SYNTHESIS AND PHYSICAL INVESTIGATION

OF

TELLURIUM DITHIOCARBAMATES

by

Mohammed Amin Karim Ahmed

A thesis submitted for the degree of

Doctor of Philosophy

at

The University of Aston in Birmingham

January 1985

DECLARATION

The work described herein was carried out at the University of Aston in Birmingham between October 1982 and December 1984. It has been done independently and submitted for no other degree.

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Mohammed Amin Karim Ahmed

January 1985

SUMMARY

The University of Aston in Birmingham

Synthesis and Physical Investigation of Tellurium Dithiocarbamates

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A range of tellurium dithiocarbamates [$Te(S_2CNR_2)_2$ and $Te(S_2CNR_2)_4$] were synthesised and used to study their ligand exchange reactions. The photo-reaction of solutions of these compounds with dioxygen was investigated. The tetrakis(dialkyldithiocarbamato)tellurium(IV) [$Te(dtc)_4$] was found to be a good stabilizer for polypropylene (PP) during photo-oxidation. In addition, [$Te(dtc)_4$] were superior stabilizers during thermal-oxidation in comparison to the metal dithiocarbamates such as zinc and nickel dithiocarbamates. It was also found that by changing the alkyl group of the dialkyldithiocarbamate, it is possible to obtain still better stabilizing activity.

The preparation of (2-phenylazophenyl-C,N')tellurium(IV) trichloride ($AzoTeCl_3$) is reinvestigated. Its crystal and molecular structure was determined. The structure of the compound is monomeric. The direct reaction of azobenzene and tellurium tetrachlorides gives $AzoTeCl_3$, the ^{13}C NMR of which is discussed. Finally its reaction with hydrazine hydrate is reinvestigated and it was found that an excess of hydrazine gives the new ditelluride; bis(2-phenylazophenyl-C,N')ditelluride.

Some new organotellurium dithiocarbamates [ArTe(dtc) and $ArTe(dtc)_3$, where Ar=2-phenylazophenyl- group and dtc=R_2NCS_2] were prepared. The crystal and molecular structure of dimethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II) was determined. The structure consists of monomeric molecules. Their I.R. and mass spectra have been studied. Also, $ArTe(dtc)_3$ was used as a stabilizer for PP. These compounds appear to be good stabilizers during photo-oxidation but they show very low efficiency during thermal-oxidation.

The crystal and molecular structure of acetato(2-phenylazophenyl-C,N')-tellurium(II) and (2-phenylazophenyl-C,N')thiocyanatotellurium(II) were determined. The structure of the former consists of discrete molecules in which weak intramolecular Te....O interactions occur. However, the structure of the latter compound shows a very weak intermolecular Te....N interaction; which links the molecules in the form of dimers. Their preparation and I.R. spectra are discussed.

KEY WORDS

TELLURIUM DITHIOCARBAMATES
POLYPROPYLENE
AZOBENZENE

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LIST OF ABBREVIATIONS

Te(dtc)$_4$	Tetrakis(dialkyldithiocarbamato)tellurium(IV)
Te(dbdtc)$_4$	Tetrakis(dibenzyldithiocarbamato)tellurium(IV)
Te(dedtc)$_4$	Tetrakis(diethyldithiocarbamato)tellurium(IV)
Te(didtc)$_4$	Tetrakis(diisobutyldithiocarbamato)tellurium(IV)
Te(dmdtc)$_4$	Tetrakis(dimethyldithiocarbamato)tellurium(IV)
Te(dtc)$_2$	Bis(dialkyldithiocarbamato)tellurium(II)
Te(dbdtc)$_2$	Bis(dibenzyldithiocarbamato)tellurium(II)
Te(dedtc)$_2$	Bis(diethyldithiocarbamato)tellurium(II)
Te(dmdtc)$_2$	Bis(dimethyldithiocarbamato)tellurium(II)
Te(dpidtc)$_2$	Bis(dipiperidyldithiocarbamato)tellurium(II)
Nadtc	Sodium dialkyldithiocarbamate
Ni(dedtc)$_2$	Bis(diethyldithiocarbamato)nickel(II)
Zn(dedtc)$_2$	Bis(diethyldithiocarbamato)zinc(II)
TRTD	Tetraalkylthiuram disulphide
TETD	Tetraethylthiuram disulphide
PP	Polypropylene
T.L.C.	Thin Layer Chromatography
AzoTeCl$_3$	(2-Phenylazophenyl-C,N')tellurium(IV) trichloride
AzoTe(dtc)$_3$	(2-Phenylazophenyl-C,N')tris(dialkyldithiocarbamato)tellurium(IV)
AzoTe(dedtc)$_3$	(2-Phenylazophenyl-C,N')tris(diethyldithiocarbamato)tellurium(IV)
AzoTe(dbdtc)$_3$	(2-Phenylazophenyl-C,N')tris(dibenzyldithiocarbamato)tellurium(IV)
AzoTe(dmdtc)$_3$	(2-Phenylazophenyl-C,N')tris(dimethyldithiocarbamato)tellurium(IV)

AzoTe(dtc)	Dialkyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II)
AzoTe(dbdtc)	Dibenzyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II)
AzoTe(dmdtc)	Diethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II)
AzoTe(dedtc)	Diethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II)
I.R.	Infra-red
U.V.	Ultra violet
N.M.R.	Nuclear Magnetic Resonance

CHAPTER ONE

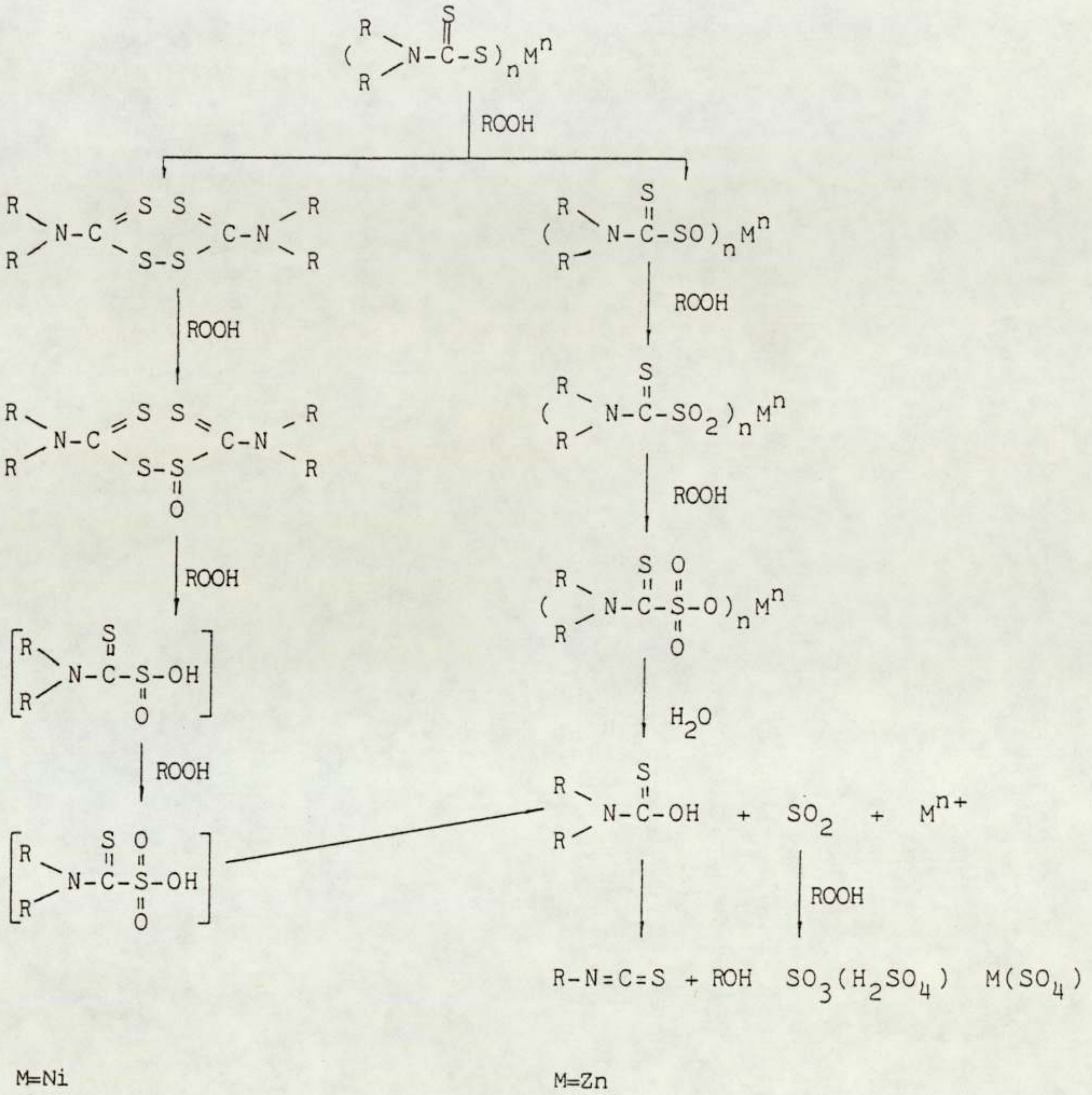
GENERAL INTRODUCTION

1.0 General Introduction

It is well known that metal dithiocarbamates, such as bis-(diethyldithiocarbamato)nickel(II) [$Ni(dedtc)_2$] and bis-(diethyldithiocarbamato)zinc(II) [$Zn(dedtc)_2$], act as both good thermal and U.V. stabilizers in polymer technology(1-6,7a). The main role of the metal dithiocarbamates acting as anti-oxidants for polymers is in the decomposition of peroxides(8,9).

It has been found(10,11,7b) that the metal dithiocarbamates are not themselves the actual catalysts for peroxide decomposition, but acidic species formed from their interaction with peroxides are the main antioxidant species. The acidic species is probably the SO_3 formed in later stages of the oxidation of metal dithiocarbamates(2,4,5).

In 1983 Marogi(7c) pointed out that different metal dithiocarbamates decompose peroxides in different ways. He has shown that metal dithiocarbamates can react with peroxides either through initial conversion to the corresponding disulphides and then to the sulphur acids, or via their further oxidation products. Also, Marogi claimed that he identified the disulphide in the case of $Ni(dedtc)_2$, but in the case of $Zn(dedtc)_2$, the oxygenated oxidation products. In the light of this evidence, the following mechanism has been proposed for the antioxidant action of metal dithiocarbamates (Scheme (1)).

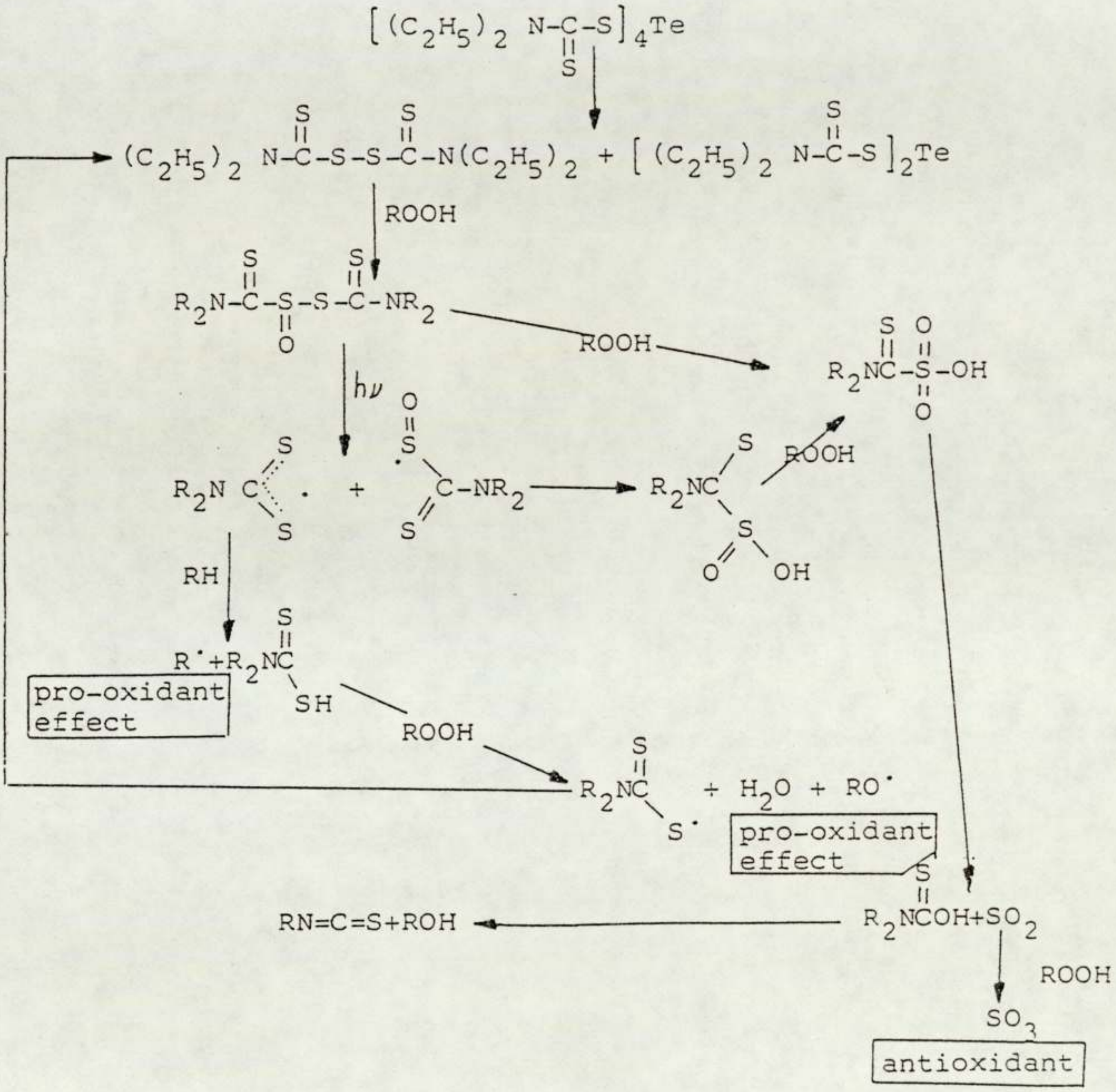


Scheme (1)

Tellurium dithiocarbamates, which are now playing important roles in polymer technology, appear to give up both sulphur and tellurium during the vulcanization of rubber and tellurium is itself a vulcanizing agent and is in some respects analogous to sulphur in its properties$^{(12,13)}$.

Recently one of our group, Abed-Ali$^{(14)}$, has used tetrakis-(diethyldithiocarbamato)tellurium(IV) [Te(dedtc)$_4$] and bis(diethyldithiocarbamato)tellurium(II) [Te(dedtc)$_2$] as stabilizers (antioxidants) for polypropylene (PP) and he has shown that these compounds exhibit both enhanced thermal and U.V. stabilization$^{(14)}$.

Abed-Ali has also indicated that Te(dedtc)$_4$ showed better stabilizing action than Te(dedtc)$_2$ and he referred that to the decomposition of Te(dedtc)$_4$ into tetraethylthiuram disulphide (TETD) and Te(dedtc)$_2$ during the processing at a temperature of 180°C. Hence the TETD is itself a stabilizer for polymers$^{(6,7a)}$. Abed-Ali has concluded that tellurium dithiocarbamates exhibit better stabilizing action than Zn(dedtc)$_2$, but were comparatively less efficient than Ni(dedtc)$_2$ during photo-oxidation, and also that they show better stabilizing action than both Zn(dedtc)$_2$ and Ni(dedtc)$_2$ during thermal oxidation$^{(14)}$. He suggested a similar mechanism for Te(dedtc)$_2$ and Te(dedtc)$_4$ as the metal dithiocarbamates have in the peroxide decomposition$^{(14)}$ (Scheme (2)).


ROOH
hν
RH
pro-oxidant effect
pro-oxidant effect
antioxidant

Scheme (2)

1.1 Tellurium Dithiocarbamates

These compounds in general can be classified according to the oxidation state of tellurium into two main groups: tellurium(IV) dithiocarbamates and tellurium(II) dithiocarbamates. Tellurium(IV) dithiocarbamates can be sub-divided into the following categories: TeL_4(12), $ArTeL_3$(15), $XTeL_3$(16) and X_2TeL_2(16) where L is dithiocarbamato group ($R_2N-\overset{S}{\overset{\|}{C}}-S^-$ or $R_2N-C\ll^{S}_{S}-$ =dtc), Ar is the phenyl (C_6H_5-), p-ethoxyphenyl ($C_2H_5OC_6H_4-$) or p-methoxyphenyl ($CH_3OC_6H_5-$) group and $X=Cl^-$, Br^-, I^-, NCS^- or O^{2-}. Hence a brief review of the chemistry of tellurium dithiocarbamates is now given.

1.1.1 $Te^{IV}L_4$

The first tellurium dithiocarbamate, tetrakis(diethyldithiocarbamato)tellurium(IV) [Te(dedtc)$_4$], was prepared by Murrill(12) in 1930 representing a new class of tetrakis (dialkyldithiocarbamato)tellurium(IV) [$Te(S_2CNR_2)_4$] . Murrill(12) has published a patent for its preparation and use in rubber vulcanization, since his methods were found to be both convenient and economic. The preparation(12) of this and analogous compounds [$Te(S_2CNR_2)_4$] where R=aliphatic group, involves mixing aqueous solutions of sodium diethyldithiocarbamate with sodium tellurite and thereafter adding an acid. The reaction obeys the following general equation:

$$4Et_2NCS_2Na + Na_2TeO_3 + 6HCl \longrightarrow Te(S_2CNEt_2)_4 + 6NaCl + 3H_2O$$

It has been reported that(17) Te(dedtc)$_4$ can be prepared by adding a 10% aqueous solution of sodium diethyldithiocarbamate to a 0.1M solution of potassium tellurite (pH 8.4 phosphate-borate buffer).

The I.R., U.V. and NMR spectra of Te(dedtc)$_4$ have been discussed by Nikolav et al(17) who claimed that two of the (dedtc) ligands are unidentate and the other two are bidentate. Thus, according to this study, tellurium in Te(dedtc)$_4$ is in a distorted octahedral environment. Husebye et al(18) reported the crystal and molecular structure of Te(dedtc)$_4$ and he found that all four (dedtc) ligands were bidentate. The central tellurium atom is bonded to all eight sulphur atoms in the molecule in a slightly distorted dodecahedral configuration (Figure 1.1).

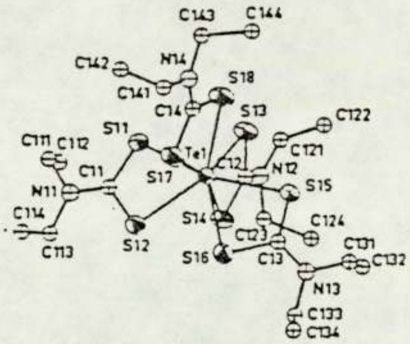
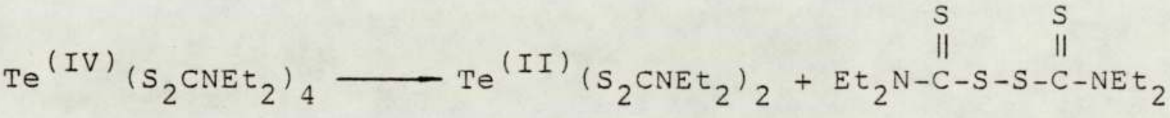


Figure 1.1

Foss(19) has shown that on heating tellurium(IV) dialkyl dithiocarbamates [$Te(dtc)_4$] in solution, an equi-molecular mixture of $Te(dtc)_2$ and the corresponding disulphide is produced:



$$Te^{(IV)}(S_2CNEt_2)_4 \longrightarrow Te^{(II)}(S_2CNEt_2)_2 + Et_2N\text{-}\overset{\overset{S}{\|}}{C}\text{-}S\text{-}S\text{-}\overset{\overset{S}{\|}}{C}\text{-}NEt_2$$

(TETD)

1.1.2 $ArTeL_3$

Compounds of the type [$ArTe(S_2CNR_2)_3$] (Ar=Aryl group such as phenyl, p-ethoxyphenyl, p-methoxyphenyl) were first prepared by Foss(15) either by reacting the corresponding diarlyditelluride with tetraalkylthiuram disulphide in solution and heating:

$$(ArTe)_2 + 3(R_2NCS_2)_2 \longrightarrow 2ArTe(S_2CNR_2)_3$$

or by reacting aryltellurium trichloride with sodium dialkyldithiocarbamate in dioxane solution:

$$ArTeCl_3 + 3R_2NCS_2Na \longrightarrow ArTe(S_2CNR_2)_3 + 3NaCl$$

Upon heating aryltris(diethyldithiocarbamato)tellurium(IV) in solution, the original greenish yellow colour of the solution changes reversibly to red. This is probably due to a reversible dissociation into the red ditelluride and the disulphide(15).

Husebye et al(20) have studied the crystal and molecular structure of phenyltris(diethyldithiocarbamato)tellurium(IV) and found that the central tellurium atom is bonded to all six sulphur atoms in the molecule and to one carbon atom in the phenyl group in a distorted pentagonal bipyramidal configuration (Figure 1.2). The crystals are built up of monomeric phenyltris(diethyldithiocarbamato)tellurium(IV) species (Figure 1.3).

1.1.3 $XTeL_3$

There is now an extensive literature dealing with compounds of the type $XTeL_3$, where L is the dithiocarbamato(dtc) ligand and X is Cl^-, Br^-, I^-, O^{2-} and NCS^- as is shown below.

Aravamudan et al(21,22) have reported the synthesis of a wide range of this type of compound ($XTeL_3$), where L is (2-hydroxyethyl)methyldithiocarbamato $[\,{}^{CH_3}_{HOCH_2CH_2}{>}NCSS^-]$ and di(2-hydroxyethyl)dithiocarbamato $[(HOCH_2CH_2)_2NCSS^-]$ and $X=O^{2-}$, NCS^-, Cl^-, Br^- and I^-. These compounds were synthesised by adding methanolic solutions of the ligands to the acidic solutions of tellurium dioxide or sodium tellurite(21,22).

It has been reported that chlorotris(diethyldithiocarbamato)-tellurium(IV) can be prepared by reacting sodium diethyldithiocarbamate with tellurium(IV) tetrachloride in a 2:1 molar ratio in dioxane(16).

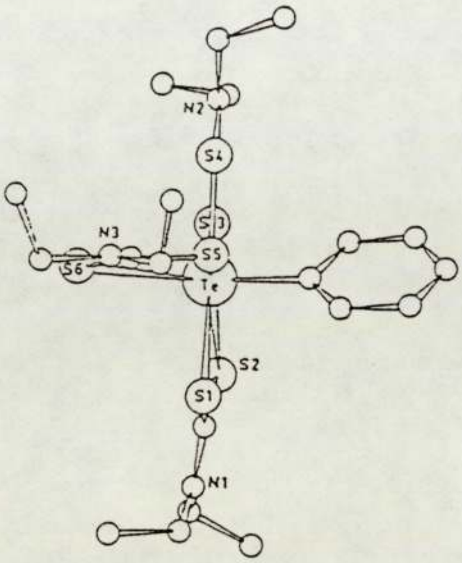


Figure 1.2 Structure of $C_6H_5Te(S_2CNEt_2)_3$

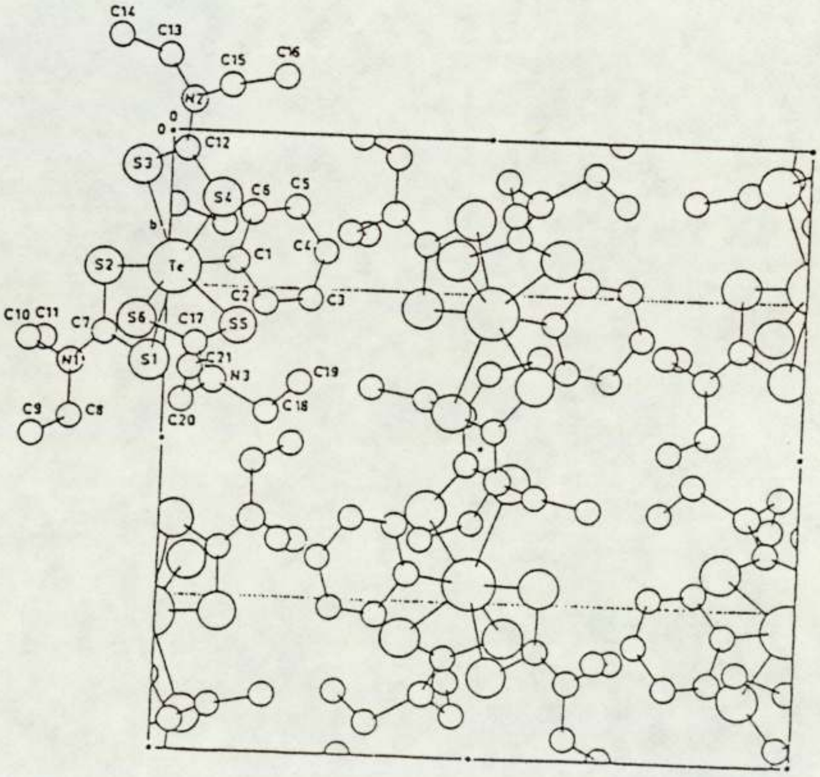


Figure 1.3 The arrangement of molecules in the unit cell of $C_6H_5Te(S_2CNEt_2)_3$

The molecular structures of the title compounds, $XTeL_3$, where L = dialkyldithiocarbamato ligand and X = Cl^-, Br^-, I^- and NCS^-, show that tellurium is bonded to the six sulphur atoms in the molecule and to X. The resulting structure is distorted pentagonal bipyramidal with X in an axial position (see Figure 1.4)$^{(16,22-25)}$. The lone pair of electrons in the valency shell of the tellurium atom is thought to be largely inert in the sense that it does not occupy a position in the co-ordination polyhedron$^{(22,23,25)}$.

Aravamudan et al$^{(21,22)}$ have observed that infra-red (I.R.) data of the title compounds ($XTeL_3$) showed the characteristic C-N stretching frequency of the dithiocarbamate moiety in the majority of complexes to be in the range 1470-1500 cm^{-1} and in the compound $(NCS)TeL_3$, the thiocyanate band occurs at 2080 cm^{-1}. The electronic spectra of these compounds showed bands at ∿40 KK, 35 KK, 30 KK and 23 KK. The first three bands have been referred to interligand transitions of the dithiocarbamate moiety while the later band which occurred in the long wavelength region is attributed to the L→M charge transfer.

1.1.4 TeL_2X_2

Only a few reports are available dealing with compounds of the type TeL_2X_2, where L is the dialkyldithiocarbamato ligand (R_2NCSS^-) and X is Cl^- or I^- only$^{(16,21,22)}$. Aravamudan et al$^{(21,22)}$ have reported the synthesis of

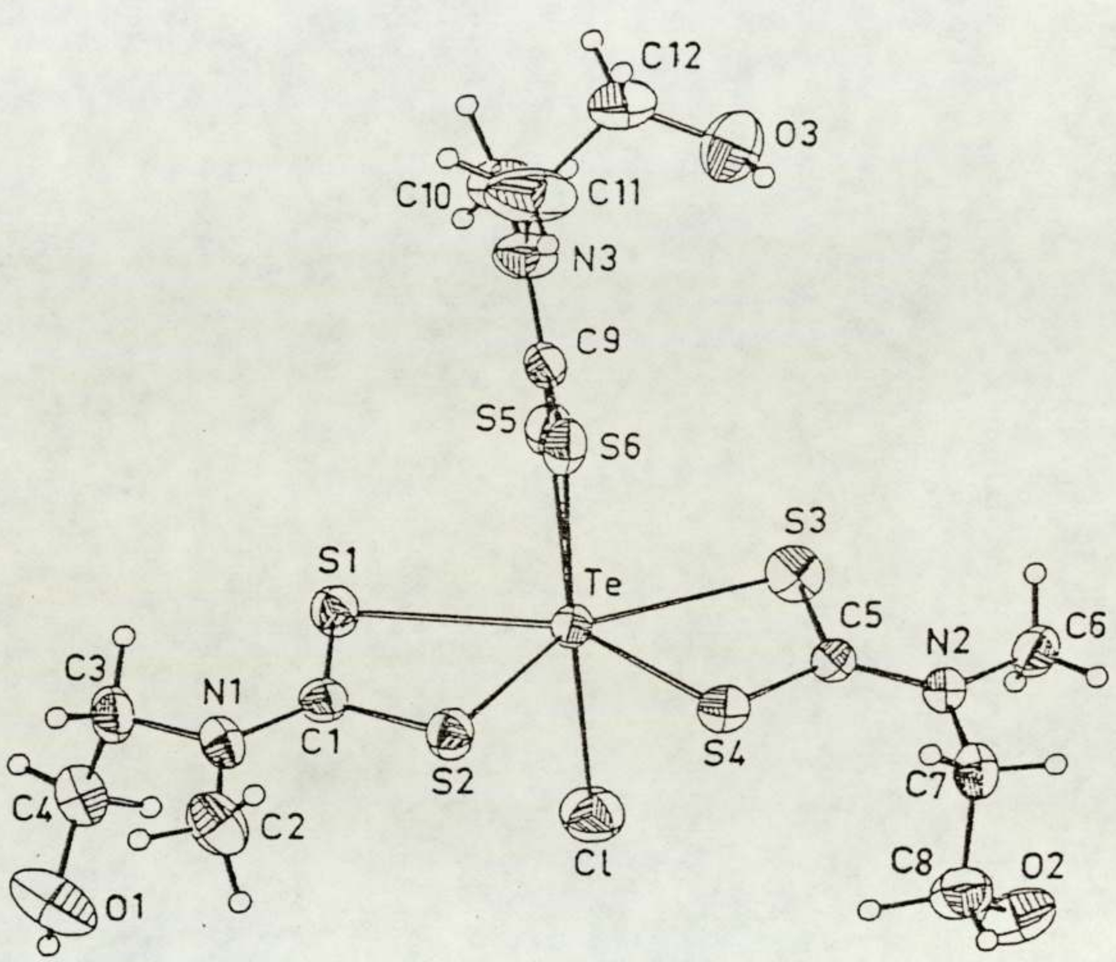


Figure 1.4 The structure of chlorotris[(2-hydroxyethyl)-methyldithiocarbamato]tellurium(IV)

compounds such as TeL_2I_2, where L = di(2-hydroxyethyl)dithiocarbamato $[(HOCH_2CH_2)_2NCSS^-]$(22) and (2-hydroxyethyl)methyldithiocarbamato $[\genfrac{}{}{0pt}{}{HOCH_2CH_2}{CH_3}{>}NCSS^-]$(21). These compounds were prepared by treating an aqueous solution of sodium tellurite, which was acidified using 1N H_2SO_4 with 20% aqueous methanol containing the appropriate dialkyldithiocarbamic acid, then adding an aqueous solution of KI(22) or by adding a methanolic solution of KI to a methanolic solution of the appropriate $ClTeL_3$(21) species.

Klar et al(16) have reported the synthesis of bis(dimethyldithiocarbamato)dichlorotellurium(IV), $Te(dmdtc)_2Cl_2$, the preparation of this compound involving the reaction of tellurium(IV) tetrachloride with sodium dimethyldithiocarbamate in a molar ratio of 1:2 in dioxane.

1.1.5 TeL_2

An extensive literature is available dealing with the title compounds (TeL_2) where L is the dialkyldithiocarbamato ligand ($R_2N\text{-}CSS^-$ or dtc). The synthesis of these compounds can be achieved by using the following methods:-

(a) In 1949, Foss(26,27) reported the synthesis of bis(diethyldithiocarbamato)tellurium(II) $[Te(dedtc)_2]$ as the first example of the title compounds (TeL_2), this being followed by another report(28) in the same year in which the synthesis of bis(dimethyldithiocarbamato)tellurium(II)

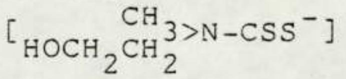
[Te(dmdtc)$_2$] and bis(piperidyldithiocarbamato)tellurium(II) [Te(dpidtc)$_2$] were described. The synthesis of these compounds is by the reaction of sodium telluropentathionate [$Na_2Te(S_2O_3)_2$] with sodium dialkyldithiocarbamate (Nadtc) in aqueous solutions and at room temperature, following the general equation:

$$Te(S_2O_3)_2^{2-} + 2R_2NCSS^- \longrightarrow Te(SSCNR_2)_2 + 2S_2O_3^{2-}$$

(b) It has also been reported that the title compounds (TeL$_2$) can be prepared by reacting tetraalkylthiuram disulphide with the divalent tellurium thiosulphonates, thiosulphates and xanthates in chloroform solutions and heating for a few minutes with a slight excess of the disulphide$^{(19)}$:

$$TeX_2 + (R_2NCSS)_2 \longrightarrow Te(S_2CNR_2)_2 + X_2$$

where X = methanthiosulphonate, aromatic thiosulphonate, thiosulphate or xanthate.

(c) Aravamudan et al$^{(21,22)}$ have reported that the title compounds (TeL$_2$), where L is di(2-hydroxyethyl)dithiocarbamato [$(HOCH_2CH_2)_2NCSS^-$] and (2-hydroxyethyl)methyldithiocarbamato [ $\overset{CH_3}{HOCH_2CH_2}{>}N{-}CSS^-$] ligand, can be prepared by adding a 20% aqueous methanol solution containing dialkyldithiocarbamic acid to tetrathioureatellurium(II) dichloride ($Te(NH_2CSNH_2)_4Cl_2$) suspended in methanol at room temperature.

(d) It has been found that bis(dialkyldithiocarbamato)tellurium(II) can be prepared by refluxing an equi-molar mixture of powdered tellurium and tetraalkylthiuram disulphide in xylene or water$^{(29)}$:

$$Te + (R_2NCSS)_2 \longrightarrow Te(SSCNR_2)_2$$

The I.R. and U.V. spectra of $Te(dtc)_2$ have been studied by two groups of investigators; Nikolov et al$^{(17)}$ and Aravamudan et al$^{(21,22)}$. The first group$^{(17)}$ has concluded from their study that the two dithiocarbamato ligands of $Te(dtc)_2$ are unidentate. The second group$^{(21,22)}$ has assigned the band at $\sim$1460 cm^{-1} to the C-N vibration of the coordinated dtc group in $Te(dtc)_2$ and they have also explained the electronic spectra of $Te(dtc)_2$ as being mainly due to intra-ligand transitions.

The crystal and molecular structure studies have so far shown that $Te(dtc)_2$ compounds have a tendency to take up a planar configuration around the central tellurium atoms. In all $Te(dtc)_2$ compounds studied so far, the four sulphur atoms in the molecule are bonded to tellurium forming an asymmetric planar complex with two short and two long bonds. Each tellurium atom is approached by a sulphur atom of a neighbouring molecule indicating a tendency towards five-coordination around tellurium$^{(30-32)}$ (Figure 1.5).

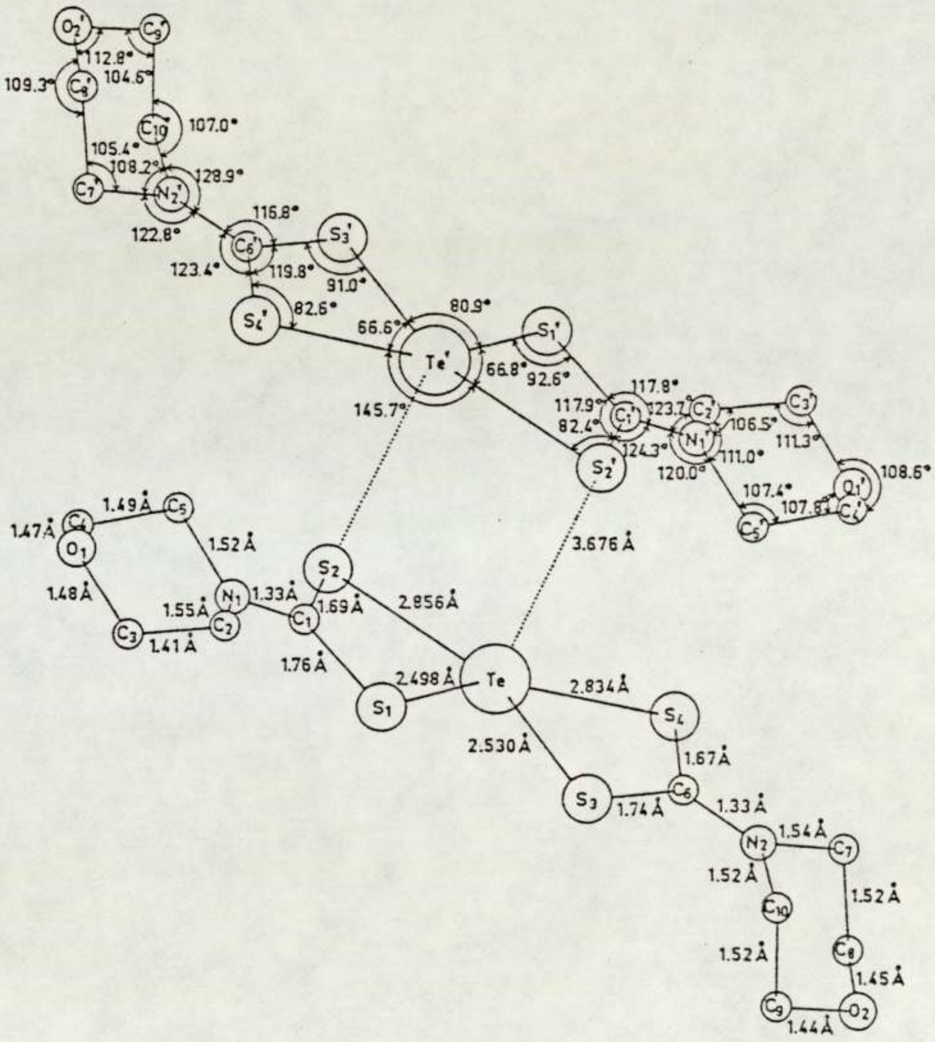


Figure 1.5 A pair of bis(morphyolyldithiocarbamato)tellurium(II) molecules

1.2 Ligand Exchange Reaction Between Tellurium Dithiocarbamates

Foss(28) has shown that tellurium dithiocarbamates readily exchange their dithiocarbamate groups in reactions with dithiocarbamate ions. In the above work it has been stated that if an excess of sodium dimethyl or piperidyldithiocarbamate, dissolved in methanol or ethanol, is added to a solution of bis(diethyldithiocarbamato)tellurium(II) in ethylacetate or chloroform, a displacement takes place and bis(dimethyldithiocarbamato)tellurium(II) or bis(piperidyldithiocarbamato)tellurium(II) separates out as is shown below:

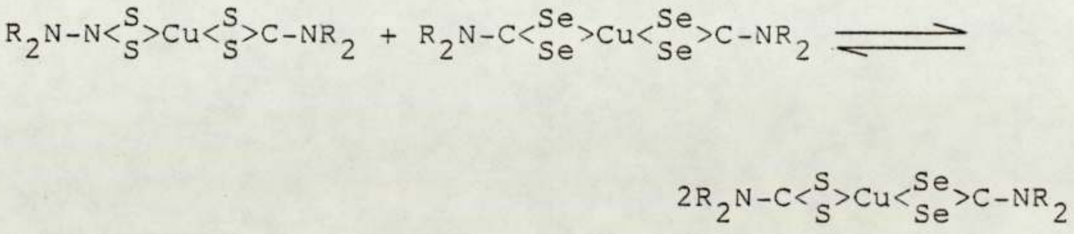
$$Te[SSCN(C_2H_5)]_2 + 2R_2NCSS^- \longrightarrow Te(SSCNR_2)_2 + 2(C_2H_5)_2NCSS^-$$

where R is methyl or piperidyl.

Foss(19) has also pointed out that tetraalkylthiuram disulphide on heating with bis(dialkyldithiocarbamato)tellurium (II) in chloroform solutions, reacts to produce the corresponding bis(dialkyldithiocarbamato)tellurium(II) according to the general equation below:

$$(R_2NCSS^*)_2 + Te(SSCNR_2)_2 \longrightarrow (R_2NCSS)_2 + Te(^*SSCNR_2)_2$$

It has been reported that bis(dialkyldithiocarbamato)copper(II) reacts with bis(dialkyldiselenocarbamato)copper(II) giving ligand exchange and forming mixed ligand complexes (33) according to the following equation:

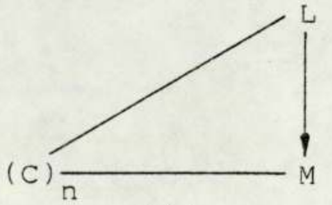


$$\mathrm{R_2N{-}N}{<}\begin{smallmatrix}\mathrm{S}\\ \mathrm{S}\end{smallmatrix}{>}\mathrm{Cu}{<}\begin{smallmatrix}\mathrm{S}\\ \mathrm{S}\end{smallmatrix}{>}\mathrm{C{-}NR_2} + \mathrm{R_2N{-}C}{<}\begin{smallmatrix}\mathrm{Se}\\ \mathrm{Se}\end{smallmatrix}{>}\mathrm{Cu}{<}\begin{smallmatrix}\mathrm{Se}\\ \mathrm{Se}\end{smallmatrix}{>}\mathrm{C{-}NR_2} \rightleftharpoons 2\mathrm{R_2N{-}C}{<}\begin{smallmatrix}\mathrm{S}\\ \mathrm{S}\end{smallmatrix}{>}\mathrm{Cu}{<}\begin{smallmatrix}\mathrm{Se}\\ \mathrm{Se}\end{smallmatrix}{>}\mathrm{C{-}NR_2}$$

It is therefore of interest to extend these studies of tellurium dithiocarbamates containing mixed ligand complexes of Te(II) and Te(IV) which might exist in dynamic equilibrium in solution.

1.3 Ortho-metallation of Azobenzene

Organometallic intramolecular co-ordination compounds, as the term indicates, are those which have at least one metal-carbon (M-C) bond and at least one donor group (L) within the molecule forming an intramolecular co-ordination bond(i) (34)

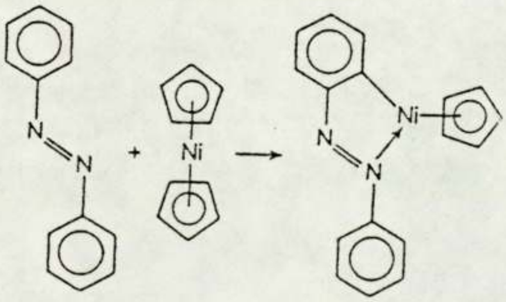


L=donor group
M=metal
n>1

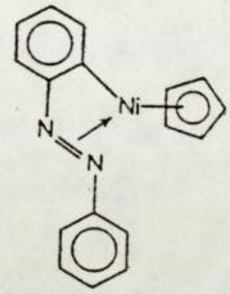
(i)

The presence of a donor group such as oxygen, nitrogen, phosphorus or sulphur in an ortho-position to the metal atom in an organic compound, has been found to be a convenient way of stabilizing organometallic compounds. In general the ortho-metallation reactions of azobenzene show a strong tendency to form five-membered rings, and the existence of ring structures has been confirmed by different physical techniques(35-37). A number of direct and indirect metallations of azobenzene have been reported and in all cases metallation occurs in the ortho-position(36,38,39). Most of the azobenzene ortho-metallation studies have involved transition metals.

Kleiman and Dubeck(40) reported first in 1963 that bis-(cyclopentadienyl)nickel reacted with azobenzene at 135°C to produce n-cyclopentadienyl-2-(2-phenylazophenyl-C.N')-nickel (Scheme (3)). The originally assumed structure (ii) was one in which the nickel atom was coordinated by the N.Nπ-electron such as in Ni(π-PhN=NPh)(CN-t-Bu)$_2$(41) and not by the nitrogen lone pair. However, the structures of the similar azobenzene complexes have been shown by X-ray diffraction studies to have co-ordination of the nitrogen lone pair(36,42,43).

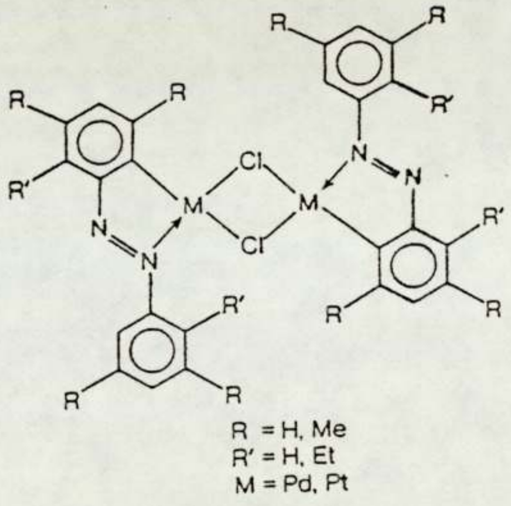


Scheme (3)



(ii)

Cope and Siekman$^{(44)}$ reported first in 1965 that the reaction of aromatic azo-compounds, azobenzene and its derivatives, with potassium tetrachloroplatinate(II) or palladium(II) dichloride easily affords the five-membered ring structure:



The crystal structure (Figure 1.6) of the trans-µ-dichloro-bis(2-phenylazophenyl-C,N')diplatinum(II) was determined by X-ray diffraction$^{(35)}$. Each platinum atom is co-ordinated to the two bridging chloride ions, an ortho-carbon atom of a phenyl ring and the distant azo nitrogen atom such that the azobenzene ligand forms a five-membered chelate. The whole molecule is planar with the exception of the free phenyl rings which are twisted 39° about the C-N bond away from the bridging chloride ions.

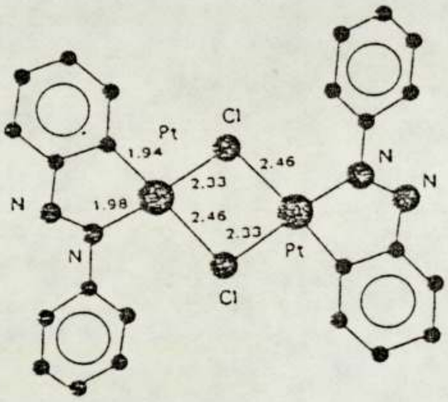
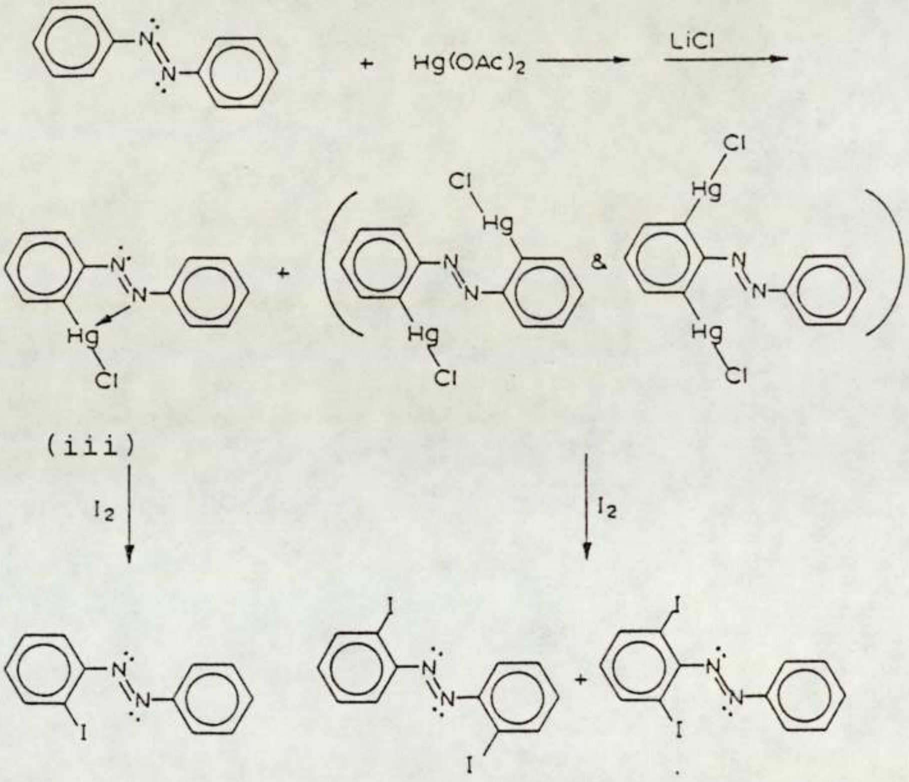


Figure 1.6

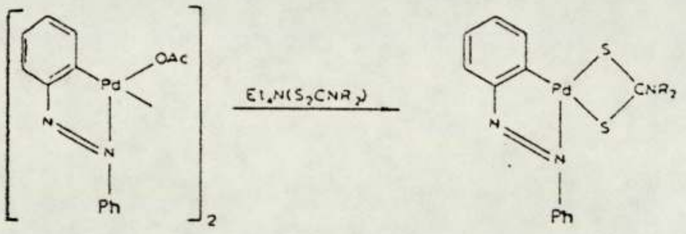
The mercuration(38,39) of azobenzene occurs exclusively in the ortho-position to yield (2-phenylazophenyl-C,N')mercury (II)chloride(iii) and a mixture which, on iodination, gives 2.2'- and 2,6-diiodoazobenzenes. The usual ortho-metallation mechanism presumed from the regiospecificity(40) of the reaction is that the mercury is directed into an ortho-position by co-ordination of the mercury to an azo nitrogen and then subsequent electrophilic substitution occurs (Scheme (4)).

The N.N-dialkyldithiocarbamato(phenylazophenyl-C^2,N') palladium(II) (iv) has been prepared by reacting di-μ-



Scheme (4)

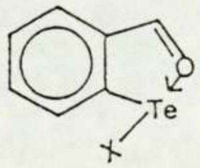
acetato-bis(2-phenylazophenyl-C,N')dipalladium with tetraethylammonium dialkyldithiocarbamate in 1:2 molar ratio(45):



(iv)

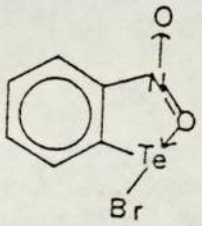
A detailed review of the ortho-metallation of transition metals would be out of the scope of the present study and therefore will not be presented here(34).

In organotellurium chemistry, ortho-metallation has been successfully used to stabilize the rather unstable organotellurenyl compounds. It has been reported that o-carbonyl-containing groups, in the solid state and in solution, have an ability to co-ordinate to the tellurium atom in aryltellurenyl halides (v)(46).



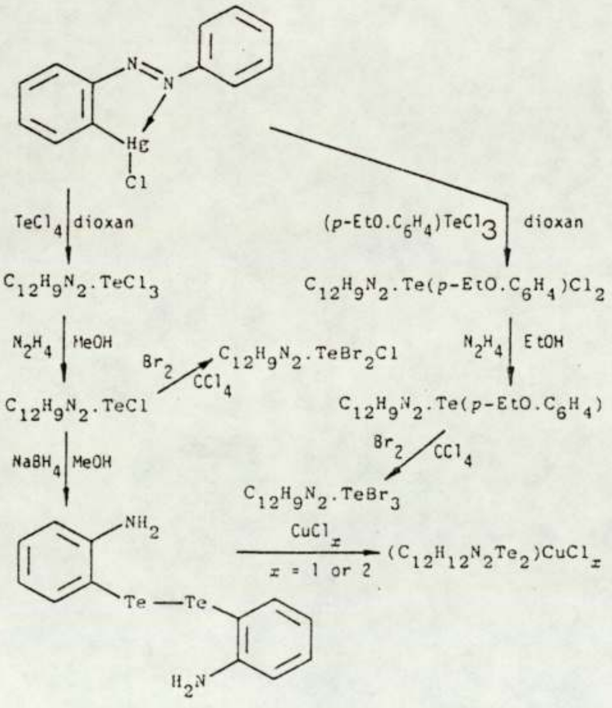
(v)

Cava et al(47) reported that the o-nitro group can also serve as an efficient stabilizing ligand (vi).



(vi)

Recently McWhinnie et al(36) reported the first examples of compounds in which azobenzene is ortho-metallated by tellurium(IV) and tellurium(II) (Scheme (5)).



Scheme (5)

The crystal structure of (2-phenylazophenyl-C,N')tellurium(II) chloride was determined by X-ray diffraction (Figure 1.7). An association through a weak secondary interaction occurred, Te....Cl=3.66Å. ^{125}Te Mössbauer studies showed that the quadrupole splitting (Δ) was less than calculated values and was interpreted in terms of delocalisation of the spare pair p electrons in the heterocyclic ring.

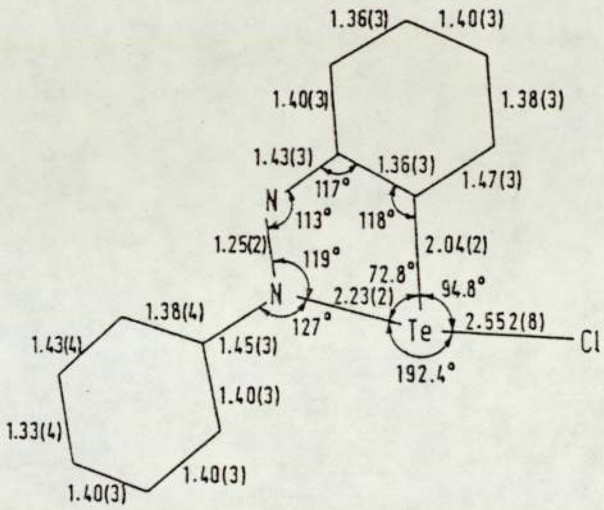


Figure 1.7

It is interesting to extend the studies of azobenzene derivatives of tellurium(II) and tellurium(IV) with monodentate ligands (Cl and Br) to bidentate ligands (dithiocarbamates) which will increase the co-ordination number of Te from three to four in Te(II) and from five to eight in Te(IV). The co-ordination number eight is very rare for this element however, it has been reported for tellurium(IV) dithiocarbamates ($Te(dtc)_4$)$^{(18,48)}$. Thus, the preparation of (2-phenylazophenyl-C,N')tellurium(IV) trichloride and (2-phenylazophenyl-C,N')tellurium(II) chloride were repeated with the view that the ligand substitution reactions might readily occur and also to obtain further evidence for or against the previous work.

CHAPTER TWO

GENERAL EXPERIMENTAL TECHNIQUES

2.0 Experimental

2.1 Chemicals

The starting materials for many reactions were obtained from British Drug House (BDH). All the known tellurium compounds used in the present study, were prepared by literature methods starting from either $TeCl_4$(BDH) or TeO_2 (BDH). All chemicals had satisfactory melting points and spectra (I.R., ^{1}H NMR). Azobenzene was obtained from BDH. Unstabilized polypropylene (PP) in a powder form identified as "propathane" HF22/GS0921 was supplied by Imperial Chemical Industries (ICI) and normally stored in the dark inside a deep freezer.

2.2 Solvents

All solvents were obtained from commercial sources. They were purified where necessary by literature methods(49). In general. solvents were dried and distilled prior to use and stored over molecular sieves in dark containers.

2.3 Techniques Used in Complex Characterization

2.3.1 Elemental Analysis

Analysis for carbon, hydrogen, nitrogen, sulphur and halogen were carried out by the Analytical Services Unit of the Chemistry Department of Aston University.

2.3.2 Melting Points

These were determined using a Gallenkamp electrically heated Melting Point Apparatus.

2.3.3 Conductivity Measurements

Molar conductance of the new compounds and some of known compounds in anhydrous nitromethane was measured at room temperature using a Mullard conductivity bridge, and a standard conductivity cell type E 7591B with a cell constant of 1.46 and with bright platinum electrodes.

2.3.4 Mass Spectra

Mass spectra were recorded with an AEl MS9 Spectrometer at an ionisation potential of 70 eV*. Measurements were carried out on ^{130}Te isotope which is the isotope of largest mass number and highest relative abundance.

2.3.5 Mössbauer Measurements

Mössbauer data were determined at Birmingham University by Dr. F. J. Berry, to whom my thanks are due. These were obtained using a ^{125}Sb/Rh source. Both source and absorber were at 77°K.

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* leV=1.60 x 10^{-19} J

2.3.6 X-ray Measurements

Crystals were obtained by recrystallisation from suitable solvents. Preliminary examination by photographic methods were used to check the quality of the crystals. Accurate cell dimensions and reflection intensities were measured with graphite-monochromated Mo-Kα radiation on an Enraf-Nonius CAD-4 diffractometer operating in the w-2θ scan mode. Two standard reflections were measured every 2 hours to check the stability of the system. Absorption corrections were not applied.

Structures were solved by Patterson and Fourier methods. The refinements were by least squares, using anisotropic temperature factors for the non-hydrogen atoms. Hydrogen atoms were either placed in calculated positions (C-H=1.08Å) "riding" on their respective carbon atoms or located from difference Fourier maps; their parameters were not refined. Refinement was terminated when all calculated shift/error ratios were <0.1.

Computations were carried out on the University of Birmingham Honeywell computer and on the CDC 7600 computer at the University of Manchester Regional Computer Centre with the SHELX(50) programme.

2.3.7 Thin Layer Chromatography

Thin layer chromatography(T.L.C) was carried out by using silica gel plates to identify the product or to separate the species. Chromatographs were developed with iodine.

2.3.8 Infra-red Spectra

All infra-red (I.R.) spectra in the range 4000-200 cm^{-1} were recorded using a Perkin-Elmer infra-red spectrophotometer model 599B, at a normal scan speed which took 12 minutes for each run. In general, solid state samples were examined as solid discs. prepared by pressing a mixture of sample and powdered KBr or CsI.

2.3.9 Ultraviolet and Visible Spectra

U.V. and visible absorption spectra of samples in solution or in polymer films were recorded on a Unicam SP800 B spectrophotometer. For the latter, a processed additive-free polymer film of identical thickness was used (as a compensator) in the reference beam. In the case of the solution, the spectra were recorded using quartz cells of 10 mm path length with the pure solvent being used in the reference beam.

2.3.10 Nuclear Magnetic Resonance Spectra

^{1}H NMR spectra were determined with a Perkin-Elmer R12B instrument (60 MHz) using tetramethylsilane (TMS) as internal standard.

Proton decoupled natural abundance ^{13}C NMR were obtained on an FX 90Q (JEOL) spectrometer at 22.5 MHz.

The ^{125}Te NMR spectra were measured on a Bruker WH 90C spectrometer, at the Université de Rouen in France, as described previously(51).

CHAPTER THREE

LIGAND EXCHANGE REACTIONS, PHOTOCHEMICAL REACTION WITH DIOXYGEN OF Te(dtc)$_4$ AND Te(dtc)$_2$ AND STABILISATION OF POLYPROPYLENE

3.1 Introduction

In 1930 Murril(12,13) reported, and published a patent, on the first preparation of tetrakis(dialkyldithiocarbamato)-tellurium(IV) compounds [Te(dtc)$_4$] and their subsequent use in the vulcanization of rubber. He claimed that these compounds are vulcanizing agents, as well as accelerators of vulcanization. Also he claimed that they appear to give up both sulphur and tellurium during the vulcanization of rubber. Brooks(29) confirmed that these compounds act as accelerators of vulcanization. Recently Abed-Ali(14) has used $Te(S_2CNEt_2)_4$, Te(dedtc)$_4$, and $Te(S_2CNEt_2)_2$, Te(dedtc)$_2$, as stabilisers for polypropylene (PP) and found that these compounds act as thermal and U.V. stabilisers. Also he found that Te(dedtc)$_4$ showed better stabilising action than Te(dedtc)$_2$.

Dialkyldithiocarbamate anions are strong nucleophiles and form stable binary complexes with both divalent and tetravalent tellurium(52). Extensive literature is available on the formation, structure and properties of Te(dtc)$_4$ and Te(dtc)$_2$. A variety of methods have been employed to effect the formation of Te(dtc)$_4$ and Te(dtc)$_2$. These involve, in general, TeO_2, in the case of Te(dtc)$_4$, or either TeO_2 or Te in the case of Te(dtc)$_2$, as starting materials.

X-ray crystallographic studies have shown that in all these and related compounds, the dithiocarbamate group acts as a bidentate, chelating ligand. However, there is unequal participation in the bonding of the two sulphur atoms from the same group. The crystal structure of $Te(S_2CNEt_2)_4$ was the first example in which tellurium was shown to have as high a co-ordination number as eight(18). Crystal structures of bis(dialkyldithiocarbamato)tellurium(II),$Te(S_2CNR_2)_2$, complexes show that each tellurium atom is bonded to all four sulphur atoms of the two ligands forming an asymmetric planar complex. A fifth sulphur atom, belonging to the neighbouring molecule approaches the tellurium atom indicating a tendency towards five-co-ordination around tellurium(30-32).

Foss(28) has shown that tellurium dithiocarbamates readily exchange their dithiocarbamate groups during reaction with dithiocarbamate ions. Other workers, also, observed the exchange reaction between tellurium dithiocarbamates and dithiocarbamate anions(53).

Aravamudan et al(30) reported that Te(II) in a methanolic solution of bis[di(2-hydroxyethyl)dithiocarbamato]tellurium(II) undergoes ready oxidation to Te(IV) forming TeO_2.

In order to extend the studies of $Te(dtc)_4$ and $Te(dtc)_2$, several of these compounds were prepared. Ligand exchange reactions between tellurium dithiocarbamates and the effect of U.V. in the presence of dioxygen, in solution, were studied. Also, the complexes were used as stabilisers for polypropylene (PP). The results may be of importance in the elucidation of the chemistry of tellurium dithiocarbamates.

3.2 Experimental

3.2.1 Synthesis of Known Tellurium Dithiocarbamates

Tellurium dithiocarbamates were synthesised following the indicated literature methods:

Tetrakis(diethyldithiocarbamato)tellurium(IV) and tetrakis-(dimethyldithiocarbamato)tellurium(IV)(17); the yield was quantitative in each case and m.p. = 123-124°C (lit. 124°C) and 165°C (lit. 165°C) respectively.

Bis(diethyldithiocarbamato)tellurium(II) and bis(dimethyldithiocarbamato)tellurium(II)(26,27); the yield was quantitative in each case and m.p. = 162-163°C (lit. 164°C) and 265°C (lit. above 250°C) respectively.

3.2.2 Synthesis of Some New Tellurium Dithiocarbamates

3.2.2.1 Synthesis of Tetrakis(dibenzyldithiocarbamato)tellurium(IV)

This compound was synthesised by adapting Murril's method(12).

A solution of sodium tellurite was prepared by dissolving sodium hydroxide (1.6 g, 0.04 mole) in water (8 cm^3), tellurium dioxide (3.19 g, 0.02 mole) then being added to the solution with heating and stirring. When the tellurium dioxide had dissolved, the solution was allowed to stand and settle until clear; it was then filtered. A solution of sodium dibenzyldithiocarbamate was prepared by adding 10 cm^3 of sodium hydroxide (3.2 g, 0.08 mole) solution to a solution of dibenzylamine (17.8 g, 0.08 mole) in ethanol (70 cm^3) with cooling and stirring. Carbon disulphide (6.08 g, 0.08 mole) was added gradually with continued cooling, the temperature being kept below 10°C, and stirring continued until dissolution. Stirring was continued for a further 30 minutes, during which time a heavy precipitate formed. Water (60 cm^3) was added to dissolve the precipitate. To the latter solution was added gradually, the solution of sodium tellurite with stirring, both being cooled by the addition of ice and being well stirred. A dilute solution (5%) of hydrochloric acid, containing about 0.12 mole of anhydrous HCl, was added slowly with stirring, and with cooling by addition of ice. Further water was added till the final volume reached 300 cm^3. The yellow precipitate was filtered off, washed with water and methanol, and dried in the usual way. The solid was recrystallized from benzene to yield an orange product of m.p. 160°C(dec). The yield was quantitative.

3.2.2.2 Synthesis of Tetrakis(diisobutyldithiocarbamato)-tellurium(IV) and Tetrakis(diphenyldithiocarbamato)-tellurium(IV)

These compounds were prepared in a similar fashion (Table 3.1), except that sodium diphenyldithiocarbamate was prepared by following another method(54). The yield was quantitative in each case.

3.2.2.3 Synthesis of Bis(dibenzyldithiocarbamato)tellurium(II)

This compound was prepared according to Foss's(26) methods. Sodium telluropentathionate was prepared following the literature method(26) and sodium dibenzyldithiocarbamate was prepared as described previously. To a solution of sodium telluropentathionate (2.18 g, 0.005 mole) in water (100 cm^3) was added 50 cm^3 of a 0.3M solution of sodium dibenzyldithiocarbamate. A flesh-coloured product immediately separated out, stirring being continued for a further 5 minutes. The precipitate melted with decomposition at 175°C and the yield was quantitative.

3.2.3 Investigation For Ligand Exchange Reaction in Solution and in the Solid State

3.2.3.1 Refluxing Solutions of Tellurium Dithiocarbamates

To study the exchange reaction, the following equi-molar mixtures were refluxed in xylene for 2->10 hours and thereafter examined:

$Te[S_2CNEt_2]_4$ + $Te[S_2CN(CH_2ph)_2]_4$ (i)

$Te[S_2CNEt_2]_2$ + $Te[S_2CN(CH_2ph)_2]_4$ (ii)

$Te[S_2CNEt_2]_4$ + $Te[S_2CNMe_2]_4$ (iii)

Thin layer chromatography (T.L.C.) examination of the solutions confirmed that they contained $Te[S_2CNR_2]_4$, $Te[S_2CNR_2]_2$ and $(R_2NCS_2)_2$; however, many other spots were observed which may arise from the mixed ligand species.

3.2.3.2 Heating a Mixture of Tellurium Dithiocarbamates in Solid State

An equi-molar mixture of $Te[S_2CNEt_2]_4$ and $Te[S_2CNMe_2]_4$ was heated in a sealed tube for different periods of time ranging from 10 minutes to 1 hour. In the case of heating for a short time, the T.L.C. examination (in chloroform) showed $Te[S_2CNR_2]_4$, $Te[S_2CNR_2]_2$, $(R_2NCS_2)_2$ and many other spots. But in the case of 1 hour heating, T.L.C. examination showed two spots less than in the first case, namely those corresponding to $Te[S_2CNR_2]_4$. As in the previous section, this may arise from the mixed ligand species.

3.2.3.3 ^{1}H NMR Spectra of Tellurium Dithiocarbamate Mixtures

^{1}H NMR spectra of the following mixtures were obtained:

$Te[S_2CNEt_2]_4$ + $Te[S_2CN(CH_2ph)_2]_4$ (i)

$Te[S_2CNEt_2]_2$ + $Te[S_2CN(CH_2ph)_2]_4$ (ii)

The ^{1}H NMR chemical shifts of these two equi-molar mixtures showed no difference from the individual pure compounds, and the spectra were the sum of the contributions from each component (Table 3.2). It is useful to mention here that tetrakis(dimethyldithiocarbamato)tellurium(IV) and bis(dimethyldithiocarbamato)tellurium(II) have a very low solubility in ordinary organic solvents. Therefore they are not suitable for NMR investigation.

3.2.3.4 ^{125}Te NMR Spectra of Tellurium Dithiocarbamates

The following equi-molar mixture was studied:

$Te[S_2CNEt_2]_4$ + $Te[S_2CN(CH_2C_6H_5)_2]_4$ (i)

When an equi-molar mixture is prepared in $CDCl_3$ and examined in a conventional 10 mm tube, the new resonance is broad with a chemical shift centred between those of the

the pure compounds. From this experiment, we have positive proof that exchange occurs. The exchange reaction is not slow since no individual lines are observed. In an attempt to obtain individual lines, the solution was cooled. However, on cooling, the solution crystallised and is therefore unsuitable for further investigation by NMR spectroscopy.

3.2.4 Photochemical Reaction of $Te(dtc)_4$ and $Te(dtc)_2$ With Dioxygen in Solution

During the course of the ligand exchange reaction, in solution, it was noted that a white precipitate formed and the colour of the solution gradually faded. In order to investigate this phenomenon, the following experiments were carried out:

(1) The irradiation of $Te(S_2CNEt_2)_4$, $Te(S_2CNEt_2)_2$ and $Te[S_2CN(CH_2C_6H_5)_2]_4$ in chloroform and benzene by U.V. light for a long period (i.e., 14 days) in the presence of dioxygen, yielded a white precipitate and the colour of the solutions faded. In the case of very low concentrations ($<10^{-6}M$) the solutions were rendered colourless after only a few minutes (about 10 minutes) from the start of irradiation. The white precipitate was identified by infra-red (I.R.) to be TeO_2. The solution was examined by thin layer

chromatography (T.L.C.) and was shown to contain only the corresponding tetraalkylthiuram disulphide (TRTD).

(2) U.V. irradiation of the solutions of the same compounds was carried out, using deoxygenated solvents. No white precipitate formed, nor did the colour of the solutions change.

(3) The solutions were kept in the dark in the presence of dioxygen. Similar results as in (2) were obtained.

3.2.5 Techniques Used in Characterization of Polymer

3.2.5.1 Processing of the Polymer

The polymer sample was processed using a proto-type RAPRA torque-rheometer$^{(55)}$ which is essentially a small mixing chamber containing mixing screws contra rotating at different speeds. Two rotor speeds are available, high, 60 r.p.m., and low, 40 r.p.m. All of the processing was done using high speed, 60 r.p.m. The chamber may be operated either open to the atmosphere or sealed by a pneumatic ram. The charge was 35 g of PP and when this charge was used, the chamber was sealed with the ram down, calculated weights of additives were mixed with the polymer charge and processed for varying periods. All processes were carried out at 180°C.

On the completion of processing, the polymer samples were rapidly removed and quenched in cold water to prevent further thermal oxidation. The polymer samples in the form of crepe were then stored in the dark at 0°C.

3.2.5.2 Preparation of Polymer Films

Films were compression moulded using stainless steel glazing plates. The plates were thoroughly washed and cleaned before use to ensure smooth surfaces and a special grade of cellophane paper was used to prevent the film from sticking to the plate. Control of film thickness was achieved by using a standard quantity of polymer; about 8.5 g was found to produce a film of approximately 0.008 in thickness. The weighed amount of polymer additive mixture in the form of crepe was placed between the glazing plates and inserted into the press whose platens were maintained at 180±2°C. The platen was closed and 2 minutes was allowed for the material to heat up and soften. The pressure was then slowly raised to a maximum of 28 ton/6" ram and left at full pressure for 1½ minutes. The platen was then cooled to about 40°C by running cold water while maintaining full pressure. The plates were then removed from the press and the films were stored in the dark at 0°C. The required thickness was then measured with a micrometer for further examination.

3.2.5.3 Measurement of U.V. Stability

U.V. irradiation of the polymer samples was carried out in an U.V. cabinet. The U.V. cabinet consists of a metal cylinder of about 110 cm in outer diameter having a concentric circular rotating sample drum whose circumference is 15 cm from the periphery of the metal cylinder. Twenty-eight fluorescent tube lamps are mounted on the inside of the cylinder. The rotating arrangement of the samples allows an identical amount of total radiation to fall on every sample. The cylinder cabinet is open to the atmosphere on both the lower and upper sides and the circulation of the air in the cabinet is ensured by the driven ventilator situated under the rotating frame. The sample films were attached to separate sample holders which were mounted vertically on the circumference of the rotating wheel fixed inside the cabinet. In this position, the light beam falls perpendicularly onto the surface of the film. The temperature recorded inside the cabinet with the lamp on was $30\pm1^{\circ}C$. The radiation source consisted of a cylindrical array of 20 W fluorescent tube lamps, positioned on the inner side of the cabinet. Twenty-one lamps, type C (Actinic blue) and 7 lamps, type Al (Westinghouse sunlamps FS20) were used, which were symmetrically distributed so that the combination was one lamp type Al for every 3 lamps of type C. The spectral distribution of both types of lamps is shown in Figure 3.1. Figure 3.2 compares the spectral distribution of lamp Al and lamp C

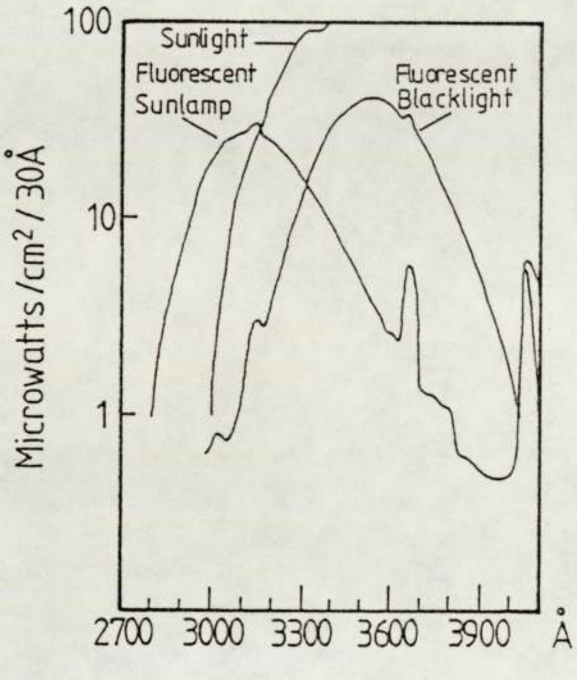


Figure 3.1 Ultra violet spectral distributions of the fluorescent sunlamp and fluorescent black light

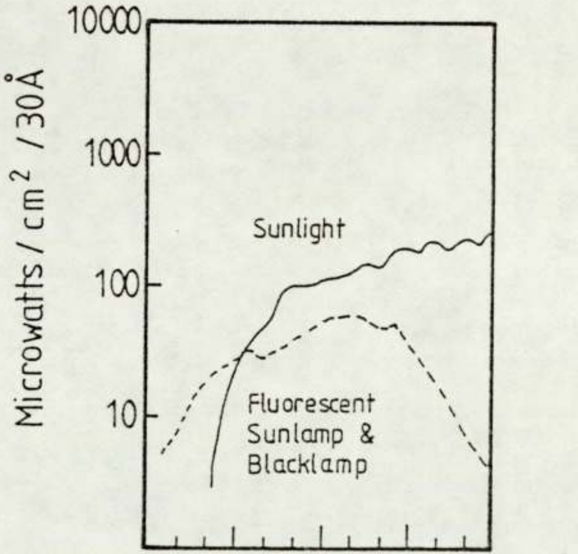


Figure 3.2 Combination of fluorescent sunlamp and blacklamp compared with sunlight

with sunlight(56). The maximum in the relative intensity of lamp A1 is at 317 nm and of lamp C, 374 nm. The available wavelength with the above combination of lamps was between 285 and 500 nm and the radiation intensity I_o at the sample surface was 44 W/m^2.

To minimise the problem of decline in lamp output, the tubes were replaced sequentially every 300 hours of exposure. Exposure times are indicated on a counter clock to the nearest 3 seconds.

3.2.5.4 Infra-red Spectroscopy

Infra-red absorption spectra were obtained by using the Perkin-Elmer (Model 599B) spectrophotometer. The spectra from 4000-200 cm^{-1} were recorded at medium scan speed. Spectra were obtained for each sample prior to and after heating-ageing and U.V. irradiation at regular intervals of time.

In all quantitative analyses, the following combined form of the Beer-Lambert equation was used(57):

$$A = \log_{10}\frac{I_o}{I} = ECL$$

where A = absorbance of optical density

I_o = intensity of radiation effectively entering the sample

I = intensity of radiation emerging from the sample

E = extinction coefficient expressed in litres $mol^{-1}cm^{-1}$

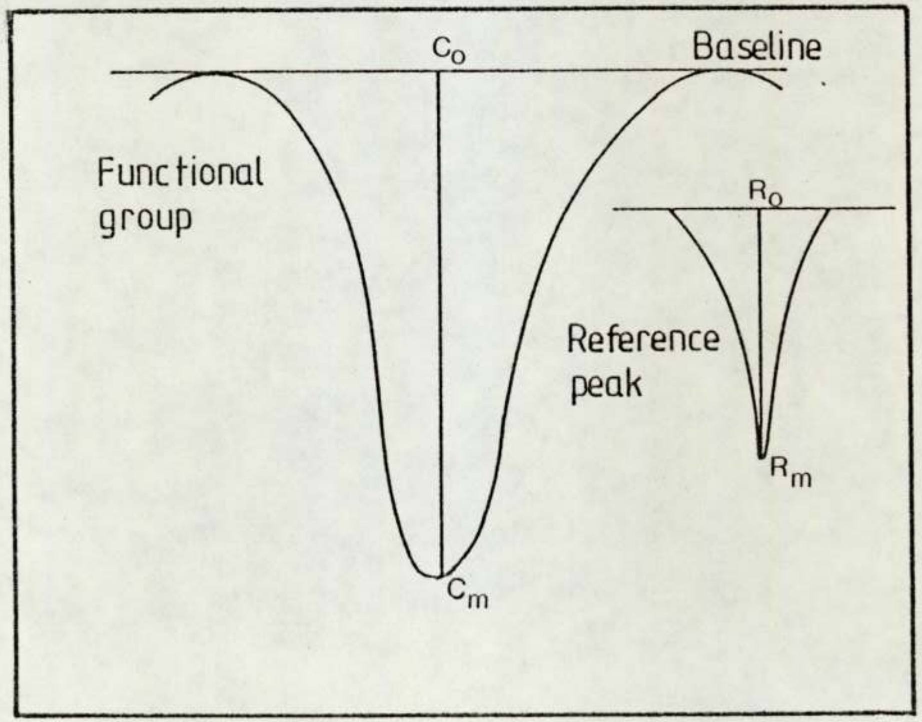
C = concentration of absorbing group present in mole $litre^{-1}$

L = path length of radiation of the sample in cm

To minimise errors due to variation in film thickness, as well as errors due to the instrument, an internal standard; a characteristic absorption peak of PP, was used as reference. The growth and decay of observed absorption peaks (for functional groups) were expressed as indices which were defined as the ratio of the absorbance of functional group peaks to that of the reference peak.

$$\text{Index} = \frac{\text{Absorbance of functional group}}{\text{Absorbance of a standard peak}}$$

The concentration of carbonyl modifications in PP films was expressed as an index relative to the polymer reference peak at 2720 cm^{-1}, which is due to C-H bond stretching. The carbonyl index was calculated from the carbonyl absorption at 1710 cm^{-1} in the following manner:



Carbonyl index measurement

where R_m = absorbance at reference peak maximum

R_o = absorbance at reference peak baseline

C_m = absorbance at carbonyl peak maximum

C_o = absorbance at carbonyl peak baseline

so the carbonyl index = $\dfrac{\log C_o/C_m}{\log R_o/R_m}$

3.2.5.5 Measurement of Embrittlement Time

This is a destructive test method. Films of identical size and of uniform thickness containing different additives along with a control sample were irradiated (U.V.) and were periodically checked for embrittlement time by folding the film back on itself through 180° manually. Each determination was carried out in duplicate. This test can serve as a qualitative guide for the durability of the films.

3.2.5.6 Measurement of Thermal-oxidative Stability

A Wallace oven (conforms to the British Standards for thermal testing of polymer films) was used for thermal oxidative ageing tests. The oven consists of 6 separate identical compartments, fitted with temperature control ($\pm 2^\circ$C) and an air flow of 3 ft^3/h was maintained throughout the tests. Each test film was suspended in one of the compartments to prevent the cross-contamination of the additives by volatilisation and was subjected to the correct temperature (140°C).

3.3 Results and Discussion

Table 3.1 combines preparative and analytical data. I.R. and ^{1}H NMR data are gathered in Table 3.2.

The reaction of sodium tellurite and sodium telluropentathionate with sodium dialkyldithiocarbamates give Te(dtc)$_4$ and Te(dtc)$_2$, following literature methods$^{(12,26)}$. All compounds have satisfactory elemental analysis (Table 3.1) and I.R. data (Table 3.2).

3.3.1 I.R. Spectra

Figures 3.3, 3.4, 3.5 and 3.6 show the infra-red spectra of the new tellurium dithiocarbamates; $Te[S_2CN(CH_2C_6H_5)_2]_4$, $Te[S_2CN(CH_2C_6H_5)_2]_2$, $Te[S_2CN(C_6H_5)_2]_4$ and $Te[S_2CN(C_4H_9)_2]_4$ respectively. In the infra-red spectra of the tellurium dithiocarbamates, the most characteristic bands are those that are attributed to the ν(C-N), ν(C-S) and ν(Te-S) vibrations. The I.R. data showed that the characteristic ν(C-N) stretching frequency of the dithiocarbamate moiety was observed in all the complexes in the range 1490-1510cm^{-1}, as a very strong band (Table 3.2). The ν(C-S) vibration

Compound	m.p. ^{o}C	Colour	C%(calc)	H%(calc)	N%(calc)	S%(calc)
$Te(S_2CNEt_2)_2$	162-163	red	28.4 (28.3)	5.0 (4.72	6.55 (6.61)	30.0 (30.2)
$Te(S_2CNEt_2)_4$	123-124	yellow	33.4 (33.4)	5.75 (5.56)	8.20 (7.78)	34.0 (35.6)
$Te(S_2CNMe_2)_2$	265	orange-red	19.9 (19.6)	3.45 (3.26)	7.85 (7.62)	33.8 (34.8)
$Te(S_2CNMe_2)_4$	165	yellow	24.3 (23.7)	3.95 (3.95)	9.35 (9.22)	42.1 (42.5)
$Te[S_2CN(CH_2C_6H_5)_2]_2$	175	flesh	53.0 (53.6)	4.15 (4.17)	4.0 (4.17)	19.1 (19.9)
$Te[S_2CN(CH_2C_6H_5)_2]_4$	160	orange	59.8 (59.2)	5.15 (4.61)	4.75 (4.61)	21.2 (21.1)
$Te[S_2CN(C_4H_9)_2]_4$	124	yellow	45.3 (45.8)	6.75 (7.63)	5.42 (5.94)	26.3 (27.1)
$Te[S_2CN(C_6H_5)_2]_4$	209-210	orange	55.9 (56.5)	3.60 (3.63)	5.0 (5.07)	23.2 (24.1)

Table 3.1 Analytical data for tellurium dithiocarbamates

Compound	ν(C-N) cm^{-1}	ν(C-S) cm^{-1}	ν(Te-S)cm^{-1}		^{1}HNMR (σ ppm vs TMS) J-Hz ($CDCl_3$)
			Asym.	sym.	
$Te[S_2CNMe_2]_4$	1510 s	970 s	350 s	310 w	
$Te[S_2CNMe_2]_2$	1510 s	970 s 980 sh	350 s	310 w	
$Te[S_2CNEt_2]_4$	1490 s	990 m 1005 sh	360 s	320 s	1.08-1.62(CH_3,triplet,40H) 3.61-4.02(CH_2,quartet,16H)
$Te[S_2CNEt_2]_2$	1490 s	990 m 1005 sh	365 s	305 s	1.12-1.53(CH_3,triplet,20H) 3.53-4.04(CH_2,quartet,8H)
$Te[S_2CN(C_4H_9)_2]_4$	1480 s	975 s 968 sh	350 s	285 s	
$Te[S_2CNPh_2]_4$	1495 s	1010 s	320 m	280 s	
$Te[S_2CN(CH_2Ph)_2]_4$	1500 s	1000 s 1010 sh	270 s	230 m	5.15(CH_2,singlet,16H) 7.35(aromatic,singlet,40H)
$Te[S_2CN(CH_2Ph)_2]_2$	1500 s	1000 s 1010 sh	330 w	285 m	

Table 3.2 I.R. and ^{1}H N.M.R. data

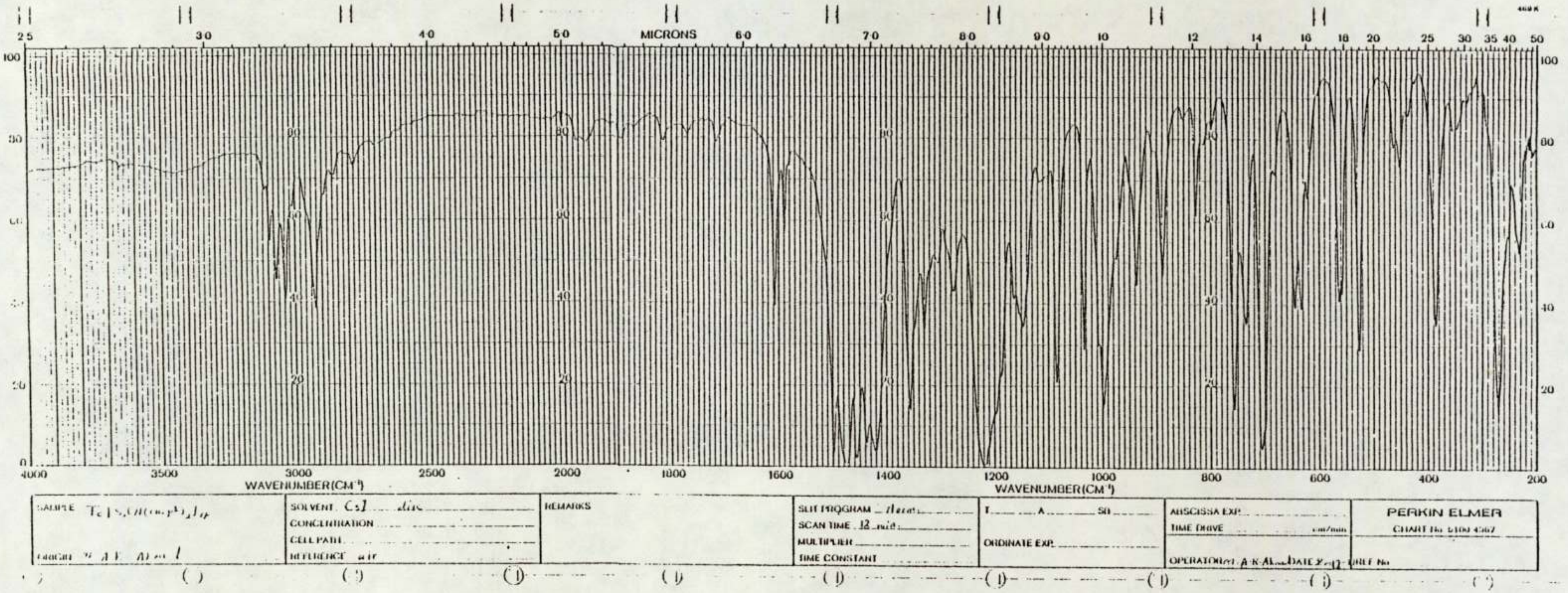
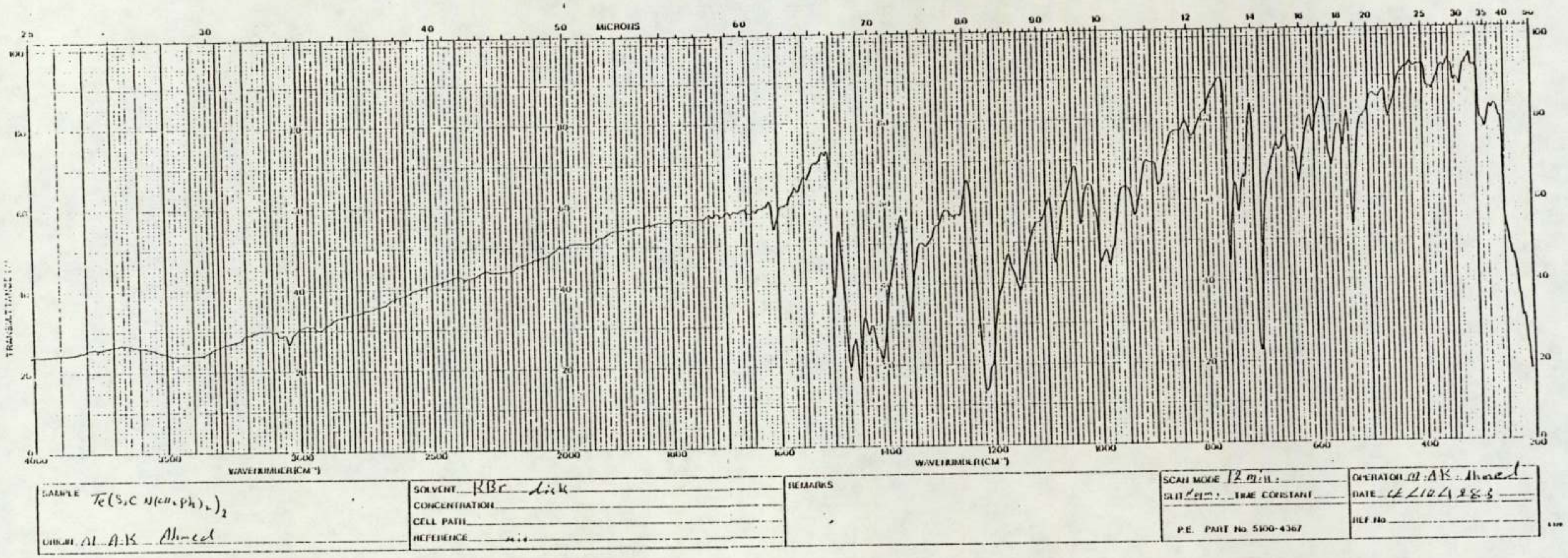


Figure 3.3 I.R. spectrum of $Te[S_2CN(CH_2C_6H_5)_2]_4$



SAMPLE $Te(S_2C N(CH_2Ph)_2)_2$
ORIGIN M.A.K. Ahmed
SOLVENT KBr disk
CONCENTRATION
CELL PATH
REFERENCE nil
REMARKS
SCAN MODE 12 min
SLIT 4mm TIME CONSTANT
P.E. PART No. 5100-4367
OPERATOR M.A.K. Ahmed
DATE 06/10/1983
REF No

Figure 3.4 I.R. spectrum of Te$[S_2CN(CH_2C_6H_5)_2]_2$

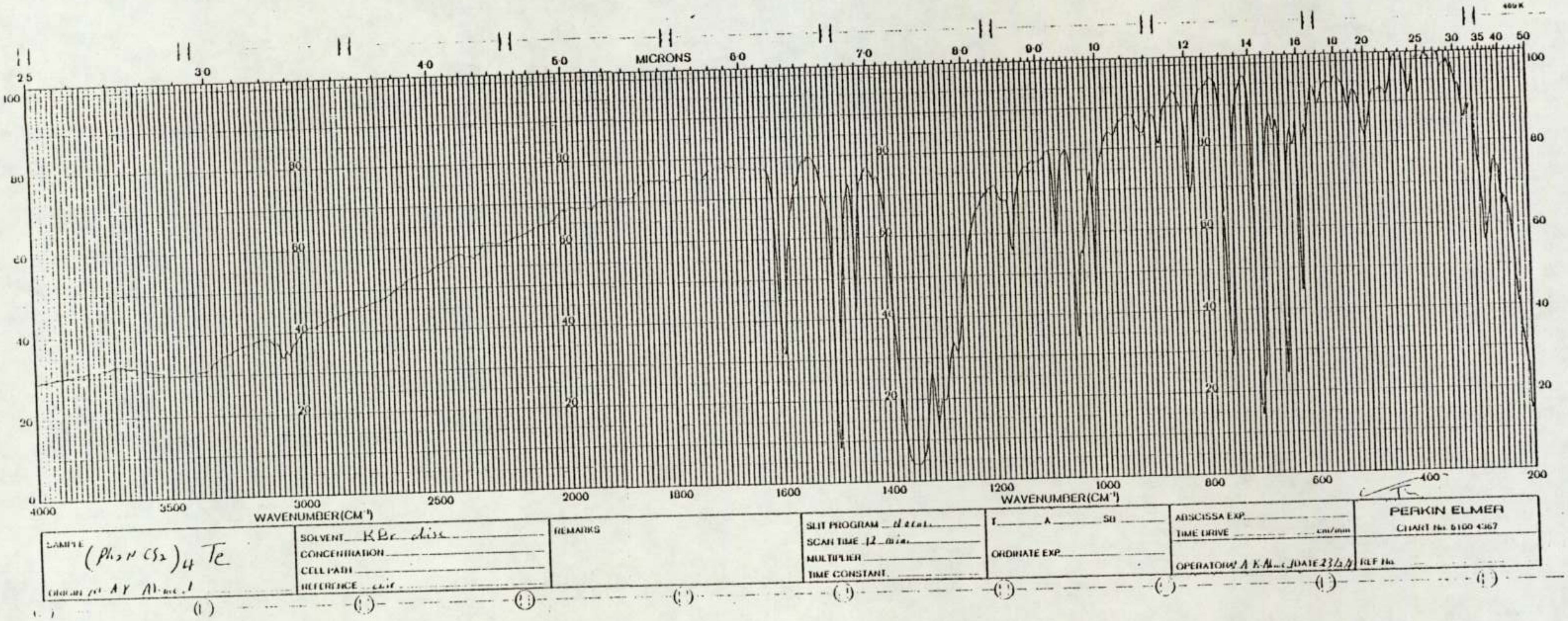


Figure 3.5 I.R. spectrum of $Te[S_2CN(C_6H_5)_2]_4$

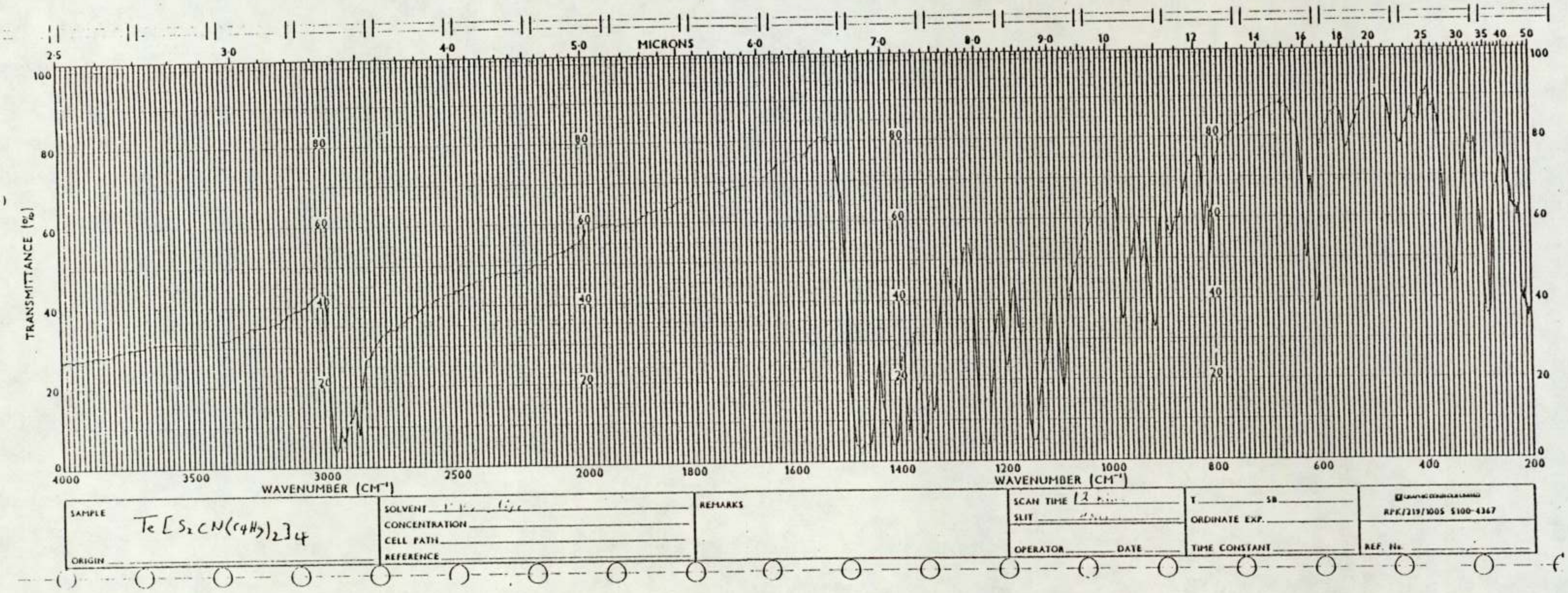


Figure 3.6 I.R. spectrum of Te$[S_2CN(C_4H_9)_2]_4$

occurred, as a strong or medium band, with a little shoulder, in the range 970-1010 cm^{-1}. For almost all compounds, the symmetric and unsymmetric ν(Te-S) could be assigned as indicated in Table 3.2.

Aravamudan et al (21,53) reported the I.R. data for a range of tellurium dithiocarbamates. They observed that the ν(C-N) vibrations occurred as a strong band in the range 1460-1500 cm^{-1}, in all complexes. Also these workers have assigned the symmetric and unsymmetric ν(Te-S) frequencies. Generally speaking, our data are in agreement with the previous reports (21,53).

The I.R. spectra of chloroform solutions of $Te[S_2CNEt_2]_4$ and $Te[S_2CNEt_2]_2$ were interpreted by Nikolov et al (17). For $Te[S_2CNEt_2]_2$, a band at 1510 cm^{-1}, whereas for $Te[S_2CNEt_2]_4$ two bands at 1500-1510 cm^{-1} and 1525 cm^{-1} were assigned as ν(C-N) vibrations. Also two bands at 992 and 1011 cm^{-1} for $Te[S_2CNEt_2]_2$ and three bands at 992, 997 and 1013 cm^{-1} for $Te[S_2CNEt_2]_4$, have been assigned as ν(C-S) vibrations. However, the I.R. spectra, as KBr discs, of both compounds were obtained by us. A very strong band at 1490 cm^{-1} was observed, in both compounds, which was assigned as ν(C-N) vibration. Also a medium band at 990 cm^{-1} with a little shoulder at 1005 cm^{-1} in both compounds, was observed and assigned as ν(C-S) vibration.

The I.R. spectra are unreliable for determining whether the dithiocarbamate group in a complex is bidentate or monodentate. The criteria used by Nikolov et al(17) and other workers(58) i.e., the splitting of ν(C-S) bands (∿1000 cm^{-1}) to indicate the bidentate or monodentate nature of dithiocarbamate group is in conflict with the crystallographic results, have shown that dialkyldithiocarbamate acts as bidentate in all complexes(18,30-32).

3.3.2 Ligand Exchange Reaction Between Tellurium Dithiocarbamates

No chemical exchange reaction between tellurium dithiocarbamates or tellurium dithiocarbamates containing mixed dithiocarbamate ligands has been reported. The following work was designed to study the exchange reaction of the title compounds in solution. It shows that tellurium NMR spectroscopy is a powerful tool for the investigation of such a system. Furthermore, it has been found that dioxygen naturally dissolved in solvents gives tellurium dioxide and the corresponding TRTD, under U.V. irradiation.

The exchange reaction between tellurium dithiocarbamates was attempted first by refluxing a mixture of two different tellurium dithiocarbamates in equimolar portions, in xylene for different periods of time and thereafter examining the solutions by T.L.C. The results showed that $Te[S_2CNR_2]_4$,

$Te[S_2CNR_2]_2$, $[R_2NCS_2]_2$ and many other spots do exist in the solutions. This may arise from the mixed ligand species. However, at the moment it is very difficult to separate or identify these spots. The reason for the large number of spots can be explained from the fact that these compounds and their products are decomposed on heating. For example:

(I) $Te[S_2CNR_2]_4$ compounds decompose on heating to $Te[S_2CNR_2]_2$ and the corresponding $[R_2NCS_2]_2$ (14,19,29);

$$Te[S_2CNR_2]_4 \xrightarrow{\Delta} Te[S_2CNR_2]_2 + [R_2NCS_2]_2 \qquad (iv)$$

(II) Tetraalkylthiuram disulphide compound decomposes on heating to tetraalkylthiourea, carbondisulphide and sulphur(59):

$$[R_2NCS_2]_2 \xrightarrow{\Delta} R_2N\text{-}CS\text{-}NR_2 + CS_2 + S \qquad (v)$$

^1H NMR was attempted as an alternative technique and the spectra were examined for the following two mixtures:

$$Te[S_2CNEt_2]_4 + Te[S_2CN(CH_2C_6H_5)_2]_4 \qquad (i)$$

$$Te[S_2CNEt_2]_2 + Te[S_2CN(CH_2C_6H_5)_2]_4 \qquad (ii)$$

The ^1H chemical shifts of these two equimolar mixtures show no differences from the individual pure compounds and the spectra are the sum of the contributions from each component (Figures 3.7, 3.8 and 3.9). The probable reason is that the protons are remote from the reaction centre (Te) and the shifts are not sensitive to other dithiocarbamato-ligands bound to the same tellurium atom. In other words, the protons in pure compounds and in the mixed ligand compounds have almost the same chemical environment. The values obtained from ^{1}H NMR data for pure tellurium dithiocarbamates, in $CDCl_3$, are given in Table 3.2. The literature(17) reports on ^{1}H NMR data for $Te(S_2CNEt_2)_4$ and $Te(S_2CNEt_2)_2$ and these values (Table 3.2) are in good agreement with those previously reported.

It has been found that tellurium NMR is a powerful tool for the study of such systems. In 1981, McWhinnie et al(51) reported the exchange reaction between diarylditellurides, in solution, by means of ^{125}Te NMR and they demonstrated the following exchange reactions:

$$(p\text{-}ClC_6H_4)_2Te_2 + (p\text{-}EtOC_6H_4)_2Te_2 \rightleftharpoons (p\text{-}ClC_6H_4)Te(H_4C_6OEt\text{-}p) \qquad (vi)$$

$$(p\text{-}CH_3C_6H_4)_2Te_2 + (p\text{-}EtOC_6H_4)_2Te_2 \rightleftharpoons (p\text{-}CH_3C_6H_4)Te(H_4C_6OEt\text{-}p) \qquad (vii)$$

$$(p\text{-}CH_3C_6H_4)_2Te_2 + (p\text{-}ClC_6H_4)_2Te_2 \rightleftharpoons (p\text{-}CH_3C_6H_4)Te(H_4C_6Cl\text{-}p) \qquad (viii)$$

From the above paper(51), it has been shown that the exchange was a thermal process, which was very slow and it was established also that dioxygen reacts with diarylditellurides to give new compounds; as a result of the

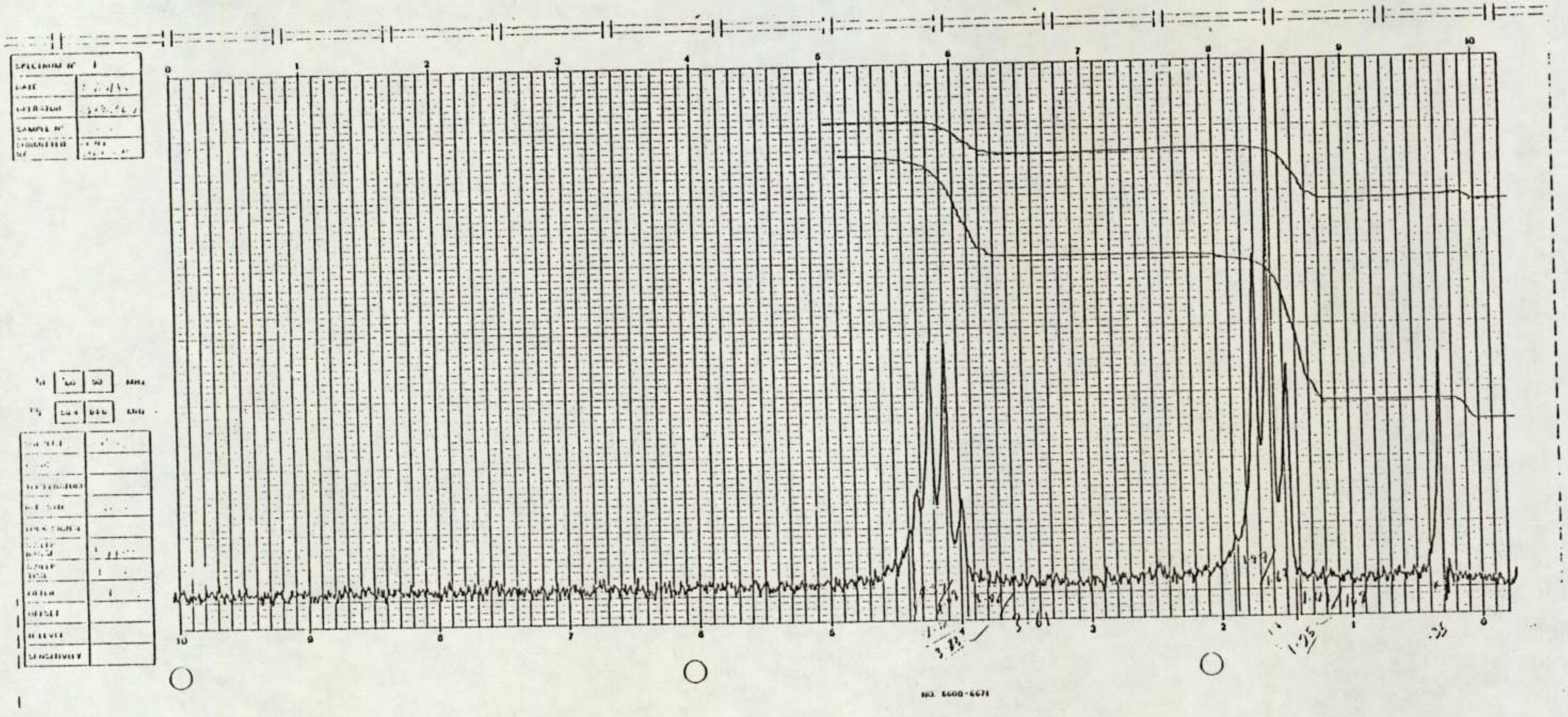


Figure 3.7 ^{1}H N.M.R. spectrum of Te[S_2CNEt_2]$_4$

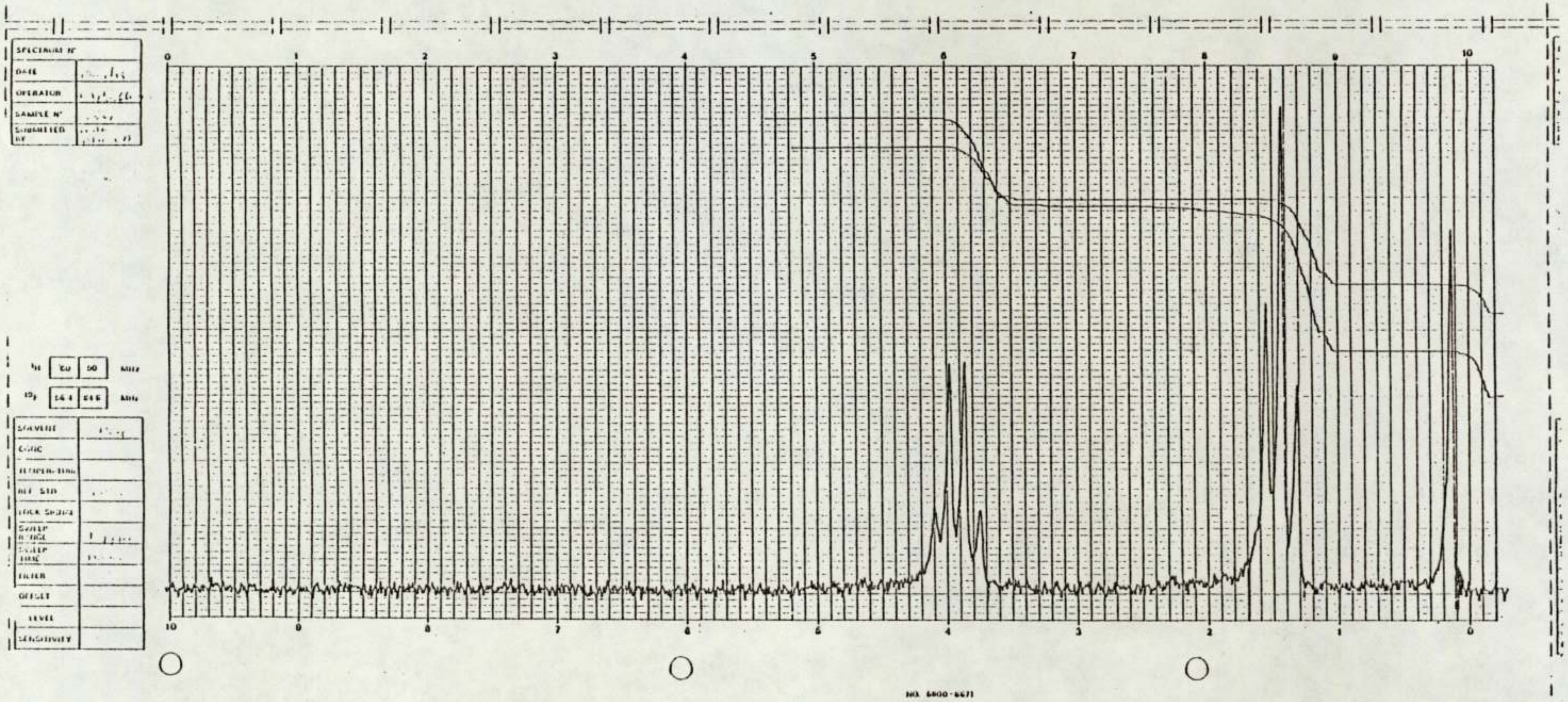


Figure 3.8 ^{1}H N.M.R. spectrum of $Te(S_2CNEt_2)_2$

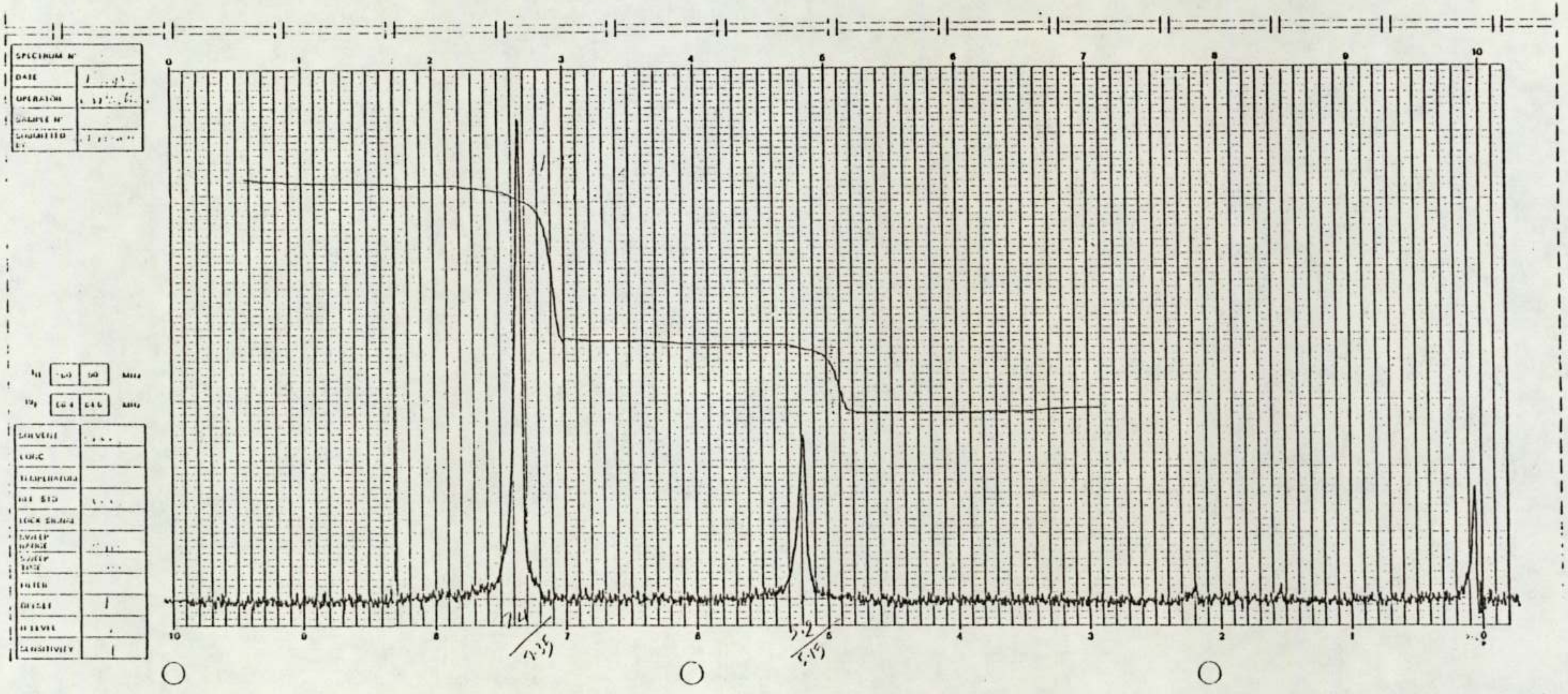


Figure 3.9 ^{1}H N.M.R. spectrum of $Te[S_2CN(CH_2C_6H_5)_2]_4$

latter reaction, the reaction can be influenced by dioxygen in the solvent. Therefore, we extended the investigation for our mixtures by tellurium NMR and hoped that the new molecular species containing mixed dithiocarbamate ligands may be identified.

The following mixture was chosen to give the maximum tellurium concentration in solution:

$Te(S_2CNEt_2)_4 + Te[S_2CN(CH_2C_6H_5)_2]_4$ (i)

Tetrakis(diethyldithiocarbamato)tellurium(IV) [Te(dedtc)$_4$] and tetrakis(dibenzyldithiocarbamato)tellurium(IV) [Te(dbdtc)$_4$] give distinct ^{125}Te NMR signals, as mentioned before. When an equimolar mixture is prepared in $CDCl_3$, the new resonance is broad and centred between those of the pure compounds. This is the indication of an exchange reaction which is within the NMR time scale, since no individual lines are obtained. On cooling, in order to slow the reaction and obtain individual lines, the solution crystallised and hence no additional information relating to the individual species could be obtained.

The mechanism of the ligand exchange reaction between tellurium dithiocarbamates may proceed via one of the two alternative pathways. The first pathway involves a dissociation mechanism:

$$\mathrm{TeL_4 + S \rightleftharpoons TeL_3S + L}$$

$$\mathrm{TeL'_4 + S \rightleftharpoons TeL'_3S + L'}$$

$$\mathrm{TeL_3S + L' \rightleftharpoons L'TeL_3 + S}$$

$$\mathrm{TeL'_3S + L \rightleftharpoons LTeL'_3 + S}$$

$$\mathrm{L'TeL_3 + S \rightleftharpoons L'TeL_2S + L}$$

$$\mathrm{LTeL'_3 + S \rightleftharpoons LTeL'_2S + L'}$$

$$\mathrm{L'TeL_2S + L' \rightleftharpoons TeL_2L'_2 + S}$$

$$\mathrm{LTeL'_2S + L \rightleftharpoons TeL'_2L_2 + S}$$

(where L and L' = dithiocarbamato ligands and S = solvent)

The probable general equation from the above mechanism is as shown below:

$$\mathrm{TeL_4 + TeL'_4 \rightleftharpoons TeL_2L'_2 + LTeL'_3 + L'TeL_3} \qquad \text{(ix)}$$

The second mechanistic pathway might involve redox chemistry:

$$\mathrm{TeL_4 \rightleftharpoons TeL_2 + L{-}L}$$

$$\mathrm{TeL'_4 \rightleftharpoons TeL'_2 + L'{-}L'}$$

$$\mathrm{TeL_2 + L'{-}L' \rightleftharpoons TeL_2L'_2}$$

$$\mathrm{TeL'_2 + L{-}L \rightleftharpoons TeL'_2L_2}$$

The general equation for this mechanism could be written as follows:

$$TeL_4 + TeL'_4 \rightleftharpoons TeL_2L'_2 \qquad (x)$$

The dissociation of $Te(dtc)_4$ to $Te(dtc)_2$ and TRTD, by heating, has been demonstrated by many workers$^{(14,19,29)}$. Therefore it is possible that dissociation could occur partially even without heating. On the other hand, Brooks$^{(29)}$ reported that $Te(dedtc)_2$ reacts with TRTD to give $Te(dedtc)_4$, in water, when the pH of the slurry is adjusted to between 2-4 and with heating. From this discussion, the partial dissociation of TeL_4 is depicted as shown:

$$TeL_4 \rightleftharpoons TeL_2 + L\text{-}L$$

i.e., the reaction could be forward or backward or in equilibrium. Given that the reduction elimination-oxidation addition steps have been demonstrated in particular case, this mechanism may currently be preferred.

3.3.3 Photochemical Reaction of $Te(dtc)_4$ and $Te(dtc)_2$ With Dioxygen

The reaction of dioxygen with tellurium dithiocarbamates in chloroform and benzene solutions under U.V. irradiation resulted in TeO_2 and TRTD. A review of literature showed that no studies have been made on photo-reactions of tellurium dithiocarbamates. Thus this small contribution is a first example of this aspect of the chemistry of tellurium dithiocarbamates.

The irradiation of tellurium dithiocarbamate solutions by U.V. light in the presence of dioxygen, produced a white precipitate and the colour of the solutions gradually faded. The I.R. spectrum of the white precipitate showed a strong broad band at $\sim 650\ \text{cm}^{-1}$ (Figure 3.10). This was assigned to a $\nu(\text{Te=O})$ vibration(14). The I.R. spectra of the white precipitate and the commercial TeO_2 are identical. This indicates that the white precipitate may be TeO_2. On the other hand, the examination of the colourless solutions by T.L.C. showed only one spot, which was shown to correspond to TRTD. From the above evidence, it can be suggested that tellurium dithiocarbamates, in solution, react with dioxygen under U.V. irradiation to produce TeO_2 and the corresponding TRTD:

$$Te(S_2CNR_2)_4Te \xrightarrow{h\nu/O_2} TeO_2 + 2(R_2NCS_2)_2 \qquad (xi)$$

$$Te(S_2CNR_2)_2 \xrightarrow{h\nu/O_2} TeO_2 + (R_2NCS_2)_2 \qquad (xii)$$

The plots of absorbance at wavelength 255 and 420 nm versus concentration of $Te(dedtc)_4$ are straight lines (Figures 3.11 and 3.12). However, at wavelength of 255nm,

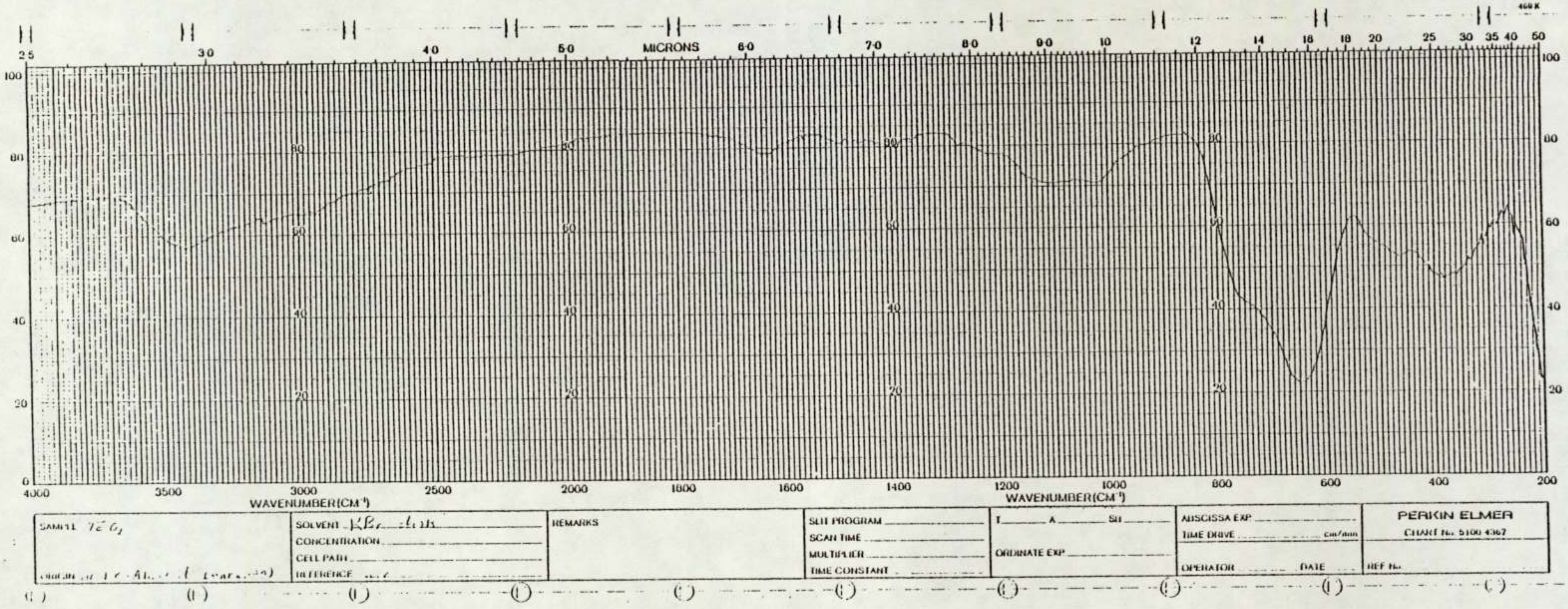


Figure 3.10 I.R. spectrum of TeO_2

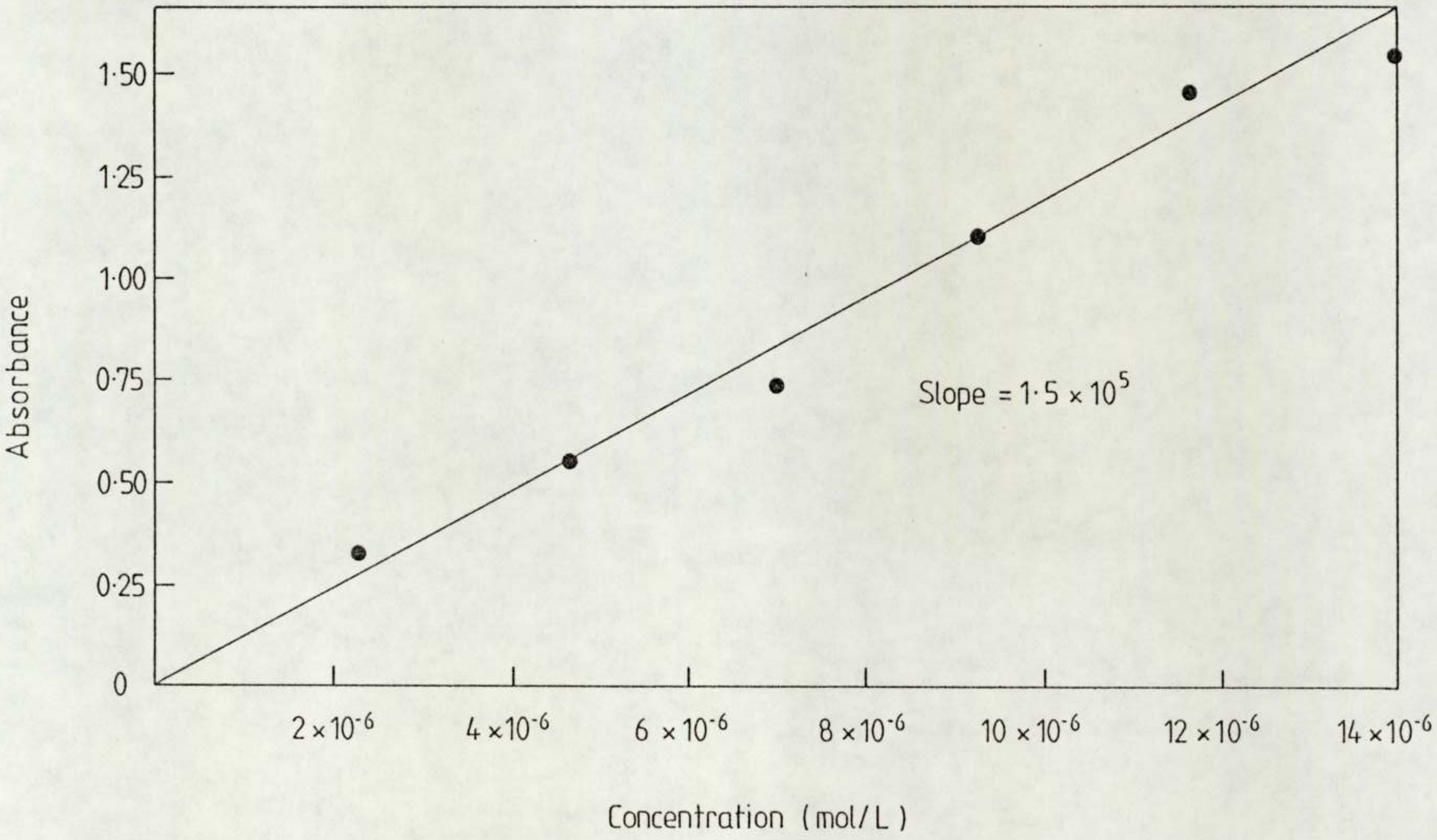


Figure 3.11 The plot of absorbance versus concentration for $Te(dedtc)_4$ in $CHCl_3$, at 25^{o}C, λ_{max} = 255 nm

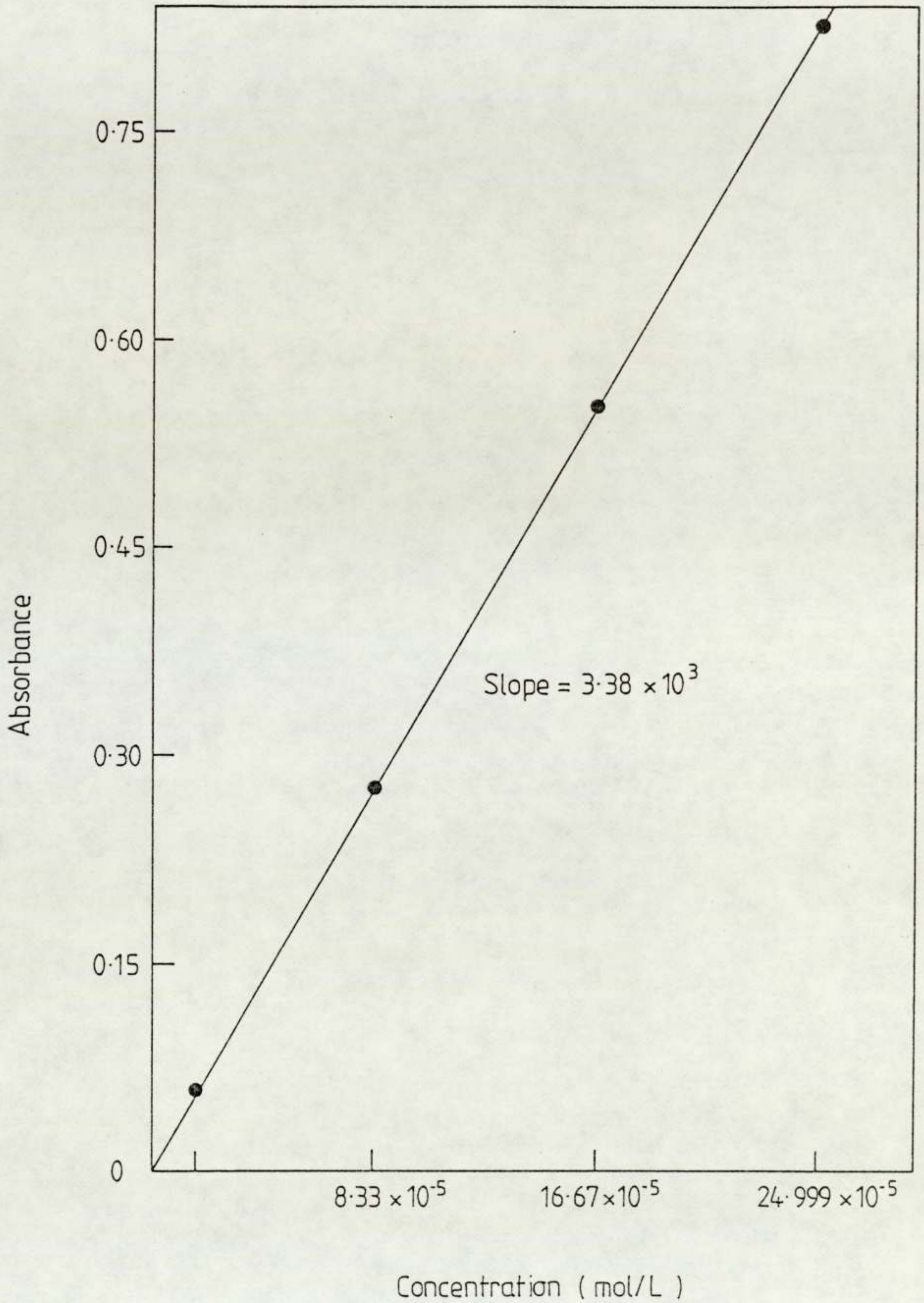


Figure 3.12 The plot of absorbance versus concentration for $Te(dedtc)_4$ in $CHCl_3$, at 25°C, λ_{max} = 420 nm

there is some scatter on the points. This may be related to the high absorption and reactivity of these compounds under U.V. irradiation. The slopes represent the molar extinction coefficient (ε) of the Te(dedtc)$_4$ at wavelengths of 255 and 420 nm respectively. The experimental values obtained for the slopes are 1.5×10^5 and 3.38×10^3 $dm^3 mol^{-1} cm^{-1}$ respectively. The plots show that Beer's law is valid over a considerable range of concentrations for the solutions of Te(dedtc)$_4$ in different solvents (chloroform and benzene).

The conclusion from the above observation is that, U.V. irradiation and dioxygen are playing an important role in the reactions of tellurium dithiocarbamates in solution.

3.4 Stabilisation of Polypropylene (PP)

The significance of hydroperoxides as the key initiator during both thermal and photo-oxidative processes of polyolefins has been well established(9,60,61). It follows then, that any additives which can remove peroxide (or their decomposition radicals) during processing will be efficient melt stabilisers(6,62). It has been shown that metal dithiocarbamates (such as Zn, Ni and Te) are efficient melt stabilisers(7,14,62) for polypropylene since they decompose hydroperoxides in non radical mechanisms.

Figure 3.13 shows the effect of tetrakis(diisobutyldithiocarbamato)tellurium(IV) [Te(didtc)$_4$] and tetrakis(dibenzyldithiocarbamato)tellurium(IV) [Te(dbdtc)$_4$] as melt stabilisers for PP during processing. It is clearly shown that the carbonyl index remains almost constant up to 20 minutes processing in a closed mixer at 180°C. This indicates that both additives effectively inhibit oxidation of PP during processing.

The effect of varying the concentration of Te(didtc)$_4$ and Te(dbdtc)$_4$ on the photo-oxidative stability of PP is shown in Figures 3.14 and 3.15 respectively. On U.V. irradiation, it appears that both additives at all concentrations used, show a stabilising action as evidenced by the embrittlement times; the time taken for the PP sample to disintegrate completely (Table 3.3). Increasing the concentration of the additives increased the U.V. life time of PP. The Te(dbdtc)$_4$ was less effective than Te(didtc)$_4$. This could be due to the phenyl group, which in other contents has been shown to produce pro-oxidant behaviour(14).

The effects of processing time on photo-oxidation of PP film containing Te(didtc)$_4$ and Te(dbdtc)$_4$ (2.8×10^{-4} mole/100 g) are shown in Figures 3.16 and 3.17 respectively. Increasing the processing time results in a slight increase in the photo-stability of PP (Table 3.3). A similar behaviour is also observed at 1.4×10^{-4} and 0.7×10^{-4}

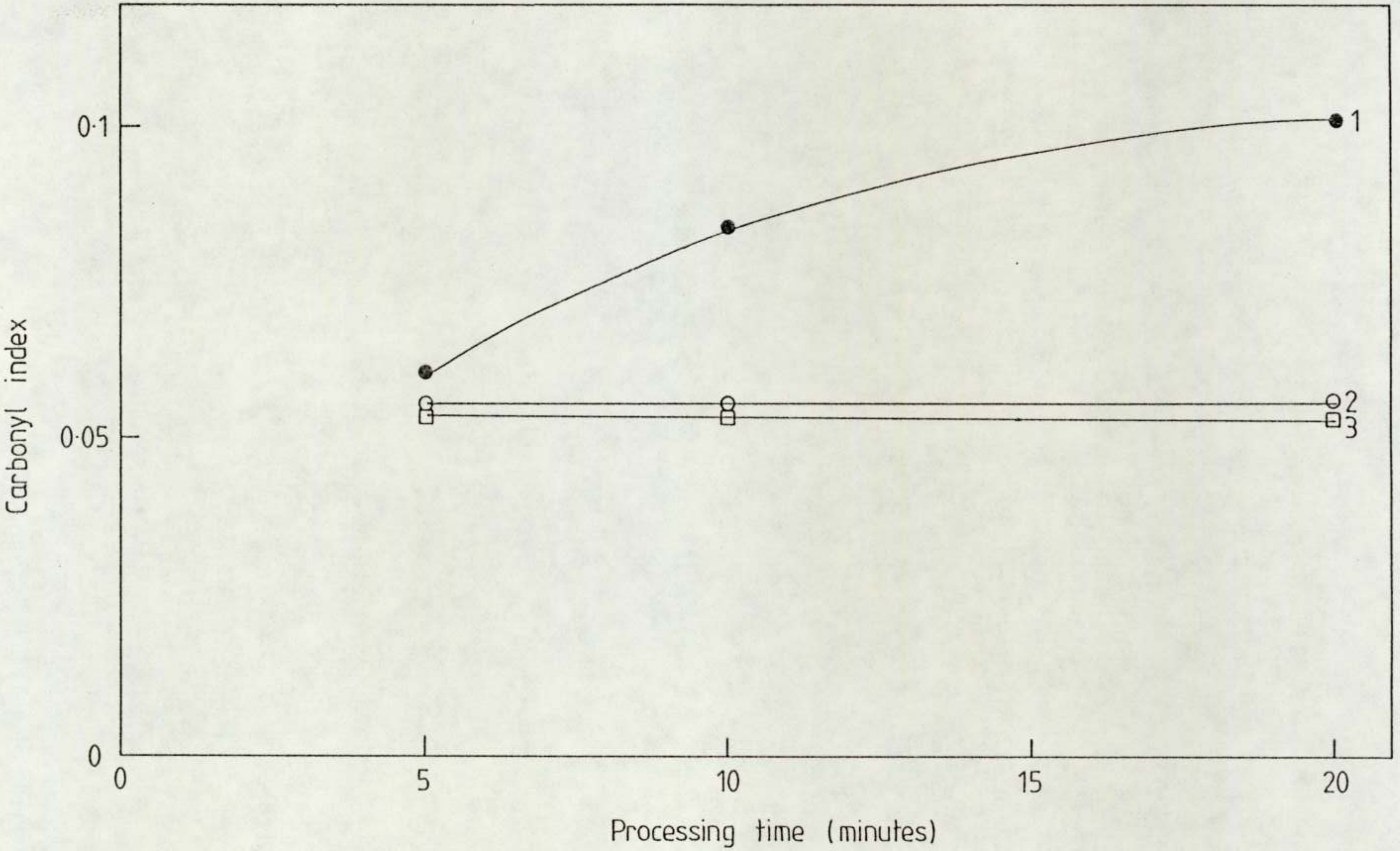


Figure 3.13 The effect of different additives on the oxidative stability of PP during processing in a closed mixer (concentration of the additives is 2.8x10^{-4} mole/100 g) 1. PP without additives 2. Te(didtc)$_4$ 3. Te(dbdtc)$_4$

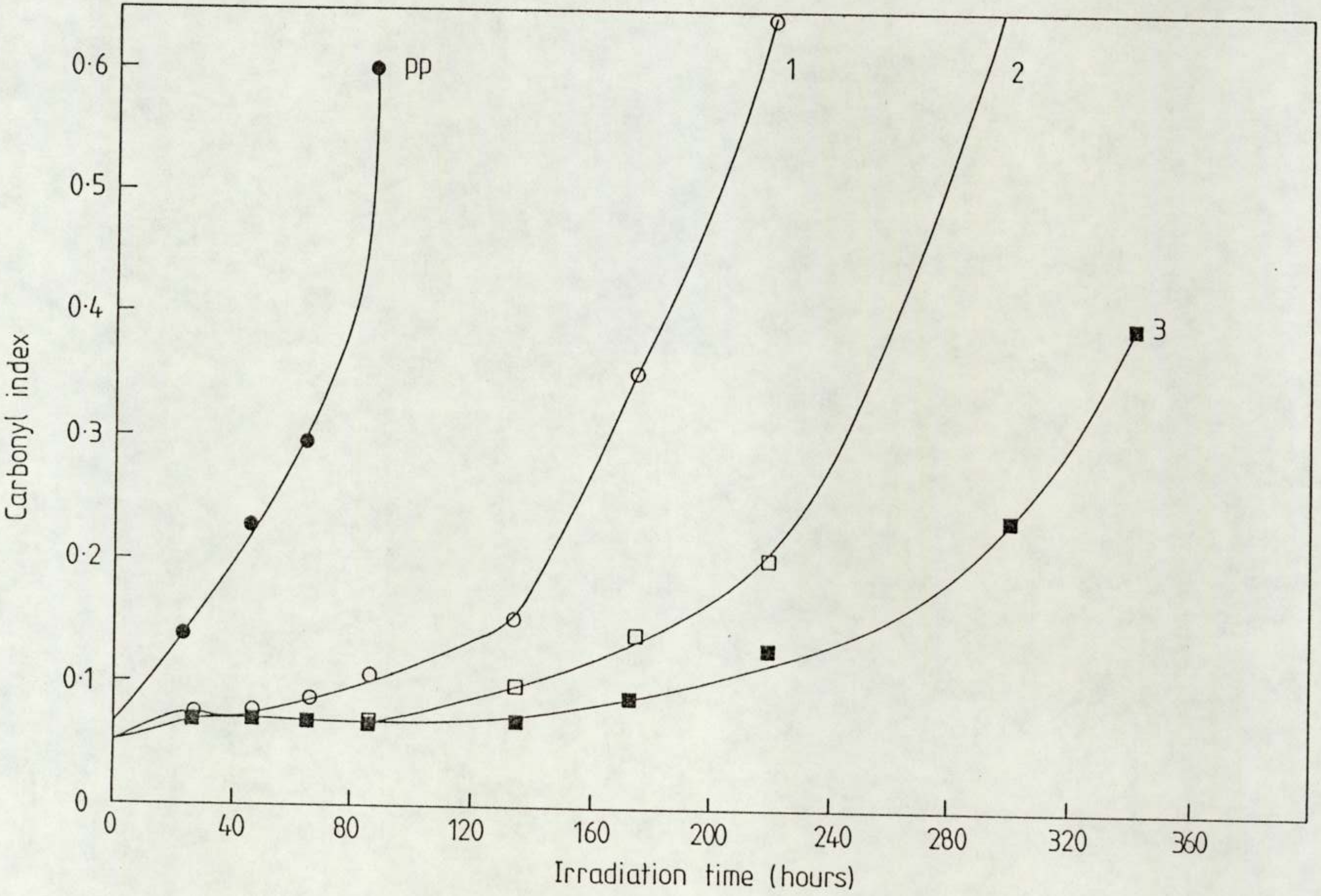
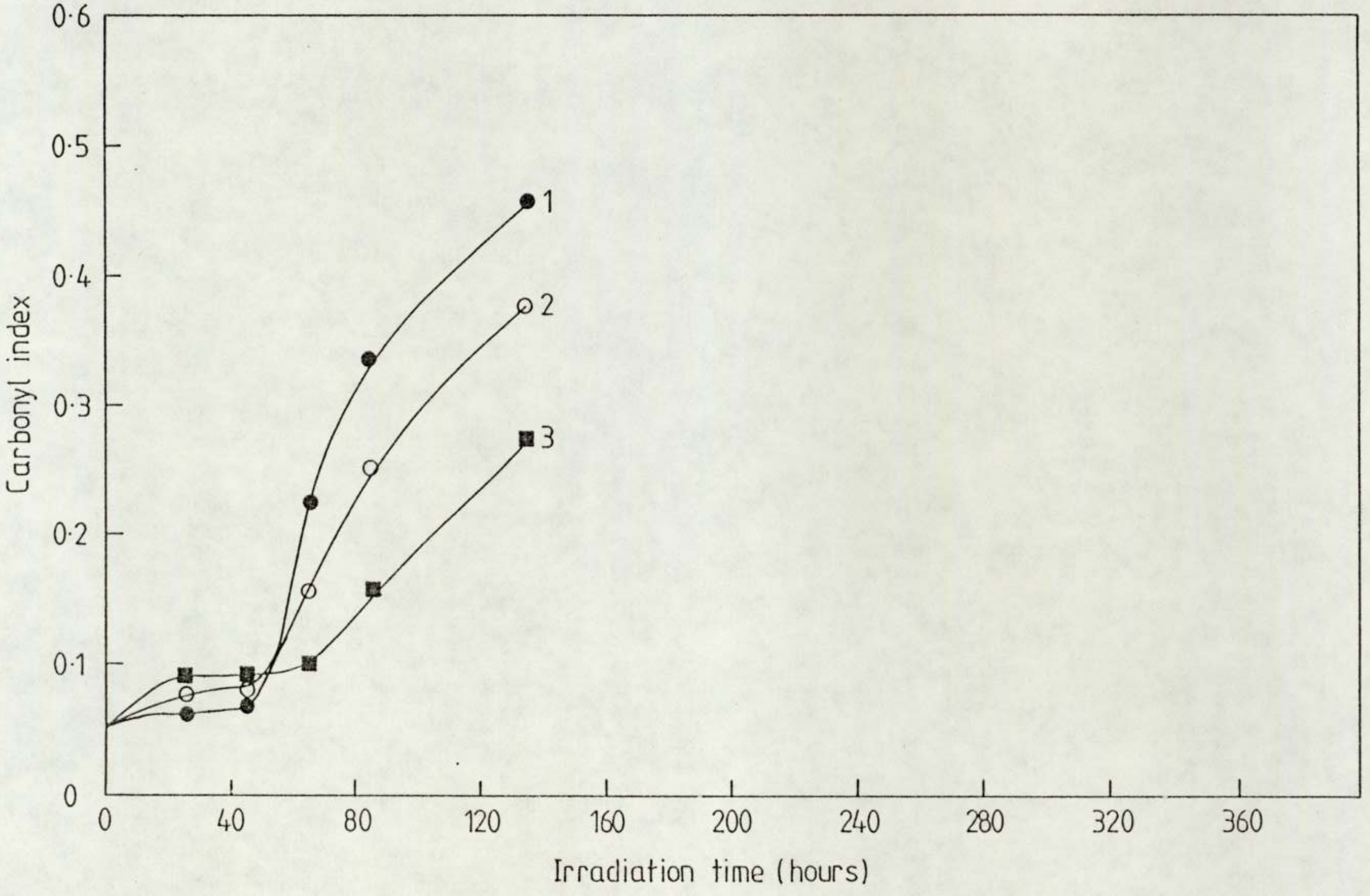


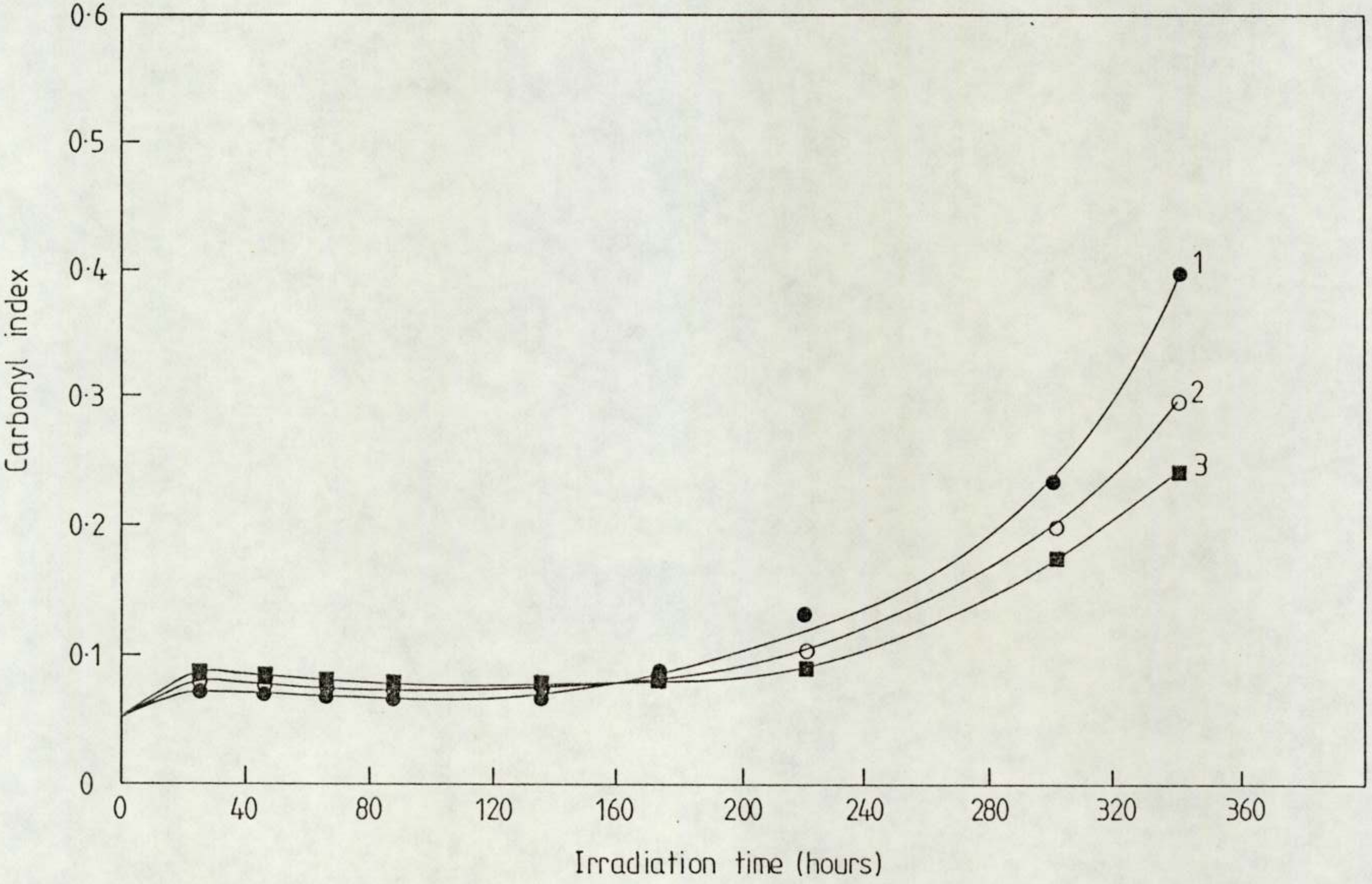
Figure 3.14 Effect of Te(didtc)$_4$ at various concentrations on photo-oxidation of PP (processed in a closed mixer at 180°C for 5 minutes) 1. 0.7x10^{-4}mole/100g 2. 1.4x10^{-4} mole/100g 3. 2.8x10^{-4} mole/100g



<u>Figure 3.15</u> Effect of Te(dbdtc)$_4$ at various concentrations on photo-oxidation of PP (processed in a closed mixer at 180°C for 5 minutes) 1. 0.7x10^{-4}mole/100g 2. 1.4x10^{-4} mole/100 g 3. 2.8x10^{-4} mole3100g

Sample	Concentration mole/100 g	Processing time (mins)	Embrittlement time (hrs)
Control		5	80
$Te(didtc)_4$	0.7×10^{-4}	5	160
	1.4×10^{-4}	5	270
	2.8×10^{-4}	5	340
$Te(didtc)_4$	0.7×10^{-4}	10	190
	1.4×10^{-4}	10	290
	2.8×10^{-4}	10	360
$Te(didtc)_4$	0.7×10^{-4}	20	220
	1.4×10^{-4}	20	310
	2.8×10^{-4}	20	395
$Te(dbdtc)_4$	0.7×10^{-4}	5	120
	1.4×10^{-4}	5	140
	2.8×10^{-4}	5	159
$Te(dbdtc)_4$	2.8×10^{-4}	10	185
$Te(dbdtc)_4$	2.8×10^{-4}	20	199

Table 3.3 Embrittlement time for PP with and without additives during photo-oxidation



<u>Figure 3.16</u> Effect of processing time at 180°C (closed mixer) on photo-oxidation of PP containing $2.8\text{x}10^{-4}$mole/100g of Te(didtc)_4 1. 5 minutes 2. 10 minutes 3. 20 minutes

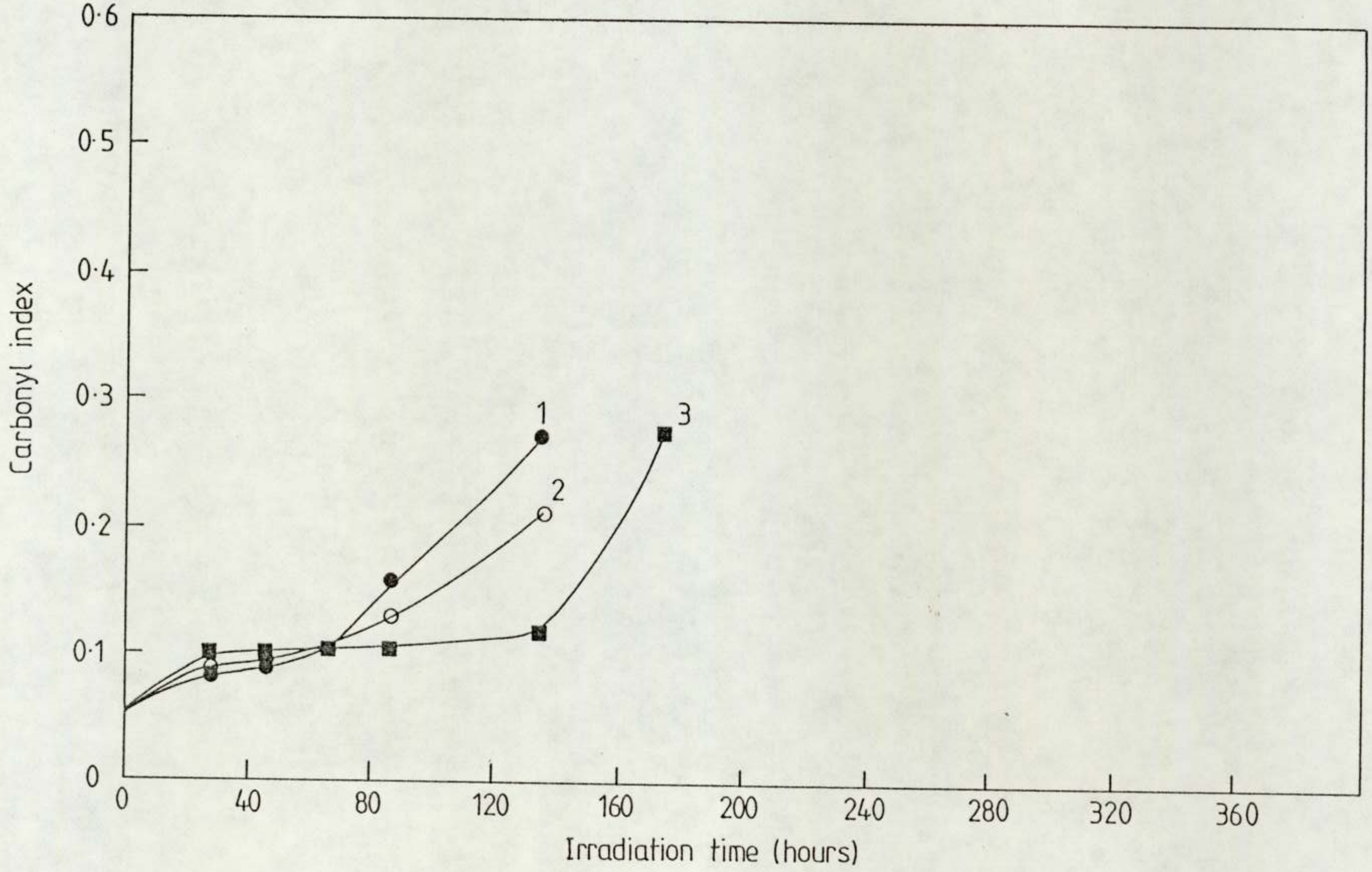
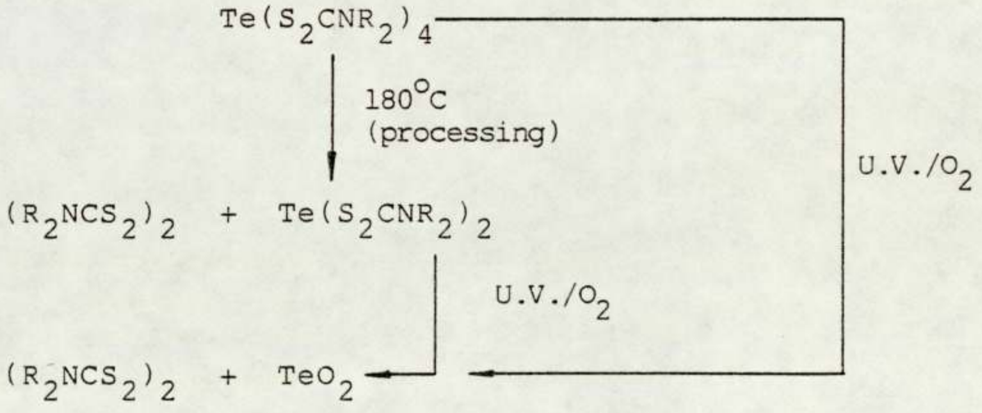


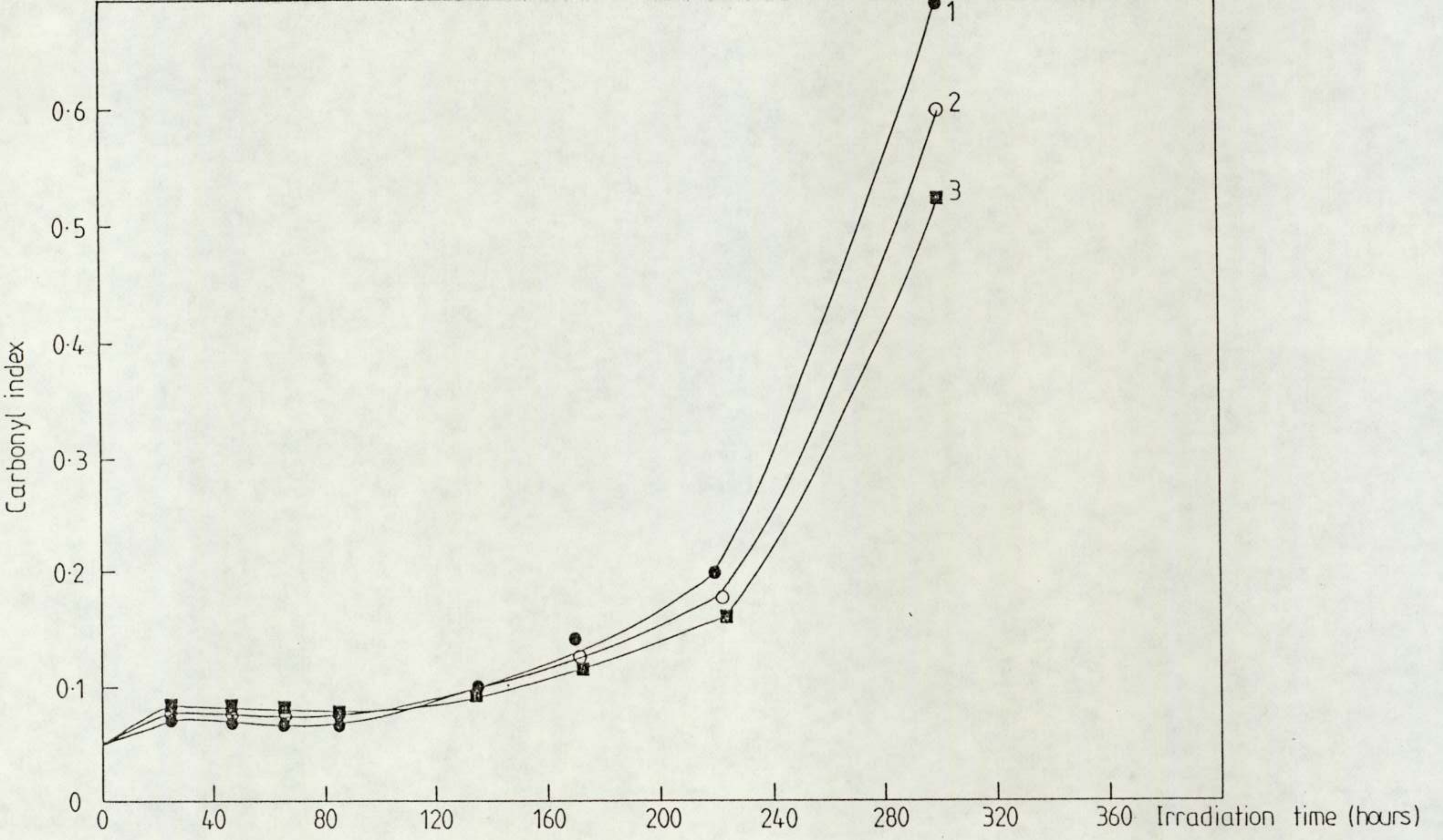
Figure 3.17 Effect of processing time at 180°C (closed mixer) on photo-oxidation of PP containing 2.8×10^{-4} mole/100g of $Te(dbdtc)_4$ 1. 5 minutes 2. 10 minutes 3. 20 minutes

mole/100 g of Te(didtc)$_4$ (Figures 3.18 and 3.19 respectively). The increase in the U.V. stability of PP and the initial pro-oxidant effect with increasing the processing time could be due to the formation of the disulphide(TRTD), from the decomposition of tetrakis(dialkyl)-dithiocarbamato)tellurium(IV) during processing at a temperature of 180°C$^{(14)}$.

The ability of tellurium dithiocarbamates as U.V. stabilisers during the photo-oxidation of PP may be due to the formation of disulphide, which has the ability to decompose the peroxide$^{(14)}$, as a result of the reaction of tellurium dithiocarbamate with dioxygen under U.V. irradiation (see Section 3.3.3):



Figures 3.20 and 3.21 show the effect of Te(didtc)$_4$ and Te(dbdtc)$_4$ respectively at different concentrations (0.7 x 10^{-4}, 1.4 x 10^{-4} and 2.8 x 10^{-4} mole/100 g) on the thermal oxidative stability of PP in a Wallace oven at 140°C. It appears, from the results, that as the



<u>Figure 3.18</u> Effect of processing at 180°C (closed mixer) on photo-oxidation of PP containing 1.4×10^{-4} mole/100g of $Te(didtc)_4$ 1. 5 minutes 2. 10 minutes 3. 20 minutes

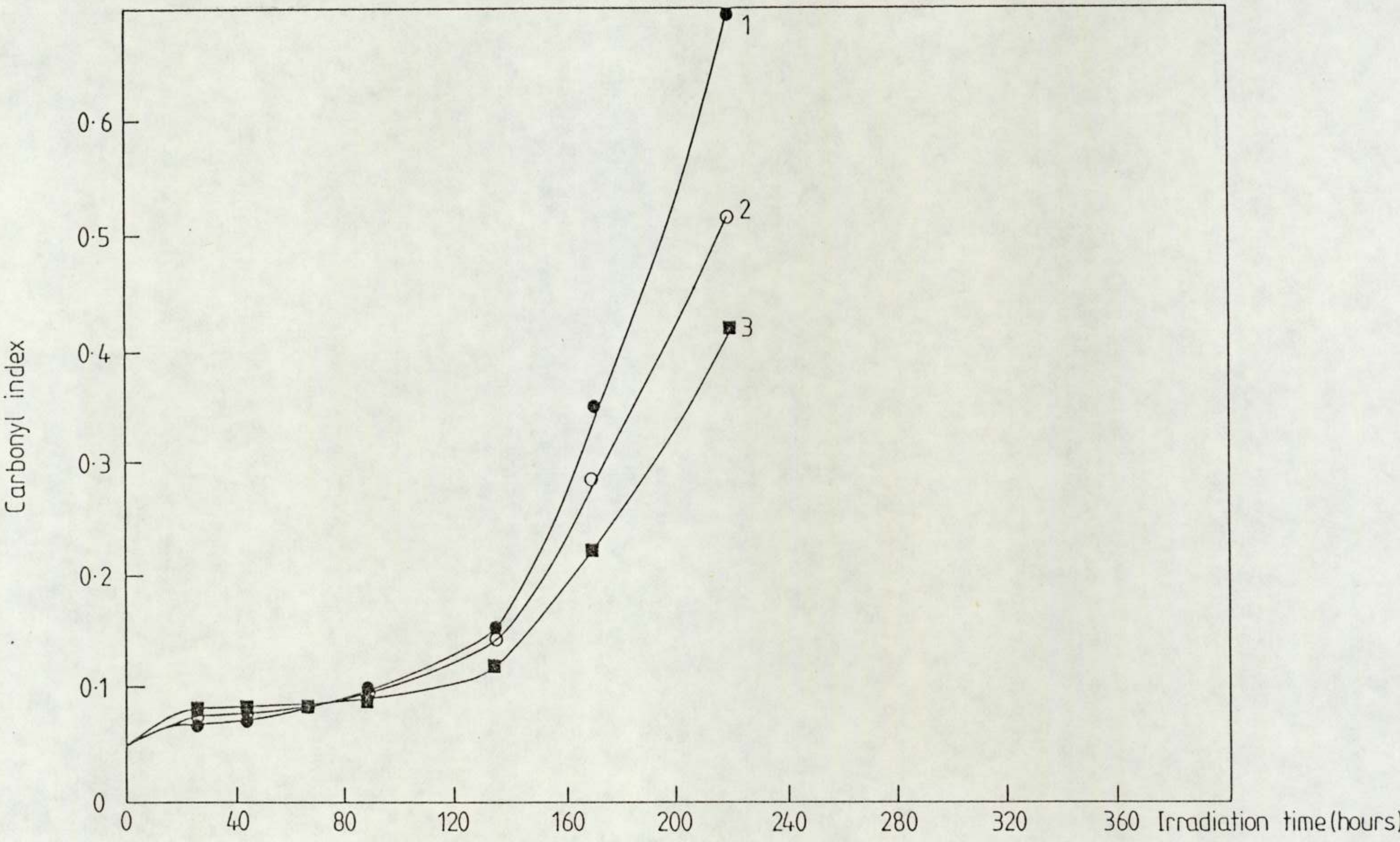
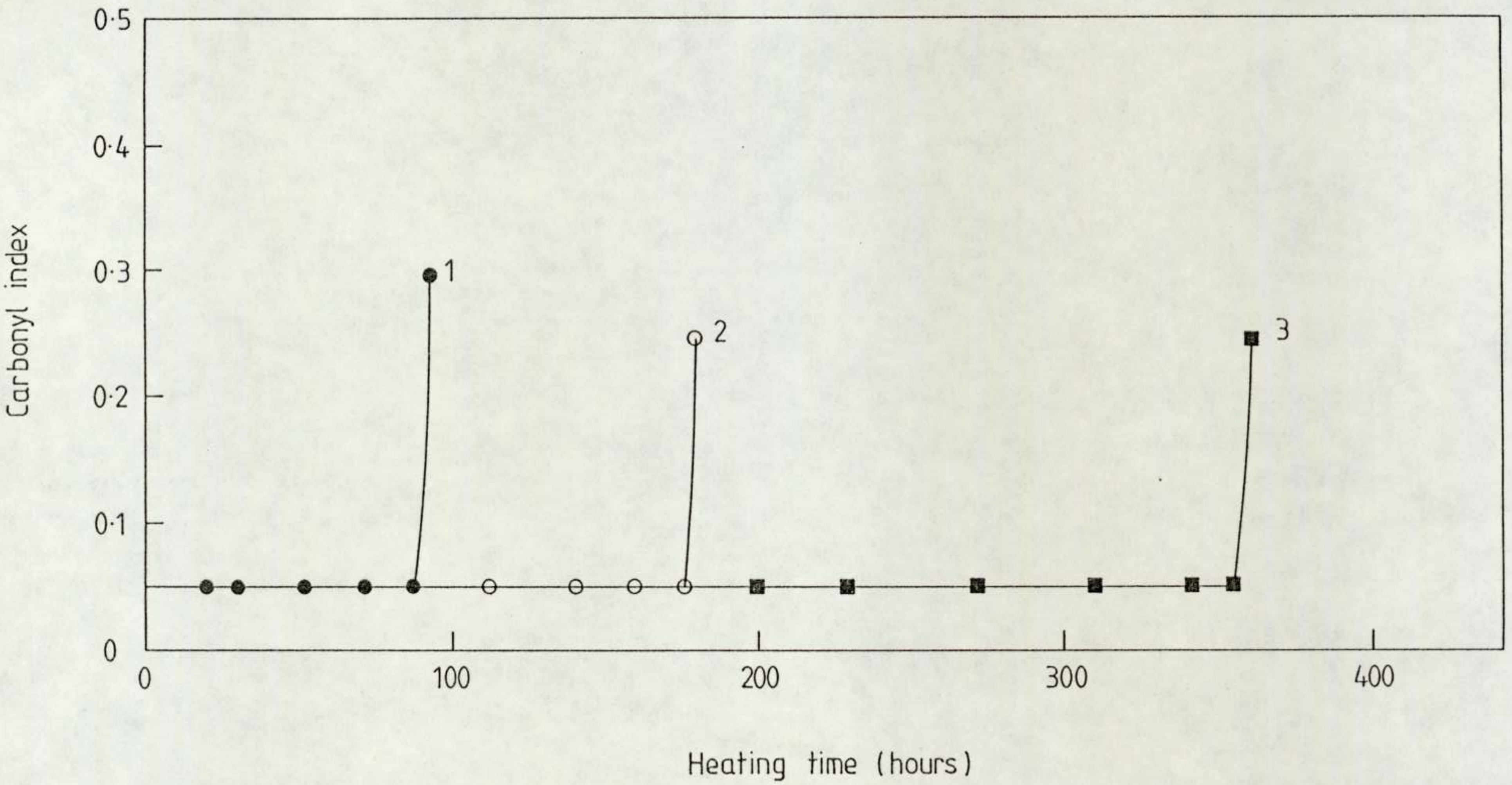


Figure 3.19 Effect of processing at 180°C (closed mixer) on photo-oxidation of PP containing 0.7×10^{-4} mole/100g of $Te(didtc)_4$ 1. 5 minutes 2. 10 minutes 3. 20 minutes



<u>Figure 3.20</u> Effect of Te(didtc)$_4$ at different concentrations on thermal-oxidation of PP at 140^{o}C processed for 5 minutes (closed mixer) 1. 0.7x10^{-4}mole/100g 2. 1.4x10^{-4} mole/100g 3. 2.8x10^{-4}mole/100g

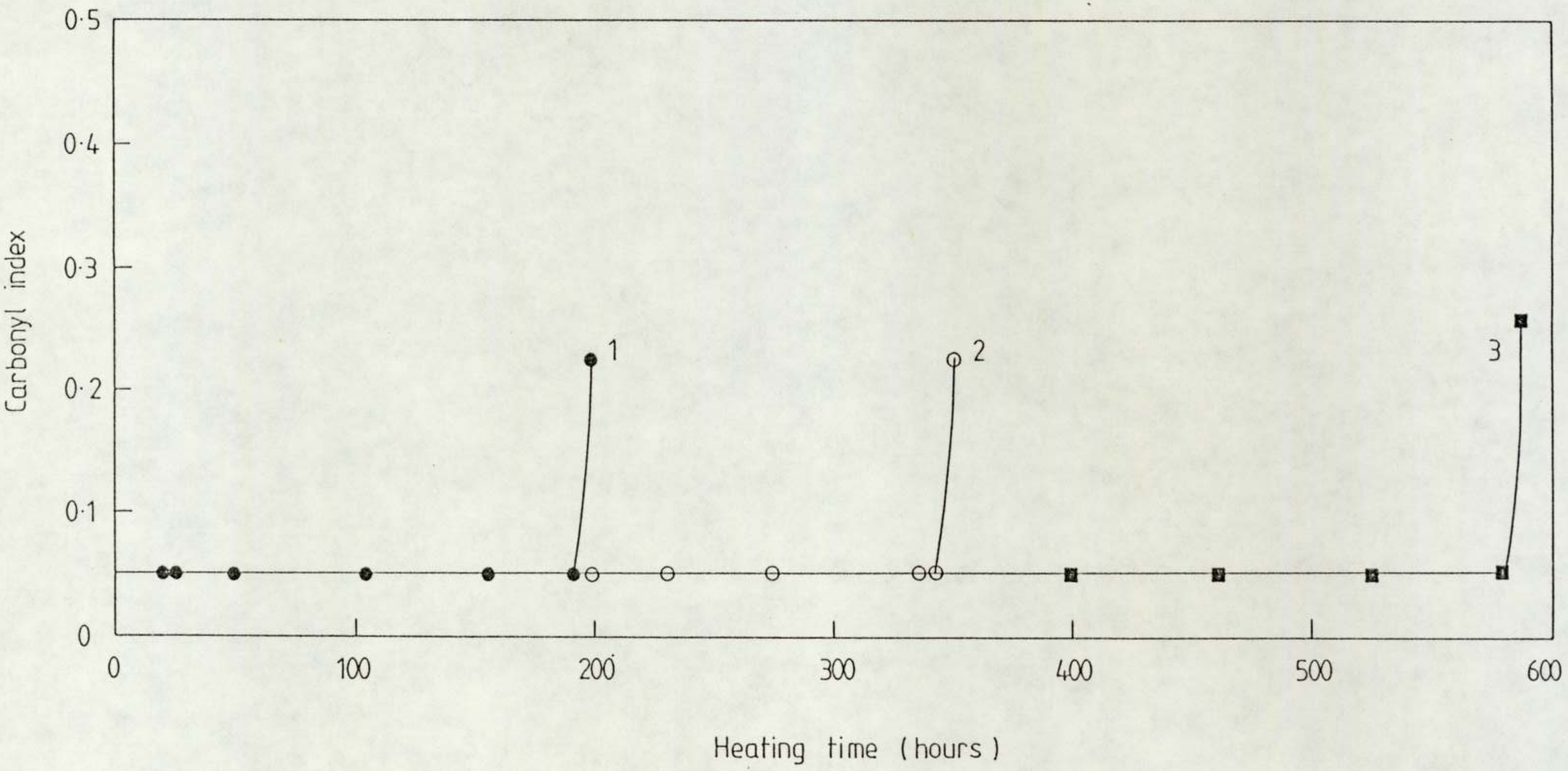


Figure 3.21 Effect of Te(dbdtc)$_4$ at different concentrations on thermal-oxidation of PP at 140°C processed for 5 minutes (closed mixer) 1. 0.7x10^{-4}mole/100g 2. 1.4x10^{-4}mole/100g 3. 2.8x10^{-4}mole/100g

concentration of the additives increases, the induction period increases e.g., $Te(didtc)_4$ and $Te(dbdtc)_4$ (2.8 x 10^{-4} mole/100 g) gave about 370 and 600 hours respectively.

$Te(dbdtc)_4$ was found to be a more effective thermal stabiliser than $Te(didtc)_4$. However, both compounds gave much better stability than $Te(dedtc)_4$(14); in the case of $Te(dbdtc)_4$ ∿10 times more effective than $Te(dedtc)_4$, a compound which was, at that time, better than zinc and nickel dithiocarbamates for thermal stabilisation. This could be due to the long alkyl substitutions, in the case of the new additives, which are presumably more compatible with the polymer than the shorter alkyl substitution as has been reported for metal dithiocarbamates (such as Zn and Ni)(63,64).

It is more likely that these two additives are involved in the same mechanisms for peroxide decomposition, during the thermal stabilisation of PP, as the $Te(dedtc)_4$(14).

From this study it can be concluded that, tetrakis(dialkyldithiocarbamato)tellurium(IV) exhibits better stabilising power for PP than bis(dialkyldithiocarbamato)zinc(II), but they were less efficient than bis(dialkyldithiocarbamato)nickel-(II) during photo-oxidation(62). However, they show much better stabilising action than bis(dialkyldithiocarbamato)-

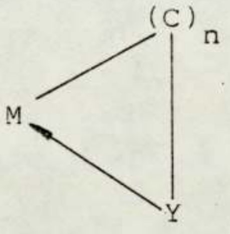
zinc(II) and bis(dialkyldithiocarbamato)nickel(II) during thermal oxidation(63).

CHAPTER FOUR

THE TELLURATION OF AZOBENZENE

4.0 Introduction

Organometallic intramolecular-coordination compounds are, in general, those which have at least one metal-carbon bond and at least one group forming an intramolecular coordination (i).



M=Metal
Y=Coordination atom or donor group
n=$\geq$ 1

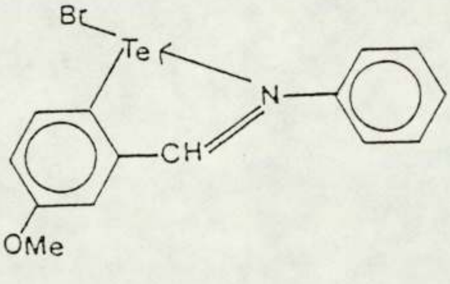
(i)

Introduction of built-in donors such as oxygen, nitrogen, phosphorous and sulphur, into the *ortho*-position of the aryl group in organometallic compounds has been shown to be a useful method of stabilizing organometallic compounds. The *ortho*-metallated complexes generally, form strain free five-membered ring structures. Recently, a large number of organometallic intramolecular-coordination compounds having the five-membered ring structure have been reported(34) and many five-membered chelate ring structures have also been confirmed subsequently by X-ray diffraction studies(34).

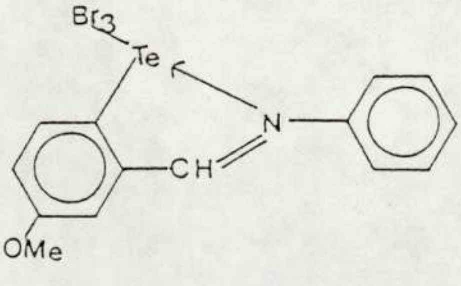
Azobenzene derivatives of transition metals have been known for some years. They are commonly prepared from the reaction between azobenzene itself and a metal compound(34,38,40,65).

The crystal and molecular structures for some of them have been studied and the existence of ring structures has been confirmed(34). The first metallation of azobenzene was in 1963. Kleiman and Dubeck reported that bis(cyclopentadienyl)-nickel reacted with azobenzene to produce η-cyclopentadienyl-2-(2-phenylazophenyl-C,N')nickel(40). A detailed review of the ortho-metallation reactions of transition metals(34) would be beyond the scope of the present study and therefore, will not be presented.

McWhinnie et al(36) reported the first examples of compounds in which azobenzene is ortho-metallated by tellurium(IV) and tellurium(II). The crystal and molecular structure of (2-phenylazophenyl-C,N')tellurium(II) chloride was described, which was, at the time one of the first compounds containing an intramolecular Te-N bond to be crystallographically characterised. As an extension to the previous work, another worker in the laboratory reported the tellurated derivatives of m-methoxybenzylideneaniline(ii) and (iii)(37).



(ii)



(iii)

We recently decided to extend the known range of tellurated azobenzenes, and to this end, (2-phenylazophenyl -C,N')-tellurium(IV) trichloride was required as a starting material. In new hands the original synthesis did not seem to proceed exactly as reported$^{(36)}$, hence it seemed sensible to probe the preparation more deeply and also to investigate further the possibility of the direct metallation of azobenzene with tellurium.

To establish beyond doubt that (2-phenylazophenyl-C,N')-tellurium(IV) trichloride had been prepared, the crystal and molecular structure was determined. This determination is timely in view of recent structural interest in organotellurium(IV) trihalides$^{(66-72)}$, and organotetrahalotellurates(IV)$^{(73)}$.

4.1 Experimental

4.1.1 Synthesis of (2-Phenylazophenyl-C.N')tellurium(IV) Trichloride$^{(36)}$

The synthesis was carried out, as reported previously$^{(36)}$, via a trans-metallation reaction with (2-phenylazophenyl-C,N')mercury(II) chloride$^{(38)}$. The reaction proceeded as reported by Musa$^{(74)}$ until the final stage, which involved formation of the orange product; his synthetic method being as follows: (2-phenylazophenyl-C.N')mercury(II) chloride (3.2 g. 7.7 m mole) and tellurium(IV) tetrachloride

(2.08 g, 7.7 m mole) were refluxed in dry dioxane (20 cm^3) for 6 hours under dry nitrogen. On cooling, the $HgCl_2$.(dioxane)$_2$ separated and was removed by filtration. The filtrate was concentrated on a rotary evaporator and nitromethane (20 cm^3) was added. Evaporation was taken to dryness which gave an orange product.

It was noted that the white crystals of $HgCl_2$.(dioxane)$_2$ were heavily contaminated with dark, almost black, well formed crystals of another substance which could be separated from the mercury complex by dissolution of the latter in methanol. The black material, which was orange-yellow when finely ground was pure $(C_{12}H_9N_2)TeCl_3$. Recrystallization of the orange product from nitromethane gave a mixture of orange and black crystals. Treatment with methanol left the black material (pure trichloride) and evaporation of methanol gave the orange product.

The orange product gave an analysis that was close to that expected for the trichloride, but the figures fluctuated over a few percent from preparation to preparation. However reduction of both the orange and black materials with hydrazine(36) gave pure (2-phenylazophenyl-C,N')tellurium(II) chloride, m.p. 125°C. The literature m.p. was 80°C but the discrepancy is not as worrying as may appear since others have informed us that a crystallographically characterized polymorphous form of this material exists(75), and the earlier sample has also been crystallographically characterized.

We believe that the orange material is essentially (2-phenylazophenyl-C,N')tellurium(IV) trichloride which is slightly contaminated with the rather soluble (2-phenylazophenyl-C,N')mercury(II) chloride. This would explain the fluctuating analysis, the fact that the m.p. reported by Musa was 235°C as opposed to 244-245°C for the black material; also the chemical behaviour on hydrazine reduction.

Given the identification of these problems, it seemed desirable to confirm the identity of (2-phenylazophenyl-C,N')tellurium(IV) trichloride by ^{13}C NMR and X-ray crystallographic studies.

Found: C,35.0; H,2.00; N,6.75; Cl,25.1% $C_{12}H_9Cl_3N_2Te$
Requires:C,34.7; H,2.17; N,6.75; Cl,25.7%

4.1.2 (2-Phenylazophenyl-C,N')tellurium(IV) Trichloride by Direct Reaction of Azobenzene and Tellurium Tetrachloride

Tellurium tetrachloride (5.39 g, 0.02 mol) and azobenzene (21.84 g, 0.12 mol) were heated together under dinitrogen, the temperature of the stirred mixture being maintained in the range 135°-150°C. When evolution of HCl ceased, the mixture was cooled to <100°C and methanol was added to dissolve excess azobenzene. The precipitate was then washed with methanol until colourless washings were obtained. The precipitate was shown by analysis and ^{13}C NMR to be $(C_{12}H_9N_2)TeCl_3$. Yield 40%.

Found: C,34.6; H,2.10; N,6.85; Cl,25.9%

4.1.3 Bis(2-phenylazophenyl-C,N')ditelluride

Hydrazine hydrate (1.9 g,0.038 mol) in ethanol (8 cm^3) was added very slowly to a refluxing mixture of (2-phenylazophenyl-C,N')tellurium(IV) trichloride (2.08 g, 0.005 mol) and ethanol (38 cm^3). Initially, each addition was accompanied by the vigorous evolution of dinitrogen and the trichloride gradually dissolved. On completing the addition, and when no further dinitrogen was evolved, the mixture was cooled to 0°C to give a golden brown precipitate which was filtered, washed with methanol and dried in a vacuum dessicator to m.p. 134°C. Yield 65-70%.

Found: C,46.7; H,2.90; N,8.85% $C_{24}H_{18}N_4Te_2$
Requires:C,46.7; H,2.92; N,9.07%

4.2.0 Results and Discussion

The preparation of (2-phenylazophenyl-C,N')tellurium(IV) trichloride by trans-metallation is slightly more complex than had previously seemed to be the case(36) (see Section 4.1.1).

The title compound has been described by Musa$^{(74)}$ as orange crystals, m.p. 235°C being soluble in methanol, chloroform etc. It was noted that (2-phenylazophenyl-C,N')tellurium(IV) trichloride is nearly yellow or orange-yellow when finely ground, its m.p. is 244-245°C and it is insoluble in methanol and moderately soluble in chloroform, acetonitrile and benzene. The discrepancy is not as worrying as may appear since it was confirmed that the orange product is essentially $(C_{12}H_9N_2)TeCl_3$ which is contaminated with the rather soluble $(C_{12}H_9N_2)HgCl$ (see Section 4.1.1).

The I.R. spectrum of the pure $(C_{12}H_9N_2)TeCl_3$ was identical to that previously reported$^{(74)}$.

4.2.1 X-ray Structure Analysis of (2-Phenylazophenyl-C,N')-tellurium(IV) Trichloride

After preliminary examination by photographic methods, the final cell dimensions and reflection intensities were measured with graphite-monochromated Mo-Kα radiation on an Enraf-Nonius CAD-4 diffractometer operating in the ω-2θ scan mode, 2640 reflections were scanned in the range $2<\theta<25°$. Two standard reflections remeasured every 2 hours showed no significant variation. Lorentz and polarisation factors were applied; 2289 unique reflections $[F>5\sigma(F)]$ were observed and used in the structure analysis.

4.2.2 Crystal Data

$C_{12}H_9N_2TeCl_3$

M = 415.1

Triclinic, space group $P\bar{1}$

$\underline{a} = 8.734(2)Å$, $\underline{b} = 9.219(3)Å$, $\underline{c} = 10.363(3)Å$

$\alpha = 113.75(2)^\circ$, $\beta = 91.20(2)^\circ$, $\gamma = 109.26(2)^\circ$

$\underline{V} = 709.49A^3$, $Z = 2$

$D_m = 1.93\ g\ cm^{-3}$ (by flotation in bromoform/carbon tetrachloride), $D_c = 1.945\ g\ cm^{-3}$

$F(000) = 396$, $\mu(M_o\text{-}K_\alpha,\ \lambda = 0.71069Å)\ 2.48\ mm^{-1}$

The structure was solved by Patterson and Fourier methods. Following least squares refinement, first with isotropic temperature factors and then anisotropically, hydrogen atoms were located from a difference map but not refined. The calculations were terminated when all shifts were less than 0.10σ and R and R_w 0.0506 and 0.0674 respectively with $w = 1/[\sigma^2(F) + 0.005F^2]$.

Computations were carried out on the Honeywell computer at the University of Birmingham and on the CDC 7600 computer at the University of Manchester Regional Computer Centre, largely with SHELX(50) program. Atomic co-ordinates are given in Table 4.1. Bond distances, angles and torsion angles are given in Table 4.2. Table 4.3 gives deviations of atoms from mean planes.

Atom	X	Y	Z
Te(1)	0.22689(3)	0.14123(3)	0.24503(3)
Cl(1)	0.1919(2)	0.2286(2)	0.4990(1)
Cl(2)	0.2825(2)	0.0273(2)	-0.0040(2)
Cl(3)	0.3487(2)	0.4314(2)	0.2771(2)
N(1)	0.1775(5)	-0.1393(5)	0.2302(4)
N(2)	0.3036(5)	-0.1642(6)	0.2604(4)
C(1)	0.4510(6)	-0.0173(7)	0.3059(5)
C(2)	0.4553(6)	0.1373(7)	0.3118(5)
C(3)	0.5998(7)	0.2773(8)	0.3607(6)
C(4)	0.7436(7)	0.2578(9)	0.4036(6)
C(5)	0.7392(7)	0.1057(10)	0.3973(6)
C(6)	0.5917(7)	-0.0378(9)	0.3458(6)
C(7)	0.0237(6)	-0.2803(6)	0.1875(5)
C(8)	-0.1129(7)	-0.2560(7)	0.1420(6)
C(9)	-0.2640(7)	-0.3916(9)	0.0954(7)
C(10)	-0.2782(8)	-0.5426(8)	0.0961(6)
C(11)	-0.1412(9)	-0.5621(8)	0.1449(7)
C(12)	0.0136(7)	-0.4301(7)	0.1896(1)
H(3)	0.6003	0.3999	0.3726
H(4)	0.8587	0.3702	0.4486
H(5)	0.8366	0.0832	0.4235
H(6)	0.5877	-0.1625	0.3359
H(8)	-0.0992	-0.1397	0.1460
H(9)	-0.3612	-0.3639	0.0653
H(10)	-0.3830	-0.6510	0.0539
H(11)	-0.1401	-0.6764	0.1400
H(12)	0.1277	-0.4457	0.2251

Table 4.1 Fractional atomic co-ordinates with standard deviations in parentheses

Te-Cl(1)	2.483(1)	C(6)-C(1)	1.382(7)
Te-Cl(2)	2.491(1)	C(1)-N(2)	1.423(7)
Te-Cl(3)	2.406(2)	N(2)-N(1)	1.255(6)
Te-N(1)	2.417(4)	N(1)-C(7)	1.431(7)
Te-C(2)	2.114(5)	C(7)-C(8)	1.390(8)
C(1)-C(2)	1.390(8)	C(8)-C(9)	1.392(8)
C(2)-C(3)	1.374(8)	C(9)-C(10)	1.359(11)
C(3)-C(4)	1.413(9)	C(10)-C(11)	1.382(11)
C(4)-C(5)	1.365(11)	C(11)-C(12)	1.399(8)
C(5)-C(6)	1.405(9)	C(12)-C(7)	1.363(8)
Cl(1)-Te-Cl(2)	171.7(1)	C(5)-C(6)-C(1)	117.4(6)
Cl(1)-Te-Cl(3)	93.0(1)	C(6)-C(1)-C(2)	121.7(5)
Cl(2)-Te-Cl(3)	92.3(1)	C(6)-C(1)-N(2)	115.3(5)
N(1)-Te-Cl(1)	87.0(1)	C(2)-C(1)-N(2)	123.1(4)
N(1)-Te-Cl(2)	86.3(1)	C(1)-N(2)-N(1)	113.6(5)
N(1)-Te-Cl(3)	165.2(1)	N(2)-N(1)-Te	115.3(3)
C(2)-Te-Cl(1)	86.3(1)	C(7)-N(1)-Te	128.0(3)
C(2)-Te-Cl(2)	87.0(1)	C(7)-N(1)-N(2)	116.7(5)
C(2)-Te-Cl(3)	92.9(1)	C(8)-C(7)-N(1)	116.1(5)
C(2)-Te-N(1)	72.3(2)	C(12)-C(7)-N(1)	121.5(5)
C(1)-C(2)-C(3)	121.0(5)	C(12)-C(7)-C(8)	122.4(5)
C(1)-C(2)-Te	115.6(4)	C(9)-C(8)-C(7)	118.0(6)
Te-C(2)-C(3)	123.4(4)	C(10)-C(9)-C(8)	121.0(7)
C(2)-C(3)-C(4)	117.6(6)	C(11)-C(10)-C(9)	119.8(6)
C(3)-C(4)-C(5)	121.3(6)	C(12)-C(11)-C(10)	120.8(6)
C(4)-C(5)-C(6)	121.0(5)	C(11)-C(12)-C(7)	117.9(6)
C(2)-C(1)-N(2)-N(1)	- 2.0(7)		
C(7)-N(1)-N(2)-C(1)	-178.1(7)		
C(6)-C(1)-N(2)-N(1)	177.3(7)		
N(2)-N(1)-C(7)-C(12)	4.3(7)		
N(2)-N(1)-C(7)-C(8)	-174.1(7)		

Table 4.2 Bond distances (Å), angles (°) and torsion angles

P_1 Plane defined by N(1),N(2),C(1),C(2),C(3),C(4),C(5),C(6),C(7),C(8), C(9),C(10),C(11) and C(12).

P_2 Plane defined by Te,N(1),C(2) and Cl(3).

P_3 Plane defined by Te,N(1),N(2),C(1) and C(2)

Atom	P_1	P_2	P_3
Te	0.00953	-0.01224	-0.01480
Cl(1)	2.48460	2.48714	2.46437
Cl(2)	-2.47564	-2.47323	-2.49504
Cl(3)	-0.01807	-0.00704	-0.08198
N(1)	-0.00267	-0.00735	0.02313
N(2)	-0.07279	-0.07687	-0.01982
C(1)	-0.05225	-0.05137	-0.00346
C(2)	-0.00257	0.00214	0.01495
C(3)	0.05785	0.06730	0.07261
C(4)	0.05817	0.06845	0.10294
C(5)	0.00535	0.01187	0.08082
C(6)	-0.07139	-0.06971	0.00684
C(7)	0.02074	0.01115	0.04883
C(8)	-0.02352	-0.03372	-0.02568
C(9)	-0.04394	-0.05887	-0.04498
C(10)	-0.00463	-0.02345	0.02410
C(11)	0.06988	0.05176	0.12828
C(12)	0.06177	0.04834	0.12012

Table 4.3 Deviations of atoms (Å) from mean planes

4.2.3 The Crystal and Molecular Structure of (2-Phenylazophenyl-C,N')tellurium(IV) Trichloride

The structure of the complex and the atom numbering are shown in Figure 4.1; the stereoscopic packing diagram is shown in Figure 4.2. The co-ordination about tellurium can be considered as essentially octahedral with a lone pair of electrons occupying the fourth equatorial site. The whole molecule apart from the apical chlorine atoms, Cl(1) and Cl(2), is planar to within ± 0.07Å. Cl(1) and Cl(2) lie 2.48Å on either side of the molecular plane. The organic ligand's deviation from planarity is illustrated by the torsion angles listed in Table 4.2, the major component being a twist of ca. 5° of the free phenyl ring around C(7)-N(1).

The distortions of the co-ordination geometry from ideal octahedral values, particularly N(1)-Te-Cl(3) (165.2°) can be explained from the view of a lone pair of electrons occupying an equatorial position between N(1) and Cl(3). The small value of the angle N(1)-Te-C(2) (72.3°) and somewhat large value of the angle Cl(3)-Te-C(2) (92.9°) are due to constraints arising from the five-membered chelate ring. The axial atoms are displaced away from the lone pair electrons reducing the Cl(2)-Te-Cl(1) angle to 171.7° from an ideal value of 180°.

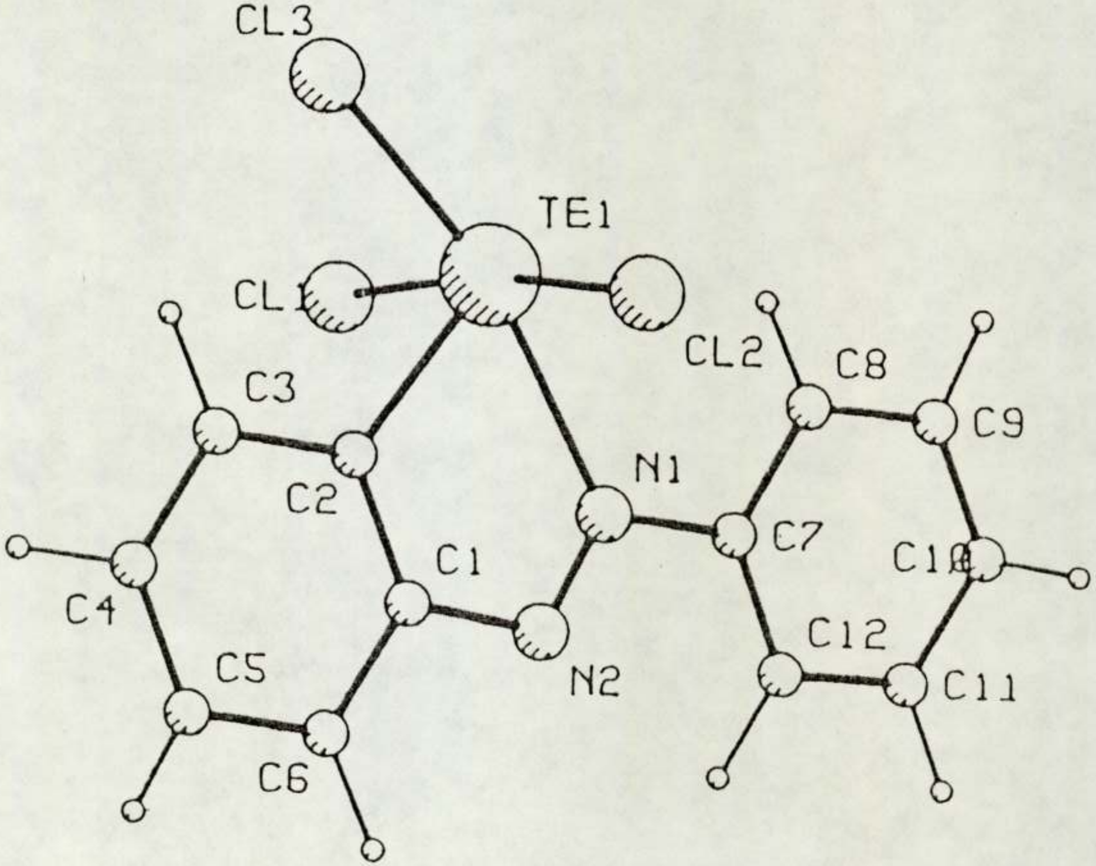
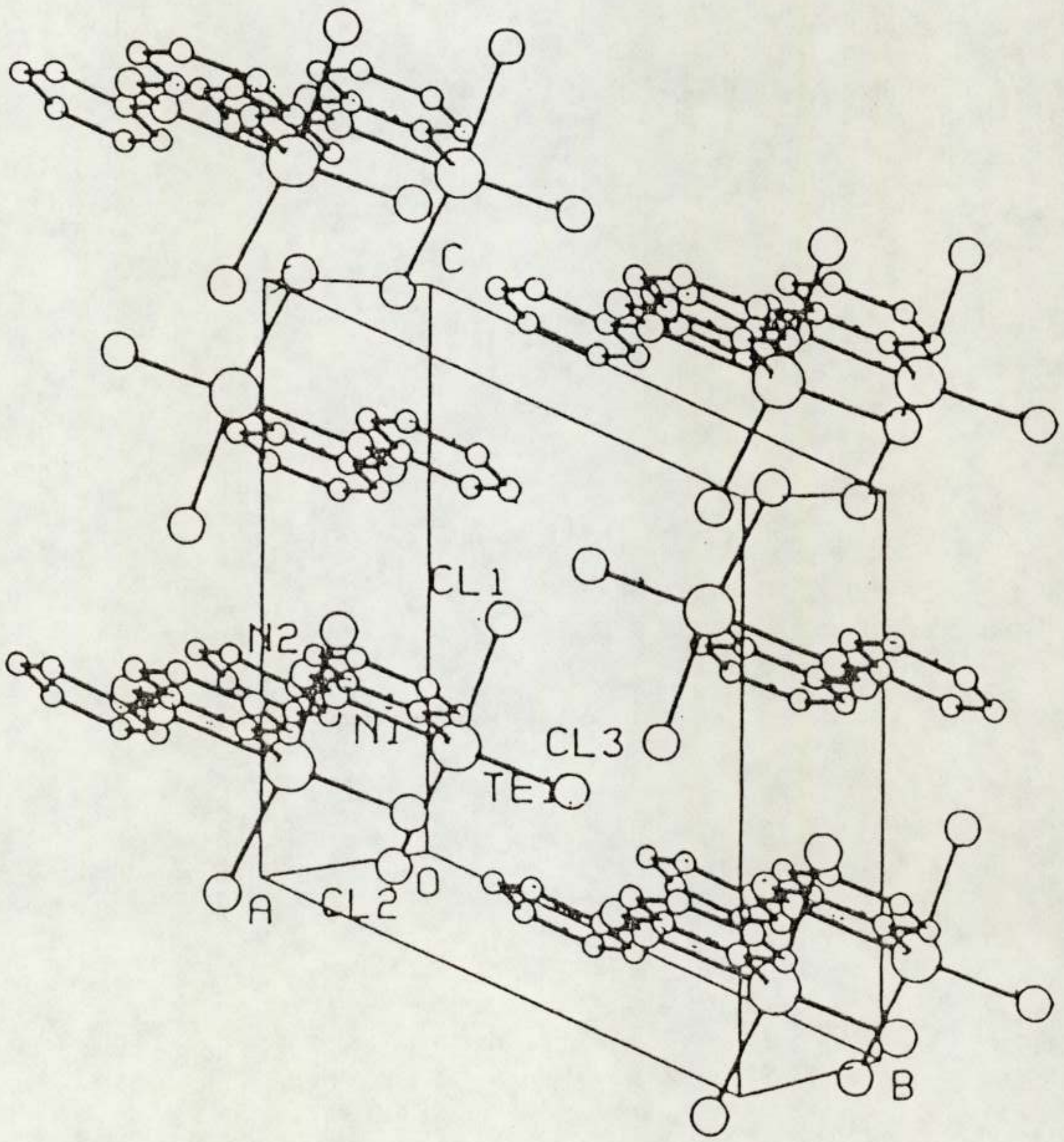


Figure 4.1 The structure of $(C_{12}H_9N_2)TeCl_3$ showing the atom numbering



<u>Figure 4.2</u> Stereoscopic packing diagram of $(C_{12}H_9N_2)TeCl_3$

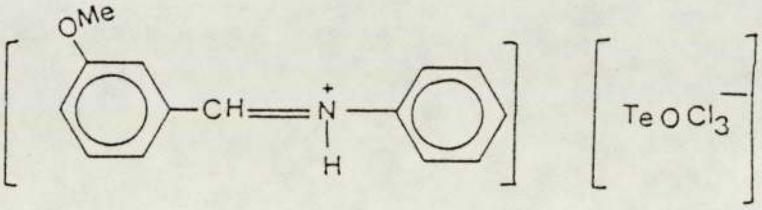
The distance Te-C(2) (2.114Å) is in good agreement with the sum of the Pauling(76) single bond covalent radii of Te (1.37Å) and sp^2-hybridised carbon (0.74Å), and with values in the crystal structures of the analogous compounds, $\mathrm{PhTeCl_3}$(72.77), [4-$\mathrm{EtOPhTeCl_3}$(78) and $\mathrm{(C_7H_7O)_2TeCl_2}$(79), which fall in the range 2.09-2.13Å. The Te-N distance (2.417Å) is much larger than the sum of the covalent radii (2.07Å)(76), but is close to the value in the crystal structure of $\mathrm{(C_9H_8NO_2)TeCl_3}$ (2.402Å)(71), however it is much shorter than the sum of the van der Waals radii of Te and N (3.70Å) according to Pauling(76) or (3.61Å) according to Bondi(80). The Te-Cl distances (2.406Å equatorial, 2.483 and 2.491Å axial) are longer than the sum of covalent radii (2.36Å)(76) or the Te-Cl distance in $\mathrm{TeCl_4}$, mean 2.311Å(81) but agree well with values commonly found for analogous compounds(69,71). These lengths are, however, very much shorter than the sum of the van der Waals radii of Te and Cl (4.00Å) according to Pauling(76), or (3.81Å) according to Bondi(80), and the Te-Cl bonds can be considered to be essentially covalent in nature. The title compound is monomeric. There are no Te....Cl or Cl....Cl intermolecular contact distances less than the sum of the van der Waals radii. In this respect, it is similar to the monomeric 2,6-diacetylpyridine(C,N,O)tellurium(IV) trichloride(71), where, however, the organic ligand is tridentate, unlike the bidentate nature of the ligand in the title compound. In 4-oxo-2-methylpent-2-en-1-yl tellurium(IV) trichloride(82) and 8-ethoxy-4-cyclooctenyltellurium(IV) trichloride(69) some association through weak secondary interactions occurs with Te....Cl=3.74 and Te....O=3.30Å in the former and Te....Cl=3.56Å in the latter. In three other structures $PhTeCl_3$(72,77), $4\text{-}EtOPhTeCl_3$(78) and $ClCH_2CH_2TeCl_3$(83). association into polymers by relatively strong covalent-type Te-Cl-Te linkages takes place with Te-Cl(bridging) bond lengths in the range 2.72-2.77Å.

4.2.4 *Ortho*-telluration of Azobenzene by Direct Reaction of Azobenzene and Tellurium(IV) Tetrachloride

After the successful synthesis and characterization of the pure (2-phenylazophenyl-C,N')tellurium(IV) trichloride via a *trans*-metallation, the direct reaction between tellurium (IV) tetrachloride and azobenzene was attempted.

Musa(74), attempted the direct telluration of azobenzene, but his attempt was unsuccessful. Other workers(37,84) in the laboratory, also attempted the direct telluration of some typical Schiff bases by tellurium(IV) tetrachloride and found that the reaction gave only ionic compounds containing the protonated bases (iv).

Although many reactions of $TeCl_4$ with aromatic compounds are believed to involve the electrophile $(TeCl_3)^+$, it was surprising that the direct telluration of azobenzene was



(iv)

not observed(74). We find that, by using more forcing conditions (135-150°) for the reaction of $TeCl_4$ with molten azobenzene under dinitrogen that the tellurated compound is formed in moderate yield. The material produced by this route gave m.p., I.R. and ^{13}C NMR spectra identical with those obtained for the material produced via trans-metallation.

In fact, the low m.p. of azobenzene and high m.p. of (2-phenylazophenyl-C,N')tellurium(IV) trichloride prompted us to react them by heating a mixture of the two, using excess of azobenzene to act as a solvent when finally melted. When the temperature is raised, it is noted that at >135°C. HCl is evolved. The HCl was identified qualitatively using NH_3 and pH paper as indicators. Also the completion of HCl evolution was taken as indicating the end of the reaction. As mentioned before (Section 4.2.0), the (2-phenylazophenyl-C,N')tellurium(IV) trichloride is nearly insoluble in methanol whereas azobenzene is soluble. Therefore, methanol was used to separate the trichloride (insoluble) from unreacted azobenzene and any ionic compounds (byproducts), if any.

4.2.5 ^{13}C NMR Spectra

^{13}C NMR spectra were determined using a Jeol FX-90Q Fourier transform multi-nuclear magnetic resonance spectrometer operating on 22.5 MHz. Solvent$^{(37)}$ was used as internal standard. The normal operating temperature was ca. 290°K and a pulse width of 12 μsec and repetition rate of 2 seconds were used. The spectral width was approximately 10.00 Hz. The ^{13}C NMR spectra of azobenzene, $(C_{12}H_9N_2)HgCl$ and $(C_{12}H_9N_2)TeCl_3$ are shown in Figures 4.3-4.5. The products from trans-metallation and from the direct telluration of azobenzene gave identical ^{13}C NMR spectra. The ^{13}C NMR data are given in Table 4.4 and nicely illustrate the telluration. Spectra of azobenzene and $(C_{12}H_9N_2)HgCl$ are included for comparison. The greater solubility of the mercury compound allowed observation of the coupling constant between ^{199}Hg-^{13}C (2333 Hz) atoms, measured using ^{13}C resonances and observing the ^{199}Hg satellites, but the one bond coupling to ^{125}Te could not be extracted from the random noise. Recently Singh$^{(37)}$ reported ^{13}C NMR for some mercurated Schiff bases, $(C_{12}H_9N_2)HgCl$ and azobenzene. The ^{13}C NMR spectra for the latter two compounds were

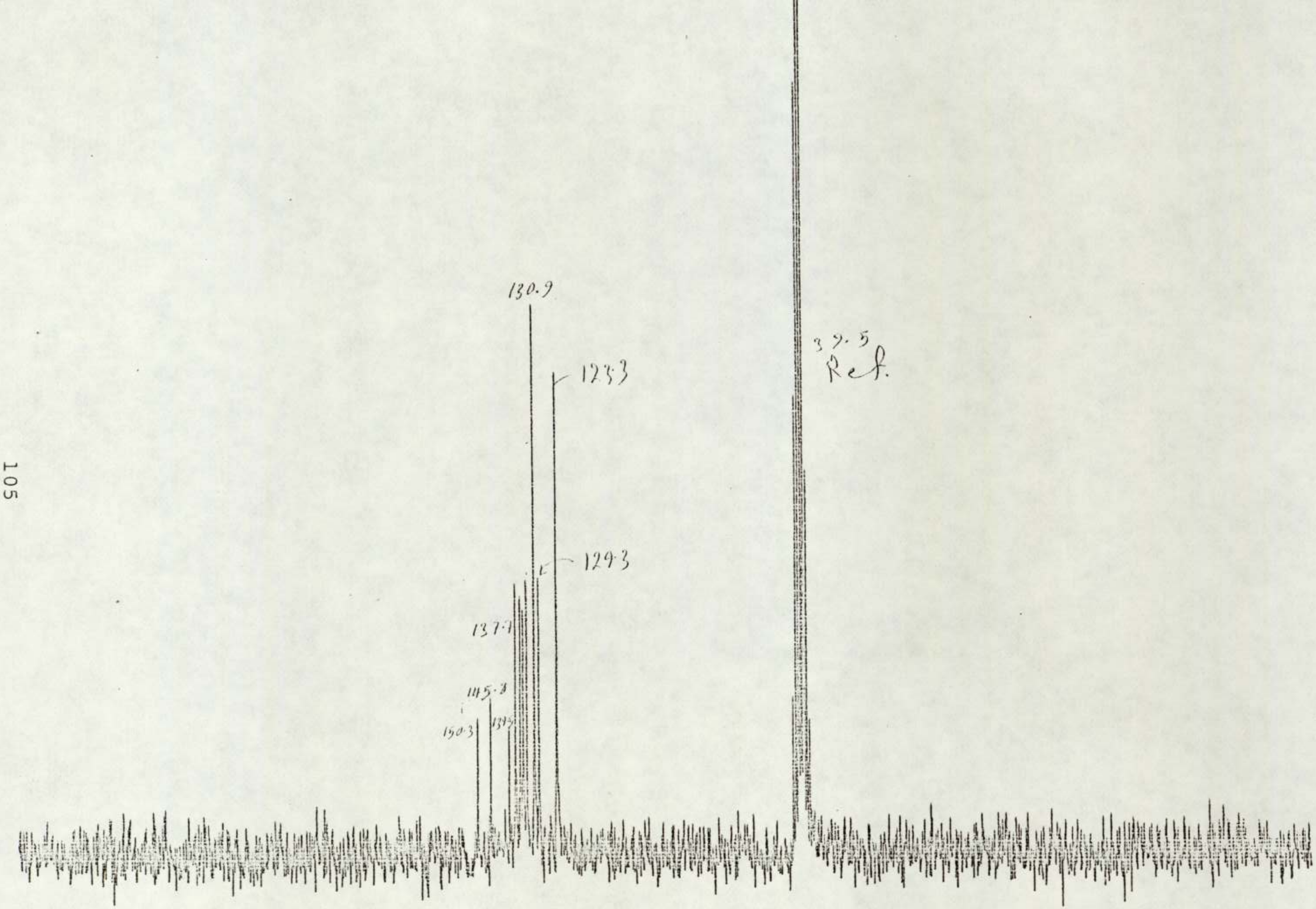


Figure 4.3 ^{13}C N.M.R. spectrum of (2-phenylazophenyl-C,N')tellurium(IV) trichloride

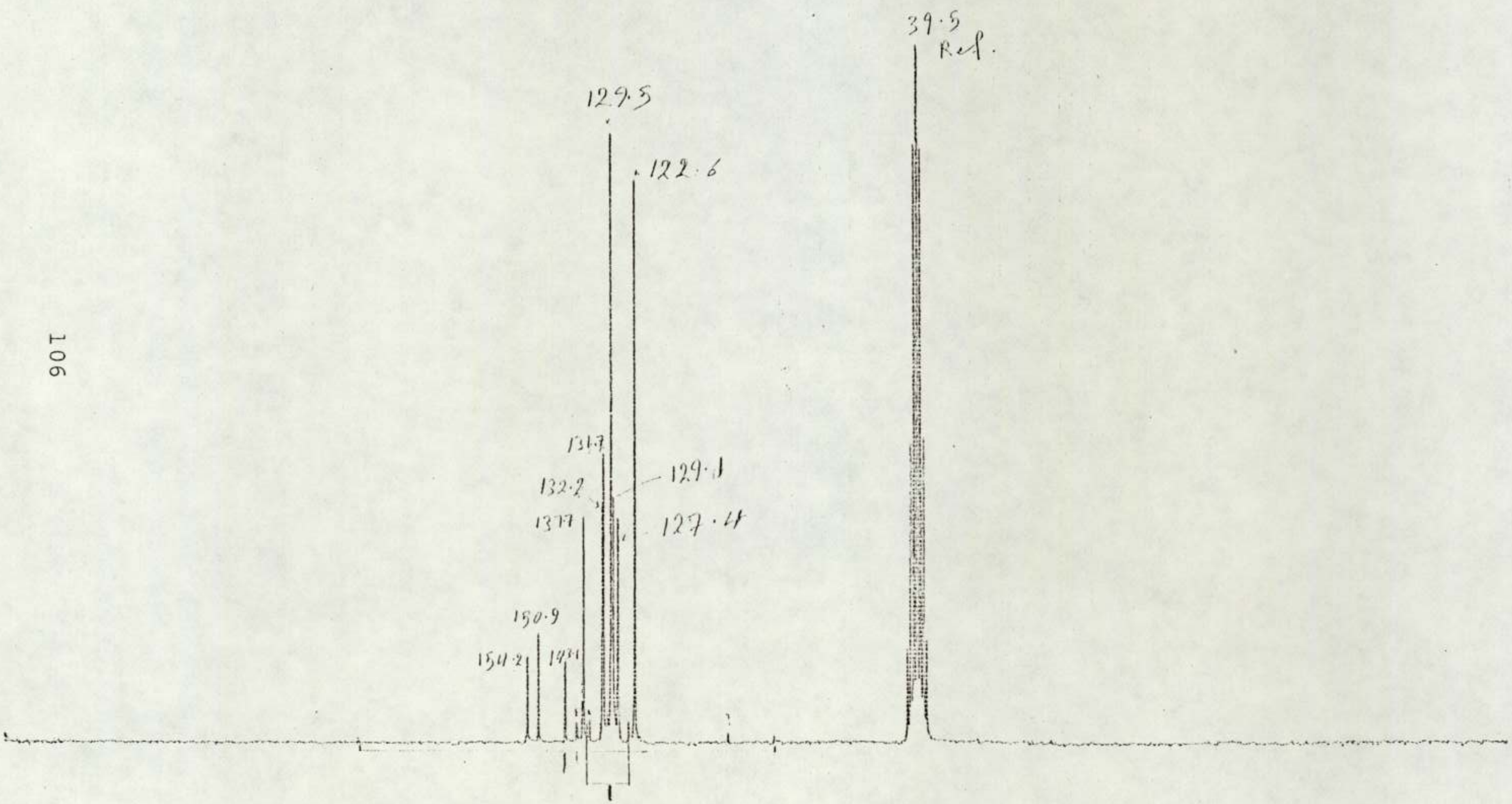


Figure 4.4 ^{13}C N.M.R. spectrum of (2-phenylazophenyl-C,N')mercury(II) chloride

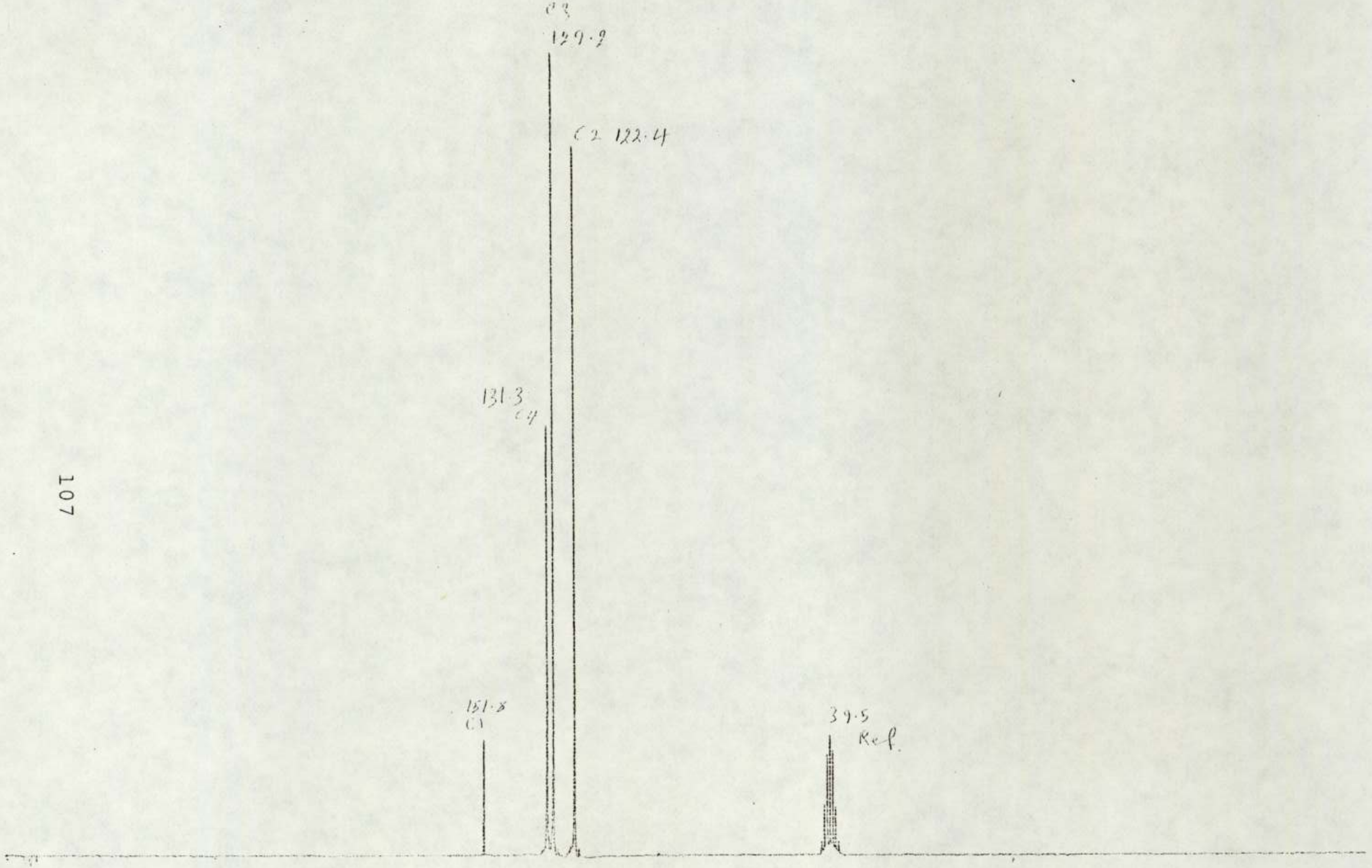
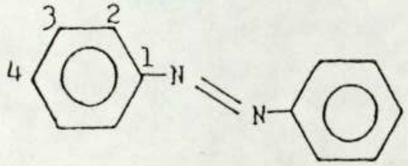
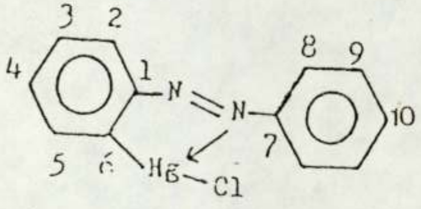
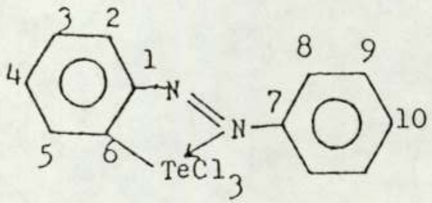


Figure 4.5 ^{13}C N.M.R. spectrum of azobenzene

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
	151.8	122.4	129.2	131.3						
	154.2*	122.6	129.1	131.7	137.7	143.1	150.9	127.4	129.5	132.2
	150.3	123.3	130.9	134.8	137.2	139.5	145.8	129.3	133.6	135.6

* $J_{^{199}Hg-^{13}C} = 2333$ Hz

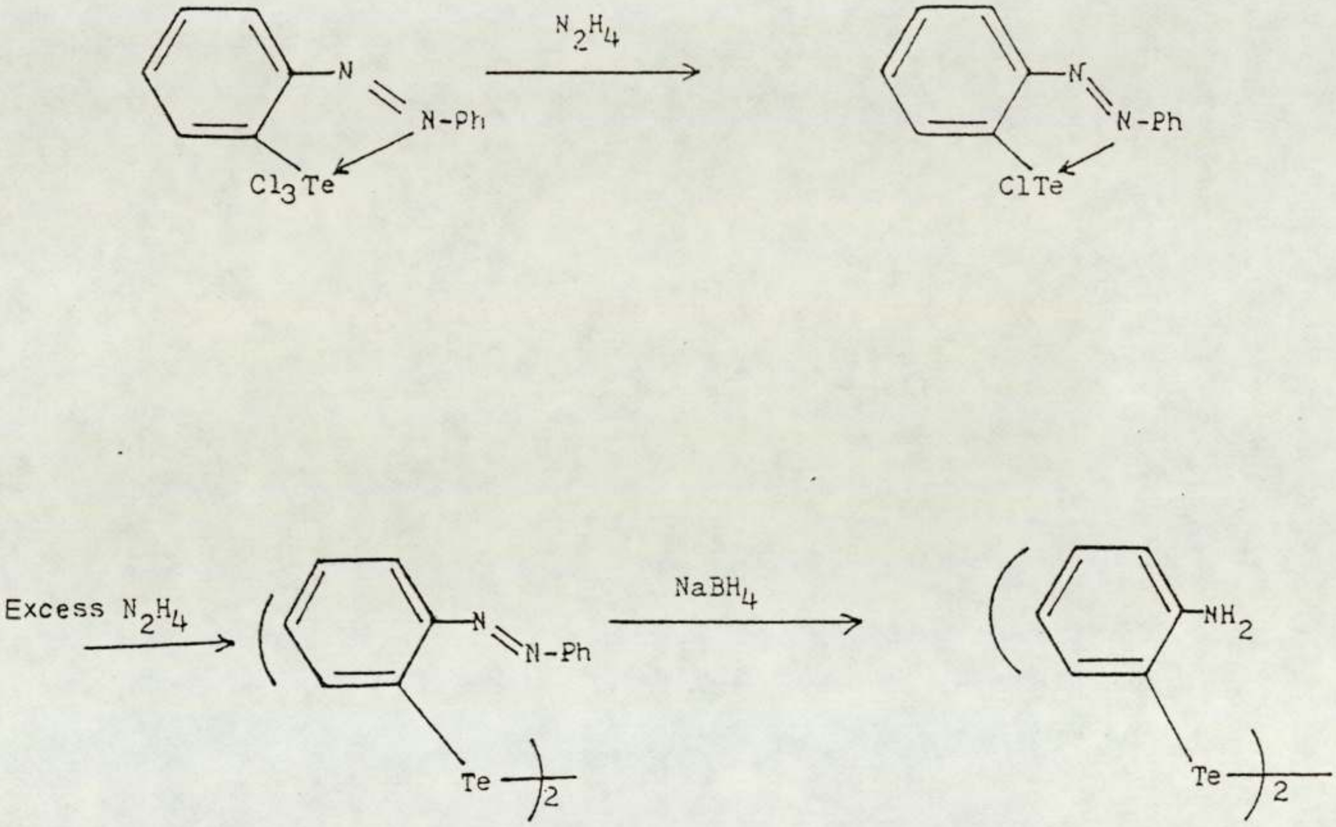
Table 4.4 ^{13}C NMR data in DMSO-d_6 (ppm, vs Me_4Si)

reproduced here and confirmed the previous work(37). ^{13}C chemical shift assignments were based on comparison with suitable model compounds; $(C_{12}H_9N_2)HgCl$ and azobenzene. as well as estimates of the effects of substituents on the aryl moiety, and on consideration of peak intensity. To assign substituted phenyl carbons by simple additivity relationships. the values of ^{13}C chemical shifts of unsubstituted benzene (128.5 ppm) and monosubstituted benzene were taken from reference(85).

As might be anticipated. the $(C_{12}H_9N_2)TeCl_3$ and $(C_{12}H_9N_2)HgCl$ spectra are very similar. One point of interest is that the carbon resonances of the "free" phenyl-ring are clearly more sensitive to the presence of tellurium than of mercury. This may imply a stronger co-ordinate intraaction of the azo-nitrogen atom with tellurium(IV) than with mercury(II).

4.2.6 $(C_{12}H_9N_2)_2Te_2$

It is known that hydrazine reduction of $(C_{12}H_9N_2)TeCl_3$ will give $(C_{12}H_9N_2)TeCl$, and that use of $NaBH_4$ as reducing agent will afford bis(o-aminophenyl)ditelluride(36). It seemed probable that the latter compound arose from bis(2-phenylazophenyl-C,N')ditelluride as implied in Scheme (1). The observation by Bergman(86). that hydrazine reacts with aryltellurium trichloride to give diaryl ditelluride, led us to reinvestigate the hydrazine reduction of $(C_{12}H_9N_2)TeCl_3$.



Scheme (1)

We now find that treatment of $(C_{12}H_9N_2)TeCl_3$ with an excess of hydrazine does indeed produce the ditelluride thus completing the series. The later compound was identified by elemental analyses (Section 4.1.3) and I.R. (Figure 4.6). The I.R. spectrum showed that all the characteristic ν(Te-Cl) bands$^{(36)}$ disappeared, while the other bands remained unaltered. This confirmed that the product is the new ditelluride $[(C_{12}H_9N_2)_2Te_2]$.

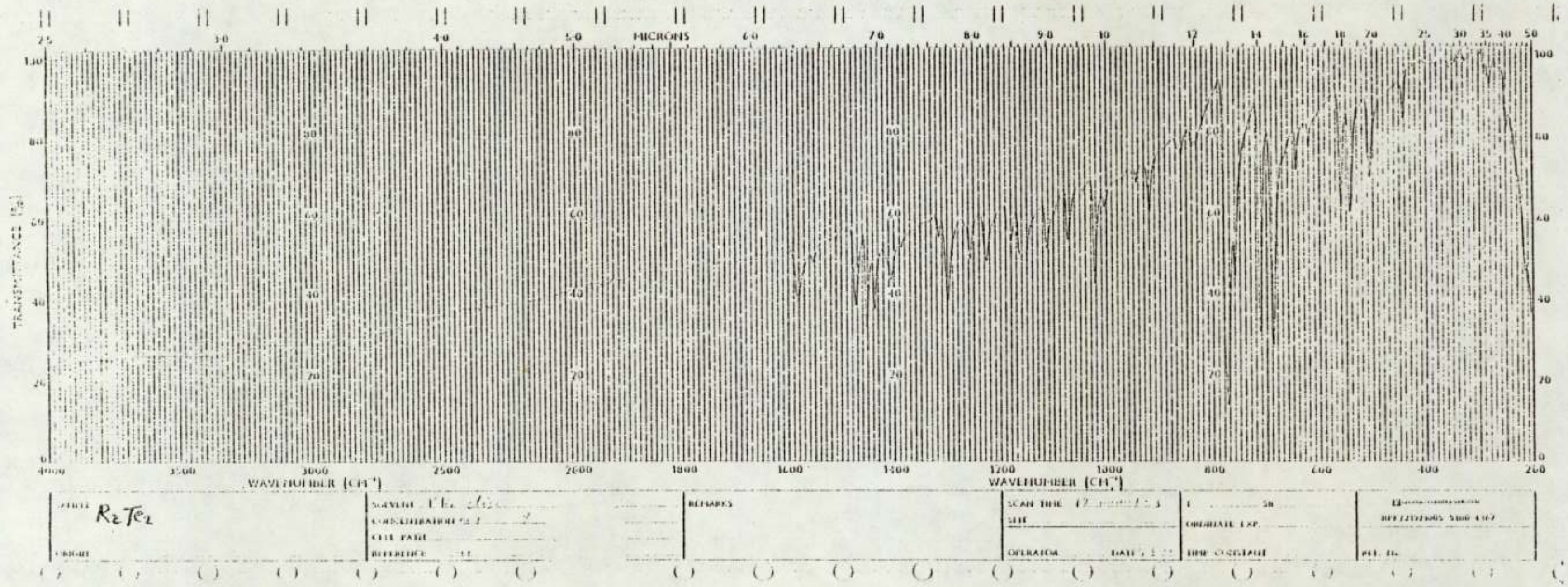


Figure 4.6 I.R. Spectrum of $(C_{12}H_9N_2)_2Te_2$

CHAPTER FIVE

SOME NEW ORGANOTELLURIUM DITHIOCARBAMATES

5.0 Introduction

It has been mentioned (Chapter's One and Three) that, tetrakis(diethyldithiocarbamato)tellurium(IV) [Te(dedtc)$_4$] and bis(diethyldithiocarbamato)tellurium(II) [Te(dedtc)$_2$] have been used as thermal and U.V. stabilisers for polypropylene (PP). In Chapter Three, the previous work has been extended by using two other compounds, namely tetrakis(diisobutyldithiocarbamato)tellurium(IV) [Te(didtc)$_4$] and tetrakis(dibenzyldithiocarbamato)tellurium(IV) [Te(dbdtc)$_4$]. It was concluded that tellurium dithiocarbamates are better stabilisers than bis(diethyldithiocarbamato)zinc(II), but are comparatively less efficient than bis(diethyldithiocarbamato)nickel(II) during photo-oxidation(62). However, they show much better stabiliser efficiency than nickel(II) and zinc(II) dithiocarbamates during thermal oxidation(63).

Also, we have demonstrated (Chapter Three) that, by changing the alkyl group (R) of the dithiocarbamate ligand ($\underline{R}_2NCS_2$) it is possible to obtain better stabilisers (see Chapter Three for more detail).

An extensive literature is available, in which the preparation and X-ray studies of tellurium dithiocarbamates have been described. The compounds; $Te(S_2CNR_2)_n$ (where n=2 and 4), $LTe(S_2CNR_2)_3$ (where L=Ph, Cl, Br, SCN) and

$L_2Te(S_2CNR_2)_2$ (where L=Br) are well known and have been the subject of X-ray studies, which showed that the dithiocarbamate group acts as an unsymmetric bidentate ligand (more detail is in Chapter's One and Three).

In Chapter Four, the preparation of the (2-phenylazophenyl-C,N')tellurium(IV) trichloride via a trans-metallation route is reinvestigated and also its synthesis by direct telluration of azobenzene is demonstrated. Its crystal and molecular structure is determined. In addition, the preparation of (2-phenylazophenyl-C,N')tellurium(II) chloride as reported by Musa(74) was confirmed (for more detail see Chapter Four).

We also recently developed an interest in the compounds; $ArTe(S_2CNR_2)_3$ and $ArTe(S_2CNR_2)$. The first type is well known(20) (where Ar=Ph). However, the second type is still unknown. To achieve the desired results, phenylazophenyl, which is known as a bidentate group and forms stable Te(IV) and Te(II) compounds(74), was chosen as the organic group. Subsequently, we have successfully prepared two new classes of tellurium dithiocarbamates. The second class prepared is the first example of a compound of the type, $ArTe(S_2CNR_2)$. The crystal and molecular structure of dimethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II) (AzoTedmdtc) is determined as representative for this new class [$ArTe(S_2CNR_2)$] of tellurium dithiocarbamates.

After the successful preparation and characterisation of these two new classes of tellurium dithiocarbamates, the first class is evaluated as a stabiliser for PP.

5.1 Experimental

5.1.1 Synthesis

5.1.1.1 Dimethyldithiocarbamato(2-phenylazophenyl-C,N')-tellurium(II)

A solution of sodium dimethyldithiocarbamate (0.185 g, 1.03 m mole) in dry methanol (15 cm^3) was added, with stirring and under dinitrogen, to a solution of (2-phenylazophenyl-C,N')tellurium(II) chloride(74) (0.344 g, 1 m mole) in dichloromethane (25 cm^3) at room temperature. The reaction mixture was stirred for a further 20 minutes, and the solvents were removed on a rotary evaporator. Dichloromethane (100 cm^3) was added to the residue with vigorous stirring. The solution was filtered to remove insoluble sodium chloride and the solvent was removed on a rotary evaporator. Methanol (5 cm^3) was added to the product, which was stirred well and filtered off.

The crude product was crystallised from methanol, purple crystals being obtained which melted with decomposition at 155-156°C, yield 85%.

5.1.1.2 Dibenzyldithiocarbamato(2-phenylazophenyl-C.N')-tellurium(II)

This compound was prepared using the same method as for the previous compound. Sodium dibenzyldithiocarbamate was used instead of sodium dimethyldithiocarbamate, with the same molar ratio, and the final product was a purple precipitate which melted with decomposition at 102-103°C, yield 97%.

5.1.1.3 Diethyldithiocarbamato(2-phenylazophenyl-C,N')-tellurium(II)

The title compound was prepared by the same method as for AzoTe(dmdtc). Sodium diethyldithiocarbamate was used instead of sodium dimethyldithiocarbamate, with the same molar ratio. It was noted that after the final evaporation, the product consisted of a dark oil which solidified after half an hour on the addition of methanol. Upon recrystallisation from methanol, dark-purple crystals were obtained which melted with decomposition at 113-115°C, yield 48%. The solubility of this compound is much higher than the previous compounds, which led to a significant decrease of the yield, upon washing and recrystallisation.

5.1.1.4 (2-Phenylazophenyl-C,N')tris(dimethyldithiocarbamato)tellurium(IV)

To a solution of (2-phenylazophenyl-C,N')tellurium(IV) trichloride (1.25 g, 3 m mole) in dichloromethane (200 cm^3) was added, with stirring and under dinitrogen, a solution of sodium dimethyldithiocarbamate (1.77 g, 10 m mole) in dry methanol (100 cm^3) at room temperature. After stirring for a further half an hour, the solvents were removed on a rotary evaporator. Dichloromethane (200 cm^3) was added to the residue and well stirred. The solution was filtered to remove insoluble sodium chloride and the solvent was evaporated on a rotary evaporator. Methanol (10 cm^3) was added to the crude product, stirred well and filtered off. The purple product melted with decomposition at 124-125°C, yield 92%.

5.1.1.5 (2-Phenylazophenyl-C,N')tris(dibenzyldithiocarbamato)tellurium(IV)

This compound was prepared using the same method as for the previous compound. Sodium dibenzyldithiocarbamate was used instead of sodium dimethyldithiocarbamate, with the same molar ratio. The final product was a purple precipitate which melted with decomposition at 95°C, yield 89%.

5.1.1.6 (2-Phenylazophenyl-C,N')tris(diethyldithiocarbamate)tellurium(IV)

The title compound was prepared using the same method as for the previous two compounds. Sodium diethyldithiocarbamate was used instead of sodium dimethyldithiocarbamate, with the same molar ratio. The final product was a dark oil, as in the case of diethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II), which solidified after half an hour on the addition of methanol. The dark-purple precipitate melted with decomposition at 102-104°C, yield 60%.

5.1.2 Thermal Stability of (2-Phenylazophenyl-C,N')tris(dialkyldithiocarbamato)tellurium(IV) [AzoTe(dtc)$_3$]

It was observed that AzoTe(dtc)$_3$ (for example $(C_{12}H_9N_2)$Te$(S_2CNMe_2)_3$) is a rather unstable compound. Its solution in methanol, chloroform and in other solvents, when brought to boiling for ∼10 minutes or more, decomposed to AzoTe(dmdtc) and the corresponding disulphide (TMTD). The AzoTe(dmdtc) was identified positively by T.L.C. and X-ray techniques, which gave identical data to that obtained for AzoTe(dmdtc) (Section 5.1.5.3). Also TMTD was identified by T.L.C., which showed three spots corresponding to the parent compound, AzoTe(dmdtc) and TMTD. Tetrakis(diethyldithiocarbamato)tellurium(IV) also undergoes a similar reaction(29,87).

5.1.3 Attempt to Synthesise Dibromodimethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(IV)

Dimethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium (II) (0.428 g, 1 m mole) in boiling carbontetrachloride (30 cm^3) was treated with a solution of bromine (0.2 g) in carbontetrachloride (10 cm^3). The reaction mixture was heated for a further 10 minutes. The solution was filtered and cooled to afford orange crystals of m.p. 245°C, which on analysis were found to be (2-phenylazophenyl-C,N')tellurium(IV) tribromide(74), even though it was expected to be the title compound.

	C%	H%	N%	m.p. °C	colour
Product	26.2	1.60	5.10	245	orange
$C_{12}H_9N_2TeBr_3$	26.3	1.64	5.10	245	orange
$C_{15}H_{15}N_3S_2TeBr_2$	36.6	2.55	7.14	-	-

5.1.4 Sample Preparation and Processing of the Polymer

PP was processed at 180°C with additives for various periods of time (5, 10 and 20 minutes) in a closed mixer and the processed samples were then compressed into films, as described in Chapter 3, to study the thermal and photo-oxidation.

5.1.5 Crystal and Molecular Structure of Dimethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II)

5.1.5.1 Experimental

Small fine dark red needle shaped crystals were obtained by recrystallisation from methanol and these were reasonably stable in the presence of air and light. A density column was prepared from bromoform and carbon tetrachloride and the density was found to be 1.71 ± 0.03 g cm^{-3} at 20°C.

5.1.5.2 X-ray Measurements

After preliminary oscillation and equiinclination Weissenberg photographs had been taken, a crystal with dimensions 0.03 mm x 0.03 mm x 0.83 mm was mounted along its z axis on an Enraf-Nonius CAD-4 diffractometer. The automatic centering, indexing and least-squares routines of the instrument were applied to 25 reflections to obtain lattice parameters using graphite monochromated M_o-K_α radiation. The intensity data were collected in the $\omega/2\theta$ scan mode. The scan range (ω^o) was calculated from $(1.0+0.35 \tan \theta)$ and the scan speed varied from 0.3-1.3 min^{-1} depending on the intensity. 4189 reflections were scanned in the range $2<\theta<27^o$ at room temperature. Three standard reflections were monitored every two hours and the orientation of the crystal was checked every one hundred reflections. No decomposition or movement of the crystal was observed during the collection of the reflection intensities. Lorentz and polarisation corrections were applied to the data and 2135 independent observed reflections with $F>5\sigma(F)$ were used in the structure analysis. The crystals were found to be monoclinic with no general absences, hol was present only when h+l=2n and oko was present only when k=2n consistent with the centrosymmetrical space group $P2_1/n$. The number of formula weights in the unit cell was calculated to be four.

5.1.5.3 Crystal Data

$C_{15}H_{15}N_3S_2Te$, M=428.6, monoclinic
$a = 6.225(5)$, $b = 12.133(9)$, $c = 21.784(14)$ Å, $\beta = 92.88(5^{\circ})$,
$V = 1643.19$ Å^3, $D_m = 1.71$ g cm^{-3}, $D_c = 1.73$ g cm^{-3}
$z = 4$
$F(000) = 839.78$, $\lambda(M_o-K_{\alpha}) = 0.71069$ Å
$\mu = 20.37$ cm^{-1}

5.1.5.4 Structure Analysis and Refinement

The atomic parameters for tellurium were found by direct methods using SHELX 76$^{(50)}$ and confirmed by analysis of the Patterson map. The positions of the sulphur, nitrogen and carbon atoms were found using difference maps. Anisotropic temperature factors were calculated for all non hydrogen atoms. The positional and temperature factor parameters for tellurium, sulphur, nitrogen and carbon were refined by three cycles of blocked full-matrix least squares refinement with hydrogen atoms included in the calculation in their theoretical positions. The weighting scheme used was $W=1.4559/\sigma^2F + 0.00247F^2$ and the refinement converged to $R=0.0517$ and $R_w=0.0526$. The fractional atomic co-ordinates and thermal parameters are as listed in Tables 5.1 and 5.2 respectively.

5.2 Results and Discussion

Generally, the reaction of (2-phenylazophenyl-C,N')tellurium(II) chloride or (2-phenylazophenyl-C,N')tellurium (IV) trichloride with sodium dialkyldithiocarbamate in solution and in molar ratio of 1:1 or 1:3 respectively afforded complexes of new tellurium dithiocarbamates. Table 5.3 lists the complexes isolated and their melting points and analytical data. The colours of the complexes are purple and all of them were found to be stable in air for several months. All compounds have satisfactory elemental analysis (Table 5.3) and I.R. data (Section 5.2.2).

5.2.1 The Crystal and Molecular Structure of Dimethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II)

The structure of the complex and atom numbering are shown

Atom	X	Y	Z
Te	2356(1)	1868(0)	976(0)
S(1)	4830(4)	1264(2)	1893(1)
S(2)	6119(5)	3509(2)	1480(2)
N(1)	-1943(10)	1202(6)	278(3)
N(2)	- 557(10)	1962(5)	256(3)
C(11)	-1023(13)	2859(7)	- 130(4)
C(12)	-3133(15)	3092(9)	- 345(5)
C(13)	-3513(20)	3966(10)	- 741(6)
C(14)	-1831(18)	4604(9)	- 934(5)
C(15)	276(17)	4380(9)	- 720(5)
C(16)	655(14)	3513(8)	- 314(5)
C(21)	-1380(12)	375(7)	693(4)
C(22)	536(13)	423(7)	1064(4)
C(23)	1019(16)	- 443(7)	1463(4)
C(24)	- 394(17)	-1325(8)	1494(5)
C(25)	-2300(16)	-1363(8)	1135(5)
C(26)	-2809(15)	- 514(8)	731(4)
N(3)	8309(12)	2294(7)	2302(4)
C(31)	6574(12)	2382(7)	1914(4)
C(32)	9814(17)	3216(9)	2381(5)
C(33)	8781(18)	1299(9)	2670(5)

Table 5.1 Atomic co-ordinates with standard deviations in parentheses ($\times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te	290 (3)	409 (3)	478 (3)	40 (3)	- 29 (2)	- 11 (3)
S(1)	399 (12)	450 (13)	632 (15)	113 (11)	-144 (10)	- 67 (10)
S(2)	573 (15)	507 (14)	891 (21)	207 (14)	-186 (14)	-131 (12)
N(1)	264 (33)	427 (38)	513 (41)	- 4 (32)	- 27 (29)	- 14 (30)
N(2)	280 (32)	413 (37)	413 (35)	6 (30)	- 16 (27)	- 28 (29)
C(11)	271 (38)	427 (46)	489 (47)	- 10 (35)	8 (35)	- 14 (32)
C(12)	321 (42)	699 (64)	703 (63)	225 (55)	- 97 (42)	- 0 (45)
C(13)	590 (64)	780 (76)	854 (84)	222 (64)	-254 (61)	- 38 (59)
C(14)	588 (60)	619 (63)	566 (59)	188 (49)	- 40 (51)	160 (50)
C(15)	491 (55)	569 (57)	792 (74)	138 (55)	91 (53)	- 24 (48)
C(16)	331 (45)	545 (52)	673 (61)	134 (47)	- 10 (42)	- 43 (40)
C(21)	268 (36)	437 (45)	399 (43)	- 51 (34)	23 (33)	- 52 (33)
C(22)	325 (40)	374 (42)	428 (45)	- 28 (34)	- 8 (35)	- 2 (34)
C(23)	521 (52)	466 (50)	530 (53)	- 5 (42)	-135 (43)	- 21 (43)
C(24)	565 (59)	447 (53)	733 (66)	109 (48)	- 60 (50)	- 34 (47)
C(25)	485 (52)	510 (50)	550 (55)	- 5 (42)	9 (43)	-149 (44)
C(26)	444 (46)	458 (48)	527 (49)	- 41 (42)	48 (40)	- 96 (40)
N(3)	348 (38)	562 (45)	551 (45)	- 34 (38)	- 72 (33)	- 7 (36)
C(31)	267 (37)	454 (45)	479 (46)	- 36 (38)	- 49 (34)	5 (36)
C(32)	485 (50)	756 (68)	588 (57)	-150 (53)	- 26 (45)	-132 (51)
C(33)	625 (61)	701 (70)	588 (61)	0 (54)	-238 (52)	137 (57)

Table 5.2 Atomic thermal parameters and their estimated standard deviations in parentheses ($\times 10^4$)

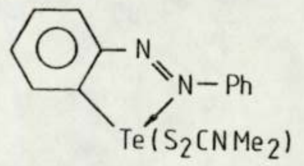
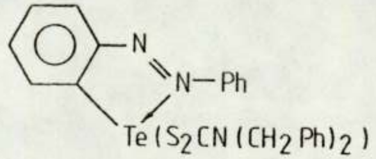
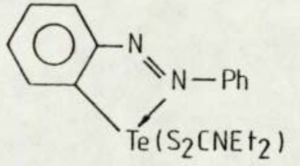
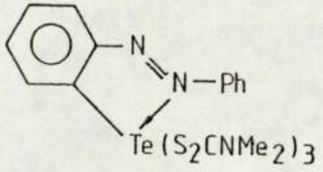
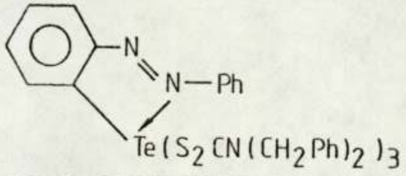
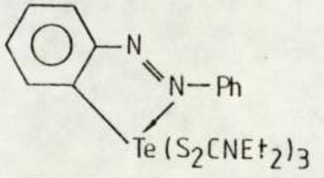
Compound	m.p. °C	colour	yield (%)	C% (calc)	H% (calc)	N% (calc)	S% (calc)
	155-156	purple	85	42.05 (42.0)	3.45 (3.50)	9.65 (9.80)	14.5 (14.9)
	102-103	purple	97	56.3 (55.8)	3.80 (3.96)	6.80 (7.23)	11.2 (11.0)
	113-115	dark-purple	48	45.0 (44.7)	4.25 (4.16)	9.35 (9.20)	
	124-125	purple	92	38.1 (37.7)	3.90 (4.04)	10.3 (10.5)	27.9 (28.7)
	95	purple	89	61.3 (60.8)	4.60 (4.54)	6.25 (6.22)	17.0 (17.1)
	102-104	dark-purple	60	42.5 (43.1)	5.35 (5.18)	9.05 (9.30)	

Table 5.3 Analytical data for the new complexes

in Figure 5.1 and the unit cell diagram is shown in Figure 5.2. Table 5.4 gives deviations of atoms from the mean planes. Bond distances, angles and torsion angles are given in Table 5.5. The structure consists of one discrete repeating molecule. The co-ordination about tellurium can be considered as essentially distorted square-planar. The four co-ordinate tellurium atom is bonded to carbon, nitrogen and two sulphur atoms, with all five atoms being approximately in one plane (a square-plane or a trapezoid). The trapezoid planar is a more correct description of such configurations as it has been reported for many four-co-ordinate tellurium(II) complexes with bidentate ligands(88). Calculations on the deviations of the atoms from the least square planes in the molecule (Table 5.4) show that the central group of atoms S(1), S(2), Te, N(2) and C(22) are almost planar with a mean deviation of 0.034 Å. The phenyl ring C(21)-C(26) is planar (mean deviation = 0.004 Å) with N(1) and N(2) lying slightly below it. The free phenyl ring C(11)-C(16) is also planar (mean deviation = 0.006 Å) but is twisted about the C(11)-N(2) bond by approximately 19° away from coplanarity with the N(1)-N(2) bond (Table 5.5 and Figure 5.3). This free phenyl group makes an interplanar angle of 25° with the Te, N(12), N(1), C(21), C(22) ring which is itself tilted at an interplanar angle of 2.5° to the attached phenyl group. This five membered nitrogen containing ring has an interplanar angle of 6.8° relative to the Te and the attached dithiocarbamate group

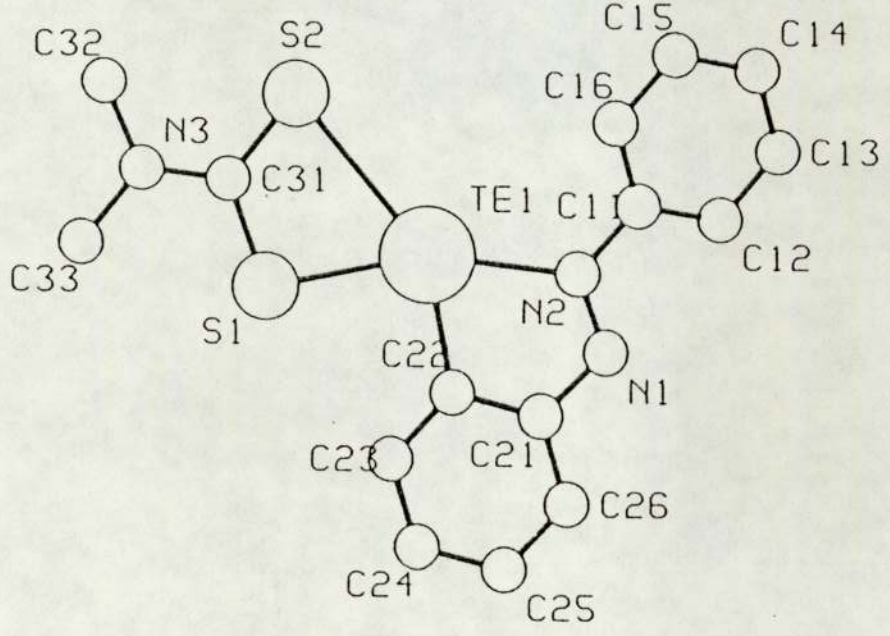


Figure 5.1 Molecular structure of $C_{12}H_9N_2Te(S_2CNMe_2)$

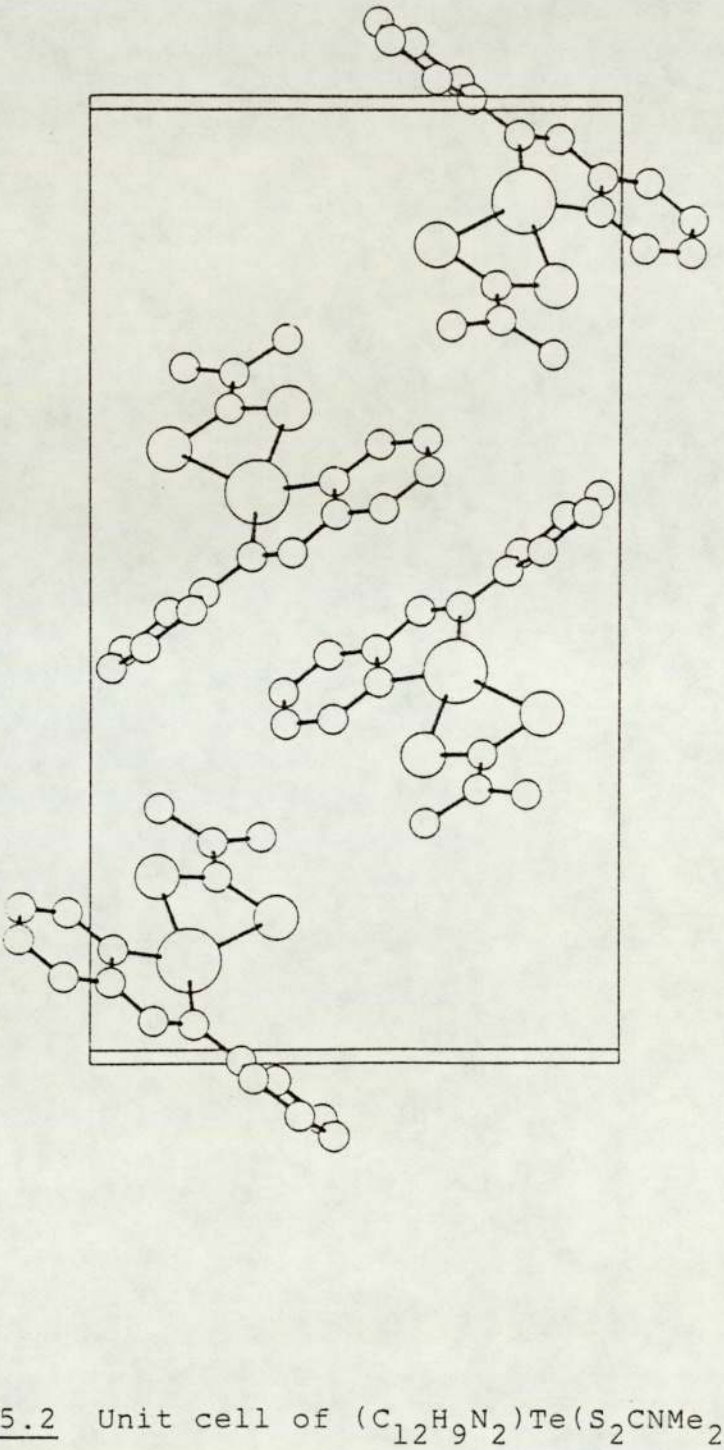


Figure 5.2 Unit cell of $(C_{12}H_9N_2)Te(S_2CNMe_2)$

No. of plane	atoms included
1	S(1),S(2),Te,N(2) and C(22)
2	C(21),C(22),C(23),C(24),C(25) and C(26)
3	Te,N(2),N(1),C(21) and C(22)
4	C(11),C(12),C(13),C(14),C(15) and C(16)
5	Te,S(1),C(31) and S(2)
6	C(31),N(3),C(32) and C(33)

Plane 1		2		3		4		5		6	
S(1)	0.0081	C(21)	-0.0068	Te	0.0306	C(11)	-0.0062	Te	-0.0213	C(31)	0.0018
S(2)	0.0255	C(22)	0.0064	N(2)	-0.0430	C(12)	-0.0022	S(1)	0.0459	N(3)	-0.0048
Te	-0.0860	C(23)	-0.0010	N(1)	0.0317	C(13)	0.0076	C(31)	-0.0629	C(32)	0.0015
N(2)	0.0273	C(24)	-0.0042	C(21)	0.0149	C(14)	-0.0048	S(2)	0.0383	C(33)	0.0016
C(22)	0.0251	C(25)	0.0038	C(22)	-0.0342	C(15)	-0.0035	(mean dev. = 0.0421)		(mean dev. = 0.0024)	
(mean dev. = 0.0344)		C(26)	0.0017	(mean dev. = 0.0309)		C(16)	0.0090			S(1)	0.0901
		(mean dev. = 0.0040)				(mean dev. = 0.0056)				S(2)	-0.0623
		N(1)	-0.0220								
		N(2)	-0.0650								

Table 5.4 Least-squares planes and deviations (Å) of atoms from the planes

Te-S(1)	2.568(2)	N(1)-C(21)	1.384(10)
Te-S(2)	3.225(3)	C(21)-C(22)	1.408(11)
Te-N(2)	2.340(7)	C(22)-C(23)	1.387(12)
Te-C(22)	2.101(8)	C(23)-C(24)	1.389(14)
C(11)-C(12)	1.401(12)	C(24)-C(25)	1.389(14)
C(12)-C(13)	1.380(14)	C(25)-C(26)	1.381(14)
C(13)-C(14)	1.384(16)	C(26)-C(21)	1.403(12)
C(14)-C(15)	1.396(15)	S(1)-C(31)	1.736(9)
C(15)-C(16)	1.387(13)	S(2)-C(31)	1.679(9)
C(16)-C(11)	1.387(13)	C(31)-N(3)	1.342(11)
C(11)-N(2)	1.396(10)	N(3)-C(32)	1.464(12)
N(2)-N(1)	1.265(9)	N(3)-C(33)	1.470(13)
S(1)-Te-S(2)	60.9(1)	N(1)-C(21)-C(26)	117.1(7)
S(1)-Te-C(22)	89.8(2)	C(22)-C(21)-C(26)	121.3(8)
C(22)-Te-N(2)	72.5(3)	C(21)-C(22)-C(23)	118.7(8)
N(2)-Te-S(2)	136.3(2)	Te-C(22)-C(23)	126.0(6)
C(11)-N(2)-Te	124.9(5)	Te-C(22)-C(21)	115.3(6)
C(11)-N(2)-N(1)	118.0(7)	C(22)-C(23)-C(24)	119.7(9)
N(1)-N(2)-Te	116.5(5)	C(23)-C(24)-C(25)	121.5(9)
C(12)-C(11)-N(2)	121.4(8)	C(24)-C(25)-C(26)	119.8(9)
C(16)-C(11)-N(2)	118.9(8)	C(25)-C(26)-C(21)	119.0(8)
C(12)-C(11)-C(16)	119.7(8)	Te-S(1)-C(31)	98.5(3)
C(11)-C(12)-C(13)	119.5(9)	Te-S(2)-C(31)	77.8(3)
C(12)-C(13)-C(14)	120.7(10)	S(1)-C(31)-S(2)	122.3(5)
C(13)-C(14)-C(15)	120.2(9)	S(1)-C(31)-N(3)	115.9(7)
C(14)-C(15)-C(16)	119.1(9)	S(2)-C(31)-N(3)	121.8(7)
C(15)-C(16)-C(11)	120.8(9)	C(31)-N(3)-C(32)	120.2(8)
N(2)-N(1)-C(21)	113.7(6)	C(31)-N(3)-C(33)	122.7(8)
N(1)-C(21)-C(22)	121.7(7)	C(32)-N(3)-C(32)	117.0(8)
C(11)-N(2)-N(1)-C(21)	-177.2(7)	N(2)-N(1)-C(21)-C(26)	-178.2(7)
C(12)-C(11)-N(2)-N(1)	18.5(6)	N(2)-N(1)-C(21)-C(22)	2.1(7)
C(16)-C(11)-N(2)-N(1)	-159.9(6)		

Table 5.5 Bond distances (Å), angles (°) and torsion angles (°) in $(C_{12}H_9N_2)Te(S_2CNMe_2)$

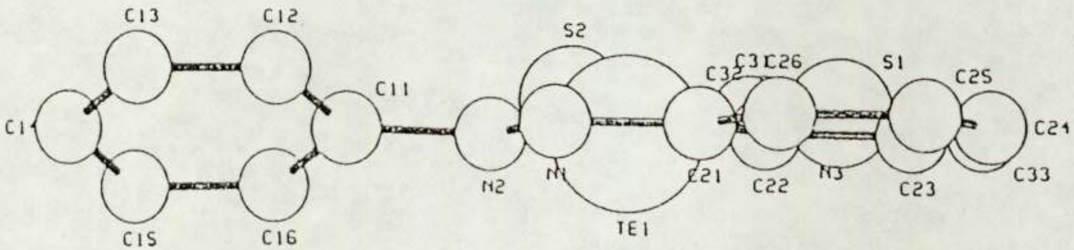
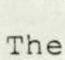


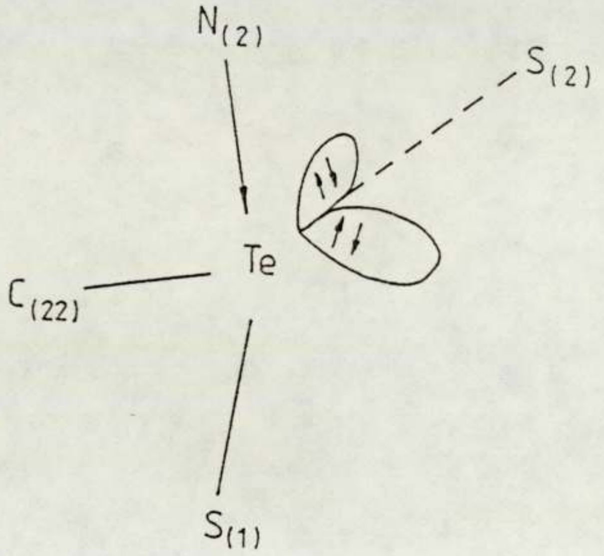
Figure 5.3 Perspective view of $C_{12}H_9N_2Te(S_2CNMe_2)$

(S(1), C(31), S(2), N(3), C(32) and C(33)).The planes through Te, S(1), C(31), S(2) and C(31), N(3), C(32), C(33) are at an angle of 7.1° to one another. The dithiocarbamate group is coplanar (mean deviation=0.028 Å).

The distance Te-C(22) (2.101 Å) is in good agreement with the sum of Pauling$^{(76)}$ single bond covalent radii of Te (1.37 Å) and sp^2-hybridised carbon (0.74 Å), and with values in the Te(II) complexes$^{(88)}$, $[PhTe(tu)_2]Cl$, $Me_4N[PhTe(SCN)_2]$, $Me_4N[PhTe(SeCN)_2]$ and [PhTe(trsu)Cl] where tu=thiourea and trsu=trimethyleneselenourea, which lie in the range 2.10-2.104 Å. The Te-N distance (2.340 Å) is much larger than the sum of the covalent radii (2.07 Å)$^{(76)}$ and also is larger than the values in the $C_{12}H_9N_2TeCl$$^{(74)}$, $C_{12}H_9N_2Te(OOCCH_3)$ and $C_{12}H_9N_2Te(SCN)$ (Chapter Six) which lie in the range 2.23-2.26 Å. However it is comparable with the values in the crystal structure of $C_{12}H_9N_2TeCl_3$ (2.417 Å) (Chapter Four) and $(C_9H_8NO_2)TeCl_3$ (2.402 Å)$^{(71)}$. The Te-S bonds differ in length, one being 2.568(2) Å and the other 3.225(3) Å. The Te-S(1) bond length, 2.568 Å, is longer than the sum of Pauling$^{(76)}$ single bond covalent radii (2.38 Å) but is close to the values found for Te(II) complexes$^{(88)}$ with bidentate sulphur-containing ligands e.g., $Te(S_2COEt)_2$, $Te(S_2COMe)_2$, $Te(S_2CN$-$)_2$, $Te(S_2CNEt_2)_2$, which fall in the range 2.49-2.52 Å. The Te-S(2) length (3.225 Å) is longer than the sum of the covalent radii$^{(76)}$, but shorter than the sum of the van der Waals radii, 4.05 Å, according to Pauling(76) or 3.91 Å according to Bondi(80), indicating a weak bond. Similar bonds have been found in the crystal structures of some other Te(II) complexes with bidentate sulphur-containing ligands e.g., $Te[S_2P(OMe)_2]_2$(88), $Te[S_2P(OEt)_2]_2$(88) and $PhTe(S_2CNEt_2)_3$(20), which fall in the range 3.209-3.311 Å.

On the other hand, the co-ordination about tellurium (in this compound) can be described as ψ-trigonal bipyramidal with C(22) and the two lone pairs in the equatorial positions and N(2) and S(1) in the axial positions. The tellurium atom is approached by a fourth atom S(2) at a distance of 3.225 Å which illustrates the tendency of Te(II) to achieve square planar geometry, as it has been reported for many Te(II) complexes(88). However, this approach is significant in this compound and is not an unusual one, but has been reported for tellurium with bidentate sulphur containing compounds(88). McWhinnie et al(89) pointed out that a fourth (secondary) bond may form along an axis bisecting the angle between the lone pairs.

By taking this geometry [ψ-trigonal bipyramidal]; the Te-S(1) distance 2.568 Å is in good agreement with the sum of covalent radii for Te (axial direction)(89) of 1.54 Å and sulphur of 1.04 Å(76). Also, the Te-N distance 2.34 Å is comparable to the sum of covalent radii of Te (axial direction)(89) and nitrogen(76) of 2.28 Å. Thus the observed geometry can be viewed as in the figure shown below:



Bond lengths in the phenylazophenyl group are generally in good agreement with those found for $(C_{12}H_9N_2)Te(OOCCH_3)$ and $(C_2H_9N_2)Te(SCN)$ (see Chapter Six). The dimensions of the dithiocarbamate group are in good agreement with those found in the crystal structure of many tellurium dithiocarbamates e.g., $Te[S_2CN(CH_2CH_2OH)_2]_2$ (30), $Te[S_2CN{<}^{CH_2-CH_2}_{CH_2-CH_2}{>}O]_2$ (32), $Te(S_2CNEt_2)_2$ (31) and $PhTe(S_2CNEt_2)_3$ (20).

5.2.2 Infra-red Absorption Spectroscopy

The spectra of dimethyldithiocarbamato(2-phenylazophenyl-

C,N')tellurium(II) and (2-phenylazophenyl-C,N')tris(dimethyldithiocarbamato)tellurium(IV), as a representative type, are given in Figures 5.4 and 5.5 respectively. Some infra-red data are given in Table 5.6. It is well established that the dithiocarbamate moiety acts as an unsymmetrical bidentate ligand in tellurium complexes (see Chapters One, Three and Section 5.2.1). Also, X-ray studies showed that the phenylazophenyl group is a bidentate ligand in tellurium complexes(74) (Chapters Four, Six and Section 5.2.1 in this Chapter). As mentioned in Chapter Three, the most characteristic bands in the infra-red spectra of tellurium dithiocarbamates are those attributed to the ν(C-N), ν(C-S) and ν(Te-S) vibrations.

The assignments of the infra-red bands were made by following the previous work (Chapter Three) with simple telluruim dithiocarbamates. The ν(C-N) band, in all compounds, is a strong band at ca. 1490 cm^{-1}. Also the ν(C-S) band occurred with a strong intensity at ca. 990 cm^{-1}. The Te-S vibration is found as a weak band at ca. 295 cm^{-1} (see Table 5.6). These results are similar in positions to that for simple tellurium dithiocarbamates (Chapter Three).

It was noted that the infra-red spectra of Te(II) and Te(IV) compounds, for the same alkyl group ($\underline{\underline{R}}_2NCS_2$), showed the same positions for the ν(C-N), ν(C-S) and ν(Te-S) bands.

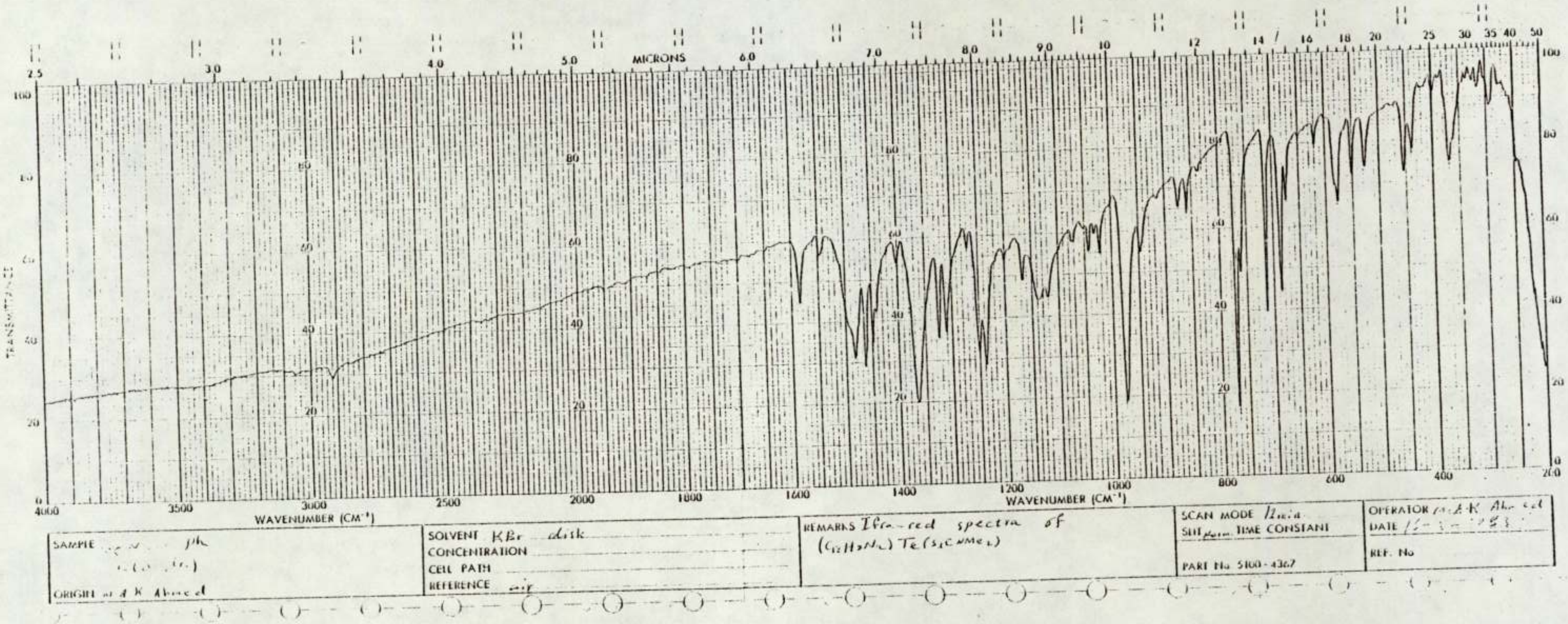
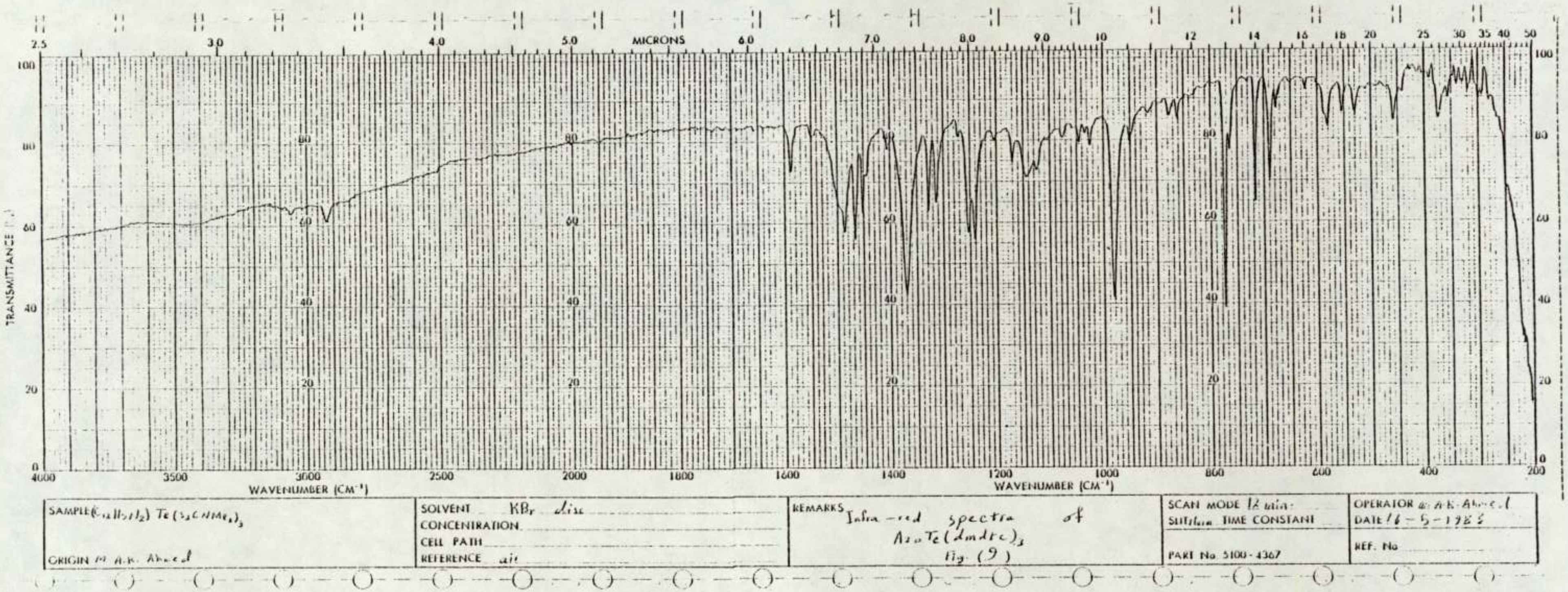


Figure 5.4 I.R. spectrum of $C_{12}H_9N_2Te(S_2CNMe_2)$



SAMPLE ($C_{12}H_9N_2$) Te (S_2CNMe_2)$_3$

ORIGIN M A.K. Ahmed

SOLVENT KBr disc

CONCENTRATION

CELL PATH

REFERENCE air

REMARKS Infra-red spectra of AzoTe(dmdtc)$_3$ Fig. (9)

SCAN MODE 12 min.

SLIT 1/cm TIME CONSTANT

PART No 5100-4367

OPERATOR M A.K. Ahmed

DATE 16-5-1985

REF. No

Figure 5.5 I.R. spectrum of $C_{12}H_9N_2Te(S_2CNMe_2)_3$

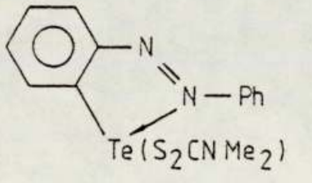
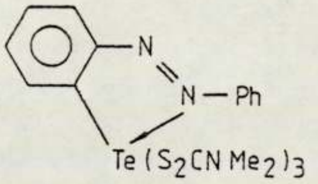
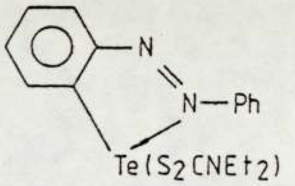
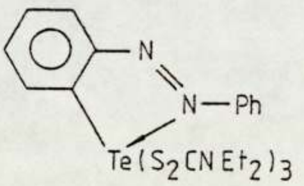
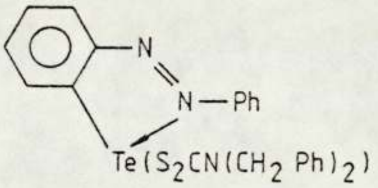
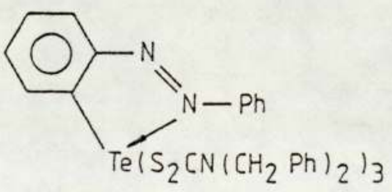
Compound	ν(CN)	ν(CS)	ν(TeS)
	1485	980	295
	1485	980	295
	1480	985	300
	1500	990	300
	1492	1000	295
	1492	1000	295

Table 5.6 Some I.R. data for the new complexes

The observation of ν(C-N) and ν(C-S) bands suggests the bidentate nature of the dithiocarbamate ligand, if splitting of both the ν(C-N) and ν(C-S) bands is taken as indicative of a unidentate and single bands as a bidentate ligand(17,58). However, we believe that the dithiocarbamate in these compounds does act as a bidentate ligand as has been demonstrated by the X-ray data (Section 5.2.1).

Comparison between the infra-red spectra of the starting materials and products showed that the phenylazophenyl-Te complex bands are almost identical to those previously reported(74). However, in some of the spectra, overlapping of bands from the phenylazophenyl- and dithiocarbamato-groups is seen.

5.2.3 Mass Spectra

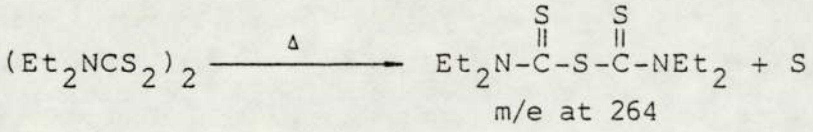
The mass spectra of (2-phenylazophenyl-C,N')tris(diethyldithiocarbamato)tellurium(IV) [AzoTe(dedtc)$_3$] and diethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II) [AzoTe(dedtc)] were determined as representative of the two types of compound. The spectrum of AzoTe(dedtc)$_3$ did not show the peak of the molecular ion. The highest peak observed corresponds to [AzoTe(dedtc)$^+$], m/e at 459 ($^{12}C_{17}$, $^{1}H_{19}$, $^{14}N_3$ and $^{130}Te_1$). In addition the disulphide [$(Et_2NCS_2)_2^+$ or TETD] was identified as a major peak at 296. These results confirm previous observations. Thus it was demonstrated (Section 5.1.2) that AzoTe(dtc)$_3$ undergoes decomposition (on heating) to AzoTe(dtc) and the corresponding disulphide (TRTD).

The fragmentation of the tetraethylthiuram disulphide ion to give the tetraethylthiuram monosulphide ion with loss of sulphur was also observed, and parallels the previously reported thermal decomposition of TRTD$^{(59)}$. The fragmentation patterns are represented as shown below, as it was observed from the mass spectrum.

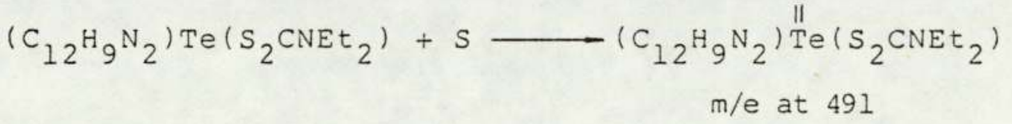
The mass spectrum of AzoTe(dedtc) shows the presence of the peak of the molecular ion, m/e at 459, in addition to other characteristic fragments for [AzoTe(dedtc)$^+$](Scheme 5.1)

The most interesting feature of the mass spectrum of AzoTe(dedtc) is that, the spectrum showed an ion appearing at higher mass charge ratio (m/e at 491) than that corresponding to the parent ion (m/e at 459). From X-ray crystallographic data (Section 5.2.1) we have positive proof that these compounds are monomeric. It is possible, therefore, that the existence of this higher peak may arise from the following redistribution reactions:

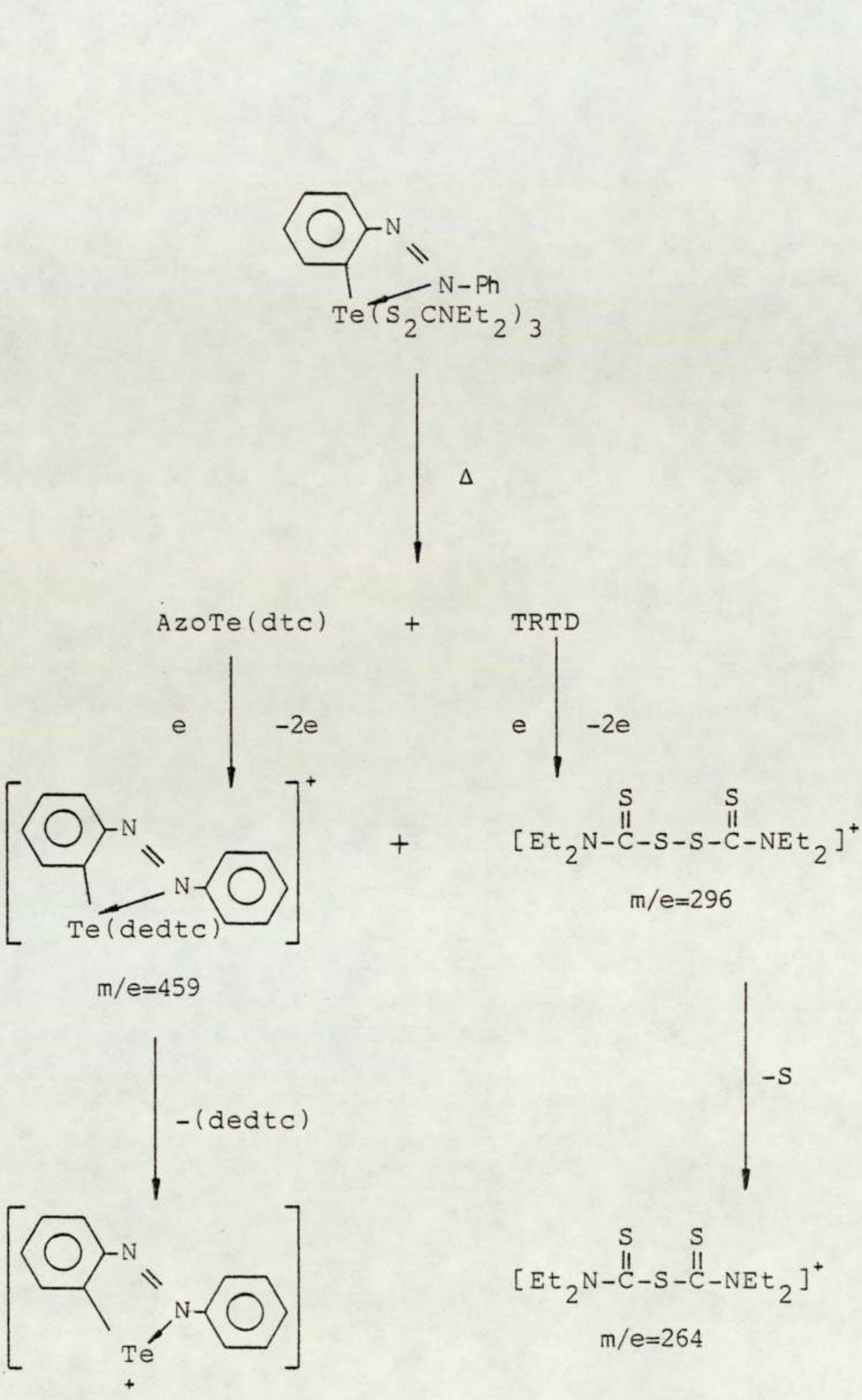
$$2C_{12}H_9N_2)Te(S_2CNEt_2) \xrightarrow{\Delta} (C_{12}H_9N_2)_2Te_2 + (Et_2NCS_2)_2$$



$$(Et_2NCS_2)_2 \xrightarrow{\Delta} \underset{\text{m/e at 264}}{Et_2N\text{-}\overset{\overset{S}{\|}}{C}\text{-}S\text{-}\overset{\overset{S}{\|}}{C}\text{-}NEt_2} + S$$



$$(C_{12}H_9N_2)Te(S_2CNEt_2) + S \longrightarrow \underset{\text{m/e at 491}}{(C_{12}H_9N_2)\overset{\overset{S}{\|}}{Te}(S_2CNEt_2)}$$


N
N-Ph
Te(S2CNEt2)3
Δ
AzoTe(dtc)
+
TRTD
e
-2e
e
-2e
N
N
Te(dedtc)
+
S
S
[Et2N-C-S-S-C-NEt2]+
m/e=296
m/e=459
-S
-(dedtc)
N
N
Te
+
S
S
[Et2N-C-S-C-NEt2]+
m/e=264
m/e=311

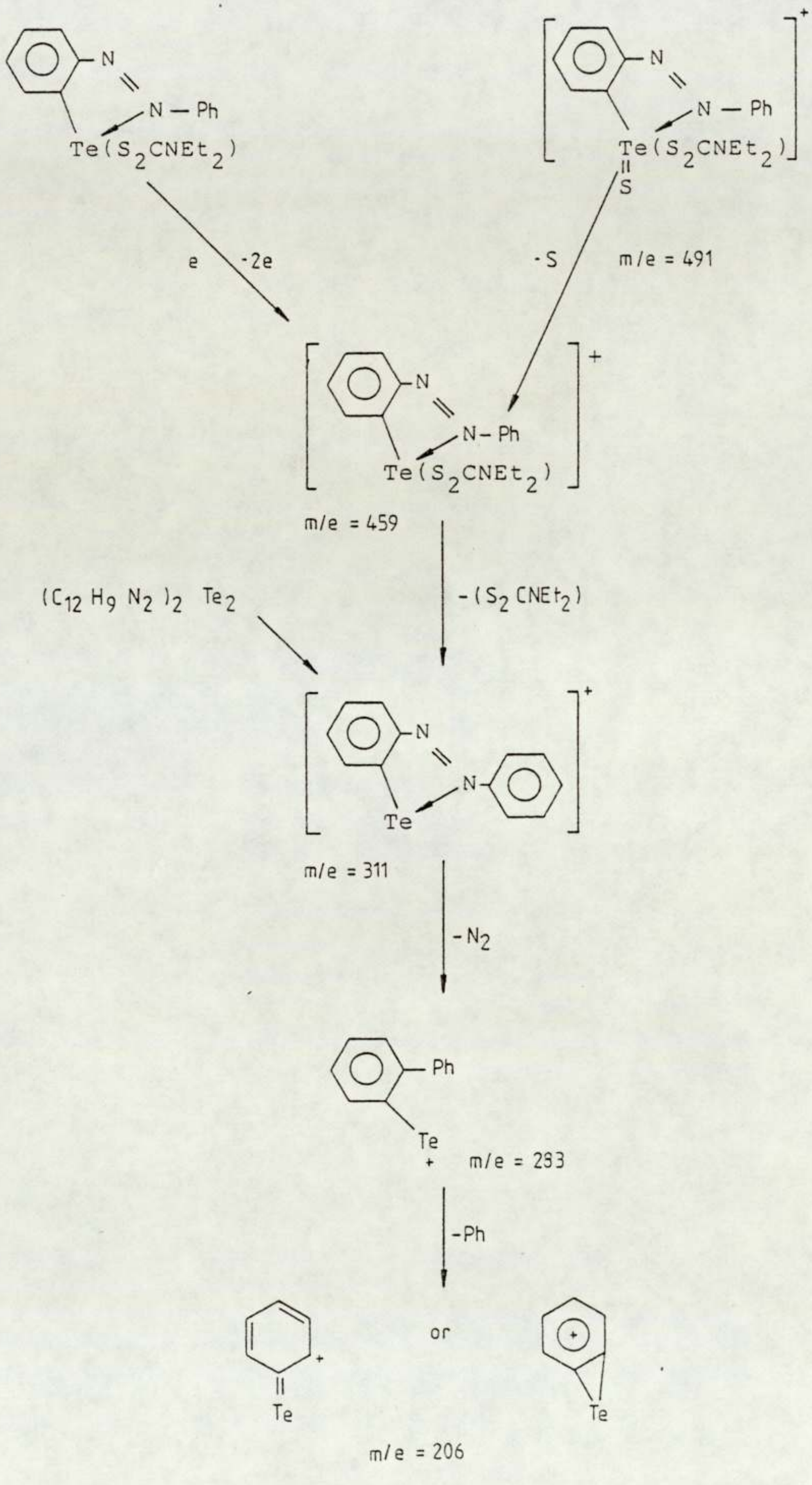
It is not surprising that the peaks corresponding to ditelluride and disulphide were not observed. This might be due to the high temperature (250°C) which was much higher than for the previous compounds (180°C), which was selected to obtain a better spectrum. From this interesting observation, it is possible to say that the peaks corresponding to the parent compounds may arise from this possible new compound $[(C_{12}H_9N_2)\overset{S}{\overset{\|}{Te}}(S_2CNEt_2)]$.

The most probable scheme of the fragmentation is as shown overleaf.

5.2.4 Stabilisation of PP

Figure 5.6 shows that the compound (2-phenylazophenyl-C,N')tris(dialkyldithiocarbamato)tellurium(IV) [alkyl= Me or Et] is a good melt stabiliser for PP during processing.

The effect of varying the concentration of (2-phenylazophenyl-C,N')tris(dimethyldithiocarbamato)tellurium(IV) [AzoTe(dmdtc)$_3$] on photo- and thermal-oxdiation of PP, in the form of a compression moulded film processed for 5 minutes at 180°C in a closed mixer, is shown in Figures


N
N — Ph
Te(S2CNEt2)
N
N — Ph
Te(S2CNEt2)
S
+
e
-2e
-S
m/e = 491
N
N- Ph
Te(S2CNEt2)
+
m/e = 459
-(S2CNEt2)
(C12H9N2)2 Te2
N
N
Te
+
m/e = 311
-N2
Ph
Te
+
m/e = 283
-Ph
+
Te
or
+
Te
m/e = 206

Scheme 5.1

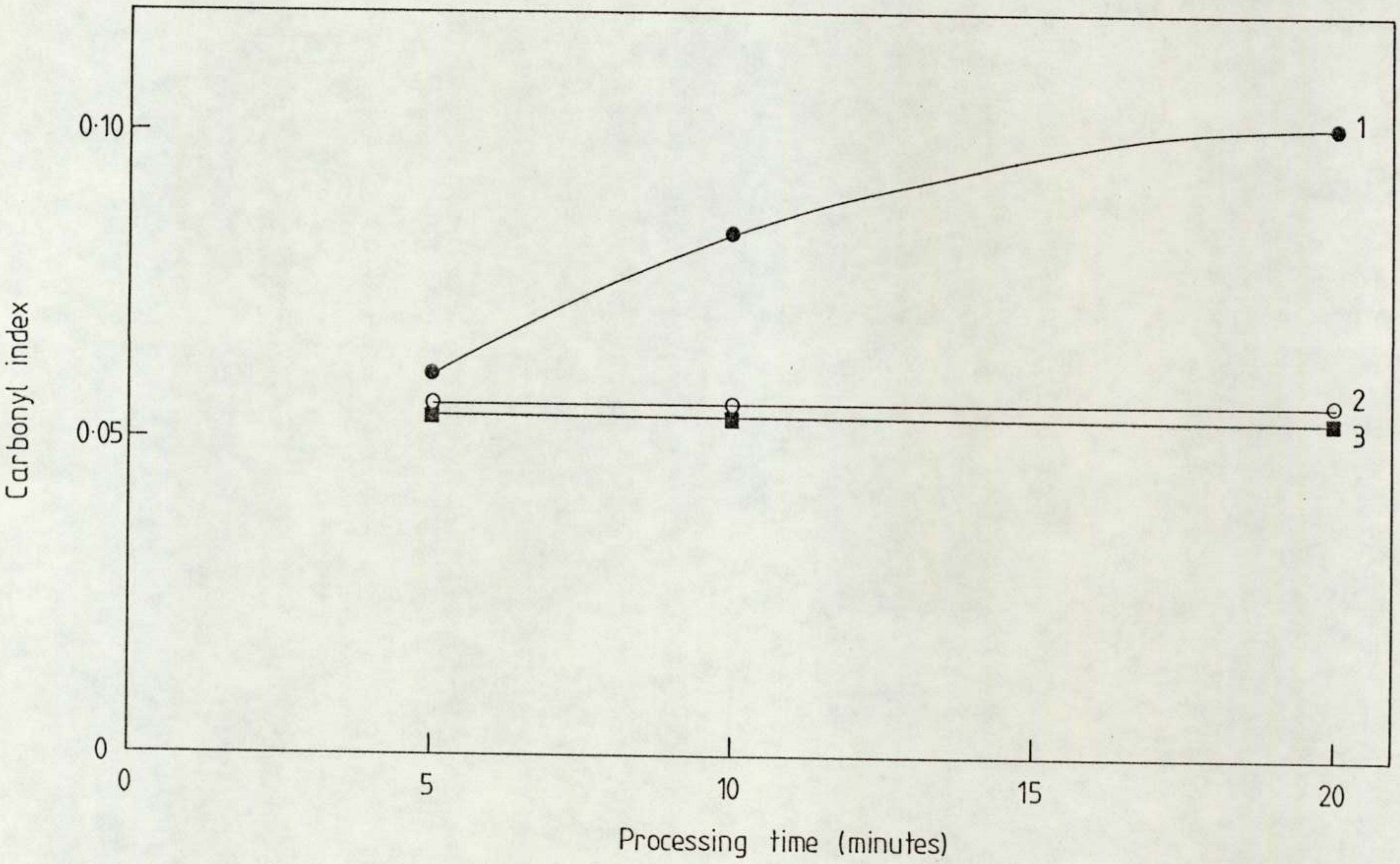


Figure 5.6 The effect of different additives on the oxidative stability of PP during processing in closed mixer (concentration of additives is 2.8 x 10^{-4} mole/100g) 1. PP (without additives) 2. AzoTe(dmdtc)$_3$ 3. AzoTe(dedtc)$_3$

5.7 and 5.8 respectively. On U.V. irradiation and heating in a Wallace oven at 140°C, it appears that the above additive, at all concentrations used, shows a stabilising action as evidenced by the length of the induction period and time to embrittlement (Table 5.7). It is also clearly shown that as the concentration of AzoTe(dmdtc)$_3$ in PP increased, the photo and thermal stability of the PP increased (Figures 5.7, 5.8 and Table 5.7).

A similar behaviour to AzoTe(dmdtc)$_3$ is shown by (2-phenylazophenyl-C,N')tris(diethyldithiocarbamato)tellurium(IV) [AzoTe(dedtc)$_3$] (Figures 5.9 and 5.10) except that the stability of PP in this case is better. This could be due to the fact that the ethyl compound is more soluble in the polymer than the methyl compound (see Chapter Three).

Figure 5.11 shows the effect of the processing time on photo-oxidation stability of PP containing 2.8×10^{-4} mole/100 g of AzoTe(dedtc)$_3$. Increasing the processing time results in a slight increase in the photo-stability of PP. This behaviour was similar to that of Te(didtc)$_4$ and Te(dbdtc)$_4$ (Chapter Three).

From these results, it is clear that AzoTe(dtc)$_3$ compounds are good stabilisers during the photo-oxidation. In this respect they are similar to Te(dedtc)$_4$(14) and Te(didtc)$_4$ (Chapter Three). As has been mentioned in Chapter Three,

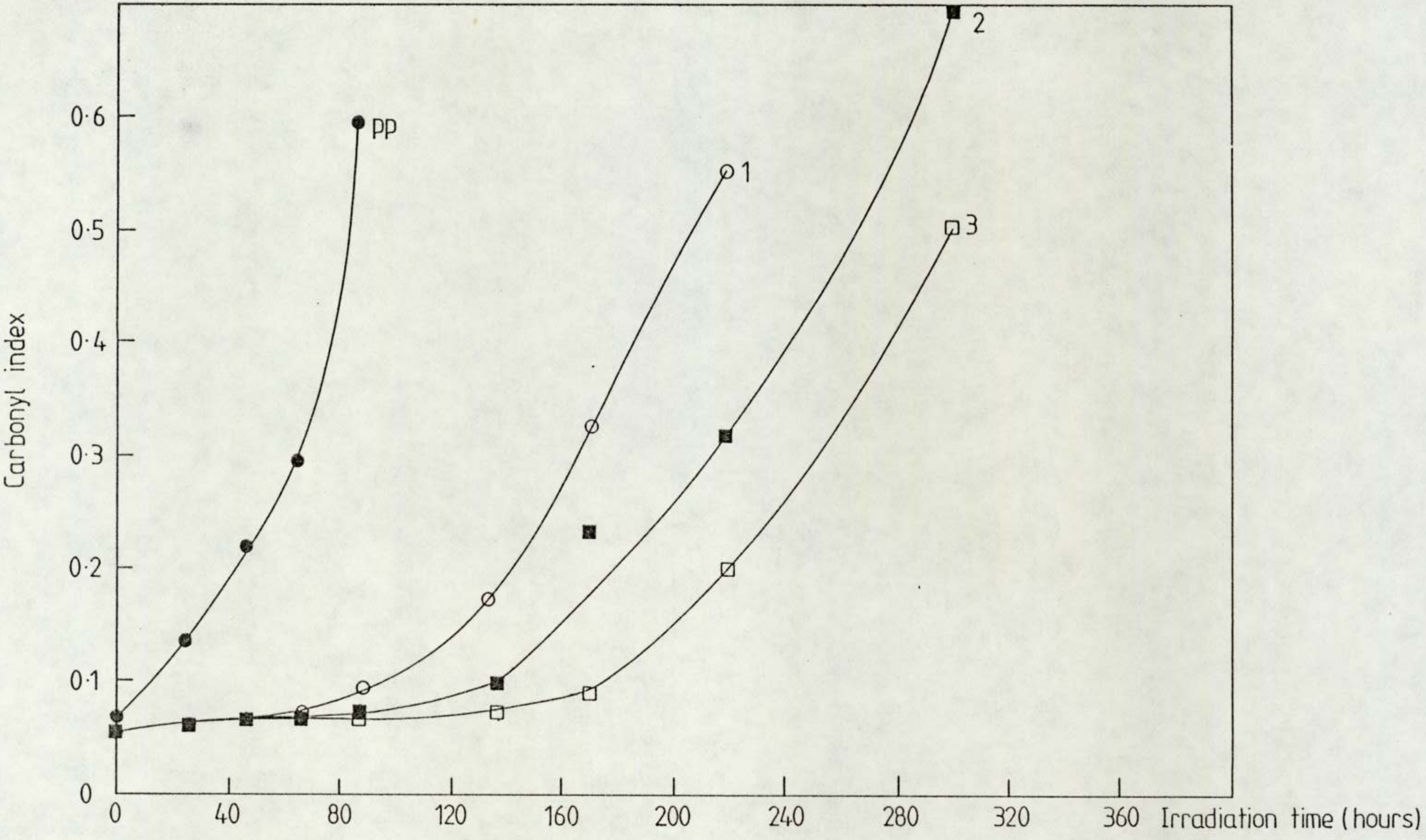
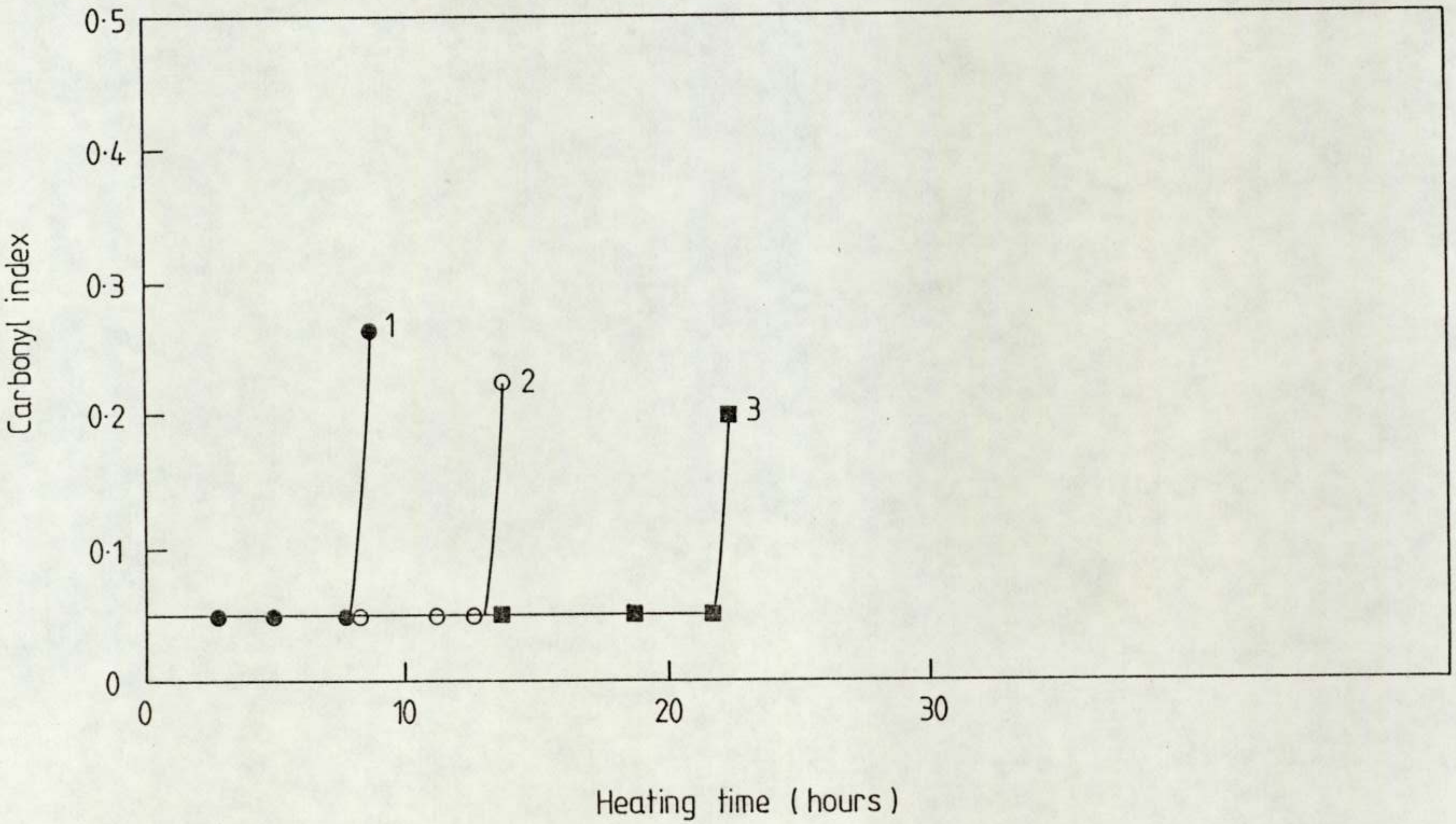


Figure 5.7 Effect of AzoTe(dmdtc)$_3$ at various concentrations on photo-oxidation of PP (processed in closed mixer at 180^{o}C for 5 minutes) 1. 0.7x10^{-4} mole/100g. 2. 1.4x10^{-4} mole/100g 3. 2.8x10^{-4} mole/100g



<u>Figure 5.8</u> Effect of AzoTe(dmdtc)$_3$ at various concentrations on thermal-oxidation of PP at 140^{o}C processed for 5 minutes (closed mixer) 1. 0.7x10^{-4} mole/100g 2. 1.4x10^{-4} mole/100g 3. 2.8x10^{-4} mole/100g

Sample	Concentration (mole/100 g)	Processing time (mins)	Embrittlement time (hrs)
AzoTe(dmdtc)$_3$	0.7×10^{-4}	5	170
	1.4×10^{-4}	5	220
	2.8×10^{-4}	5	330
AzoTe(dedtc)$_3$	0.7×10^{-4}	5	200
		10	215
		20	247
AzoTe(dedtc)$_3$	1.4×10^{-4}	5	255
		10	270
		20	290
AzoTe(dedtc)$_3$	2.8×10^{-4}	5	360
		10	375
		20	400

Table 5.7 Embrittlement time for PP with additives during photo-oxidation

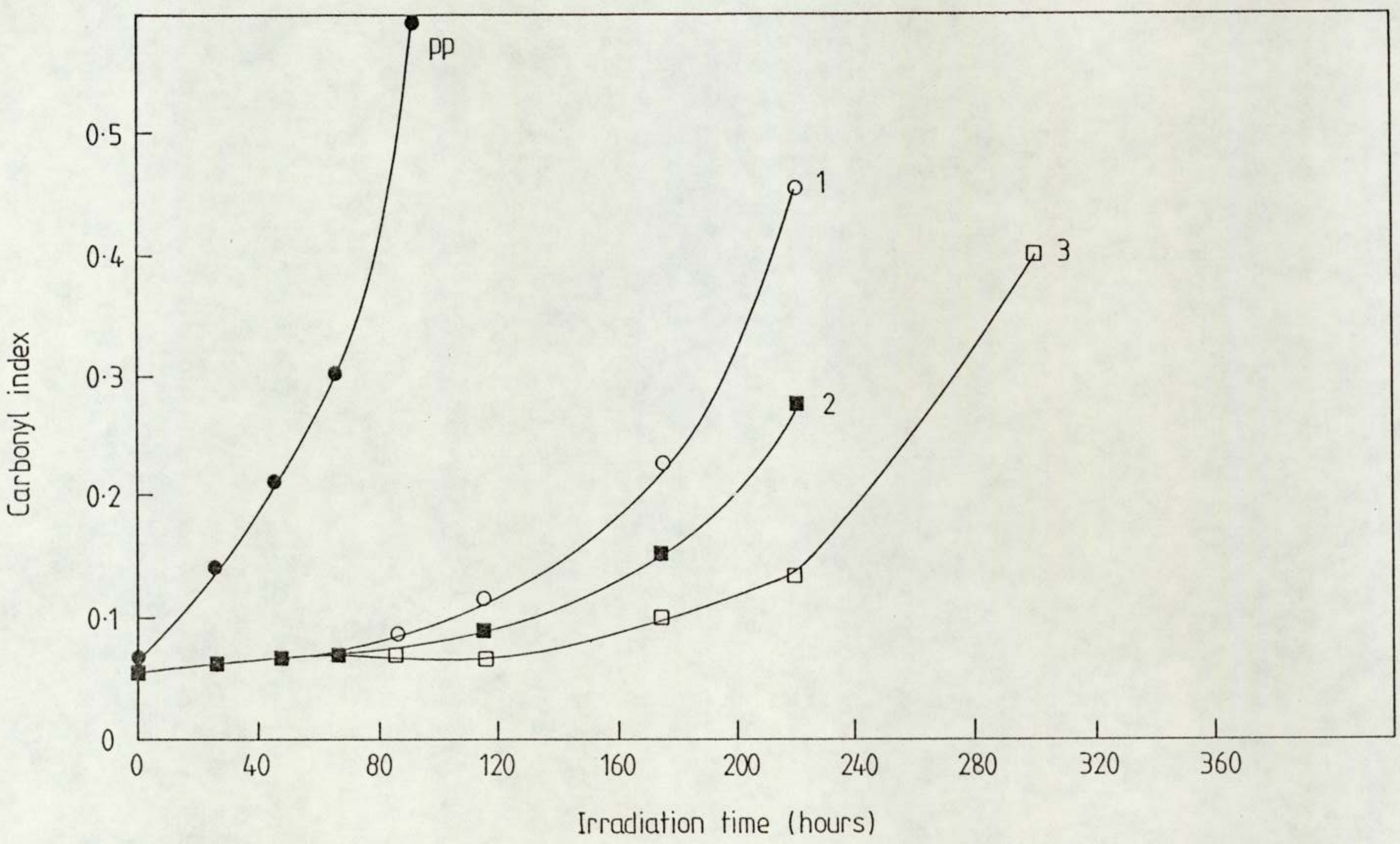


Figure 5.9 Effect of AzoTe(dedtc)$_3$ at various concentrations on photo-oxidation of PP (processed in closed mixer at 180^{o}C for 5 minutes) 1. 0.7x10^{-4} mole/100 g 2. 1.4x10^{-4} mole/100 g 3. 2.8x10^{-4} mole/100 g

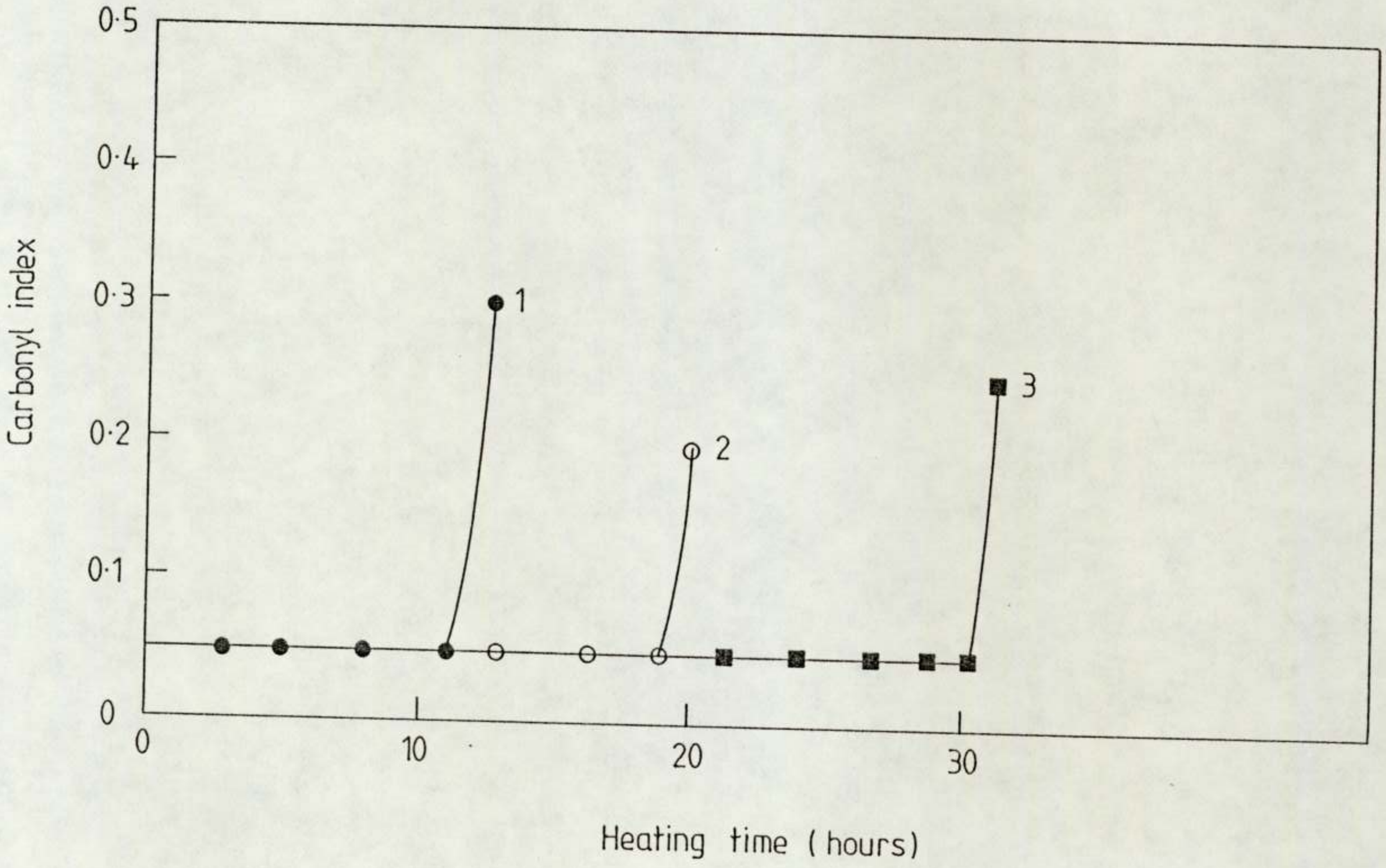
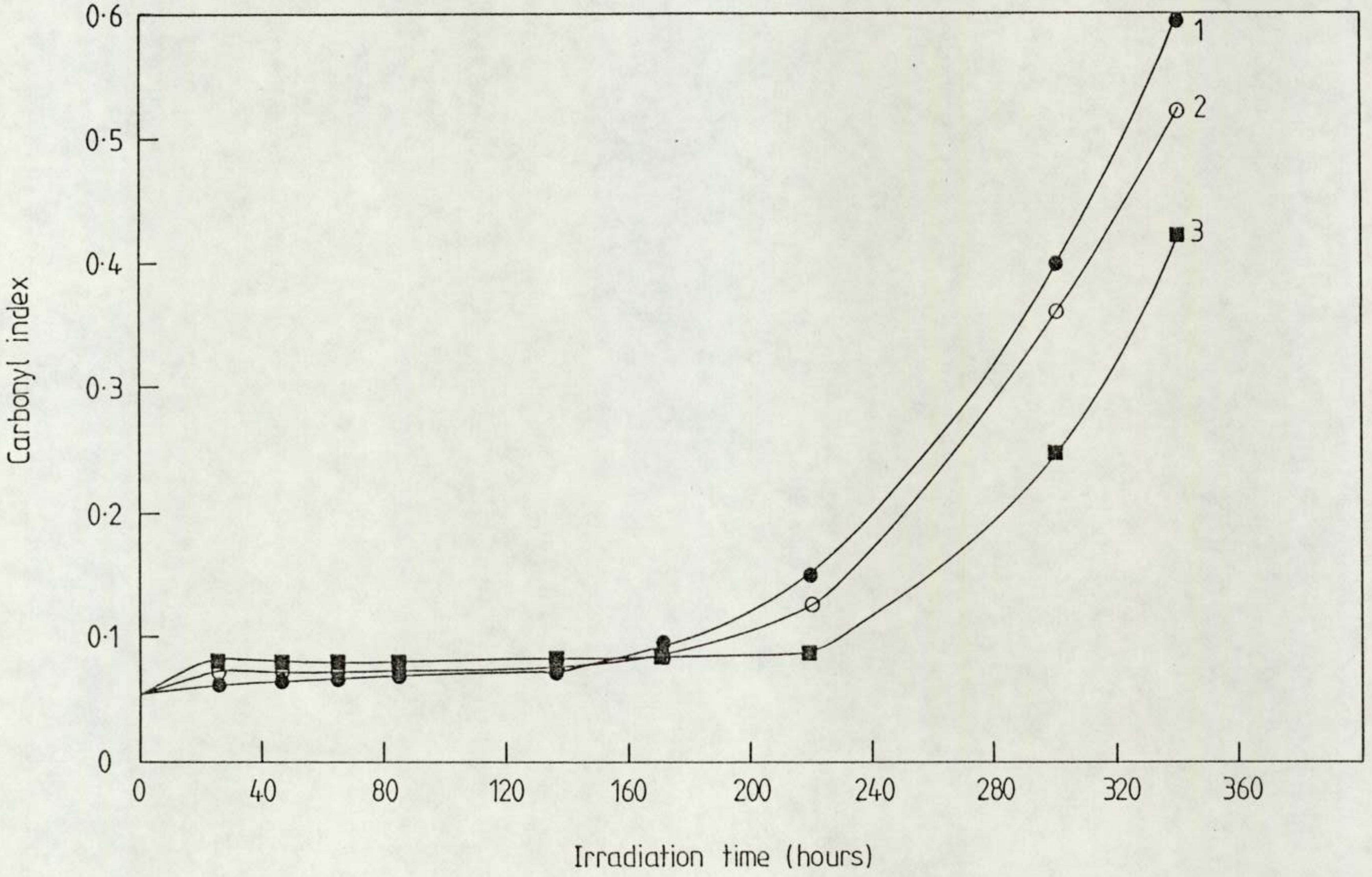


Figure 5.10 Effect of AzoTe(dedtc)$_3$ at various concentrations on thermal-oxidation of PP at 140^{o}C processed for 5 minutes (closed mixer) 1. 0.7x10^{-4} mole/100 g 2. 1.4x10^{-4} mole/100 g 3. 2.8x10^{-4} mole/100 g



<u>Figure 5.11</u> Effect of processing at 180°C (closed mixer) on photo-oxidation of PP containing 2.8×10^{-4} mole/100 g AzoTe(dedtc)$_3$ 1. 5 minutes 2. 10 minutes 3. 20 minutes

the simple tellurium dithiocarbamates ($Te(dtc)_n$, where n=2 and 4) react with dioxygen to give TeO_2 and the corresponding disulphide (TRTD), under U.V. irradiation. TRTD acts here as a hydroperoxide decomposer(14). Also the previous reaction will remove some of the dioxygen from the system. As a result, the $Te(dtc)_4$ compounds were found to be good stabilisers during the photo-oxidation of PP(14) (and Chapter Three).

However, the $AzoTe(dtc)_3$ treated material involves a different mechanism during the photo-oxidation of PP. These compounds decompose on heating to AzoTe(dtc) and TRTD (Section 5.1.2). Thus it is more probable that a similar decomposition is taking place during the thermal processing at 180°C:

$$AzoTe(dtc)_3 \xrightarrow{180^{\circ}C} AzoTe(dtc) + TRTD$$

It is well known that TRTD's are good hydroperoxide decomposers during photo-oxidation as has been postulated previously. It has also been reported that azo compounds in general are good U.V. absorbers(90). Thus the efficiency of $AzoTe(dtc)_3$ compounds as stabilisers for PP during photo-oxidation could be due to their decomposition products [AzoTe(dtc) and TRTD].

On the other hand, these compounds [$AzoTe(dtc)_3$] were found to be very much less effective as thermal stabilisers by comparison with the simple tellurium dithiocarbamates [$Te(dtc)_4$]. It was mentioned (Chapter Three) that $Te(dtc)_4$ decomposes on heating (during thermal processing at 180°C) to $Te(dtc)_2$ and TRTD. The TRTD's act as stabilisers during thermal-oxidation(14) and $Te(dtc)_2$ are good stabilisers for PP during thermal-oxidation(14). Also, it was demonstrated that different alkyl groups (of the dithiocarbamates) act differently (Chapter Three).

The $AzoTe(dtc)_3$ materials behave differently during thermal-oxidation of PP. They undergo decomposition to AzoTe(dtc) and TRTD during thermal processing at 180°C. As a result, it is clear that in both cases [$Te(dtc)_4$ and $AzoTe(dtc)_3$] TRTD is formed in the same molar ratio and the only difference is the Te(II) compound [$Te(dtc)_2$ and AzoTe(dtc)]. Abed-Ali(14) has found that $Te(dedtc)_2$ is a good stabiliser during thermal-oxidation. Thus, the low efficiency of $AzoTe(dtc)_3$ compounds as thermal stabilisers might be due to the organic group (phenylazophenyl) which was found to be a strong bidentate organic ligand with tellurium compounds (see Chapters Four, Six and Section 5.2.1).

5.2.5 ^{125}Te N.M.R.

Table 5.8 presents the chemical shifts of some azobenzene derivatives of tellurium(II) and tellurium(IV). The results show that the ^{125}Te N.M.R. chemical shifts reflect

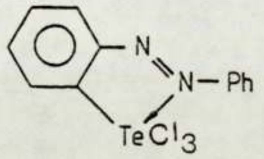
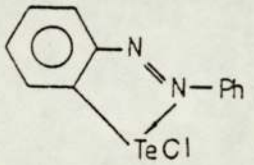
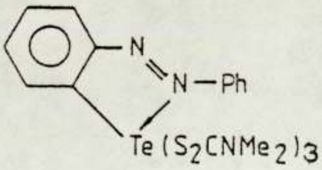
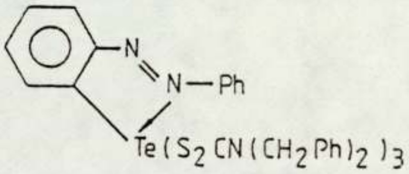
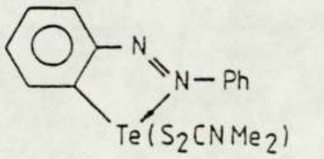
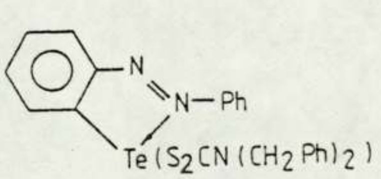
Compound	Solvent	Chemical shift (δ) ppm
	$CDCl_3$	1278.2
	DMSO	1486.5
	$CDCl_3$	1225.4
	$CDCl_3$	1239.6
	$CDCl_3$	1228.6
	$CDCl_3$	1239.1

Table 5.8 ^{125}Te N.M.R. data

the oxidation state of tellurium. Thus in going from Te(+IV) [$C_{12}H_9N_2TeCl_3$] to Te(+II) [$C_{12}H_9N_2TeCl$] a large downfield shift occurs (208.3 ppm, see Table 5.8).

These results also showed that the all tellurium dithiocarbamate compounds are in the same oxidation state in solution, since there are no significant differences between the chemical shifts of Te(II) and Te(IV) compounds. This is probably due to the dissociation of AzoTe(dtc)$_3$ to AzoTe(dtc) and TRTD in solution, since it is well known that these compounds are rather unstable compounds (see Section 5.1.2 and 5.2.3).

The other interesting observation of these data is that: electron donation causes shielding and electron withdrawal causes deshielding at tellurium. For example, in going from the electron donating dithiocarbamate group to the electron withdrawing chlorine causes large downfield shift change (∿254 ppm).

From this study it can be concluded that ^{125}Te N.M.R. will be a useful tool in determining and confirming the structures of the products in solution.

CHAPTER SIX

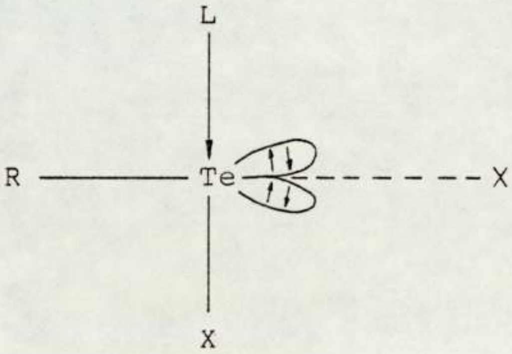
ACETATO(2-PHENYLAZOPHENYL-C,N')TELLURIUM(II)

AND

(2-PHENYLAZOPHENYL-C,N')THIOCYANATOTELLURIUM(II)

6.0 Introduction

All organotellurenyl compounds whose structures have been determined are stabilised by complex formation which may occur either via reaction with Lewis bases, or it may be intramolecular. The basic molecular structure is generally a "T" shape. A reasonable view of the structure would be one in which five electron pairs (two of which are non-bonding) distribute themselves around the metal atom to define a ϕ-trigonal bipyramid(i). When the tellurium atom is not part of a ring system, observed bond angles are close to 90° and 180°. A fourth (secondary) bond may form along an axis bisecting the angle between the lone pairs.



L=Lewis base
X=halogen

(i)

Phenyltellurenyl halides have been stabilised by co-ordination to a range of thioureas and selenoureas(91-94) (Table 6.1).

*Compound		Te-C (A)	Te-S or Te-Se (A)	Te-X (A)	Reference
PhTe(tu)Cl		2.12	2.50	3.00	91
PhTe(tu)Br		2.12	2.50	3.11,3.77	91
PhTe(etu)Cl		2.12	2.521	2.849,3.74	92
PhTe(etu)Br	I	2.116	2.556	2.835	93
(two forms)	II	2.123	2.523	2.969,3.831	93
PhTe(etu)I		2.124	2.614	3.003	94
PhTe(esu)Br		2.118	2.616	3.054,3.849	92

*Where tu=thiourea, etu=ethylenethiourea and esu=ethyleneselenourea

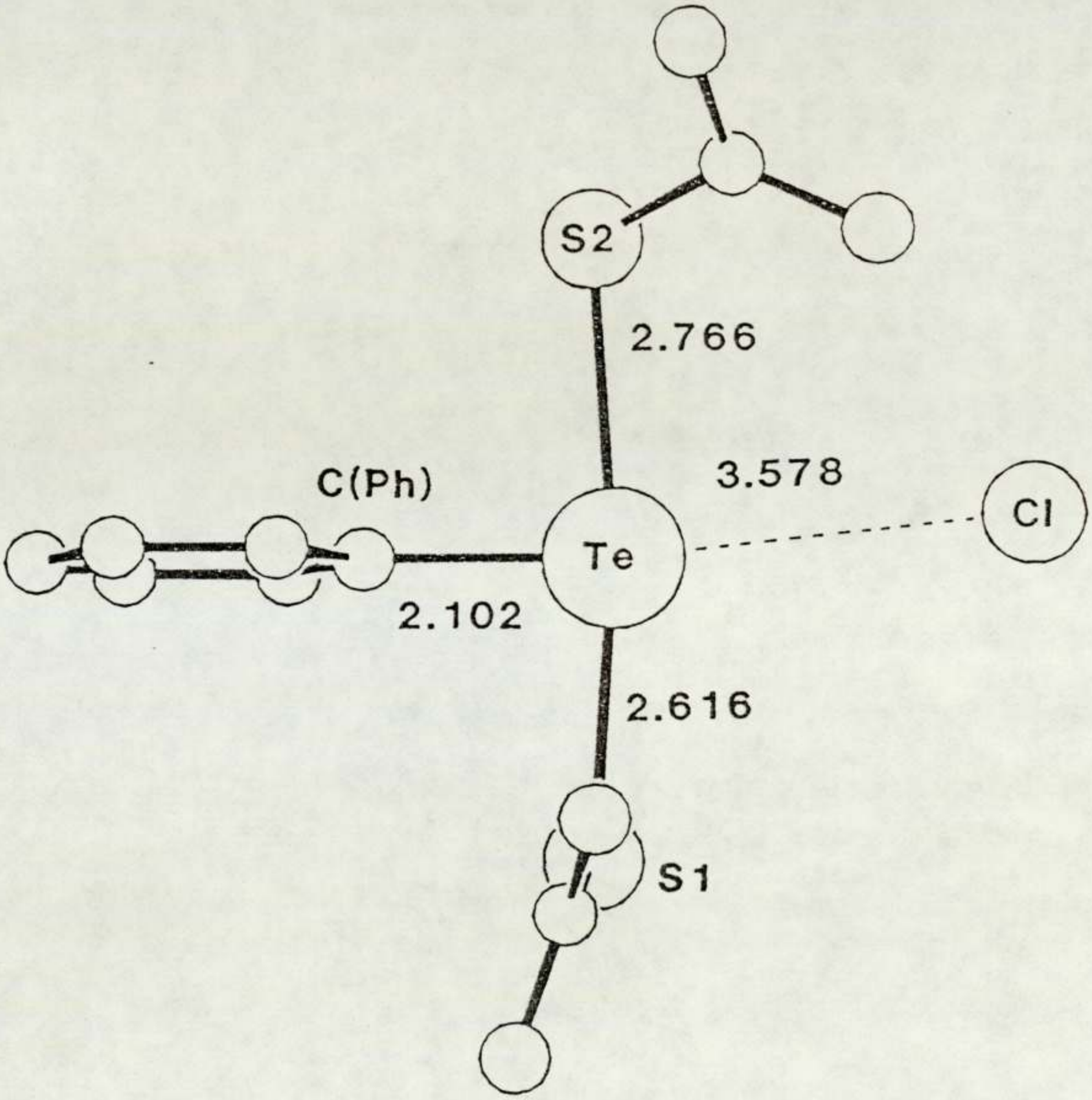
Table 6.1 Thiourea and selenourea complexes of phenyltellurenyl halides

It is noticeable that generally the Te-S and Te-Se bonds are of normal length whereas the Te-halogen bonds are longer than expected and hence the halogen carries a greater share of the non-bonding electron density. Sometimes a fourth, longer halogen contact is seen. The preferance of Te(II) for "soft" ligands is shown by the structures of $PhTe(tu)_2Cl$(95,96) and $PhTe(su)_2Cl$(96) (su=selenourea). The second compound is virtually ionic whereas the thiourea derivative has a long secondary Te.....Cl contact of 3.578 Å (ii).

The structure of the pseudo-halide derivatives $[Me_4N][PhTe(SCN)_2]$ and $[Me_4N][PhTe(SeCN)_2]$ are known(97) but in these cases the Te-S (2.665,2.702 Å) and Te-Se (2.764,2.823) distances are more comparable than when sulphur or selenium shares the axial position with a more electronegative element.

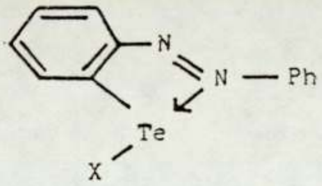
The presence of a donor group in an ortho-position to a tellurium atom in an aryl-chalcogen compound is a convenient way of achieving co-ordination. For example, o-carbonyl-containing groups have been shown, both in solution and in the solid state, to co-ordinate to the tellurium atom in aryltellurenyl halides(46) (see Chapter One).

More recently it has been shown that the o-nitro group also serves as an efficent stabilising ligand(47) (see Chapter One).



(ii)

An extensive series of azobenzene derivatives of tellurium(II) is now known (iii) where X=Cl$^{(36)}$, Br, I, CH_3COO, SCN$^{(98)}$ and R_2NCS_2 (Chapter Five). Ligand substitution reactions are readily carried out and the structures of compounds with X=Cl and Me_2NCS_2 have been determined. A very long Te.....Cl contact is seen in the former, having the value 3.66 Å, which is barely significant. However, in the later compound, a long Te-S intramolecular interaction (3.225 Å) is seen which is more significant.



(iii)

As part of the research currently taking place in our laboratory on azobenzene derivatives of Te(II), the molecular and crystal structures of acetato(2-phenylazophenyl-C,N')tellurium(II) and (2-phenylazophenyl-C,N')-thiocyanatotellurium(II) were determined, in order to confirm the co-ordination number and establish the stereochemistry of these compounds. Also the preparation*, I.R. and Mössbauer data for these two compounds which

---

*Two samples of these two complexes were kindly obtained from Dr F H Musa, but they were not in good condition, therefore were not used in the present investigation.

are the first examples of "RTeX" in which X is a CH_3COO or SCN group, are reported.

6.1 Experimental

6.1.1 Synthesis of Acetato(2-phenylazophenyl-C,N') Tellurium(II) [Compound I]

A solution of sodium acetate (0.082 g, 0.001 mol) in dry methanol (20 cm^3) was added, with stirring and under dinitrogen, to a solution of (2-phenylazophenyl-C,N')-tellurium(II) chloride(36) (0.344 g, 0.001 mol) in dichloromethane (25 cm^3) at room temperature. On completing the addition, the mixture was stirred for a further 20 minutes and the solvents were removed on a rotary evaporator. Dichloromethane (100 cm^3) was added to the residue with vigorous stirring. The solution was filtered to remove insoluble sodium chloride and the solvent was removed on a rotary evaporator. Methanol (5 cm^3) was added to the residue, which was stirred well and filtered off. The crude product was recrystallized from petroleum ether (60-80), under conditions of slow evaporation, golden-orange crystals being obtained which melted with decomposition at 121-122°C (Yield 75%).

Found: C,45.8; H,3.15; N,7.65% $C_{14}H_{12}N_2O_2Te$
Requires:C,45.7; H,3.26; N,7.62%

6.1.2 Synthesis of (2-Phenylazophenyl-C,N')thiocyanatotellurium(II) [Compound II]

A solution of ammonium thiocyanate (0.152 g, 0.002 mol) in dry methanol (40 cm^3) was added slowly, with stirring and under dinitrogen, to a refluxing mixture of (2-phenylazophenyl-C,N')tellurium(II) chloride$^{(36)}$ (0.688 g, 0.002 mol) and dichloromethane (50 cm^3). On completing the addition, the mixture was heated for a further 5 minutes and cooled to room temperature, with continuous stirring. The solvents were removed on a rotary evaporator and dichloromethane (200 cm^3) was added to the residue with vigorous stirring. The solution was filtered to remove insoluble sodium chloride and the solvent was removed on a rotary evaporator. Methanol (8 cm^3) was added to the product, which was stirred well and filtered off. The crude product recrystallized from methanol to give orange-red crystals, which melted with decomposition at 122°C. (Yield 60%).

Found: C,42.2; H,2.25; N,11.1; S,7.80 $C_{13}H_9N_3STe$
Requires: C,42.6; H,2.46; N,11.5; S,8.73%

Conductivity ($\Lambda^{-1}cm^2mol^{-1}$) = 5.25, in nitromethane at room temperature (concentration = 10^{-3} mole.litre^{-1})

6.1.3 X-ray Structure Analysis of I and II

After preliminary examination by photographic methods, the final cell dimensions and reflection intensities were measured with graphite-monochromated M_o-K_α radiation on an Enraf-Nonius CAD-4 diffractometer operating in the ω-2θ scan mode. Two standard reflections were measured every hour to check the stability of the system. Absorption corrections were not applied.

The structures were solved by Patterson and Fourier methods. The refinements were by least squares, using anisotropic temperature factors for the non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps and included in the calculations but their parameters were not refined. Refinement was terminated when all calculated shift/error ratios were <0.1. Details of crystal and experimental parameters are in Table 6.2. Final atomic co-ordinates for I and II are in Tables 6.3 and 6.4. Computation were carried out on the Honeywell computer at the University of Birmingham with SHELX(50). Pictures were drawn with PLUTO(99).

6.2 Results and Discussion

The reaction of (2-phenylazophenyl-C,N')tellurium(II) chloride with sodium acetate or sodium thiocyanate gave acetato(2-phenylazophenyl-C,N')tellurium(II) or

		I	II
Molecular formula		$C_{14}H_{12}N_2O_2Te$	$C_{13}H_9N_2STe$
Molecular weight		367.6	366.6
Crystal size (mm)		0.55x0.45x0.05	0.45x0.125x0.025
Cell constants(Å)	a	5.420(4)	7.357(5)
	b	11.361(2)	9.300(1)
	c	12.321(3)	10.188(1)
(°)	α	65.24(3)	70.50(1)
	β	79.57(3)	85.65(2)
	γ	86.94(3)	83.09(2)
Cell volume ($Å^3$)		677.40	651.86
Space group		$P\bar{1}$	$P\bar{1}$
Z		2	2
Density (g cm^{-3}) calc		1.802	1.868
" " m		1.791	1.872
Absorption coefficient (mm^{-1})		2.06	2.27
Data collection range (λ=0.71069 Å)2θ(°)		4-50	4-55
Scan range (ω°)		1.1+0.35tanθ	1.2+0.35tanθ
Scan speed range(°min^{-1})		3.3-0.9	3.3-1.2
Total data measured		2712	3134
Significant data[$I>2.5\sigma(I)$]		2152	2457
Least-squares weights $w=[\sigma^2(F)+KF^2]^{-1}$		K=0.0015	K=0.0010
Final R (%)		4.05	3.73
Final R_w (%)		5.06	4.72
Residual electron density in final difference map($eÅ^{-3}$)		-1.14 to +1.52	-0.85 to +1.58

Table 6.2 Crystal and experimental parameters

Atom	X	Y	Z
Te(1)	0.0365(1)	0.2436(0)	0.2610(0)
O(1)	-0.1815(7)	0.2181(3)	0.1410(4)
O(2)	0.0519(8)	0.0492(4)	0.1592(4)
N(1)	0.1287(8)	0.4547(4)	0.3430(4)
N(2)	0.1837(7)	0.3374(3)	0.3670(3)
C(1)	-0.0242(9)	0.5051(4)	0.2560(4)
C(2)	-0.1055(9)	0.4289(4)	0.2036(4)
C(3)	-0.2682(11)	0.4817(5)	0.1203(5)
C(4)	-0.3491(12)	0.6062(5)	0.0920(5)
C(5)	-0.2700(13)	0.6807(5)	0.1458(5)
C(6)	-0.1088(11)	0.6309(4)	0.2264(5)
C(7)	0.3382(8)	0.2785(4)	0.4563(4)
C(8)	0.3278(10)	0.1443(4)	0.5196(4)
C(9)	0.4780(12)	0.0855(5)	0.6065(5)
C(10)	0.6390(11)	0.1604(6)	0.6303(5)
C(11)	0.6490(10)	0.2937(5)	0.5659(5)
C(12)	0.4986(9)	0.3526(4)	0.4798(4)
C(13)	-0.1209(9)	0.1165(4)	0.1225(4)
C(14)	-0.2850(11)	0.0880(5)	0.0493(6)

<u>Table 6.3</u> Fractional atomic co-ordinates for $C_{12}H_9N_2TeOAc(I)$

Atom	X	Y	Z
Te(1)	-0.2168(0)	-0.2376(0)	-0.0315(0)
S(1)	-0.1508(3)	0.0560(2)	-0.1409(2)
N(1)	-0.2555(5)	-0.4848(4)	0.0105(4)
N(2)	-0.2430(5)	-0.5329(4)	-0.0932(4)
N(3)	-0.4975(10)	0.1805(6)	-0.2455(6)
C(1)	-0.2020(6)	-0.4213(5)	-0.2170(5)
C(2)	-0.1800(6)	-0.2721(5)	-0.2230(4)
C(3)	-0.1406(7)	-0.1648(5)	-0.3503(5)
C(4)	-0.1270(7)	-0.2063(60)	-0.4689(5)
C(5)	-0.1505(8)	-0.3544(6)	-0.4648(5)
C(6)	-0.1873(8)	-0.4621(5)	-0.3384(5)
C(7)	-0.2948(6)	-0.5959(5)	0.1433(4)
C(8)	-0.3090(6)	-0.7479(5)	0.1582(5)
C(9)	-0.3482(8)	-0.8481(6)	0.2879(6)
C(10)	-0.3733(8)	-0.7990(6)	0.4023(5)
C(11)	-0.3575(8)	-0.6490(6)	0.3873(5)
C(12)	-0.3184(7)	-0.5439(6)	0.2586(5)
C(13)	-0.3547(10)	0.1288(6)	-0.2015(6)

Table 6.4 Fractional atomic co-ordinates for $(C_{12}H_9N_2)TeSCN(II)$

(2-phenylazophenyl-C,N')thiocyanatotellurium(II) respectively. Both compounds were found to be stable in air for several months and have satisfactory elemental analysis (Sections 6.1.1 and 6.1.2) and I.R. data (Section 6.3).

6.2.1 The Crystal and Molecular Structure of Acetato(2-phenylazophenyl-C,N')tellurium(II) and (2-Phenylazophenyl-C,N')thiocyanatotellurium(II)

Pertinent distances, angles and torsion angles are given in Tables 6.5 (compound I) and 6.6 (compound II). The tellurium co-ordination geometries in both compounds are illustrated in Figures 6.1 and 6.2. The packing arrangements are shown in Figures 6.3 and 6.4. In both compounds, the co-ordination about tellurium is approximately trigonal bipyramidal with the carbon atom and the two lone pairs in the equatorial positions and either N(2) and O(1) (compound I) or N(2) and S(1) (compound II) in the axial positions. Thus in both structures the position trans to the bonded carbon atom is unoccupied. Both compounds are almost T-shaped. In compound I the tellurium atom is approached by a fourth atom, O(2) of the acetate group at a distance of 2.953(4) Å which illustrates the tendency of Te(II) to achieve square planar geometry as has been reported for many Te(II) complexes(88). However, in the present structure, distortions from square planar geometry

Te-O(1)	2.167(4)	N(1)-N(2)	1.270(5)
Te...O(2)	2.953(4)	N(2)-C(7)	1.420(6)
Te-N(2)	2.260(4)	C(7)-C(8)	1.391(6)
Te-C(2)	2.074(4)	C(8)-C(9)	1.383(8)
C(1)-C(2)	1.404(6)	C(9)-C(10)	1.397(9)
C(2)-C(3)	1.396(8)	C(10)-C(11)	1.383(8)
C(3)-C(4)	1.375(7)	C(11)-C(12)	1.378(8)
C(4)-C(5)	1.397(8)	C(12)-C(7)	1.386(6)
C(5)-C(6)	1.363(9)	O(1)-C(13)	1.283(6)
C(6)-C(1)	1.393(7)	O(2)-C(13)	1.205(6)
C(1)-N(1)	1.387(7)	C(13)-C(14)	1.509(7)
N(2)-Te-O(1)	159.0(1)	C(7)-N(2)-Te	126.2(3)
C(2)-Te-O(1)	85.3(2)	N(2)-C(7)-C(8)	118.8(4)
C(2)-Te-N(2)	73.9(2)	N(2)-C(7)-C(12)	121.0(4)
C(2)-C(1)-C(6)	120.2(5)	C(8)-C(7)-C(12)	120.2(4)
C(1)-C(2)-C(3)	119.2(4)	C(7)-C(8)-C(9)	119.4(5)
C(2)-C(3)-C(4)	119.8(5)	C(8)-C(9)-C(10)	120.3(5)
C(3)-C(4)-C(5)	120.7(5)	C(9)-C(10)-C(11)	119.7(5)
C(4)-C(5)-C(6)	120.2(5)	C(10)-C(11)-C(12)	120.2(5)
C(1)-C(6)-C(5)	120.0(5)	C(11)-C(12)-C(7)	120.2(4)
C(1)-N(1)-N(2)	113.1(4)	Te-O(1)-C(13)	112.3(3)
N(1)-C(1)-C(6)	118.6(4)	Te-C(2)-C(3)	126.4(3)
N(1)-C(1)-C(2)	121.0(4)	Te-C(2)-C(1)	114.5(3)
N(1)-N(2)-Te	117.4(3)	O(1)-C(13)-O(2)	123.7(5)
N(1)-N(2)-C(7)	116.4(4)	O(1)-C(13)-C(14)	114.0(4)
N(2)-Te-O(2)	152.9	O(2)-C(13)-C(14)	122.3(4)
O(2)-Te-O(1)	47.8		
C(7)-N(2)-N(1)-C(1)	-179.460	N(2)-N(1)-C(1)-C(2)	0.450
N(1)-N(2)-C(7)-C(8)	155.651	N(2)-N(1)-C(1)-C(6)	176.626
N(1)-N(2)-C(7)-C(12)	-24.878		

Table 6.5 Bond distances (Å), angles (°) and torsion angles (°) in I

Te-S(1)	2.672(1)	N(2)-N(1)	1.270(5)
Te-N(1)	2.243(3)	N(1)-C(7)	1.436(6)
Te-C(2)	2.073(4)	C(7)-C(8)	1.386(6)
C(1)-C(2)	1.397(6)	C(8)-C(9)	1.372(7)
C(2)-C(3)	1.382(6)	C(9)-C(10)	1.380(8)
C(3)-C(4)	1.379(9)	C(10)-C(11)	1.370(8)
C(4)-C(5)	1.395(7)	C(11)-C(12)	1.383(7)
C(5)-C(6)	1.374(7)	C(12)-C(7)	1.405(7)
C(6)-C(1)	1.403(6)	S(1)-C(13)	1.646(7)
C(1)-N(2)	1.379(7)	C(13)-N(3)	1.158(9)
S(1)-Te-N(1)	166.8(1)	C(2)-C(1)-N(2)	121.7(4)
S(1)-Te-C(2)	92.6(1)	C(1)-N(2)-N(1)	112.9(4)
N(1)-Te-C(2)	74.2(2)	N(2)-N(1)-C(7)	115.9(3)
Te-S(1)-C(13)	98.4(2)	N(2)-N(1)-Te	117.4(3)
S(1)-C(13)-N(3)	179.3(6)	Te-N(1)-C(7)	126.7(3)
Te-C(2)-C(3)	127.1(3)	N(1)-C(7)-C(12)	117.0(4)
Te-C(2)-C(1)	113.7(3)	N(1)-C(7)-C(8)	121.9(4)
C(1)-C(2)-C(3)	119.1(4)	C(8)-C(7)-C(12)	121.1(4)
C(2)-C(3)-C(4)	119.5(4)	C(7)-C(8)-C(9)	119.1(5)
C(3)-C(4)-C(5)	122.1(4)	C(8)-C(9)-C(10)	120.7(5)
C(4)-C(5)-C(6)	118.7(5)	C(9)-C(10)-C(11)	120.0(5)
C(5)-C(6)-C(1)	119.8(4)	C(10)-C(11)-C(12)	121.3(5)
C(6)-C(1)-C(2)	120.8(4)	C(11)-C(12)-C(7)	117.8(5)
C(6)-C(1)-N(2)	117.4(4)		
C(1)-N(2)-N(1)-C(7)	-178.963	N(1)-N(2)-C(1)-C(6)	-179.232
N(2)-N(1)-C(7)-C(8)	3.114	N(1)-N(2)-C(1)-C(2)	-0.747
N(2)-N(1)-C(7)-C(12)	-176.886		

Table 6.6 Bond distances (Å), angles (°) and torsion angles (°) in II

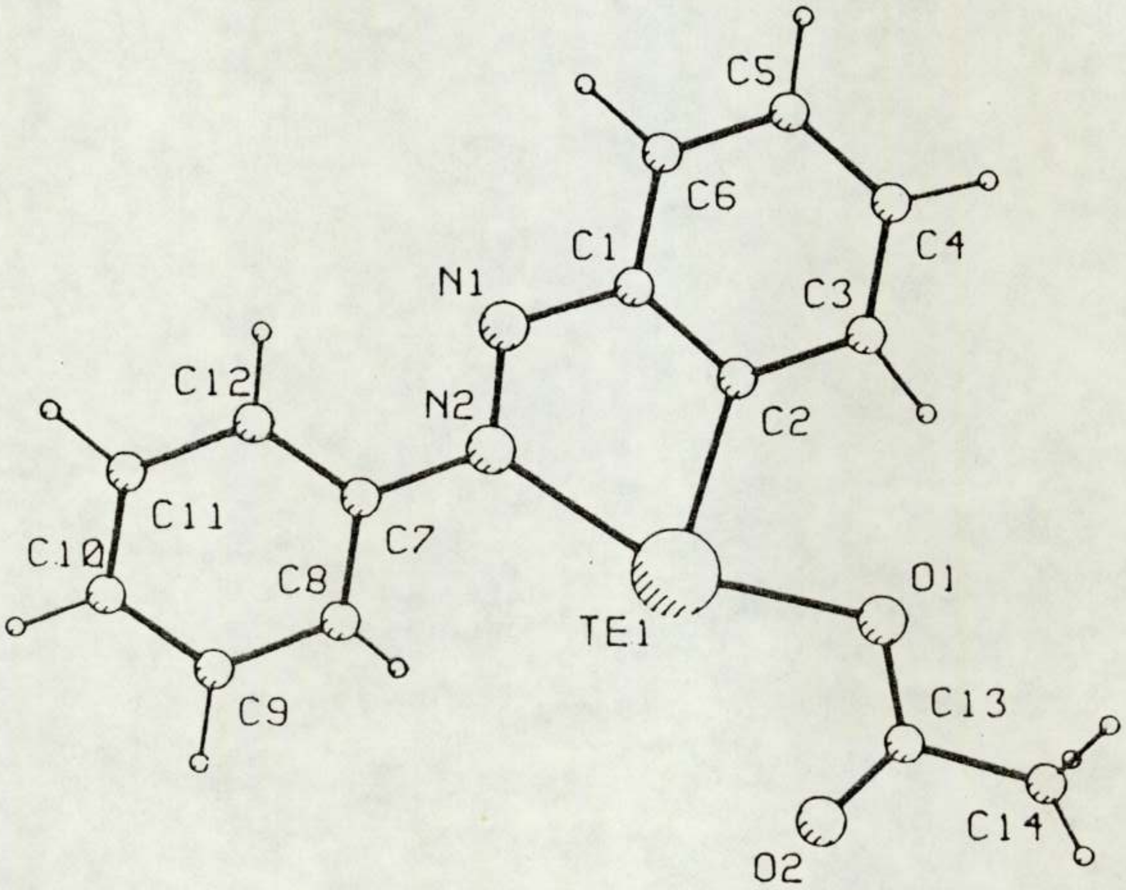


Figure 6.1 The structure of $(C_{12}H_9N_2)Te(OAc)$ showing the atom numbering

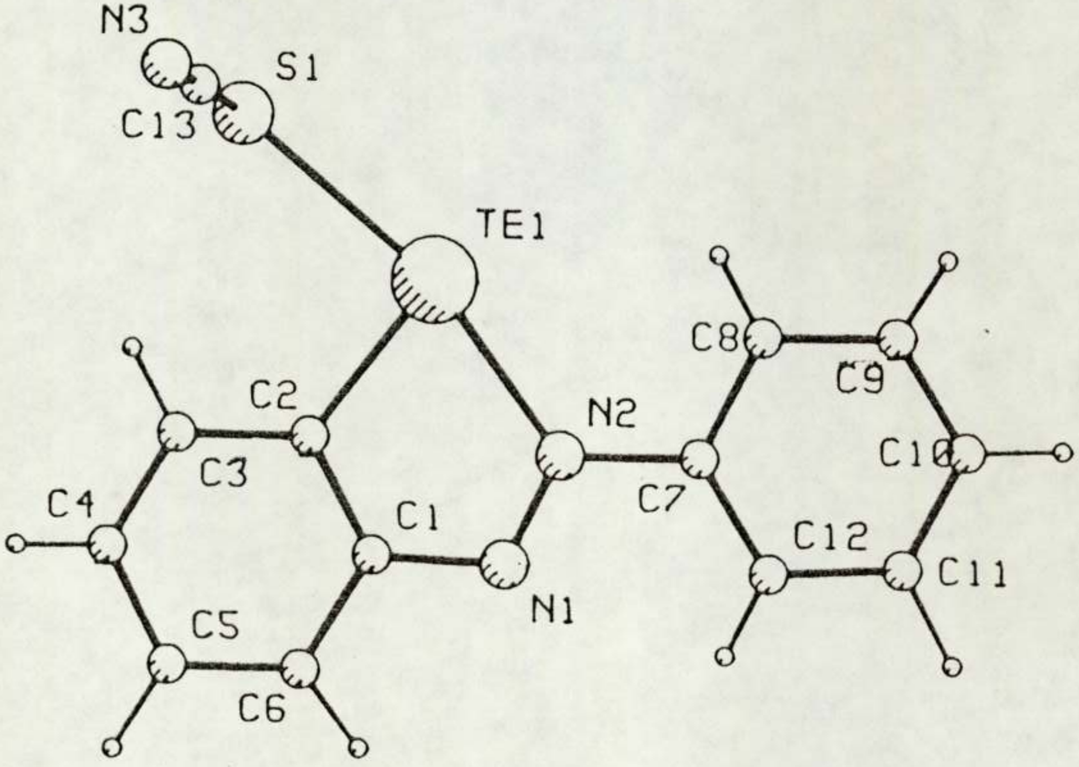


Figure 6.2 The structure of $(C_{12}H_9N_2)Te(SCN)$ showing the atom numbering

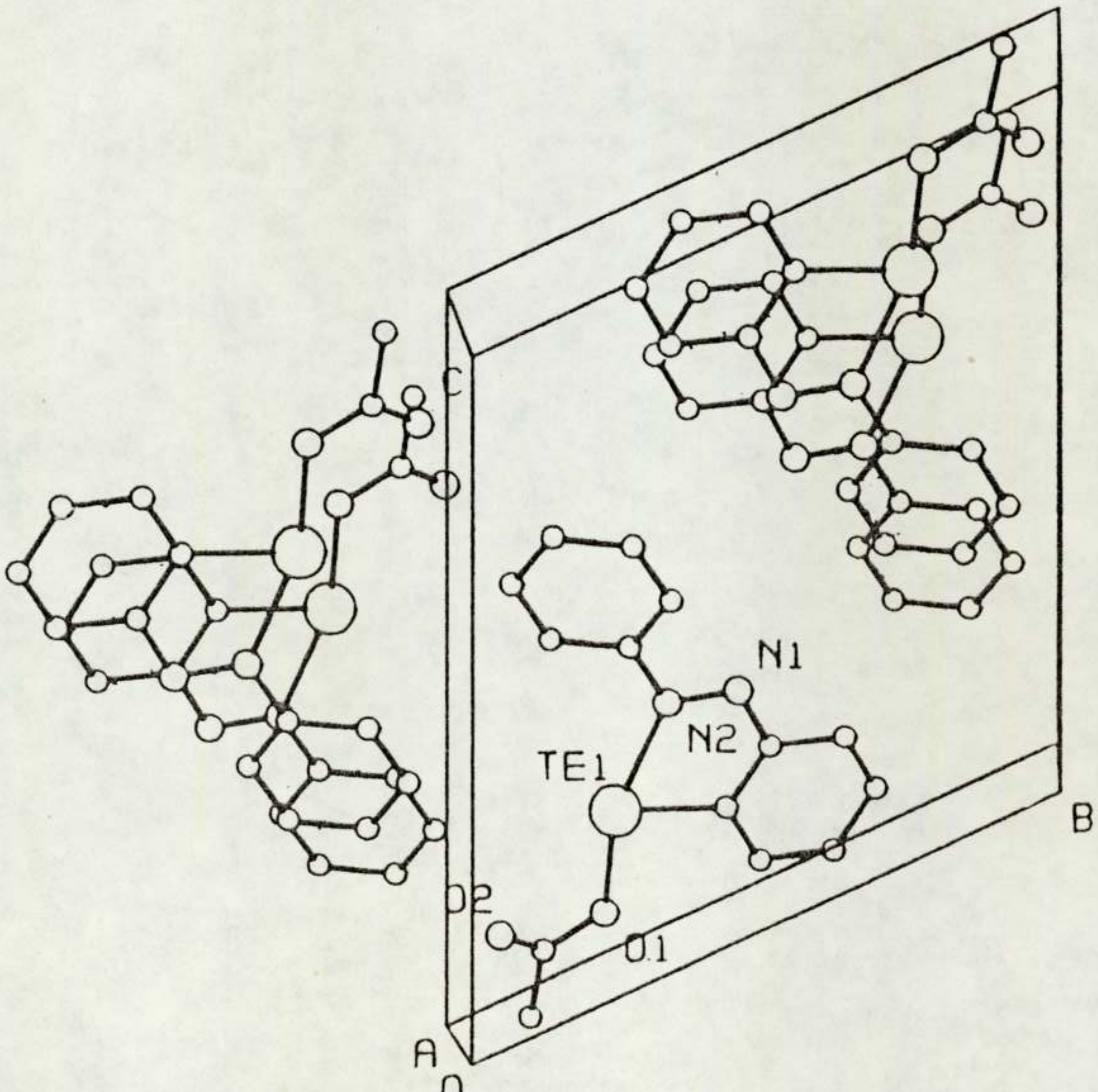


Figure 6.3 The packing diagram of $(C_{12}H_9N_2)Te(OAc)$

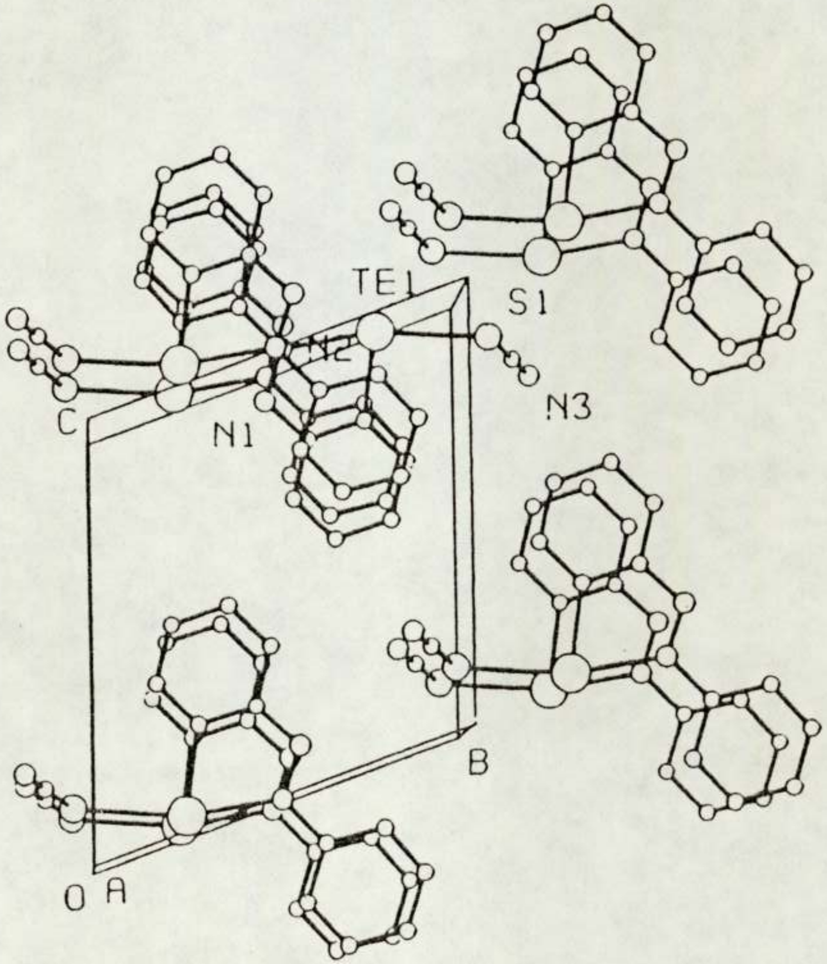


Figure 6.4 The packing diagram of $(C_{12}H_9N_2)Te(SCN)$

are very considerable (see Table 6.4). In compound II, tellurium is approached by N(3) of a neighbouring molecule at a distance of 3.535(3) Å, indicating a possible very weak interaction. This nitrogen atom is situated 1.660(5) Å from the tellurium co-ordination plane (see Figure 6.4).

In (I) the organic ligand is not planar. There is a twist of ca 25° of the free phenyl ring relative to the other phenyl ring and the nitrogen atoms, which are coplanar to within ± 0.025 Å. The tellurium atom lies in this plane and O(1) and O(2) deviate by 0.039 and -0.55 Å respectively. C(13) and C(14) of the acetate group are displaced by -0.22 and -0.07 Å from the plane. The acetate group itself is accurately coplanar (Table 6.7). A similar twist of the free phenyl ring occurs in the crystal structure of dimethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II) (Chapter Five).

In compound (II) the situation is different. The organic ligand is planar to within ± 0.04 Å with the tellurium atom close to the plane (deviation from mean plane 0.02Å). The sulphur atom is displaced by 0.10 Å. The thiocyanato-group is nearly linear (N-C-S angle 179.3(6)°) and is oriented approximately perpendicular to the Te-organic ligand plane, angle Te-S-C, 98.4(2)° (see Figure 6.2 and Table 6.8). Similar geometries have been reported for

P_1 Plane defined by $C_{(1)}$, $C_{(2)}$, $C_{(3)}$, $C_{(4)}$, $C_{(5)}$, $C_{(6)}$, $N_{(1)}$, $N_{(2)}$, $C_{(7)}$, $C_{(8)}$, $C_{(9)}$, $C_{(10)}$, $C_{(11)}$ and $C_{(12)}$

P_2 Plane defined by $C_{(1)}$, $C_{(2)}$, Te, $N_{(1)}$ and $N_{(2)}$

P_3 Plane defined by $C_{(2)}$, $N_{(2)}$, Te, $O_{(1)}$ and $O_{(2)}$

P_4 Plane defined by $O_{(1)}$, $C_{(13)}$, $C_{(14)}$ and $O_{(2)}$

Atom	P_1	P_2	P_3	P_4
Te	-0.5871	-0.0170	0.1007	0.1994
$O_{(1)}$	-0.8069	0.0740	0.1781	-0.0007
$O_{(2)}$	-1.7385	-0.5649	-0.1450	-0.0008
$N_{(1)}$	0.0665	-0.0102	-0.1824	-0.0721
$N_{(2)}$	-0.1238	0.0199	0.0319	0.2901
$C_{(1)}$	-0.0009	-0.0146	-0.2951	-0.4286
$C_{(2)}$	-0.2477	0.0218	-0.1657	-0.3648
$C_{(3)}$	-0.2495	0.0749	-0.2280	-0.6769
$C_{(4)}$	0.0089	0.1110	-0.3940	-1.0210
$C_{(5)}$	0.2717	0.0930	-0.5034	-1.0641
$C_{(6)}$	0.2613	0.0255	-0.4601	-0.7770
$C_{(7)}$	-0.0582	0.0384	0.1711	0.6824
$C_{(8)}$	0.2544	0.5720	0.8874	1.5432
$C_{(9)}$	0.3166	0.5919	1.0270	1.9300
$C_{(10)}$	0.0658	0.0790	0.4520	1.4586
$C_{(11)}$	-0.2550	-0.4587	-0.2669	0.5944
$C_{(12)}$	-0.3102	-0.4732	-0.4014	0.2133
$C_{(13)}$	-1.3205	-0.1934	0.0801	0.0020
$C_{(14)}$	-1.3677	-0.0109	0.2635	-0.0006

Table 6.7 Deviations of atoms (Å) from mean planes $[(C_{12}H_9N_2)Te(OAc)]$

P_1 Plane defined by $C_{(2)}$, $C_{(3)}$, $C_{(4)}$, $C_{(5)}$, $C_{(6)}$, $C_{(1)}$, $N_{(1)}$, $N_{(2)}$, $C_{(7)}$, $C_{(8)}$, $C_{(9)}$, $C_{(10)}$, $C_{(11)}$ and $C_{(12)}$

P_2 Plane defined by Te, $N_{(2)}$, $N_{(1)}$, $C_{(1)}$ and $C_{(2)}$

P_3 Plane defined by S, Te, $N_{(2)}$ and $C_{(2)}$

P_4 Plane defined by Te, S, $C_{(13)}$ and $N_{(3)}$

Atom	P_1	P_2	P_3	P_4
Te	0.0212	-0.0068	-0.0161	-0.00001
S	0.0970	0.0293	0.0083	-0.0021
$N_{(1)}$	0.0055	0.0101	-0.0066	-0.5092
$N_{(2)}$	-0.0175	-0.0080	0.0103	-1.7208
$N_{(3)}$	-2.6250	-2.6996	-2.7226	-0.0031
$C_{(1)}$	0.0048	-0.0019	-0.0029	-2.5417
$C_{(2)}$	0.0327	0.0066	-0.00253	-2.0448
$C_{(3)}$	0.0421	0.0005	-0.0134	-2.9141
$C_{(4)}$	0.0005	-0.0372	-0.0501	-4.2460
$C_{(5)}$	-0.0423	-0.0606	-0.0679	-4.7549
$C_{(6)}$	-0.0344	-0.0373	-0.0398	-3.8999
$C_{(7)}$	0.0077	0.0284	0.0335	0.3988
$C_{(8)}$	0.0499	0.0902	0.1011	-0.0338
$C_{(9)}$	0.0398	0.0948	0.1101	0.8855
$C_{(10)}$	-0.0120	0.0383	0.0525	2.2245
$C_{(11)}$	-0.0416	-0.0108	-0.0022	2.6465
$C_{(12)}$	-0.0350	-0.0194	-0.0156	1.7557
$C_{(13)}$	-1.5024	-1.5741	-1.5963	0.0052

Table 6.8 Deviations of atoms (Å) from mean planes $[(C_{12}H_9N_2)Te(SCN)]$

other thiocyanate complexes of Te(II) and Te(IV) e.g., $Te(etu)_2(SCN)_2$(100) (where etu=ethylenethiourea), $[(CH_3)_4N][C_6H_5Te(SCN)_2]$(97) and $[Te(HOCH_2CH_2(CH_3)NCS_2)_3SCN]$(25).

The bonding between tellurium and the (2-phenylazophenyl) group is quite similar in the two compounds. The Te-N bonds are 2.260(4) Å in (I) and 2.243(3) Å in (II) and the Te-C bonds 2.074(4) and 2.073(4) Å. These values may be compared with the results obtained in the crystal structures of (2-phenylazophenyl-C,N')tellurium(II) chloride(36) and dimethyldithiocarbámate (Chapter Five) [Te-C 2.04(2), 2.10(8) and Te-N 2.23(2), 2.340(7) Å]. They also agree with the sum of covalent radii for Te (axial direction)(89) and nitrogen (2.24 Å) and Te (equatorial direction)(89) and sp^2-hybridised carbon (2.08 Å), considering the Te co-ordination to be essentially trigonal bipyramidal as previously postulated. The N-Te-C angles are also similar in the four compounds.

Te-O distances (compound I) 2.167(4) and 2.953 Å, are in good agreement with those found in bis(p-methoxyphenyl)-tellurium(IV) diacetate [2.161 and 2.988 Å (av.)](101). The Te-O(I) bond length, 2.167(4) Å, is in good agreement with the sum of covalent radii if the axial radius of tellurium is taken to be 1.54 Å(89) giving an estimated length of 2.20 Å for Te-O. However, the length is approximately 0.1-0.2 Å longer than many other previously reported values (102-104), but differences in geometry make comparisons difficult.

The Te-O(2) length (2.953 Å) is longer than the sum of covalent radii (89,76), but shorter than the sum of the van der Waals radii 3.6 Å according to Pauling (76) or 3.46 Å according to Bondi (80), indicating a weak intramolecular interaction. Long Te-O bonds also have been reported in e.g., 2,6-diacetylpyridine(C,N,O)tellurium(IV) trichloride (2.878 Å) (71) and in two modifications of TeO_2 (2.89 and 2.73 Å) (105).

Weak interactions clustered around the tellurium lone pairs of electrons in the equatorial plane, roughly <u>trans</u> to the carbon atom of an organic ligand, appear to be common in organotellurium(II) derivatives (88,89).

The Te-S(1) distance (compound II) of 2.672(1) Å is slightly larger than the sum of the covalent radii (2.58 Å) (89,76) but agrees well with values found for other Te(II)-thiocyanate complexes (97,100), range 2.665-2.702 Å. The next closest interaction involves a nitrogen atom from a neighbouring molecule (-x,-y,-z), Te....N(3)=3.535 Å, which is close to the van der Waals distance (3.7 Å) (76) or (3.56 Å) (80). If this weak interaction is significant, it would link the molecules into dimers. Bond length in the phenylazophenyl groups are generally in good agreement with those found for free azobenzene(106). However, in the moiety involved in bonding to tellurium, significant differences occur. Thus the N=N double bond, 1.270(5) Å in both (I) and (II) is slightly, but significantly, longer than the value (1.243(3) Å) in free azobenzene, or than the sum of the covalent radii (1.24 Å)(76). The C-N bond to the complexed phenyl ring is 1.387(7) in (I) and 1.379(7)Å in (II) compared with 1.420(6) (I) and 1.436(6) Å (II) to the free phenyl ring and 1.433 Å in free azobenzene. This significant shortening of the C-N bond and lengthening of the N=N bond in the complexed moieties may indicate electron delocalisation in the five-membered heterocyclic ring. Such an effect has been predicted on the basis of Mössbauer data for (2-phenylazophenyl-C,N)-tellurium(II) chloride(89).

C-S (1.646(7) Å) and C≡N (1.158(9) Å) in the thiocyanate group (compound II) are in good agreement with those found for Te(II) thiocyanate complexes(97,100) range 1.594-1.643 for C-S and 1.128-1.179 Å for C≡N. The C-S distance is considerably shorter than the expected value (1.81 Å)(76).

The dimensions of the acetate group (compound I) are in good agreement with those found in bis(p-methoxyphenyl)-tellurium(IV) diacetate(101), C-C 1.503 (av.) C=O 1.216 (av.) and C-O 1.307 (av.) Å.

6.3 Vibrational Spectroscopy

Figures 6.5 and 6.6 show the infra-red spectra of acetato(2-phenylazophenyl-C,N')tellurium(II) and (2-phenylazophenyl-C,N')thiocyanatotellurium(II) respectively. Because of the great difference between acetate and thiocyanate groups, the I.R. spectra of these two compounds will be discussed separately. The acetate compound will be considered initially.

The I.R. spectrum of acetato(2-phenylazophenyl-C,N')tellurium(II) is complex, the reason for that being the coupling of vibrations of the acetato and phenylazophenyl groups in the region beyond 1600 cm^{-1}. However, we were able to assign three major bands $\nu_{as}(OCO)$, $\nu_s(OCO)$ and $\nu(TeO)$, following the vibrational study of organotellurium carboxylates by McWhinnie et al(107). The $\nu_{as}(OCO)$ stretching frequency of acetato(2-phenylazophenyl-C,N')-tellurium(II) occurs at 1640 cm^{-1}, which is similar in position to that band found in $Ph_2Te(OOCCH_3)_2$(107) which was interpreted as being characteristic of a unidentate acetate group. In comparison, compounds where chelation by the carboxylate is considered to occur, this frequency is at 1600 cm^{-1}(108).

Further, the $\nu_s(OCO)$ stretching frequency occurred at $\sim$1298 cm^{-1} which is also close to the value found for

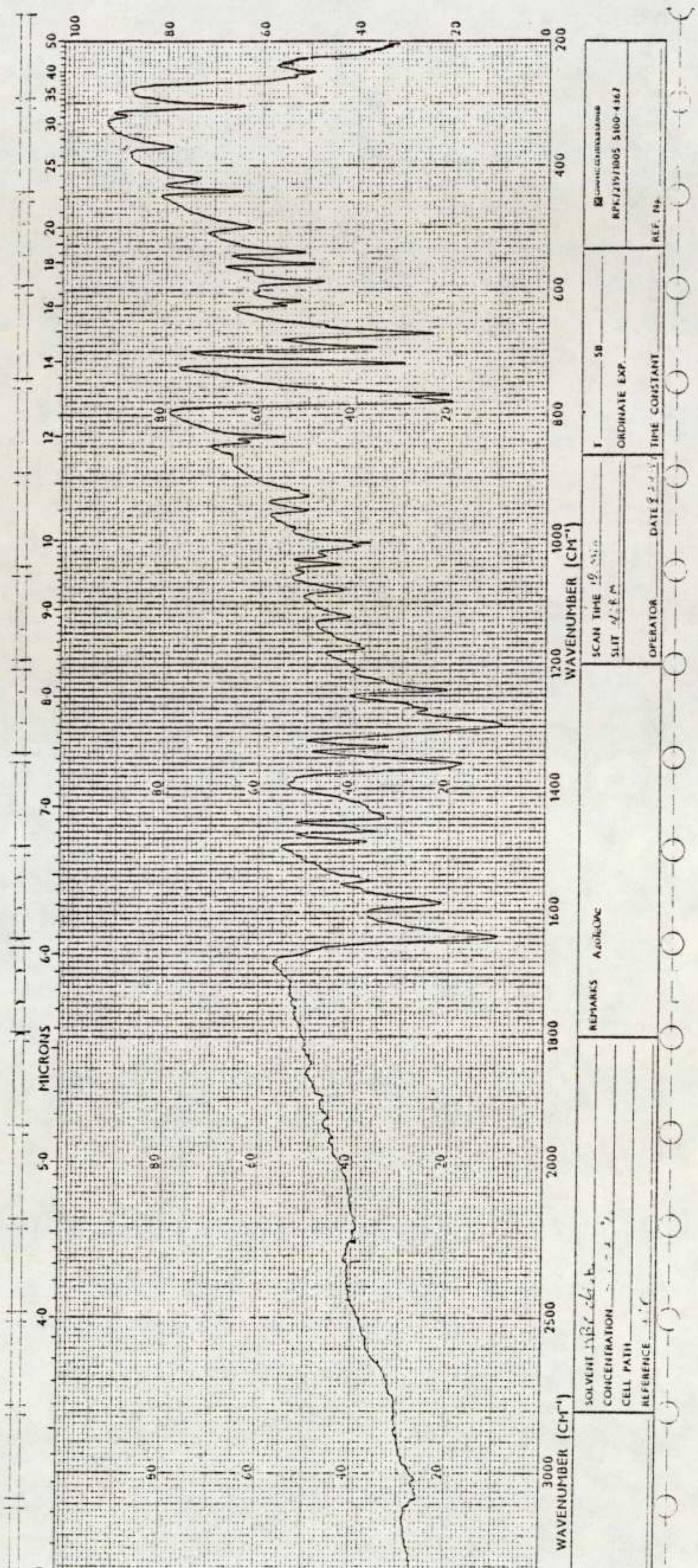


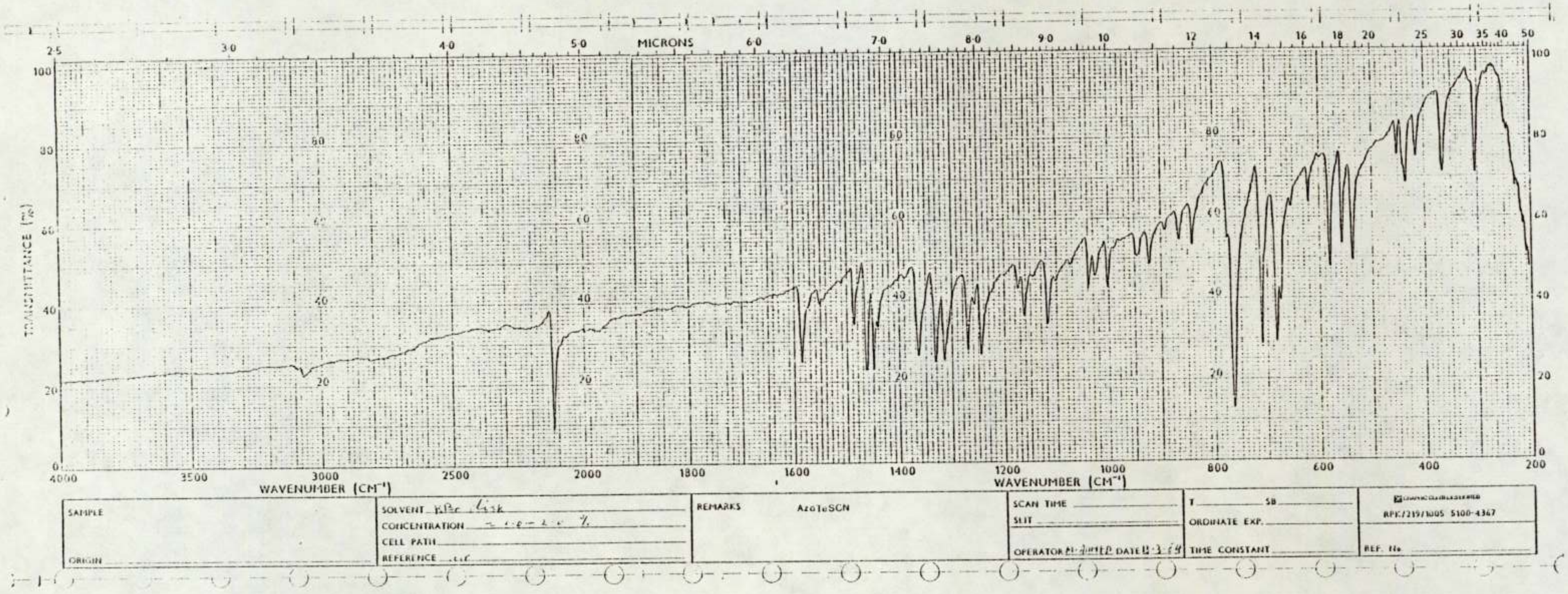
Figure 6.5 I.R. spectrum of $(C_{12}H_9N_2)Te(OOCCH_3)$

the compounds $ph_2Te(OOCCH_3)_2$ and $(p\text{-}EtOC_6H_4)_2Te(OOCCH_3)_2$ (1280 cm^{-1} in both compounds$^{(107)}$). The separation of ν_{as}(OCO) and ν_s(OCO) is 342 cm^{-1} which suggests a unidentate or very unsymmetrically bidentate acetate group. The X-ray data (Section 6.2) is consistent with the I.R. data. Hence the O(1) and O(2) atoms are 2.167 and 2.953Å from the tellurium atom (Table 6.4) respectively. Thus, any chelation by the acetate group must therefore be very weak. In other words, the acetate group in this compound is acting as a very unsymmetric bidentate ligand.

From the above discussion, it can be concluded that the tellurium atom is best considered as being three-coordinate in acetato(2-phenylazophenyl-C,N')tellurium(II), the structure being that of a pseudotrigonal bipyramidal, as has been described in Section 6.2.2.

The tellurium-oxygen stretching vibration for $ph_2Te(OOCCH_3)_2$$^{(107)}$, has been assigned as a shoulder at 280 cm^{-1}. This assignment led us to search a similar region of the spectrum for ν(Te-O). Comparison of the low frequency infra-red spectra of acetato(2-phenylazophenyl-C,N')-tellurium(II) and (2-phenylazophenyl-C,N')tellurium(II) chloride$^{(36)}$ reveals a band at ~250 cm^{-1} in the acetate spectrum and this is assigned as the tellurium-oxygen stretching frequency.

The SCN group may co-ordinate to a metal through the nitrogen (M-NCS) or the sulphur atom (M-SCN) or both (M-NCS-M'). In general, class a (hard metal) metals form the M-N bond, whereas class b (soft metal) metals form the M-S bond(109). However, other factors such as the oxidation state of the metal, the nature of other ligands in a complex, and steric considerations also influence the mode of co-ordination(110,111). Mitchell and Williams(112) have shown that the CN stretching frequencies are generally lower in the M-NCS complexes than in the M-SCN complexes. Sabatini and Bertini(113) concluded, from their study, that the most reliable feature for diagnosing bond type in the complexes $[PdL_2(SCN)_2]$ is the C-N stretching bond: it is sharp and above 2100 cm^{-1} in the S-bonded complexes and broad and below 2100 cm^{-1} in the N-bonded complexes. However, the value of the C-S stretching frequency is more useful in distinguishing these two isomers: 780-860 cm^{-1} for the M-NCS and 690-720 cm^{-1} for the M-SCN group(113-115). The value of the NCS bending frequency also differs between two isomers: 450 -490 cm^{-1} for the M-NCS and 400-440 cm^{-1} for the M-SCN group(113,115). Clark and Williams(110) have obtained the infra-red spectra of tetrahedral $[M(NCS)_2L_2]$ and octahedral $[M(NCS)_2L_4]$-type complexes (M=Fe, Co, Ni etc.; L=pyridine etc.) and discussed the stereochemistry from infra-red spectra. Bennett et al(111) have obtained the infra-red spectra of $[Cr(NCS)_4L_2]^-$, where L is an



SAMPLE
ORIGIN
SOLVENT KBr disk
CONCENTRATION ~ 1·0 – 2·0 %
CELL PATH
REFERENCE [illegible]
REMARKS AzoTeSCN
SCAN TIME
SLIT
OPERATOR [illegible] DATE 13·3·84
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ORDINATE EXP.
TIME CONSTANT
REF. No.

Figure 6.6 I.R. spectrum of $(C_{12}H_9N_2)Te(SCN)$

amine or phosphine, and have assigned the Cr-N and Cr-L stretching bands in addition to the NCS group vibrations. In [M(NCS)$_2$L$_2$]-type complexes in which M is Pt(II) or Pd(II), the NCS group is S-bonded if L is an amine and N-bonded if L is a phosphine(114). This is because a strong π-acceptor such as a tertiary phosphine makes the d-orbitals of the metal less available for bonding with the π-orbitals of sulphur.

In tellurium compounds, only a few reports are available in which tellurium is bonded to the NCS group. X-ray studies show that in compounds: [Te(HOCH$_2$CH$_2$(CH$_3$)NCS$_2$)$_3$-(SCN)](25), [(CH$_3$)$_4$N][C$_6$H$_5$Te(SCN)$_2$](97) and Te(etu)$_2$(SCN)$_2$(100), the NCS group is S-bonded. However, in the compound [Ph$_2$Te(NCS)$_2$]$_2$O(102) the NCS group is N-bonded.

McWhinnie et al(116) reported the I.R. data for diorganotellurium diisothiocyanates. From the I.R. data of these compounds, it has been concluded that the NCS group is N-bonded. Aravamudan et al(21) have assigned the band at 2080 cm^{-1} as a CN stretching frequency, for the compounds [Te(HOCH$_2$CH$_2$(CH$_3$)NCS$_2$)$_3$(SCN)]. As a consequence, they have suggested that the NCS group is N-bonded in that compound. However, the X-ray study showed that it is S-bonded(25).

The X-ray data of the (2-phenylazophenyl-C,N')thiocyanatotellurium(II), showed that the NCS group is S-bonded as expected (Section 6.2). The I.R. data for this compound is also consistent with the X-ray crystallographic data. The CN stretching frequency occurred at 2120 cm^{-1}, as a sharp band, which is also indicative of the S-bonded compound. The CS stretching and the NCS bending frequencies cannot be assigned, since the regions 690-720 cm^{-1} and 400-440 cm^{-1} are obscured by the organic group (phenylazophenyl) absorptions (Figure 6.6).

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