	23	1380	1.230	0.813
16.5	7.5	29	1740	1.217	0.875
15.5	9.0	36	2160	1.190	0.984
11	12.5	51	3060	1.041	1.099
7.5	16.0	71	4260	0.875	1.204
5.0	18.0	91	5460	0.699	1.255
4.0	19.5	110	6600	0.602	1.290
2.0	22.0	130	7800	0.301	1.342
1.0	22.5	150	9000	0.000	1.352
0	23.5	00		-	1.371

'H n.m.r. spectra, a = initial concentration, x = concentration at time t. for $Ph_2MeTe(NCS)$ in $CDCl_3$

TABLE 8

COMPOUND	SOLVENT	Methyl group resonance (from TMS in PPm)	
		RESONANCE (1)	RESONANCE (2)
$MePh_2TeNCS$	DMSO(d_6)	2.73, $J(^{125}Te-'H)$ = 24Hz	2.56 (growing)
	$CDCl_3$	2.90 (diminishing) $J(^{125}Te-'H)$=25Hz	
MeSCN	EtOH		2.60
$MePh_2TePF_6$	DMSO (d_6)/ benzene (50:50)	2.68, $J(^{125}Te-'H)$ = 25Hz	
	DMSO(d_6) /$CDCl_3$	2.72(diminishing slowly)	3.01 (growing) slowly
MeCl	$CDCl_3$	-	2.96
$MePh_2TeBF_4$	DMSO(d_6)	2.71, $J(^{125}J-'H)$ = 24Hz	-

'H n.m.r. Data for Telluronium Salts DMSO (d_6), $CDCl_3$ or mixed Solvents



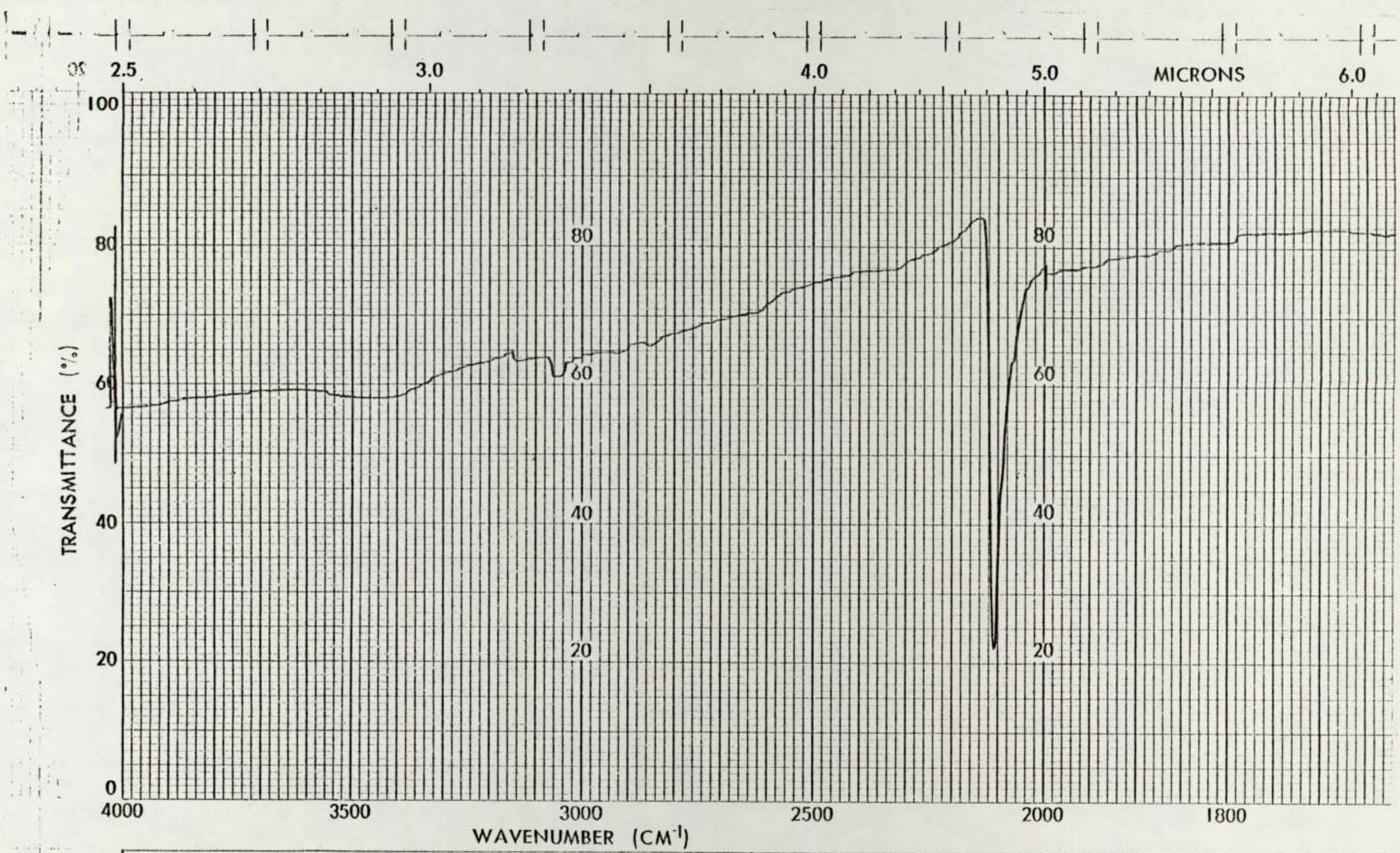
NT KBr.
ENTRATION approx. 1·0%
PATH 13·0 m/m. dia. disc
ENCE Air.

REMARKS Infra-red spectra of K SCN

Fig. (1)

SCAN SPEED Medium.
SLIT Standard.
RPK/219/1002 457-5001
Intek

OPERATOR V.H.Clenton.
DATE 14th January 1977
REF. No. 437.

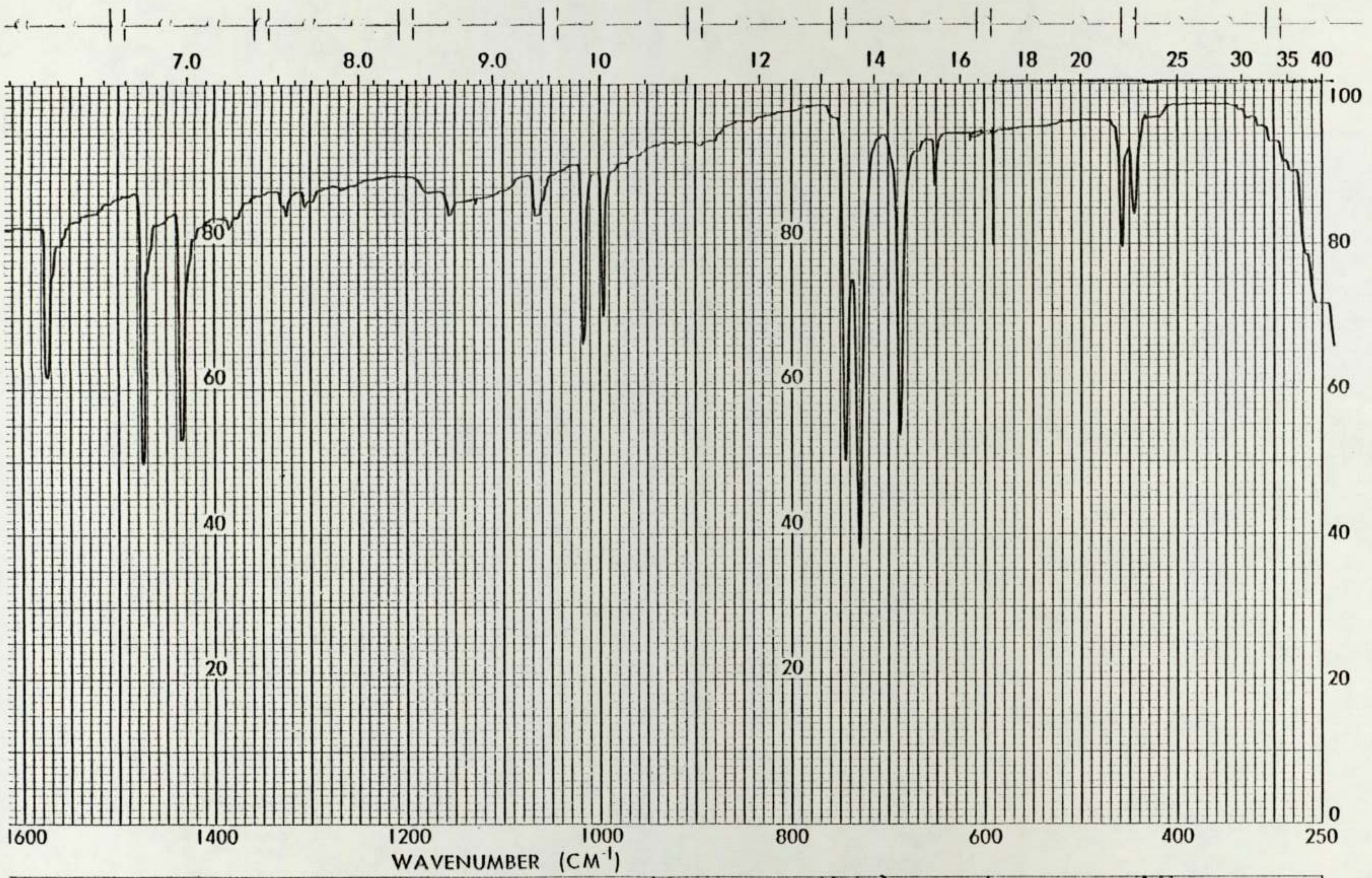


SAMPLE Infra-red spectra of $Ph_2MeTeNCS$

Fig. (2)

ORIGIN F. H. Musa.

SOLVENT KBr.
CONCENTRATION approx. 1.0%.
CELL PATH 13.0 m/m. dia. disc.
REFERENCE Air.



REMARKS

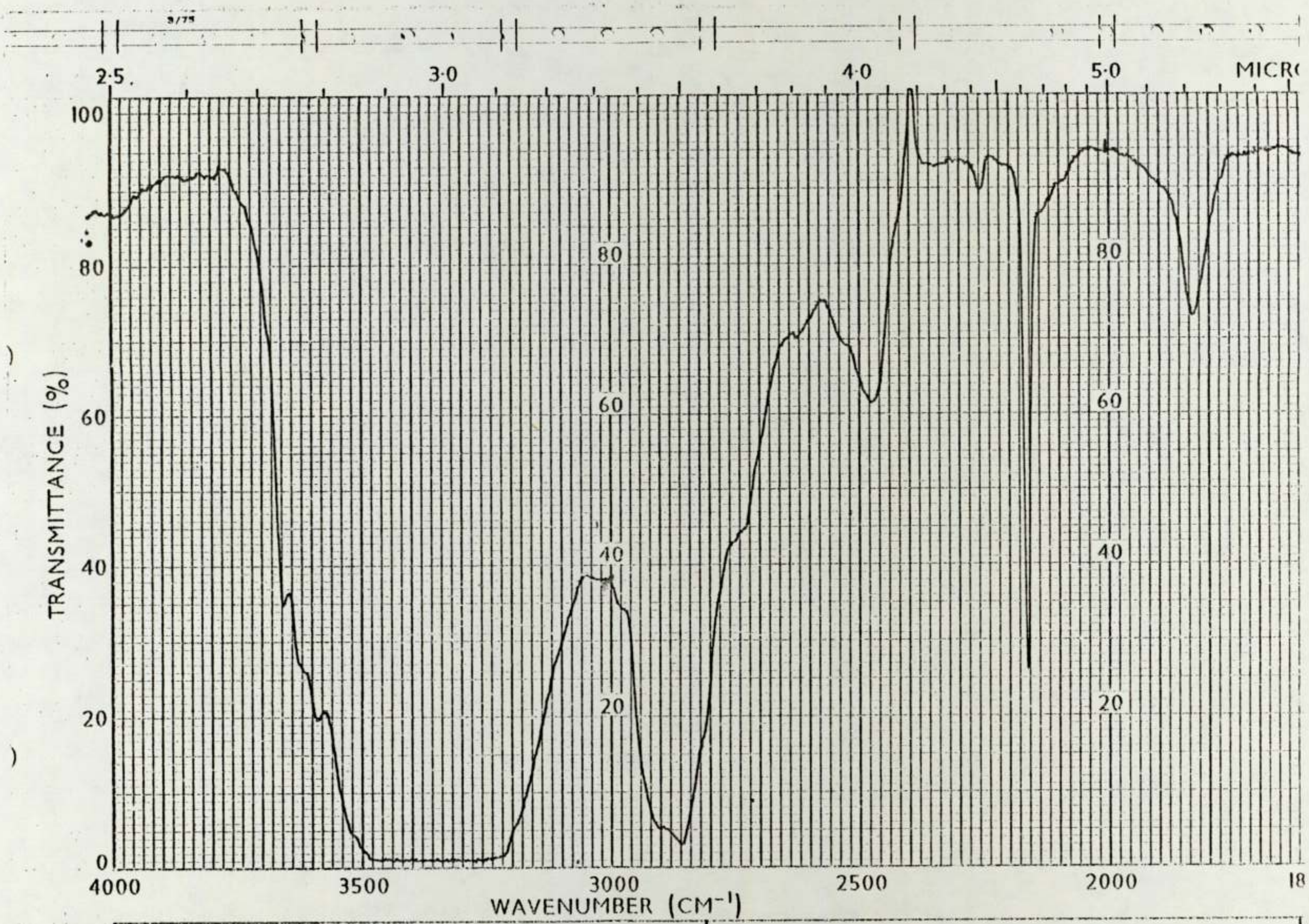
Infra-red spectra of $Ph_2MeTeNCS$
Fig. (2) cont.

SCAN SPEED Medium.
SLIT Standard.

No 457-5001

OPERATOR V.H. Clanton.
DATE 20th. July 1977

REF. No 9213

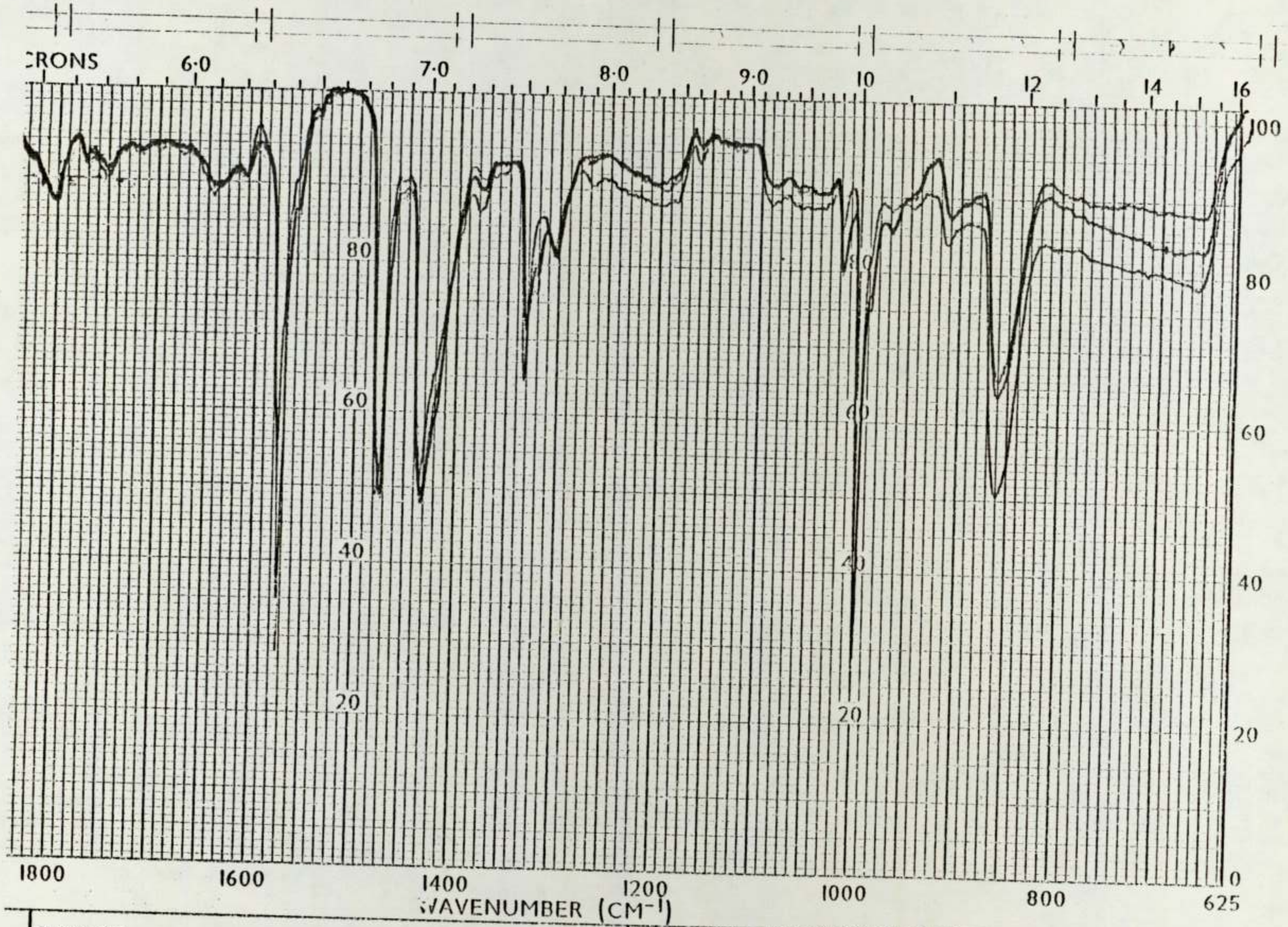


SAMPLE Infra-red spectra of CH_3SCN

Fig. (3)

ORIGIN F.H. Musa.

SOLVENT $CHCl_3$
CONCENTRATION approx. 1·5%.
CELL PATH 0·50 m/m fixed NaCl cell.
REFERENCE $CHCl_3$



REMARKS Infra-red spectra of $ph_2MeTeNCS$

in $CHCl_3$

Fig. (4)

SCAN SPEED

SLIT

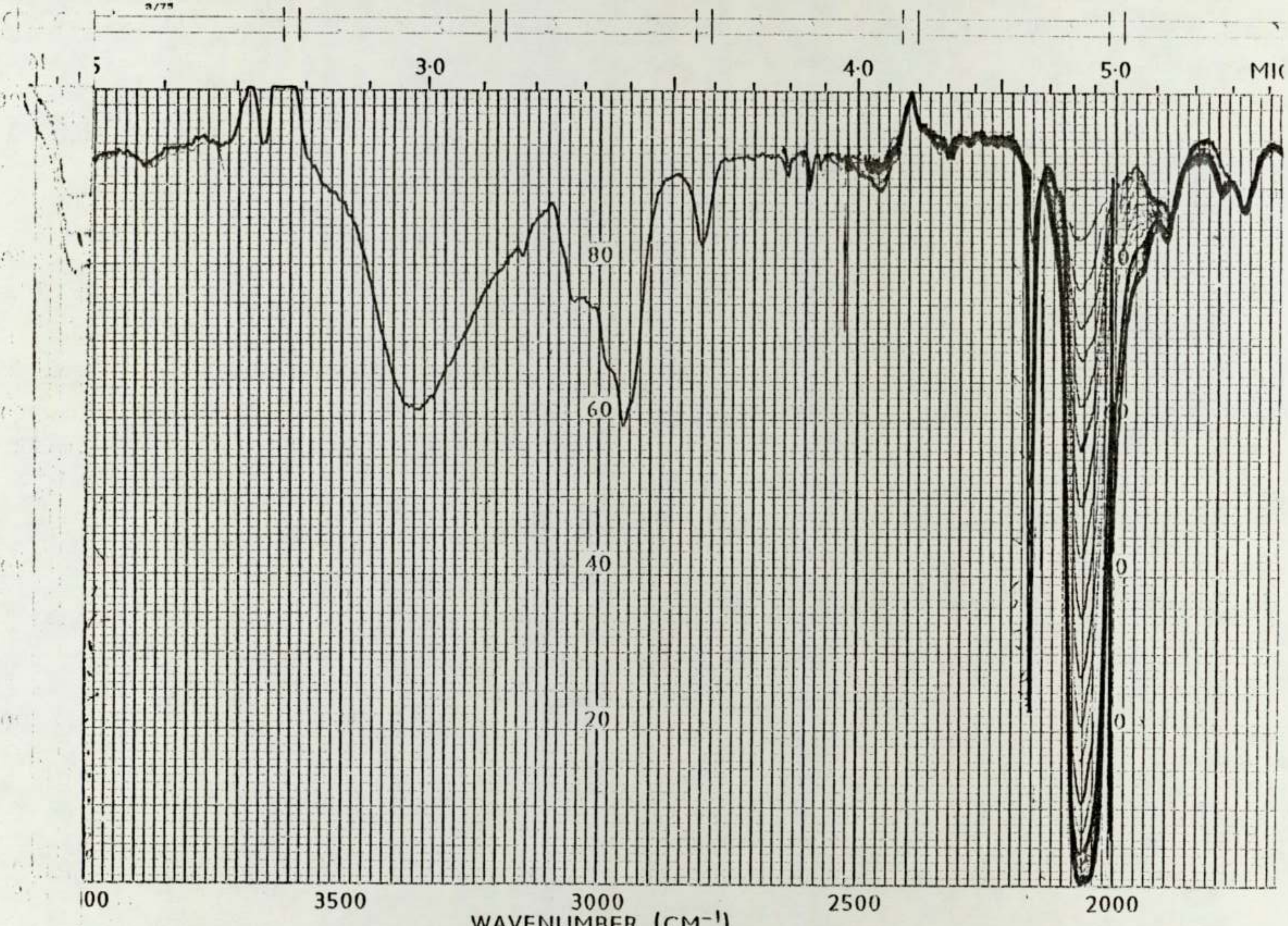
RPK/215/1001 472-5089

Intek

OPERATOR

DATE

REF. NO.



SAMPLE Infra-red spectra of $Ph_2MeTeNCS$ in $CHCl_3$ Fig(4) Cont.

ORIGIN

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE

REMARKS Infra-red spectra of $Ph_2MeTeBF_4$ (KBr)

Fig. (5)

SCAN SPEED [illegible]

SLIT [illegible]

No 457-5001

OPERATOR J. L. [illegible]

DATE [illegible]

REF. No [illegible]

SAMPLE Infra-red spectra of $Ph_2MeTeBF_4$

ORIGIN Fig. (6)

SOLVENT Mull

CONC.

CELL PATH

REFERENCE

SCAN SPEED

SLIT

OPERATOR

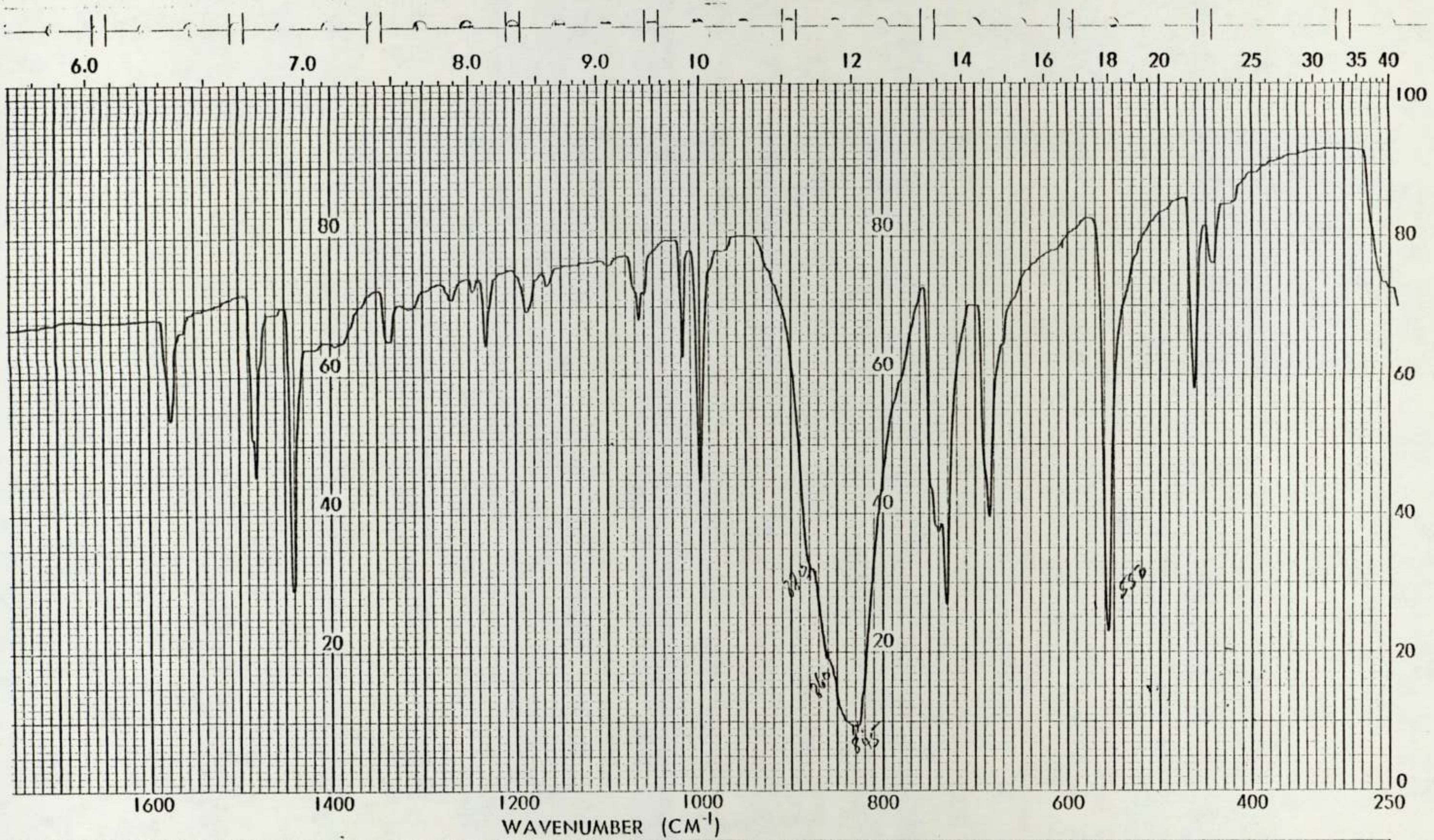
DATE

REMARKS

No.

PART No. 237E - 1035/C2

SENSITISED COATINGS LTD., COULSDON, SURREY



REMARKS Infra-red spectra of $Ph_2MeTePF_6$ (KBr)

Fig. (7)

SCAN SPEED [illegible]
SLIT [illegible]
No 457 - 5001

OPERATOR [illegible]
DATE [illegible]
REF. No [illegible]

SAMPLE Infra-red spectra of $Ph_2\,MeTePF_6$

Fig. (8)

ORIGIN

SOLVENT mull

CONC

CELL PATH

REFERENCE

SCAN SPEED

SLIT

REMARKS

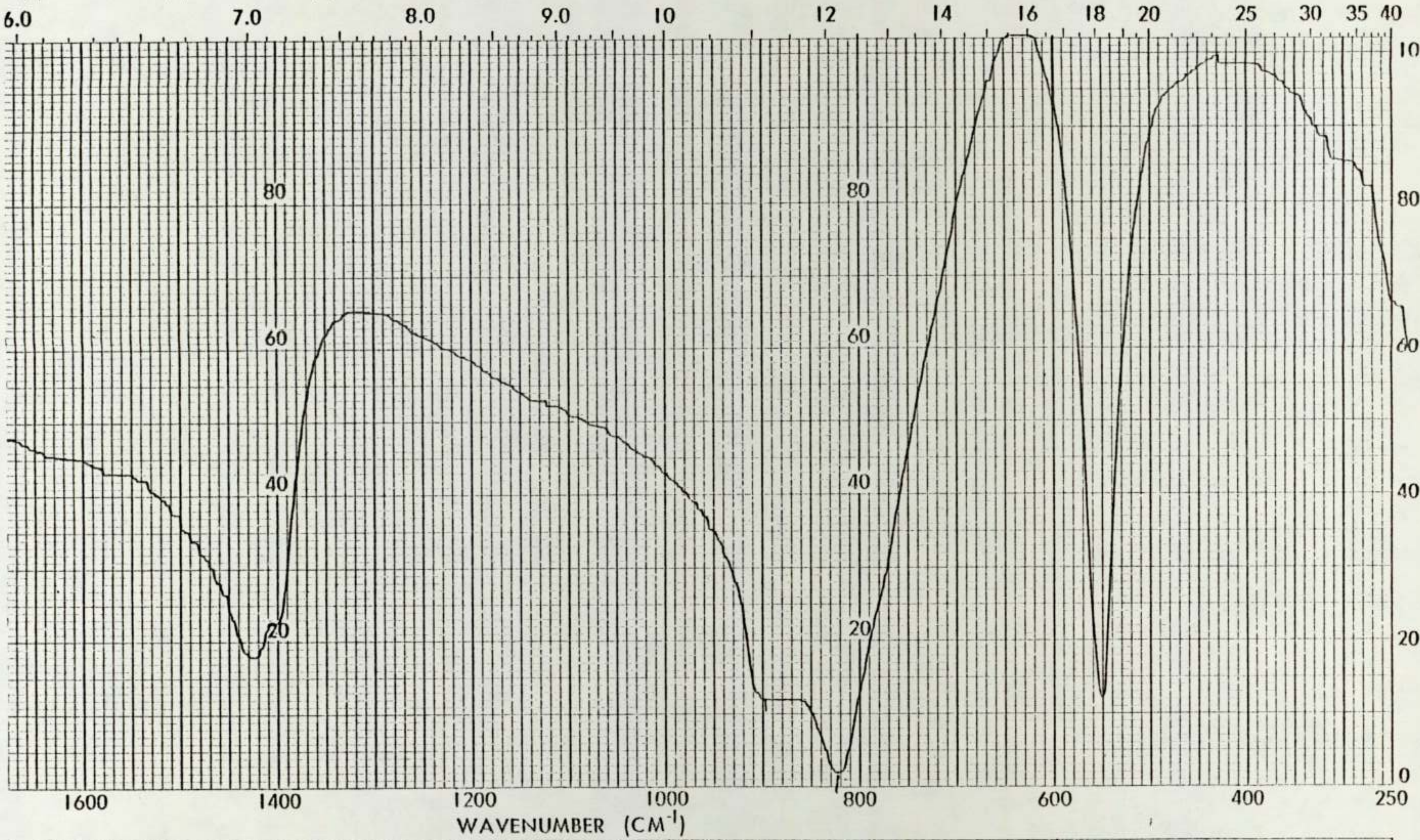
OPERATOR

DATE

No

PART No. 237E - 1035/C2

SENSITISED COATINGS LTD., COULSDON SURREY 4783



REMARKS Infra-red spectra of NH_4PF_6

Fig. (9)

SCAN SPEED [illegible]

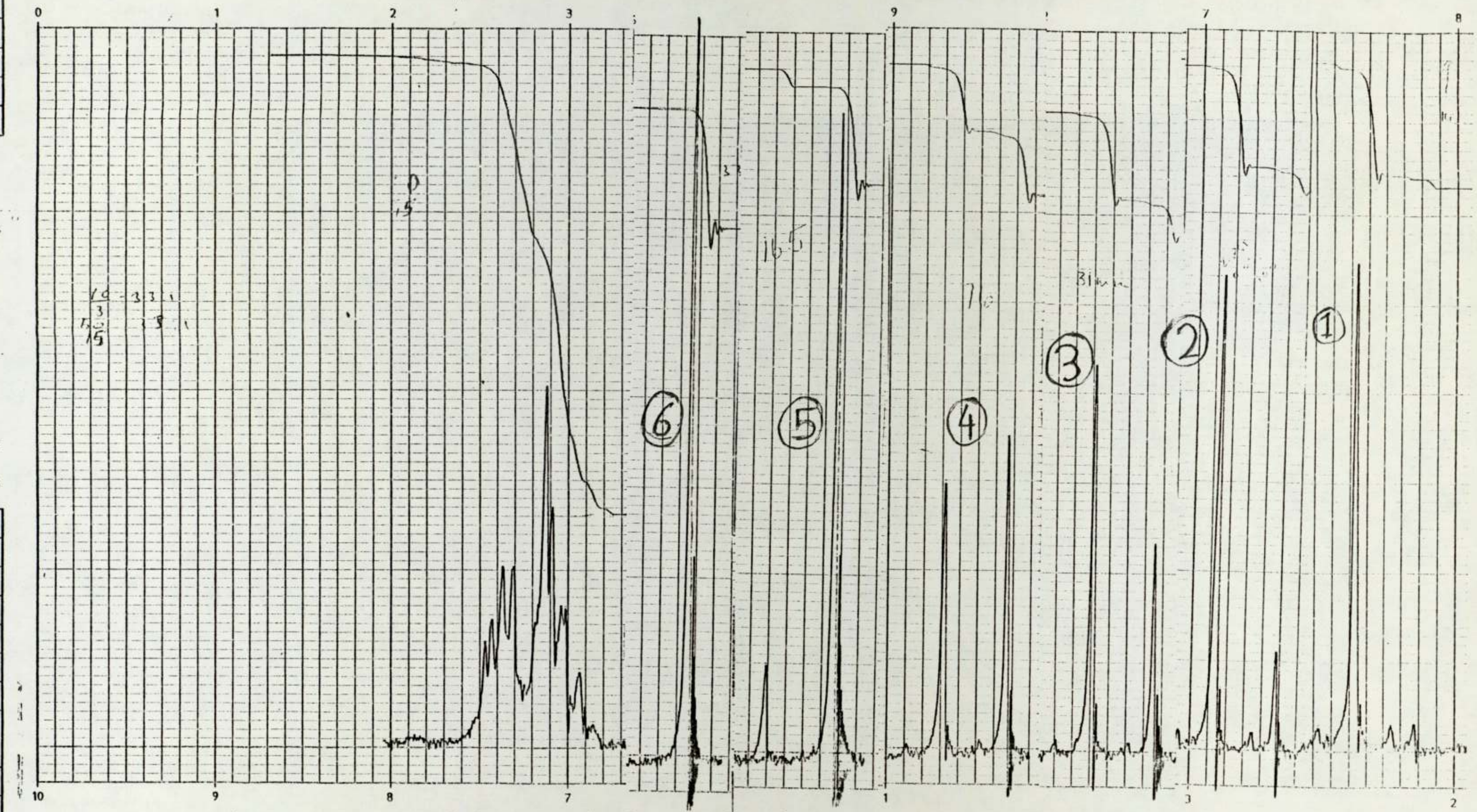
SLIT [illegible]

No 457-5001

OPERATOR [illegible]

DATE [illegible]

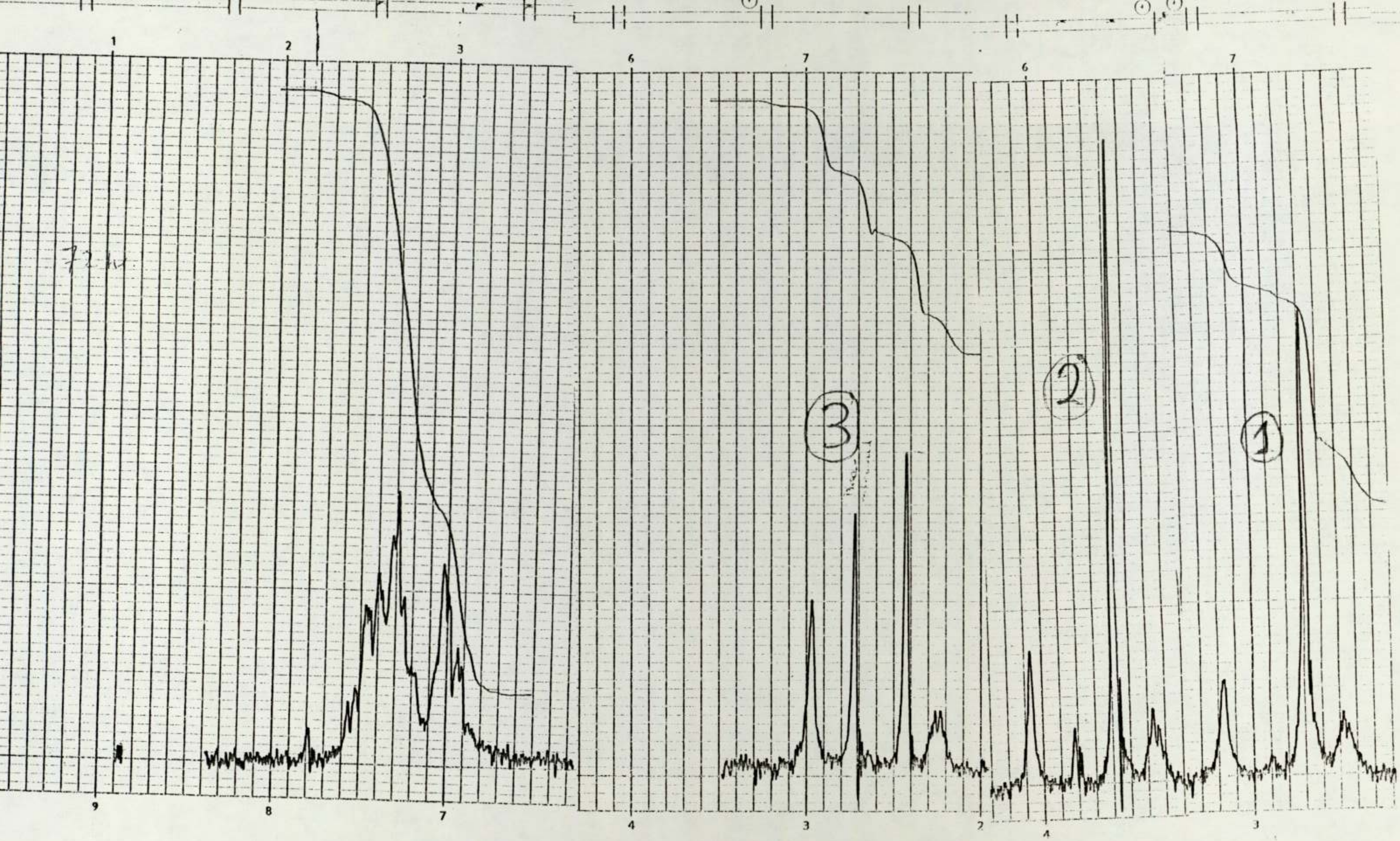
REF. No [illegible]



'H n.mrr spectrum of $Ph_2MeTeNCS$ in deuterated $CDCl_3$

Spectrum 1 recorded soon as dissolving
  "   2,3,4,5, recorded various times
  "   6 recorded after 3 hours

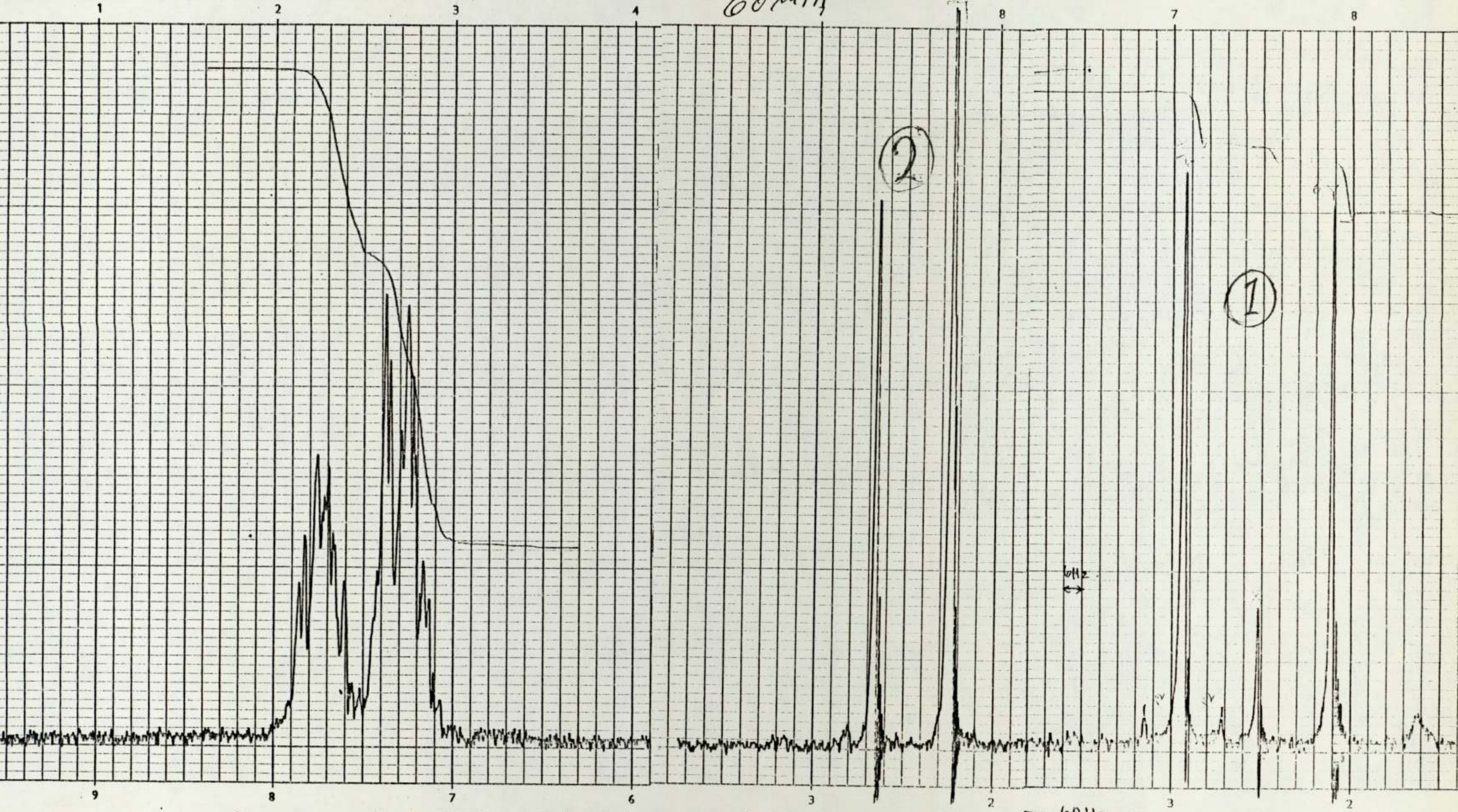
Fig. (10)



^{1}H n.m.r. spectrum of $Ph_2MeTePF_6$ in deuterated $CDCl_3$ and DMSO

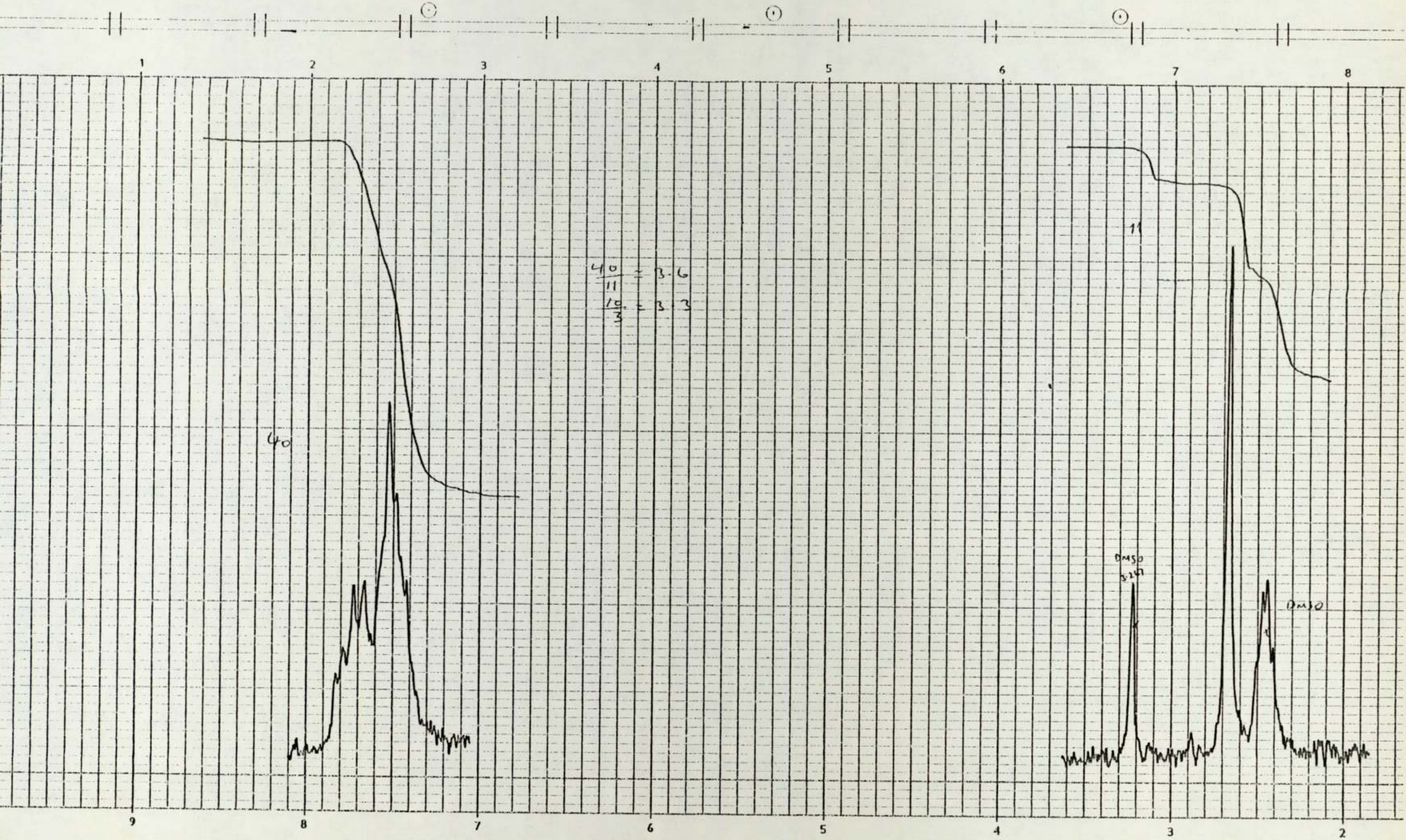
Spectrum 1 recorded soon after dissolving
" 2 recorded 5 hours later
" 3 recorded 24 hours later

(Fig 11)

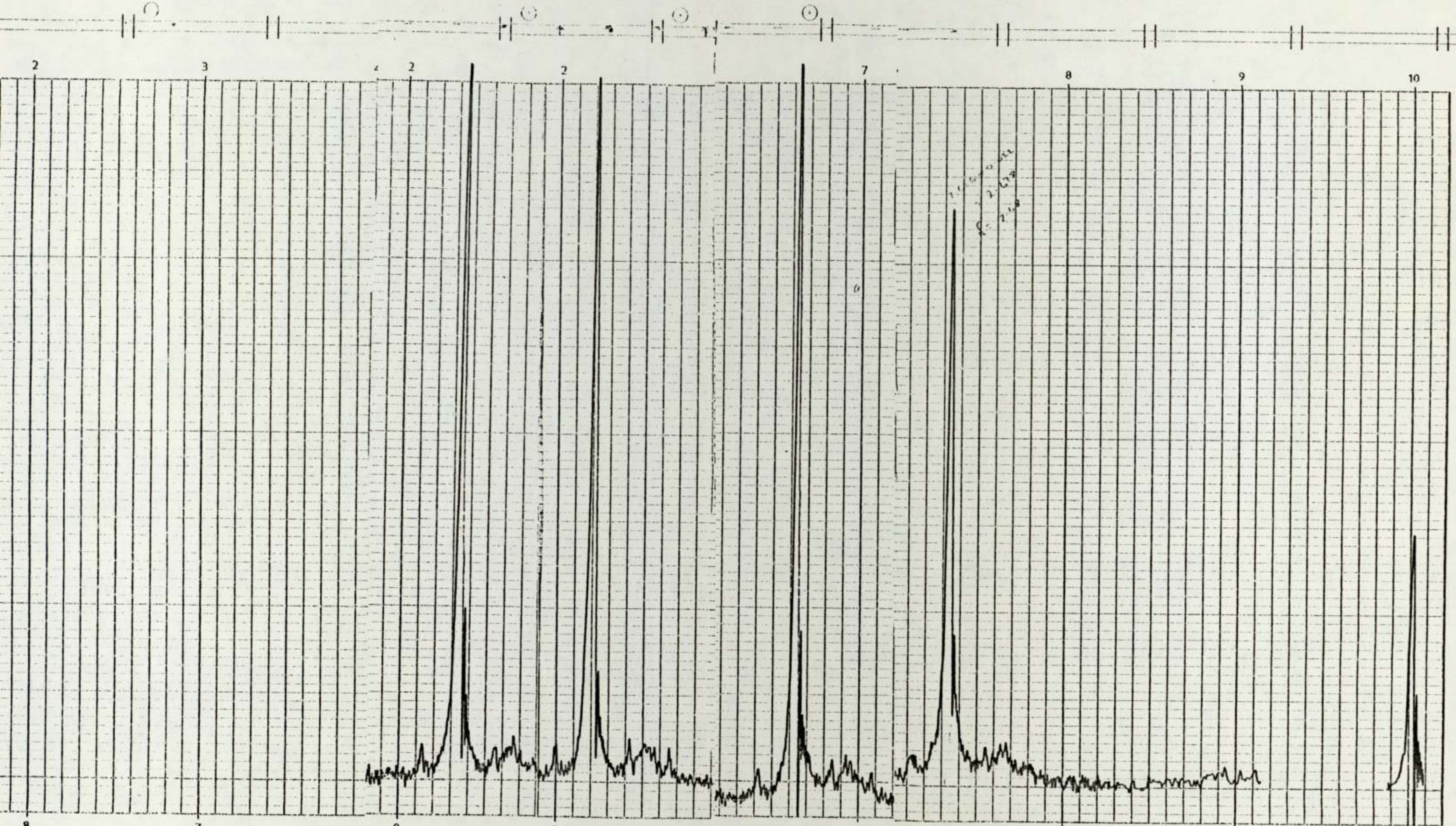


'H n.m.r. spectrum of Ph_2MeTeI (NCS) in deturated $CDCl_3$
Spectrum 1 recorded soon after dissolving
" 2 recorded 3 hrs later

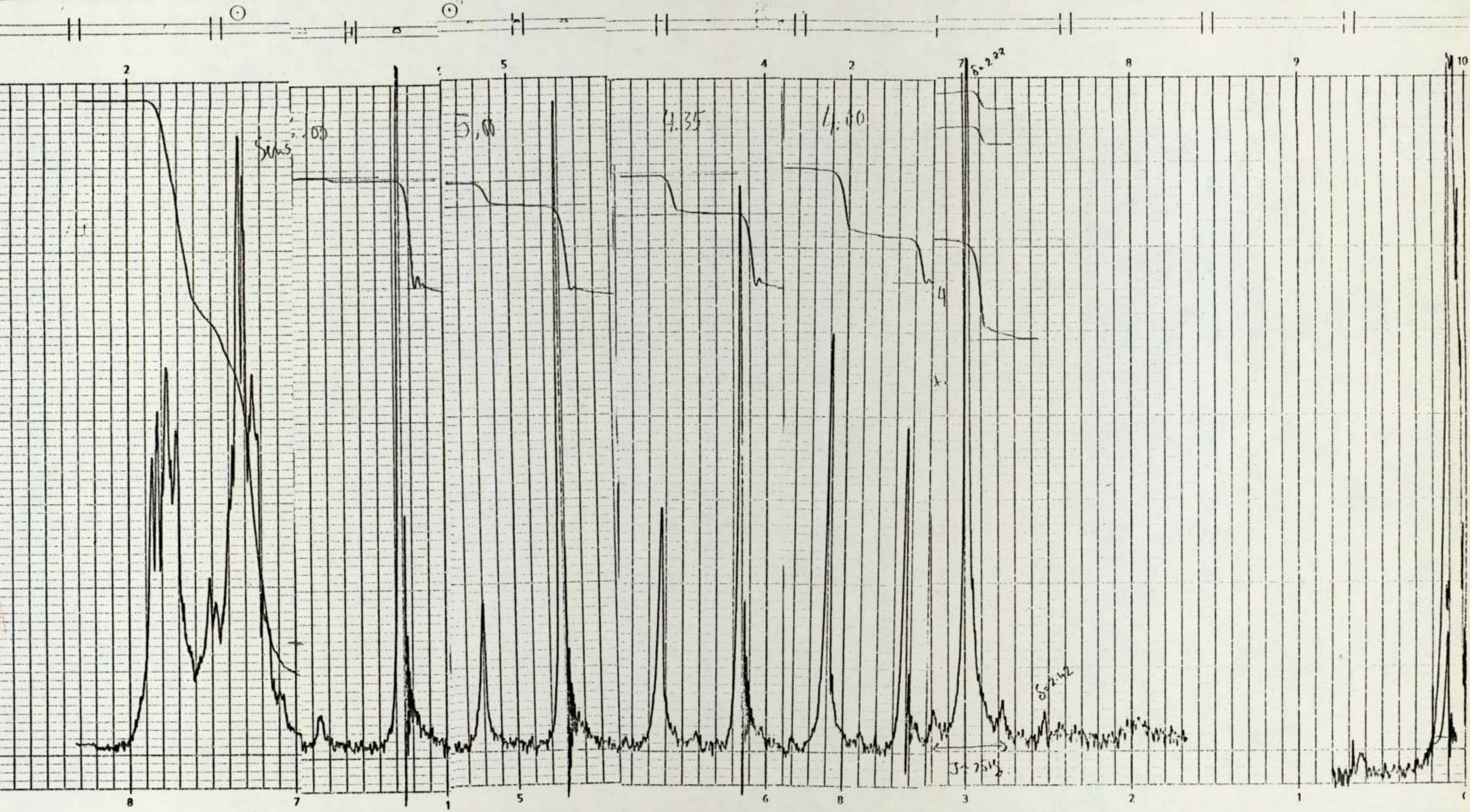
Fig. (12)



" 'Hnmr Spectrum of $Ph_2MeTeBF_4$ in deuterated DMSO Fig. (13)



^{1}H n.m.r. spectrum of $Ph_2MeTePF_6$ in DMSO/benzene   Fig. (10)



'Hn.m.r. spectrum of $Ph_2MeTe(NCS)$ + Ph_2Te in $CDCl_3$ Fig. (15)

4

Fig. (16) plot of molar conductivity (Λm) against (concentration)$^{\frac{1}{2}}$ for $Ph_2MeTe(NCS)$ in DMSO

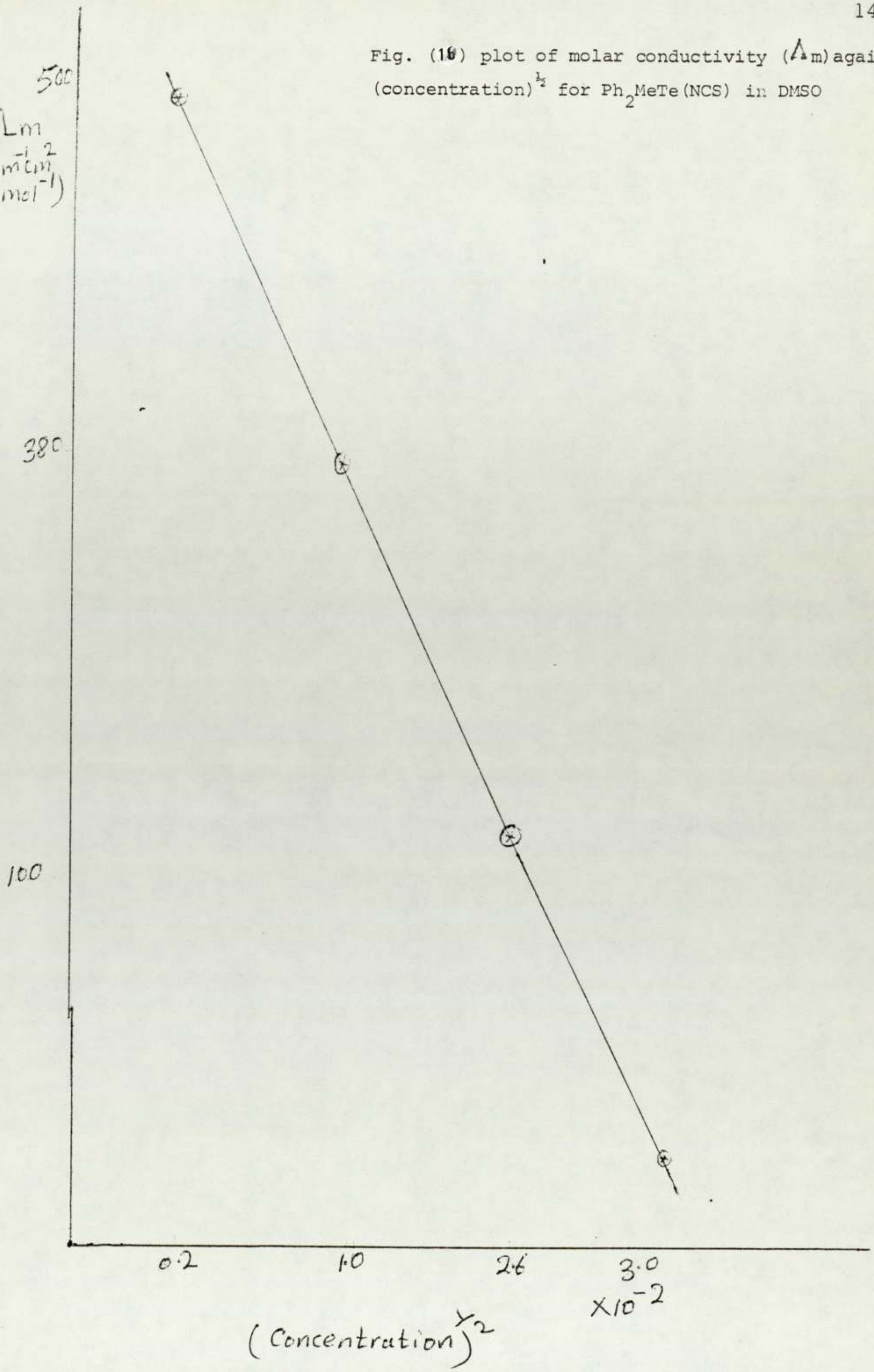


Fig. (17) Plot of molar conductivity (Λ m) against (concentration)$^{\frac{1}{2}}$ for $Ph_2MeTe(NCS)$ in DMF.

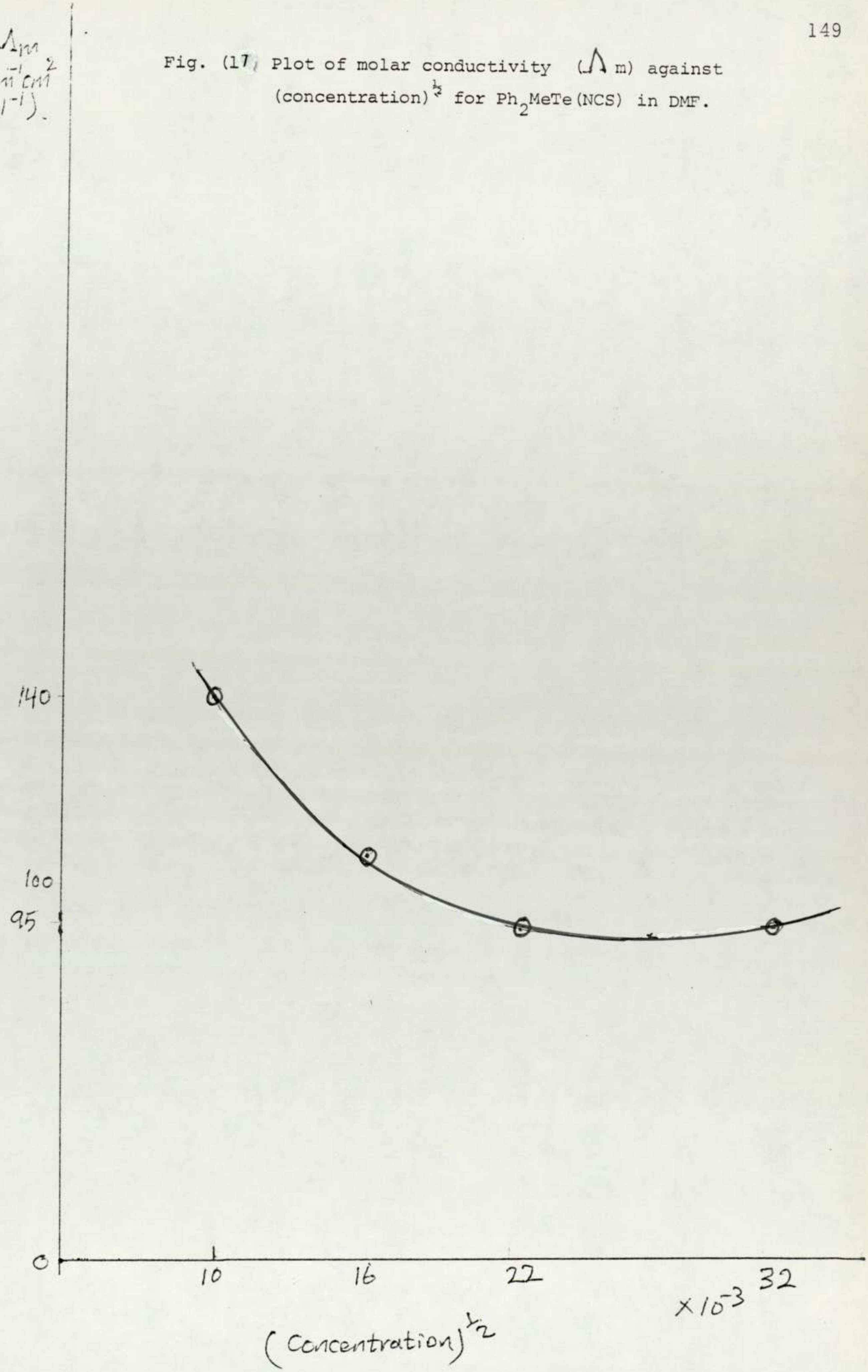
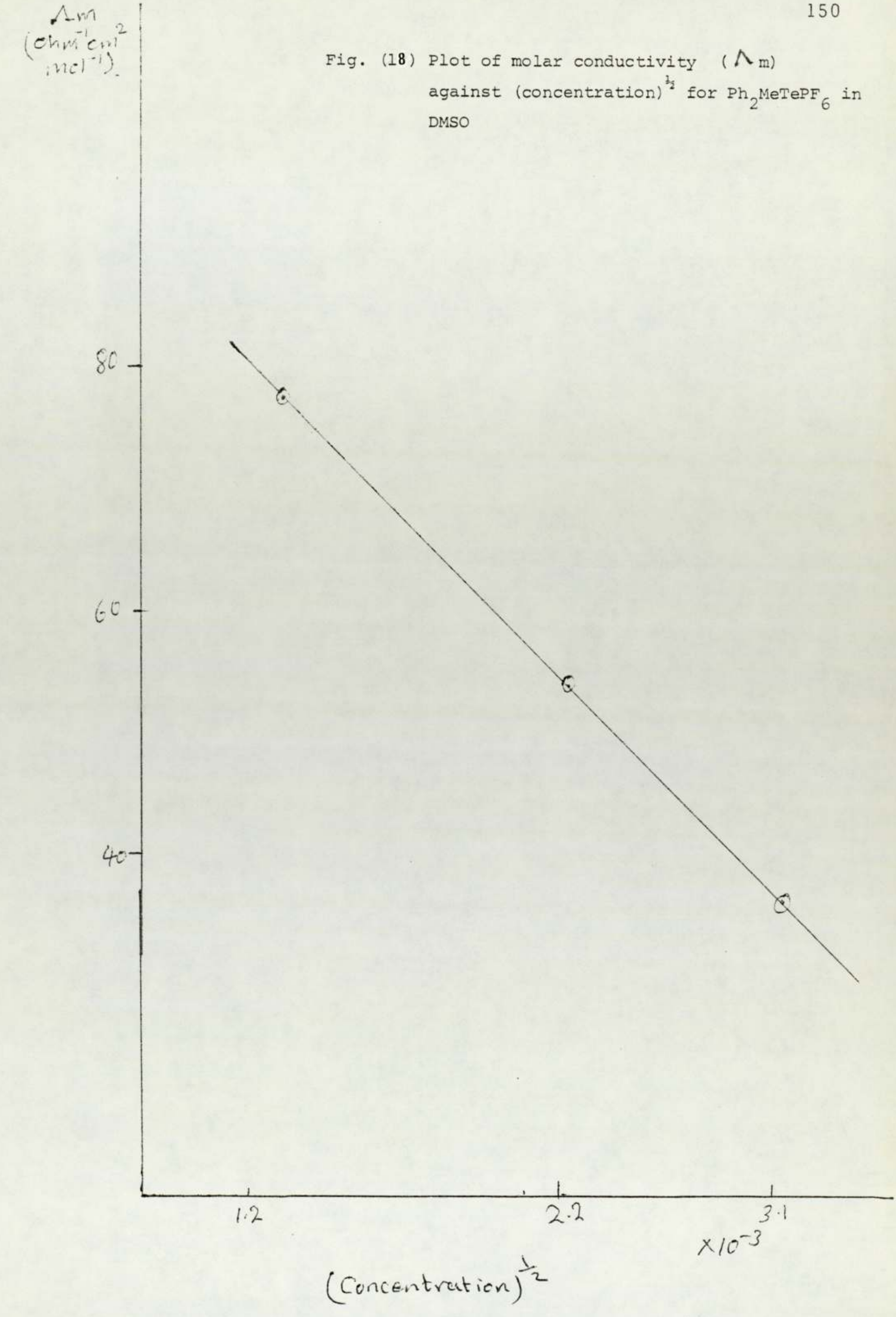


Fig. (18) Plot of molar conductivity (Λm) against (concentration)$^{\frac{1}{2}}$ for $Ph_2MeTePF_6$ in DMSO



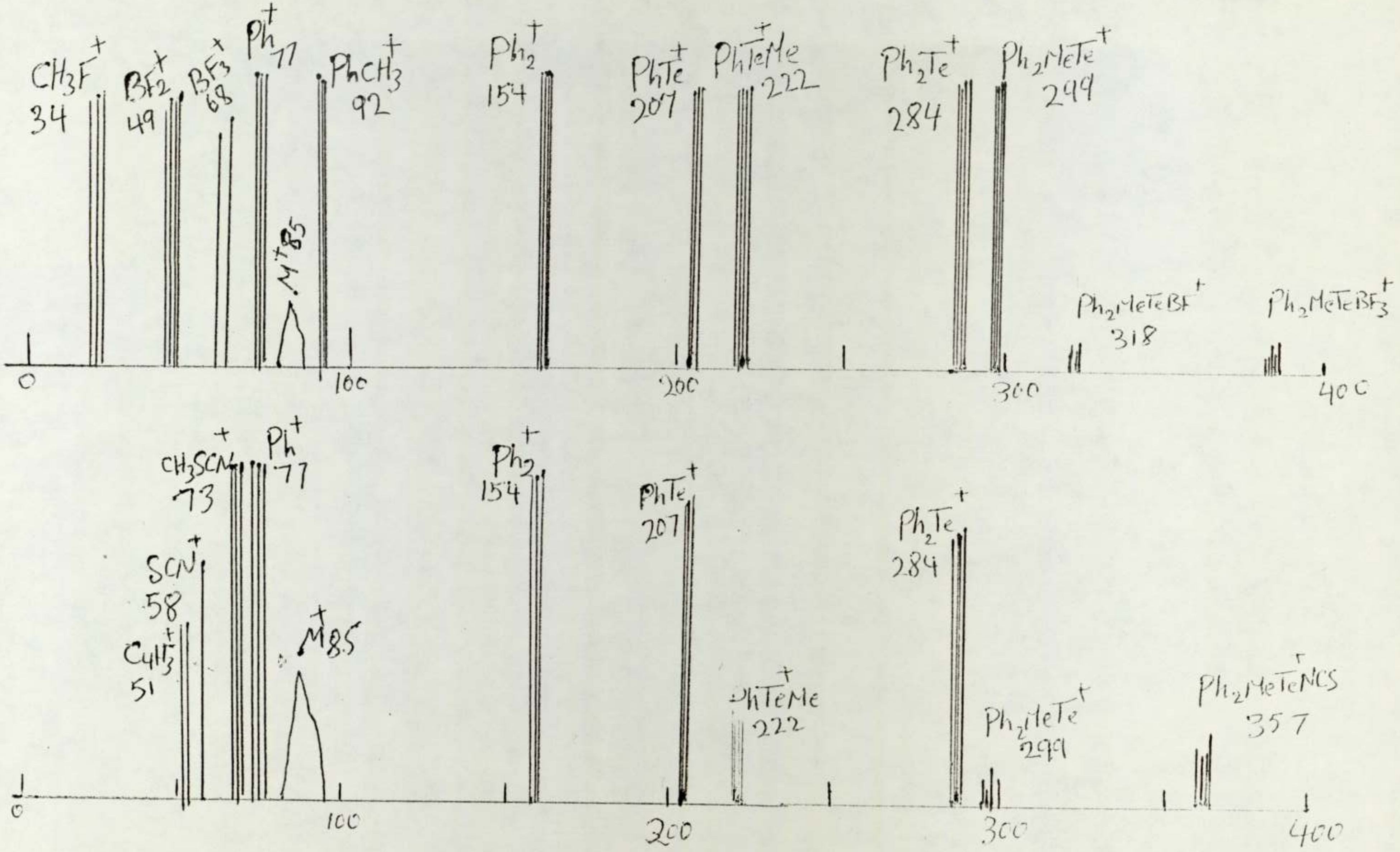
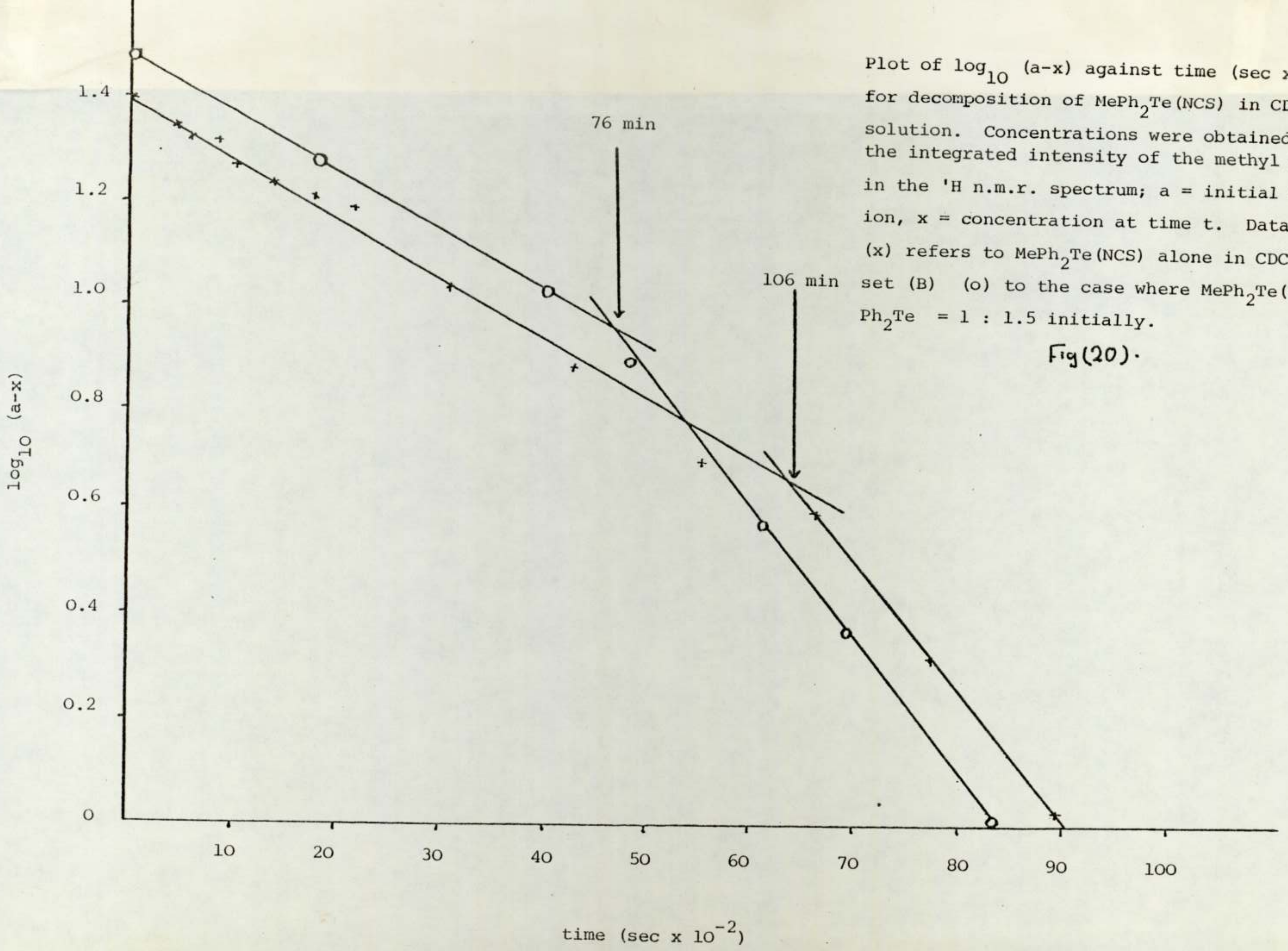
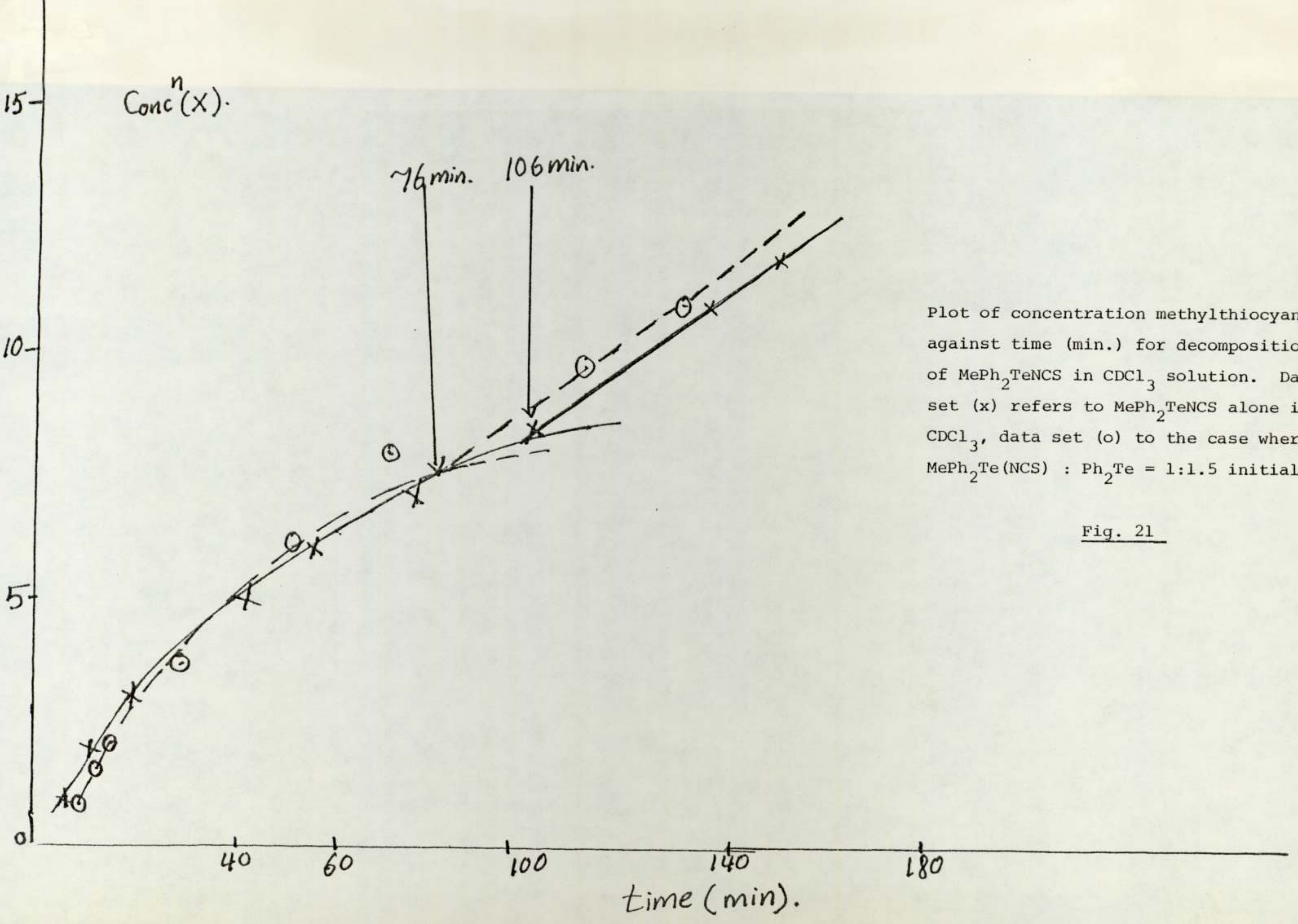


Fig. (19) Mass spectrum of ($Ph_2MeTeBF_4$ Ph_2MeTe NCS)



Plot of $\log_{10}$ (a-x) against time (sec x 10^{-2}) for decomposition of $MePh_2Te(NCS)$ in $CDCl_3$ solution. Concentrations were obtained from the integrated intensity of the methyl resonance in the 'H n.m.r. spectrum; a = initial concentration, x = concentration at time t. Data set (A) (x) refers to $MePh_2Te(NCS)$ alone in $CDCl_3$, data set (B) (o) to the case where $MePh_2Te(NCS)$: Ph_2Te = 1 : 1.5 initially.

Fig(20).



Plot of concentration methylthiocyanate against time (min.) for decomposition of $MePh_2TeNCS$ in $CDCl_3$ solution. Data set (x) refers to $MePh_2TeNCS$ alone in $CDCl_3$, data set (o) to the case where $MePh_2Te(NCS)$: Ph_2Te = 1:1.5 initially.

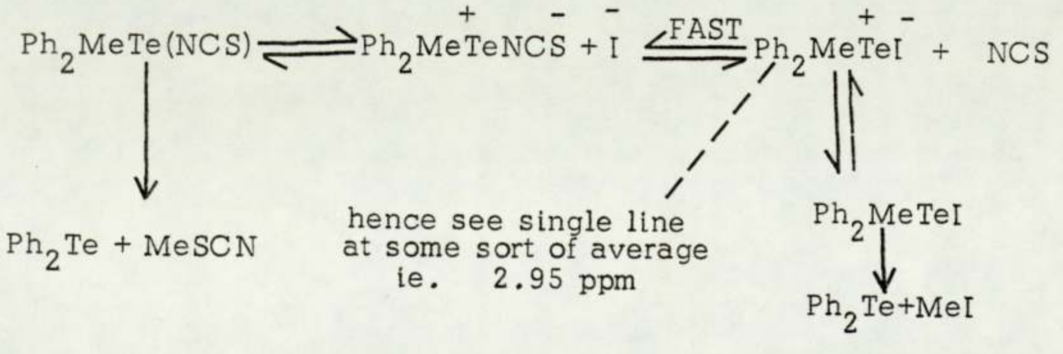
<u>Fig. 21</u>

DISCUSSION

Synthesis :-

Reaction of diphenylmethltelluronium iodide with silver thiocyanate :-

Crystalline Ph_2 MeTe(NCS) was prepared from Ph_2MeTeI and AgSCN. The product has a melting point at 125°C. The n.m.r. technique was used to study this compound. The n.m.r. data should provide unambiguous proof of the constitution of this compound. The n.m.r. spectrum of $Ph_2MeTeNCS$ in $CDCl_3$(page 142) showed that the aromatic groups absorb between δ = 8-7 ppm and a single methyl resonance, with satelites, at δ = 2.90 ppm. As time passes, the initial methyl resonance decays to be replaced by another one at δ = 2.56 ppm subsequently shown to be due to methyl thiocyanate. But sometimes the synthetic reaction gave a different product, which has the same melting point, and a different n.m.r. spectrum. The n.m.r. spectrum of the latter compound gave a single methyl resonance, with satellites, at δ = 2.95 ppm. This decayed with time, being replaced by another two, at δ = 2.56 ppm (due to methyl thiocyanate) and at δ = 2.12 ppm (due to methyl iodide) (fig. 12). The point is that I^- and N C S are often interchangeable in a lattice and could give a possible solid state structure such as $(Ph_2MeTe)_2$ (NCS) (I). We might have expected two resonances due to Ph_2MeTeI (δ = 3.04) and $Ph_2MeTeNCS$ (δ = 2.90 ppm). The fact,that we see only one may mean that we have an even more complex spectrum which involved fast exchange :-



hence see single line at some sort of average ie. 2.95 ppm

Vibrational Spectroscopy of Ph_2MeTeX, = SCN, BF_4, PF_6

$Ph_2MeTe(NCS)$, in solid state

The recent literature contains several papers which indicate a a growing interest in triorganotelluronium salts. Dance [52] has investigated the assignment of bands in the infra-red spectrum of methyldiphenyltelluronium iodide, using isotopic substitution techniques. Ziolo prepared a series of triphenyltelluronium pseudohalides and studied their infra-red spectra [43a].

The infra-red spectrum of methyldiphenyltelluronium isothiocyanate in solid state and in solution are shown on pages 132, 135,. The infra-red spectroscopy provides some useful information on the type of interaction between the thiocyanate groups and the tellurium atoms. Thiocyanate groups may be linked to tellurium by sulphur, which should give a sharp band above 2100 cm^{-1}. Or they may be linked by nitrogen, and that would be expected to give a broad band $\approx 2000 - 2100$ cm^{-1}. The solid state infra-red spectrum of $Ph_2MeTe(NCS)$ has been recorded (table 3). We find the ν (CN) is insensitive to the sampling technique; thus in a KBr matrix is 2078 cm^{-1}. The band differs in frequency from that in a typically ionic thiocyanate e.g. KCNS has ν (CN) at 2053 cm^{-1}. The infra-red of the triphenyl telluronium isothiocyante showed three infra-red ν (CN) stretching vibration around 2062 cm^{-1}. due to three bridging crystallographically independent (NCS) groups . The solid infra-red spectra of $R_2Te(NCS)_2$, (R = Ph, MeOPh-p) and the infrared of $R_2Sn(NCS)_2$ (R = alkyl) show two infra-red ν (CN) stretching vibrations around 2060, 2080 cm^{-1} subsequently, they are both believed to have weakly bridging groups, as has $Ph_3Te(NCS)$. The NCS group gives at least two bands. But $Ph_2MeTe(NCS)$ gives only one, hence it is relatively ionic.

The solution- infra-red of $Ph_2MeTe(NCS)$ in $CDCl_3$

The infra-red spectrum of $Ph_2MeTe(NCS)$ in $CDCl_3$ is shown on page 135 , and recorded in table 3 . The infra-red spectrum of $Ph_2MeTe(NCS)$ in $CDCl_3$ is different than in the solid state. The initial solution gave a broad band due to ν (CN) centred on 2059 cm^{-1}, this decays with time to be replaced by an extremely sharp band at 2161 cm^{-1}. A solution of MeSCN in $CHCl_3$ exhibits ν (CN) as a sharp band at 2161 cm^{-1}. (Fig. 3) . MeNCS exhibit a broad band and is very strongly centred around 2100 cm^{-1} due to the isothiocyanate group[115] . Thus, there is good evidence that, over a period of about 3h., the telluronium salt is decomposing to methyl thiocyanate and, presumably, diphenyl telluride (subsequently confirmed by 'Hn.m.r), as follows ;

$$Ph_2MeTeNCS \longrightarrow Ph_2Te + MeSCN$$

Although the maximum of ν (CN) in the inital solution is close to the free ion value, we believe that in fact the thiocyanate group is co-ordinated, as isothiocyanato-ligand, to tellurium (IV). The considerable breadth of the band would appear to indicate some covalent interaction ($\Gamma_{\frac{1}{2}} = 62\ cm^{-1}$).

$Ph_2MeTeBF_4$:-

The infra-red spectrum of diphenylmethyltelluronium tetrafluoroborate is shown on page 136 . The infra-red of potassium tetrafluoroborate was investigated in the region 400-500 cm^{-1}., by Cote and Thompson [117], using sublimed films and paraffine mulls at room temperature, and it revealed that the strong broad ν_3 band had two maxima and two shoulders between 1000 and 1100 cm^{-1} and a doublet at 521, 534 cm^{-1} assigned as ν_4. The complex structure of the fundemental ν_3 and ν_4 was discussed in terms of the isotopic species boron 10 and boron 11. The infra-red spectrum of $(CH_3)_3Sn-BF_4$ was investigated as well by Clark and O'Brien [118]. The ν_3 vibration is clearly resolved into three strong bands at 930, 1070 and 1170 cm^{-1}. The ν_4 vibration isa broad band at 446 cm^{-1} in the trimethyl tin compound. The infra-red of diphenylmethyltelluronium tetrafluoroborate is recorded (table 3). Three infra-red ν (B-F) stretching vibration is shown at 1088, 1060, 1038 cm^{-1}.

$Ph_2MeTePF_6$

The infra-red spectrum of diphenylmethyltelluronium hexaflurophosphate is shown on(page 139). The majority of complex fluorides have an octahedral arrangement of fluoride ions about the central atom, these octahedra sometimes sharing corners. An octahedral molecule or ion, MF_6^-, should have two ν_3 and ν_4 infra-red active vibrations,The higher frequency is due to the vibration ν_3 and that at the lower to the vibration ν_4 [119].
The infra-red spectra of $Ph_2MeTePF_6$ and NH_4PF_6 are shown on (pages 139, 141) . The ν_3 vibration (asymmetric P-F stretch triply degenerate is resolved into three components at 880, 860, 840 cm^{-1} . The appearance of the sharp band at 556 cm^{-1} was assigned to ν_4 in the $Ph_2MeTePF_6$, in contrast to NH_4PF_6; The broad band with two componentsat 825, 900 cm^{-1} which is due to ν_3 and sharp band at 553 cm^{-1} was assigned to ν_4.

Since $\nu_4$is a sharp and single band, it is unlikely that the splitting of the ν_3 implies an interaction with the tellurium. I think the spectra show the structure to be relatively ionic and it would be misleading to say that they are similar to the $Ph_2MeTeNCS$.

Mass Spectra :-

Dance [52] has studied the mass spectra of the Ph_2MeTeX, X = Cl, Br, I. The highest observed mass observed for Ph_2MeTeX is that of diphenyltelluride. The decomposition involved thermolysis to give diphenyl telluride and methyl halides. The most important feature of the mass spectrum table 5 . (fig. 19), of methyldiphenyltelluronium isothiocyanate is that there is a parent ion appearing at m/e = 357 ($^{12}C_{14}{}^{1}H_{13}{}^{14}N_{1}{}^{32}S_{1}{}^{130}Te_{1}$), together with the major peaks(page 126), due to methyldiphenyltelluronium ion at m/e = 299 and $(\text{diphenyltelluride})^+$ at m/3 = 284. As is often the case with such organo metallic compounds, the fragmentation pattern observed probably arises both from fragmentation of $Ph_2MeTeNCS^+$ and elimination of methyl thiocyanate in the source of the instrument. Ethane was not observed in the mass spectrum of $Ph_2MeTe(NCS)$, but methyl thiocyanate was observed. This therefore, provides an interesting parallel with the observed (the decomposition of this telluronium thiocyanate in chloroform solution) . The evidence for the step :

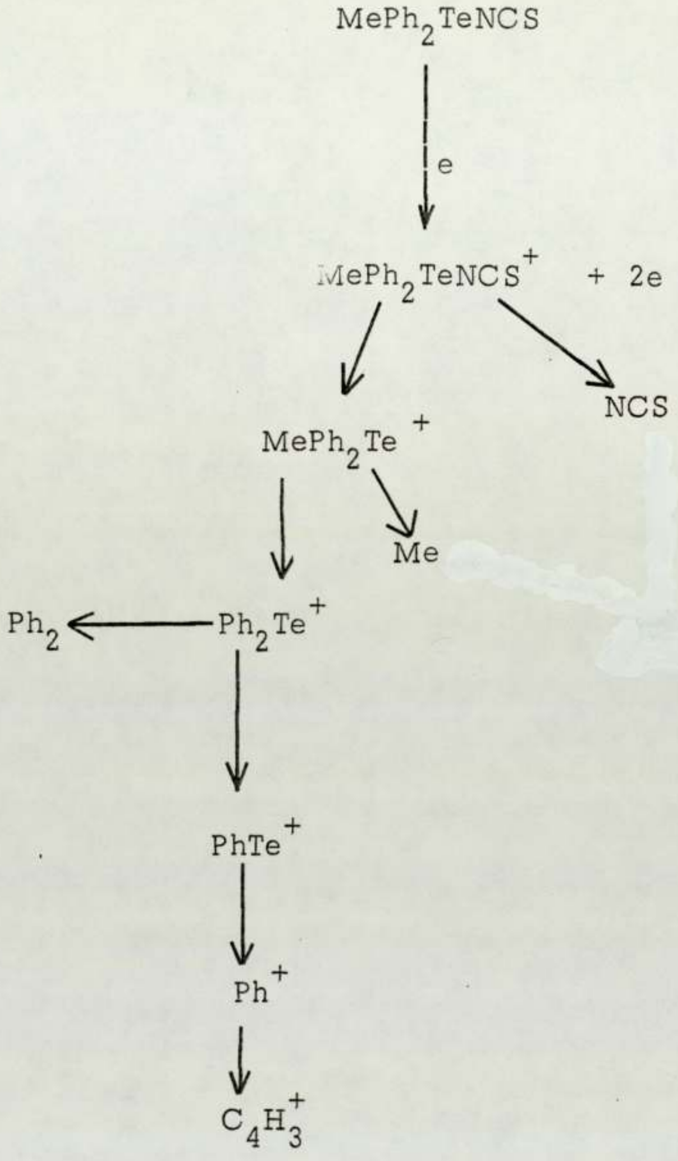
$$Ph_2Te^+ \longrightarrow C_6H_5^+$$

was supported by the metastable ion at m/e = 84 and the step :

$$C_6H_5^+ \longrightarrow C_4H_3^+$$

was supported by the metastable ion at m/e = 33.8.

The thiocyanate ion was observed at m/e = 58, thus, the decomposition sequence might be formed by ionisation of the telluronium salt, as over ;



The mass spectrum of $Ph_2MeTeBF_4$,(table 5) ,(Fig. 19) showed a weak ion at m/e = 367 $(^{12}C^{1}H_3)$ $(^{12}C_6{}^{1}H_5)_2$ $^{130}Te^{11}B^{19}F_3$, together with a weak isotopic ion at m/e = 366 $(^{12}C^{1}H_3)$ - $(^{12}C_6{}^{1}H_5)_2$ $(^{130}Te^{11}B^{19}F$, together with a isotopic ion at m/e = 328 $(^{12}C^{1}H_3)$ $(^{12}C_6{}^{1}H_5)_2$ $^{130}Te^{10}B^{19}F$. Two major peaks showed at m/e = 299 $(MePh_2Te^{+})$ and m/e = 284 (Ph_2Te^{+}). No parent ion $(MePh_2TeBF_4^{+})$ could be detected from $MePh_2TeBF_4$. But $^{11}B^{19}F_3^{+}$ was identified m/e = 68 together with an isotopic ion at m/e = 67 ($^{10}B^{19}F_3$). The two ions having relative abandances of about 66.6 : 22.2. Ethane and methyl tetrafluoroborate were not observed, but methyl fluoride m/e = 34 was observed. The step;

$$Ph_2Te^+ \longrightarrow C_6H_5^+$$

was supported by the metastable ion at m/e = 84 of $MePh_2Te^+$ and the step of ;

$$C_6H_5^+ \longrightarrow C_4H_3^+$$

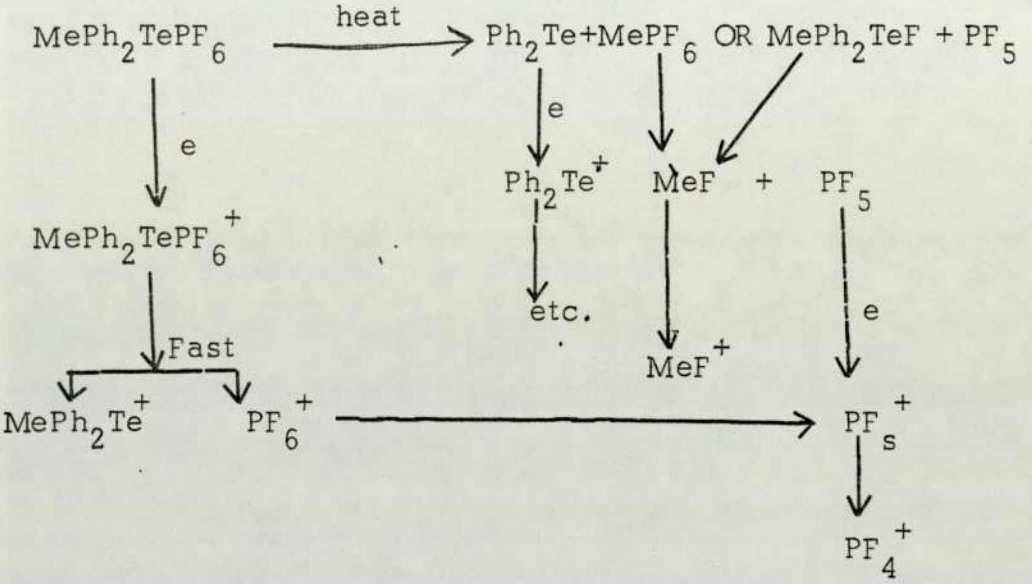
was supported by the metastable ion at m/e = 33.8 of the same compound.

In the light of above two distinct things appeared to be happening :

$$\begin{tikzcd}
1.\ Ph_2MeTeBF_4 \arrow[r, "e"] & Ph_2MeTeBF_4^+ \arrow[r, "v.fast"] & Ph_2MeTeBF_3^+ \arrow[dl] \\
\text{etc.}\ (Ph_2MeTeBF^+) & (Ph_2MeTeBF_2)^+ \arrow[l] & \\
 & \text{not seen} &
\end{tikzcd}$$

$$\begin{tikzcd}
2.\ Ph_2MeTeBF_4 \arrow[r, "heat"] & Ph_2Te \arrow[d] & + & MeBF_4 \arrow[d] & & \\
Ph_2^+ \arrow[ddr] & Ph_2Te^+ \arrow[l] \arrow[d] & & MeF \arrow[dd, "e"] & + & BF_3 \arrow[dd, "e"] \\
 & PhTe^+ \arrow[d] & & & & \\
 & Ph^+ & & MeF^+ & & BF_3^+
\end{tikzcd}$$

The mass spectrum of $Ph_2MeTePF_6$ is very similar indeed with the mass spectrum of $Ph_2MeTeBF_4$, but no parent ion could be detected from $Ph_2MeTePF_6$. The $(^{31}P^{19}F_6)^+$ was identified m/e = 145. Again ethane was not observed. Methyl fluoride was observed. There could be thermolysis or ionization taking place, as follows :



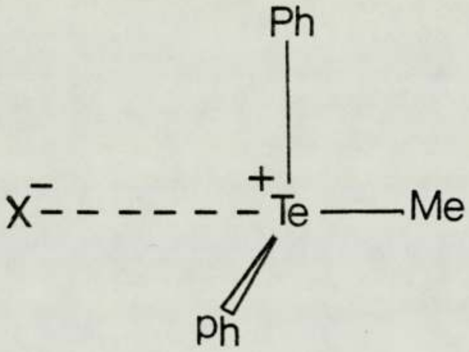
The most important evidence from the mass spectrum of these telluronium salts is that; the thiocyanate ion was observed in the mass spectrum of $Ph_2MeTe(NCS)$, this must be from thermolysis. It would imply some association in the solid like, that seen by Ziolo et. al., for $Ph_3Te\ NCS$. In the gas phase, the $MePh_2TeX$, $X = BF_4$, PF_6 are in covalent form and the reductive elimination of $MeBF_4$ and $MePF_6$ can occur; but both rapidly breakdown to MeF. (Alternatively, we may consider

$$MePh_2TeBF_4 \xrightarrow{heat} MePh_2TeF + BF_3$$

$$MePh_2TePF_6 \longrightarrow MePh_2TeF + PF_5)$$

The conductivity measurements

Single concentration (10^{-3}M) conductivity studies of the Ph_2MeTeX, X = SCN, BF_4, PF_6 in DMSO give values of the molar conductivity Λ_m; 27, 34, 36 mhos, $cm^2.mol^{-1}$. subseqeutnly. This represents within a 1:1 electrolyte in this solvent. However, the conductivity was studied as a function of concentration (Λm versus $\sqrt{c}$), Straight lines were obtained for Ph_2TeMeX X = SCN, BF_4, PF_6 (pages 148, 150.) Thus strong electrolytes were indicated. Hence the species in solution is probably best represented as ;



The molar conductivity of $Ph_2MeTeSCN$ in DMF gives the value of the Λm = 95 mhos cm^2 mol^{-1}. Also the graph of $\sqrt{c}$ against Λm, the curved plot(fig. 17) . Thus some degree of ion pairing is indicated in this solvent. The molar conductivity of Ph_2MeTeX, X = BF_4, PF_6 gavea low value in DMF 39 mhos cm^2 mol^{-1}, as observed by Dance [52], for Ph_2MeTeX, X = Cl, Br, I in DMF

The H n.m.r. spectra of Ph_2MeTeX, X = SCN, BF_4, PF_6

Since Dance[52] has found 'H n.m.r. to be useful in the investigation of the reductive elimination of alkyl halide from Ph_2MeTeX, X = Cl, Br, I, (more detail on page 16), we decided to examine the 'H n.m.r. spectrum of diphenylmethyltelluronium isothiocyanate in solvents of differing polarity and to compare the behaviour with that of other new organotelluronium compounds, e.g. Ph_2MeTeX, X = BF_4, PF_6.

The 'H n.m.r. spectra of a solution of a Ph_2MeTeX where X = SCN, BF_4, PF_6 in deuterated DMSO were recorded(table 8) . In DMSO (d_6) a simple spectrum is obtained with a single methyl resonance at δ = 2.70 ppm. for $Ph_2MeTeSCN$ at δ = 2.72, for $Ph_2MeTeBF_4$. For $Ph_2MeTePF_6$ at 2.71 ppm. (relative to TMS). The singlet has satellite peaks caused by coupling between 'H and ^{125}Te (spin = ½) and must therefore, be due to the methyl group, which is still attached to the tellurium atom ($J^{125}Te$-'H ^{24}Hz). The low δ value of the resonance indicates that the methyl group is attached to an electropositive centre, as would be expected for a telluronium salt.

The Ph_2MeTeX,where X = BF_4, PF_6,are insoluble in chloroform, but the $Ph_2MeTeNCS$ is soluble in chloroform. The 'H n.m.r. spectrum of the $Ph_2MeTe(NCS)$, dissolved in deuterochloroform also contains a singlet with satellite peaks, but this is in a different position to that in DMSO and it decreased with time. The singlet for diphenylmethyltelluronium isothiocyanate is at δ = 2.9 ppm, and within 3h., this resonance had vanished, being replaced by another singlet and δ = 2.56 ppm, due to methyl thiocyanate,since it was shown that methyl thiocyanate,in deuterochloroform gave a singlet at δ = 2.56 ppm. This compares with

Dance's [52] work on the 'H n.m.r. spectra investigated for Ph_2MeTeX, ($X = Cl, Br, I$) in deuterochloroform. The iodide gave a singlet with satellite peaks at δ = 3.04 ppm, within ½ h., this resonance had vanished, being replaced by methyliodide at δ = 2.15 ppm. The bromide gave a singlet at δ = 2.90 ppm, which vanished over a period of 24 hrs. and was replaced by resonance at δ = 2.61ppm due to methyl bromide. The chloride produced a singlet at δ = 2.76 ppm, which decreased very slowly, while a peak at δ = 2.96 ppm, due to methyl chloride, was formed. However, the diphenylmethyltelluronium isothiocyanate had decomposed to give diphenyltelluride and methyl thiocyanate;

$$Ph_2MeTe(NCS) \longrightarrow Ph_2Te + MeSCN$$

No other product was observed. In the light of the above we conclude that the position of methyl resonance of $Ph_2MeTe(NCS)$ is identical with that for $Ph_2MeTeBr$. The relative rates of dissociation of Ph_2MeTeX in $CDCl_3$ are then $X = I > NCS \approx Br > Cl$

and appears to parallel the electronegativity of the groups.

Kinetic Study :-

Kinetic studies provide important evidence for the reaction mechanism. Foremost is the identification of what species reacts, what products are formed, and what stoichiometry is obeyed. Closely allied to this is the recognition and identification of intermediates, sometimes by actual isolation and structure determination but more often through physical detection.

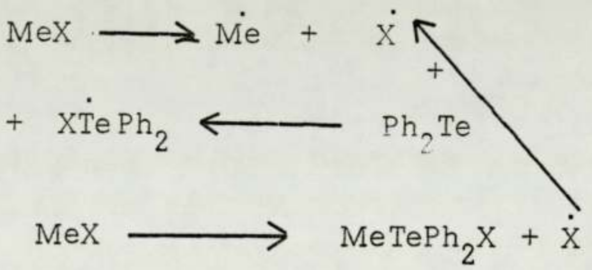
A few of the methods more commonly used, with the sampling technique and for direct instrumental monitoring are now mentioned with some commentary e.g. u-v, i.r., n.m.r. spectra.

N.M.R. is a useful for rate determination in two quite different ways. On the one hand, rate information concerning relatively fast processes can be obtained from line-shape analysis. On the other hand, n.m.r. is a useful, static analytical technique for the study of reactions with half-lives of minutes or hours.

In a preceding investigation, Dance [52] studied the kinetics of the reaction between diphenyltelluride and methyl iodide which indicated that the dissociation occurred from a covalent, rather than an ionic form. Thus the following equilibria were shown to be shifted to the right or the left by selecting solvents of differing polarity:

$$\underset{\text{ionic}}{Ph_2MeTe^+X^-} \rightleftharpoons \underset{\text{covalent}}{Ph_2MeTeX} \rightleftharpoons Ph_2Te + MeX \qquad X = Cl,\ Br,\ I.$$

It has been suggested that the mechanism of the formation of the covalent form involves a radical pathway; Ph_2Te I + Me



However, from i.r. data of Ph_2MeTe NCS, we postulate that the $Ph_2MeTeNCS$ behaves as an essentially ionic telluronium salt $MePh_2Te^+$ $(NCS)^-$. But in $CDCl_3$ solution it exists in a covalent form, $MePh_2Te(NCS)$, from which reductive elimination of, exclusively, methyl thiocyanate occurs. We followed the decomposition of Ph_2MeTe (NCS) in $CDCl_3$ using the n.m.r. technique. The total integrated intensity of the methyl resonances remain constant throughout the reaction, thus, within the sensitiveity of the continuous wave n.m.r. technique, no other methyl containing products than methyl thiocyanate were formed.

$$Ph_2MeTe(NCS) \xrightarrow{CDCl_3} Ph_2Te + MeSCN$$

By monitoring the 'H n.m.r. spectrum at time intervals over the occurrence of the reaction, we might consider the total integrated intensity of the methyl resonance which remains constant equivalent to a, (initial concentration). After a time t, X, of, a, decomposes. The remaining concentration of $Ph_2MeTeNCS$. is (a - x). If the plot of log (a-x) against time is a straight line, implies that the reaction of a pseudo-first order. We were able to construct pseudo first order rate plots from the data, (table 6). A typical result is shown in figure (20, 21). Over a period of 90 mins. a linear plot is obtained, however, the rate then changes and the slope alters. A further linear plot is then obtained. The plot of concentration for growth of methyl thiocyanate which forms (from decomposition of Ph_2Me TeNCS in $CDCl_3$) against time was shown in(fig.20) . This reaction was repeated in more dilute solution the same observations as above were made (fig.20). It would therefore, appear that there were two mechanisms operative, the second of which becomes dominant during the latter stages of the reaction. The most probable mechanism for the initial stage of the reaction is one involving loss of a methyl radical at a rate determinend in step :

Initiation $MePh_2TeNCS \xrightarrow{slow} \dot{M}e + Ph_2\dot{T}eNCS$

followed by a sequence of fast steps, e.g.

propagation $\dot{M}e + SCNTePh_2Me \longrightarrow MeSCN + \dot{T}ePh_2Me$

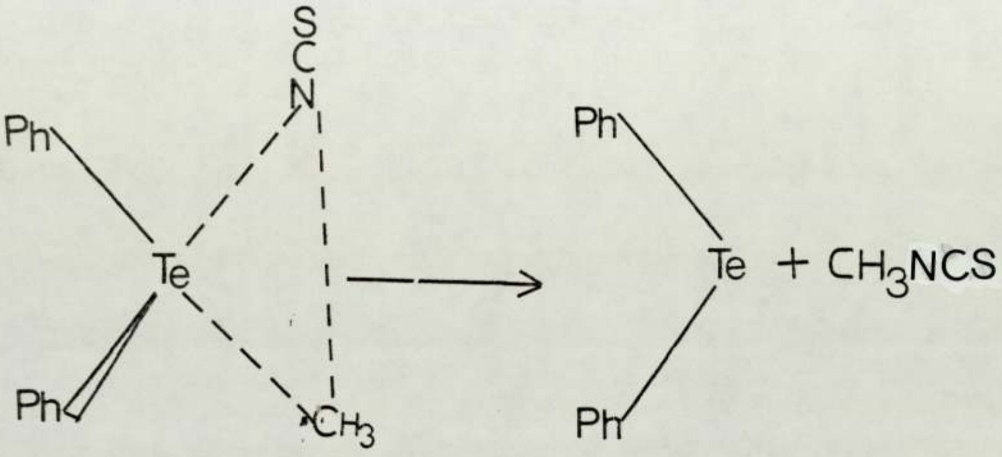
$\dot{T}ePh_2Me \longrightarrow Ph_2Te + \dot{M}e$

Termination $\dot{\mathrm{Me}} + \mathrm{SCNTePh_2} \longrightarrow \mathrm{MeSCN} + \mathrm{Ph_2Te}$

Some evidence that the proposed radical mechanism may be involved comes from studies of $Ph_2MeTePF_6$ in DMSO (d_6) /$CDCl_3$ and DMSO (d_6)/benzene. The n.m.r. spectrum of $Ph_2MeTePF_6$ in DMSO(d_6)/$CDCl_3$ 1:1 is shown in (fig. 11.).

In the presence of chloroform the compound produced a singlet at δ = 2.72 ppm, which decreased very slowly with time, while a peak at δ = 3.01 ppm, which is assigned to methylchloride was formed. The 50% of the starting material remained after about 6 hours, compared with methyl chloride. The methyl chloride probably arises from the attack on chloroform by methyl radicals. The n.m.r. spectrum of $Ph_2MeTePF_6$ in DMSO/benzene is shown in (fig.14) gave a singlet at δ = 2.68 ppm, no change in the spectrum with time was detected over 5 hours (N.B. ($MePh_2TePF_6$) is insufficiently soluble in $CDCl_3$ or benzene for the pure solvent to be used). These results suggest that methyl radicals can be released and may attack chlorinated solvents in a slow reaction, however, the n.m.r. spectrum of $Ph_2MeTeNCS$ in deuterochloroform clearly indicates the presence only methyl thiocyanate and eliminates the possibility of MeCl being formed (the attack of the solvent is a slow reaction compared with formation of MeSCN).

If the above speculation is accepted, it is resonable to postulate that material whose concentration grows during the reaction may exercise some catalytic influence. The two candidates are diphenyl telluride and methyl thiocyanate. Methyl thiocyanate has been shown to be inert under these conditions. No direct reaction between methyl thiocyanate and diphenyl telluride was seen in the n.m.r. tube for more than 48 hrs., hence a role for diphenyl telluride is possible. An alternative explanation is that a concerted mechanism may become dominant. Barton [120] has shown that the tetraaryltellurium compound decomposed thermally to biaryls and diaryl tellurides; but the suggestion seems less likely to be true here. Given that dissociation occurs from an isothiocyanate species, $MePh_2Te(NCS)$, it would be expected that methyl isothiocyanate would be formed as follows :

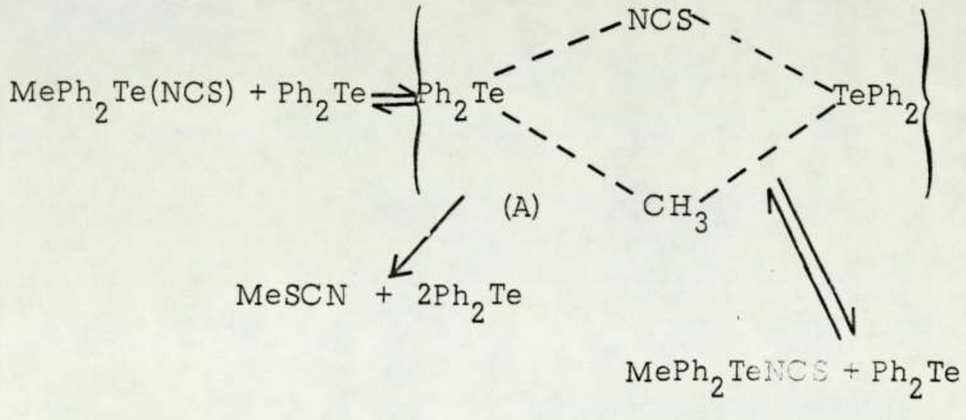


However, methyl thiocyanate is the exclusive product, hence we argue the concerted mechanism, as unlikely in the light of the data presently available.

A further possibility is that diphenyl telluride, the concentration of which increases during the reaction, may play some catalytic role causing a speeding up of the reaction. We therefore, carried out the kinetic experiments in the presence of an initial concentration of diphenyl telluride. Also illustrated in (fig.20) are the results of an experiment for which, initially, $Ph_2Te : MePh_2TeNCS$ = 1.5:1, and the compound with the experiment in which the decomposition of $Ph_2MeTeNCS$ in $CDCl_3$ is shown (fig.20). In the presence of an excess of Ph_2Te, the initial rates of decomposition agree well, and the major influence of the excess telluride is to advance the onset of the faster stage of the reaction. As with the initial stage rates for the latter stage are the same within experimental error. The interpretation of these results requires care. In general rates are dependent on the solvent. Theoretical treatments of solvent effect on reaction rates have mostly taken the macroscopic dielectric constant to be the significant solvent variable. In kinetic study of Ph$_2$MeTeI,[52] , Ph$_2$Te behaved as a solvent intermediate in polarity between CDCl$_3$ and DMSO, thus, dilution of CDCl$_3$ with Ph$_2$Te might begin to favour the ionic form of the telluronium salt and hence, slow the reductive elimination reaction, ie. if the role of Ph$_2$Te is purely dielectric, kinetic effects opposite to those observed might be anticipated. The ^{1}H.n.m.r. chemical shift of the methyl group of MeSCN shows some degree of solvent dependence. Thus, in CDCl$_3$ $\delta = 2.56$ ppm, in C$_2$H$_5$OH, $\delta = 2.6$ ppm, and in CDCl$_3$/Ph$_2$Te, $\delta = 2.42$ ppm., although the variation in δ is small, some change of solvation is implied. However, apart from the changes illustrated in fig. (20), this was the only difference noted for the system in the presence of excess diphenyl telluride.

The evidence available indicates that the mechanism of reductive elimination of MeSCN from MePh$_2$TeNCS is not simple. There is support for the view that diphenyltelluride has a catalytic role. We speculate that the initial stage of the reaction is a radical process and suggest that as diphenyltelluride concentration builds up, interaction between Ph$_2$Te and a reacted MePh$_2$Te NCS may occur ;

e.g.



No concrete evidence for intermediates such as (A) above is available. Thus, if they exist, the concentration must be small. Russian workers [121] have studied the exchange reaction

$$Ph_2Te + Ph_2TeX_2 \longrightarrow Ph_2TeX_2 + Ph_2Te$$

It is possible that an associated intermediate similar to (A) may have a role to play. The work of Dance [52], together with the results presented here, indicate that the solution chemistry of telluronium salts is not simple. It is implicit in the work of Dance, and also in this work, that the reductive elimination of MeX occurs from a ψ' -trigonal bipyramidal "covalent" form of Ph_2MeTeX. From phosphorane chemistry (e.g. P. Gillespie, F. Ramirez, I. Ugi and D. Marquarding. Angew. Chem. Inst. Edu. 12 91 (1973), we anticipate that groups will enter, and depart from, an axial position in the ψ' -trigonal bipyramid. Given that the lone pair will remain equatoral and the electronegative halogen or isothiocyanate will be axial, no pseudo-rotation will interchange Me and Ph. Hence, it must be assumed that the methyl group will be preferentially axial. The electronegativities Me and Ph are similar (e.g. ^{35}Cl nqr frequency for MeCl is 34.1 MHz and for PhCl is 34.8 MHz - E.A.C. Lucken, Nuclear. Quadrupole Coupling Constants, Academic Press, London (1967). In fact, Ph is marginally the more electronegative, but it also has a greater steric requirement which may argue for the equatorial position being favoured.

It is probable that a rich solution chemistry awaits examination and elucidation in this area. It is hoped that these results will form a useful basis for future investigators.

CHAPTER 5

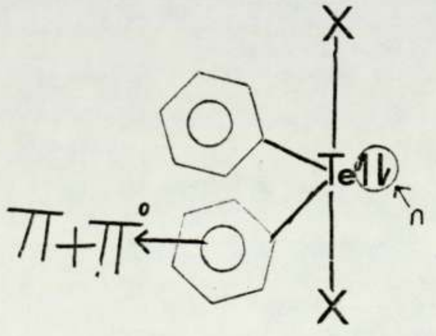
1 - The UV-spectra of Ph_2TeX_2, X = Cl, Br, I

There exist a number of different possible origins for the electronic absorption spectra of complexes, these are ; $\pi \longrightarrow \pi^{o}$, $n \longrightarrow \pi^{*}$ $n \longrightarrow 6^{\cdot}$. The spectra associated with transition metals may arise from d-d transition the transition are influenced by the ligand attached to the metal. Charge-transfer phenonmena, the transfer of an electron from the ligand to the metal or vice-versa, may also contribute to the spectrum.

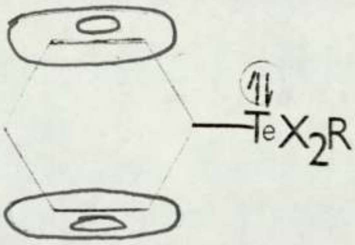
The aim of this study was to rationalize the u. v.-spectra of Ph_2TeX_2.

Ph_2TeCl_2 is colourless and gives absorption in the u.v. - region. Ph_2TeBr_2 is yellow and gives absorption bands in the ultra-violet, which partly intrude into the visible. Ph_2TeI_2 is red in the solid state and yellow in solution. Peak positions of these spectra have been tabulated in table 2.

The tellurium in these compounds has formally a d^{O}-electronic configuration, thus pure d-d transitions are not possible and the colour cannot arise in that way. If we consider;



I suppose $n \longrightarrow \pi^{o}$ is possible since, in a sense, Te is a substituent in an aromatic ring :-



e.f. $PhNH_2$, PhOH, PhOR, PhSR elec.

However, the spectra shift to longer wave length as the halogen becomes less electronegative or more polarisable. Hence it is reasonable to expect that a charge transfer transition of the type $\overset{\frown}{X - Te}$ will become easier in the order $Cl < Br < I$. Good support for this comes from the observation that ν_s(Te-Br) in Ph_2TeBr_2 undergoes resonance enhancement when the laser frequency is absorbed [10]. Christofferson and MCCullough [16] studied x-ray crystallographically of $(ClC_6H_4)_2TeI_2$. The intense red colour in R_2TeI_2 was attributed to Te-I and I_2-I_1 interaction (more detail in page 6). No short Cl_1 - Cl_2 or Br_1 - Br_2 contact were observed in R_2TeX_2, X_2 = Cl_2, Br_2.

2. A convenient method for the preparation of Organotellurium Compounds

The cleavage of a carbon-metal bond (Sn, Pb) are used widely to prepare organotellurium compounds in good yields [42, 41].

$$R_4M + TeCl_4 \longrightarrow R_2TeCl_2 + R_2MCl_2$$

$$R_3MCl + TeCl_4 \longrightarrow RTeCl_3 + R_2MCl_2$$

$$R_3MCl + R'TeCl_3 \longrightarrow RR'TeCl_2 + R_2MCl_2$$

This new arylation procedure is especially attractive because work-up of the tellurium product from reactions involving Grignard or organo-lithium reagents usually involves a hydrolysis step to destroy any residual reagent, and this can cause hydrolysis to tellurium compounds.

In continuation with this work, we would like to demonstrate the preferential cleavage of alkyl-tin or phenyl-tin bonds, in mixed tin compounds, toward tellurium tetrachloride.

Halogenation of Sn-aryl is known to be faster than that of Sn-alkyl [123] hence, it seemed probable that the reaction of a mixed alkyl aryl tin compound with tellurium tetrachloride would, give preferentially the aryltellurium halide. Thus, phenyltri -butyl tin and phenyl-tin -propyltri were prepared [124] by reaction of the appropriate trialkyl tin chloride with phenylmagnesium bromide.

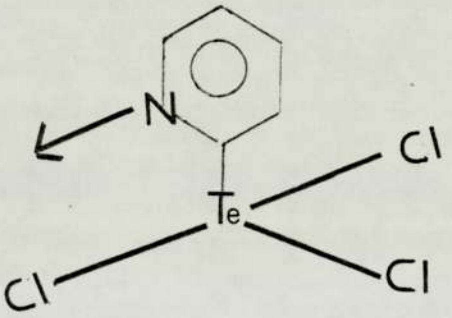
The reaction of Pr_3PhSn or Bu_3PhSn with tellurium tetrachloride in toluene gave a white precipitate together with tributyl or tripropyl-tin chlorides which were identified by infrared spectroscopy. The elemental analysis (table 1), and infrared spectrum (fig. 1) of white precipitate indicated that the material was phenyltellurium-trichloride. This reaction was repeated, but with p-ethoxyphenyl tellurium trichloride in a benzene (or in toluene) refluxed about two hours to afford a white precipitate and tributyl tin chloride. The elemental analysis (table 1) and infrared spectrum (fig. 2) of that white material showed it to be $Ph(p\text{-}EtO.C_6H_4)TeCl_2$. In fact the first reaction goes to completion at room temperature within one hour and the second one within 2hrs. refluxing. The yields of the organotellurium halides are excellent. The procedure may be used for the synthesis of a variety of organotellurium halides depending on the tin compounds. Soon after this work had been finished Kapoor and Srivastavac[125] published a paper which is of relevance to it ; they reported that the reaction of tributylphenyl-tin with tellurium tetrachloride was stirred overnight to afford phenyltellurium trichloride, but we found here only one hour was required to complete this reaction.

Attempt formation of a 2.pyridyltellurium trichloride from tributyl-2-pyridyltin and tellurium tetrachloride :-

Tributyl-2-pyridyltin was prepared following McWhinnie et. al.[126] ; from 2-pyridylmagnesium bromide (prepared by the entrainment method with ethyl bromide and 2-bromopyridine in ether) reacted normally with a benzene solution of tributyltin chloride to give tributyl-2-pyridyltin. The i.r. and n.m.r. spectra(fig. 12, 16) indicated that the butyl and 2-pyridyl-groups were present. The reaction mixture of tributyl-2-pyridyltin with tellurium tetrachloride in benzene was stirred overnight to afford a white precipitate together with tributyltin chloride. Tributyltin (IV) chloride was identified by i.r. spectroscopy.(fig. 17) . The white precipitate which was unstable, changed to black. The infra-red spectrum of this unstable material showed bands around 1600, 450, 720 cm^{-1}. which were assigned to 2-substituted pyridines(fig.7). The i.r. spectrum of 2-bromopyridine(fig. 7) showed bands around 1600, 460, 750 cm^{-1}. The unstable material was reduced by hydrazine, to give a tellurium precipitate together with 2,2' bipyridine, which was identified by the i.r. spectrum (fig. 13) compared with i.r.

spectra of 2,2 bipyridine. Also, the material was shown to give a deep red colour with iron II. The fact that tributyltin chloride was positively identified as a product of the reaction of tributyl (2-pyridyl)tin with tellurium tetrachloride, argues strongly for the view that a pyridiyl-group has been transferred to tellurium. The subsequent identification of 2,2-bipyridyl from the hydrazine reduction of the unstable material, further supports the view that a 2-pyridyl tellurium compound has been made.

If (2-pyridyl)tellurium trichloride was prepared, then it is apparently unstable. There is no immediate reason why this should be the case. The geometry of the pyridine lone pair is such that intramolecular co-ordination is unlikely :



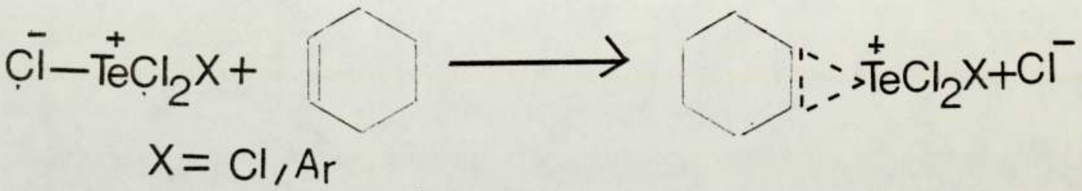
Thus, (2-pyridyl)$TeCl_3$ should either be similar in structure to $PhTeCl_3$, or possibly, has a structure involving a degree of intermolecular N → Te co-ordination.

In view of the instability of this white reaction product, the fact that hydrazine reduction should afford tellurium is not in itself surprising.

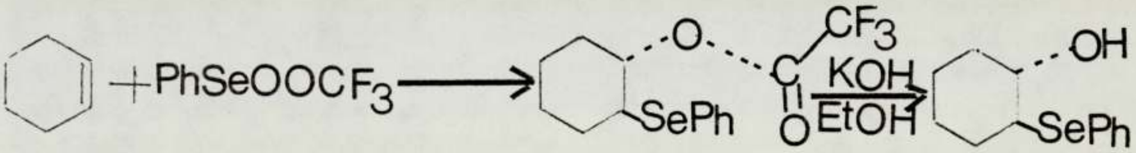
Clearly, this is an area which would repay more detailed study. Unfortunately, the present author suffered an allergic reaction to the tin compounds required as intermediates, and was unable to pursue the topic further.

3. The reaction of 2-vinylpyridine with tellurium tetrachloride or p-ethoxyphenyltellurium trichloride :-

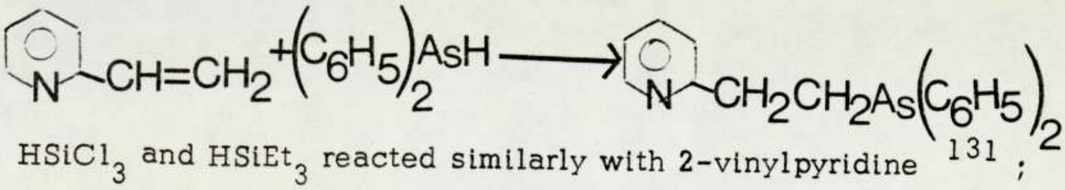
One of the methods of introducing tellurium to organic compounds is adding tellurium compounds to unsaturated organic molecules. It was found, for example, that tellurium tetrachloride and aryltellurium trichloride added to cyclohexene to afford 2-chlorocyclohexyltellurium trichloride and aryl-2-chlorocyclohexyltellurium dichloride respectively[127];



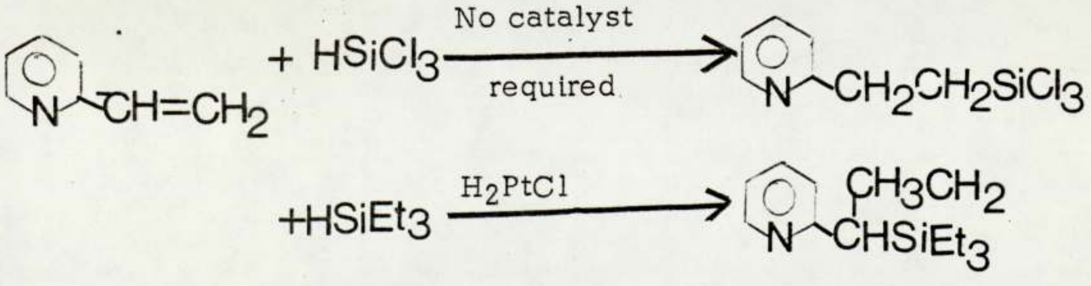
The reaction of tellurium tetrachloride with ethene in carbon tetrachloride gave β-chloroethyltellurium trichloride.[128] The addition of phenylselenyl bromide to silver trifluroacetate in benzene in the presence of cyclohexene produced trans -2-phenylseleno-1-trifluoroacetoxcyclohexane, as below[129];



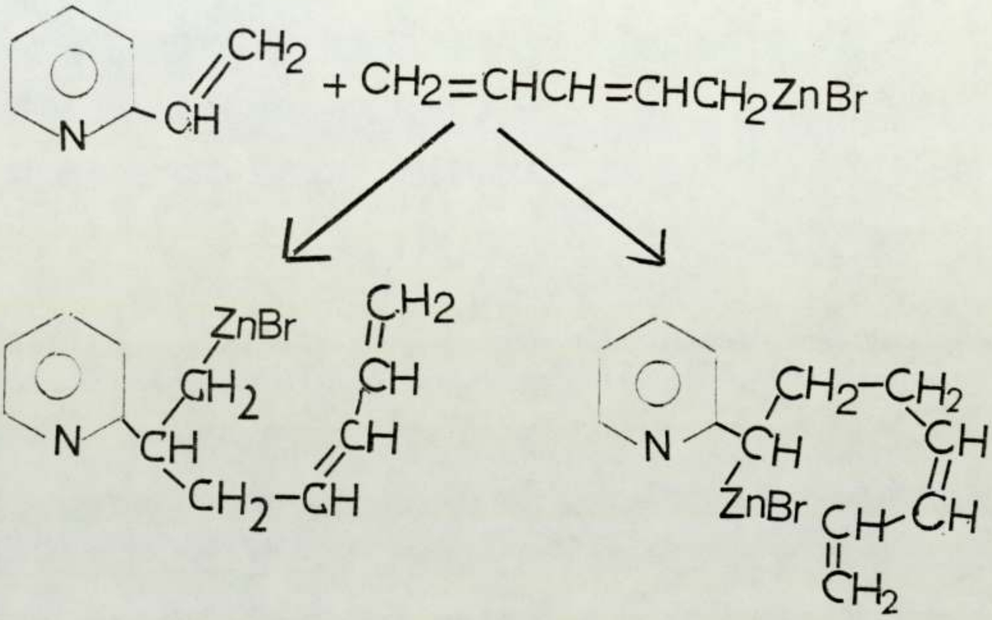
2-(diphenylarsinoethyl)pyridine has been formed by the reaction between diphenyl arsine and 2-vinylpyridine as follows [130];



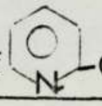
$HSiCl_3$ and $HSiEt_3$ reacted similarly with 2-vinylpyridine [131];



Allylic organozinic compounds add on either end of the ethylenic bond of 2-vinylpyridine, to give a mixture of two isomeric 2-alkylpyridines[132].

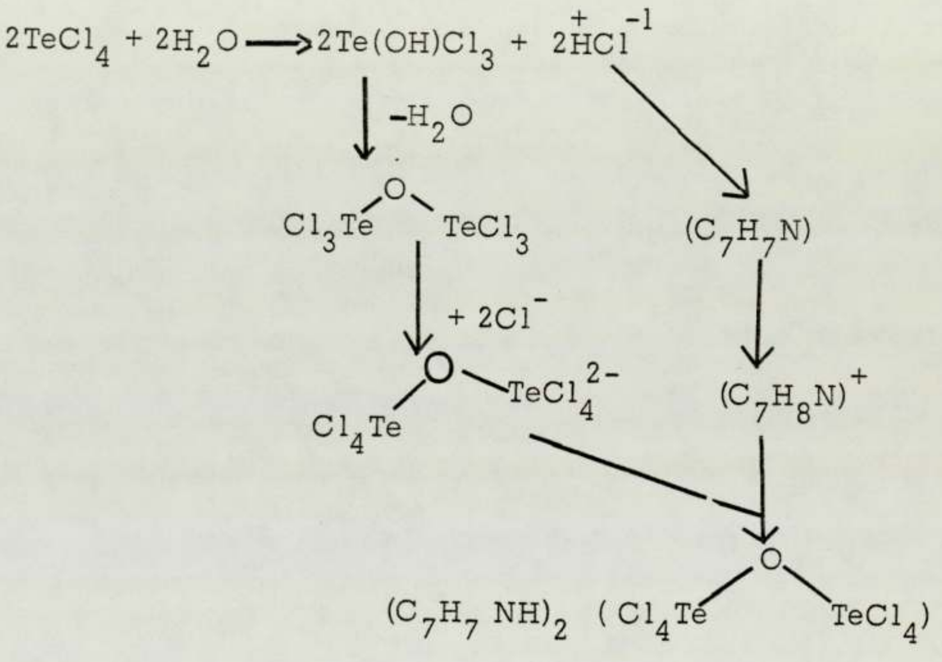


This research has been extended to react tellurium compounds with 2-vinylpyridine hoping that an addition reaction on the ethylenic bond of 2-vinylpyridine will take place.

a) Reaction of  -CH= CH_2 with $TeCl_4$:-

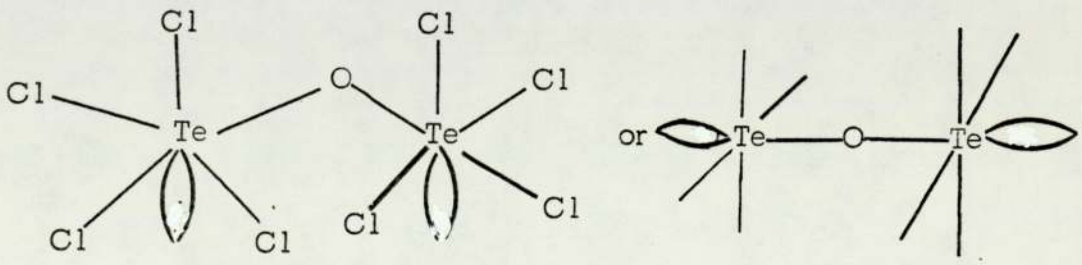
The reaction of tellurium tetrachloride with 2-vinylpyridine gave a yellow precipitate. The elemental analyses of this compound is shown in table 3 . The u.v.-spectrum of this material in ethanol gave bands at 235, 285, 355 nm. which is similar to the u.v-spectrum of the 2-vinylpyridinium cation in ethanol which produced bands at 226, 236, 288 nm. This may indicate the presence of the pyridinium cation. In other cases the N-H of the 2-vinylpyridinium cation was inferred from the infrared spectrum of the yellow compound which is shown on page 193 it showed four clearly resolved N-H stretching vibration 3060, 3100, 3160, 3260 cm^{-1} by comparison the infra-red spectrum of $(PhTeCl_4)^-(C_5H_5N)^+$ which gave N-H stretching vibration within the same range.[22] The tellurium-oxygen vibrational mode was assinged around 600 cm^{-1} [133]. the single concentration (10^{-3}M) conductivity study of this compound in acetonitrile gave the value of the molar conductivity :- $\Lambda_M = 81$ mhos cm^2 mol^{-1}., this value is expected for a 1:1 electrolyte in this solvent.

In view of above possible spectrum one might speculate that the reagents were supposedly 'dry' but that they contained sufficient water to hydrolyse tellurium tetrachloride ;



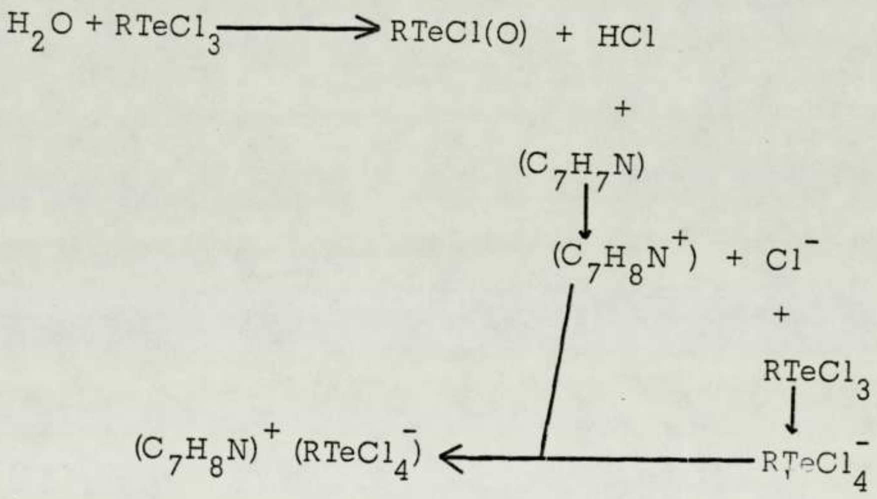
yellow precipitate

with this possible shape ;



b- Reaction of 2-vinylpyridine with p-ethoxyphenyltellurium trichloride :

The reaction of p-EtOPhTeCl$_3$ with 2-vinylpyridine produced a white precipitate. The elemental analysis of this compound is shown in (table 3) The single concentration (10^{-3}M) conductivity study of the white precipitate in acetonitrile gave the value of the molar conductivity Λm = 85 mhos cm^2 mol^{-1}. This value is expected for a 1:1 electrolyte in this solvent. The infrared spectrum of this compound (fig. 6) showed four resolved N-H stretching vibration (table 3). which is similar to the infrared spectrum of $(C_7H_7NH^+)_2$ $(Cl_4Te{-}O{-}TeCl_4)$. We might suggest that the moisture in our reagents caused hydrolysis of some of RTeCl$_3$ as follows ;



This compound is believed to be analogous with $(PhTeCl_4^-)(C_5H_5N^+)$ prepared by Thavoryutikarn[22]. The anions in these compounds are similar to the well known $MeTeI_4^-$ which occurs in the β form of $Me_2TeI_2(Me_3Te^+.MeTeI_4^-)$[134]. The structure of $MeTeI_4^-$ has been determined by X-ray crystallography and was found to be of square pyramidal configuration with iodine atoms in the base, the methyl-groups at the apex, and with the lone-pair completing an octahedron.

Therefore, a square pyramidal structure is most probable for the (p-EtOPhTeCl$_4$) anion, with the chlorine atom in the base and the p-EtOPh group at the apex. This proposal is supported by the Thavoryutikarn study of the vibrational spectra for the (PhTeCl$_4$)$^-$ (C$_5$H$_6$N)$^+$.

EXPERIMENTAL :-

Diphenyltellurium dichloride was prepared following the Bush method [122], passing chlorine gas into an ether solution of diphenyltelluride, and purified by recrystallization from xylene. M.p. 160° (lit[122] m.p. 160).

Diphenyltellurium dibromide or diiodide :- were prepared by a halogen-exchange reaction. This is similar to Petragnani's method [53] for the preparation of aryltellurium trihalides. A known amount of Ph_2TeCl_2 in methanol was treated with excess of alcoholic potassium bromide or potassium iodide solution and corresponding dihalides precipitated by the addition of a small amount of benzene. The products were recrystallized from a benzene and were yellow/red in colour M.p. (dibromide) 203°C. lit,[48] 203°C (diiodide) 237°C lit[135] 237°C.Then very dilute solutions of R_2TeX_2 in CH_2Cl_2 were made for u.v.-spectral measurements.

Tributylphenyl tin; $^{n}Bu_3PhSn$:-

The preparation of this compound was carried out according to Kerk[124] starting from tributyl tin chloride and phenylmagnesium bromide. Tributyltin chloride (14 gm) in benzene (5 0 ml) (dried over sodium wire) was slowly added to the reaction product of magnesium (1.5 gm) and of phenyl bromide (10.5 gm) in anhydrous ether (100 ml). The mixture was refluxed for three hours, then cooled, decomposed by the addition of water (25 ml.), followed by that of 20% ammonium chloride solution (400 ml.). The crude tributylphenyltin left after evaporation of the dried ethereal layer was fractionated in Vacuo.B.p(0.1 mmHg). 160°C. The purity of this compound was checked by the n.m.r. spectrum which gave correct integration.

Tripropylphenyltin $^{n}Pr_3PhSn$:-

The method above was used to prepare $^{n}Pr_3PhSn$ using tripropyltin chloride (10 gm) in benzene (50 ml.) which was added to the reaction product of magnesium (0.6 gm) and phenyl bromide (7 gm) in anhydrous ether (80 ml.). The product tripropylphenyltin was checked by the n.m.r. spectrum which gave correct integration as well.

Tributyl-2-pyridyltin $^{n}Bu_3PySn$:- was prepared following the McWhinnie method [126], magnesium (1.5 gm) and a solution of ethyl bromide (0.1 ml.) in ether (5 ml.) was placed in a flask fitted with a reflux condenser and mechanical stirrer and a crystal of iodine was added to initiate the reaction. A solution containing 2-bromopyridine (2.9 ml.) and ethyl bromide (1 ml.) in ether (25 ml) was added at a rate which maintained steady boiling and the mixture was then heated under reflux for 2h. After cooling, a solution of tributyltin chloride (12.0 gm) in benzene (30 ml.) was added, the ether was distilled off, more benzene (50 ml.) added and the mixture refluxed for 2h. Excess Grignard reagent was decomposed by the addition of saturated aqueous ammonium chloride and, after filtration, the benzene layer was separated and evaporated to give an oil (7.0 gm). An initial distillation gave tributyl-2-pyridyltin (5.33 gm) b.p 116 - 120°/0.2 mm.

Attempt to prepare tributyl-2-thienyltin :-

Starting from tributyltin chloride and 2-thienylmercury chloride

2-thienylmercury chloride Following the Volhard [136] method ; a mixture of thiophene (10 gm), ethanol (100 gm) and, aqueous $HgCl_2$ (100 gm) saturated in the cold and 33% aqueous sodium acetate (200 gm) is set aside for 4-5 days in a large flask with frequent shaking. The white crystalline precipitate, consisting of a mixture of mono and dimercurated compounds is recrystallized from alcohol. 2-thienylmercury chloride crystallized to M.p. 183 °C(lit[136] 183°C).

2.thienylmercuric chloride (3 gm) and tributyltin chloride (2.93 gm) in 1,4 dioxane (50 ml.) were refluxed for 6 hrs. The mixture was cooled. The starting materials were recorded. This reaction was repeated in different solvent such as methanol, but no reaction had taken place.

Reaction of tributylphenyltin and tellurium tetrachloride :-

A solution of tellurium tetrachloride (1.2 gm) in anhydrous toluene (30 ml.) was added to well stirred tributylphenyltin (3.1 gm) in toluene (10 ml.). During one hour, at room temperature, a white precipitate was formed, which was filtered, washed with toluene and dried. The precipitate was phenyltellurium trichloride m.p. 216°C (lit[41] 216°C).

Found	C	22.93	H.,	1.95	Cl.,	34.02
Required		23.2		1.6		34.23

Reaction of tripropylphenyltin with tellurium tetrachloride :-

The method mentioned above was used in tripropylphenyltin (3 gm) in toluene (10 ml.) and tellurium tetrachloride (1.9 gm) in toluene (30 ml.) which gave a white precipitate, which was phenyltellurium trichloride m.p. 216°C (lit 216°C.).

Reaction of tributylphenyltin and p-ethoxyphenyltellurium trichloride :-

A solution of tributylphenyltin (0.65 gm) in toluene (10 ml.) was added to suspension of p-ethoxyphenyltellurium trichloride (0.5 gm) in toluene (25 ml.). The mixture was refluxed for 3 hrs. The volume of solution was reduced to about (15 ml.) under reduced pressure, petroleum ether (10 ml.) was added giving a white precipitate which was filtered, washed with petroleum ether and dried. The precipitate was Ph(p-$C_2H_5OC_6H_4$)$TeCl_2$.M.p. 115^{o} (lit^{41} 115 ^{o}C).

Found	C.,	42.3	H.,	3.5	Cl.,	17.6
Required		42.3		3.6		17.8

Reaction of tributy-2-pyridyltin with tellurium tetrachloride :

A solution of tellurium tetrachloride (1 gm) in anhydrous toluene (30 ml.) was added to stirred tributyl-2-pyridyltin (1 gm) in toluene (10 ml.). The mixture was left stirring over night, a white precipitate was formed, which was filtered, washed with toluene, dried during that time, the colur changed to nearly black. This material was reduced by hydrazine in methanol which gave tellurium precipitate and 2,2-bipyridine.

Reaction of 2-vinylpyridine with tellurium tetrachloride

A solution of 2-vinylpyridine (1 gm) in toluene (20 ml.) was added to a well stirred solution of tellurium tetrachloride (1 gm) in toluene (25 ml.). This reaction was carried out under dry nitrogen. A yellow precipitate appeared after the addition of the first few drops. The yellow precipitate was filtered, washed with toluene and dried to m.p. 75^{o}C. The material was slightly soluble in chloroform and methanol but insoluble in carbon tetrachloride. The yellow precipitate was reduced with different reducing agents such as hydrazine or $K_2S_2O_3$ producing a tellurium precipitate in each case. The elemental analysis of the yellow precipitate showed it to be $(C_7H_7NH)_2\ (Cl_4Te{-}O{-}TeCl_4)$ Λm (10^{-3} in CH_3CN) = 81 mhos $cm^2\ mol^{-1}$.

Required	C,	21.9 ;	H,	2.08 ;	N,	3.64
Found		22.3		2.05		3.60

Reaction of 2-vinylpyridine with p-$C_2H_5OC_6H_4TeCl_3$:-

A solution of 2-vinylpyridine (1 gm) in toluene (20 ml.) was added to solution of p-ethoxyphenyltellurium trichloride (1 gm) in toluene (25 ml) under dry nitrogen. The mixture was set aside for 25 hrs. The solvent was evaporated. The white precipitate left was recrystallized from acetone and was decomposed at 135°C. The white precipitate was treated with different reducing agents such as hydrazine or $K_2S_2O_3$ and gave orange crystals which were identified as di-p-ethoxyphenylditelluride m.p. 107°C, (lit 107°C). The elemental analysis of that white precipitate showed it to be (C_7H_8N) (p-$C_2H_5OC_6H_4TeCl_4$). Λ_m (10^{-3} in CH_3CN) = 85 mhos cm^2 mol^{-1}.

Found	C.,	36.2 ;	H,	3.1 ;	N ;	2.5 ;	Cl.,	27.1
Required		36.45		3.06		2.8		28.7

Compound	Analysis (%)					
	Found			Calculated		
	C	H	Cl	C	H	Cl
$PhTeCl_3$	22.93	1.95	34.02	23.2	1.6	34.23
$Ph(p\text{-}EtOphTeCl_4)$	42.3	3.5	17.6	42.3	3.6	17.8

TABLE (1)

ANALYTICAL DATA OF TELLURIUM COMPOUNDS

Compounds	Solvent	Absorption Millmicrons
Ph_2TeCl_2	CH_2Cl_2	270, 254, 238
Ph_2TeBr_2		300, 275, 243
Ph_2TeI_2		360, 333, 283, 236

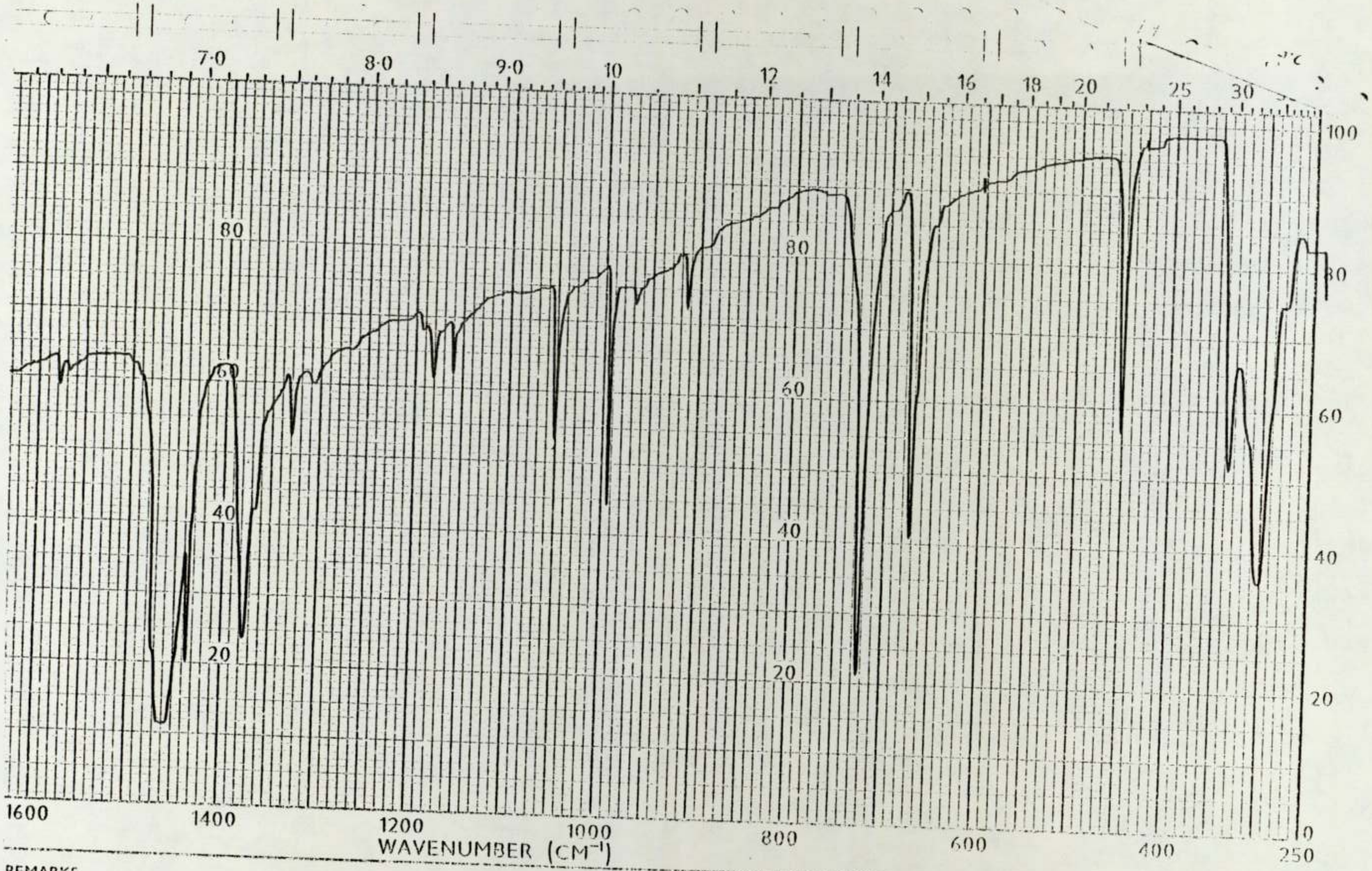
TABLE (2)

The u.v-spectra of R_2TeX_2, $X = Cl, Br, I$

Compounds	Analysis (%) Found C	Found H	Found N	Calculated C	Calculated H	Calculated N	Molar Conductivity m, 15^3 sol.	u.v. spectra n.m.	i.r. spectra cm^{-1}
$(\mathrm{C_7H_7NH})_2(\mathrm{Cl_4Te}\overset{\mathrm{O}}{\frown}\mathrm{TeCl_4})$	22.3	2.05	3.6	21.9	2.08	3.64	81	226) 236) $(\mathrm{C_7H_7N\overset{+}{H}})$ 288)	3060) 3100) (N-H) 3160) 600-(Te-o)
$(\overset{+}{\mathrm{C_7H_7NH}})(\mathrm{p\text{-}EtO.phTeCl_4})$	36.2	3.1	2.5	36.45	3.06	2.8	85	-	3060) 3100) (N-H) 3160)

ANALYTICAL, CONDUCTIVITY AND SPECTROSCOPY DATA FOR PYRIDINUM COMPOUNDS

TABLE (3)



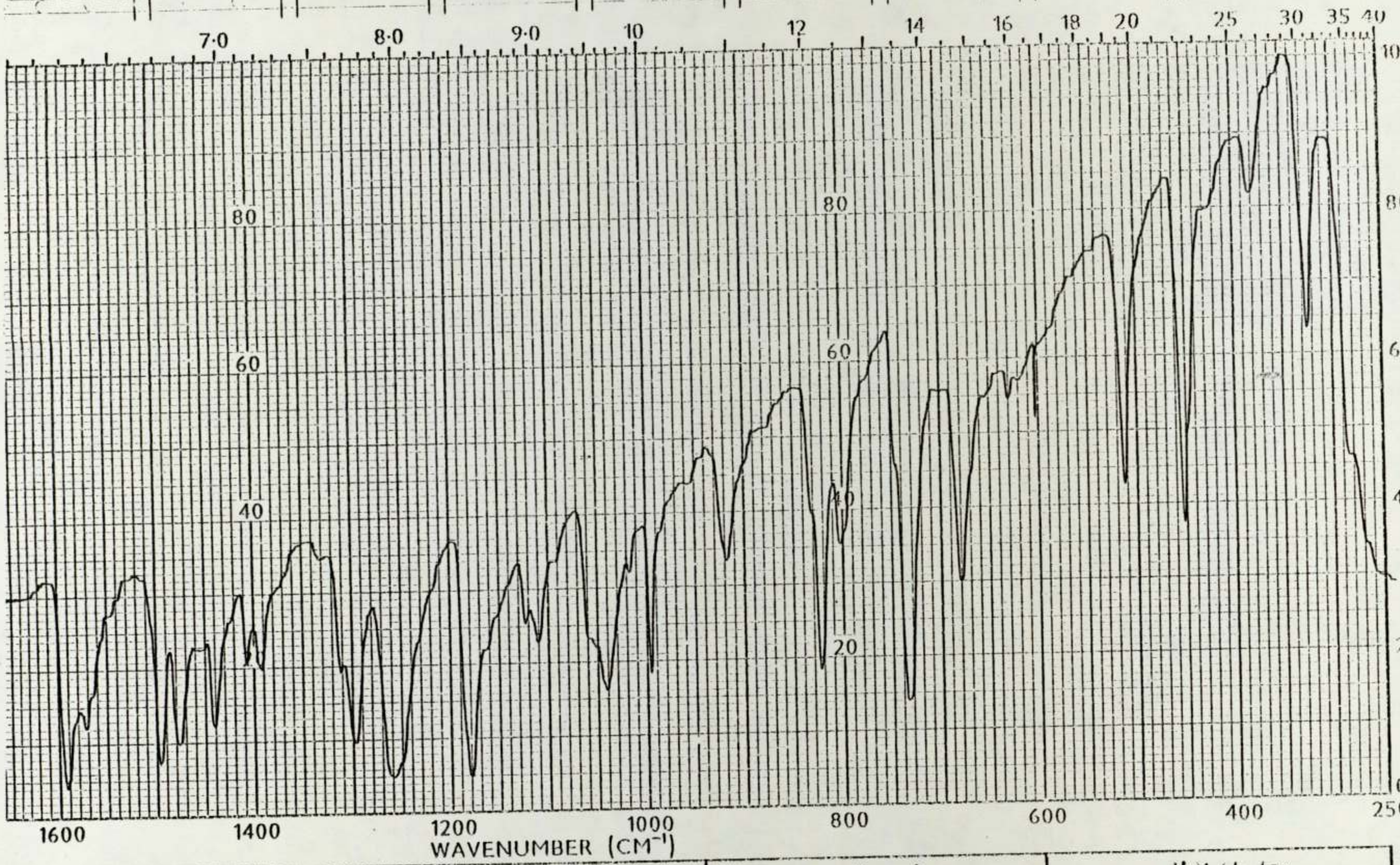
REMARKS

Infra - red spectra of $PhTeCl_3$

Fig. (1)

SCAN SPEED Medium.
SLIT Standard.
RPK/215/1002 457-5001
Intek

OPERATOR V.H. Clenton.
DATE 13th. June 1971
REF. No. 9170

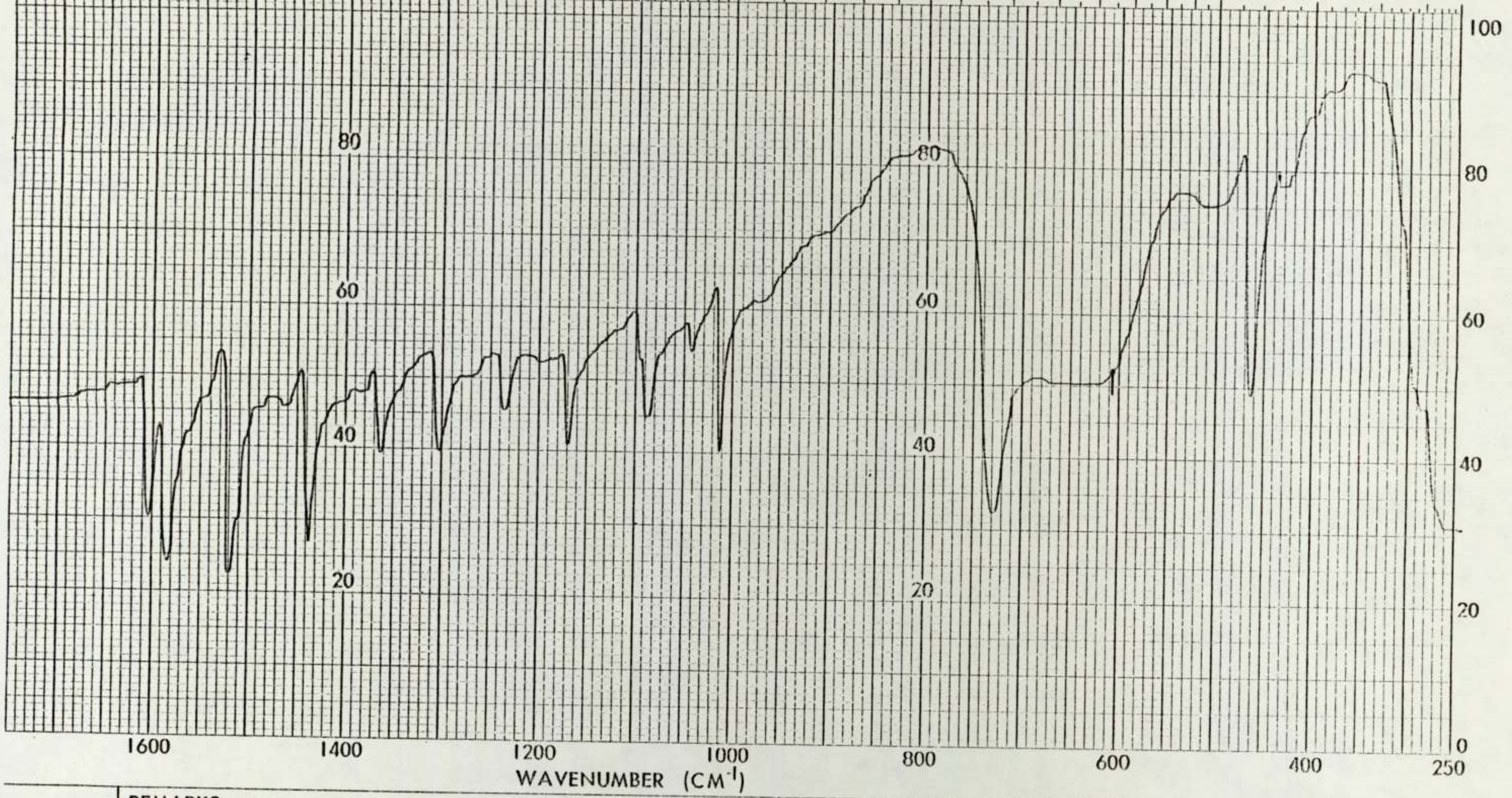


REMARKS Infra-red spectra of Ph(p-EtOph)TeCl$_2$

Fig. (2)

SCAN SPEED Medium.
SLIT Standard.
RPK/219/1002 457-5001
Intek

OPERATOR V.H. Clinton.
DATE 4th. May 1976
REF. No. 8324



REMARKS Infra-red spectra of $(C_6H_4N)TeCl_3$

Fig. (3)

SCAN SPEED [illegible]

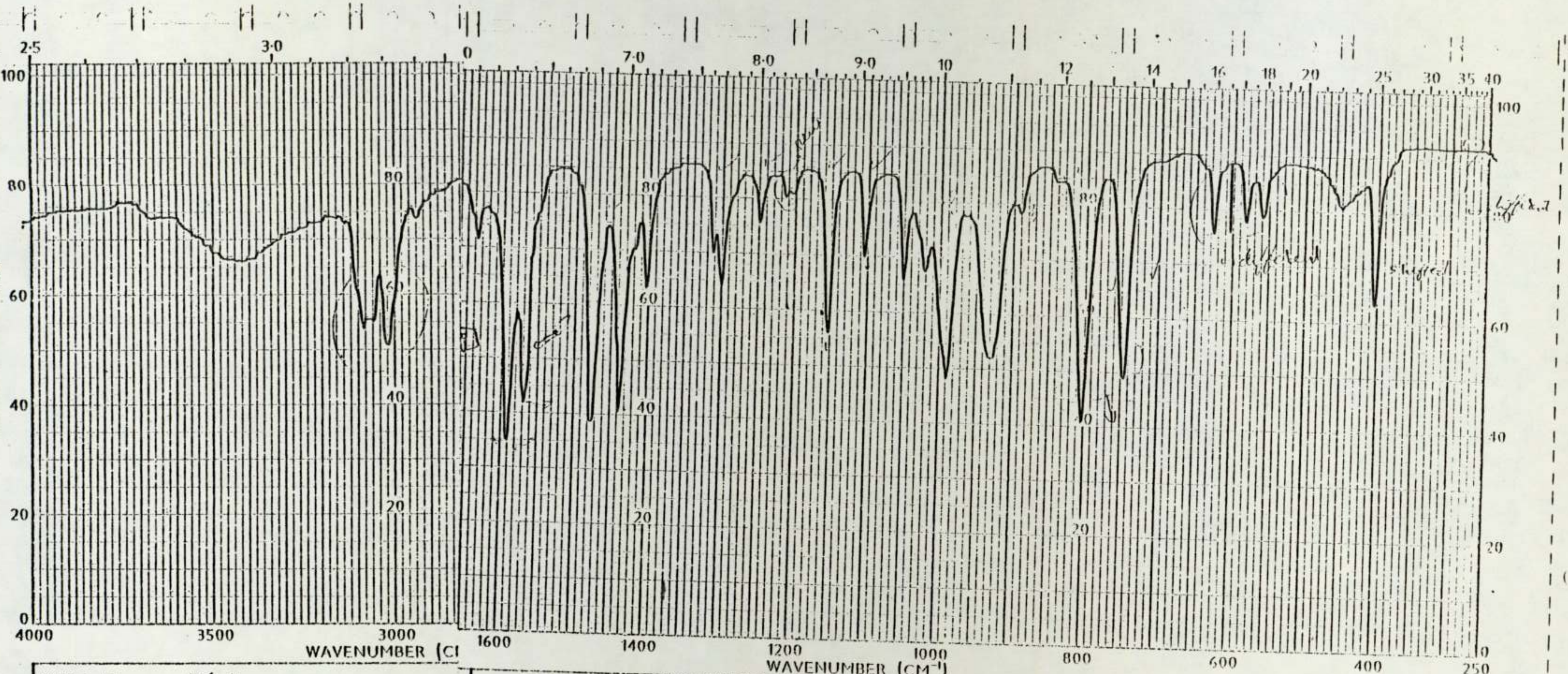
SLIT standard [illegible]

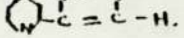
No 457-5001

OPERATOR [illegible]

DATE [illegible]

REF. No [illegible]



SAMPLE F. 

ORIGIN F.H. Muna

REMARKS Infra-red spectra of 2-vinyl pyridine Fig. (4)

SCAN SPEED Medium

SLIT Standard

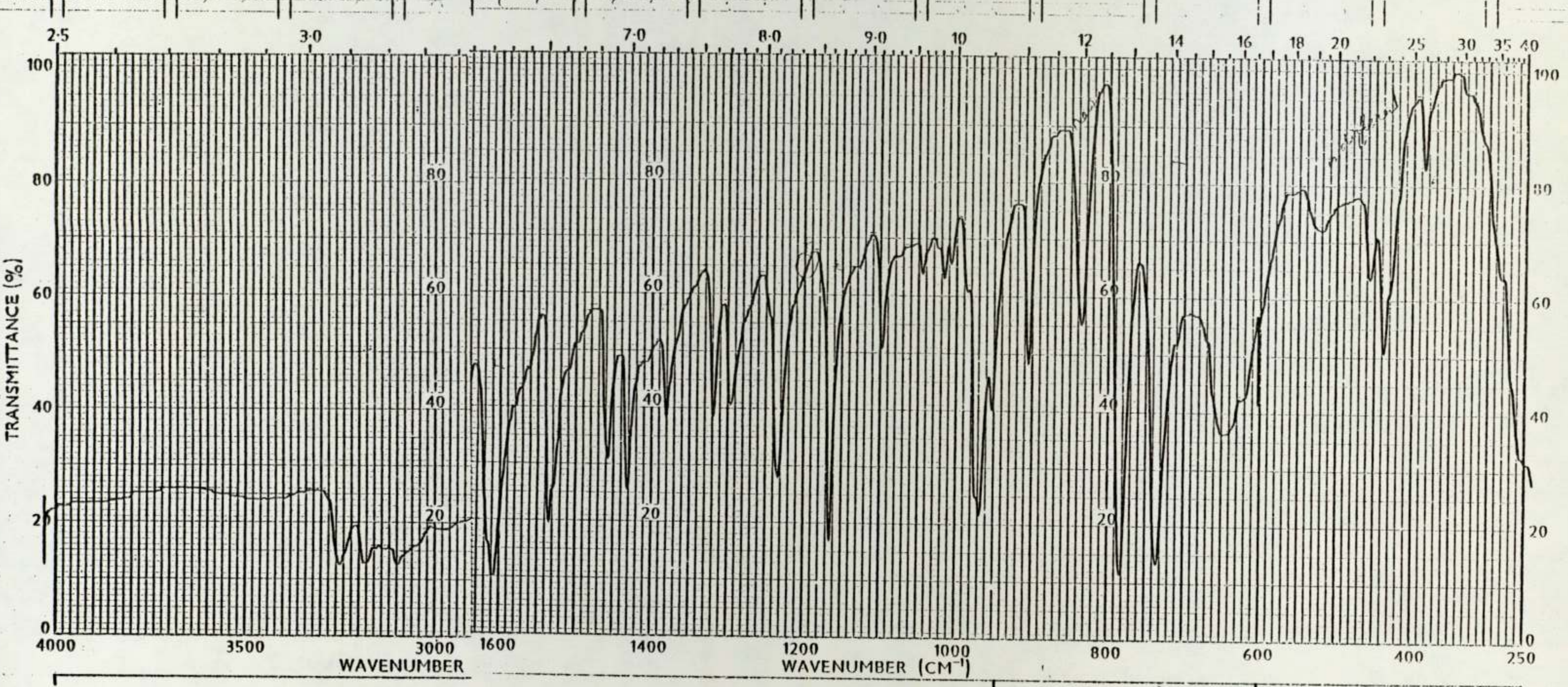
RPK/219/1002 457-5001
Intel:

OPERATOR V.H. [illegible]

DATE 15th December 1975.

REF. No. 7120.

10/74

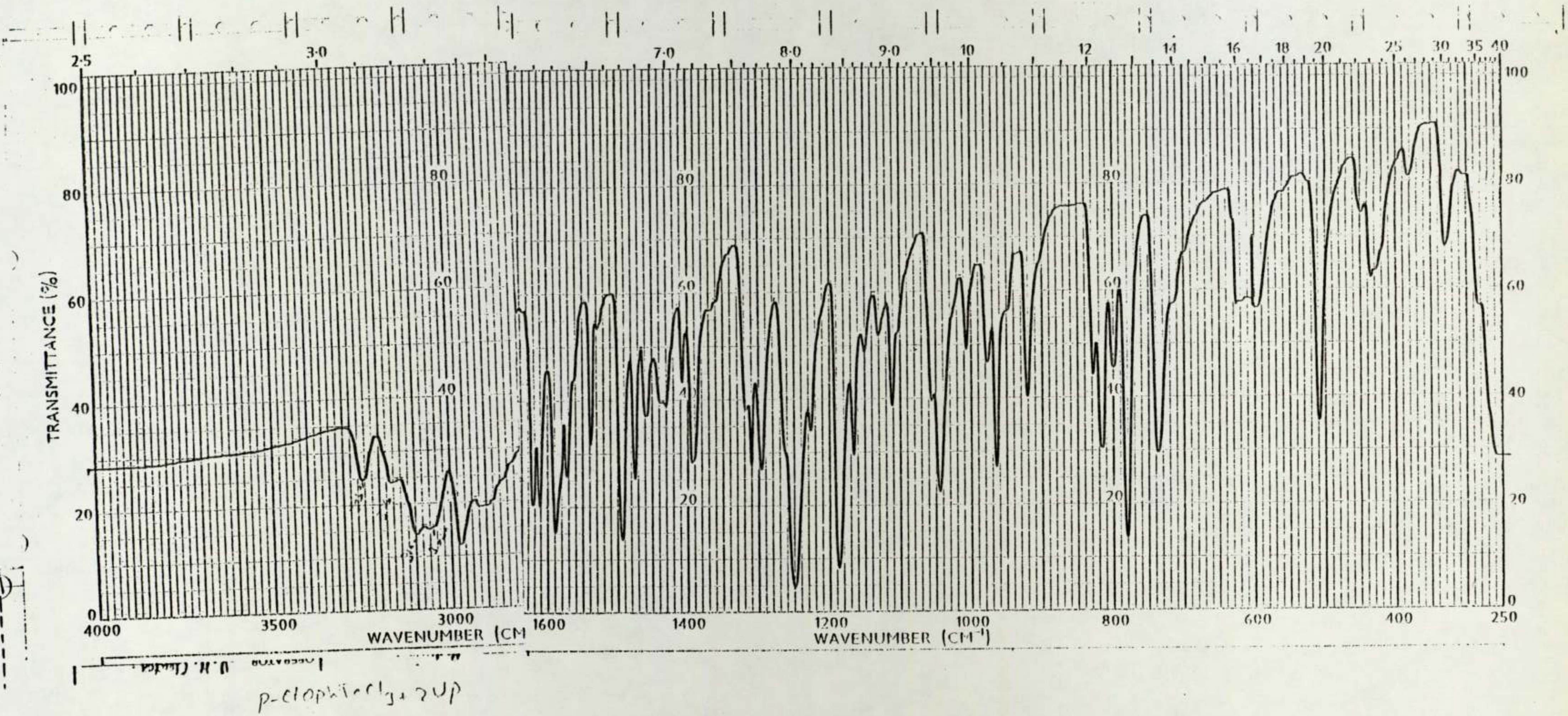


p-2vinylPyridine + TeC

p2-vinylPyrid + TeCl4

Infra-red spectrs of $(Cl_4Te{-}O{-}TeCl_4)^{-}\ (C_7H_7NH)^{+}$

Fig. (5)



Infra-red spectra of $(p\text{-EtOphTeCl}_4)^-$ $(2VPH)^+$

Fig. (6)

REMARKS

Infra-red spectra of 2-bromopyridine

Fig. (7)

SCAN SPEED [illegible]

SLIT standard

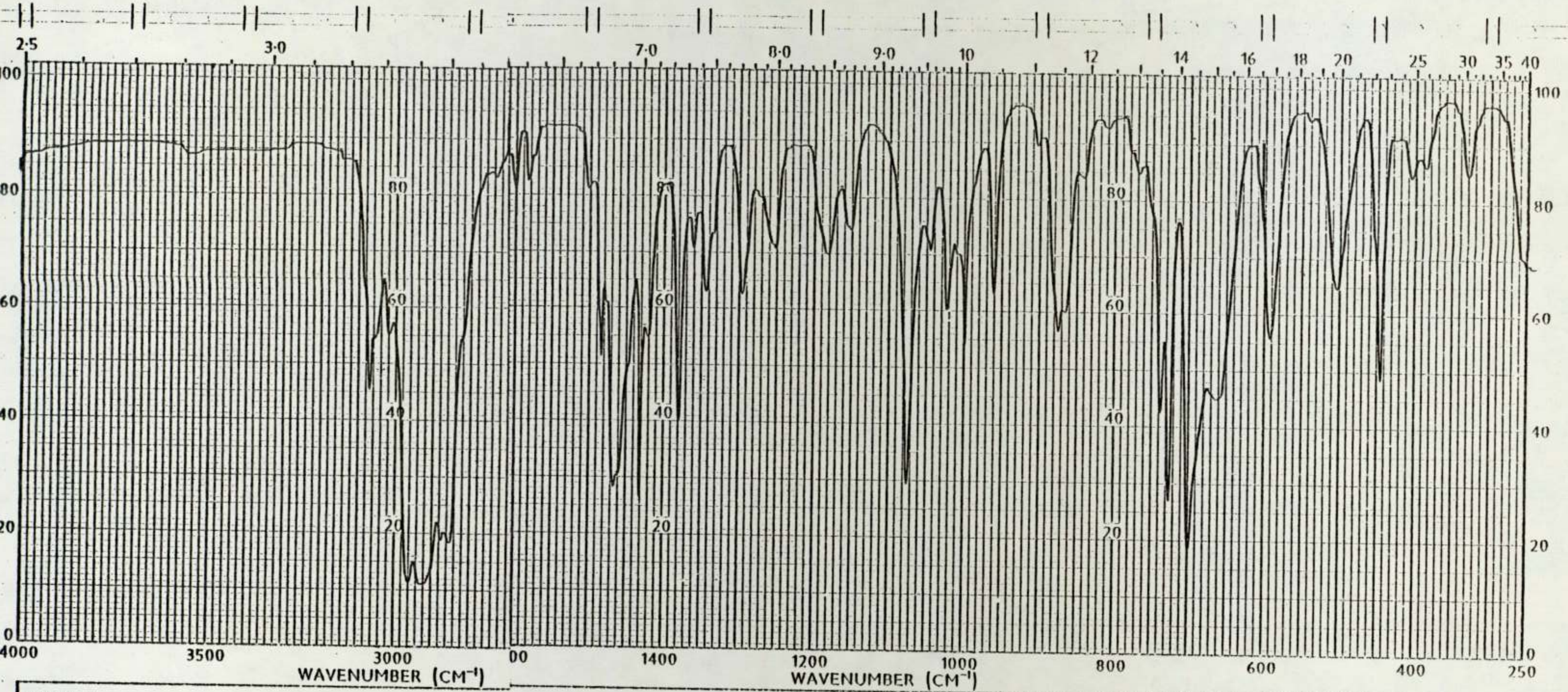
RPK/219/1002 457-5001

Intek

OPERATOR [illegible]

DATE [illegible]

REF. No. RH



SAMPLE b.p 140 ② Bu₃Snph

ORIGIN E.H.Musa.

MARKS Infra-red spectra of Bu_3PhSn

Fig. (8)

SCAN SPEED Medium.

SLIT Standard.

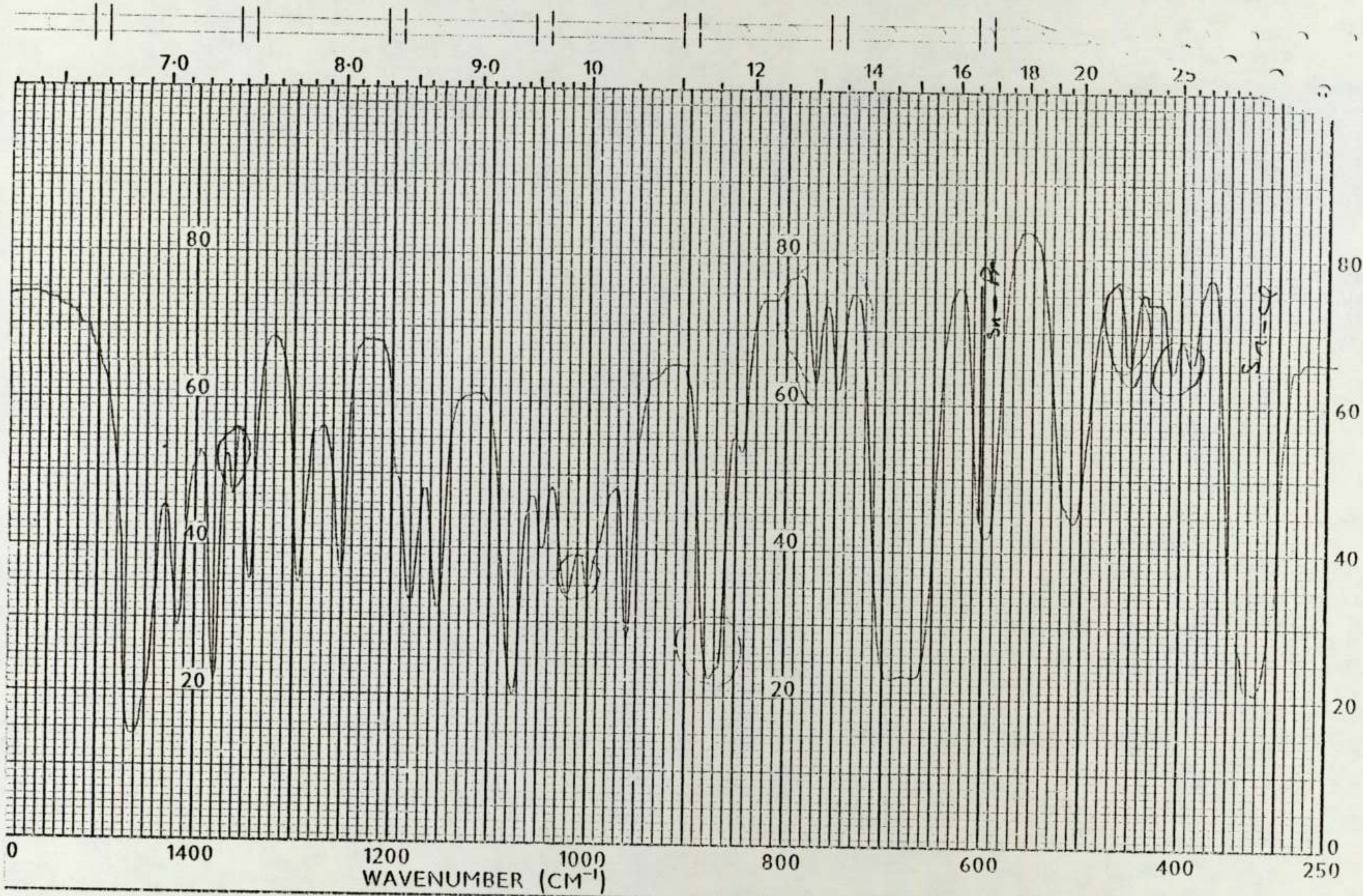
RPK/219/1002 457-5001

Intek

OPERATOR V.H. Chuten.

DATE 9th. March 1976

REF. No 8039.



IARKS

Infra-red spectra of Pr_3SnCl

Fig. (9)

SCAN SPEED Medium.

SLIT Standard

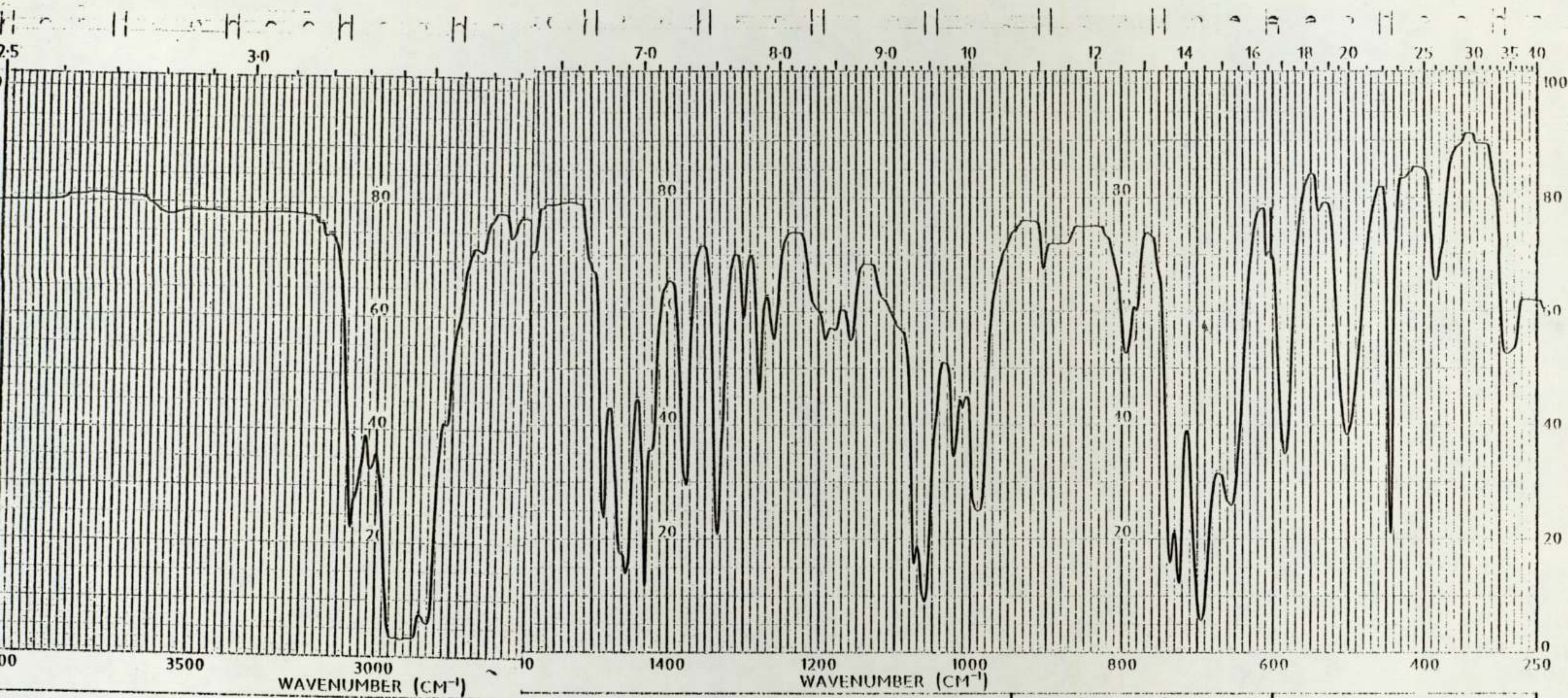
RPK/219/1002 457-5001

Intek

OPERATOR V.H. Chaton.

DATE 5th. February 1976

REF. No 7857



SAMPLE Pr_3 SnPh (F)

ORIGIN F.H. Musa.

REMARKS Infra-red spectra of Pr_3PhSn

Fig. (10)

SCAN SPEED Medium.

SLIT Standard.

RPK/219/1002 457-5001
Intek

OPERATOR [illegible]

DATE 10th February [illegible]

REF. No. 2121.

REMARKS

Infra-red spectra of $(C_4H_3S)HgCl$

Fig. (11)

SCAN SPEED Medium.

SLIT Standard.

RPK/219/1002 457-5001

Intek

OPERATOR V. H. Clenton.

DATE 7th October 1976

REF. No. 9018.

MARKS

Infra-red spectra Bu_3PySn

Fig. (12)

SCAN SPEED [illegible]

SLIT standard

RPK/219/1002 457-5001

Intek

OPERATOR [illegible]

DATE [illegible]

REF. No. [illegible]

REMARKS

Infra-red spectra of 2,2'bipyridine

Fig. (13)

SCAN SPEED

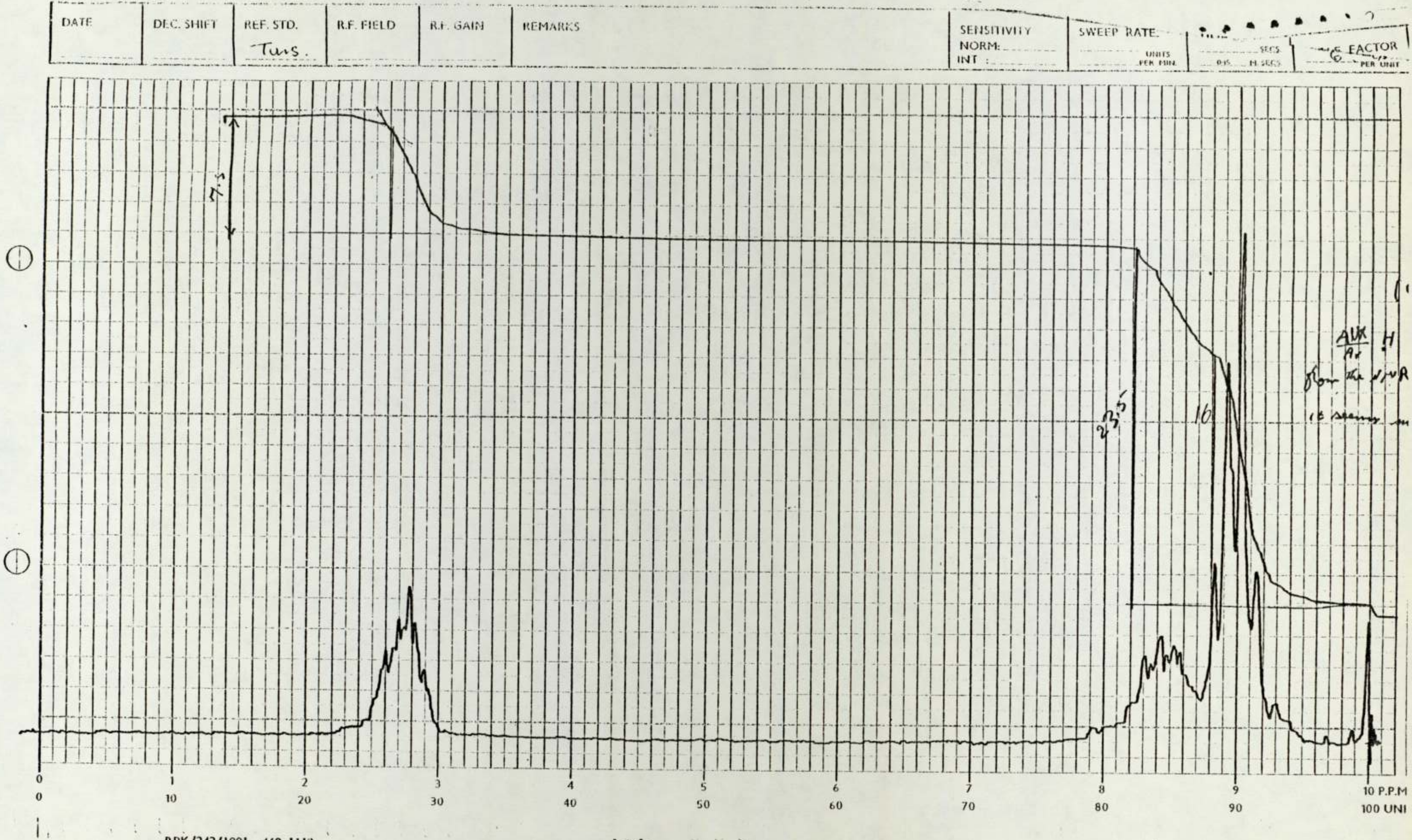
SLIT

No 457-5001

OPERATOR

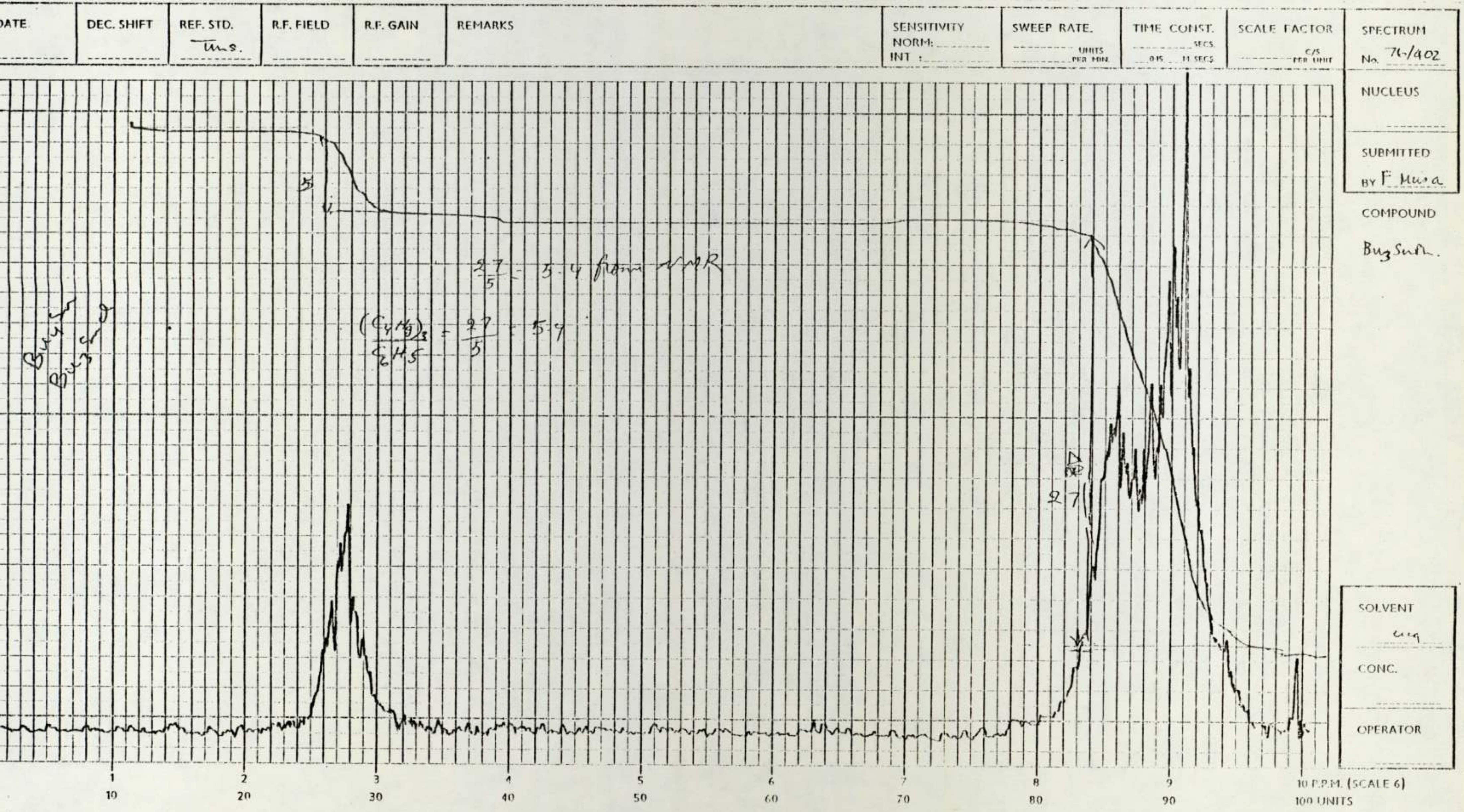
DATE

REF. No



'H n.m.r. spectra of Pr_3PhSn

Fig. (14)



RPK/242/1001 468-1112 Intek 9/72

'H n.m.r. spectra of Bu_3PhSn Fig. (15)

'H.n.m.r. spectra of Bu_3PySn Fig. (16)

Infra-red spectra of Bu_3SnCl

Fig. (17)

CONCLUSIONS

1. A series of new compounds in which azobenzene is metallated with tellurium (IV) or tellurium (II) have been prepared from the reaction of (phenylazophenyl-2C,N') mercury (II) chloride with tellurium (IV) tetrachloride or with p-ethoxyphenyl tellurium trichloride. Physical data, including infra-red spectra, are discussed. It is concluded that the new tellurium (IV) derivatives are five co-ordinate monomers.

2. Di(o-aminophenyl)ditelluride and two complexes with copper (I) and copper (II) chlorides have been made.

3. The crystal and molecular structure of (phenylazophenyl-2C,N') tellurenyl chloride has been determined in S.F.U. from three dimensional x-ray diffractometer data, and it has been found that there are two similar discrete molecules in the asymmetric unit. The co-ordination of the Te-atoms can be considered to be distorted-bipyramidal if the two Te lone pairs are considered. The phenylazophenyl ligand is bidentate, co-ordinating via an ortho carbon atom and a nitrogen atom.

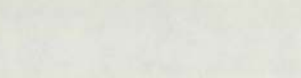
4. The synthesis of the first diorganotellurium diisothiocyanates was reported. Spectroscopic evidence indicates that the tellurium interacts more strongly with the nitrogen than with the sulphur atom of the NCS group.

5. The chemistry of $MePh_2Te(NCS)$ was studied, and found to be ionic in the solid state and, in solution ($CHCl_3$) it exists in a covalent form, $MePh_2Te(NCS)$, from which reductive elimination of exclusively methylthiocyanate occurs. The mechanism of the decomposition was not simple. Initially it is probable that a free radical pathway dominates, but after approximately 100 min.

the rate of decomposition increases. There was evidence that the second rate process was catalysed by diphenyltelluride. Other salts, $(MePh_2Te)X$, ($X = BF_4$, PF_6) were reported for comparison.

6. The ultraviolet absorption spectra of a Ph_2TeX_2 (X = Cl, Br, I) have been investigated. It is concluded that charge transfer electron influences the resonance.

7. Removal of the phenyl group was achieved by reacting tributylphenyl tin, tripropylphenyltin, with tellurium tetrachloride or with p-ethoxyphenyltellurium trichloride. An attempt to remove the pyridyl group was carried out by reacting tributyl (2-pyridyl)tin with tellurium tetrachloride.

8. The reaction of tellurium tetrachloride or p-ethoxyphenyltellurium trichloride with 2-vinylpyridine gave $(C_7H_7NH)_2^+$  $(Cl_4Te{-}O{-}TeCl_4)$, $(C_7H_7NH)(p\text{-}EtOphTeCl_4)^-$.

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Preliminary communication

DIORGANOTELLURIUM DIISOCYANATES

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Summary

Diaryltellurium diisothiocyanates are reported. The solid state structures and solution properties vary within the series $R_2Te(NCS)_2$ (R = Ph, p-$MeOC_6H_4$, p-$EtOC_6H_4$).

The recently reported synthesis of a range of triphenyltellurium pseudohalides [1], together with crystallographic data [2] and the crystal and molecular structures of $(Ph_3Te)(NCO)\cdot\frac{1}{2}CHCl_3$ [3] and $(Ph_3Te)(NCS)$ [4], prompts us to report some results for the new compounds $R_2Te(NCS)_2$ where R = Ph, p-$CH_3OC_6H_4$ and p-$C_2H_5OC_6H_4$.

Three new compounds which, to our knowledge, are the first examples of diorganotellurium dipseudohalides are conveniently prepared from the reaction of thiocyanogen [5] with the appropriate telluride. Alternatively, the compounds may be prepared by the reaction of ammonium thiocyanate and the diorganotellurium dichloride in methanolic solution. Some physical data are reported in Table 1.

The diphenyl and di-p-methoxytelluride products are pale yellow whereas that obtained using di-p-ethoxytelluride is white. Furthermore substantial differences are noted in the solid state IR spectra. Thus, for R = Ph and p-$CH_3OC_6H_4$, ν(CN) is a doublet with both components above 2000 cm^{-1}, which may imply a nonlinear SCN—Te—NCS system with relatively weak tellurium—nitrogen bonds; or which may arise from factor group splitting. By contrast, for $(p$-$C_2H_5OC_6H_4)_2$-$Te(NCS)]^+$ $(NCS)^-$. However the possibility of weak association between 2053 cm^{-1}) and the other is extremely broad ($\Gamma_{1/2}$ 100 cm^{-1}) and centred on 1980 cm^{-1}. The width and position of the latter band suggest a covalently bound isothiocyanato group [6] and a solid state structure $[(p$-$C_2H_5OC_6H_4)_2$-$Te(NCS)]^+(NCS)^-$. However the possibility of weak association between the ionic units in the crystal cannot be eliminated, a point emphasised by the oligomeric structure of $[Ph_3Te](NCS)$ [4].

TABLE 1

Compound	Colour	M.p. (°C)	Infrared data ν(CN) (cm^{-1})	Λ_m (10^{-3} M/MeNO$_2$)
$Ph_2Te(NCS)_2$	pale yellow	140	2060 s (sharp), 2050 s (sharp)	Insoluble
$(p\text{-}CH_3OC_6H_4)_2Te(NCS)_2$	pale yellow	110	2060 s (sh), 2040 s	61
$(p\text{-}C_2H_5OC_6H_4)_2Te(NCS)_2$	white	100	2040 s (sharp), 1980 s (v.br)	106

The structures of the phenyl and *p*-methoxyphenyl derivatives are believed to be similar, and most probably based on a very distorted six coordinate arrangement around tellurium. Thus we envisage diorganotellurium diisothiocyanato units (which, if the s^2 electrons are stereochemically active, may be considered trigonal bipyramids with axial isothiocyanato groups) linked to other units by long Te—S bonds. This tellurium—sulphur association probably accounts for the pale yellow colour of the solids.

The solution behaviour of these materials is also of interest. $Ph_2Te(NCS)_2$ is insoluble in solvents suitable for conductivity measurements, but both the *p*-methoxy and *p*-ethoxyphenyl derivatives dissolve in nitromethane to give colourless, conducting solutions (Table 1). Investigation of the conductivity over a range of concentration for both compounds gives non linear plots of Λ against (concentration)$^{1/2}$, hence we are probably dealing with the following equilibria:

$$R_2Te(NCS)_2 \rightleftharpoons R_2Te(NCS)^+ + NCS^-$$

$$R_2Te(NCS)^+ \rightleftharpoons R_2Te^{2+} + NCS^-$$

We believe that the interesting variation of solid state and solution properties is determined more by the effect of the increasing size of the *p*-substituent in the phenyl ring on the balance between the energies of various possible lattices and solvation energies, than it is by the electronic influence of the substituent.

The compounds gave satisfactory analyses and the full details of their synthesis together with more detailed and extensive physical properties will be given in due course.

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