SYNTHETIC APPROACHES TO ORGANYLSELENIUM AND -TELLURIUM SEMI-CONDUCTORS

by

KHALID YAHYA ABID

A Thesis Submitted for the Degree of Doctor of Philosophy

at

THE UNIVERSITY OF ASTON IN BIRMINGHAM

NOVEMBER 1987

SYNTHETIC APPROACHES TO ORGANYLSELENIUM AND -TELLURIUM SEMICONDUCTORS

by

Khalid Yahya Abid

A thesis submitted for the degree of Doctor of Philosophy

November 1987. The University of Aston in Birmingham

Summary

A range of organotellurium and -selenium(II) compounds were used as donors with some electron acceptors to form donor-acceptor complexes. 7,7,8,8-Tetracyano-p-quinodimethane (TCNQ), Chloranil (TCQ) and p-dinitrobenzene (DNB) were chosen as acceptors. Solid state conductivity measurements have been employed for the charge-transfer complexes.

Charge-transfer salts of the general formula DX(D= 1,3-Dihydro-2-selenaindene, X = PF_6^-, BF_4^-, ClO_4^-) have been synthesised electrochemically.

The reaction of 2,3-bis(bromethyl)quinoxaline with selenium and sodium iodide gives 3,4-quinoxalino-1-selenacyclopentane-1,1-diiodide, which may be reduced to 3,4-quinoxalino-1-selenacyclopentane. The same method has been used for the preparation of 7,8-dimethyl-3,4-quinoxalino-1-tellura and -selenacyclopentane. These three compounds have formed black 1:1 charge-transfer complexes with TCNQ. The solution and solid state conductivity for the above complexes have been determined. When 2,3-bis(bromomethyl)quinoxalino and dimethyl substituted were reacted with tellurium (or selenium) and potassium iodide a yellow crystalline adduct of the above diiodide and 2,3-bis-(iodomethyl)quinoxaline was isolated.

2-Butyltellurobenzaldehyde reacts with chlorine gas to give the dichloride compound which was structurally determined. The reaction of the same material with diaminopropane gave 1,7-bis-2-butyltelluro-phenyl-2,6-diazahepta-1,6-diene(Ligand L). The bromination of this ligand and the ehtylene derivative (Ligand L') led to the tribromide compounds. Both ligand tribromides were reduced with $Na_2S_2O_5$, excess N_2H_4 and $NaBH_4$. The mono bromide was produced from the $Na_2S_2O_5$ reaction. Whilst treatment with excess N_2H_4 resulted in the cleavage of $N-CH_2$ bond to give the ditelluride compound. The crystal structure of the ditelluride was investigated. On reaction $NaBH_4$ with the tribromide compounds, new tritelluride compounds were produced. Finally the complexation of the two ligands (L and L') with $HgCl_2$ and $CdBr_2$ was also studied.

KEY WORDS:

ORGANOTELLURIUM
CHARGE-TRANSFER
QUINOXALINE
LIGAND
TRITELLURIDE

TO MY PARENTS

AND BROTHER LAITH

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Professor W. R. McWhinnie for his supervison, encouragement and unfailing interest throughtout the course of this work and during the writing of this thesis, for which I am indebted and much appreciate.

My thanks are also due to Dr. T. A. Hamor (Department of Chemistry, University of Birmingham) and A. A. West for their X-ray crystallography work.

I would like to thank the Technical Staff (Department of Chemical and Applied Chemistry, Aston University) for their help in obtaining physical measurements.

I am grateful to R. S. Bassi (Department of Physics, University of Aston) for providing facilities for conductivity measurements.

I also thank my colleagues in the laboratory for their good company and co-operation. I wish to express my appreciation to my best friend Ammar Thannon who helped me with the diagrams for the thesis. My thanks are due to Mrs. Dilina Goonatilaka for the very tidy typing of the thesis.

Finally, I am most grateful to my very kind parents for their financial and moral support throught my studies. I wish to express my thanks to all my brothers and sisters (especially Laith) for their encouragement.

LIST OF CONTENTS

LIST OF TABLES

List of Tables(cont.)

LIST OF FIGURES

List of Figures (cont.)

LIST OF SCHEMES

LIST OF ABBREVIATIONS

C.T	Charge-transfer
TCNQ	Tetracyanoquinodimethane
TCQ	Tetrachloro-p-benzoquinone(chloranil)
DNB	p-Dinitrobenzene
D-A	Donor - Acceptor
Ph	Phenyl
Me	Methyl
R	Alkyl
Ar	Aryl
DMSO	Dimethylsulphoxide
THF	Tetrahydrofuran
en	Ethylenediamine
n-Bu	n-Butyl
dmdtc	Dimethyldithiocarbamato
I.R.	Infra-red
U.V.	Ultra Violet
E.S.R.	Electron Spin Resonance
N.M.R.	Nuclear Magnetic Resonance
$^{13}C[^{1}H]$N.M.R.	Proton Decoupled Natural Abundance ^{13}C NMR

CHAPTER ONE

GENERAL INTRODUCTION

1.0 Introduction

Electron donor-acceptor (EDA) complexes have been known for many years. Amongst shortrange interactions one can distinguish molecular complexes formed by hydrogen bonding or electron donor-acceptor (charge-transfer) interactions.

The definition of the term charge-transfer, has only an absolute meaning when used as a label for an electronic transition that is accompanied by a migration of charge (i.e.electron) from a donor to an acceptor.

Donor-acceptor complexes manifest themselves in many ways, such as solubility, chemical reactivity and probably the most characteristic property of EDA complexes is the appearance of an intense absorption band that is not present in the seperated donor and acceptor species. This band, often broad and structureless, usually is in the visible and/or near ultraviolet regions, giving rise in many cases to large colour changes when the individual components are mixed.

Many spectroscopic studies generating various thermodynamic parameters have been carried out on EDA complexes over the past thirty years following the classic papers by Benesi and Hildebrand[1] on 1:1 iodine complexes with aromatic hydrocarbons and Mulliken's[2,3] subsequent explanation of the absorption band based on a charge-transfer (CT) resonance model.

Bensi and Hildebrand[1] argued, that the intense electronic transition band of the benzene-iodine complex, must of necessity be attributed to a transition characteristic of some one of the two molecules which comprise the complex. The particular transition would of course be modified by the inclusion of the molecule in the complex and would produce what appears to be the new transition[4].

Following somewhat this line of reasoning, Bayliss[5] attributed the strong absorption of the benzene-iodine ($Bz-I_2$) complex with λ_{max}=2970°A and of the benzene-bromine ($Bz-Br_2$) complex with λ_{max}=2920°A to a strongly shifted halogenes occurs below 2000°A.

Similarly, Mulliken[6] at first, explained the same absorption as due to the weak 2600°A absorption of benzene. He has pointed out[7], for example, that the acceptor molecular orbital for a molecule such as I_2 is the strongly anti-bonding σ^*, which should be appreciably larger than the outer orbitals of the isolated molecule leading to overlap with donor orbitals even at large separations.

Attempts to discover infrared absorption bands for 1:1 aromatic-halogen complexes have been unsuccessful. Absorption bands attributable to a complex are not observed over the region 2.5-25 μ (1μ =10^{4} cm^{-1}) for solutions of iodine in benzene[8].

Other complexes which have been investigated early, are those between anthracene as a donor and series of 1-substituted-2,4,6-trinitrobenzenes as acceptors including picric acid in chloroform at 24°C. The equilibrium constants for the complex formation have been determined spectroscopically by Kuntz[9].

The free picric acid has an absorption in the region of 380 nm and can usually be estimated photometrically[10], providing that the hydrocarbon component does not absorb in this region.

The complex of anthracene and picric acid has melting point of 138°C and a Ruby-red colour.

The appearance of strong colour in many of charge-transfer complexes cases, is generally attributed to a loose reversible association ("Molecular Compound" or "Molecular Complex") of the original molecules in a definite ratio, most often 1:1[3].

Weiss[11], has attributed the strong colour of molecular complexes to intense charge resonance spectra arising within the ions in the complex.

In a study of the molecular complex formation, Brackman [12] attributed the strong colour to "complex resonance" meaning quantum-mechanical resonance between a no-bond structure and a structure with a bond between the two partners. A and B, but made no clear statement about ionic character in the latter structure. He[12] has insisted that (assuming colourless partners) the complex as a whole determines the colour, that is the light absorption causing colour is not localized in one of the partners. Brackman[12] also emphasized that reversible formation of a resonance complex, by reducing the activation barrier, may often be a preliminary step in an irreversible chemical reaction.

Those early studies led Murrell[13] to confirm, that the intense colour of such complexes, is due to the transfer of an electron from the donor to the acceptor.

When there is only weak interaction between the components of a charge-transfer complex, the infrared spectrum of the complex often shows only small differences, compared with the sum of the spectra of the two components[14-16]. Some of these differences which are observed in the solid phase may be the result of crystal-packing effects[17].

The general lack of change in the infrared spectrum on complex formation has been used to distinguish between weak charge-transfer complexes and the products of electron transfer. In the case of complete electron transfer from the donor to the acceptor in the ground state, the infrared corresponds closely to the sum of the spectra of two ions[18].

The increase in bond lengths which result when donor-acceptor interaction (weak interaction) takes place is generally accompanied by corresponding decreases in vibration frequencies of the components[17].

Person[19], has compared the infrared spectra of charge-transfer complexes with those of the isolated molecules which form the complexes, and has found:-

1. the vibrational frequencies in donor or acceptor (or both) may be shifted,
2. the intensities of the bands may be changed considerably,and
3. new low frequency bands appear due to the vibrations of one molecule in the complex against the other. Only slight changes are expected, because the charge-transfer complexing action is distributed over several atoms.

When the complexing action is distributed over only two atoms, as for halogens in the benzene-halogen systems, the effect is observable in the infrared spectrum[17].

It is also worthy to note that the charge-transfer products are weak complexes. The structure of the weak complex was early described[19] in terms of two limiting, idealized structures : the no-bond structure (Ψ_0) and the dative stucture (Ψ_1), as suggested by Mulliken[3] which is part of the charge-transfer theory.

Perhaps it would be useful to summarize some basic ideas of Mulliken's theory since it has played an important role in the studies of electron donor-acceptor complexes, and the development of research on charge-transfer interactions theory.

Weiss[11] proposed that all molecular complexes have an essentially ionic structure B^+A^-, and pointed out that a low ionisation potential (I_D) for the base B (donor), and a high electron affinity for the Lewis acid A (acceptor), should then favour a stable complex. He attributed the strong colour of molecular complexes to intense charge-resonance spectra arising within the ions in the complex.

The term complex resonance has been proposed[12] to describe the interaction of a donor and acceptor and formulated the structure of a 1:1 complex as a resonance hybrid of a no-bonded structure and a structure in which a bond is established between the donor and acceptor.

The interactions of nitro compounds or quinones (Acceptors) with aromatic substances (Donors) for example has been explained in terms of a one electron transfer process,

$$D\colon + A \longrightarrow D^{\dot{+}} \; .A^{-}$$

leading to the formation of odd electron ions held together by electrostatic forces[20].

Following Mulliken's treatment[2], the interaction of a no-bond ground state $\Psi(D,A)$, and a polar excited state (dative structure) $\Psi(D^{+}, A^{-})$ formed by the transfer of one electron from donor (D) to acceptor (A), to produce a stabilised ground state having a wave function,

$$\Psi_0 = \Psi(D,A) + \lambda \Psi(D^{+}-A^{-})$$

and an excited state, the charge-transfer state,

$$\Psi_1 = \Psi(D^{+}-A^{-}) + \mu \Psi(D,A)$$

λ and μ will in most cases be small compared with unity. The charge-transfer band is associated with the electronic transition $\Psi_0 \longrightarrow \Psi_1$, and occurs at the frequency $\gamma = (E_1 - E_2)/h$, where h is Plank's constant.

The energy of the electronic transition, $(D,A) \longrightarrow (D^+ - A^-)$ is given to a first approximation by the expression, $I_D - E_A - C$, where C is the mutual electrostatic energy of D^+ and A^- relative to that of D and A.

The acceptor and the donor may in general be molecules, molecule-ions, atoms or atom-ions, with the restriction, that they are both in their totally symmetric ground state[3].

The crystal structures[21,22] of some π-molecular charge-transfer crystals support the occurrence of weakly overlapping, essentially molecular D and A constituents. Their infrared and ultraviolet spectra also show absorption characteristic of D and A molecules[23]. Even the strongest π donors and acceptors, which crystallize[24] in ionic lattices of D^+ and A^- radicals, show spectra characteristic of the molecular ion-radicals.

These spectroscopic observations provide the experimental basis for the sharp separation of π-molecular charge-transfer crystals into those with largely neutral and those with largely ionic ground states.

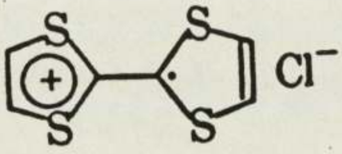
It is now quite well established that the Mulliken CT resonance model adequately represents electron donor-acceptor spectra, and thatin fact is necessary to explain some unique properties of these complexes. Associated with this model is the concept of (attractive) CT resonance forces that supplement the classical intramolecular electrostatic contributions to ground-state stability of electron donor-acceptor complexes.

It should be pointed out, however that the presence of a charge-transfer absorption band alone says nothing at all about the source, or sources of ground-state stability, in fact very strong charge-transfer absorption spectra are observed in many cases where, there is virtually no attraction between the two components in a simple encounter[25,26].

It has been stated[21], that the importance of charge-transfer resonance in determining ground state properties is still an open question.

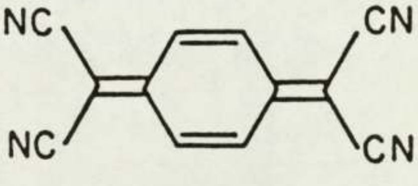
However, the question that has been developed in recent years is: "could radical ions ($X^{+}A^{\overset{-}{\cdot}}$ and $D^{\overset{+}{\cdot}}X^{-}$) be in the ground state good donors and acceptors ?".

Torrance[27], has supposed, that strong π-molecular donor (D) and acceptors (A) molecules often react to form ion-radical salts ($X^{+}A^{\overset{-}{\cdot}}$ and $D^{\overset{+}{\cdot}}X^{-}$) and charge-transfer compounds (DA and $D^{\overset{+}{\cdot}}A^{\overset{-}{\cdot}}$) e.g. $K^{+}TCNQ^{-}$(potassium tetracyanoquinodimethane) and $TTFCl^{-}$ (tetrathiafulvalene chloride).



(TTFCl$^-$)

Since the discovery of the most remarkable π^* electron-acceptor, 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) in 1962[28], several papers have been reported on the importance of this compound in forming different charge-transfer complexes.

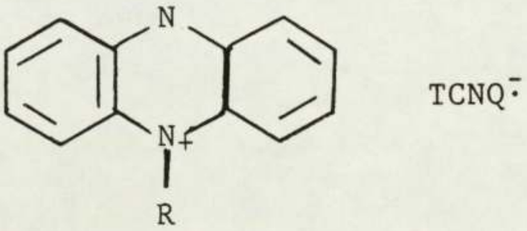


TCNQ

The ability of quinones to form stable solid salts with aromatic amines has been known for many decades[29], and it was ascribed interaction of the electron poor π-orbital system of the quinone (π-acceptor) with the electron-rich π-orbital of the amine (π-donor).

Many attempts have been made to prepare various organic and inorganic (including the simple salts comprising one cation and one $TCNQ^{\bar{\cdot}}$ anion-radical, e.g. $Li^+ TCNQ^{\bar{\cdot}}$, $Na^+ TCNQ^{\bar{\cdot}}$, $K^+TCNQ^{\bar{\cdot}}$)[30] TCNQ salts which commonly termed "charge-transfer complexes".

N,Methylphenazinium 7,7,8,8-tetracyanoquinodimethane, is one of the most important organic TCNQ salts. It is exhibits unusual volume electrical resistivity of (7×10^{-3} Ωcm) and thus is the most highly electrically conductive organic compound known at that time[30]. In marked contrast, the N-ethyl phenazinium compound had a single crystal resistivity of (10^9 Ωcm).



(a) $R = CH_3$ (7×10^{-3} Ω cm)

(b) $R = CH_3CH_2$ (10^9 Ωcm)

Here, the difference in the conductivity has been explained by X-ray measurements, i.e. in the N-methyl salt, the $TCNQ^{\cdot}$ units are stacked one above the other in a columnar manner (Figure 1.1)

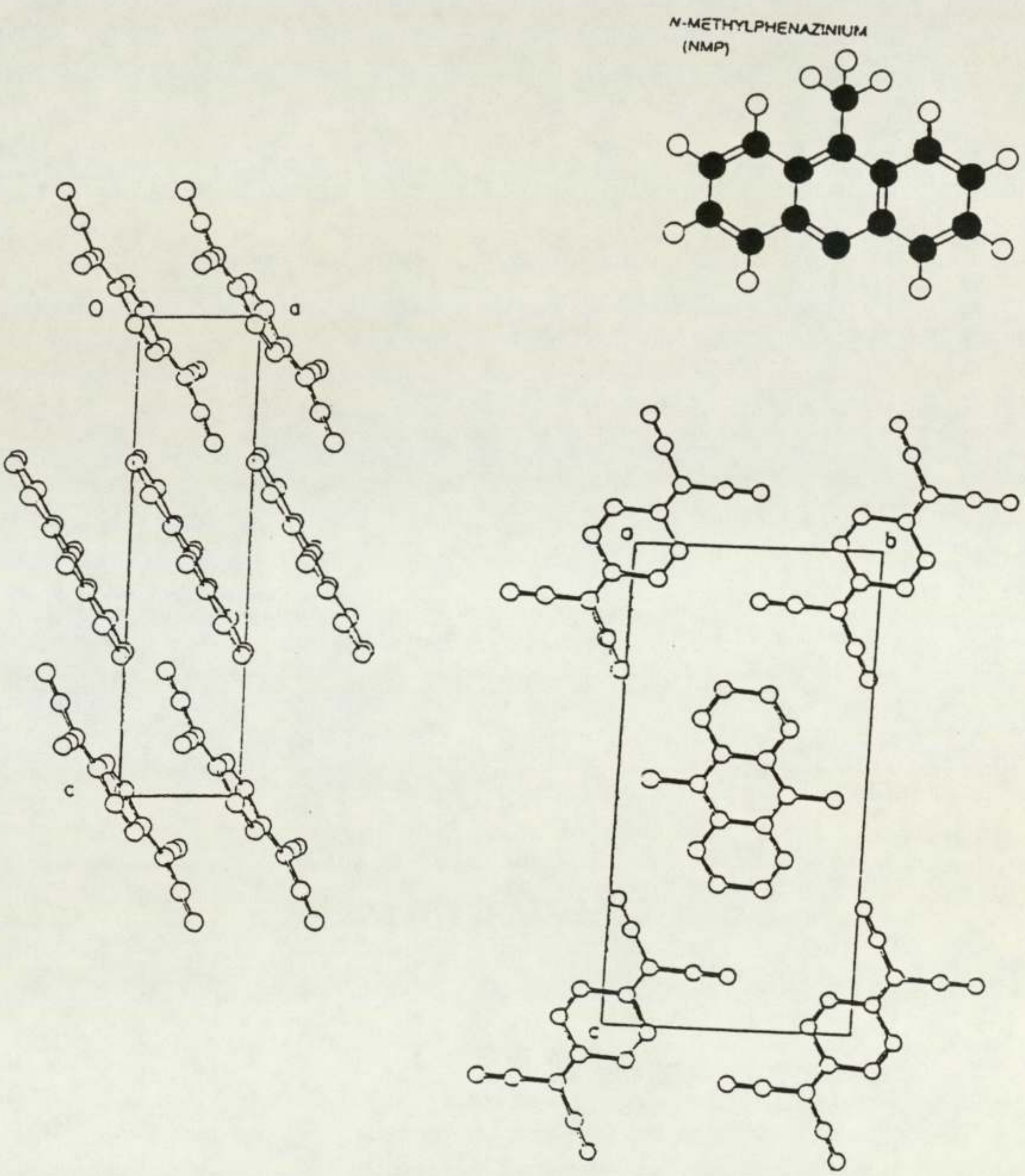


Figure 1.1. Unit cell view and packing diagram of NMP^+- $TCNQ^-$, showing $TCNQ^-$ ions pack in a columnar manner.

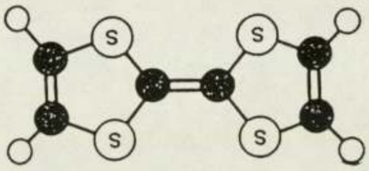
Furthermore, the compound has a remarkably high density (1.44 g/cm^3). These observations suggest that the low steric requirement of the N-methyl group in the cation allows very efficient packing of the $TCNQ^{\cdot -}$ units which presumably mediate the electronic conduction.

On the other hand, the N-ethyl derivative has a density of (1.33 g/cm^3). The bulky N-ethyl group apparently disrupts the packing, resulting in an appreciable barrier to electron movement[30].

In fact such materials form the basis of the field of "organic semiconductors", which has been actively studied[31-33] since the mid- 1950s. Besides their unusual conductivity behaviour, these compounds exhibit interesting structural, optical, and magnetic properties that are directly related to the charge transfer interactions between molecules.

The huge improvement in conductivity of these TCNQ salts, by 4-10 orders of magnitude, generated renewed interest and activity in this field[34,35].

In 1972, it was noted[36] that the chloride salt of a new organic donor, TTF (tetrathiafulvalene), has a high pellet conductivity ($0.2\Omega^{-1}cm^{-1}$), and in the following year A.J. Heeger and A.F. Garito and their co-workers[37] at the University of Pennsylvania reported observing very high conductivity in a salt made up of TCNQ and TTF (10^4 $\Omega^{-1}cm^{-1}$), at comparatively low temperatures (between 50 and 60 degrees Kelvin) and was considered as a first "organic metal".



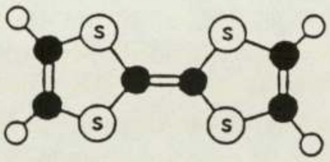
TETRATHIAFULVALENE (TTF)

Torrance[27], has argued that such materials, produced by organic chemistry preparations, can exhibit electrical properties of metals.

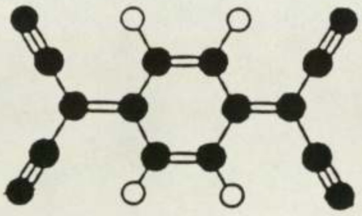
The unusual conductivity of the quasi-one-dimensional TTF-TCNQ charge-transfer is generally reflect the behaviour of electrons which are transferred from the donor TTF to the accepter TCNQ, and hence require the formation of a stable ionic (charge-transferred) ground state of the molecular crystal[38].

TTF-TCNQ is a simple (stoichiometric crystal) 1:1 complex crystallising in segregated stacks of TTF and TCNQ molecules[39].

The herringbone pattern of TTF-TCNQ charge-transfer (Figure 1.2) is formed by the planes of stacked molecules



(TTF)



(TCNQ)

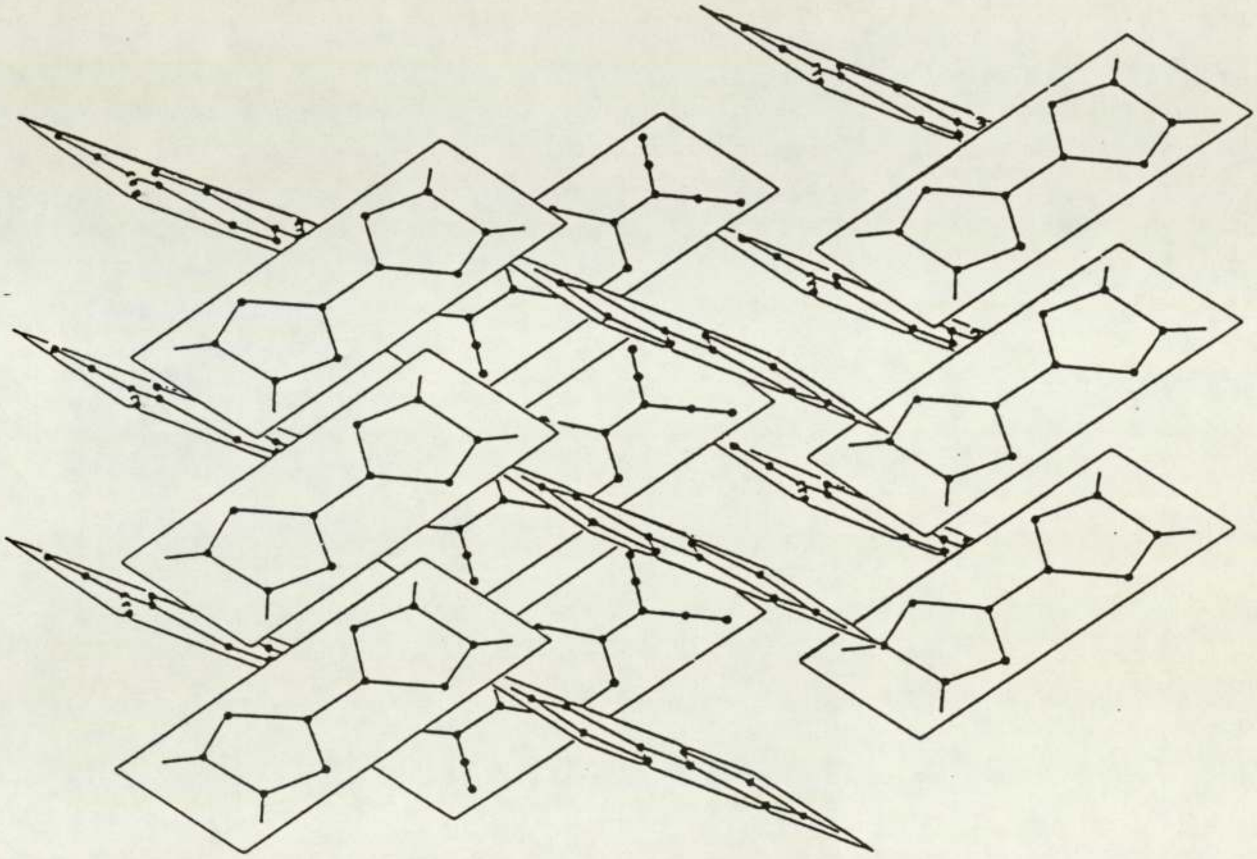


Figure 1.2. The herringbone pattern of TTF-TCNQ complex.

in the salt. Within each stack the molecules are parallel to one another, but they are inclined to the axis of the stack. Orbitals that extend above and below the plane of each molecule overlap, giving rise to an electronic conduction band along the stacks. The charge transfer from donor to acceptor (between the two conducting columns) is incomplete as demonstrated by diffuse X-ray scattering experiments[40].

It has been found that on the average 0.59 of an electron per molecule is transferred from TTF to TCNQ, which creates partially filled bands in both molecules, as a result conduction takes place in both kinds of stack.

In TCNQ the carriers of charge are electrons and in TTF they are holes, which represent the absence of electrons [41].

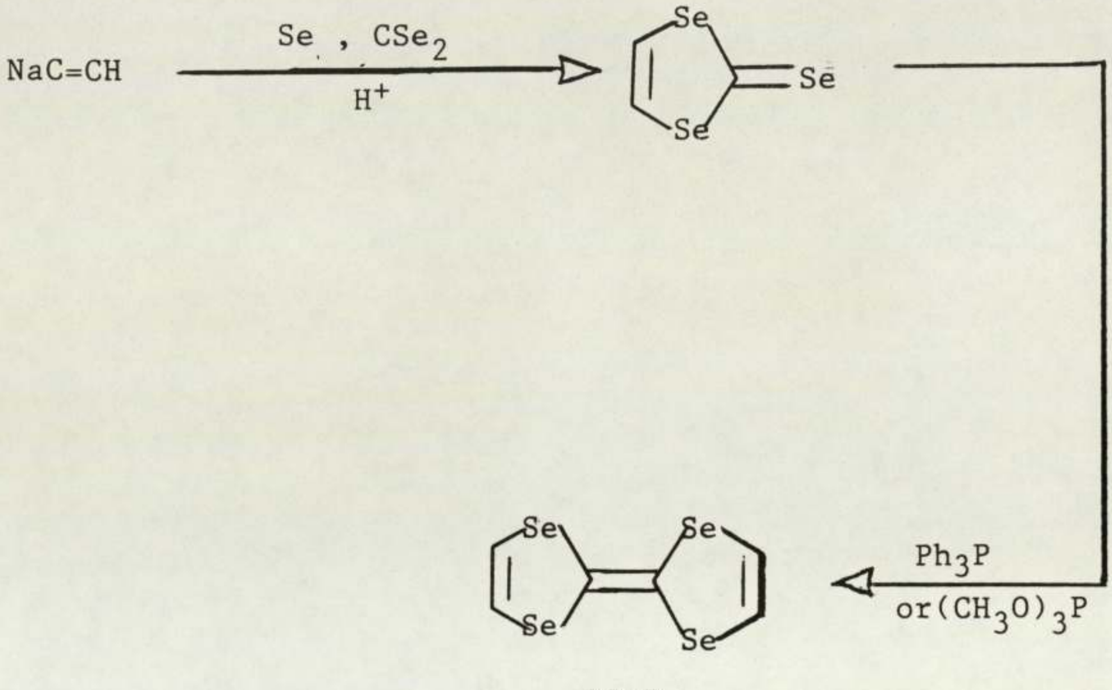
It has been pointed out that the lack of complete charge transfer in TTF- and NMP – TCNQ accounts for the greater conductivities of these salts compared to that of K-TCNQ, for example[42].

Torrance[43], has viewed the structure of such salts as sheets of charge perpendicular to the chain axis, the interaction between the cations and anions within a sheet is strong and attractive, while the interaction between sheets is strong but repulsive, due to the repulsion between like charges along the chains. For a fixed spacing within the sheets, but variable spacing between sheets, the sum of the attractive and repulsive contributions gives rise to a minimum in the Madelung energy/vol., often the optimum inter-sheet spacing is larger than the spacing observed in the structure.

In these cases it has been suggested that the solid can lower its energy by effectively increasing the separation between charges on the chains. This could be accomplished either by having incomplete charge-transfer from cation to anion, or by forming complex salts (or both). The observed structures suggest incomplete charge transfer in each of TTF-TCNQ and NMP-TCNQ.

In order to improve upon the metallic properties of fulvalenium system (TTF) in more definable and controllable fashion, Engler[44] has synthesised tetraselenafulvalene (TSeF), where the four sulphur atoms of the TTF molecule were substituted with selenium; and its charge-transfer salt with TCNQ.

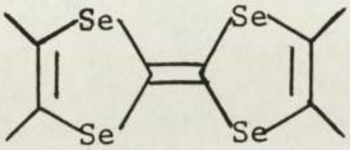
Tetraselenafulvalene was prepared in two steps as outlined in the eq. below.



TSeF

Crystals of the 1:1 charge transfer salt of TSeF with TCNQ were gained in acetonitrile as long black needles. The room temperature conductivity of $800\Omega^{-1}cm^{-1}$ for TSeF-TCNQ is one of the highest reported to date for an organic charge transfer salt, nearly double the usual values found for TTF-TCNQ.

Since the discovery of the first "organic metal", preparation of new donors analogous to TTF has received added impetus with the discovery of superconductivity in salts of tetramethyltetraselenafulvalene (TMTSF)[45-47].



TMTSF

Tetramethyltetraselenafulvalene reacts with TCNQ to form a highly conducting organic solid (Fig. 1.3).

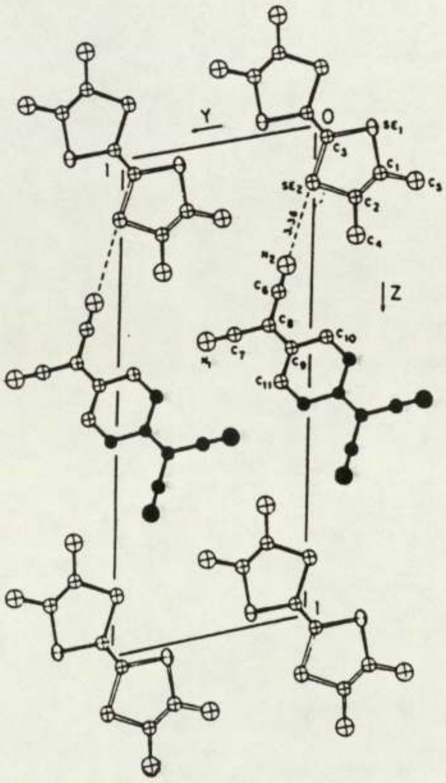


Figure 1.3 Crystal structure of TMTSF-TCNQ

The salt (TMTSF-TCNQ) was found in at least two forms, a coppery red material with a room temperature d.c. conductivity of $10^{-5}\ \Omega^{-1}cm^{-1}$ and a black organic 'metal' with a room temperature d.c. conductivity of at least 800 $\Omega^{-1}\ cm^{-1}$ comparable to the best organic conductors known[45].

It has been pointed out that it is known now that all highly conductive organic metals are formed from radical ions based on chalcogenafulvalenoids and not on TCNQ, and are single stack lattices in which the metallic conductivity is due only to long-range delocalization among donors[48].

Prior to the advent of $(TMTSF)_2X$, (X= BF_4, ClO_4, PF_6, AsF_6 SbF_6, NO_3)[49], the principal requirements to achieve metallic behaviour, Wudl[47] believed to be (a)segregated chains of donor and acceptor molecules and (b)partial charge transfer between donors and acceptors, i.e. $P<1$, (P = charge per molecule)[32].

Several electrochemical methods have been used to study the oxidation of TMTSF in the presence of different anions ($X^- = PF_6^-$, BF_4^- , ClO_4^- , AsF_6^- , ... etc.) to form a series of quasi-one-dimensional organic cation radical salts $(TMTSF)_2X$, exhibit superconductivity at moderate hydrostatic pressures of 1.2 GPa[50-52].

In each case the solid phase $TMTSF_2X$, has been isolated by electrolysis and its electrochemical behaviour deduced from the analysis of the current voltage curves obtained with a carbon-past electrode[50].

The structures of some of these salts have been determined[47,49,51], and show that some of the anions had octahedral symmetry and the others are tetrahedral.

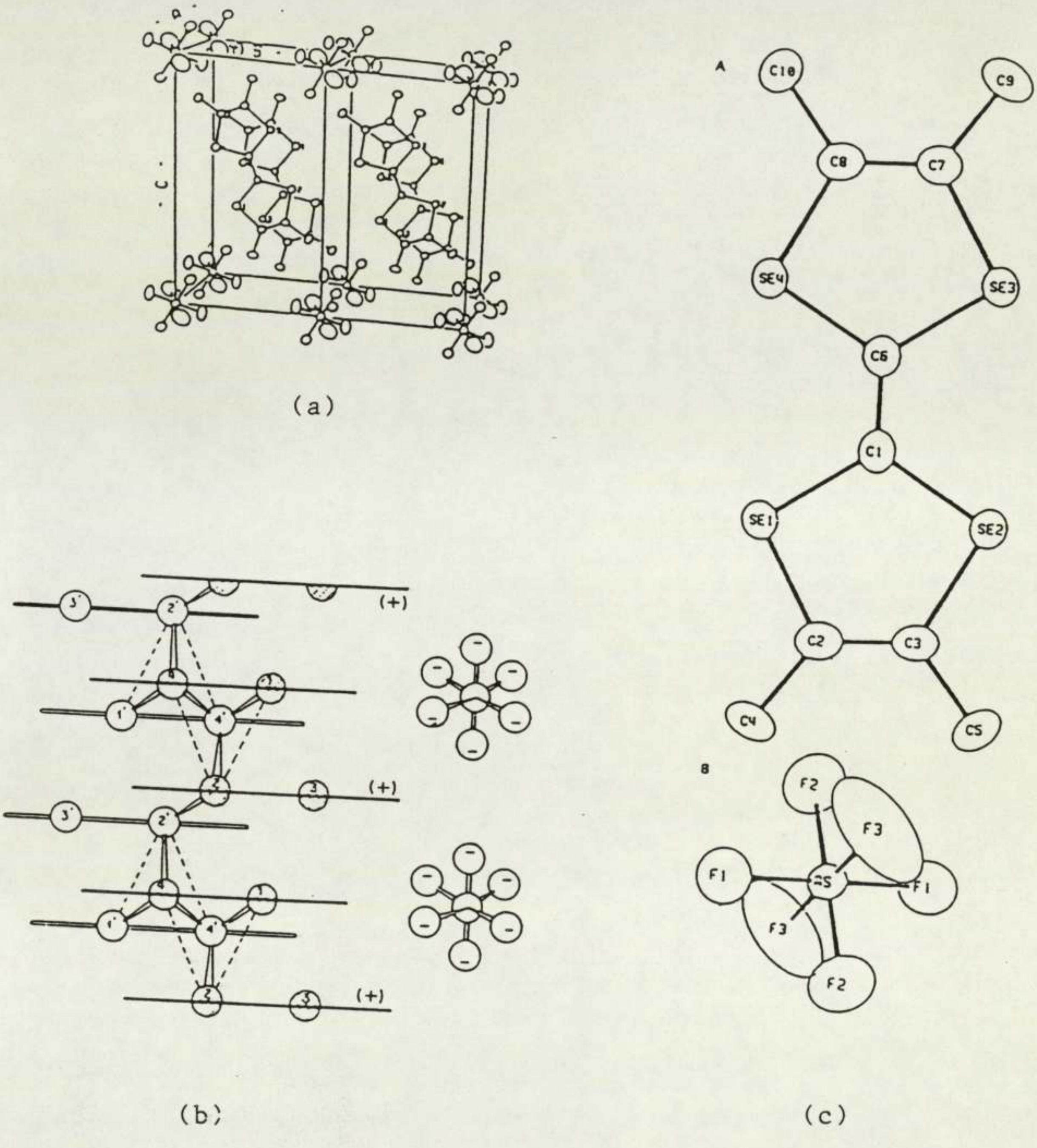
Single crystals of $(TMTSF)_2ClO_4$, were obtained by electrochemical oxidation of (TMTSF [51], according to:-

$$2n\mathrm{TMTSF} + n\mathrm{ClO_4^-} \xrightarrow{ne} [(\mathrm{TMTSF})_2\mathrm{ClO_4}]_n$$

The structure of $(TMTSF)_2ClO_4$ is similar to that of the congener $(TMTSF)_2PF_6$[49].

$(TMTSF)_2PF_6$ and $(TMTSF)_2NO_3$ salts have been prepared by similar method and has specific conductivities of $540\Omega^{-1}$ cm^{-1} below 20K.

The crystal structure of $(TMTSF)_2AsF_6$ (Figure 1.4), the unusual electric conductivity ($430\Omega^{-1}cm^{-1}$) and the magnetic properties was explained[49] in terms of unique interstack and intrastack interactions among the selenium atoms and the location and quality of the closed-shell



(a)

(b)

(c)

Figure 1.4. (a) Unit cell view along b,

(b) Schematic view of two stacks of $(TMTSF)_2AsF_6$,

(c) The molecular components of TMTSF, AsF_6.

anion lattice.

The physical properties of salts of the solid state structure of $(TMTSF)_2X$, is because of the electrostatic field associated with the X^--Se^{+3} interactions gives this family of solids a more polarized character than is possible in other organic metals[49].

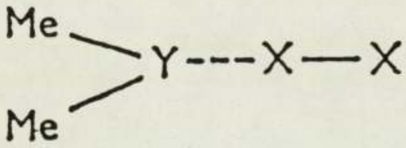
Charge-transfer compounds of organoselenium and tellurium donors are now considered.

It is known that organic sulphides, selenides and tellurides form adducts of 1:1 molecular composition with the halogens. Many of these adducts can be isolated as crystalline solids.

The structures of certain of these adducts have been studied by X-ray methods. It has been shown that, without exception, there is present an almost linear system, comprising the chalcogen atom of the other situated either centrally between the halogen atoms (covalent type structure) or at a terminal position, when the structure is said to be of charge-transfer type[53].

A considerable number of halogen adducts of dimethylsulphide,-selenide and -telluride are known. But not all of these have had their structures determined.

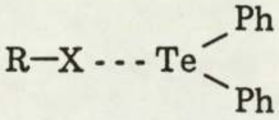
Dimethylselenide forms adducts with bromine and iodine of 1:1 stoicheiometry (R_2SeX_2). The iodine adducts of the few selenides which have been studied by diffraction techniques appear to be of the charge-transfer type with linear Se-I-I groups[54,55].



Y = Se
X = I

Over the past few years McWhinnie et al[56], have been developing an interest in the investigation of diphenyltelluride (Ph_2Te) with methyl iodide. He has suggested that the reaction underwent an intermediate which was a charge-transfer complex.

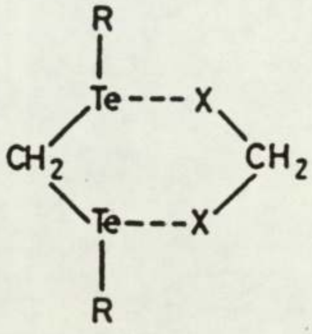
$$RX + Ph_2Te \rightleftharpoons \{RX \cdots TePh_2\}$$

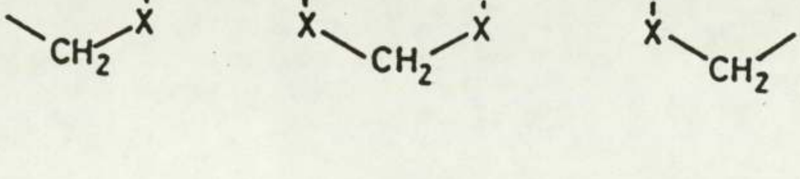


This suggestion was in very good agreement with the previous proposal of R_2SeI_2.

There is now evidence that tellurium compounds such as $(RTe)_2CH_2$[57] can mimic this behaviour with CH_2Br_2 and CH_2I_2. The products of the reaction of NaTeR with dibromo- or diiodomethane gave a pale yellow with CH_2Br_2 or deep yellow colour with CH_2I_2 solids. The analytical data showed one mole of dihalomethane and it gave an empirical formula of $[(RTe)_2CH_2.CH_2X_2]$, (X = Br, I).

It has been suggested[58], that the material is a charge-transfer complex and two possible formulations are illustrated below.





The mass spectra of telluronium salts[59-61], Ph_2MeTeX (where X = Cl, Br, I, NCS, BF_4, PF_6, PhCOO) showed the thermolysis pathway is :-

$$Ph_2MeTeX \longrightarrow Ph_2Te + MeX$$

Tellurium - 125 Mossbauer spectroscopy, which examines the electronic environment of the tellurium nucleus directly, is a powerful means by which the fundamental nature of bonding and structure in solid organotellurium compounds may be investigated.

The initial ^{125}Te Mossbauer investigations of organotellurium compounds were performed in the mid-1970's and involved the examination[62-66] of a variety of alkyl- and aryl derivatives of tellurium-(II) and-(IV).

^{125}Te Mossbauer data with the other physical measurements were obtained for $[(P.Eto\ C_6H_4)Te]_2CH_2.CH_2Br$. The results obtained are more consistent with a tellurium(II) species when compared with values obtained for other tellurium compounds[64].

The suggestion that these materials are indeed charge-transfer complexes is the only one which offers a self consistent interpretation of the data.

It was proposed that electron density is transferred from the spare-pair p-orbital on tellurium. This will decrease the p-orbital occupational imbalance and, accordingly, reduce the quadrupole splitting (Δ). Simultaneously removal of p-electron density will increase the chemical isomer shift (δ).

Similar effects have been noted for organotellurium complexes with TCNQ[67], and the implication was that the charge-transfer is considerable.

Mossbauer data for a wide range of organotellurium compounds have been reported, including compounds of the type : R_2Te, Ar_2Te, Ar_2Te_2, R_2TeX_2, Ar_2TeX_2 and $ArTeX_3$, where R = alkyl, Ar = aryl and X = Cl, Br or I. The isomer shifts and quadrupole splittings are interpreted in terms of the relative populations of the tellurium 5s and 5p orbitals. The quadrupole splittings are rationalized in terms of a simple additive model, formulated within the framework of the Townes and Dailey theory[64].

It has been pointed out that there is evidence from iodine Mossbauer data that the effect on δ of the latter term is six times that of the former term of each electron removed[68].

The isomer shifts δ lie in the order:-
tellurides < ditellurides < dihalides < trihalides. This is corresponds to an increasing s-electron density at the nucleus in that order. The bonding in the tellurides and ditellurides may be viewed as intermediate between pure p^3 and sp^3 ,as suggested by the C-Te-C and C-Te-Te bond angles in $(p\text{-}MeC_6H_4)_2Te$ (101°)[69a], $(p\text{-}ClC_6H_4)_2Te_2$ (94.4°) [69b], and Ph_2Te_2 (99°)[69c].

The chemical isomer shifts of the dihalides are more positive than those of the organotellurides, and this is consistent with the halogen ligands removing predominatly p-electron density from the tellurium and the conversion of tellurium(II) to (IV)[70].

The large quadrupole splittings Δ of the tellurides and ditellurides correspond to a considerable imblance in the 5p-orbital population on the tellurium atoms. The data are indicative of considerable covalent character in the Te-C and Te-Te bonds and suggest that the tellurium atoms have a significant number of holes in the 5p-shells. Such a situation would be expected to give rise to increased s-electron densities of the tellurium nuclei and consequently to large and positive chemical isomer shifts[70].

Structural studies[71-73] of the crystalline dihalides of R_2TeX_2, have shown the tellurium atoms to be in distorted trigonal bipyramidal coordination (Fig.1.5). In these structures the axial positions are occupied by the halide (more electronegativity) and the equatorial positions are occupied by the two remaining organic groups and the non bonding electron pairs.

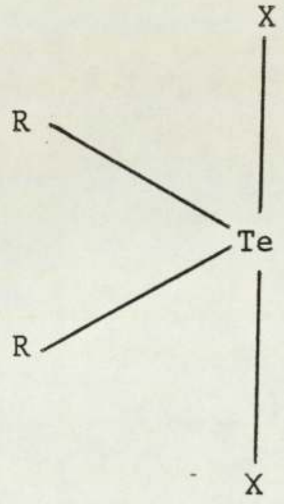


Figure. 1.5

It has been noted that there is a correlation between colour, type and the degree of secondary bonding. Recently, McCullough[74] have reported in a comparative study of secondary bonding system and colour in the diiodide of 1,3-dyhydro-2-telluraindene (β-$C_8H_8TeI_2$).

Since the colours of various organotellurium diiodides in the yellow range [75-77], it has been suggested that the darker colours of these compounds in the solid state result from two types of intermolecular bonding. Secondary Te...I bonds appear to produce red colours while I...I bonds cause purple to black colours that are usually accompanied by a metallic luster. The secondary Te...I bonds link the molecules into infinite chains of the general type(Fig.1.6)[78].

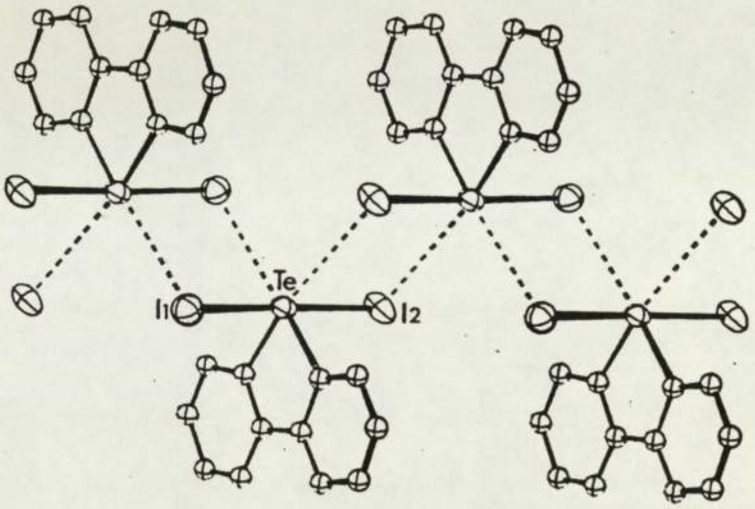


Figure. 1.6

Quite a large number of papers have been devoted to investigating the electrochemical behaviour of selenium and tellurium elements. But little has been published on the electrochemistry of organotellurium and -selenium compounds[79,80].

Latypova[81],reported the electrochemical oxidation of some of the organosulphur,selenium and tellurium at a rotating oxide-platinum disk electrode and the influence of the hetroatom on the electrochemical reactivity. It has been found that the oxidation of ethynyl sulphides, selenides and tellurides probably consists in the initial loss of one electron by the molecule and the formation of a radical cation. Also the charge transfer complexes of those compounds with tetracyanoethylene (TCE) has been investigated. It was concluded that the electrochemical reactivity and electron-donor power toward TCE rise in the order S <Se <Te.

The reduction and oxidation of arylethynylselenides and tellurides has been found as a two electron processes and the attempts to detect the ESR signal of the unstable radicals were unsuccessful[82,83].

Recently, Liftman[84] studied the electrochemical behaviour of various classes of organotellurium compounds($ArTeCl_3$, Ph_3TeCl, Ar_2Te_2) and tellurium tetrachloride $TeCl_4$ in methylene chloride containing tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. It was found that $ArTeCl_3$ were readily reduced generally to the strongly coloured ditellurides by different reducing agents[84a].

Diorganyltellurium dichloride and diperchlorate (Ar_2TeX_2) could be electrochemically reduced to the corresponding tellurides in one electron-transfer reaction preceding a disproportionation and vice versa[84b].

Ph_3TeCl was found to be oxidized electrochemically to $Ph_2(Cl)TeTePh_2(Cl)$ and reduced either in a one electron reaction to $Ph_3TeTePh_3$ or in a two electron reaction to Ph_3TeH[84c].

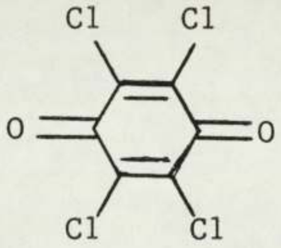
The reduction of $TeCl_4$ or $TeCl_6^{-2}$ to Te° causes coating of the electrode with metallic tellurium, on whose surface chloride ions were strongly bonded[84d].

McWhinnie[85], has reported the electrochemical oxidation of 1,3-dihydro-2-telluraindene (C_8H_8Te). The appropriate tetrabutylammonium salts were used as supporting electrolytes in dichloromethane solvent.

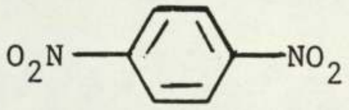
Three salts of the formula $[C_8H_8Te]^+[X]^-_{n(1-2)}$ were prepared and characterised, where X was PF_6^-, ClO_4^-, and BF_4^-. It was concluded that the obtained solids are salt-like. The failure to observe ESR signals were proposed, it may imply a diamagnetic ground state e.g. via dimerisation of radical cations.

Accordingly, it is interesting to continue these investigations to provide a more complete understanding of organotellurium and selenium charge-transfer. This was the aim of the present research, as well as designing new organic conductors with high room temperature conductivities.

It has been decided to extend Singh's[86] work, using tetracyanoquinodimethane(TCNQ), and other acceptors such as tetrachloro-o-benzoquinone [chloranil(TCQ)], and p-dinitrobenzene(DNB).



(TCQ)



(DNB)

Attempts have been carried out to extend Singh's[86] electrochemical work, in order to illuminate some of the general aspects of this area of chemistry. Also for the sake of completeness, some new donors were synthesised. Some work along this line has enabled the study to be extended to selenium via the synthesis of some new organoselenium compounds.

CHAPTER TWO

GENERAL EXPERIMENTAL TECHNIQES

2.0 Experimental

2.1 Chemicals

All chemicals were obtained from commercial sources, or prepared by literature methods starting from either $TeCl_4$ or Te and Se (BDH). All materials were assessed for purity by checking melting points and other physical data. Tetracyanoquinodimethane (TCNQ) and p-dinitrobenzene (DNB) were obtained from Aldrich Chemicals. Chloranil (TCQ) was obtained from Koch-Light Chemicals.

2.2 Solvents

Most of the solvents were obtained from commercial sources and purified by literature methods[87]. In general, all solvents were distilled prior to use and kept over molecular sieves.

2.3 Melting Points

The melting points were determined using a Gallen-Kamp electrically heated melting point apparatus. The apparatus was adjusted by calibration of some organic compounds of known melting points, which it is below 250°C.

2.4 Infra-red Spectra

A Perkin-Elmer 599B infra-red spectrophotometer of range 4000-200 cm^{-1} was used for some of the samples. Others were recorded on a Perkin-Elmer-1710 infra-red fourier transform spectrometer (model PP-1).

Solid state samples were examined as KBr discs. Liquid samples were spread between two NaCl standard liquid cells.

2.5 Mass Spectra

Mass spectra were obtained from an AEl MS9 spectrometer generally at an ionisation potential of 70 eV. Appearance potentials were measured from the variation of ion current by varying the exciting voltage from 70 eV to 6 eV gradually. Argon gas was incorporated with the sample as a standard of known ionisation potential. Measurements were carried out on ^{80}Se and ^{125}Te isotopes which are the largest mass numbers and highest relative abundances.

2.6 Elemental Analysis

Micro-elemental analysis for carbon, hydrogen, nitrogen and halogen were carried out by the Micro Analytical Laboratories of the Molecular Sciences of Aston University. Tellurium analysis was carried out volumetrically by the following method[88]:-

A known weight of the tellurium compound was oxidised with a mixture of concentrated nitric acid and perchloric acid (2:1). The volume of the mixture was then reduced to 10 cm^3. Extra $HClO_4$ (10 cm^3) was added and heated until the solution became effectively colourless. It was then cooled and diluted with distilled water to 250 cm^3 in a volumetric flask. To a 50 cm^3 of this solution was added a knowm excess of standard 0.1 N potassium dichromate solution and the mixture was allowed to stand half an hour at room temperature. Then the solution was treated with an excess of 0.1 N iron(II) ammonium sulphate solution.

The unreacted iron(II) was back titrated with a standard 0.1 N potassium dichromate solution using a few drops of diphenyl amine indicator (prepared by dissolving 2.7 g of diphenyl amine in 100 ml of conc.H_2SO_4) and about 2 cm^3 of conc. phosphoric acid as a complexing agent for iron(II) ions.

1 ml 0.1 N $K_2Cr_2O_7$ = 0.00638 g Te

2.7 Ultraviolet and Visible Spectra

The uv and visible spectra were recorded on a Unicam SP8-100 spectrometer using 10 mm pathway quartz cells.

2.8 Conductivity Measurements

Molar conductance of freshly prepared solutions were measured with Mullard conductivity bridges using a standard conductivity cell (type E759/B) with a cell constant of 1.46.

2.9 Solid State Conductivity Measurements

Samples were prepared into discs of diameter 13 mm and thickness of 0.6-1.0 mm. Silver paste was painted on each side of the pellet to function as contacts. Each side was attached with gold wire by silver paste and the conductance was measured by the two pulse method. A 610 C solid state Electrometer (Keithley instruments) and stabilised power supply (Kingshill) model 305 have been used to measure the conductivity. Facilities were available to monitor conductance in the range 25°C to -190°C.

2.10 Nuclear Magnetic Resonance

Some ^{1}H NMR spectra were determined on an FX-90 Q(JEOL) spectrometer using tetramethylsilane (TMS) as an internal standard. Other ^{1}H NMR, ^{13}C NMR and ^{125}Te NMR spectra were recorded on an Bruker AC-300 MHz instrument. The ^{125}Te NMR spectra were measured as solutions at room temperature. The data were referenced to the frequency of the standard dimethyltelluride (Me_2Te) for which is considered as zero[89].

2.11 Electron Spin Resonance Spectra

ESR spectra were obtained with a JEOL-1X spectrometer at room temperature. Calibration was done with a standard manganese(II) to check the magnetic field and as a g-marker. Solid samples were packed inside capillary glass tubes (1 mm diameter) up to about 1 cm. The small capillary tube was put in a quartz tube of 5 mm diameter, which was inserted in the resonant cavity between the magnetic poles.

2.12 X-ray Crystallography

Crystals of the tellurium compounds were obtained by recrystallisation from suitable solvents. All the crystallographic work was done by one of our group in the laboratory.

CHAPTER THREE

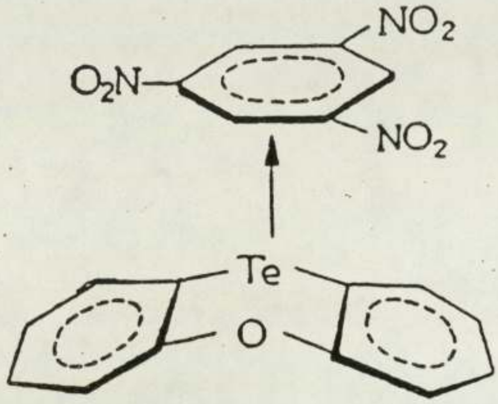
CHARGE-TRANSFER COMPLEXES OF ORGANYLTELLURIUM AND -SELENIUM COMPOUNDS

3.1 Introduction

Since the discovery of metallic conductivity in the complex of tetrathiafulvalene and tetracyanoquinodimethane (TTF - TCNQ), great interest has been focussed on the synthesis and properties of related organic and organometallic charge-transfer complexes.

A view is held that, tellurium, being both larger and more electropositive than sulphur and selenium, may enhance both intermolecular and interchain interactions.

Hetnarski[90], has employed phenoxatellurine as a model compound to examine the electron donor properties of the organic derivatives of tellurium. This choice of this compound was based on the steric rigidity of the phenyl groups arrangement due to their bonding by means of the oxygen atom which effectively unshields the tellurium atom thus increasing its ability to act as a donor. The complex of phenoxatellurine with trinitrobenzene was prepared in the form of carmine-red crystals.



Later on, same donor compound had been used together with TCNQ, TCNE and chloranil. The interaction was interpreted in terms of π to π type bonding involving a delocalised orbital of the phenoxatellurine rather than non-bonding orbitals of the tellurium[91].

In the present study, TCNQ was selected as an acceptor molecule because of the high electron affinity of the polyene system, conferred by the powerful electron withdrawing effect of the four cyano groups.

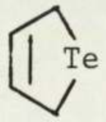
Another strong π -acceptor, tetrachloro-p-benzoquinone [chloranil(TCQ)] has similar behaviour with TTF and it forms both metallic and semiconducting complexes[92,93].

The third electron acceptor p-dinitrobenzene (DNB) was chosen because it resembles TCNQ in two important ways.

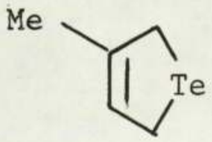
The molecules are of similar size and DNB has the same high symmetry as TCNQ (D_{2h}); also the electron spin resonance studies of the radical anions of aromatic compounds show that the electronegativity of the nitro group is similar to that of the dicyanomethylene group [94]. Thus the two acceptors, TCNQ and DNB, should have similar spin and charge distributions in their radical ions.

These three acceptors have been used in the present work, together with a range of organotellurium and selenium compounds to form various donor-acceptor complexes.

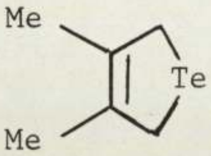
According to the molecular requirements for obtaining highly conducting charge-transfer complexes, for example, planar structure, large cation polarizability and relatively small cation size, the following organochalcogen donors were chosen:-



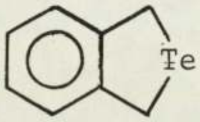
2,5-Dihydrotellurophene



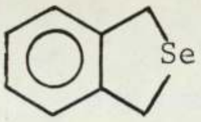
3-Methyl-2,5-dihydrotellurophene



3,4-Dimethyl-2,5-dihydrotellurophene



1,3-Dihydro-2-tellurainedene



1,3-Dihydro-2-selenaindene

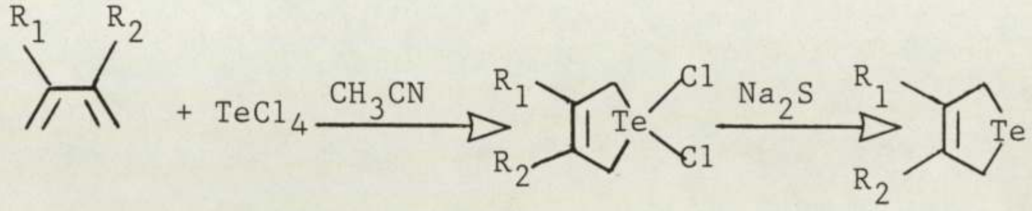
3.2 Experimental

Synthesis of Organotellurium and -selenium Compounds

Organotellurium and -selenium donors were synthesised according to the literature methods as follows:-

(1) Tellurophenes[95]:

    a. 2,5-dyhydrotellurophene
    b. 3-methyl-2,5-dihydrotellurophene
    c. 3,4-dimethyl-2,5-dihydrotellurophene,

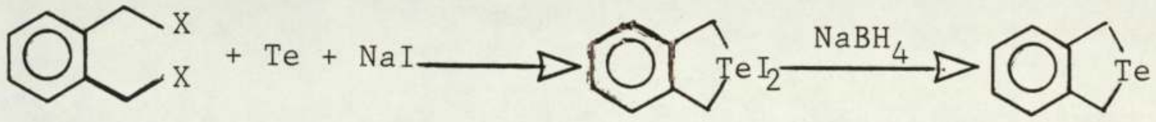


$R_1 = R_2 = H$

$R_1 = Me, \ R_2 = H$

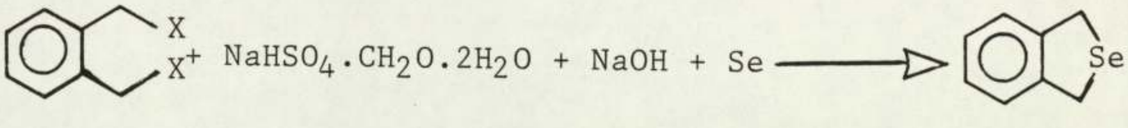
$R_1 = R_2 = Me$

(2) 1,3-dihydro-2-telluraindene[96]



X= Br

(3) 1,3-dyhydro-2-selenaindene[97]



X= Br

Synthesis of Charge-transfer Complexes

All the charge-transfer complexes were synthesised by the following typical method:-

To a hot solution of freshly prepared donor in acetonitrile solvent (20 cm^3) was added the acceptor in a hot acetonitrile (20 cm^3) (1:1 equimolar). The mixture was stirred and refluxed for one hour, after which the volume was reduced. On cooling to room temperature, small dark crystals of the complex were deposited.

3.3 Results and Discussion

In general, the charge-transfer complexes of organo-tellurium and -selenium compounds with different acceptors were found to be of 1:1 stoicheiometry. Physical and analytical data of the complexes are given in Tables (3.1 and 3.2). All the complexes were found to be stable in air for several months. The analytical data (Table 3.2), show clearly that all the complexes of the acceptor DNB are poorly fitted to the calculated figures.

On the basis of the obtained results of the work, one can conclude that the acceptor interactions with the donor under investigation are in the order TCNQ > TCQ > DNB.

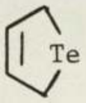
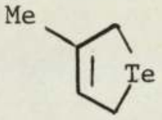
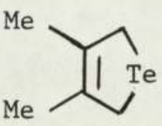
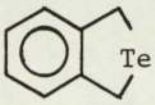
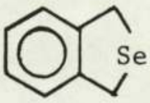
No	Compound		Colour	Yield %	MP °C
1		TCNQ	deep violet	84	102-104
2		TCQ	dark brown	78	198-200
3		DNB	brown	-	157-158
4		TCNQ	reddish black	82	92-95
5		TCQ	deep brown	80	171-173
6		DNB	brown	-	150-152
7		TCNQ	black	86	83-85
8		TCQ	brown-black	76	159-161
9		DNB	deep brown	-	145-147
10		DNB	black	82	108-110
11		TCNQ	blue-black	85	135-137
12		TCQ	violet	75	197-199

Table 3.1 Physical data for charge-transfer complexes

Compound No.	C %	(calcd)	H %	(calcd)	N %	(calcd)	Cl %	(calcd)
1	50.1	(49.8)	2.6	(2.6)	14.1	(14.5)	-	-
2	28.5	(28.0)	1.45	(1.40)	-	-	33.6	(33.1)
3	35.0	(34.0)	3.5	(2.9)	7.0	(8.0)	-	-
4	51.4	(51.0)	3.1	(3.0)	13.5	(14.0)	-	-
5	28.2	(29.9)	2.3	(1.8)	-	-	31.6	(32.1)
6	37.2	(36.2)	4.1	(3.3)	7.0	(7.7)	-	-
7	52.5	(52.2)	3.7	(3.4)	14.1	(13.5)	-	-
8	32.0	(31.6)	2.7	(2.1)	-	-	31.9	(31.2)
9	39.3	(38.1)	2.9	(3.7)	6.6	(7.4)	-	-
10	42.9	(42.0)	2.8	(3.0)	6.0	(7.0)	-	-
11	62.2	(62.0)	3.3	(3.1)	14.0	(14.4)	-	-
12	39.6	(39.0)	2.1	(1.8)	-	-	33.8	(33.1)

Table 3.2 Analytical data for charge-transfer complexes

3.4 Conductivity Measurements

The molar conductivity of each complex in acetonitrile solution and the solid state conductivity of compacted discs (at room temperature) were determined and data are given in Table (3.3).

Generally, low conductivities were observed, which show little concentration dependence. Only the complex of 2,5-dihydrotellurophene showed a significant conductivity in solution.

The numerous solid molecular conductors have been studied in recent years, because of many novel physical and chemical properties atypical of molecular solids. Particular emphasis has been placed upon understanding the temperature dependence of the conductivity of quasi-one-dimensional materials.

The conductivity of a solid is determined by its electronic structure. The distribution of the electrons in the vicinity of an atom is described by a system of orbitals, each of which has a characteristic shape and size.

In a highly conductive solid orbitals of adjacent atoms or molecules overlap, so that electrons can readily move from site to site through the lattice. Linear-chain

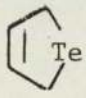
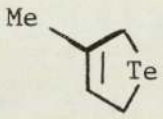
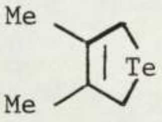
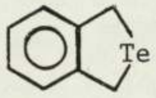
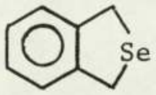
Compound		Molar Cond. $\Omega^{-1}cm^{2}mol^{-1}$	Solid Cond. $\Omega^{-1}cm^{-1}$
	TCNQ	108.0	10^{-6}
	TCQ	12.0	10^{-8}
	DNB	10.0	-
	TCNQ	25.0	10^{-8}
	TCQ	11.0	10^{-11}
	DNB	9.0	-
	TCNQ	23.0	10^{-11}
	TCQ	9.0	10^{-12}
	DNB	8.0	-
	DNB	9.0	-
	TCNQ	16.0	10^{-11}
	TCQ	9.0	10^{-13}

Table 3.3 Solution molar conductivity (10^{-3} M.) and compressed disc conductivity data at room temperature.

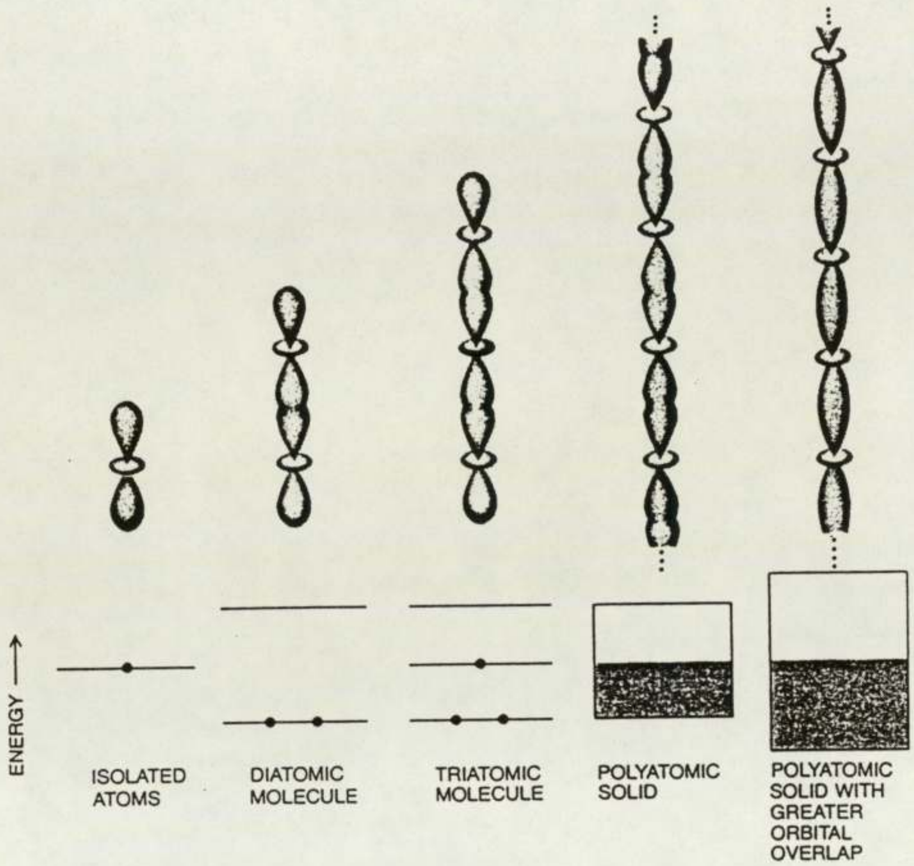
conductors are materials in which there is extensive overlapping of orbitals only along one axis.

(TTF)(TCNQ) is made up of two kinds of flat molecules, which form parallel conducting stacks. The molecules in each stack are tilted with respect to the axis of the stack and adjcent columns are arranged to form a herring-bone pattern (Fig. 1.2). Within both the TTF and the TCNQ stacks orbitals of each molecule overlap those of the molecules above and below it in same stack. The orbitals involved are associated with the molecule as a whole rather than with any particular atom. There is little contact between the orbitals of molecules in different stacks and so charge transport perpendicular to the stacks is inefficient.

In order to explain the mechanism of electrical conduction it is necessary to discuss the state of the electrons in a solid. In an isolated atom each electron occupies a particular orbital, which has a certain energy associated with it.

The orbital defines the distribution of the electron charge in space. Each orbital can be occupied by no more than two electrons. In an atom in its ground state, the first two electrons fill the lowest-energy orbital and any additional electrons must go into higher-energy orbitals. Because the electrons are confined to orbitals they can have only discrete energy levels, all intermediate energies are forbidden. If an electron is to change its energy at all, it must jump from one allowed level to another.

When two identical atoms are brought together closely enough for their orbitals to overlap, each energy level is split to create two new levels, one below the original level and the other above it. The magnitude of the splitting is determined by how extensively the orbitals overlap, or in other words by how closely the two atoms approach each other. It is important to note that the total number of electrons that can be accommodated by the system does not change when the two atoms coalesce to form a molecule. Whereas before there were two independent atomic orbitals of the same energy, each of which could hold two electrons, there are now two molecular orbitals with two different energy levels and again each level can hold two electrons. If three atoms are brought together, three new energy levels are created, one below the original level, one above it and one between these two levels.



FORMATION OF ENERGY BANDS

The extent of occupation of the energy bands and the magnitude of the gaps between them determine most of the electrical properties of a solid.

The electrons in a band are said to be delocalised they are free to wander throughout the solid. In order for an electric current to be sustained, however, there must be a net movement of electrons in one direction. If the energy levels in a band are filled continuously from the lowest available level to the highest allowed one, there can be no net motion of the electrons.

It is the presence of a partially filled electron-energy band that gives a metal its most distinctive properties. In a metal, the electrons in the highest filled energy levels can readily be promoted to unoccupied levels that are only infinitesimally higher in energy. Thus electrons are always freely available for conduction. A partially filled band is created whenever the orbitals that combine to form the band are not fully occupied. For example, if each orbital is occupied by just one electron (instead of the maximum of two electrons), the corresponding energy band in the solid will have only n electrons rather than the maximum of 2n. The remaining levels in the band are available for conduction.

Semiconductors and insulators differ from metals in that every energy band is either completely full or completely empty. In a semiconductor conduction is possible when an electron is excited by heat or light to move from a filled band to one of the vacant levels of an empty band. Such a change in the energy of an electron effectively creates two charge carriers: the electron itself and the "hole" left behind in the previously filled band. The minimum energy needed to create these charge carriers is equal to the width of the gap between the bands. Charge carriers can also be supplied by defects or by impurities, such as the dopants that are diffused into silicon semiconducting devices.

In (TTF)(TCNQ), which is a stoichiometric crystal, charge is transferred between the two conducting columns (Fig. 1.2). TTF is an electron donor and TCNQ an electron acceptor, and on the average 0.59 of an electron is transferred from each TTF molecule to the TCNQ stacks. The result is to partially empty a filled band and partially fill an empty one[40].

The preparation of (TTF)(TCNQ) complex was on the premise that the fermi surface for this solid should be more complicated than that for simple closed-shell cation salts of TCNQ because of the two bands resulting from the highest occupied molecular orbital (HOMO) of the donor (TTF) and the lowest unoccupied molecular orbital (LUMO) of the acceptor (TCNQ) with the attendant possibility that the metal-to-insulator transition temperature would be lowered and the conductivity increased[98].

The another structural feature that made TTF-TCNQ as attractive candidata for study is the polarizability of the cation portion of this molecule.

Le Blanc, proposed that when the cation is relatively small and polarizable the conduction electron-cation chain exciton coupling can facilitate conduction by reducing the effective Coulomb repulsion (U_{eff}) between two electrons on the same site[99.100].

The energy U is given by ($U = U_o - V_1$)[32], the difference between the Coulomb repulsion (U_o) of two electrons on the same molecule and that (V_1) on neighbouring molecules. The point is, presumably, that U_o and V_1 may vary for different molecules and in different environments, but the difference $U = U_o - V_1$ appears to vary only slightly.

A comparative study of the thin disc conductivity of TCNQ complexes with 2,5-dihydrotellurophene; 3-methyl-2,5-dihydrotellurophene; and 3,4-dimethyl-2,5-dihydrotellurophene is presented here.

The disc conductivities of the three complexes have been measured over a range of temperature. The measured values increase with temperature initially quite steeply (80-150°K) then more gradually to the plateau values of 350°K given in Table 3.3. This behaviour is illustrated in Figure 3.1 and Figure 3.4 expresses the plateau conductivity as a function of the number of methyl-substituents. The apparent linear relationship is regarded as fortuitous.

Figure 3.1 indicates the temperature dependence of the electrical conductivity of the three tellurophene complexes. The resistivity of the three complexes increased on lowering the temperature (10^{-9}- 10^{-13} $\Omega^{-1}cm^{-1}$) while the resistivity was stable above the room tempera-

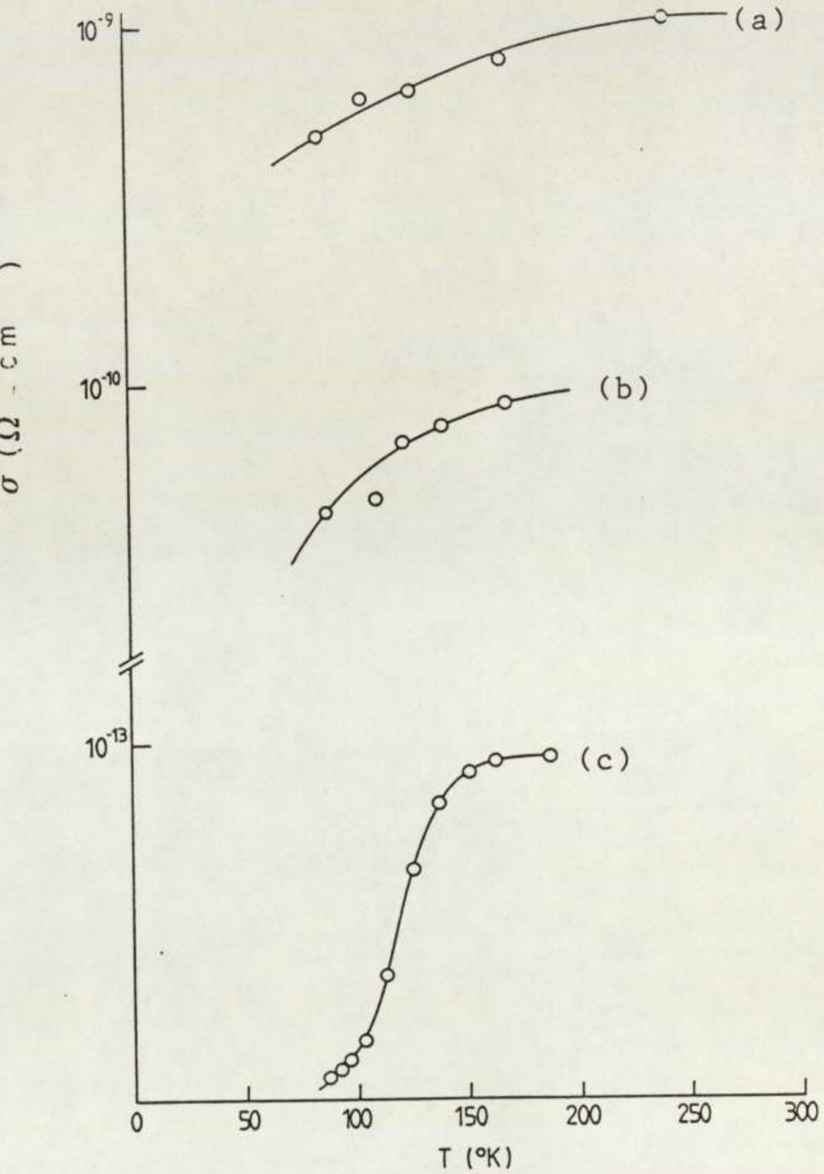
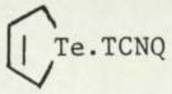
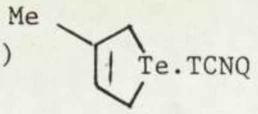


Figure 3.1 Temperature dependance of electrical conductivity of:

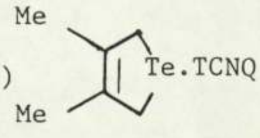
(a)



(b)



(c)



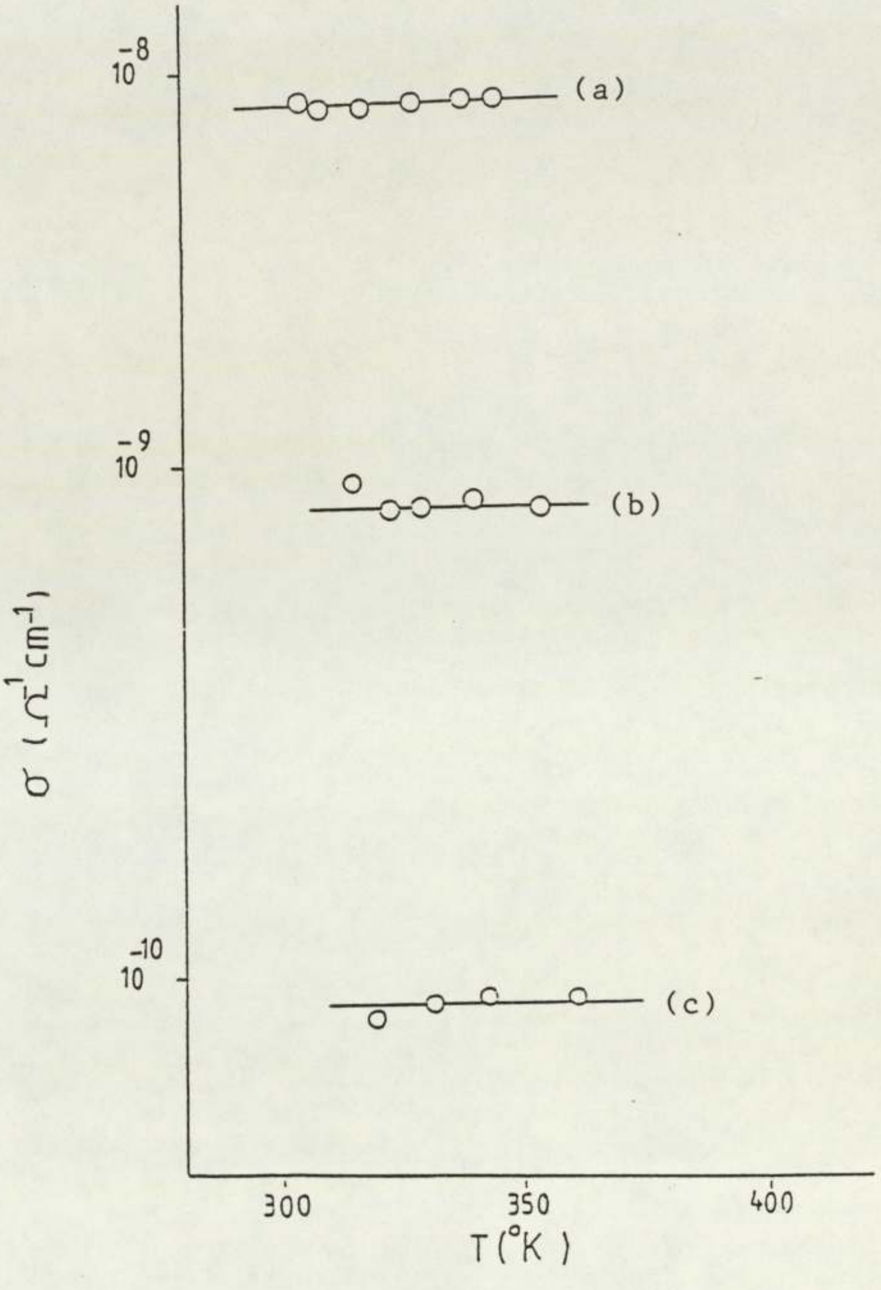
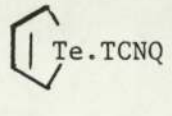
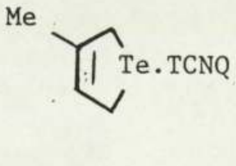


Figure 3.2 Temperature dependance of electrical conductivity of:

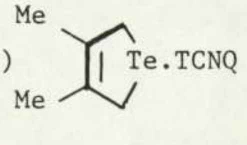
(a)



(b)



(c)



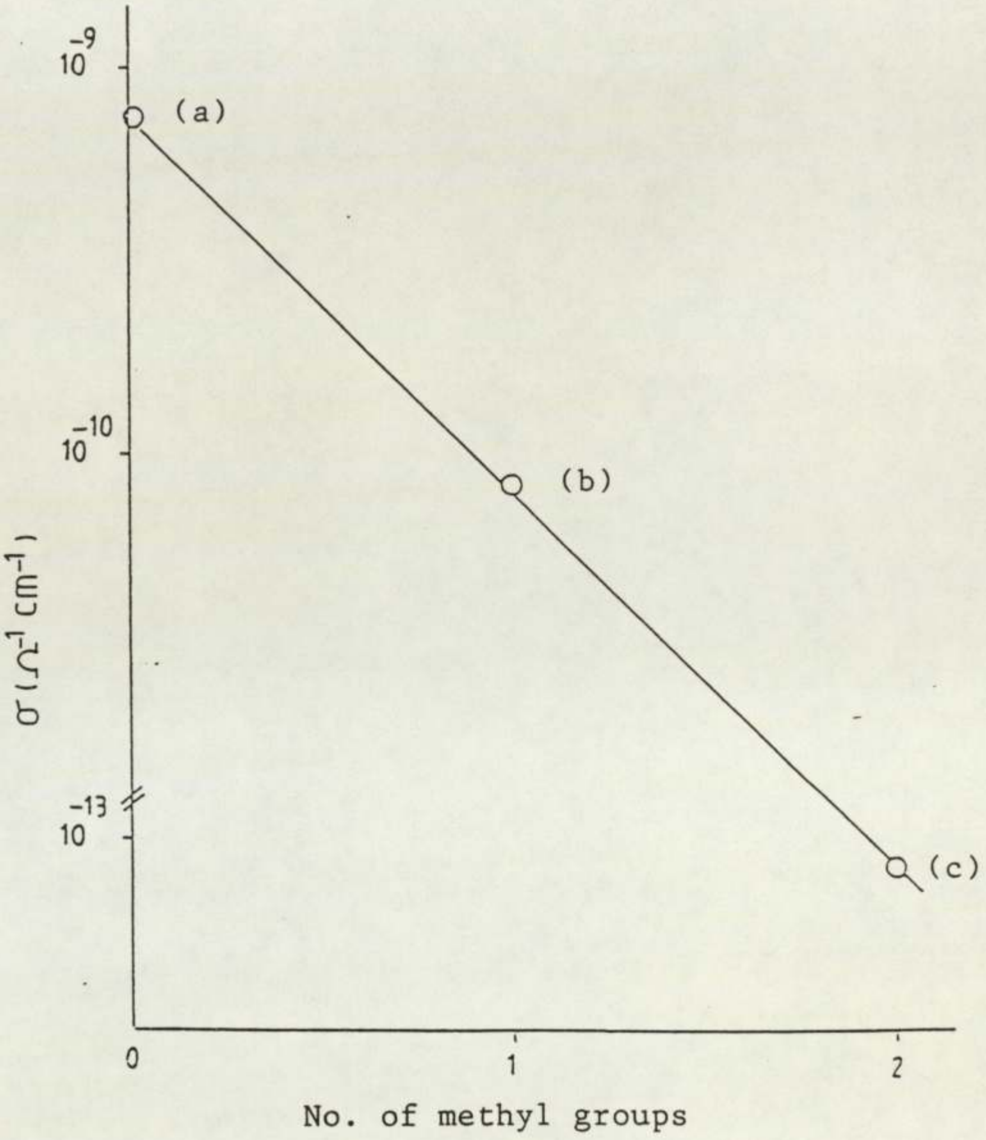
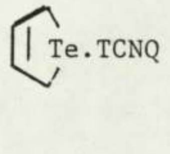
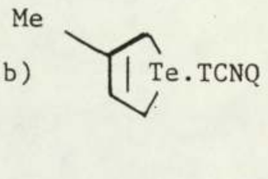


Figure 3.3 The relationship between the conductivity and the number of methyl groups at 150°K

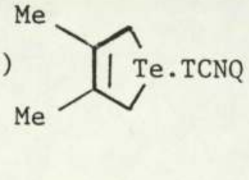
(a)



(b)



(c)



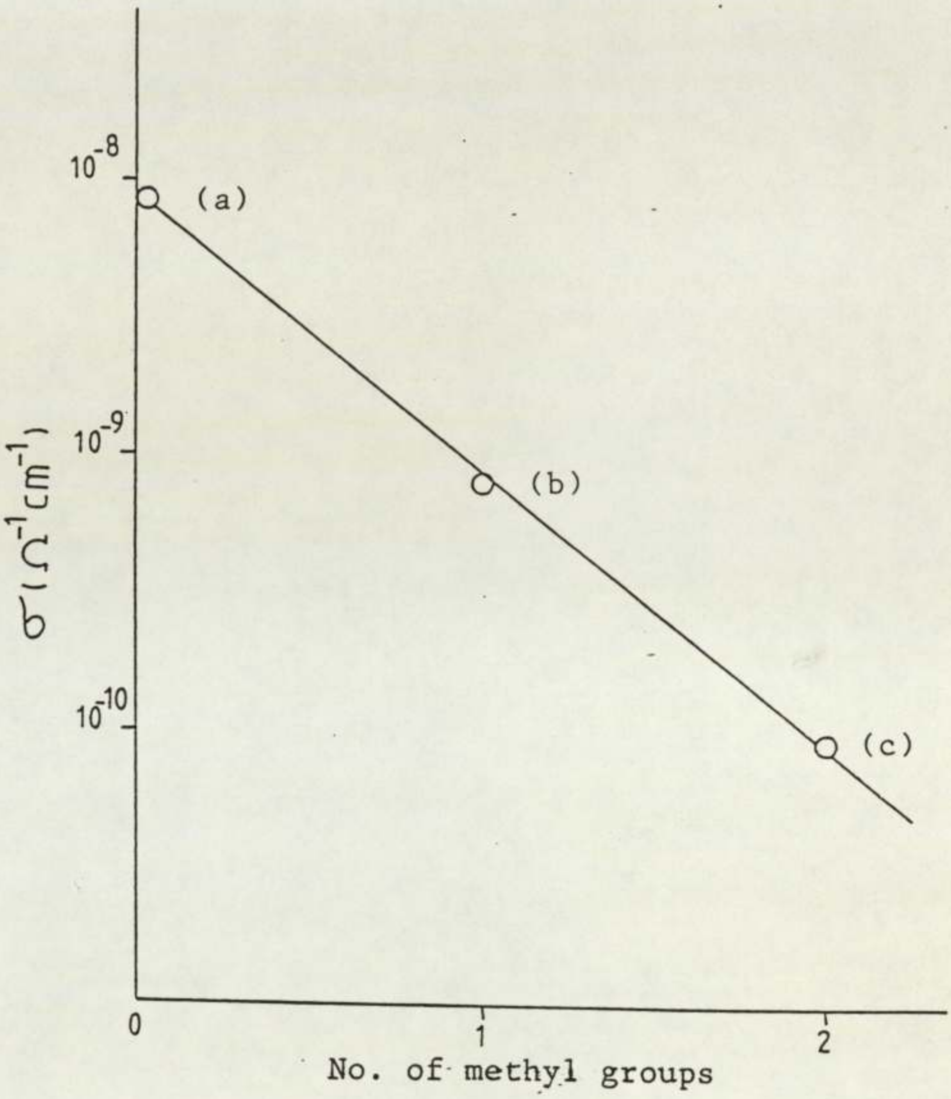
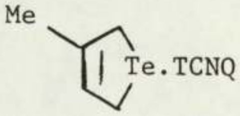


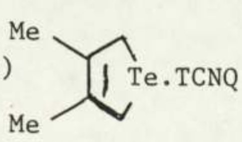
Figure 3.4 The relationship between the conductivity and the number of methyl groups at 330°K

(a)

(b)



(c)



ture. Generally semiconductors conductivity falls off as the temperature is reduced[41].

The relatively high room-temperature conductivities for the three tellurophene-TCNQ complexes may be ascribed to narrow-band formation by overlap of a combination of open-shell and closed-shell molecular orbitals as it has been explained[101] generally for the organic metals.

There are a large number of effects and interactions which are believed to have an important influence on the charge-transfer compounds such as: U_o (the Coulomb repulsion energy between two electrons on the same molecule), the number of unpaired electrons per TCNQ (ρ), the polarizability and size of the cations, the interaction between stacks, impurities, the band-width arising from the strong π-molecular, the temperature dependence of the mobility,........... Torrance[102], has proposed that polarization and disorder play only a minor role in the TCNQ charge-transfer.

It is well known that the charge transfer from the donor to acceptor can be either complete or incomplete. It is concluded, for example, that he unifying common feature of the known organic metals is an incommensurate (or non-simple fractional) value of ρ , due to incomplete charge-transfer[103]. It is further proposed[43] that ρ is determined by the ionization potential of the donor

molecule and the strength of the ionic bonding in these materials.
For the effects of the size and the shape of the cations it has been pointed out that the planar and small size of the donors gives strong intermolecular contacts and the substitution on the basic acceptor or donor skeleton is dependent upon their size. The substitution has been shown generally to lower the conductivity of charge-transfer complexes formed[104-106].

It seems that the conductivity of three tellurophene complexes with TCNQ (in this study) is related to the small size of the tellurophene donors.

Figure (3.3) and (3.4) shows the relationship between the electrical conductivity and the number of methyl groups at certain temperatures (150 and 330°K).

It reveals clearly that the attaching CH_3 groups to the tellurophene donors reduces the conductivity. This conclusion is in good agreement with Bechgaard, who points out that the substitution of the hydrogens by methyl groups in TTF makes the molecule longer and creates electronoic perturbations[48].

The relationship between the conductivity and the number of methyl groups at room temperature is shown in Figure. (3.5). Two significant considerations could be concluded

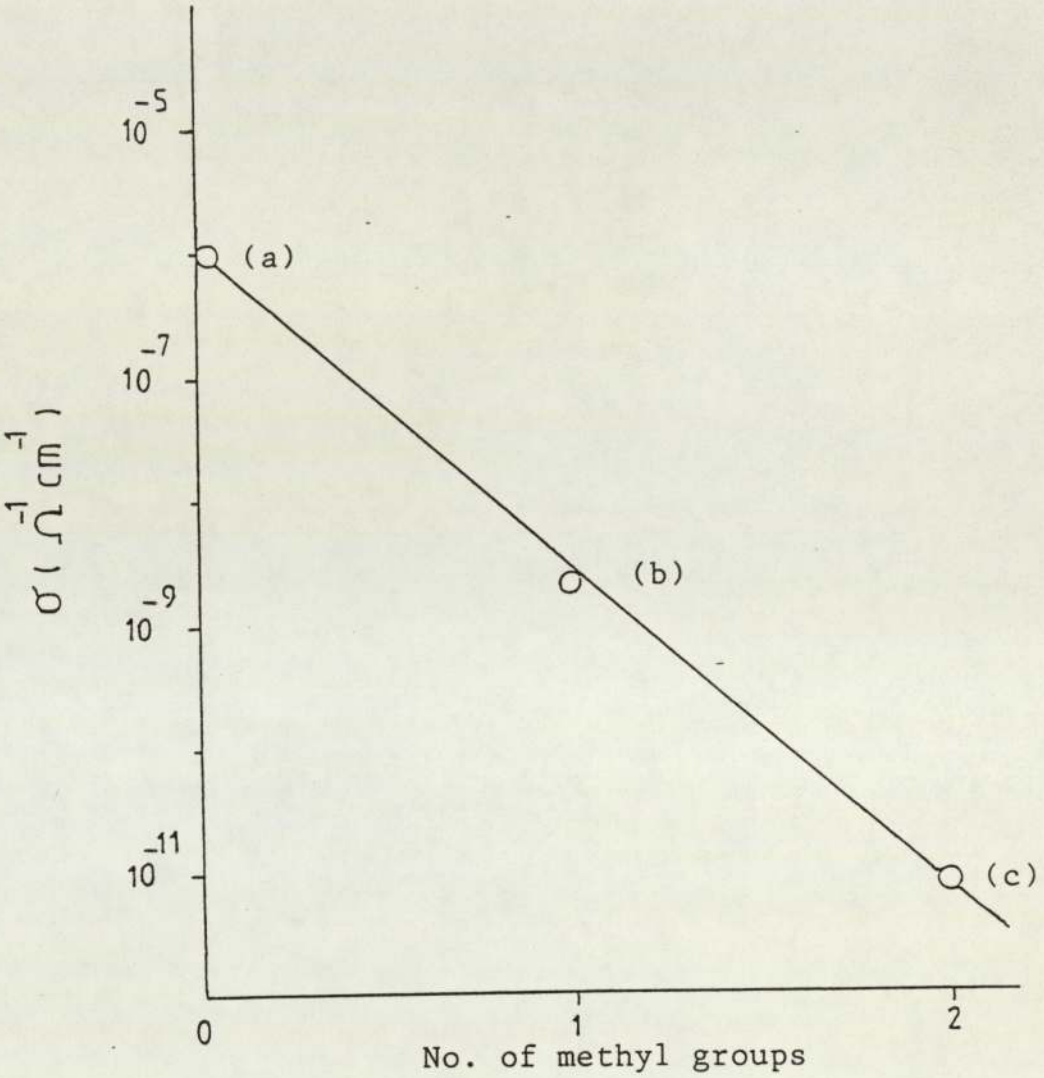
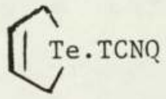
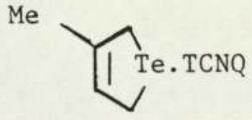


Figure 3.5 The relationship between the conductivity and the number of methyl groups at room temperature

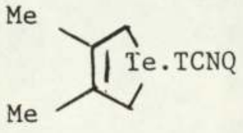
(a)



(b)



(c)



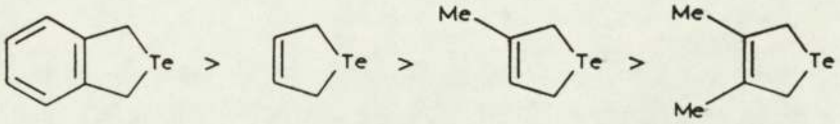
from the plot, the first is that the three tellurophene complexes can be fitted to a straight line and this may be due to the proportionality between the conductivity of those three complexes and the number of CH_3 groups at certain temperature, and the second is that the best value for the conductivity is for the complex, dihydrotellurophene (TCNQ) ($10^{-6}\,\Omega^{-1}cm^{-1}$), and the lowest value is for the complex dimethyldihydrotellurophene-TCNQ (10^{-11} $\Omega^{-1}cm^{-1}$). The three different values for the three tellurophene complexes is related to three different sizes (by substitute methyl group step-by-step).

Keller[107], has pointed out that, certainly TCNQ is an oxidizing agent, electron acceptor (A), and forms stable open-shell or free radical salts. However there are numerous examples of insulating stable free radicals and free radical salts. Even an electron acceptor, such as chloranil (TCQ), which has a planar structure and readily accepts an electron into and extended π-molecular orbital, structural characteristics shared with TCNQ,forms insulating or semiconducting radical ion salts[31,32].

The chloranil complexes in this study did not give such good solid electrical conductivities as TCNQ complexes (Table 3.3). That low conductivities might be related with the chloranil chemical structure and the withdrawing of the electrons from the donor is less than that of CN groups in TCNQ molecule.

Generally, the low ionisation potentials of both 1,3-dihydro-2-telluraindene (6.55 eV)[86] and 1,3-dihydro-2-selenaindene (7.4 eV -Chapter 4) are quite unlike those of non cyclic tellurides[59], also the detailed behaviour with TCNQ is dependant upon the 3 and 4 substituent on the 2,5-dihydrotellurophene ring (it has been regarded that the tellura-indene as a special case of a substituted 2,5-dihydrotelluraphene)[108] . If donation is from the double bond (π -system), this result is contrary to expectation. It may therefore support the idea, that the donation is from the tellurium Pz lone pair which was supported by ^{125}Te Mossbauer measurements[67].

A complex (No 10 on Table 3.1) of 1,3-dihydro-2-telluraindene with DNB was isolated, thus a combination of data in this and a pervious work[67] suggests that the order of donor is;



and of acceptor strength;

TCNQ > TCQ > DNB .

3.5 Infra-red Measurements

The observation of unusual spectroscopic effects in the infrared spectra of donor-acceptor CT complexes was reported a long time ago. It was related with the interaction between electronic states and intermolecular vibrations[109].

Matsunaga[18], has pointed out that for a complex of an ionic type, it may be expected that the infrared spectrum is close to a superposition of the spectra of the ionized components, namely the D^+ and A^- free radical ions. Consequently if there is an appreciable difference in the vibrational spectrum between D molecule and D^+ ion or A molecule and A^- ion, examination of the infrared spectrum of complex may provide a reliable method of characterizing the nature of the intermolecular bonding.

In general, for simple 1:1 organic charge-transfer salts, the highly conducting systems have a broad, intense absorption $\geqslant 2.0\mu$ ($1\mu = 10^4$ cm^{-1}). This is believed to be a mixed valence transition and indicative of the segregated stacked structure which is required for high conductivity. On the other hand, poorly conducting materials display absorptions around $1.0\ \mu$. These absorptions are typical of charge transitions in an alternating donor-acceptor stacking arrangement (i.e., the D,A structure in the solid state)[110].

It has been pointed out, that partial transfer of charge from donor to acceptor is essential for high conductivity of 'organic metals' type[107]. The degree of charge-transfer in organic conductors could be monitored by examination of ν(CN) for TCNQ[111].

In the present study, infrared data are given in Table (3.4). The spectra of the complexes were compared with those of the components alone. They are quite similar to each other. There are slight shifts in frequency and some alterations of the intensity which reflect the molecular association. The frequency of ν(CN) has been changed.

Generally the TCNQ complexes fall into two categories, (a) those which show ν(CN) around 2230 cm^{-1} (the value for neutral TCNQ), and (b) some showing ν(CN) around 2180 cm^{-1} (a value similar to that observed for the salts Na^{+} TCNQ^{-} and K^{+}TCNQ^{-}). The observed shift can be attributed to the acceptance of one electron into the antibonding level of the CN groupsof TCNQ.

Simplistically, therefore, the infrared data (Table 3.4) suggest less radical ion character in the complexes of methyl-substituted 2,5-dihydrotellurophenes. At this stage, it should be mentioned that all the infrared measurements were taken at room temperature, and since the electrical conductivity in the solid state has been

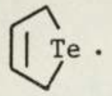
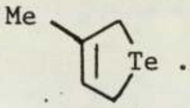
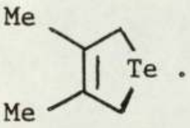
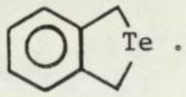
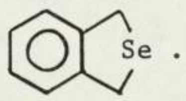
Complex		$\nu(\mathrm{CN})$	$\nu(\mathrm{CO})$	$\nu(\mathrm{CNO_2})$
	TCNQ	2198,2166		
	TCQ		1682,1694	
	DNB			1326,1348
	TCNQ	2238,2198,2160		
	TCQ		1682,1693	
	DNB			1326,1350
	TCNQ	2236,2197,2158		
	TCQ		1683,1693	
	DNB			1326,1346
	DNB			1328,1348
	TCNQ	2228,2198		
	TCQ		1684,1696	

Table 3.4 Infra-red data for TCNQ, TCQ and DNB complexes with organotellurium and -selenium donors (cm^{-1}).

found to be dependent on the temperature of the measurement (the room temperature values being the highest),one can expect also that this may bring a certain difference in the infrared spectra at the (CN) absorption region.

The infrared spectra of the DNB complexes were virtually the superposition of the spectra of the individual components and this could be in a good agreement with the poor analytical data given in Table (3.2). Also there is no shift of ν(CO) with change of donor in the chloranil complexes. This implies an extremely weak charge-transfer interaction and this observation is in line with results previously obtained for the 1,3-dihydro-2-telluraindene-TCQ complex[67].

The infrared spectra of complex 1,3-dihydro-2-selenaindene with TCNQ and TCQ (Table 3.4) implies that the selenium compound may be less ionic than the tellurium analogue. The ionisation potential of 1,3-dihydro-2-selenaindene (7.4 eV) and the low room temperature conductivity of this compound with TCNQ and TCQ (Table 3.3) could support this idea.

3.6 Electronic Absorption Spectra

There have been many comprehensive papers and reviews on the electronic absorption of TCNQ complexes. Tanaka et al[112], pointed out, that the electronic study becomes very important, since the remarkable electronic properties of highly conductive TCNQ salts may be elucidated by the analysis of their electronic spectra.

The first electronic absorption measurements on salts of TCNQ were reported by Iida[113], who found that the spectra of the compounds in class I (K-TCNQ, Na-TCNQ, Li-TCNQ,....) were all very similar to that of K-TCNQ. The spectra of the highly conducting class II salts (NMP-, TTF, TSF-TCNQ) are clearly quite distinct from those of class I. The most significant feature of the data is the striking similarity between the spectra for such a wide variety of class II and class III (Cs_2TCNQ_3, TEA-$TCNQ_2$, and Ad-$TCNQ_2$) salts with different on the conductivity.

In an optical study[114] of phenoxachalcogenine (S, Se and Te) complexes with tetracyanoethylene (TCNE) and chloranil (TCQ), a broad maximum appeared in all cases, and it was explained as a characteristic of weak 1:1 complexing systems.

For the phenoxachalcogenine charge-transfer complexes, all of the equilibrium constants are less than 10, and that all the extinction coefficients are relatively small, of the order of a few hundred to about a thousand. The small values for the equilibrium constants indicate that the complexes formed are relatively weak, probably being of the $\pi-\pi^*$ charge-transfer type. There may well be a much stronger charge-transfer band located at shorter wavelengths but the uncomplexed components absorb very strongly in this region, so that observation of such a band is precluded[114].

Hillebrand et al[115], in their study of the interaction of phenoxathiin (PS) with TCNE have suggested that the absorption band at 6700-6800°A is due to the transition from the last occupied molecular orbital (HOMO) on the donor to the lowest empty molecular orbital (LUMO) on the acceptor. The absorption peak which occurs at about 4300-4500°A was assigned to a somewhat higher energy transition from the second highest filled molecular orbital on the donor to the lowest unfilled orbital on the acceptor.

In the present study, the electronic absorption spectra were measured in acetonitrile solution and the data are given in Table (3.5). Fiugure (3.6) shows a comparison of the spectra of the tellurophene donors with TCNQ.

It has been demonstrated[113] that the charge-transfer complexes of TCNQ are completely dissociated in solution,

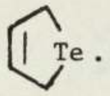
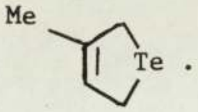
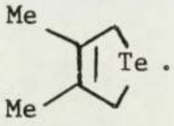
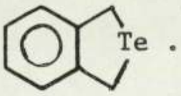
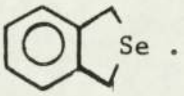
Complex		g-value (±0.003)	λ (max) nm
	TCNQ	2.0026	656
	TCQ	2.0038	508
	DNB	-	402
	TCNQ	2.0040	654
	TCQ	-	506
	DNB	-	-
	TCNQ	2.0048	648
	TCQ	-	504
	DNB	-	-
	DNB	2.0038	418
	TCNQ	2.0041	623
	TCQ	-	449

Table 3.5 ESR and E.A. data for the CT complexes

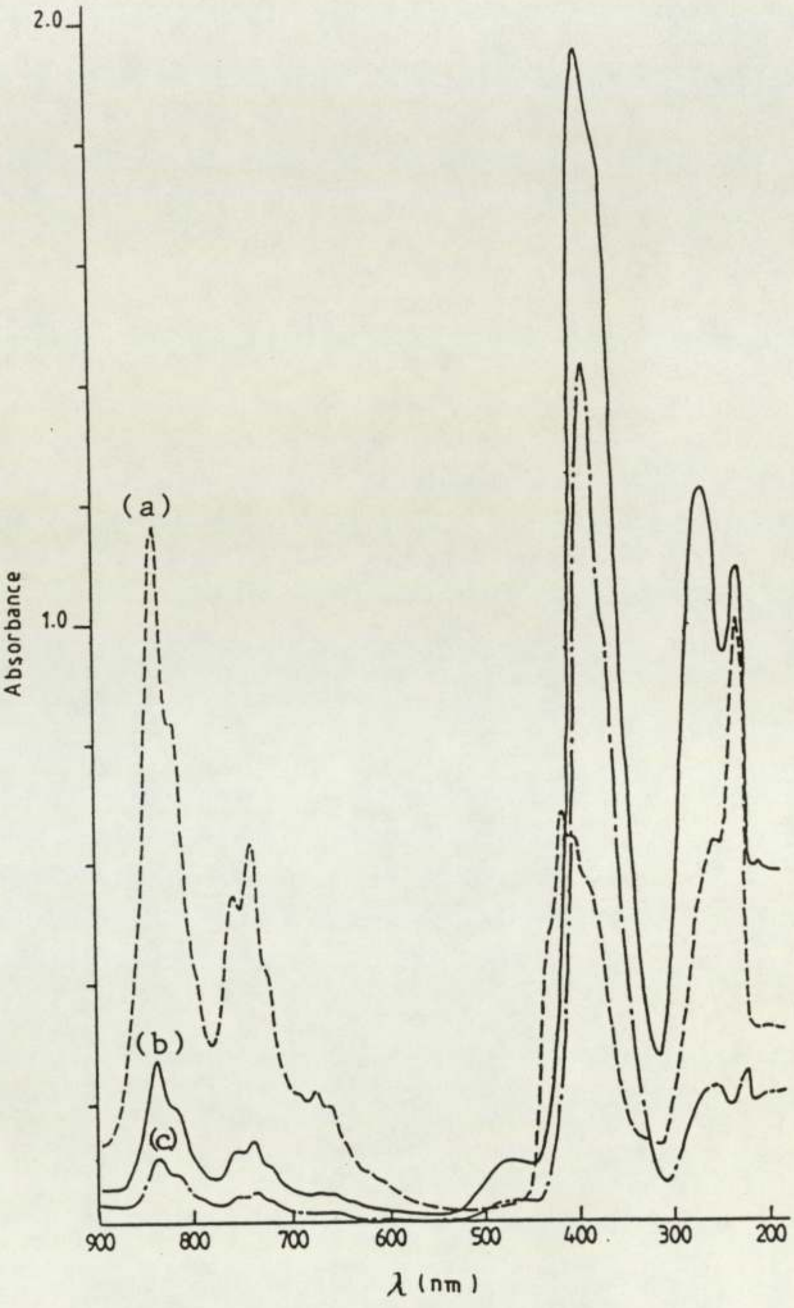
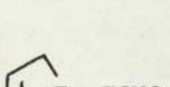
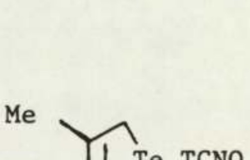


Figure 3.6 Electronic spectra of the tellurophene complexes with TCNQ

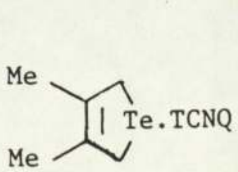
(a)



(b)



(c)



thus giving spectra consisting of these independent TCNQ and $TCNQ^{\cdot-}$ molecules. Also that the semiconducting and metallic properties arise from crystal structure with one dimensional TCNQ columns. The electronic spectra of such complexes showed CT absorption band between adjacent TCNQ in the infrared region.

The observed absorptions (Figure 3.6) around 700-900 nm are attributable to the absorption of $TCNQ^{\cdot-}$. The values of 380-420 nm are to a combination of $TCNQ^{\cdot-}$ and neutral TCNQ absorption similar to Tanaka's conclusion[112]. The greater relative intensity in the 700-900 nm region for compound no. 1 is notable, again implying greater ion character. Indeed, the acetonitrile solution of complex no.1 is quite conducting (108 $\Omega^{-1}cm^{2}\ mol^{-1}$) in contrast to those of complex no.4 and complex no. 7 again implying a greater ionic character.

Since all of the tellurophene complexes absorb at approximately the same region of the visible spectrum, it is reasonable to assume that the absorption bands at 656 nm, 654 nm and 648 nm are due to a related transition from the highest occuiped molecular orbital on the donor to the lowest unoccupied molecular orbital on the acceptor (HOMO $\longrightarrow$ LUMO). If this assignment is correct, the band for the 2,5-dihydrotellurophene complex is at marginally lower energy than those for compounds (4 and 7)[108]. This could be in good agreement with Zingaro's argument[114] that this kind of weak interaction (here the tellurophenes with TCNQ) being of $\pi - \pi$ charge-transfer type.

3.7 Electron Spin Resonance Spectra

It has been pointed out, that the interaction between donor and acceptor must be considerably strong to rise to a charge separation in the ground state. Since this can be detected by the sensitive methods afforded by ESR[116].

For molecules with great donating and accepting power a complete electron transfer can take place in the ground state. The system, then, is paramagnetic and is expected to show free radical behaviour. ESR is observed in such systems and indicates the presence of unpaired electron spins in such materials.

The electron spin resonance measurements were carried out on freshly prepared complexes at room temperature. The solid ESR data are in Table (3.5), and a typical spectrum is shown in Figure (3.7).

Strong single line and sharp signals were obtained. The g-value of ESR spectra is, within the errors, the same for each sample and is very close to the free electron value (2.0023)[117] suggesting that the signal arises from unpaired electron density on TCNQ and the other

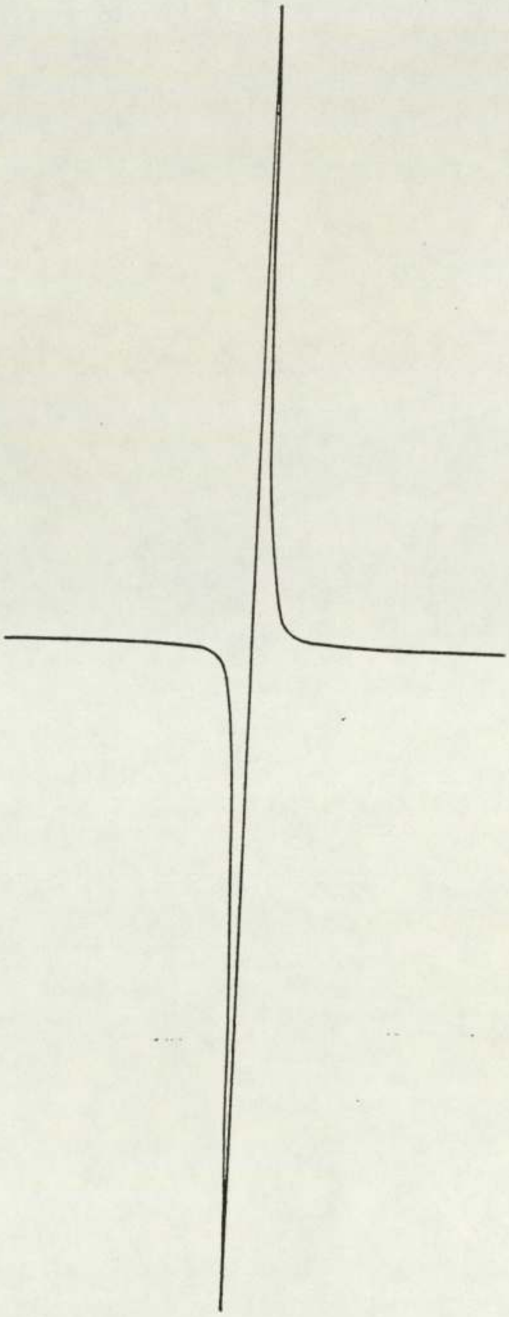


Figure 3.7 ESR spectrum of 3-methyl-2,5-dihydrotellurophene complex with TCNQ.

acceptors.

The authors attribute failure to observe signals for the electrochemical formation of a radical cation of phenoxatellurin to the rapid formation of a dimer which, in turn interacts with a neutral phenoxatellurin molecule to give a complex cation which may be isolated as the perchlorate[118]. The electrochemical reduction of nitro-substituted phenoxatellurins has shown the ESR data for anion radicals and the unpaired spin density was largely associated with the nitro-groups[119].

McWhinnie et al[67], assumed that these remarks are of particular significance for the complex of TCNQ with 1,3-dihydro-2-telluraindene which some data suggest to be ionic in the ground state. For this compound no tellurium centred resonance was observed as well as in no case was it possible to see a resonance from a tellurium centred radical. This was attributed to the fact that ESR spectra is reflect the effect of increasing spin orbit interaction as the series S < Se < Te is traversed [116].

An alternative explanation has been given for 1,3-dihydro-2-telluraindene complex with TCNQ that it contains cation dimers with a singlet ground state[67].

In a study of series of perinaphthalene-1,8-dichalcogenides, no spectrum was obtained from the ditelluride. Although, failure to observe signals from radical cations of phenoxatellurin, the selenium analogue does give a broad ESR spectrum from which ^{77}Se hyperfine splitting is just discernible[120].

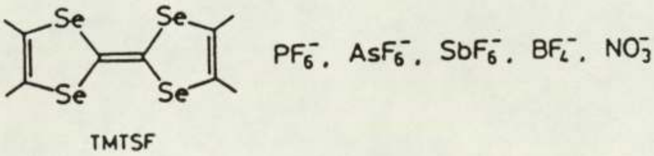
CHAPTER FOUR

ORGANOSELENIUM ELECTROCHEMISTRY

4.1 Introduction

The synthesis of the salt of tetrathiafulvalene and tetracyanoquinodimethane (TTF-TCNQ) and the discovery of its exceptionally high electrical conductivity[37,98] have encouraged attempts to prepare related organic conductors either chemically or electrochemically.

In 1979, the oxidation of tetramethyltetraselenafulvalene (TMTSF) in the presence of different anions (PF_6^-, AsF_6^-, SbF_6^-, BF_4^-, ClO_4^-, NO_3^-) was studied by several electrochemical methods[49]. Tetraalkylammonium salts of the appropriate anions were used as supporting electrolyte. In each case the solid phase $TMTSF_2X$ was isolated by electrochemical oxidation.

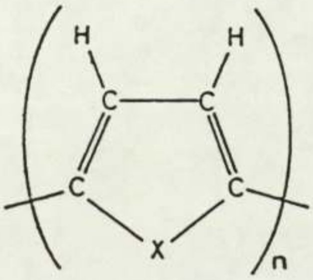


(1)

Also, heterocyclic polymers like polythiophene and polypyrrole and their derivatives have been reported to indicate high electrical conductivity and to have high quality of mechanical and thermal properties. Polymers of hetero five-membered ring compounds including atoms of the oxygen group in the periodic table, polyfuran and polythiophene are obtained by both the chemical and electrochemical polymerization methods. Polyselenophene was also prepared by the electrochemical method[121,122].

In some cases, electrochemical polymerization on conducting substrates is very convenient for applications. However, in other cases, the chemical polymerization is preferred for applications because in this case polymer films can be prepared on an non-conductive substrate[123].

Polyselenophene and polytellurophene were prepared successfully by the chemical method from selenophene and tellurophene monomers(2) using $FeCl_3$ as a catalyst. The products was deposited within a very short time as a film. The electrical conductivity of the doped state (I_2, ClO_4) is of the order of $10^{-3}\Omega^{-1}cm^{-1}$[123].

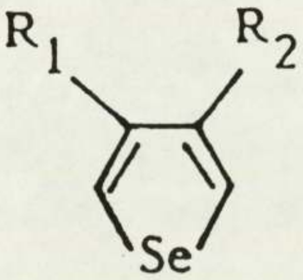


(a) X=Se
(b) X=Te

(2)

The influence of 3,4 substitutions on the selenophene has been studied by Gazard[124]. The electrochemical polymerisation products of substitued or nonsubstitued selenophene were rendered conductive by incorporating ions (e.g. BF_4^-). These materials are used in electrochemical cells designed as electrochemical recording apparatus or batteries. The polymer corresponds to the general formula $(M^+X^-)_n$, where X^- is an anion.

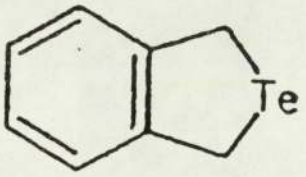
The monomers (R_1 and R_2 are H or alkyl, alkoxyl, aryl or substituted aryl groups) are selenophenes(3). The anion can be ClO_4^-, BF_4^-, PF_6^-, I^- or Br^- and the electrochemical cell consists of an electrolyte solution with an anode covered by a layer of the doped polymeric material and a counter electrode. The anode was a sheet of Pt and the cathode was a Pt wire. The electrical conductivity of the polymer containing BF_4^- is $10^{-3}\,\Omega^{-1}cm^{-1}$.



(3)

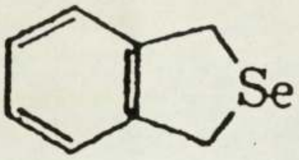
Generally, organoselenium and tellurium compounds possess many unique and desirable qualities. They possess low ionization potentials[125] and their highest occupied molecular orbitals (HOMO) are very polarizable [126].

On reconsidering the appearance potentials of different tellurides and 1,3-dihydro-2-telluraindene(4) in particular, the low value for (4) has led McWhinnie et al[85] to suggest the ionisation from p-π-molecular orbitals. It was assumed that, the appearance potential (6.55eV) for(4) would allow the compound to be oxidised electrochemically in solution to its radical cation[85]. It was therefore tempting to investigate the electrochemical oxidation of 1,3-dihydro-2-telluraindene(4).



(4)

It is interesting to continue these investigations in order to explore this area of research. Also because of the structure similarity between 1,3-dihydro-2-selenaindene(5) and (4), it has been realized that it is very useful to study its electrochemical oxidation and its appearance potential.



(5)

4.2 Ionisation Potential Measurement

The mass spectrometer is often used for the measurement of the appearance potentials of ions produced by bombardment of gaseous molecules.

The definition of the first ionisation potential of a neutral molecule is the minimum energy required to remove an electron from the highest occupied molecular orbital, both the original molecule and the resultant molecular ion being in their ground vibrational states. This energy is the difference between the $\nu=0$ and $\nu'=0$ vibrational levels and is termed the ionisation potential.

The minimum energy required to fragment an ion in its ground vibrational state from the original molecule in its ground vibrational state is referred to as the appearance potential of that ion.

Many methods have previously been used for these determinations[127-129].
The Warren's extrapolated voltage difference method[129] was applied for the measurement of the appearance potential.

4.3 Extrapolated Voltage Difference Method[129]

A standard gas, such as argon, for which an accurate value of the appearance potential is known, is incorporated with the sample. The ionisation efficiency curves are plotted for both the sample and calibrant ions. The voltage differences ΔV are measured for a series of low values of ion current, and ΔV is plotted against the ion current.

The curve obtained is then extrapolated back to zero ion current to get the value of ΔV_o, which is taken as the difference between the ionisation potential of the sample and the calibrant.

4.4 Determination of Ionisation Potential

The extrapolated voltage difference method[129] has been employed for the measurement of the appearance potentials of the molecular ions by electron bombardment of gaseous molecules.
An example of this method is given on pages(104,105 and 106).

The ionisation efficiency data for 1,3-dihydro-2-selenaindene(5) were given in Table 4.1. The mass spectroscopic measurements showed considerably lowered appearance potentials for 1,3-dihydro-2-selenaindene (7.4 eV). This value is significantly higher than the value of the tellurium analogue (6.55 eV) given by Singh [86] (the lowest value known for an organotellurium compound) which assumed the low value is indicating removal of an electron from a π (p) orbital[130].

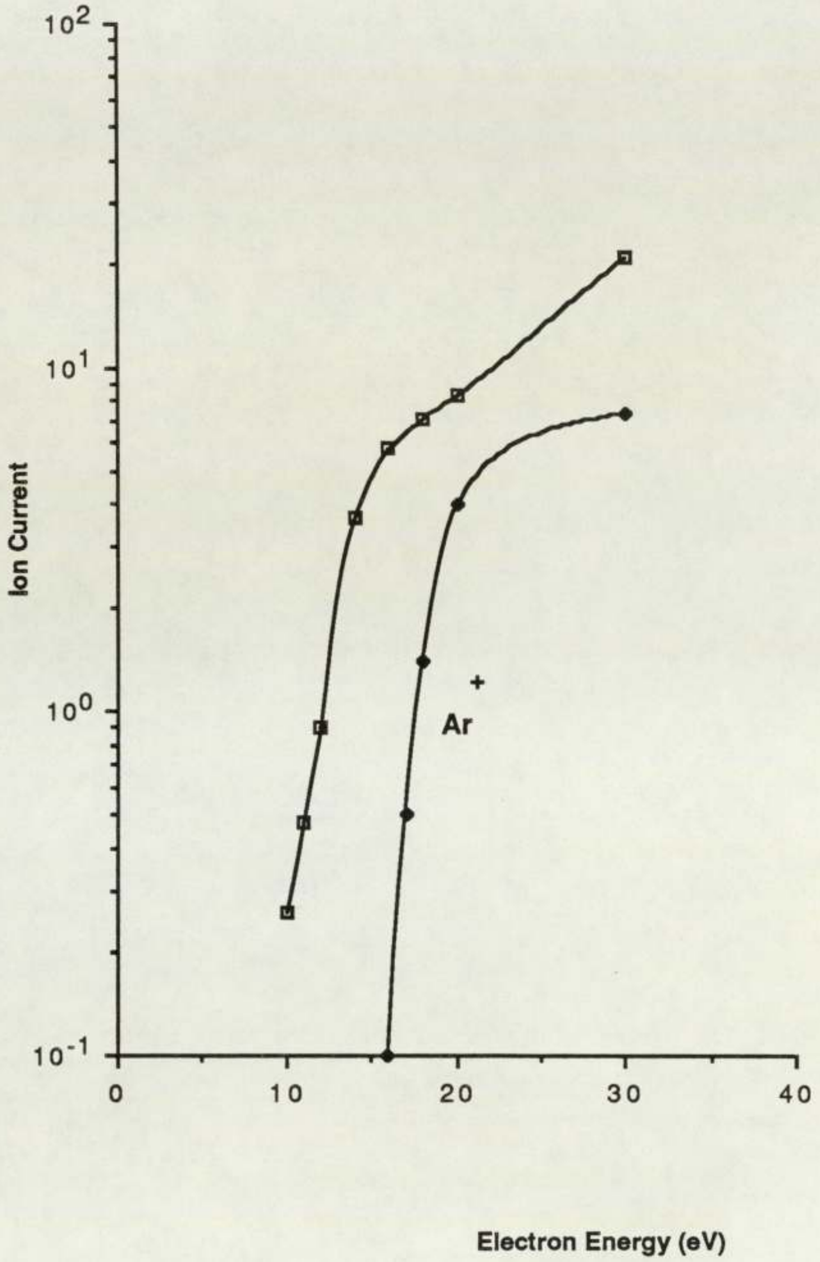
For the complex of 1,3-dihydro-2-telluraindene-TCNQ, it has been suggested, that this complex may undergo ionisation more easily in the solid state than other tellurium complexes because of its low I.P. value.

McConnell et al[131], confirmed that the slight change in the ionisation potential of the donor or in the electron affinity of the acceptor might sharply discriminate an ionic state from a nonionic state in solid charge transfer complexes.

Electron energy (eV)	% Ion current	
	$C_8H_8Se^+$	Ar^+
30	21	7.4
20	8.3	4.0
18	7.1	1.4
17	-	0.5
16	5.8	0.1
14	3.7	-
12	0.91	-
11	0.48	-
10	0.26	-

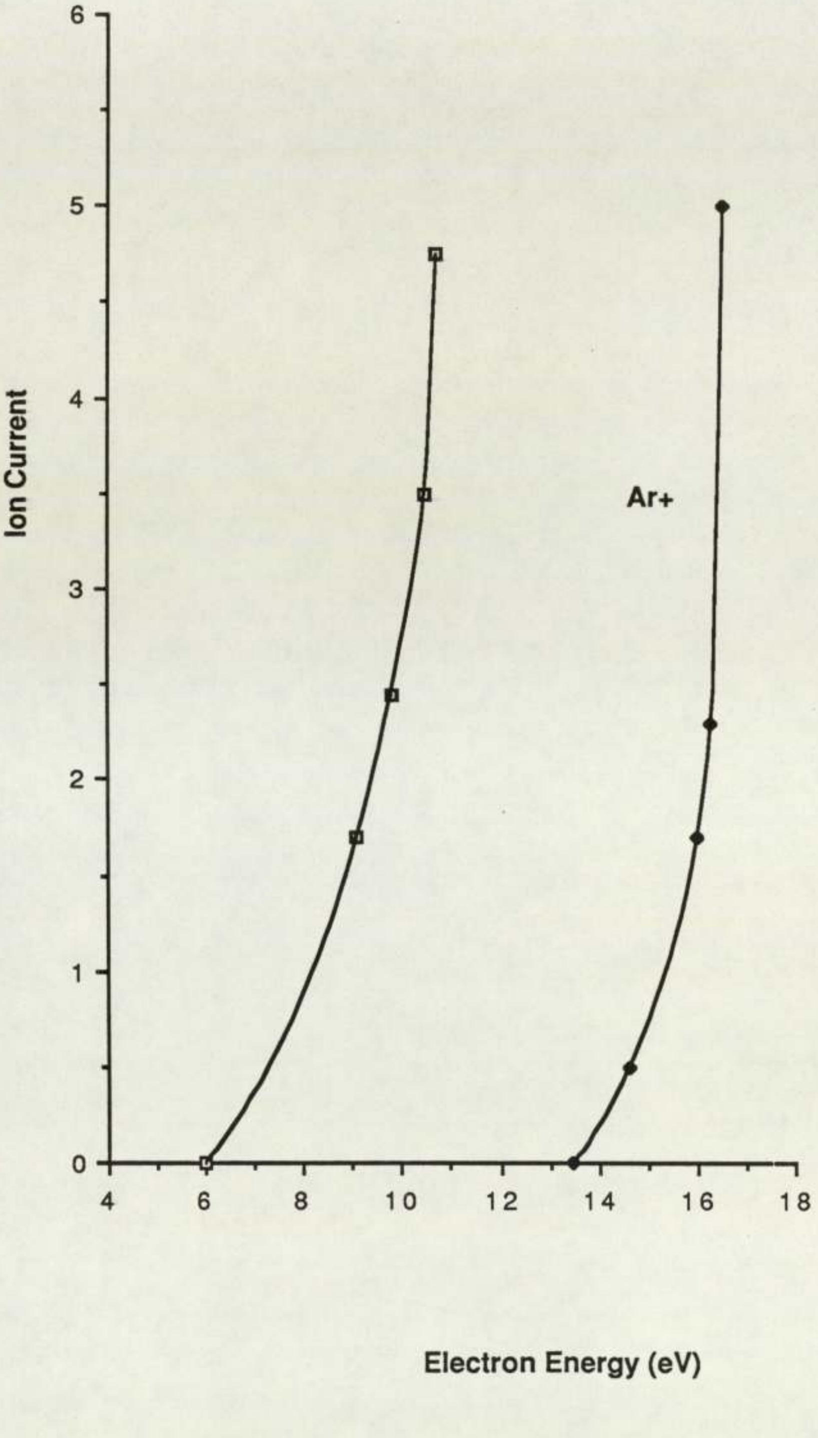
Table 4.1 Ionisation efficiency data for 1,3-dihydro-2-selenaindene(5)

In general, the easy removal of one electron from 1,3-dihydro-2-selenaindene(5) compound and its low I.P. value relatively gives an allowance to employ it in the charge transfer reactions as it was shown in the previous Chapter and to propose that C_8H_8Se(5) with TCNQ is probably ionic in the ground state i.e. $(C_8H_8Se)^{\cdot +}(TCNQ)^{\cdot -}$. Also to use it in preparing a range of new salts $(C_8H_8Se)^+X^-$ by electrochemical method.



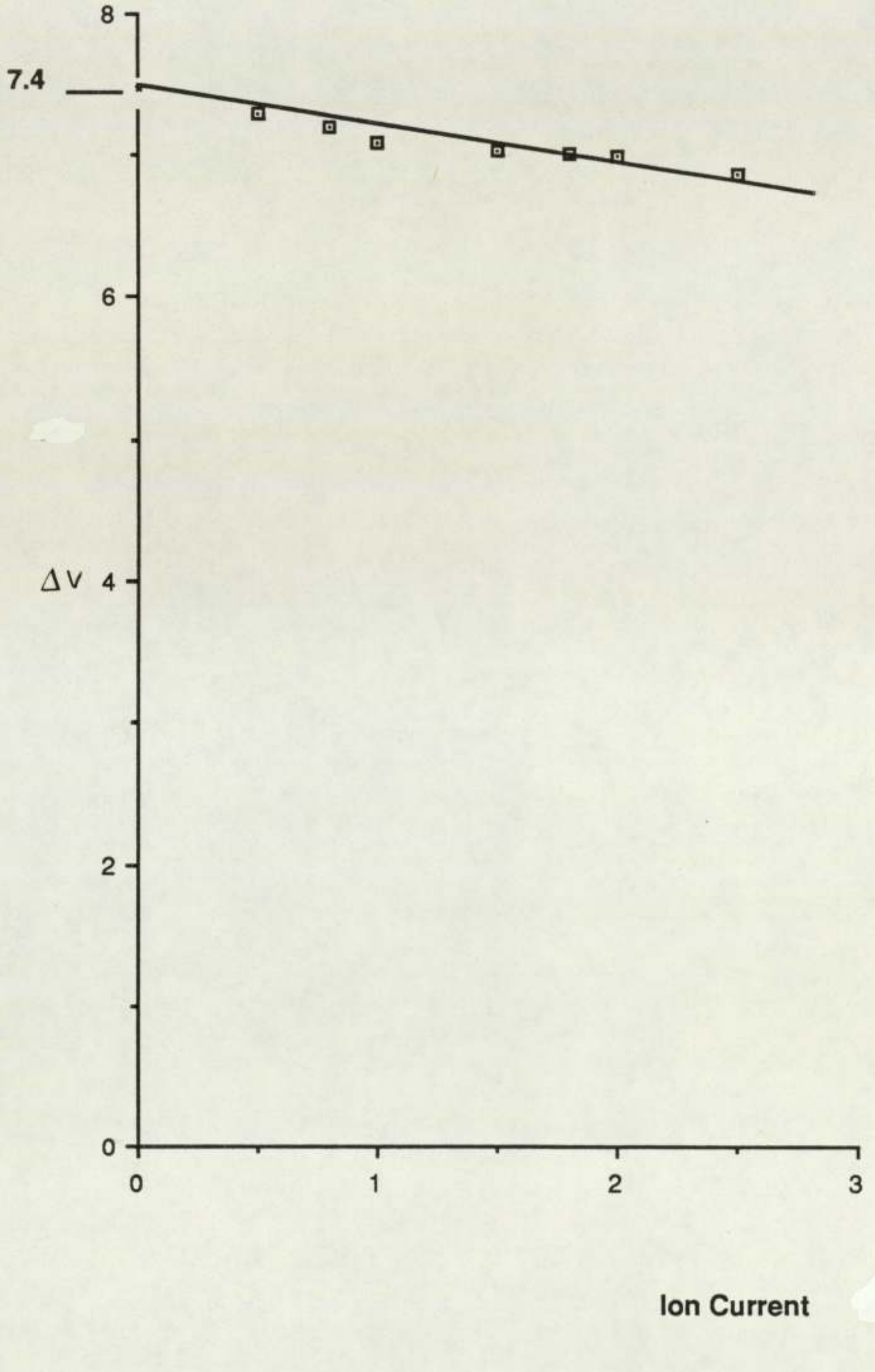
Graph of Ion Current aginst Electron Energy for

1,3-dihydro-2-selenaindene ---> (1,3-dihydro-2-selenaindene)+.



Graph of Ion Current against Electron Energy for

1,3-dihydro-2-selenaindene ---> (1,3-dihydro-2-selenaindene)+.



Graph of Ion Current against Voltage Difference (ΔV)

for 1,3-dihydro-2-selenaindene ---> (1,3-dihydro-2-selenaindene)+.

4.5 Electrochemistry Sample Preparation

Recrystallised 1,3-dihydro-2-selenaindene(5) (10 m mole) in pure dichloromethane (200 cm^3) was treated with an appropriate supporting electrolyte (20 m mole).

In successive experiments, choice of electrolyte was tetra-n-butylammonium hexafluorophosphate, tetrafluoroborate and perchlorate.

The solution was electrolysed between two platinum electrodes with a spacing of 1 cm and a constant current of 2 mA. Shiny crystals of the desired product started depositing on anode in a few minutes. The poor yield has led us to build up another system.

A cyclic platinum gauze anode with an area of 31 cm^3 and sintered platinum cathode rod were used for this purpose (Figure 4.1),

Although, the yield was improved but still not enough to do different physical measurements.

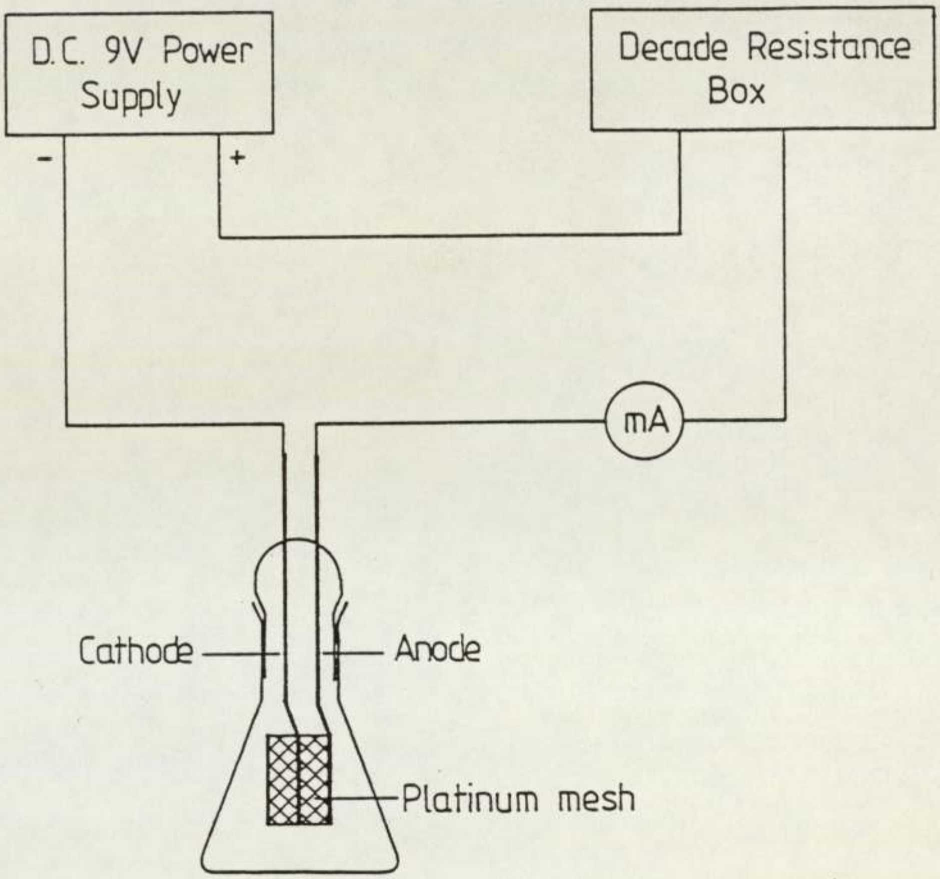


Figure 4.1. The electrochemistry cell.

4.6 Discussion

The three salts of the formula $[C_8H_8Se]^+[X]^-_{n(1-2)}$ where X is PF_6^-, BF_4^- and ClO_4^-, have been prepared and characterised. All the salts are brightly coloured.

The elemental analysis of the hexafluorophosphate salt gave a 1:1 cation to anion ratio while the cation to anion ratio for the tetrafluoroborate salt was 1:2. The perchlorate derivative exploded on heating.

Analytical, i.r. and molar conductivities data are given in Tables 4.2, 4.3 and 4.4 respectively. The three salts are stable for a long period of time. The formal oxidation state of the selenium in these salts is (III) which is not very common.

4.7 Infra-red Spectra

Several investigators have examined in detail the vibrational spectra of the simple hexafluorophosphate salts[132]. The infra-red and Raman data have clearly been interpreted in terms of octahedral symmetry for the anion. The coordination of one fluorine atom (from PF_6^- ion) to a metal, lowers the local symmetry to C_{4v} which, in turn, leads to resolution of some degeneracies and to alteration of the selection rules.

Compound	M.P.°C	Colour	C % (calc)	H % (calc)
$[C_8H_8Se]^+PF_6^-$	125	yellowish black	29.2 (29.2)	2.50 (2.43)
$[C_8H_8Se]^+BF_4^-HBF_4$	137(d)	black	26.55 (26.81)	2.48 (2.51)
$[C_8H_8Se]^+ClO_4^-$	-	black	-	-

Table 4.2 Analytical data

$[C_8H_8Se]^+PF_6^-$	$[C_8H_8Se]^+BF_4^-.HBF_4$	$[C_8H_8Se]^+ClO_4^-$	
1088 w	1090	1148	
875 v.w	1060	1116	ν_3, X^-
848 v.s	1035	1095	
828 sh		1034 sh	
570 s	540	642	
	528	631 s	ν_4, X^-
2942 w	2942 w	2941 w	$\nu(CH_2)$

Table 4.3 I.R. data/cm $^{-1}$

(N.B. compound (5) gives $\nu(CH_2)$ at 2922 cm^{-1}).

Compound	Molar Conductivity (Ω^{-1} cm^2 mol^{-1})
$[C_8H_8Se]^+PF_6^-$	117
$[C_8H_8Se]^+BF_4^-.HBF_4$	93
$[C_8H_8Se]\ ClO_4$	87.5

Table 4.4 Molar conductivity data

(10^{-3} M in acetonitrile solution)

It has been pointed out that an octahedral molecule or ion MF_6^-, should have two ν_3 and ν_4 infra-red active vibrations. The higher frequency is due to ν_3 vibration and the lower to the vibration ν_4 [133].

From (Table 4.3), the position of ν_3 and ν_4 in $[(C_8H_8Se)^+ PF_6^-]$ have been assigned to 848 cm^{-1} and 570 cm^{-1} respectively. The single and sharp ν_4 makes it unlikely that the splitting of ν_3 reflects cation-anion interaction. Similar observations have been noticed for the tellurium cation anologue salt[85].

Cote and Thompson[134], investigated the i.r. of simple tetrafluoroborates using sublimed films and paraffin mulls at room temperature and revealed that the strong broad ν_3 band had two maxima and two shoulders between 1100 cm^{-1} and 1000 cm^{-1} and a doublet at 521 cm^{-1} and 534 cm^{-1} assigned as ν_4. The complex structure of the fundamental ν_3 and ν_4 was discussed in terms of the isotopic species boron 10 and 11.

The splitting of ν_3 and ν_4 bands of $(CH_3)_3SnBF_4$ in the infra-red spectrum has been reported by Clark and O'Brien [135].

The ν_3 band of tetrafluoroborate derivative of 1,3-dihydro-2-selenaindene(5) $[C_8H_8Se]^+BF_4^-.HBF_4$ is observed as a broad and strong band between 1090 cm^{-1} and 1035 cm^{-1}

(Table 4.3), indicating an environment similar to the simple tetrafluoroborates[134] and very close to the tellurium analogue salt[85].

In the perchlorate derivative $[C_8H_8Se]^+ClO_4^-$, both ν_3 and ν_4 are different from those expected for an ionic perchlorate salt. Instead, a splitting of the ν_4 and ν_3 bands is noted. The clean split of ν_3 and ν_4 could imply a weak cation-anion interaction.

The well resolved splitting is interpreted in terms of lower symmetry for the perchlorate group. which is in a good agreement with McWhinnie et al observations for a telluronium salt of 1,3-dihydro-2-telluraindene(4)[136].

The lower symmetry of the perchlorate derivative of the tellurium analogue(4) was interpreted in terms of interaction of the anion and cation via Te-O bonding to give a dimer type[86].

It is most probably that same case was happened in the selenium compound (5) and the dimerization was carried out via Se-O bonding (Figure 4.2)

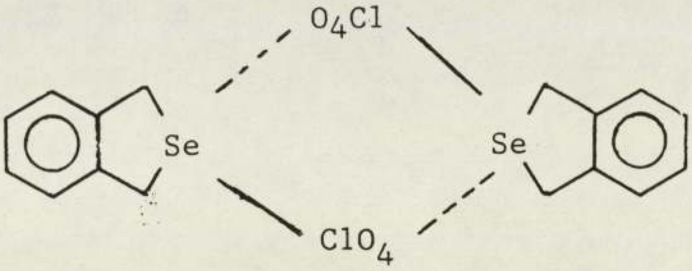


Figure 4.2

4.8 Conductivity Measurements

The molar conductivities data of the three salts are given in (Table 4.4). The molar conductivity of each salt was determined in acetonitrile solution. The values of the molar conductivity indicate that it is of 1:1 electrolyte for the PF_6 salt while it is less than this ratio for the others, specially for the perchlorate compound. Therefore, a possible explanation is that these compounds show ion pairing in solution, perhaps forms dimers such as those in (Figure 4.2). This could be a good confirmation to the argument of the i.r interpretation of the perchlorate salt which is that there was a dimerization via Se-O bonding. The low yield of these salts was not enough to do solid state conductivity despite of the encouraging molar conductivity results.

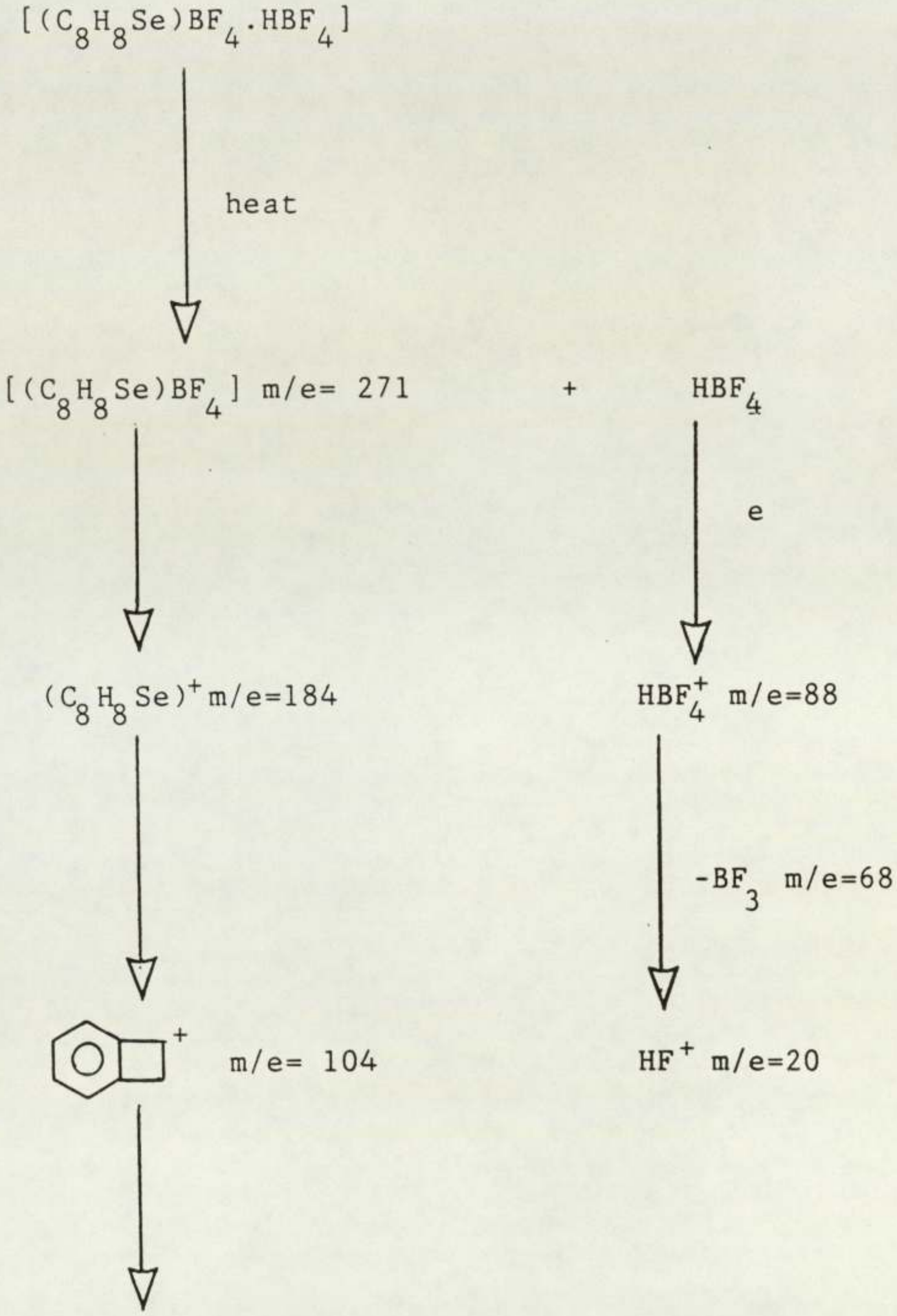
4.9 Electron Spin Resonance Spectra

Non of the compounds gave an ESR signal. this may be a consequence of large spin orbit coupling constant (λ_{Se}= 0.22 eV) leading to increased line width[114]. Similar result was obtained with the tellurium analogue (4) salts [85].

4.10 Mass Spectra

The mass spectra of the three salts shows $(C_8H_8Se)^+$ as the ion of greatest m/e= 184.

The tetrafluoroborate salt $[C_8H_8Se]^+BF_4^-.HBF_4$ did not show the peak for the molecular ion. The major peaks at m/e = 68, 67 correspond to the isotropic mass of BF_3. In addition a peak at m/e =20 could be similarly attributed to HF, which has been reported for the tellurium analogue[85] thus providing support for the proposal that HBF_4 may crystallise with the tetrafluoroborate salt and also helping to explain the broad infra-red spectrum.



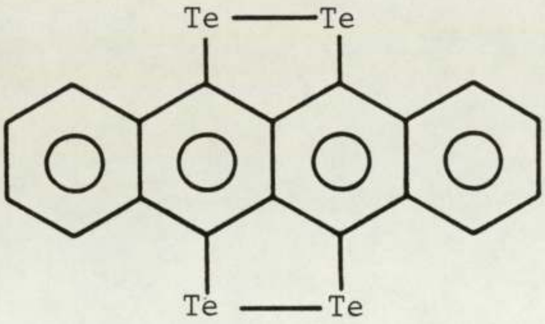
Scheme 4.1. Mass spectrum of $(C_8H_8Se)BF_4.HBF_4$.

CHAPTER FIVE

NEW ORGANOTELLURIUM AND -SELENIUM COMPOUNDS

5.1 Introduction

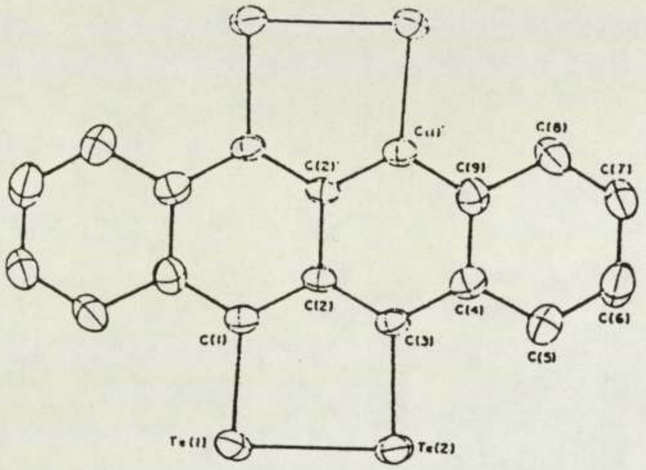
Structural studies on the compound tetratelluratetracene (TTeT) shows linear chain structure and very short Te..Te contacts[137], (Figure 5.1). The intermolecular Te-Te distance (3.707°A] is the lowest observed for any organotellurium compound.



(TTeT)

Also it has been found that there is a short intermolecular Se....Se contact for a series of $(TMTSF)_2X$ [47].

Many organotellurium compounds have revealed intermolecular bonding effects of various types and strengths. In organotellurium diiodides [72,77,138-141] interactions of the type Te....I or I....I have been shown to be very prounounced whereas in corresponding bromides either a very weak effect[142] or complete absence[71a] of such effects has been reported. Similar pronounced interactions between Te and chlorine have been



Tetratelluratetracene (T Te T)

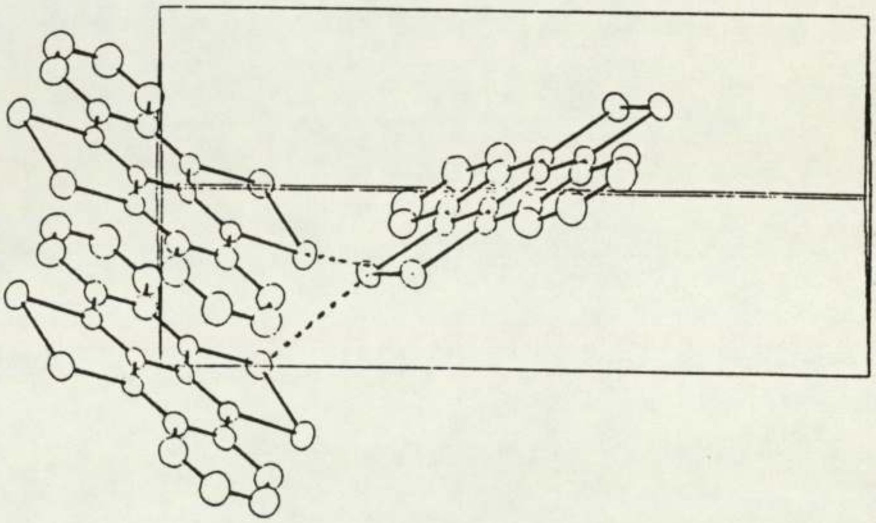
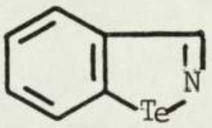


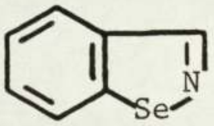
Figure 5.1. Partial packing diagram of (T Te T), showing individual molecules stacked along the b direction.

described in p-methoxy-phenyltellurium trihalides[143]. Apart from halogens, only N has been found to have short intermolecular contacts. Anomalous physical properties such as high melting point and low solubility of 1,2-benzoisotellurazole (I) were explained by very short intermolecular Te----N bonds (2.4°A)[144].

Such bonds were not presented in the crystal structure of 1,2-benzoisoselenazole (II) and the physical properties were those expected.



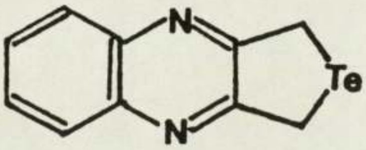
(I)

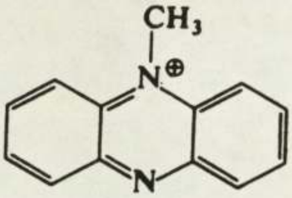


(II)

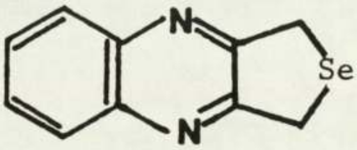
3,4-Quinoxalino-1-telluracyclopentane (III) has been synthesised[86], in order to investigate the strength of Te...N intermolecular contacts in such heterocyclic system.

The charge-transfer of compound (III) with TCNQ has been studied since it has similar structure to N-methylphenazinium (IV) ion whose C.T complex with TCNQ is known to have highest conductivity for an organic compound[30].


(III)


(IV)

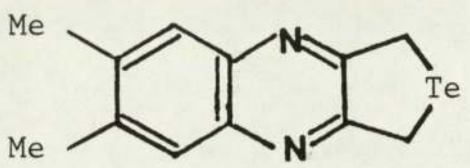
In the present study, the selenium analogue of (III) has been prepared, namely 3,4-quinoxalino-1-selenacyclopentane (V), using the same method of preparation[86], in order to explore its charge-transfer with TCNQ and compare this with the Te analogue compound (III).


(V)

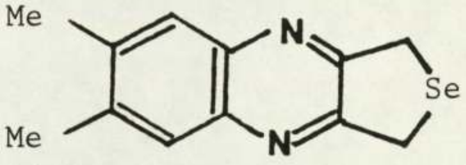
Generally, organic π-molecular donors and acceptors have been found to form a wide variety of charge-transfer salts, with a wide variety of physical properties. Historically interest has been sharply focussed on those few which have a high d.c. electrical conductivity at room temperature and on how to design new organic metals.

It should be mentioned that alkylation for example does not always have to decrease electronic overlap between donor and acceptor. More success has been achieved using weakly donating alkyl substituents (TMTTF, HMTTF..etc.) [145].

For such a purpose, 7,8-dimethyl-3-4-quinoxalino-1-tellura (VI) and selenacyclopentane (VII) have been prepared, using the same method of preparation.



(VI)



(VII)

5.2 Experimental

7,8-dimethyl-2,3-bis(bromomethyl)quinoxaline

To a warm solution of (0.48 g, 0.2 m mol) 1,4-dibromo-2,3-butanedione in (20 cm^3) benzene, was added a solution of (0.27 g, 0.2 m mol) 4,5-dimethyl-o-phenylenediamine in (20 cm^3) benzene. After refluxing the mixture for 40 minutes, it was allowed to cool. On filteration and recrystallization from ethanol, shiny white crystals of 7,8-dimethyl-2,3-bis(bromomethyl)quinoxaline were obtained, yield 75%, m.p. (149-151°C).

Found C = 41.8, H = 3.50, N = 8.5; $C_{12}H_{12}N_2Br_2$
requires C = 41.8, H = 3.48, N = 8.1

1,1-diiodo-7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane

A mixture of 7,8-dimethyl-2,3-bis(bromomethyl)quinoxaline (0.86 g, 5 m mol), sodium iodide (1.5 g, 20 m mol), and powdered selenium (0.2 g, 5m mol) in 2-methoxyethanol (50 cm^3) was stirred and heated to gentle reflux for two hours. After cooling the reaction mixture, deionized water (100 cm^3) was added to cause additional precipitation.

The precipitate was filtered off, washed with water and dried. The crude material was recrystallized from 2-methoxyethanol to give a deep violet crystalline solid, yield 54%, m.p. (168-169°C).

Found $C = 28.2$, $H = 2.0$, $N = 4.9$; $C_{12}H_{12}N_2SeI_2$
requires $C = 27.8$, $H = 2.3$, $N = 5.4$

7,8-dimethyl-1,1-diiodo-3,4-quinoxalino-1-selenacyclopentane 7,8-dimethyl-2,3-bis(iodomethyl)quinoxaline (1 : 1) complex.

In a repeat experiment, 7,8-dimethyl-2,3-bis(bromomethyl)quinoxaline (0.57 g, 10 m mol), powdered selenium (0.13 g, 10 m mol) and potassium iodide (1.08 g, 39 m mol) were stirred and heated gently in 2-ethoxyethanol) for one hour. After the reaction period, deionized water (200 cm^3) was added to the mixture. The yellow precipitate formed was filtered and air dried. The crude material was dissolved in hot acetone, filtered to remove any unreacted selenium and the filtrate was set aside to crystallise slowly. The resulting complex yield 70% had m.p. 163-164°C. Reduction of this complex with hydrazine hydrate affords a pale yellow compound m.p. (85°dec.), which readily decomposes with the elimination of selenium.

Found C = 33.5, H = 2.7, N = 6.1; $C_{24}H_{24}N_4SeI_4$
requires C = 33.5, H = 2.7, N = 6.4.

7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane(VII)

To a suspension of violet 7,8-dimethyl-1,1-diiodo-3,4-quinoxalino-1-selenacyclopentane (1.2 g) in ethanol (75 cm^3) and water (15 cm^3) was added dropwise a solution of hydrazine hydrate (0.45 g) in ethanol (15 cm^3). The resulting solution was warmed gently untill all the violet crystals of the diiodide dissolved, then the mixture was poured into water (200 cm^3) and extracted into ether. The etheral layer was separated, dried over anhydrous Na_2SO_4 and removed on a rotary evaporator. On treatment of the resulting yellow powder with charcoal and ether, yellow needles were obtained, yield 61%, m.p. 169-171°C.

Found C = 54.2, H = 4.5, N = 10.1; $C_{12}H_{12}N_2Se$
requires C = 54.8, H = 4.6, N = 10.6.

Attempted direct synthesis of 7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane.

7,8-dimethyl-2,3-bis(bromomethyl)quinoxaline (1.88 g, 6 m mol) was mixed with selenium powder (0.47 g, 6 m mol) and sodium borohydride (1.2 g, 32 m mol) in ethanol. The mixture was stirred and heated for 12 hours under dinitrogen. The initial green colour changed to red in 45 minutes. Then the mixture was poured into water (500 cm^3) when a yellow precipitate appeared. The colourless material was extracted into ether from which solution colourless needles were obtained, m. p. 109-111°C.

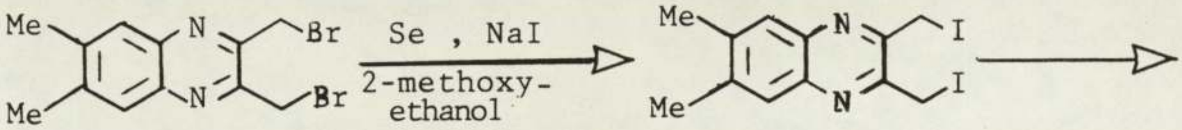
Complex of 7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane with TCNQ (1 :1)

To a solution of 7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane (0.26 g, 1 m mol) in acetonitrile (20 cm^3) was added to a solution of TCNQ (0.2 g, 1m mol) in acetonitrile (30 cm^3). The resulting solution was stirred under reflux for one hour, after which the volume of the solution was reduced to 10 cm^3 and the residue was left to crystallize. Black crystals, yield 85%, m.p. 144-146°C were obtained.

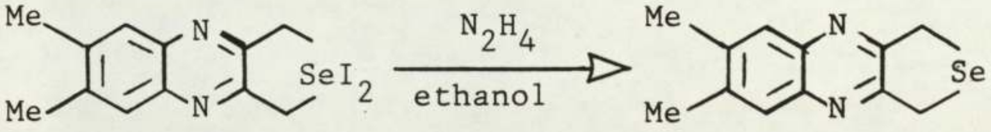
Found C = 62.2, H = 3.5, N = 18.8; $C_{24}H_{16}N_6Se$
requires C = 61.7, H = 3.4, N = 18.0.

5.3 Results and Discussion

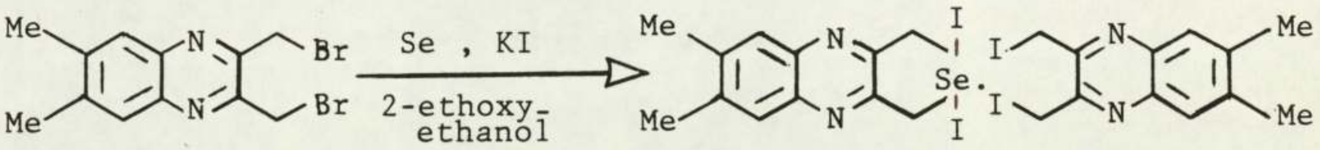
The preparative, analytical, I.R., U.V. and N.M.R. data for 3,4-quinoxalino-1-selenacyclopentane(3), are combined in Tables 5.1, 5.2 and 5.3. For 7,8-dimethyl-3,4-quinoxa-lino-1-telluracyclopentane(8) are combined in Tables 5.4, 5.5 and 5.6, also for 7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane (12) are gathered in Tables 5.7, 5.8 and 5.9. The reaction of 2,3-bis(bromomethyl)quinoxaline with powdered selenium and sodium iodide gives a violet coloured compound(I). Also the reaction of 7,8-dimethyl-2,3-bis(bromomethyl)quinoxaline with powdered tellurium or selenium and sodium iodide gives violet coloured compounds (6 and 10). The results were explained on the basis of elemental analysis and ^{1}H NMR data. The suggested[86] sequence of reactions are as follows:-


Me
Me
N
N
Br
Br
Se , NaI
2-methoxy-ethanol
Me
Me
N
N
I
I

(5)


Me
Me
N
N
SeI_2
N_2H_4
ethanol
Me
Me
N
N
Se

(10) (12)


Me
Me
N
N
Br
Br
Se , KI
2-ethoxy-ethanol
Me
Me
N
N
I
Se
I
I
I
N
N
Me
Me

(5) (11)

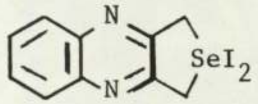
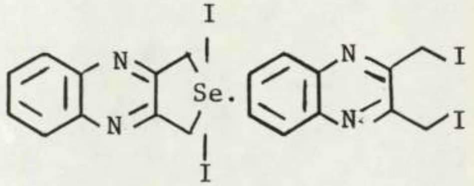
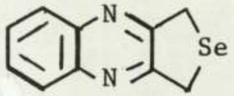
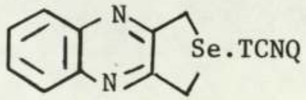
Compound	Colour	M. Point °C	Yield %	I.R. cm^{-1}
 (1)	deep violet	138 - 140	61	ν(Se-C) 504
 (2)	Yellow	145 - 147	80	ν(Se-C) 506
 (3)	pale yellow	148 - 150	62	ν(Se-C) 508
 (4)	black	135 - 136	80	ν(C≡N) 2132, 2158, 2196 ν(Se-C) 512

Table 5.1 Melting points, Yields and Infra-red data.

Compound No.	C % (calcd)	H % (calcd)	N % (calcd)
(1)	24.8 (24.5)	1.7 (1.6)	5.4 (5.7)
(2)	29.8 (29.8)	1.85 (1.90)	7.0 (6.9)
(3)	50.4 (51.0)	3.3 (3.4)	11.4 (11.9)
(4)	59.7 (60.2)	2.5 (2.7)	18.2 (19.1)

Table 5.2 Analytical data

Compound No.	U.V. maxima (CH_2Cl_2) nm	^{1}H NMR J-Hz	(δ ppm vs TMS) ($CDCl_3$)
(1)	247,270,330	4.82 7.7-8.4	(CH_2, S, 4H) (aromatic, m, 4H)
(2)	244,253,335	4.82 7.65-8.15	(CH_2-Se, S, 4H) (aromatic, m, 4H)
(3)	241,318	4.74 7.2-8.1	(CH_2, S, 4H) (aromatic, m,4H)
(4)	236,321 398(TCNQ+$TCNQ^{\overline{\cdot}}$)		———

Table 5.3 Physico - chemical data.

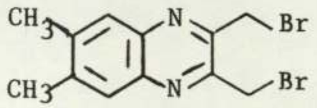
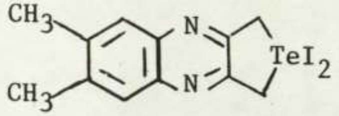
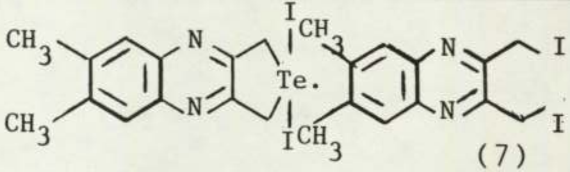
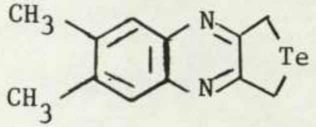
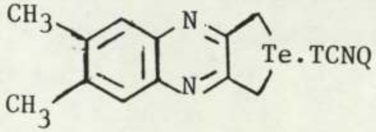
Compound	Colour	M. Point °C	Yield %	I.R. cm^{-1}
 (5)	white	149 - 151	75	$(-CH_3)$ 1365 (C-Br) 500-700
 (6)	deep violet	169-171	53	(Te-C) 508
 (7)	yellow	164-165	65	(Te-C) 512
 (8)	pale yellow	167-169	60	(Te-C) 502
 (9)	black	164-166	80	(C≡N) 2132,2182 (Te-C) 504

Table 5.4 Melting points, Yields and Infra-red data.

Compound No.	C % (calcd)	H % (calcd)	N % (calcd)	Te % (calcd)
(5)	41.75 (41.80)	3.50 (3.48)	8.5 (8.1)	
(6)	25.7 (25.4)	1.6 (2.1)	4.1 (4.9)	23.1 (22.6)
(7)	28.7 (28.7)	2.3 (2.3)	5.1 (5.5)	12.6 (12.7)
(8)	45.7 (46.2)	3.7 (3.8)	8.5 (8.9)	40.1 (40.9)
(9)	56.2 (55.8)	2.8 (3.1)	15.5 (16.2)	25.7 (24.7)

Table 5.5 Analytical data

Compound No.	U.V. maxima (CH_2Cl_2) nm	^1H NMR J-Hz	(δ ppm vs TMS) ($CDCl_3$)
(5)	255,349	4.92 2.52 7.29-7.83	(CH_2, S, 4H) (CH_3, S, 6H) (aromatic, m, 2H)
(6)	243,269,331,343	4.88 2.52 7.25-7.92	(CH_2, S, 4H) (CH_3, S, 6H) (aromatic, m, 2H)
(7)	257,347,355	4.75 2.43 7.25-7.75	(CH_2-Te, S, 4H) (CH_3, S, 6H) (aromatic, m,2H)
(8)	246,257,333	4.58 2.50 7.3-7.6	(CH_2,S, 4H) (CH_3,S, 6H) (aromatic, m, 2H)
(9)	248,324,334 394(TCNQ+$TCNQ^{\overline{\cdot}}$)		———

Table 5.6 Physico - chemical data.

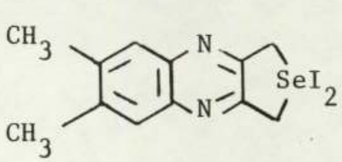
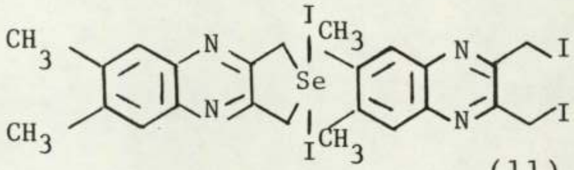
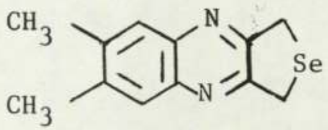
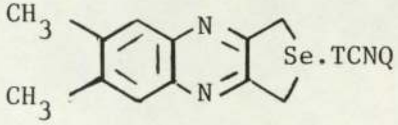
Compound	Colour	M. Point °C	Yield %	I.R. cm^{-1}
 (10)	deep violet	168-169	54	(Se-C) 504
 (11)	yellow	163-164	70	(Se-C) 500
 (12)	pale yellow	169-171	61	(Se-C) 508
 (13)	black	144-146	85	(C≡N) 2146,2188 (Se-C) 505

Table 5.7 Melting points, Yields and Infra-red data.

Compound No.	C % (calcd)	H % (calcd)	N % (calcd)
(10)	28.2 (27.8)	2.0 (2.3)	4.9 (5.4)
(11)	33.5 (33.5)	2.7 (2.7)	6.1 (6.4)
(12)	54.2 (54.75)	4.5 (4.6)	10.1 (10.6)
(13)	62.2 (61.7)	3.5 (3.4)	18.8 (18.0)

Table 5.8 Analytical data

Compound No.	U.V. maxima (CH_2Cl_2) nm	^1H NMR J-Hz	(δ ppm vs TMS) ($CDCl_3$)
(10)	251,267,348	4.8 2.57 7.3-7.79	(CH_2, S, 4H) (CH_3, S, 6H) (aromatic, m, 2H)
(11)	264,347,358	4.82 2.49 7.28-7.78	(CH_2-Se, S, 4H) (CH_3, S, 4H) (aromatic, m, 2H)
(12)	248,326,338	4.68 2.46 7.26-7.7	(CH_2-Se, S, 4H) (CH_3, S, 6H) (aromatic, m,2H)
(13)	246,324,336 398(TCNQ+$TCNQ^{\bar{\cdot}}$)		——

Table 5.9 Physico - chemical data.

5.4 Ultra-violet Spectra

In a study of the methyl derivative of thianaphthene[146], the u.v. spectrum was very similar to that of the thianaphthene. The curve showed a slight bathochromic shift and some variation in the intensity. These changes were explained as due to the hyperconjugation of the methyl group.

Similarly, the spectrum of 2-methylselenonaphthene closely resembles the spectrum of selenonaphthene. The observed maxima were at 304, 295.5, 262 and 238 nm. Also the slight bathochromic shift was observed which was due to the hyperconjugation of the methyl group. Comparing the two methyl derivatives it was considered that resemblance exists between the sulphur and selenium compounds.

The ultra-violet spectrum of 1,1-diido-7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane (10) shows bands at 251, 267 sh and 348 nm (Figure 5.2). The slight shift from 1,1-diiodo-3,4-quinoxalino-1-selenacyclopentane (1) could be also attributed to the hyperconjugation of the two methyl groups.

In an examination of solid α-$C_8H_8TeI_2$ in Nujol, two very broad bands were centered approximately at 280 and 385 nm, The β form also showed a very broad band centered approximately at 425 nm with small broad shoulders at higher frequencies.

The compound 7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane (12) shows maxima at 248, 326 and 338 nm (Figure 5.3).

In general all the compounds (Tables 5.3, 5.6 and 5.9), for the bands at 236-255 and 318-349 nm are characteristic of the quinoxaline and its dimethyl substituted nucleus. Also it should be mentioned that the bands at 270, 269 and 267sh nm must be due to the presence of Se-I and Te-I bonds in compounds (1,6 and 10).

The spectrum of complex 7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane with TCNQ (Figure 5.4) shows maxima at 246, 324, 336 nm and a broad band at 398 nm which represents the neutral molecule and radical (TCNQ+$TCNQ^{\cdot-}$) together.

This is in agreement with Zingaro's argument[114], that in all cases, the fairly broad maxima are characteristic of weak complexing systems.

Similar observations have been pointed out by Singh[86] for the Te analogue of compound (1) and its derivatives.

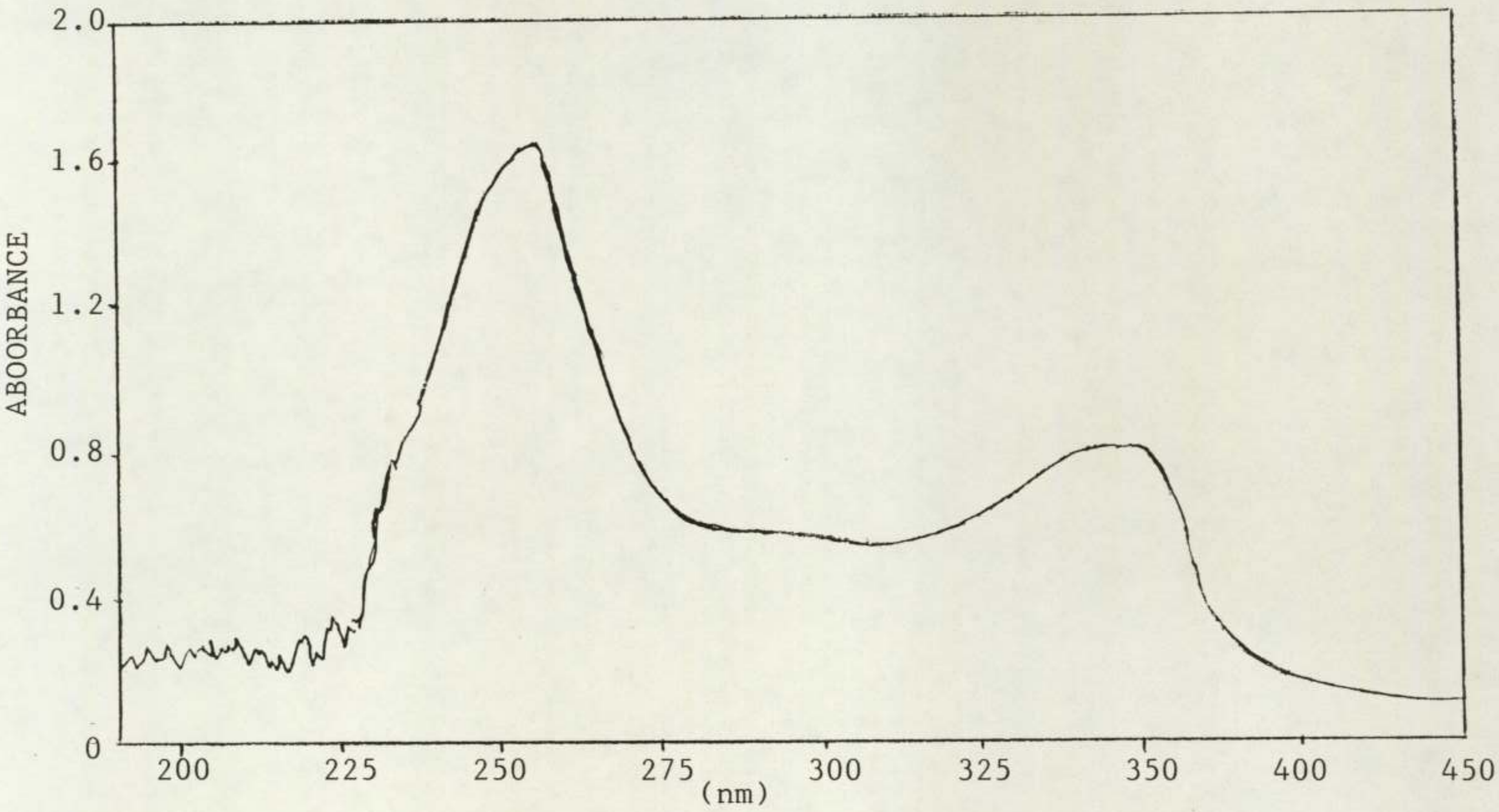


Figure 5.2 U.V. spectrum of $(CH_3)_2C_{10}H_6N_2SeI_2$.

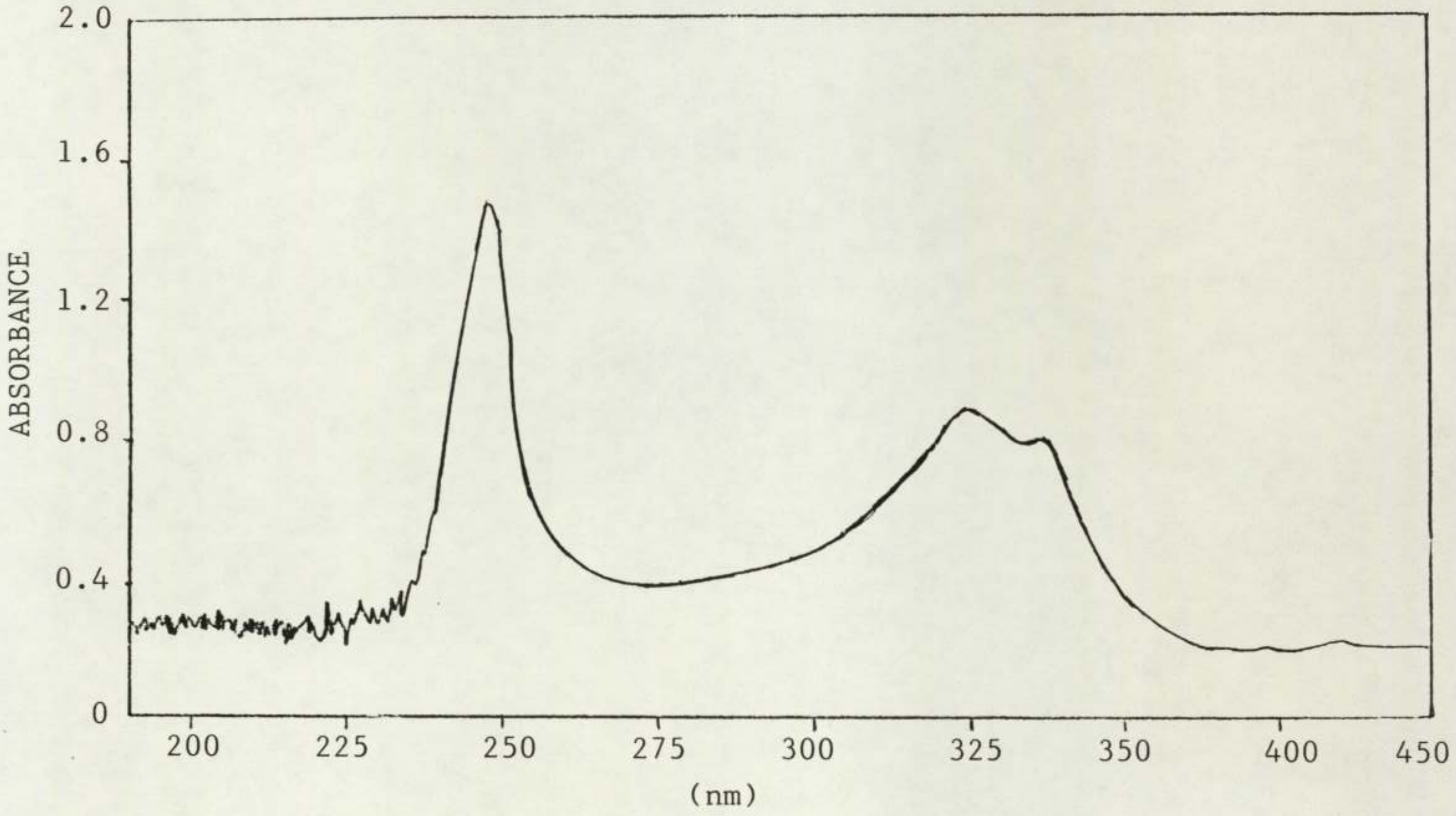


Figure 5.3 U.V. spectrum of $(CH_3)_2C_{10}H_6N_2Se$.

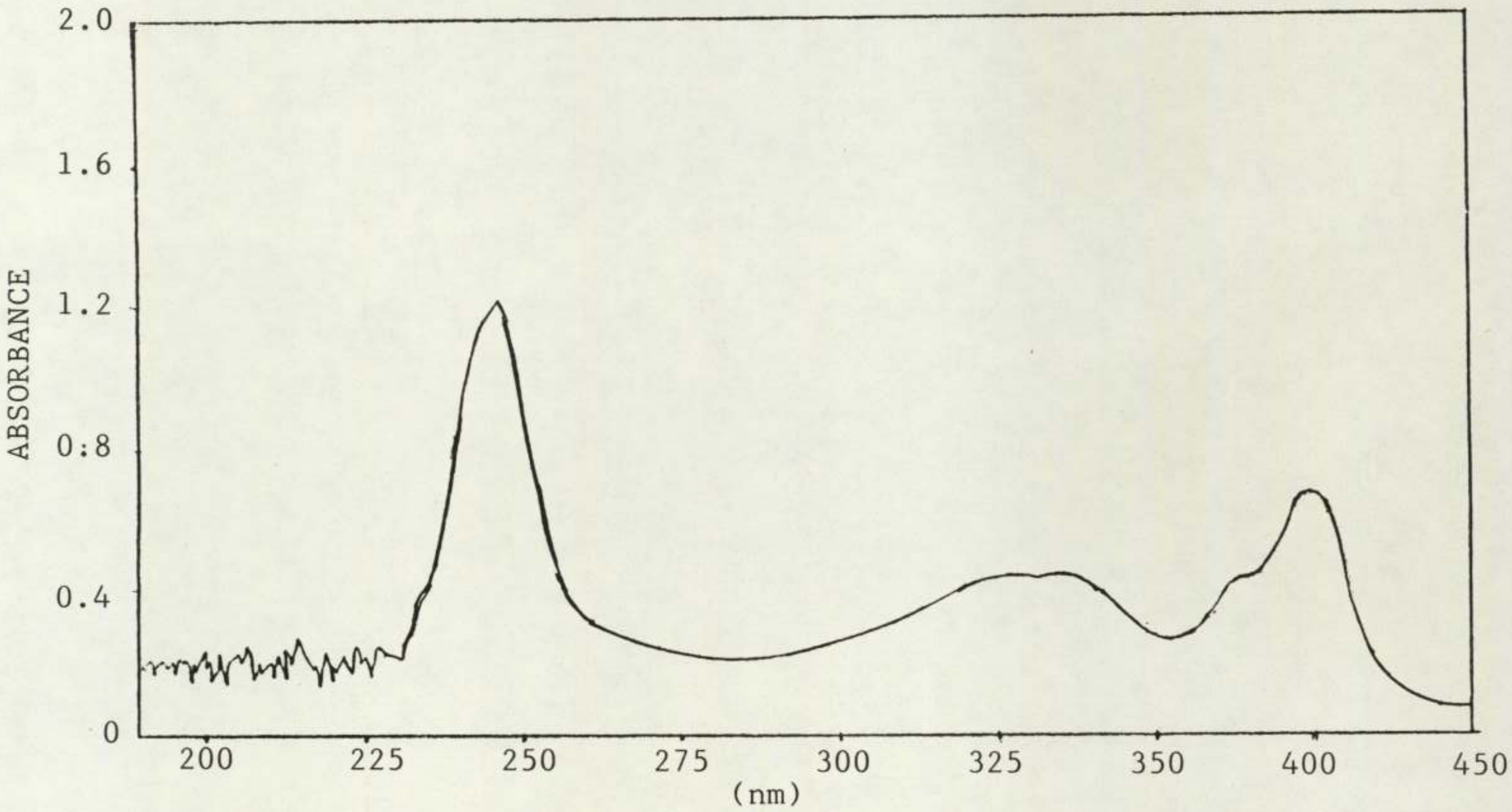


Figure 5.4 U.V. spectrum of complex $(CH_3)_2C_{10}H_6N_2Se.TCNQ$

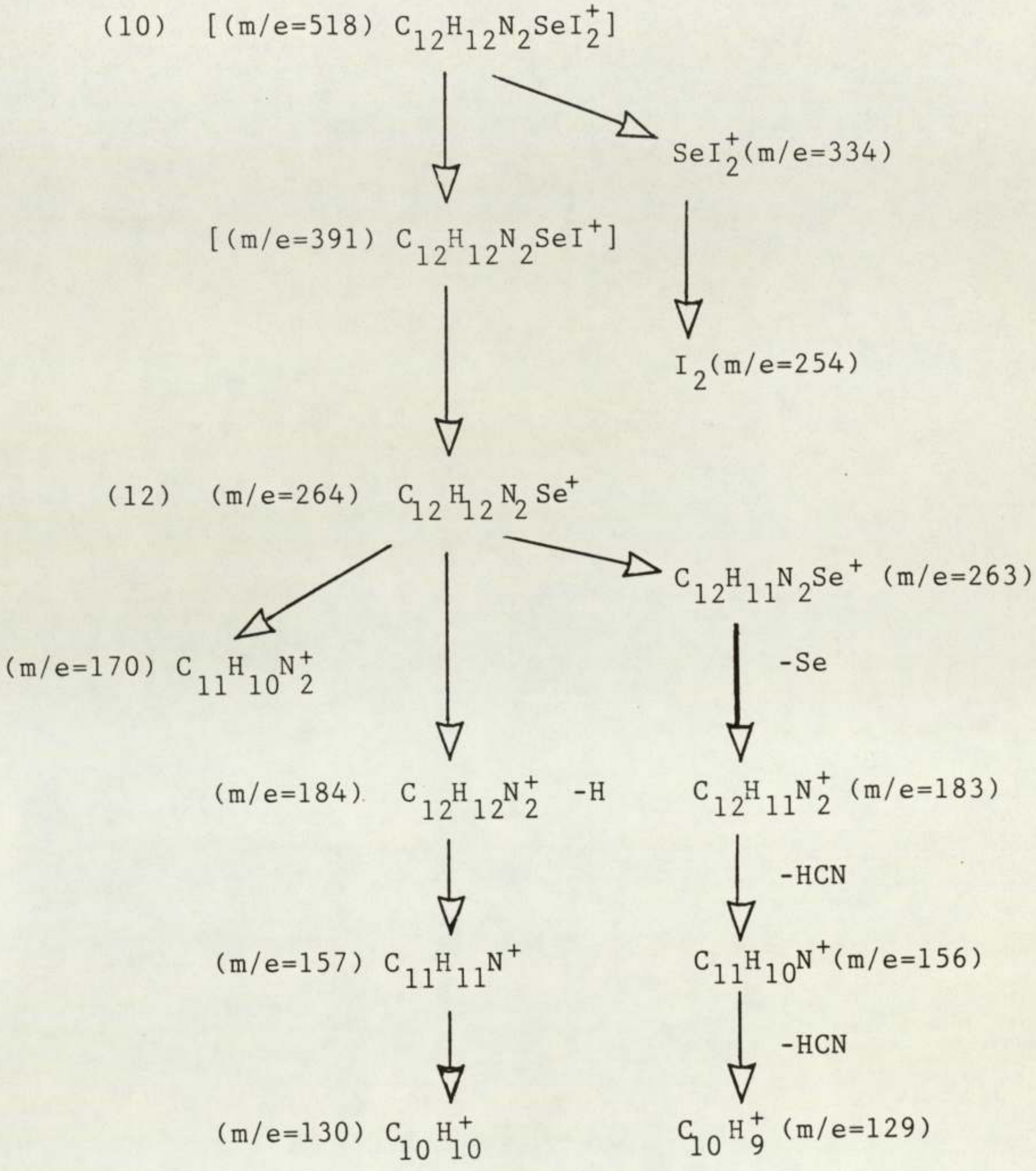
5.5 Mass Spectra

Although a great variety of organo-sulphur compounds have been studied by mass spectrometry and the results have been reviewed, comparatively few mass spectra spectra of the analogous organoselenium compounds have so far been reported.

It has been pointed out[147] that, selenium- and tellurium containing fragments are easily recognized in mass spectra from the very characteristic groups of peaks resulting from the typical distribution of natural isotopes, thus making it possible to study the fragmentation patterns involving the Se and Te atoms present in the molecule.

However, the mass spectrum of 1,1-diiodo-7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane (10) [Scheme 5.1] based on ($^{80}Se, ^{127}I$) shows no molecular ion at m/e = 518. The major fragments observed are SeI_2^+, I_2^+, $C_{12}H_{12}N_2Se^+$, $C_{12}H_{12}N_2^+$, Se^+ and I^+. Further fragmentation of $[C_{12}H_{12}N_2]^+$ proceeded by the loss of HCN to give ions $[C_{11}H_{11}N]^+$ and $[C_{11}H_{10}N]^+$ at m/e = 157 and 156.

Some other fragments were found at $[C_{10}H_8N_2]^+$ (m/e =156), $[C_8H_8N_2]^+$(m/e = 132), $[C_8H_8]^+$ (m/e = 104), and $[C_6H_2]^+$ (m/e=74).



Scheme 5.1. Mass spectra of compounds (10 and 12) based on ^{80}Se, ^{127}I, ^{12}C, ^{14}N and ^{1}H.
[species in square brackets not observed]

Generally the m/e values of the fragments are in good agreement with those of the 2,3-substituted quinoxalines[148].

Many of the proposed fragmentations are supported by the observations of metastable ions at appropriate values of m/e.

An interesting fragment at m/e = 93 may arise from the parent ion (m/e = 263) by loss of CH_2Se. However no metastable transition observed to support this suggestion.

The observation of fragments of SeI_2^+ and I_2^+ of compound (10) is very significant and similar to that of 1,3-dihydro-2-telluraindene[76] which confirms the formulation proposed of compound (10). Thus the violet colour of compound (10) is a result of strong intermolecular interactions in the solid state.

5.6 Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance (NMR) is one of the most useful techniques in the study of structural problems. The proton has previously been by far the most frequently used nucleus, and only a few n.m.r. investigations of other nuclei have been reported in the field of organoselenium and tellurium compounds.

The ^1H N.M.R. spectrum of 1,3-dihydro-2-telluraindene diiodide has been studied[76] and shows resonance at δ = 4.99 ppm (sharp singlet) and δ = 7.0-7.5 ppm (multiplet). The methylene proton signal was downfield from the methylene resonance of the starting material α, α'-dibromo-o-xylene (δ = 4.67 and 4.60 ppm respectively), consistent with the deshielding effect expected for tellurium (IV). Reduction of the same diiodide compound in ethanol with $NaBH_4$, yielded 1,3-dihydro-2-telluraindene. Hence the methylene proton resonance δ = 4.59 ppm is upfield from the diiodide compound consistent with less deshielding by tellurium (II)[76].

The ^1H N.M.R. spectrum of 2,3-bis(bromomethyl)quinoxaline [149] shows resonance at δ = 4.92 (CH_2 singlet, four protons) and δ = 7.65 - 8.17 (aromatic multiplet, four protons).

1,1-Diiodo-3,4-quinoxalina-1-selenacyclopentane(1) ^1H NMR spectrum (in $CDCl_3$) shows a singlet at 4.82 ppm ($-CH_2$,4H) and multiplet at 7.7-8.4 (aromatic, 4H) (Figure 5.5).

Here the fact that the methylene protons of compound (1) are more shielded than those in the starting material, is in accord with simple expectation from electronegativity arguments. The methylene protons reveal satellites due to coupling to the ^{77}Se (I =1/2, natural abundance 7.58) consistent with integrity of the heterocyclic structure

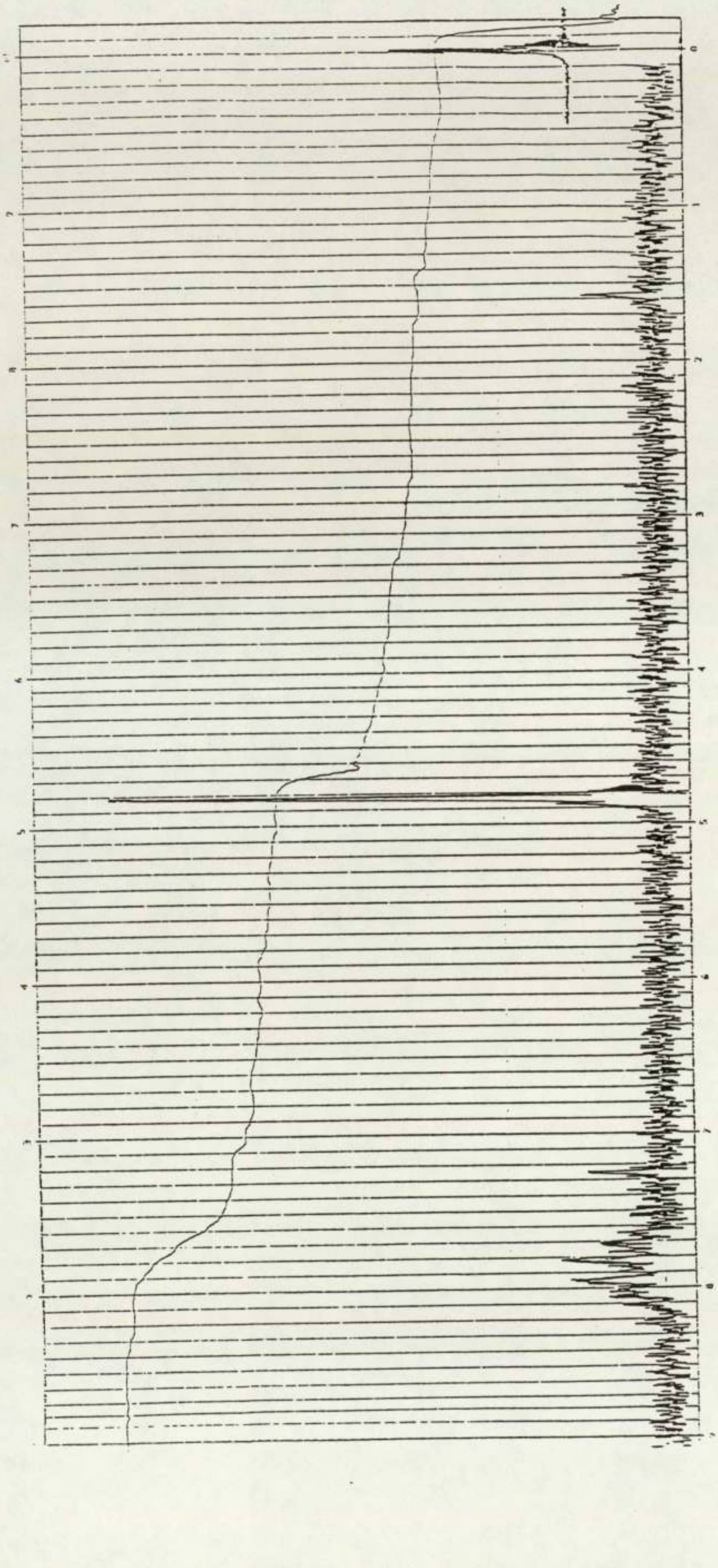


Figure 5.5. ^1H N.M.R. spectrum of $C_{10}H_8N_2SeI_2$.

in the diiodide. The reduction derivative (compound 3) displays δ = 7.2-8.1 (aromatic, 4H) and δ= 4.74 (CH_2,S, 4H) (Table 5.3). The methylene proton resonance of (3) is upfield from the diiodide compound (1) which is in accordance with less deshielding by selenium (II). The singlet at 4.74 ppm also displays two satellites due to coupling with ^{77}Se.

For the dimethyl quinoxaline compounds of tellurium and selenium (6,8,10 and 12), three sets of proton signals are available, the first is for the methyl groups, the second is for methylene groups and the third is for the aromatic protons (Tables 5.6 and 5.9),

In the last few years there has been a considerable increase in the use of Tellurium-125 and Selenium-77 nuclear magnetic resonance for the characterisation of organotellurium and selenium compounds[150-154].

A special caution needs to be given concerning the referencing of Te-125 chemical shifts. It is now generally accepted that dimethyl telluride(Me_2Te) is the zero point on the chemical shift scale. The ^{125}Te chemical shifts and $^{125}Te-^{1}H$ coupling constants for 1,3-dihydro-2-telluraindene and its dihalo oxidation products have been measured (in DMF-d7) and the electronegativity of the halo substituent[155].

Gysling[155], has pointed out that the dihalides of 1,3-dihydro-2-telluraindene display greater coupling constants than the parent compounds and fine structure due to small long-range couplings to the aromatic protons (2.3 Hz) begins to appear. The larger coupling constants observed for the Te(IV) compounds reflect the increasing s-character of tellurium bonding orbitals compared to Te(II), which used pure p-orbitals for bonding[156].

For the compound 1,1-diiodo-3,4-quinoxalino-1-telluracyclopentane, it was found[86] that the ($^{125}Te-^{1}H$) coupling was 31Hz and for 3,4-quinoxalino-1-telluracyclopentane was 23 Hz.

In an N.M.R. study of 7,8-dimethyl-1,1-diiodo-3,4-quinoxalino-1-telluracyclopentane (6), it has been found that J($^{125}Te-^{1}H$) coupling was 39Hz. Figures (5.6 and 5.7) show that ^{125}Te N.M.R. proton decoupled and the coupled spectra of compound (6). The difference in the J coupling value between 1,1-diido-3,4-quinoxalino-1-telluracyclopentane and the dimethyl substituted (6) is 8Hz. There is only one explanation for such difference in the J coupling value which it is due to the dimethyl influence on the electronic structure of compound (6).

In the dihalides of 1,3-dihydro-2-telluraindene, a correlation between halogen electronegativities and tellurium

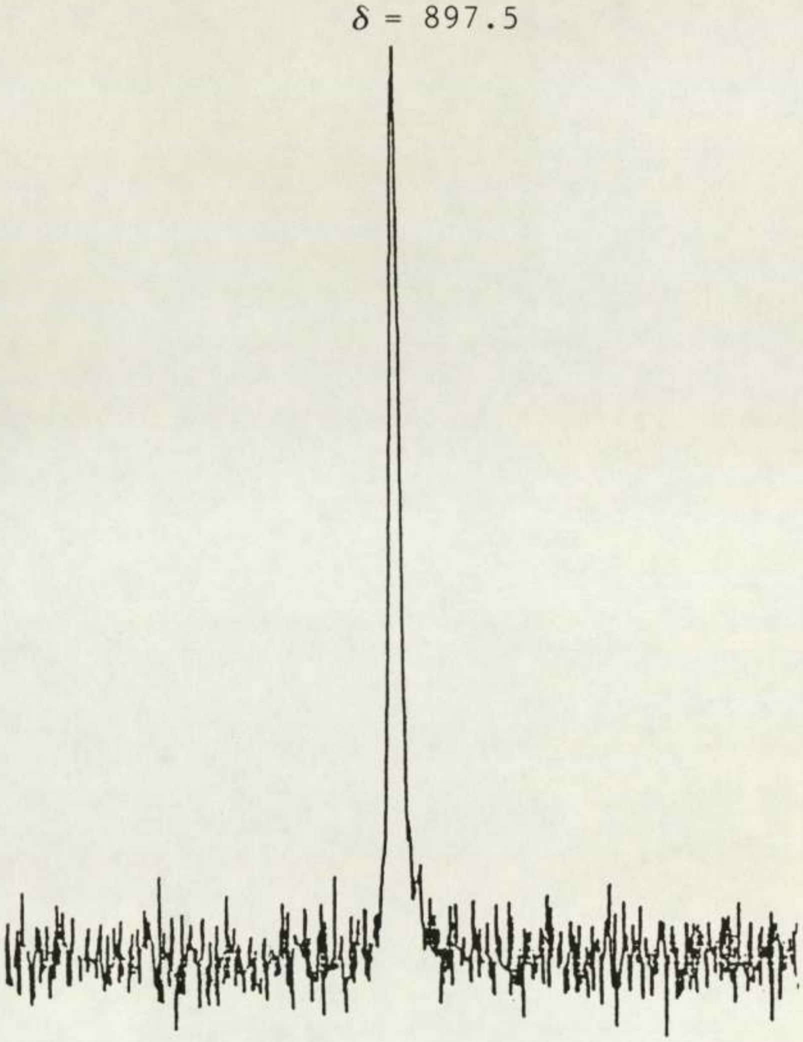


Figure 5.6. ^{125}Te NMR decoupling of compound $(CH_3)_2C_{10}H_6N_2TeI_2$.

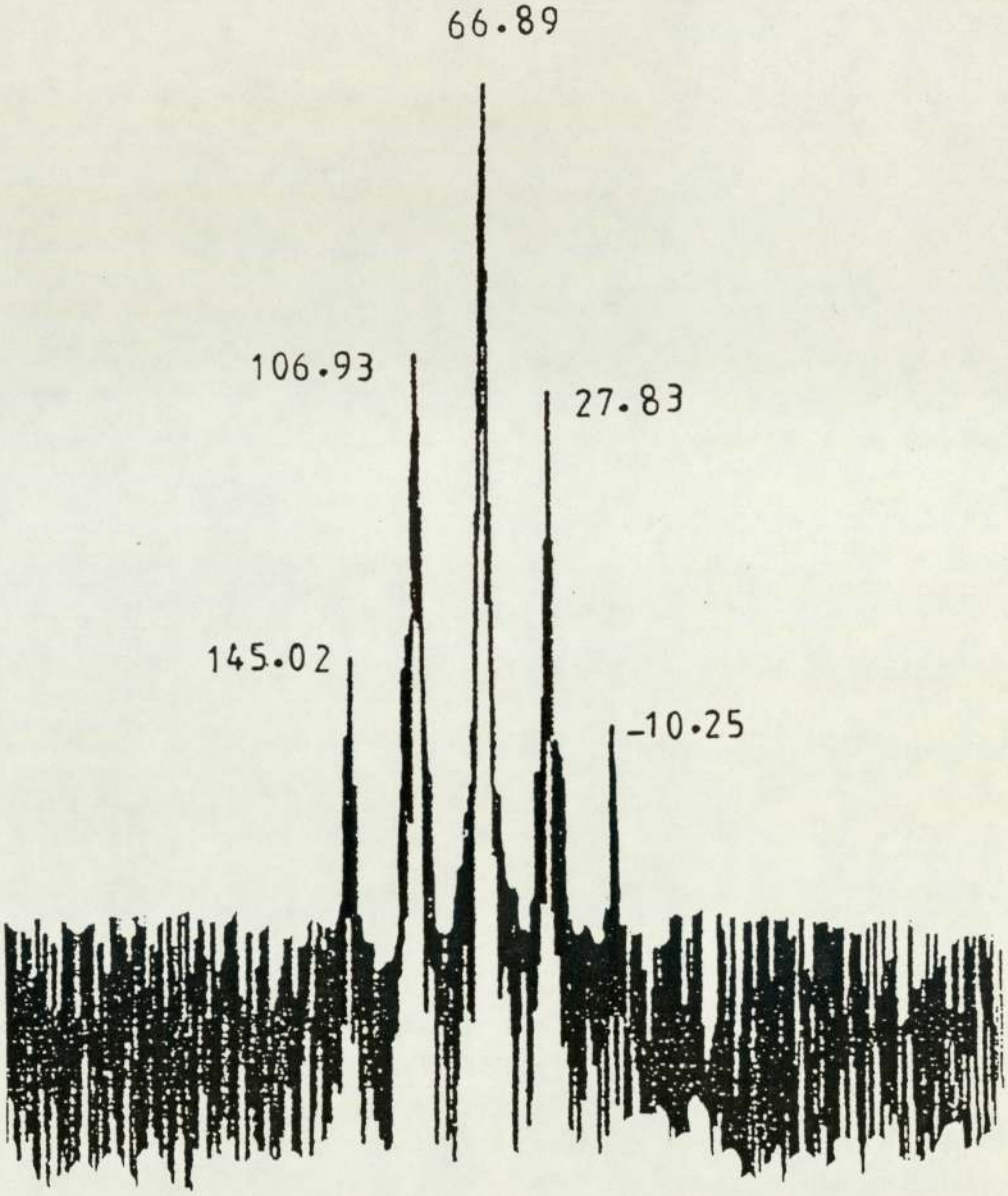


Figure 5.7. ^{125}Te NMR proton coupling of compound $(CH_3)_2C_{10}H_6N_2TeI_2$.

chemical shifts was observed[155]. The chlorine induces the largest shemical shift (^{125}Te) 994 ppm and iodine is the smallest δ(^{125}Te) 831 ppm.

Hence the chemical shift of compound (6) in dimethyl sulphoxide (DMSO) is δ(^{125}Te) 897.5 ppm (relative to dimethyl telluride), which it is in agreement with the results of Gysling[155].

5.7 Conductivity Measurements

The molar and electrical conductivity data for the complexes (4,9 and 13) are given in Table (5.10). Low conductivity values in (10^{-3} mol) acetonitrile solutin were observed which showed little concentration dependence.

The solid conductivity of compacted discs for the three complexes (4, 9 and 13) are clearly insulators.

complex no.	molar cond. $\Omega^{-1}\,cm^2 mol^{-1}$	solid cond. $\Omega^{-1} cm^{-1}$	ESR-g factor (±0.003)
4	14.5	10^{-13}	2.0036
9	23.4	10^{-13}	2.0025
13	13.6	10^{-14}	2.0038

Table 5.10 Solution and solid state conductivity data, together with the ESR data.

5.8 Electron Spin Resonance Spectroscopy

The electron spin resonance measurements were carried out on the freshly prepared charge-transfer samples at room temperature.

Solid state e.s.r. data of complexes (4,9 and 13) (Table 5.10) have a g- value of 2.0 consistent with a free electron of a π-radical.

The single e.s.r. signals are sharp and no hyperfine splitting was observed.

Figure (5.8) shows a typical spectrum of complex (4).

5.9 Infra-red Absorption Spectroscopy

The infra-red data are given in Tables (5.1, 5.4 and 5.7). It has been noted that thers is a slight change in ν(Te-C) frequency of compounds (1,6 and 10) (tellurium IV) on reduction to compounds (3,8 and 12) (tellurium II).

The stretching frequency ν (C≡N) of the three complexes (4,9 and 13) are around 2180 cm^{-1} , a value similar to that of the insulating alkali metal-TCNQ salts.

To date, structure of some organotellurium iodides have been reported[72,141,157-159].

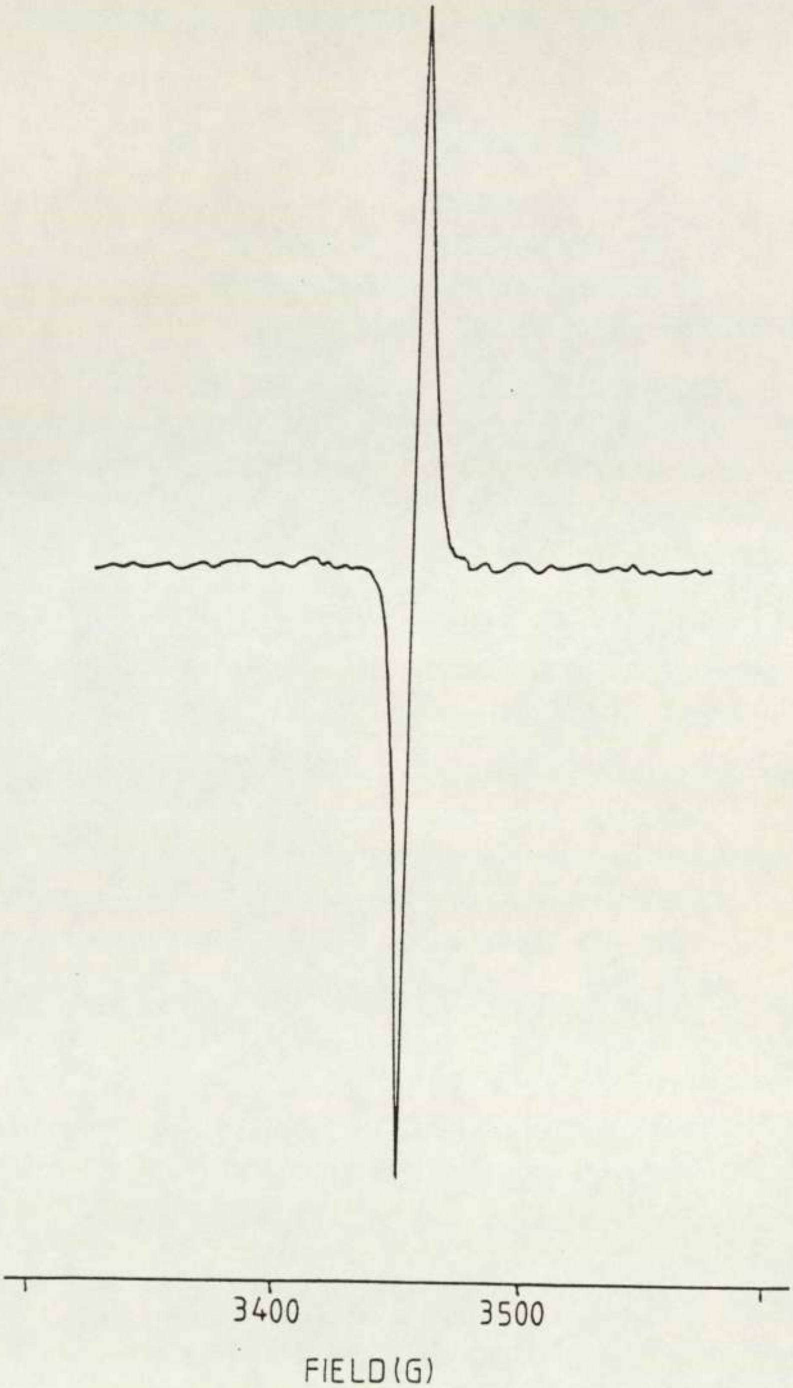


Figure 5.8. E.S.R. spectrum of complex $C_{10}H_8N_2Se$.TCNQ.

These range in colour from the yellow-orange α-polymorph of diiodo-1,3-dihydro-2-telluraindene[157] through reds and purples to the black α-polymorph of 2-biphenyltellurium triiodide[159].

It has been suggested[38,77], that the darker colours of these compounds in the solid state form two types of intermolecular bonding. Secondary Te---I bonds appear to produce red colours while I---I bonds cause purple to black colours that are usually accompanied by a metallic lustre .

The crystal and molecular structure of the Te analogue of (compound 2) (Figure 5.9) showed[86] that the shortest I---I distance was 3.864°A, which is considerably less than the sum of the van der Waals radii, 4.30°A but greater than distances which would be considered to indicate a bonding interaction[158,160]. However there were no abnormally short contact distances. Furthermore, it has been pointed out[86], that the yellow colour of the compound supports the weak bonding found in crystal structure, whereas deep violet colour of the Te analogue of compound (1) suggests strong intermolecular interactions according to McCullough's arguments[38,77].

Similarly, the compounds (1, 6 and 10) are of deep violet colours and the compounds (2, 7 and 11) are fine yellow crystalline materials. Unfortunately the proton N.M.R.

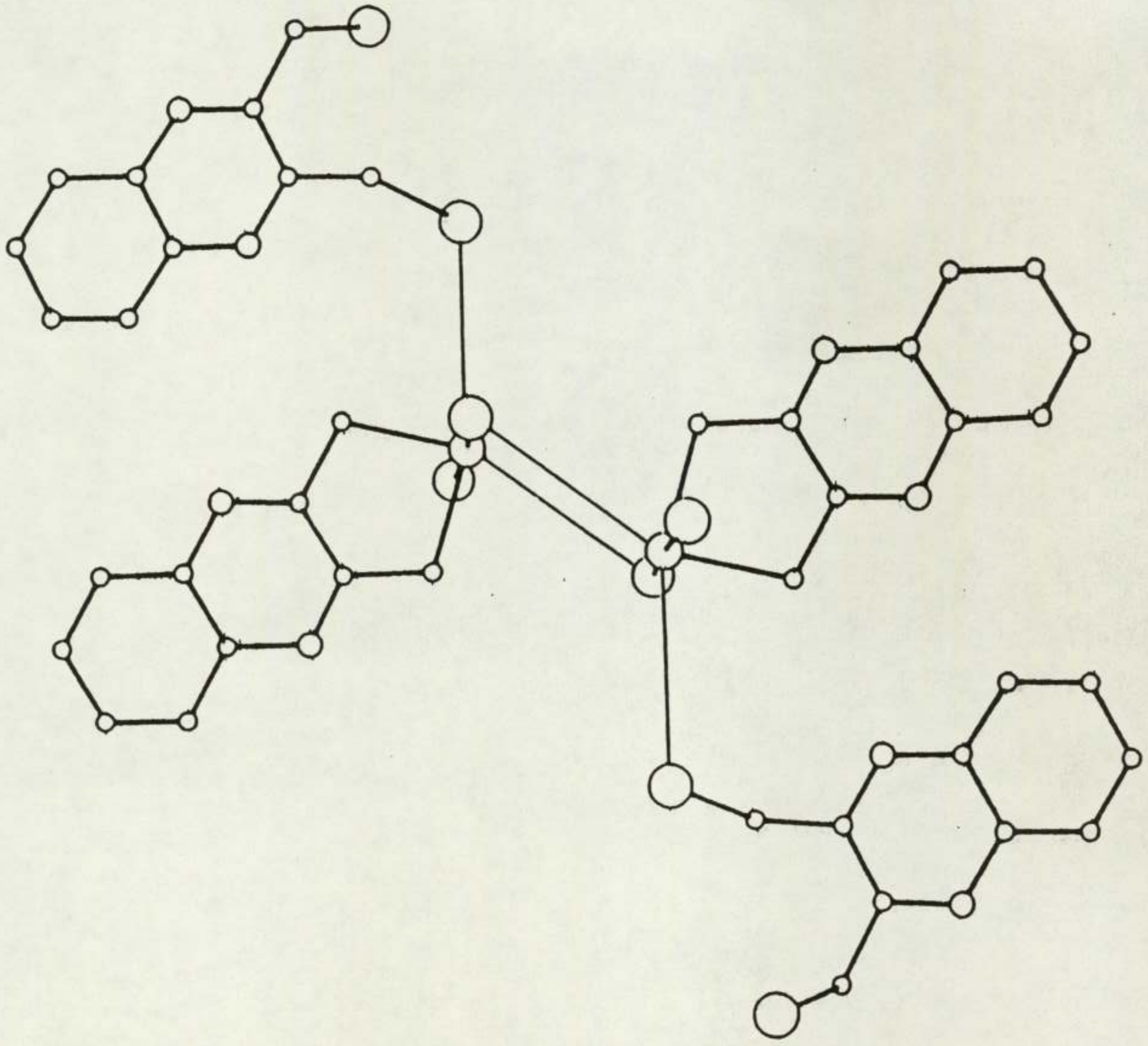


Figure 5.9. The molecular structure of complex $C_{10}H_8N_2TeI_2.C_{10}H_8N_2I_2$.

does not show clear evidence for the doublet of CH_2 in compounds (2, 7 and 11) and the only evidence is the correct analysis data for the suggested structure.

It should be mentioned here that the compounds (2,7 and 11) and the Te analogue are charge-transfer complexes of the organotellurium and selenium (IV) iodide with organic diiodides (the starting materials) and this could be very useful in the view of charge-transfer in organotellurium and selenium chemistry. However a tellurium (II) compound has also been found to form charge-transfer complexes with dihalomethane (halogen = Br, I)[58].

Also it was suggested[161] that the oxidative addition reaction of diorganotelluride (R_2Te) with methyl iodide underwent an intermediate which was a charge-transfer complex (Figure 5.10).

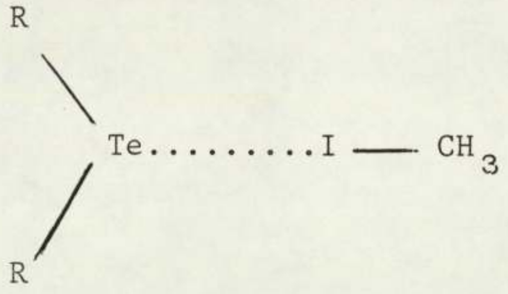


Figure 5.10

Generally, it has been noticed that there were two main stages in the overall reaction of Ar_2Te_2 with I_2[162]. The initial reaction is fast and the follow is by slow stage. The first stage involves the formation of 1:1 and 1:2 donor:acceptor charge-transfer complexes, that is $Ar_2Te:I_2$ and $Ar_2Te_2:2I_2$ respectively.

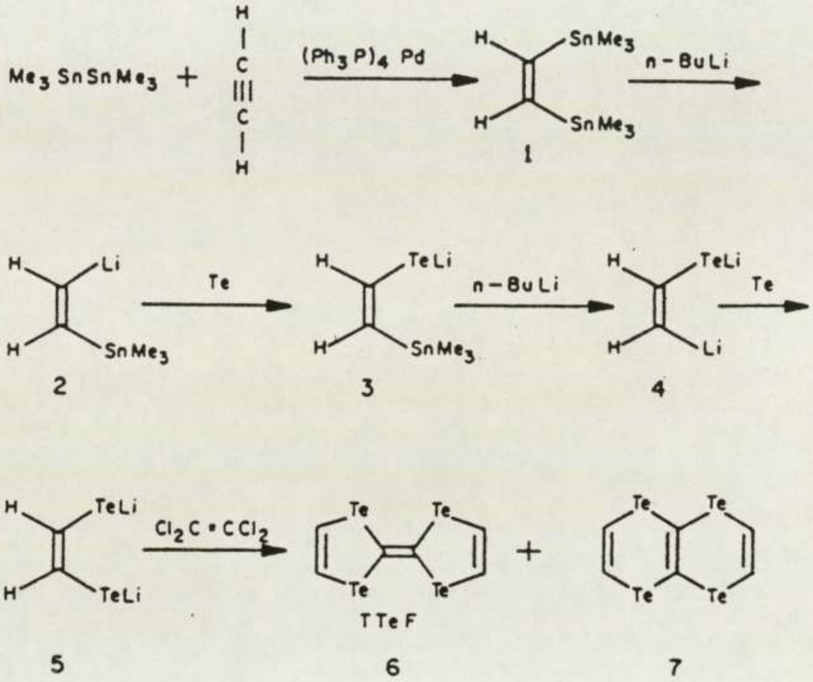
CHAPTER SIX

TOWARDS METAL COMPLEX CONDUCTORS AND SEMI-CONDUCTORS

6.1 Introduction

In the previous chapters the study of charge-transfer complexes of some organotellurium compounds gave materials which showed poor conductivity and the work was terminated. However in this chapter attempts to seek other kinds of molecular conductors are made.

Very recently the synthesis of tetratellurafulvalene (TTeF,6) has been reported in the U.S.A.[163]. This compound completes the interesting series starting with tetrathiafulvalene(TTF), first prepared by Wudl[164] and followed four years later by the selenium analogue,tetraselenafulvalene(TSF), synthesised by Engler[44]. The synthesis of TTeF adds to a small but growing list of tellurium heterocyclic π-donors recently prepared[165]. With the preparation of this compound, it should be possible not only to compare the sulphur, selenium and tellurium series of compounds but also to construct a variety of charge-transfer complexes and highly conductive materials.



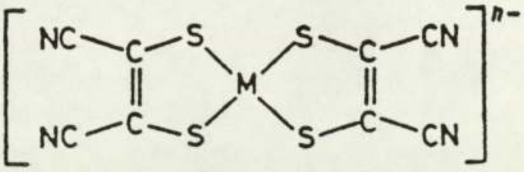
Also, there has been valuble recent work in our laboratory. Several ligands containing both tellurium and donor atoms such as nitrogen and oxygen have been prepared with a wide range of transition metal and post transition metal complexes[166]. The present task is an attempt to develop this line of work.

In fact since the last decade, there has been considerable interest in the molecular design of bimetallic complexes bridged by a quadridentate or a bis-bidentate ligand with a highly delocalized system. [167-169].

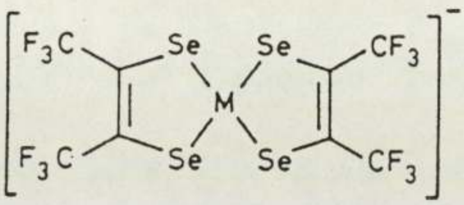
The crystal and molecular structure of the 1:1 charge-transfer molecular compound formed between the transition metal donor complex bis(propene-3-thione-1-thiolato)-platinum(II), $Pt(PTT)_2$ and the organic acceptor 7,7,8,8-tetracyanoquinodimethane(TCNQ) has been reported [170]. The crystals of $Pt(PTT)_2$ and TCNQ consist of individual centrosymmetric $Pt(PTT)_2$ and TCNQ molecules stacked approximately coplanar to each other in a D-A-D-A arrangement along the a axis[170].

The synthesis and electrical conduction properties of compounds containing planar $[M(S_2C_4N_2)_2]^{n-}$, (M = Ni, Pd or Pt), anions have been extensively studied[171-173].

However one-dimensional metallic properties have only been established in compounds where the organic cation and not the $[M(S_2C_4N_2)_2]^{n-}$(I) is responsible for the high conductivities[173].



(I)



(1) M = Ni
(2) M = Pt

(II)

Recently, the crystal and band-electronic structures of (BEDT-TTF)Ag$_4$(CN)$_5$, (BEDT-TTF) is bis(ethylenedithio)-tetrathiafulvalene, $C_{10}H_8S_8$ or simply "ET" has been studied as a first conducting organic radical-cation salt which contains a polymeric anion[178].

Later, the perparation, crystal structure and electrical properties of ET silver iodide, $(ET)_3\ Ag_xI_8 (x \sim 6.4)$ were reported[180]. This new truly two-dimensional polymeric anion, one which combines the structural features of both an organic electronic conductor and an inorganic solid electrolyte (ionic conductor)[180].

It has been decided to extend the recent work in the laboratory[166] and to synthesise some more new ligands and complexes. This chapter reports new synthetic work directed to these ends, i.e. some further steps to synthesise organotellurium ligands which can encircle ions prefering square planar stereochemistry.

Underhill[174], reported the first observation of metallic behaviour in single crystals of a $[Pt(S_2C_4N_2)_2]^{n-}$ salts in which conduction must occur through interacting anions. The electrical conductivity of $Li_x[Pt(S_2C_4N_2)_2]$ $.2H_2O$ (where x= ca. 0.75) at room temperature was found to vary from 30 to 200 $\Omega^{-1}cm^{-1}$ with an average value of 96 $\Omega^{-1}cm^{-1}$.

Also planar metal bis-dithioalkene complexes are attractive precursors for molecular metals because of their delocalized electronic structure and range of stable oxidation states[175]. Furthermore, close intermolecular contacts mediated by the chalcogen atoms of these complexes can produce conductive crystals that exhibit quasi-2- or 3-dimensional character[176], as is found in the organic superconductors[177].

In principle, the selenium analogues of such complexes (metal bis-diselenoalkenes) would be better suited for the formation of extended, multi-dimensional molecular networks because of the increased van der Waals radius and greater polarizability of selenium[178].

Salts of the monoanions $[M(Se_2(C_2(CF_3)_2)_2]^-$ (M= Ni, Pt) (II) were prepared and shown to conduct well along the needle axis (20 and 65 $\Omega^{-1}cm^{-1}$ respectively)[178].

6.2 Experimental

6.2.1 The Preparation of 2-butyltellurobenzaldehyde

2-Bromobenzaldhyde (25 g, 0.135 mole) was reacted with triethylorthoformate (20 g, 0.135 mole) in the presence of 0.5 g potassium hydrogen sulphate ($KHSO_4$) in ethanol (20 cm^3). After reflux for three hours, ethanol was removed under vacuum and extraction with diethyl ether(100 cm^3) and water (100 cm^3) was carried out. The organic layer was dried over anhydrous Na_2SO_4. The result was the liquid diethyl acetal derivative, yield 95%.

2-Bromobenzaldehyde diethyl acetal (13 g, 0.05 mole) in dry diethylether (50 cm^3) was placed in 3-necked flask and n-butyl lithium (4.8 ml, 10.4 molar in 15 cm^3 ether /cyclohexane solution) was added slowly undr N_2 gas from a separating funnel over 15 mimutes.

The mixture was cooled to room temperature and tellurium powder (6.5 g, 0.05 mole) was added slowly, with stirring. After 30 minites refluxing, the mixture was cooled, poured on ice and extracted with ether. After drying over Na_2SO_4, the solvent was removed and the result was a yellow liquid (2-butyltellurobenzaldehyde diethyl acetal), boiling point 148-150°C at 0.1 mmHg and yield 68%.

The hydrolysis of the above compound was carried out by heating it gently with concentrated hydrochloric acid (10 cm^3). The mixture was then cooled to room temperature, extracted with diethylether and dried over anhydrous $MgSO_4$. After removing the solvent, the product was distilled under vacuum at 141-143°C and 0.1 mmHg (l:t. 140-142°C) [181] to give bright yellow liquid (2-butyltellurobenzaldehyde) yield 82%.

Found C = 43.2%, H = 4.02%, ; $C_{11}H_{14}OTe$
requires C = 43.5%, H = 3.83%.

6.2.2 The Chlorination of 2-Butyltellurobenzaldehyde

2-Butyltellurobenzaldehyde (5 g, 0.014 mole) in carbon tetrachloride (30 cm^3) was treated with a stream of chlorine gas (Figure 6.1).

On completion of the reaction, the solvent was removed and the solid resdue was recrystallised from a mixture of hexane and benzene. Bright white needle-like crystals of 2-butyldichlorotellurobenzaldehyde were formed, yield 85%, m.pt. 107-109°C (lit. 105-110°C)[181].

Found C = 36.6%, H = 3.90%, $C_{11}H_{14}OTeCl_2$
requires C = 36.6%, H = 3.88%.

6.2.3 The Preparation of the Ligand 1,7-Bis-2-butyltellurophenyl-2,6-diazahepta-1,6-diene (Ligand L)

2-Butyltellurobenzaldehyde (5.2 g,0.018 mole) in absolute ethanol (10 cm^3) was reacted with dry 1,3-diaminopropane (0.67 g, 0.009 mole) in absolute ethanol (10 cm^3). The mixture was refluxed for 30 minutes, then cooled to room temperature. The solvent was eliminated under reduced pressure to afford light yellow liquid material, yield 70%.

Found C = 48.4%, H = 5.61%, N = 4.50% ; $C_{25}H_{34}N_2Te_2$ requires C = 48.9%, H = 5.50%, N = 4.53%.

6.2.4 Bromination of the Ligand 1,6-Bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene (ligand L')

A solution of excess bromine in carbon tetrachloride was added slowly to a solution of the ligand 1,6-bis-butyltellurophenyl-2,5-diazahexa-1,5-diene[166]. (2.41 g,0.004 mole) in carbon tetrachloride. The mixture was stirred and gently warmed for two hours. The yellow precipitate was separated by filtering and washed with CCl_4 solvent several times. It was recrystallised from dioxane to give a yellow crystalline 1,6-bis-2-tribromotellurophenyl-2,5-diazahexa-1,5-diene, yield 90%, m. p. 296-298°C (dec.).

Found $C = 20.2\%$, $H = 1.10\%$, $N = 2.70\%$, $Br = 49.4\%$,

$C_{16}H_{14}N_2Te_2Br_6$

requires $C = 19.8\%$, $H = 1.40\%$, $N = 2.89\%$, $Br = 49.5\%$.

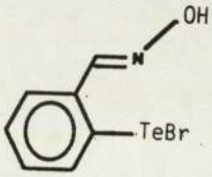
6.2.5 Reduction of 1,6-Bis-2-tribromotellurophenyl-2,5-diazahexa-1,5-diene.

Method (A)

A suspension of 1,6-bis-2-tribromotellurophenyl-2,5-diazahexa1,5-diene (1.94 g,0.002 mole) in ethanol (30 cm^3) was treated with hydrazine hydrate (0.004 mole) in ethanol (10 cm^3). The mixture was refluxed for 15 minutes and filtered off. Recrystallisation from benzene gave a yellow crystalline material which was the hydroxylamine derivative of the tellurium mono bromide, yield, 35%, m. p. 176-178°C.

Found $C = 24.7\%$, $H = 2.32\%$, $N = 4.57\%$,

$C_7H_6NOTeBr$,



requires $C = 25.6\%$, $H = 1.83\%$, $N = 4.27\%$.

Method (B)

1.6-Bis-2-tribromotellurophenyl-2,5-diazahexa-1,5-diene (1.94 g, 0.002 mole) in THF solvent (50 cm^3) was stirred with sodium metabisulphate ($Na_2S_2O_5$) (0.76 g, 0.004 mole) in water (50 cm^3)for one hour at room temperature.

The filtered yellow material was washed with THF many times and recrystallised from benzene to give a yellow crystalline compound, yield 35%, M. p. 228-230°C(dec.).

Found C = 29.3%, H = 1.91%, N = 4.50%, Br = 24.5%

$C_{16}H_{14}N_2Te_2Br_2$

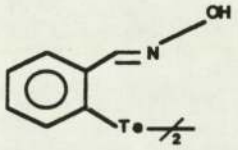
requires C = 29.6%, H = 2.16%, N = 4.31%, Br = 24.6%

6.2.6 Attempt to Synthesise a Cyclic Ditelluride

1,6-Bis-2-tribromotellurophenyl-2,5-diazahexa-1,5-diene (1.94 g, 0.002 mole) was suspended in ethanol (30 cm^3). Hydrazine hydrate (0.6 g, 0.012 mole) in ethanol (15 cm^3) was added and refluxed together for 20 minutes. The mixture was then filtered off and recrystallisation from benzene was carried out to give yellow orange crystals. All the data suggest this to be a non cyclic ditelluride of unexpected composition, yield 75%, m. p. 276-278°C.

Found C = 34.9%, H = 2.50%, N = 5.45%

$C_{14}H_{12}N_2O_2Te_2$,



requires C = 33.9% H = 2.42%, N = 5.65%.

6.2.7 Synthesis of a Tritelluride Compound

1,6-Bis-2-tribromotellurophenyl-2,5-diazahexa-1,5-diene (3.87 g, 0.004 mole) was suspended in ethanol (30 cm^3) and tellurium powder (0.26 g, 0.002 mole) was added. The mixture was stirred under argon gas. Sodium borohydride ($NaBH_4$) (1.1 g, 0.03 mole) was then added to the mixture slowly, until all the tellurium powder disappeared. The resulting reddish solution was refluxed for 30 minutes and filtered. On cooling to room temperature an orange precipitate appeared which was recrystallised from benzene to give an orange compound, yield 65%, m. p. 127-128°C.

Found C = 30.8%, H = 2.50%, N = 4.10% ;$C_{16}H_{14}N_2Te_3$
requires C = 31.1%, H = 2.27%, N = 4.54%.

6.2.8 Attempted Synthesis of an Unsymmetrical Ditelluride

Di(p-ethoxyphenyl)ditelluride (3 g, 0.006 mole) and sodium borohydride ($NaBH_4$) (0.45 g, 0.012 mole) in absolute ethanol (50 cm^3) were stirred and refluxed under argon gas. Dimethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium (II)[182], (5.14 g, 0.012 mole) was added to the mixture and refluxed for another 60 minutes. After filtering off the mixture, recrystallisation from benzene was carried out to give a red colour crystals.

yield 85%, m. p. 83-84°C

Found C = 42.8%, H = 3.30%, N = 4.90%; $C_{20}H_{18}N_2OTe_2$
requires C = 43.0%, H = 3.23%, N = 5.02%

6.2.9 The Preparation of the Complex $HgCl_2.L$

The ligand (L) (0.88 g, 0.001 mole) was dissolved in a mixture of acetone and absolute ethanol (30 cm^3) and heated. A warm solution of mercury(II) chloride (0.27 g, 0.001 mole) in ethanol (15 cm^3) was added slowly to the ligand and refluxed together under nitrogen gas for 30 minutes. The white solid was filtered off and washed with hot ethanol several times. Recrystallisation from hot nitromethane gave white yellowish crystals, yield 65%, m.p. 137°C.

Found C = 33.6%, H = 3.71%, N = 3.00%;
$C_{25}H_{34}N_2Te_2.HgCl_2$
requires C = 33.8%, H = 3.83%, N = 3.15%

Conductivity (10^{-3}mole.litre^{-1}) in CH_3NO_2=3.2 ohm^{-1}cm^{2}mole^{-1}

6.2.10 The Preparation of the Complex $CdBr_2.L'$

The ligand (L') (0.60 g, 0.001 mole) was dissolved in ethanol (30 cm^3) and mixed with a solution of cadmium bromide ($CdBr_2.4H_2O$) (0.34 g, 0.001 mole) in methanol (20

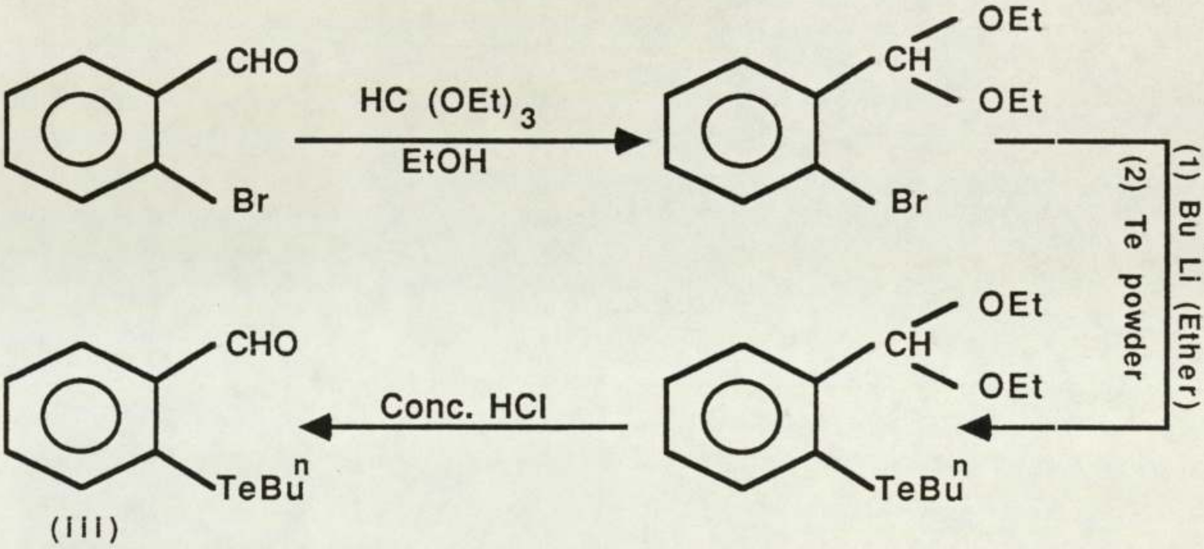
cm^3). The mixture was gently heated for 30 minutes under nitrogen gas. The solid material was washed with hot ethanol and methanol, then recrystallised from nitromethane to give white crystalline compound, yield 85%, m.pt. 151-152 C.

Found C = 32.8%, H = 3.40%, N = 2.93%
$C_{24}H_{32}N_2Te_2$-$CdBr_2$
requires C = 32.9%, H = 3.65%, N = 3.20%

Conductivity (10^{-3} mole $litre^{-1}$) in DMSO=4.1 $ohm^{-1}cm^2mole^{-1}$

6.3 Results and Discussion

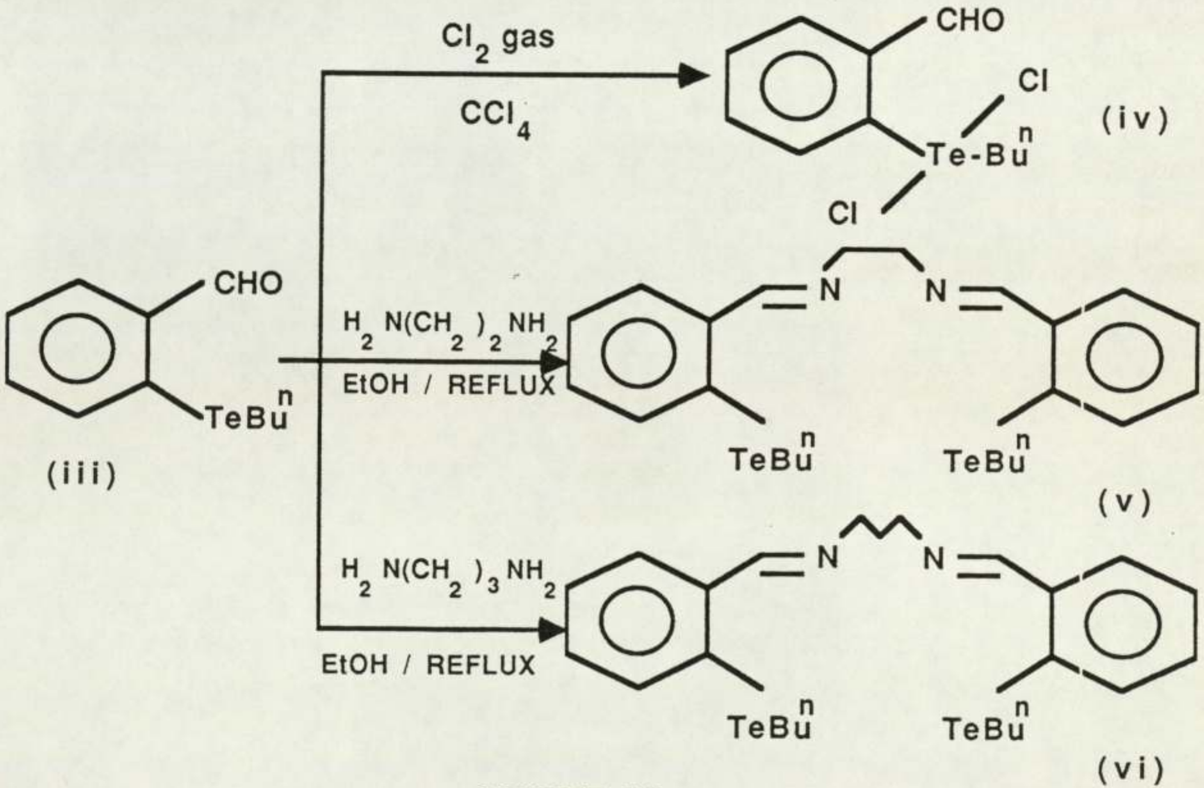
The preparation of the starting material, 2-butyltellurobenzaldehyde(III) is illustrated in Scheme(6.1).



SCHEME 6.1

The first step was the conversion of the aldehyde group in 2-bromobenzaldehyde to an acetal, which is insensitive to butyl-lithium. The second step was the telluration and the finalstep was the conversion of the acetal group back to aldehyde (2-butyltellurobenzaldehyde).

The reaction of compound (III) with a stream of chlorine gas gave 2-butyldichlorotellurobenzaldehyde (IV). While compound (III) reacts with primary amine groups such as 1,2-diaminoethane to give the ligand 1,6-bis-2-butyltelluro-phenyl-2,5-diazahexa-1,5-diene (V)[166] and with 1,3-diaminopropane to give the ligand 1,7-bis-2-butyltelluro-phenyl-2,6-diazahepta-1,6-diene (VI). The amine compounds were used to link two tellurium compounds by the elimination of water, to afford ligands containing two tellurium and two nitrogen atoms, Scheme(6.2)



SCHEME 6.2

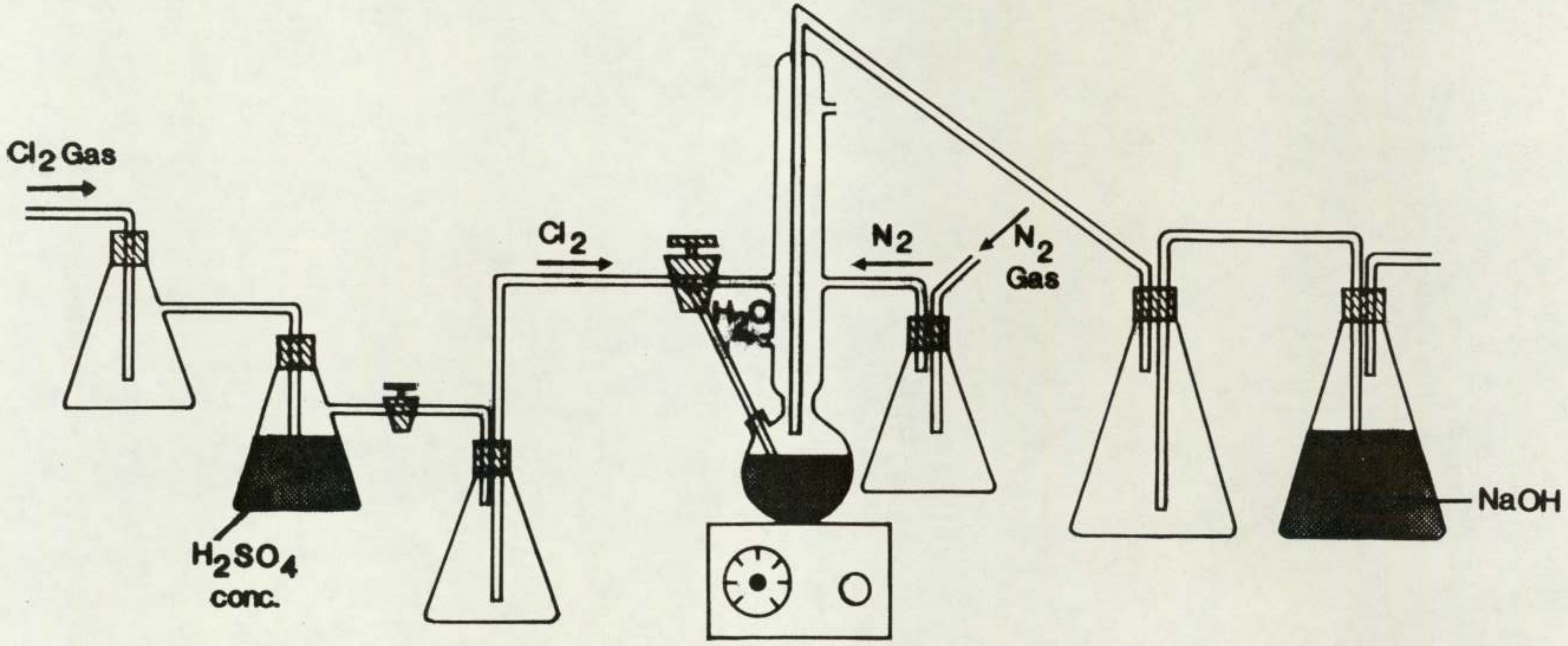
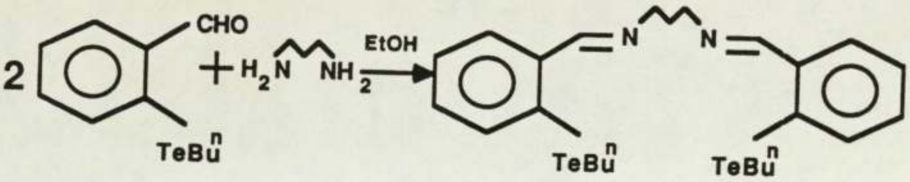


Figure 6.1 The chlorination system of 2-butyltellurobenzaldehyde.

6.3.1 Characterisation of the New Ligand (L)

The ligand 1,7-bis-2-butyltellurophenyl-2,6-diazahepta-1,6-diene (L) was the esult of the reaction of 2-butyltellurobenzaldehyde (III) with diaminopropane which proceeded via the condensation on both amino-groups (equation 6.1).



.. (Eq. 6.1)

The reaction of the same starting material (compound III) with diaminoethane (en) and hydrazine under similar conditions gave the two amine derivative ligands[166]. Such ligands have two tellurium and two nitrogen donor atoms. However ligand L was a liquid material, while the other two ligands (ethylenediamine and hydrazine derivatives) were crystalline materials[166]. The work was confirmed by the analytical data, i.r(Table 6.1) and ^{1}H, ^{13}C, ^{125}Te NMR.

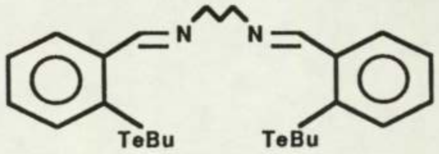
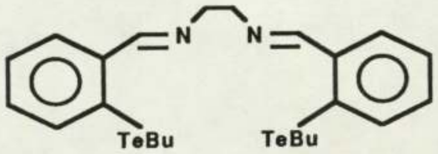
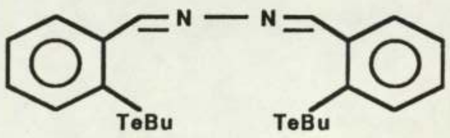
	Ligand	Yield%	Colour	M.Pt.°C	$(C=N)cm^{-1}$
L		70	shiny yellow liquid	-	1638
*L'		68	yellow needles	83-85	1637
*L''		70	orange crystals	113-115	1616

Table 6.1 Analytical and infra-red data. * reference [166]

The infra-red spectrum of the ligand (L) showed the absence of the aldehyde carbonyl group (1695 cm^{-1}) and the appearance of lower energy band, at 1638 cm^{-1} in spectrum for the stretching frequency of the imine group, ν(C=N), in the ligand. The same band has appeared at 1637 and 1616 cm^{-1} in the ethylenediamine and hydrazine derivatives (Table 6.1).

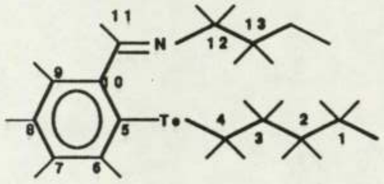
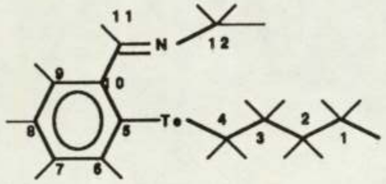
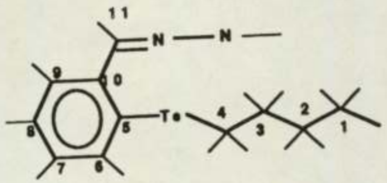
The ^{1}H N.M.R. data of ligand (L) together with ligand (L') and (L") are in Table(6.2). $CDCl_3$ was used as solvent. The spectra showed a peak at (2.20 ppm) in ligand (L) which belongs to the resonance of the protons attached to the carbon atoms of the propane chain.

The ^{13}C-[^{1}H] N.M.R. data of the three ligands were gathered in Tables (6.3 and 6.4) and the spectra recorded in $CDCl_3$. These spectra can be divided into two distinct regions:-

1. the aliphatic region
2. the aromatic region

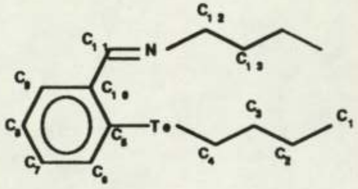
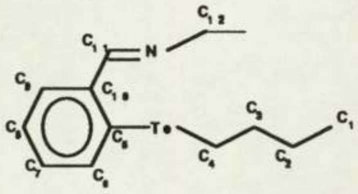
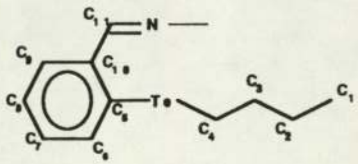
The 7% natural abundance of ^{125}Te did not allow observation of C-Te coupling in the ^{13}C-[^{1}H] N.M.R. spectra of these ligands.

The assignments of the ^{13}C-[^{1}H] resonances follow the available literature data for alkyl phenyltellurides[183] and aromatic Schiff bases [184].

δ Ligand (L)	(a) δ Ligand (L')*	(a) δ Ligand(L")*
H_1 = 0.96 (t), 6H	H_1 = 1.00 (t), 6H; J=7.03Hz	H_1 = 0.95 (t), 6H; J=6.88Hz
H_2 = 1.42 ( ), 4H	$H_{2,3}$= 1.46-2.55 (m), 8H	$H_{2,3}$= 1.36-1.92 (m), 8H
H_3 = 1.80 ( ), 4H	H_4 = 2.54 (t), 4H	H_4 = 2.72 (t), 4H; J=7.32Hz
H_4 = 2.59 (t), 4H		
H_{Ar} = 7.22-7.62 (m), 8H	H_{Ar} = 7.13-7.52 (m), 8H	H_{Ar} = 7.20-7.10 (m), 8H
H_{11} = 8.51 (s), 2H	H_{11} = 8.53 (s), 2H	H_{11} = 8.38 (s), 2H
H_{12} = 3.88 (s), 4H	H_{12} = 4.10 (s), 4H	
H_{13} = 2.20 (s), 2H		
		

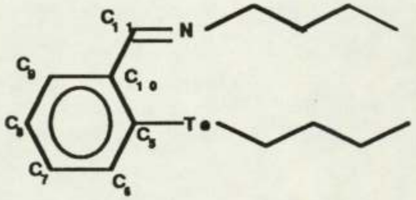
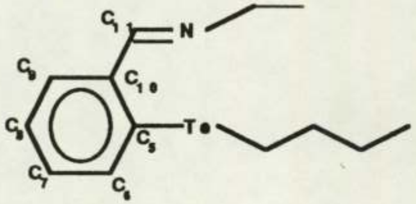
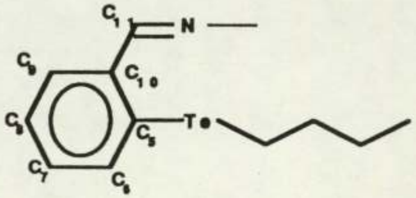
(a) chemical shift in ppm relative to Me_4Si, (t)-triplet, (m)-multiplet, (s)-singlet
* reference [166].

Table 6.2 ^{1}H. N.M.R. data

ligand		chemical shift$^{(a)}$					
		C-1	C-2	C-3	C-4	C-12	C-13
L		13.48	26.91	32.06	8.09	57.04	32.62
*L'		13.51	25.54	31.93	8.20	60.43	-
*L''		13.51	25.54	32.25	9.17	-	-

(a) In ppm relative to Me_4Si. * Reference [166]

Table 6.3 ^{13}C N.M.R. data (aliphatic region)

	Ligand	chemical shift$^{(a)}$						
		C-5	C-6	C-7	C-8	C-9	C-10	C-11
L		120.77	132.15	132.94	124.89	129.69	136.10	161.83
*L'		121.22	132.27	133.14	124.90	129.67	136.17	162.94
*L''		120.24	133.25	133.68	125.55	130.43	135.20	162.61

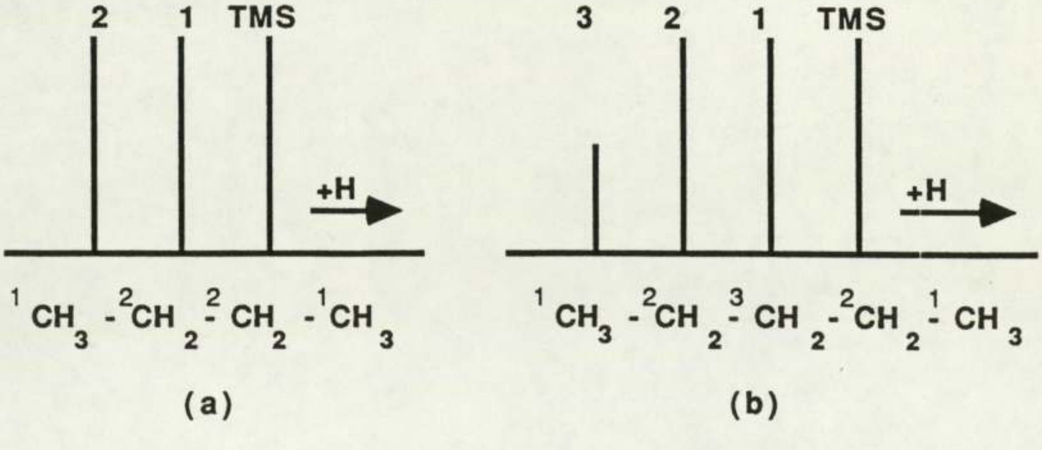
(a) In ppm relative to Me_4Si. * Reference [4]

Table 6.4 ^{13}C N.M.R. data (aromatic region)

1. The aliphatic region:

Although there have been numerous publications in recent years on the ^{13}C N.M.R. spectra of organometallic compounds, only limited data on organotellurium compounds are available and the literature lacks systematic investigations of these compounds.

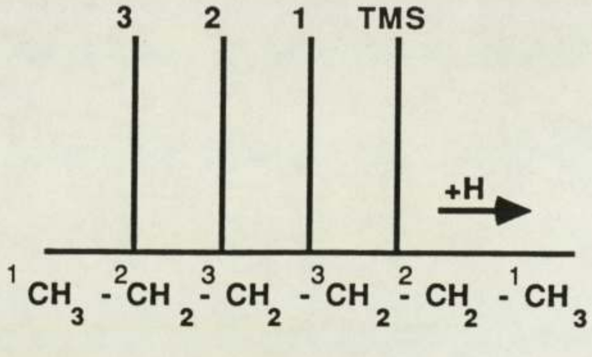
The absence of ^{13}C-^{125}Te coupling in the spectra of the Schiff base- and the hydrazone-tellurium ligands and the lack of data in the literature about similar n-butyl-tellurium compounds makes the assignment difficult. The ^{13}C N.M.R. spectra of the linear alkanes could be considered. The trend observed for linear alkanes up to n-hexane is simple. The schematic spectra of some of n-alkanes shown in Figure(6.2).



(a)

(b)

(Figure 6.2 cont.)



(C)

Figure 6.2 Schematic $^{13}C-[^{1}H]$ N.M.R spectra of some n-alkanes

Figure(6.3) shows that the terminal carbon has the lowest chemical shift (highest field) and it has been assigned at 13 to 13.7 ppm [185,186]. The next carbon, C2 resonates at a lower field than C1, while the middle carbon, C3, still lower (31.5-34 ppm).

If a phosphorus atom is attached to one of the terminal carbon atoms, the symmetry of the alkane chain and the trend in chemical shift will change. Tri-n-butylphosphine, has four carbon resonances for the butyl chain attached to the phosphorus atom (Figure 6.3). The highest chemical shift (δ =29.3 ppm) was assigned to the carbon attached to the phosphorus atom, whilst the terminal carbon gave the lowest chemical shift (δ =14.7 ppm)[187].

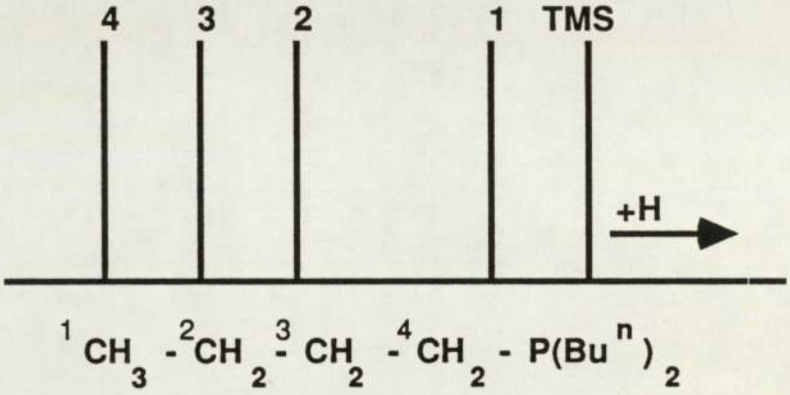


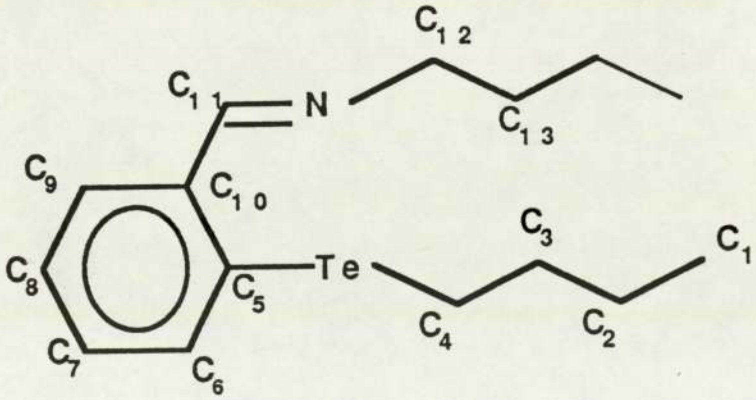
Figure 6.3. Schematic $^{13}C[^1H]$N.M.R. of tri-n-butylphosphine.

Also dibutylphenylphosphine has similar chemical shift values[187].

It has been noted that the chemical shift of the carbon attached to phosphorus is relatively high [188,189]. These values are close to that found for n-heptane and n-octane [186]. The similarity between ^{13}C chemical shift values of the tertiary phosphines and linear alkanes and the small influence of phosphorus on ^{13}C chemical shifts have been attributed to the similarity in the electronegativities of -PMe (-2.28) and -CHMe (-2.28)[187].

The C1 and C2 alkyl resonances are inconsistent with those for other (alkyl)Te(aryl) compounds reported and discussed in the literature[183,188,189].

Comparing the present Schiff-base and the hydrazone tellurium compounds (Table 6.3), similar results were seen. The additional signals at a lower field (δ C=60.43 ppm) in ligand L'(V) (which were assigned for the ethylene carbons (C12) attached to the nitrogens)[166] and (δC =57.04 ppm) for C12 and δC =32.62 ppm for C13) the extra methylene group in ligand L(VI).



(VI)

C4 in L' and L" has been assigned at 8.20 and 9.17 ppm for the carbon attached to tellurium atom[166] and very close to that reported for ArTe(CH$_2$)nTeAr δC1= 9 ppm[190]; in the same trend, δ C4=8.09 ppm for the ligand L. All these data are in good agreement with the argument that the nitrogen-tellurium interaction has no significant influence on δ C4, although the nitrogen is <u>trans</u> to C4 in such ligands[166].

The remaining three carbon signals in the aliphatic region are very close to that reported for n-hexane (Figure 6.4)[185,186], thus they are assigned as C1,C2 and C3 in the three ligands at lower fields.

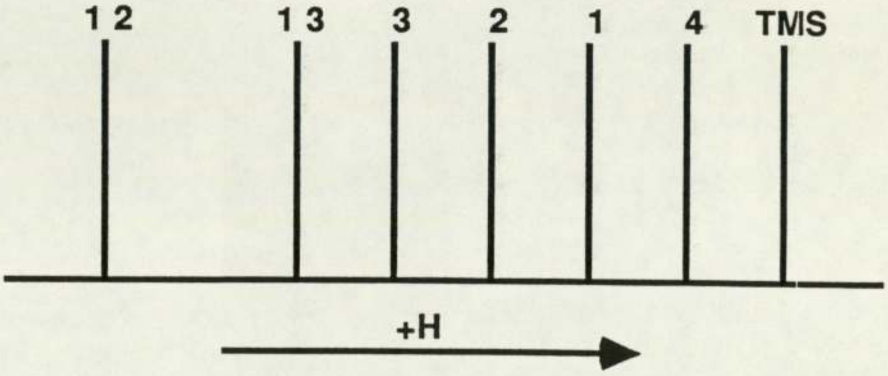


Figure 6.4. Schematic ^{13}C representation for ligands L, L' and L", numbering is as shown in (VI).

This trend of chemical shift is similar to that reported for Bu_2Te[191], in spite of the chemical shift values difference. But this trend is different than in the spectrum of tri-n-butylphosphine[187].

2. The aromatic region

The ^{13}C NMR spectra showed six resonances for the phenyl carbons and one for imine carbon (Table 6.4). The C11 signal appeared at δC= 161.83 ppm in ligand L and it is very close to the values δC=162.94 and 162.61 for the same carbon position in ligand L' and L"[166]. The three values are in agreement with the value of the imine carbon in N-methylphenylimine[192], which appeared at 162.2 ppm.

C5 and C10 (compound VI) does not possess a directly bound hydrogen atom, such carbons usually show signals of low intensity. Therefore, the low intensity peak which appeared at 136.10 ppm in ligand L and at 136.17 and 135.5 ppm in ligands L' and L"[166], is assigned as C10 in the three ligants. In the compound N-methylphenylimine a similar value was obtained at (δ 137.13) for the phenyl carbon attached to the imine group [192].

In the spectrum of ligand L, the lowest chemical shift value in the aromatic region is for the low intensity peak at δC=120.77 ppm. A value has been reported for ligand L' (121.2 ppm) and ligand L''(120.2 ppm) which was assigned to the carbon attached to tellurium atom[166].

It has been pointed out that the effect of a "heavy atom" like tellurium on the directly attached carbon of phenyl ring is to decrease the chemical shift value [183]. For example in PhTeEt (δC= 112 ppm) relative to benzene (δC= 128 ppm).

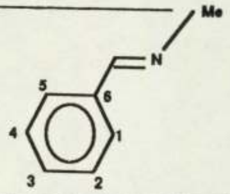
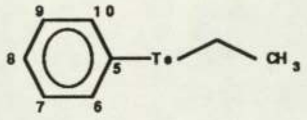
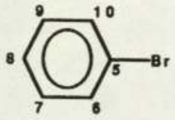
Also a "large highfield" shift in the phenyl carbons attached to tellurium in diaryltellurides Ph_2Te (δC= 114.7 ppm), has been reported as a result of shielding effects of the electropositive tellurium atom[193]. The lower values have been reported down to 100 ppm for the <u>ipso</u>-carbon of some aromatic tellurium (II) compounds[190].

Therefore the peak at 120.77 ppm in ligand L was assigned as C5 (the <u>ipso</u>-carbon). However this value which is higher than that reported for simple aromatic tellurium compounds ca-114 ppm[193] could be similarly attributed to Te---N interaction in ligand L' and L''[166] which tends to increase the electron density on tellurium atom, thus Te will effectively have more than two unpaired electrons.

The number of unpaired electrons of the heavy atom (has been reported) plays an important role in the chemical shift of the ipso carbon[183].

In the present work, the signals with the highest resonating field, apart from C5(ipso), are those at 124.89 ppm in ligand L, 124.9 ppm in ligand L' and 125.5 ppm in ligand L". These resonances could be assigned to the para-carbon to tellurium (i.e. C8) in the three ligands. However, these values are slightly lower than that reported in the literature[183,189,191,193] for a para-carbon atom, for which δC ranges between 126.6 to 128.2 ppm depending on the other organic groups bonded to tellurium. This may imply that the tellurium atoms in these compounds (Ligands L, L' and L") are possessing more π-donor properties than the simple phenyltellurium (II) compounds.

The additivity principle was used comparatively with the chemical shifts of similar compounds (Table 6.5) to assign C6, C7 and C8 in the three ligands (L, L' and L"). This table showed that C5 (from A+B) is very different than that of the obtained value of C5 in ligand L (Table 6.4). The difference in the chemical shift is (-8.77 ppm) from the ligand L value and similarly from ligand L' and L". While the values of (A+C) in the Table 6.5 are closer to the three ligands values. This result indicates the failure of the additivity principle for

compound	chemical shift (ppm) relative to Me_4Si(a)						ref.
	C-5	C-6	C-7	C-8	C-8	C-10	
(A) 	129.0 (+0.3)	128.6 (-0.1)	130.8 (+2.1)	128.6 (-0.1)	129.0 (+0.3)	137.3 (+8.6)	192
(B) 	111.7 (-17.0)	138.9 (+10.2)	128.4 (-0.3)	127.2 (-1.5)	128.4 (-0.3)	138.9 (+10.2)	183
(C) 	123.3 (-5.4)	132.0 (+3.3)	130.9 (+2.2)	127.7 (-1.0)	130.9 (+2.2)	132.0 (+3.3)	194
(A + B)	112.0	138.8	130.5	127.1	128.7	147.5	
(A + C)	123.6	131.9	133.0	127.6	131.2	140.6	

(a) values between parentheses are the deviation $\Delta\delta C$ from δC(benzene) taken as 128.7 ppm.

Table 6.5 Application of the additivity principle to compounds which are related to ligands L, L', L".

closely related aromatic group 6 compounds. In addition it shows that tellurium atom influence (in the three ligands) is close to that of bromine on δC of the phenyl carbon atoms. From this the remaining three signals at 132.15, 132.94 and 129.69 ppm in ligand (L) were assigned as C6, C7 and C9 respectively and similarly for ligands L' and L"[166].

The different ranges in δC(ipso) of $PhER_n$ formula compounds (where E =group 4A, 5A, 6A or 7A; n=0,1,2,3) were attributed to the numbers of unshared electron pairs :zero for G4A, one for G5A, two for G6A and three for G7A[183]. Also it has been proposed that the observed trends in such compounds are the result of nonbonded interactions of the substituents with the unshared electron pairs of the hetroatoms[183]. In the present work tellurium also has two unshared electron pairs and should show similar chemical shift for the ipso-carbon atom.

The crystal structure determination of ligand (L')[166], showed that there is a weak but considerable interaction between tellurium and nitrogen in the compound. The nitrogen lone pair of electrons is partially donated to the tellurium atom (acting as Lewis acid). Consequently the effective electron density on tellurium is more than two electron pairs and to behave similar to the halogens, thus will increase its π-donor property. That could be

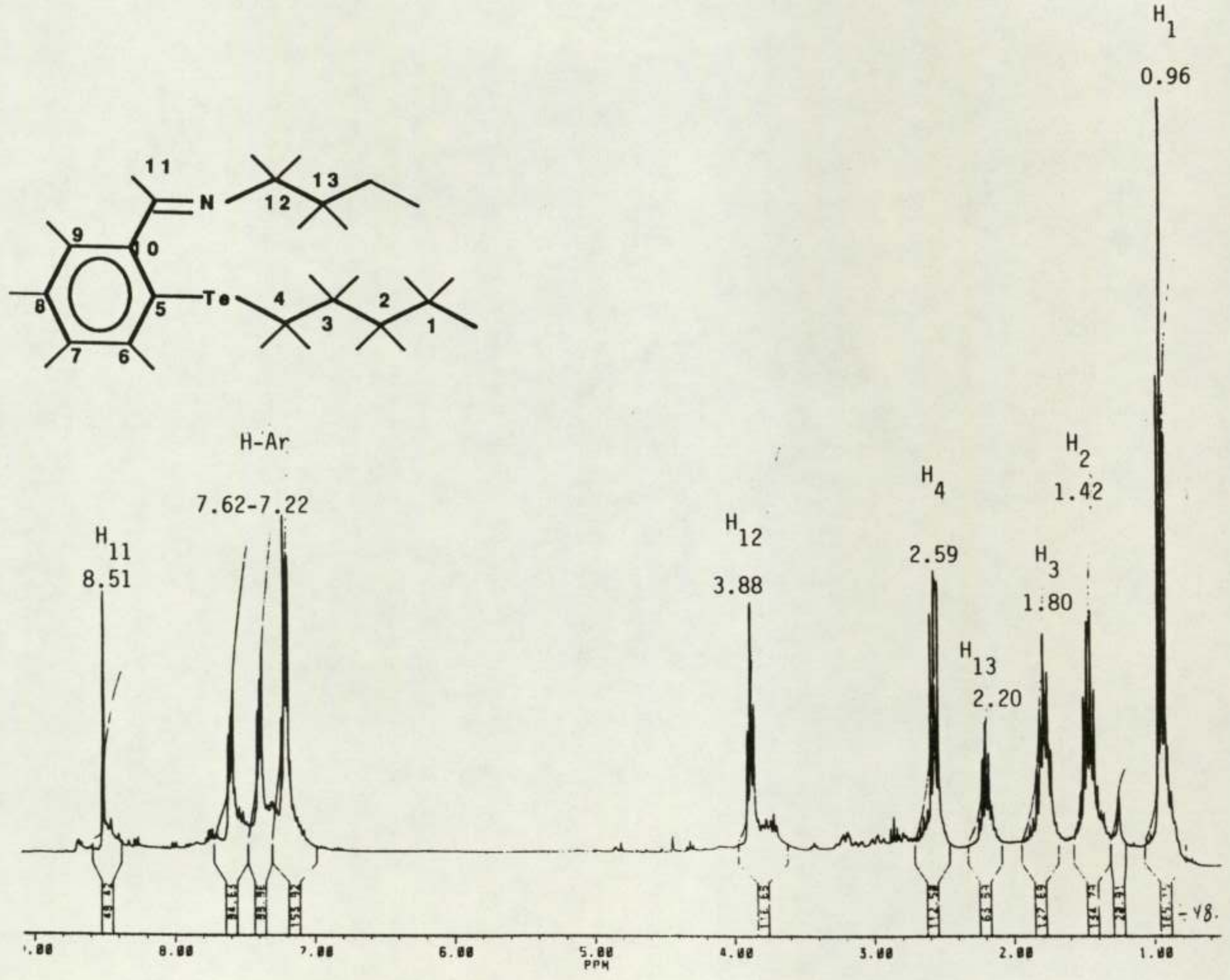


Figure 6.5 ^{1}H NMR spectrum of ligand L.

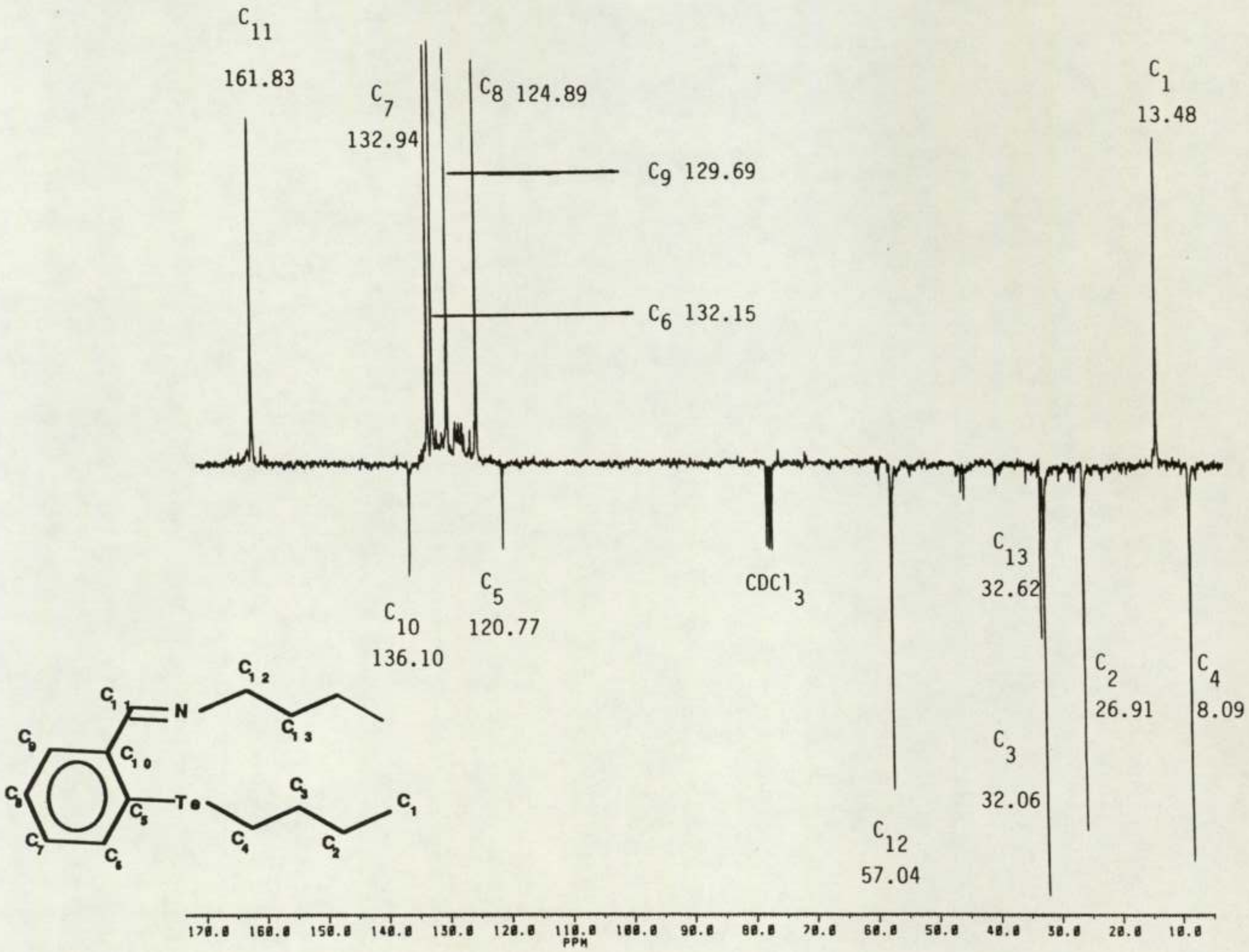


Figure 6.6 $^{13}C[^{1}H]$ NMR spectrum of ligand L.

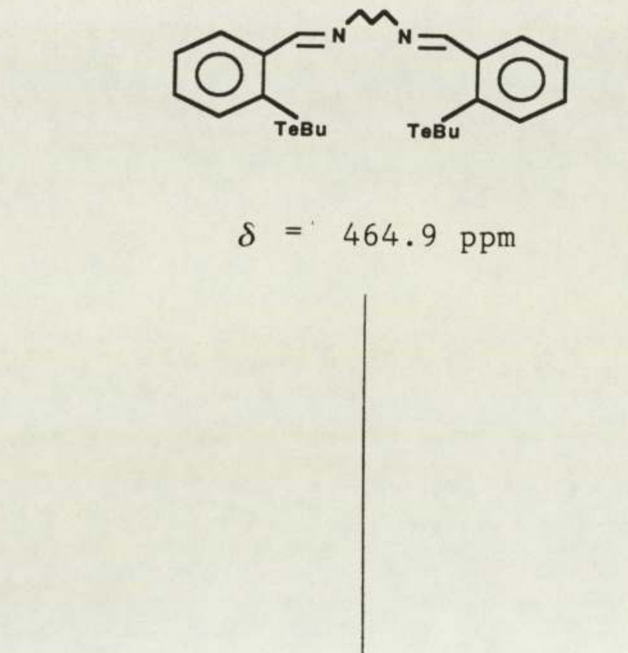


Figure 6.7 $^{125}Te[^{1}H]$ NMR spectrum of ligand L in $CDCl_3$.

the reason for the observed chemical shifts compared to that in (Table 6.5). Thus to explain the high value for δC(<u>ipso</u>) and the low value for δC(<u>para</u>) in the three ligands (Table 6.4) relative to compound (C) in Table 6.5.

The proton-decoupled ^{125}Te N.M.R. spectra of ligand L showed one signal at (δ = 464.9 ppm). While the signals for ligand L' and L" appeared at 464.4 and 464.1 ppm respectively[166].

The close chemical shift values for the three ligands indicate that the tellurium atoms are in similar environments in the three compounds. The Te---N interaction is also expected in ligand L as well as in ligands L' and L"[166], for which no crystal structure is available for ligand L because it is a liquid.

Generally the chemical shifts of the ligands of the three structures were close to each other. These values are close to that reported for PhTeBu^n (468 ppm)[194] and comparable with the value reported for ArTe$(CH_2)_n$TeAr (454.7 ppm)[190].

6.3.2. The Formation of 1,6-Bis-2-tribromotellurophenyl-2,5-diazahexa-1,5-diene

It has been reported that the interaction between tellurium and nitrogen, Te <--- N in ligand L' has a distance of 2.773°A[166]. The question is, does the same interaction occur in Te(IV) compounds?.

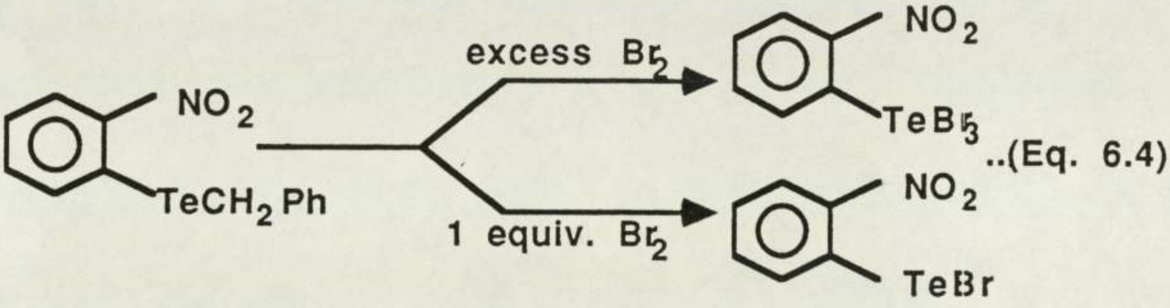
The reaction of ligand L or L' with bromine gave $RTeBr_3$ with a loss of the Bu group from the two ligands. The reaction of diorganyltellurides with the elemental halogen is a widely used method for the synthesis of diorganyl tellurium dihalides (eq. 6.2)[195].

$$R_2Te^{II} + X_2 \longrightarrow R_2Te^{IV}X_2 \qquad \text{(eq. 6.2)}$$

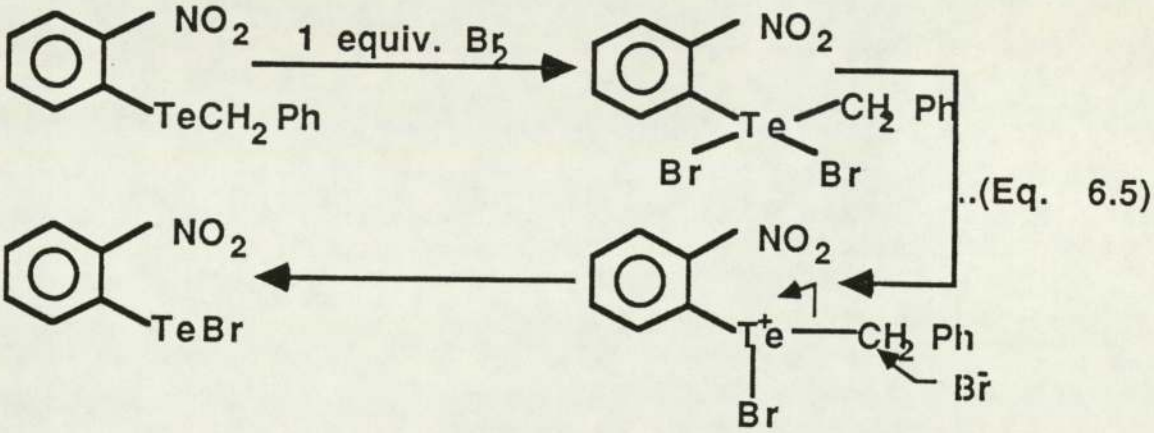
Recently further examples of Te-C bond rupture with Br_2 have been noted thus the reaction of bis-aryltelluroalkanes $ArTe(CH_2)_6TeAr$ with excess bromine led to rupture of the Te-aryl linkage and resulted in bis-tribromotelluroalkanes (eq. 6.3)[190].

$$ArTe(CH_2)_6TeAr + \text{excess } Br_2 \longrightarrow Br_3Te(CH_2)_6TeBr_3 \qquad \text{(eq.6.3)}$$

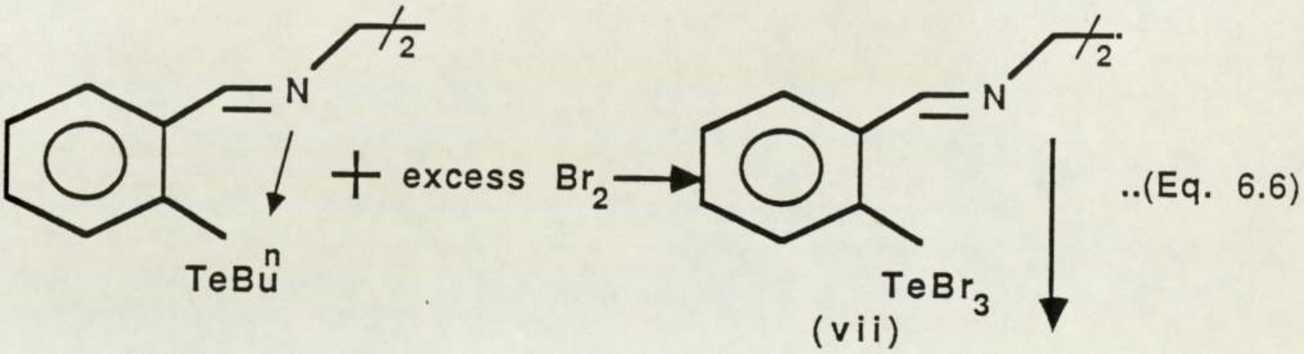
Cava et. al.[196] reported that o-nitrophenyl benzyl telluride reacts smoothly with excess bromine in CCl_4 solution to give (o-nitrophenyl)tellurium tribromide (eq. 6.4). While the direct treatment of o-nitrophenyl benzyl telluride with 1 equiv. of bromine in CCl_4 solution yielded the tellurenyl mono bromide.


..(Eq. 6.4)

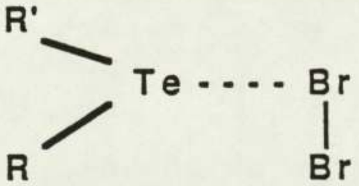
It has been proposed[196] for the second of the above reaction that the initial product was an (arylbenzyl)-tellurium dibromide, which collapses to benzyl bromide and the tellurenylbromide by way of the transient ion pair (eq. 6.5)


..(Eq. 6.5)

In the present work, the addition of excess bromine to the ligand L' (or ligand L) in CCl_4 led to the formation of $RTeBr_3$(VII) (eq. 6.6) with involvement of Te-alkyl cleavage.

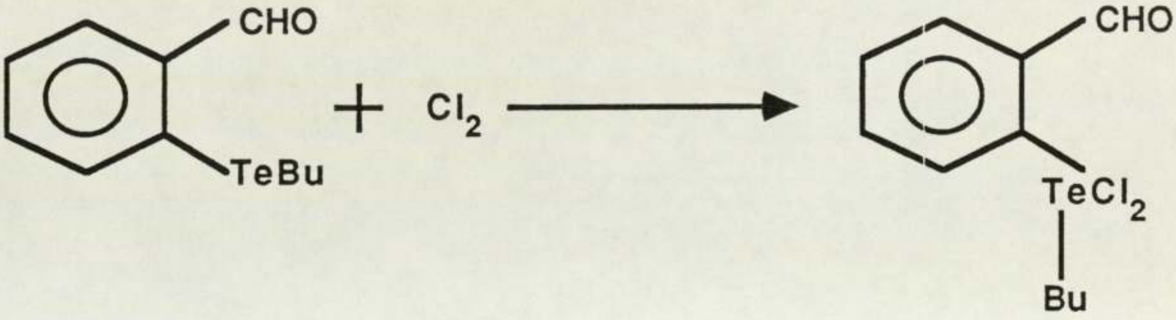


An alternative view of the mechanism is that the "dibromide is in fact a charge-transfer complex(VIII),



(viii)

Which can decompose to give R'TeBr and RBr. If this is the case then Br should form a stronger complex than Cl_2, furthermore the Te...N interaction should make Te a better donor than it would be in a telluride compound without such an interaction, consistant with this we observed the following reaction (see page 167):-



(iv)

6.3.3 Characterisation of the Tribromide Compounds.

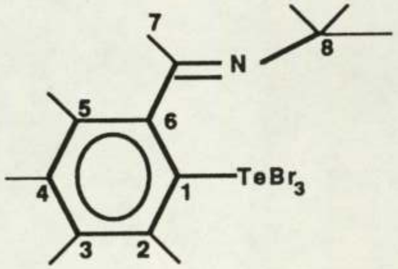
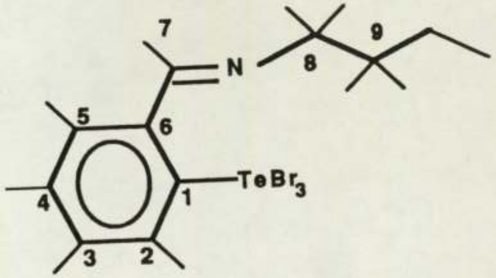
The infra-red, ^1H and ^{13}C N.M.R. spectra for the two new tribromide compounds indicate the absence of the alkyl group (C_4H_9).

The infra-red spectra of the two tribromides showed two bands in the lower frequency region between 247-274 cm^{-1} (for the ethylene derivative ligand tribromide(VII)) and 241-266 cm^{-1} (for the propylene derivative ligand tribromide(IX)), which may be a combination of ν(Te-C) and ν(Te-Br).

McWhinnie et.al.[197], investigated the infra-red frequency spectra of isotopically pure ^{126}Te- and ^{130}Te-, in $(C_6H_5)_2TeX_2$ (X =Cl, Br) and found that bands at 270 and 245 cm^{-1} underwent shifts on isotopic substitution for ν(Te-C). The ν(Te-Cl) modes at 286 and 265 cm^{-1} were also shifted.

^{1}H and ^{13}C N.M.R. chemical shifts are presented in Tables 6.6-6.8 and the spectra are produced in Figures(6.8-6.11) ^{13}C N.M.R. chemical shift assignments were based on comparison with suitable model compounds. Also the estimates of the substituents influence on the aryl moiety of the starting materials using the simple additivity relationship (Table 6.9), and on consideration of peak intensity.

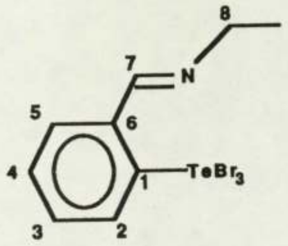
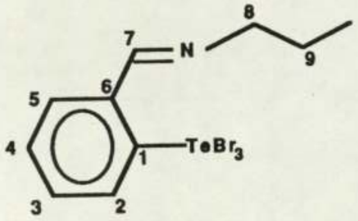
The ^{13}C N.M.R. chemical shift values shows that the effect of $TeBr_3$ group and Te<--N interaction is almost equal to the effect of chlorine (Cl) atom on the δC of benzene ring. This may indicate that there are two factors effecting the chemical shift, the first is the size of the substituent and the second is the electronegativity of the attached group, as well as the number of the unshared electrons on tellurium as mentioned by Kalabin[183].

(a) δ (compound VII)	δ (compound IX)
H_7 = 9.74 (s), 2H	H_7 = 9.79 (s), 2H
H_8 = 4.65 (s), 4H	H_8 = 4.25 (s), 4H
	H_9 = 2.49 (s), 2H
H_{Ar} = 7.58-8.50 (m), 8H	H_{Ar} = 7.63-8.53 (m), 8H
	

(a)-chemical shifts in ppm relative to Me_4Si.

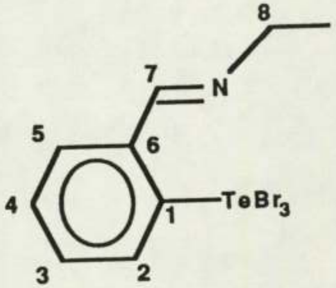
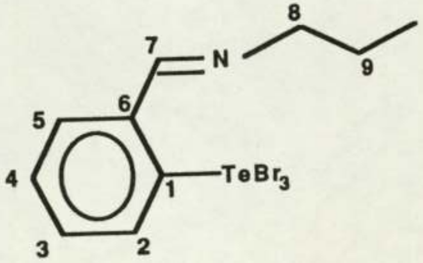
(s)-singlet, (m)-multiplet

Table 6.6 ^1H N.M.R. data of new organotellurium compounds.

compound		chemical shift (a)		
		C-7	C-8	C-9
(vii)		166.71	56.66	-
(ix)		165.62	52.45	34.92

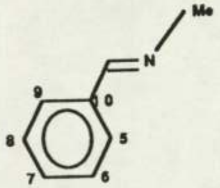
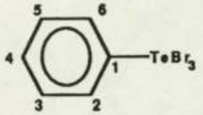
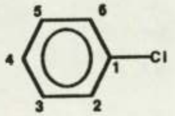
(a) In ppm relative to Me_4Si.

Table 6.7 ^{13}C N.M.R. data (aliphatic region)

Compound		chemical shift (a)					
		C-1	C-2	C-3	C-4	C-5	C-6
(vii)		138.38	133.70	126.85	133.06	131.58	135.64
(ix)		138.17	133.69	126.83	132.90	131.35	136.06

(a) In ppm relative to Me_4Si.

Table 6.8 ^{13}C N.M.R. data (aromatic region)

compound	chemical shift (ppm) relative to $Me_4Si^{(a)}$ C-1	C-2	C-3	C-4	C-5	C-6	ref.
(A) 	129.0 (+0.3)	128.6 (-0.1)	130.8 (+2.1)	128.6 (-0.1)	129.0 (+0.3)	137.3 (+8.6)	192
(B) 	143.8 (+15.1)	135.4 (+6.7)	128.2 (-0.5)	130.0 (+1.3)	128.2 (-0.5)	135.4 (+6.7)	193
(C) 	135.0 (+6.3)	129.1 (+0.4)	130.1 (+1.4)	126.8 (-1.9)	130.1 (+1.4)	129.1 (+0.4)	184
(A + B)	144.1	135.3	130.3	129.9	128.5	144.0	
(A + C)	135.3	129.0	132.2	126.7	130.4	137.7	

(a) values between parentheses are the deviation $\Delta\delta C$ from δC(benzene) taken as 128.7 ppm.

Table 6.9 Application of the additivity principle to compounds related to (VI) and (IX).

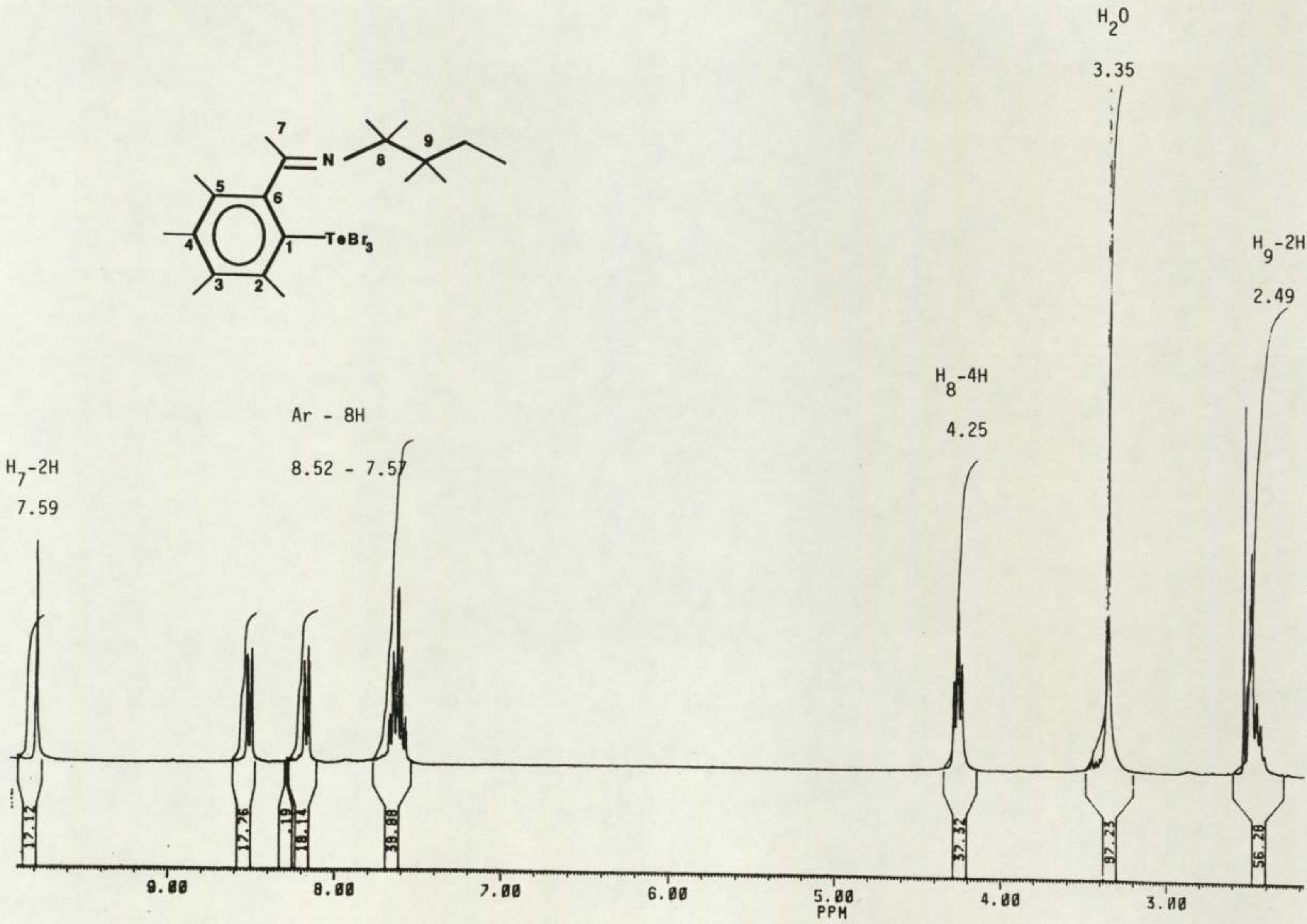


Figure 6.8 ^{1}H NMR spectrum of compound (IX).

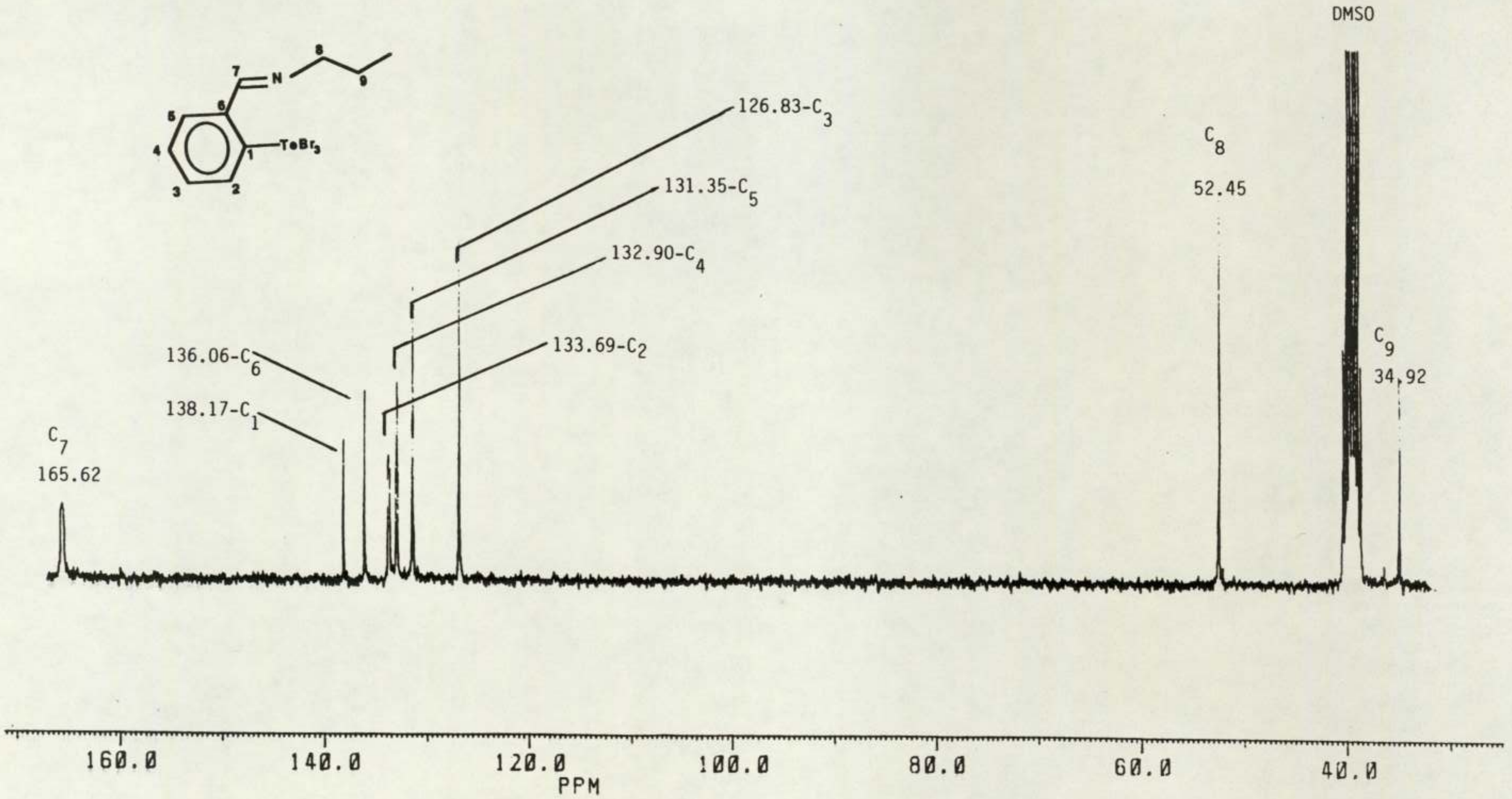


Figure 6.9 $^{13}C[^{1}H]$ NMR spectrum of compound (IX).

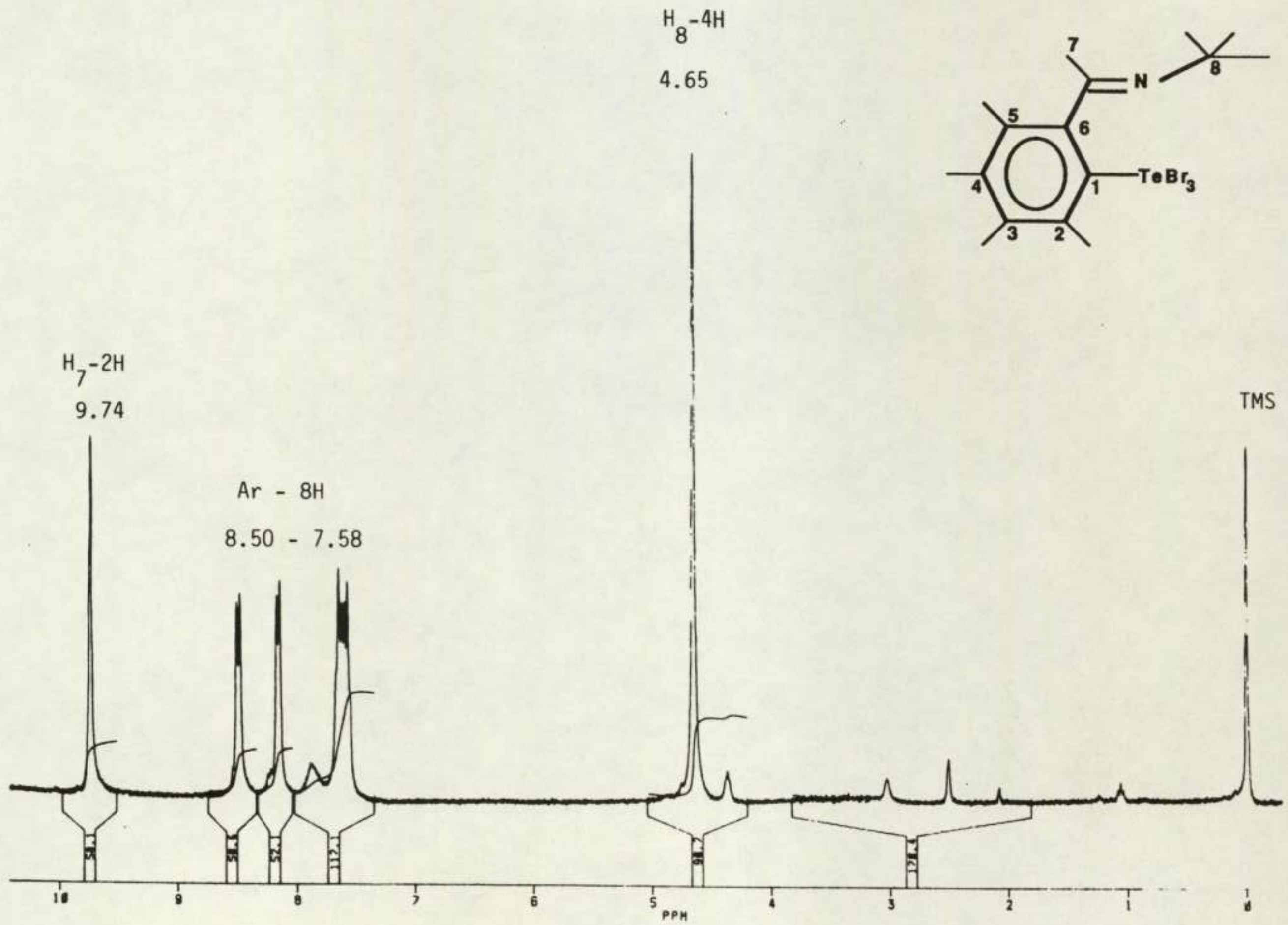


Figure 6.10 ^{1}H NMR spectrum of compound (VII).

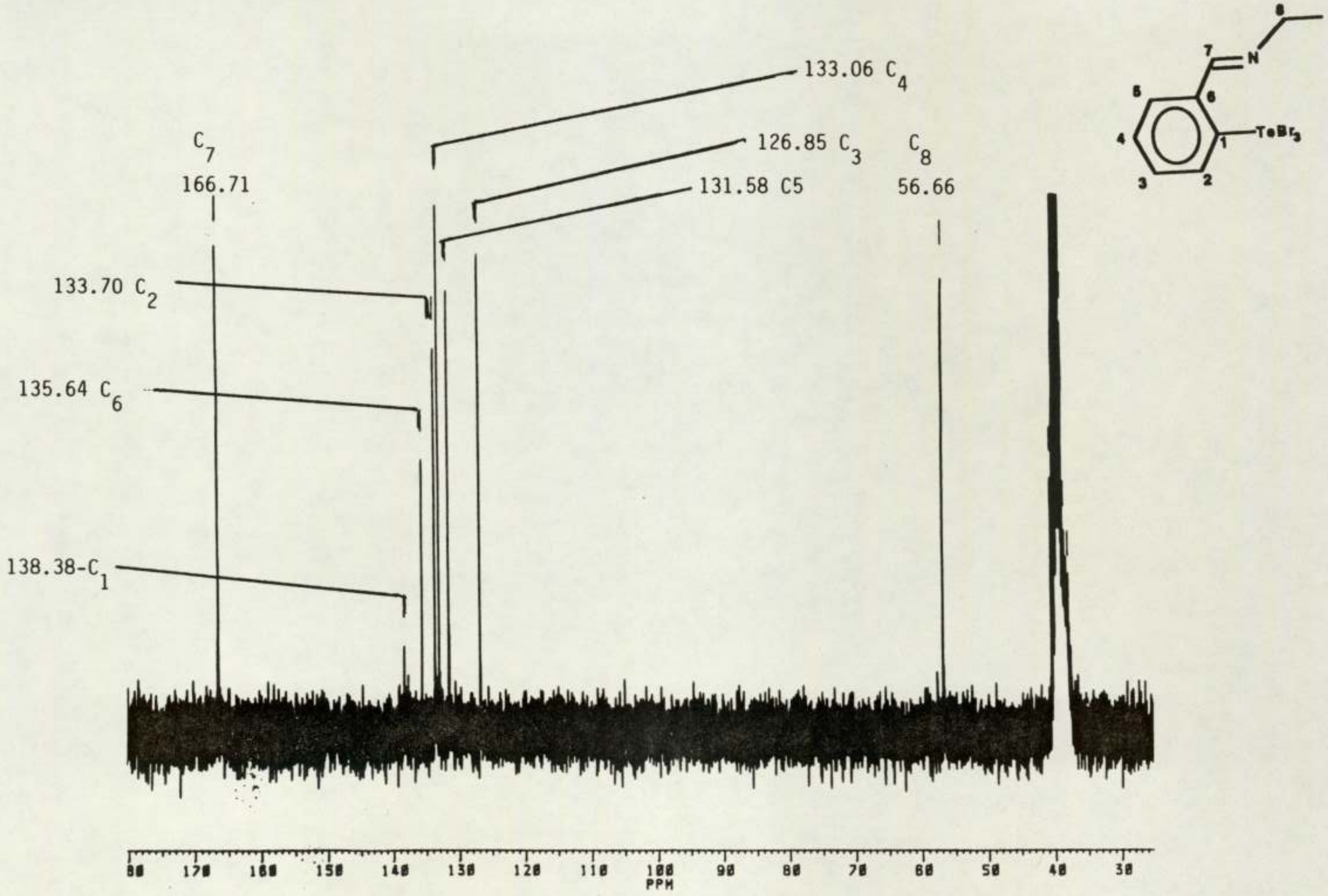


Figure 6.11 $^{13}C[^{1}H]$ NMR spectrum of compound (VII).

6.3.4 Description of 2-Butyldichlorotellurobenzaldehyde Structure

Diorganotellurium(IV) dihalides of the type R_2TeX_2(X = Cl Br or I) have been known for many years. They have been shown to adopt similar molecular structures[71,72,138] with some intermolecular association between tellurium and the halogen atoms.

In these structures the tellurium atom is in distorted trigonal bipyramidal coordination and the halogens, occupy trans axial positions. The organic group are situated in the equatorial plane in which the third position is occupied by a lone pair of electrons. The coordination number may sometimes be increased by a intermolecular bonding through bridging halogens (Figure 1.5, Chapter 1).

The several diorganyltellurium dichlorides which have been structurally characterised tend, at best, to show weak interactions[71,198-200], but two compounds are worth special mention. Ph_2TeCl_2 has the expected trigonal bipyramidal primary structure[201] with one significant long contact of 3.677°A approximately trans to a phenyl group. In one sense the structure becomes a distorted square based pyramid with the lone pair preventing the approach of a sixth ligand.

By contrast phenoxatellurin-10,10-dichloride[202] has discrete stepped tetrameric clusters with intermolecular Te....Cl contacts between 3.368 and 3.504°A (van der Waal's distance, 3.81°A[203]).

It has been pointed out that the structures of other diorganotellurium(IV) dihalides have been described as distorted trigonalbipyramidal, distorted tetrahedral and distorted octahedral according to the significance which has been attributed to intermolecular associations through bridging halogens and the mixing of s with p electrons[204].

The structure analysis of the title compound (IV) reveals a distorted octahedral arrangement (Figure 6.12 and 6.13) in which the chlorine atoms occupy the axial positions. The tellurium atom has a distorted octahedral coordination consisting of two carbon atoms (one from phenyl ring and the other from the alkyl group) to form two sides of the octahedral plane. While the bonds from the oxygen atom (from the aldehyde group in the molecule) are bent to form the third side .The fourth position is (to be) the lone pair of electrons (from the Te atom). The two axial chlorine atoms could complete the octahedral structure of 2-butyldichlorotellurobenzaldehyde molecule (Figure 6.12).

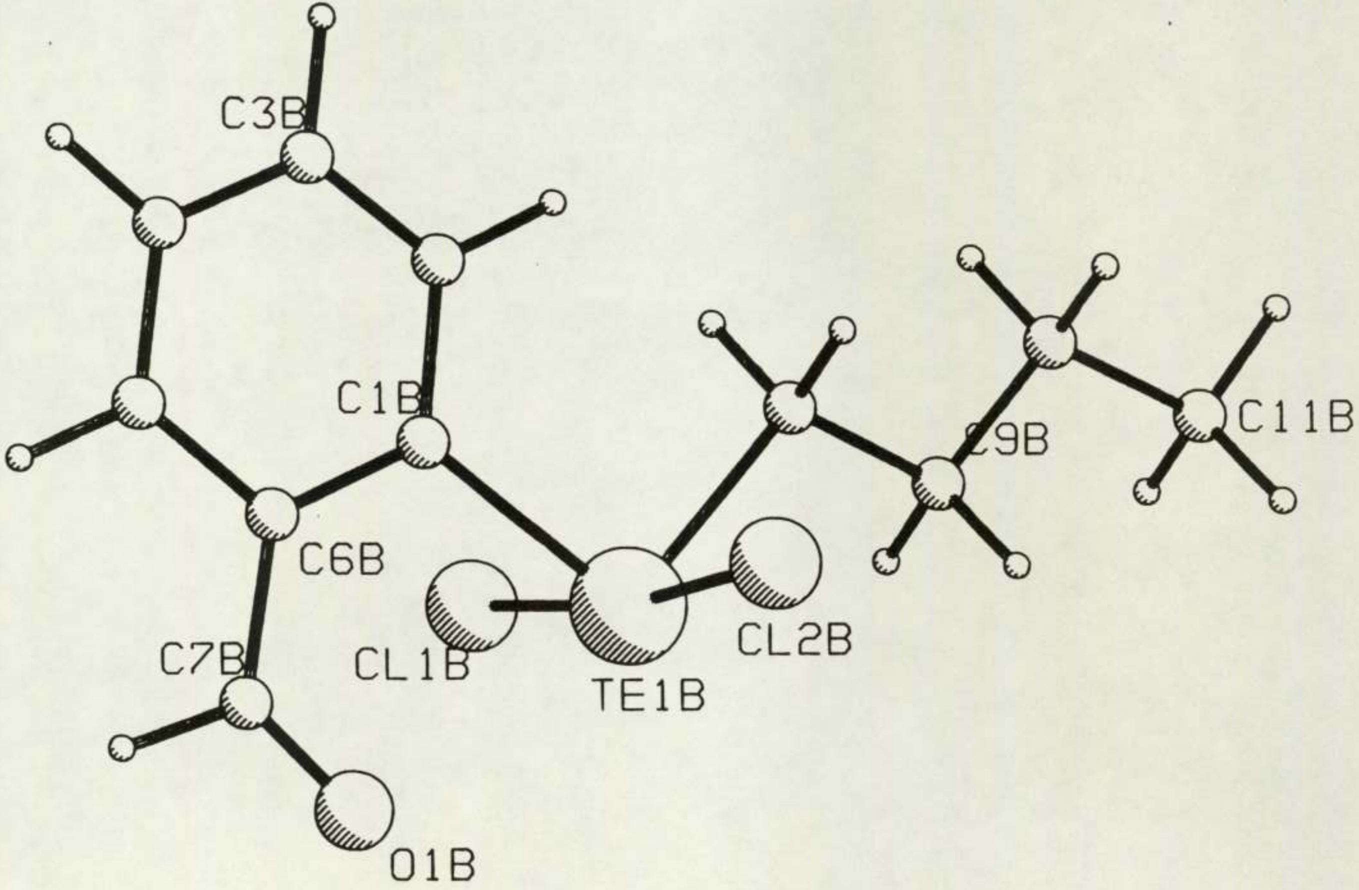


Figure 6.12 The molecular structure of $C_{11}H_{14}OTeCl_2$.

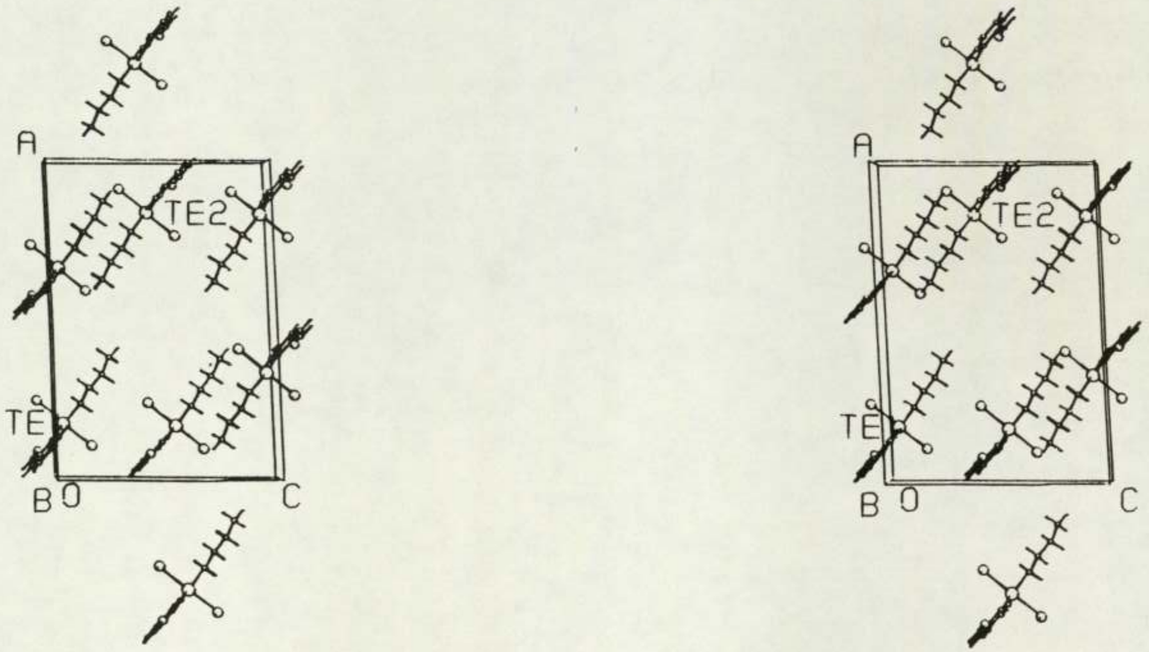
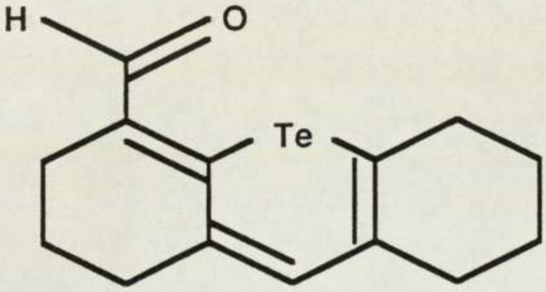


Figure 6.13 A stereoscopic view of unit cell of $C_{11}H_{14}OTeCl_2$.

Compound (IV) has not very strong intramolecular distances (Te....O) of 2.847 and 2.830°A and it contrasts with the tellurium(II) compound(X)[205], which has a Te...O distance of 2.574°A (van der Waal's distances of 3.6[206] or 3.58°A[203].



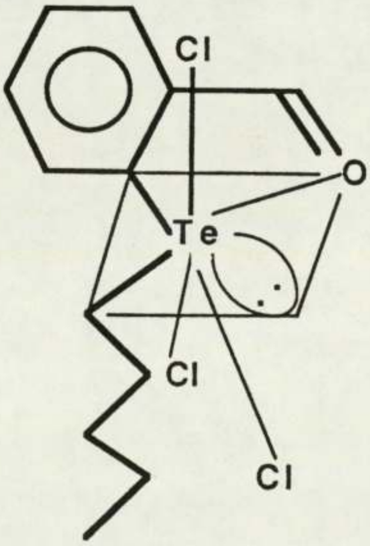
(x)

Also in the title compound (IV), the (Te-Cl) distances are of 2.504 and 2.512°A. These are close to those observed for $(C_6H_5)_2TeCl_2$, (2.53 and 2.48 A)[201] and $(C_{12}H_8O)TeCl_2$ (2.47 and 2.58°A)[202], but longer than those of $TeCl_4$ (mean 2.31°A)[207].

Secondary interactions in different R_2TeX_2 compounds give rise to differing overall structures. In the case of phenoxatellurin-10,10-dichloride[202], four molecules are held together to form discrete tetrameric units, whereas all the other compounds are loosely packed in sheets or chains.

The secondary bonds in compound(IV) range from 3.79 to 3.755°A. They show consiiderably weak intermolecular interaction and are shorter than the sum of the van der Waal's radii for these atoms (4.00°A according to Pauling[206] and 3.81°A according to Bondi[203]). These figures are not unusual for this type of compound if we consider two important factors:

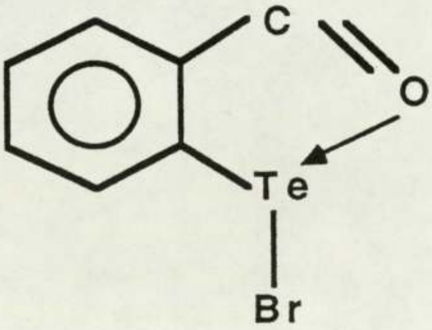
1. The repulsion between Te....Cl (secondary bonds) and the tellurium lone pair, because the chlorine approaches Te is almost in the same direction of the Te lone pair of electrons. This could cause a significant repulsion and elongation of the Te...Cl intermolecular interaction(XI).



(xi)

2. The presence of a donor atom (oxygen from carbonyl group in this case) may increase the electron density at the tellurium atom which makes less favourable the interaction with an approaching chlorine atom from an adjacent molecule. Now it is not surprising that the Te....Cl contact is weak when compared to that of $C_{12}H_{10}TeCl_2$[201] and $C_{12}H_8OTeCl_2$[202].

Dupont at.al.[208] have reported the molecular structure of compound (XII). This compound has a Te-Br of 2.618°A and intermolecular distance of Te...O between 3.586 and 3.944°A also Te....Br distance of 3.919°A.

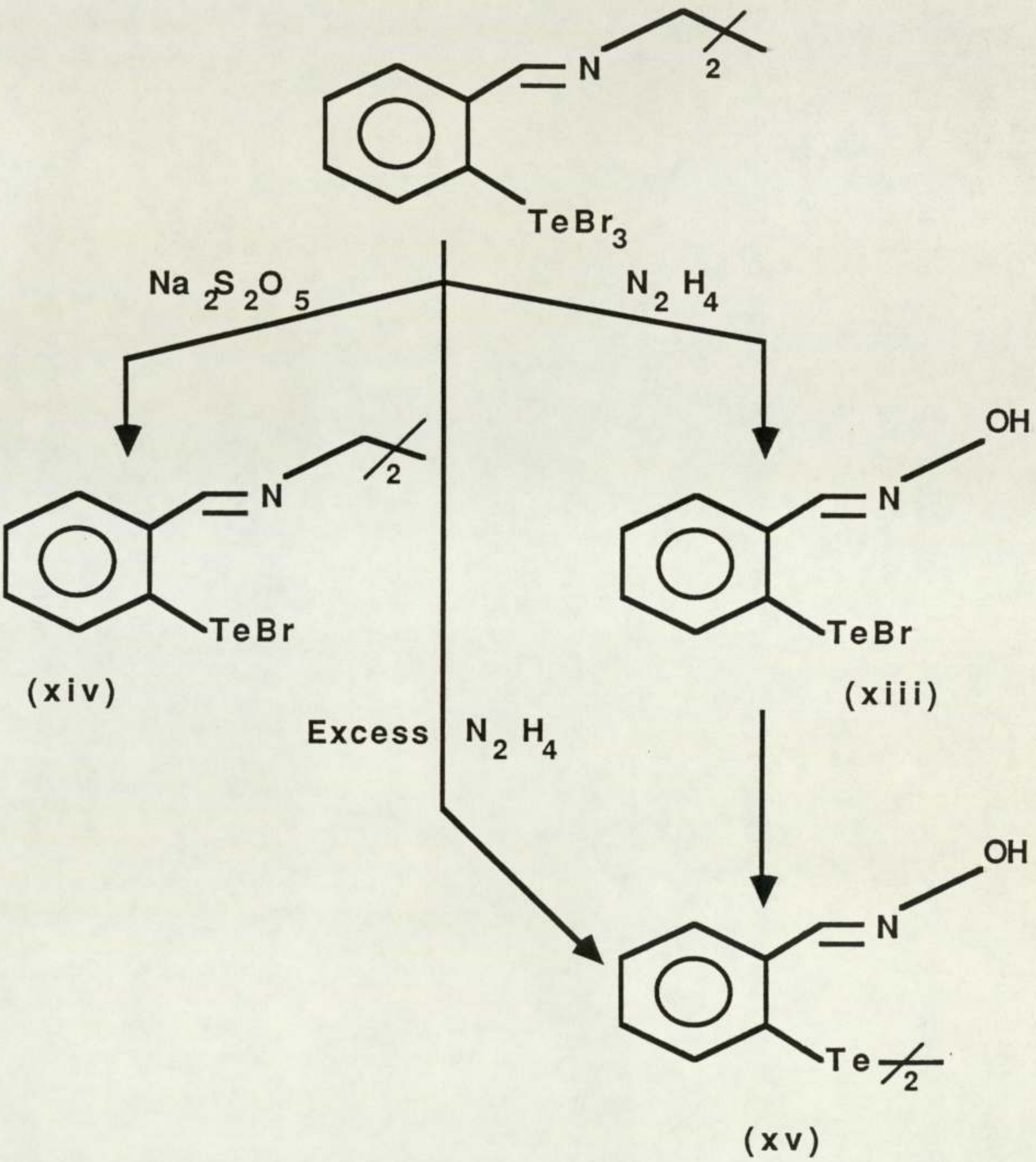


(xii)

6.3.5. Reduction of $RTeBr_3$ Compounds

It was stated recently that the reduction of organotellurium(IV) trihalides, which have a donor group in the ortho- position, with N_2H_4[166,182,209] or with sodium bisulphite [196] gives organotellurenylhalides. The mono halide products could be stabilised by the intramolecular interaction. It has also been reported that the reduction of such trihalide compounds with excess of hydrazine could afford the corresponding ditellurides [182].

Since the trihalide compounds (VII and IX) were available attempts have been made to reduce them with the stoicheimetric quantity of hydrazine hydrate (Scheme 6.3). An unexpected product was obtained as a result of the reduction. This substrate apparently underwent $N-CH_2$ bond cleavage and the nitrogen (from the compound) was hydrolyzed to give the hydroxylamine derivative of the tellurium mono bromide(XIII). While the reduction with sodium metabisulphite ($Na_2S_2O_5$) gave the desired mono bromide compound (XIV) without any trouble. When an excess of hydrazine hydrate was reacted with tribromides, yellow-orange compounds were obtained. The elemental analysis of the new compounds showed that they were ditellurides (XV).



SCHEME 6.3

The elemental analysis data and the strong ν(OH) at 3260 cm^{-1} in the infra-red agree with the formatiom of compound (XIII). The crystal structure of the ditelluride compound (XV) is showm in Figure (6.14). This compound was formed through the further reduction of compound (XIII) or by using excess of hydrazine hydrate with the tribromide compound (VII) (Scheme 6.3). Some of the bond lengths (°A) of compound (XV) are shown below[210].

Te_1-Te_2	2.746
Te_1-C_1	2.136
Te_2-C_8	2.142
N_1-O_1	1.415
N_2-O_2	1.399

The Te...N distance of 2.822 and 2.876°A is well within the van der Waal's distance 3.61°A (Bondi)[203] or 3.7°A(Pauling)[206]. This differs from the covalent bond Te-N (2.1°A) in 1,2-benzisotellurazole(XVI), which has an intermolecular Te...N interaction of 2.47°A. This intermolecular interaction was considered to account for the "anomalous" physical properties of compound (XVI)[144].

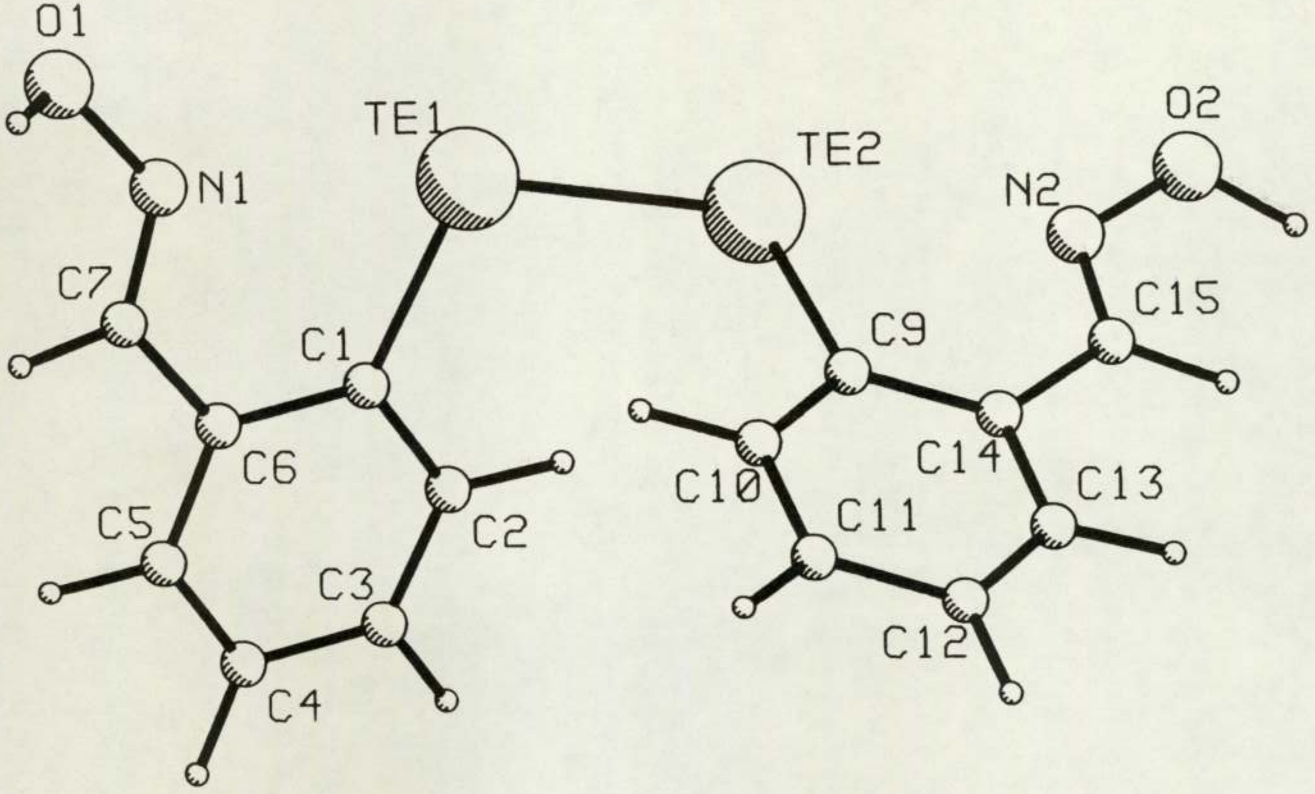
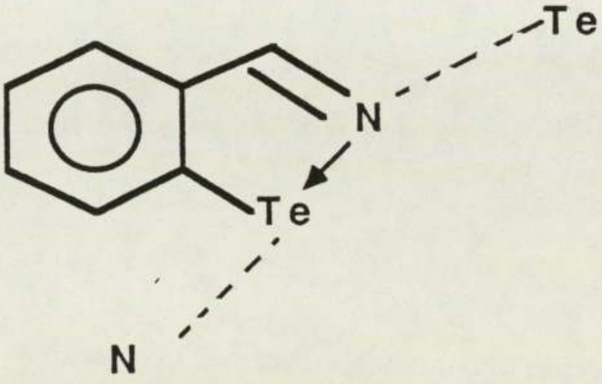


Figure 6.14 The molecular structure of $C_{14}H_{12}N_2O_2Te_2$.

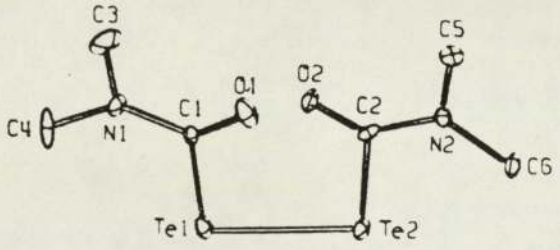


(xvi)

Also it is longer than that of Te...N distance in ligand L' (2.773°A)[166]. This could be due to the lack of a withdrawing group on Te, which causes the unusual strong interaction between N and Te atoms in the compound.

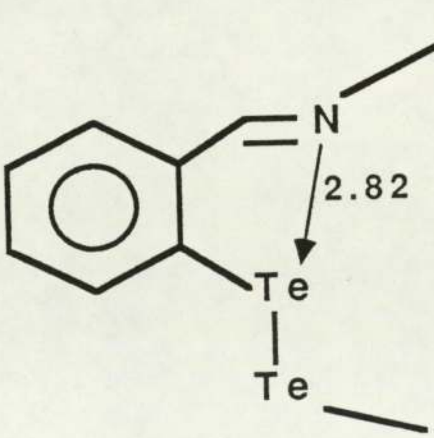
The Te-Te bonded distance (2.746°A) is the longer when compared to some other known ditellurides e.g. Ph_2Te_2 (2.712°A)[193], (p-Cl-C_6H_4)$_2$$Te_2$ (2.69°A)[193], $Ph_2C_4H_2Te_3$ (2.71°A)[211], (p-MeO-C_6H_4)$_2$$Te_2$ (2.72°A)[58] and (p-Cl-C_6H_4)Te_2 (2.68°A)[212].

Recently, the crystal structure of bis(N,N-dimethylaminoformyl)ditelluride has been determined[213], with a very short Te-Te bond distance (2.665°A) and Te-C distance of (2.184°A) (XVII) which is longer than that of Te-C distance (in compound XV) (2.14°A).

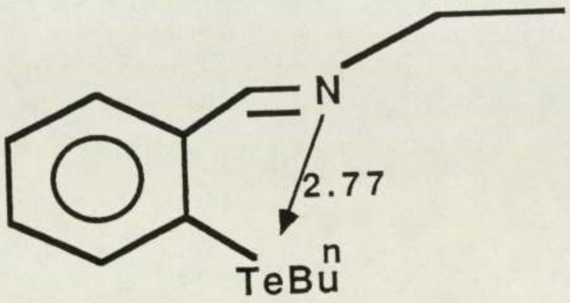


(XVII)

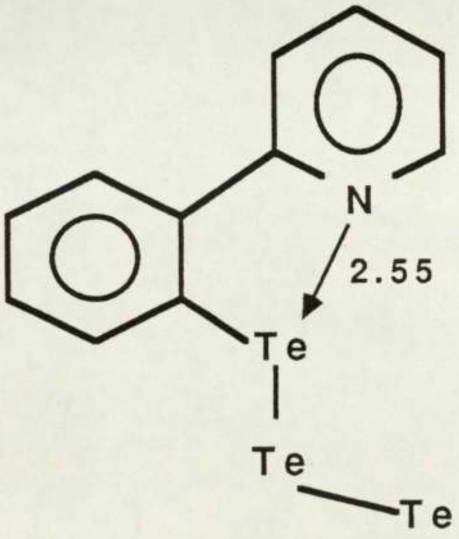
In the above compound (XVII), there is a Te_1...O_1 contact of (2.984°A), Te_1 ...O_2 of (3.341°A) and Te_1 ...N_1 of (3.019°A). While in compound (XV), the Te...N contacts are 2.822 and 2.876°A. Also the Te...N distance in compound (V) is 2.77°A and 2.55°A in compound (XVIII)[166].



(xv)

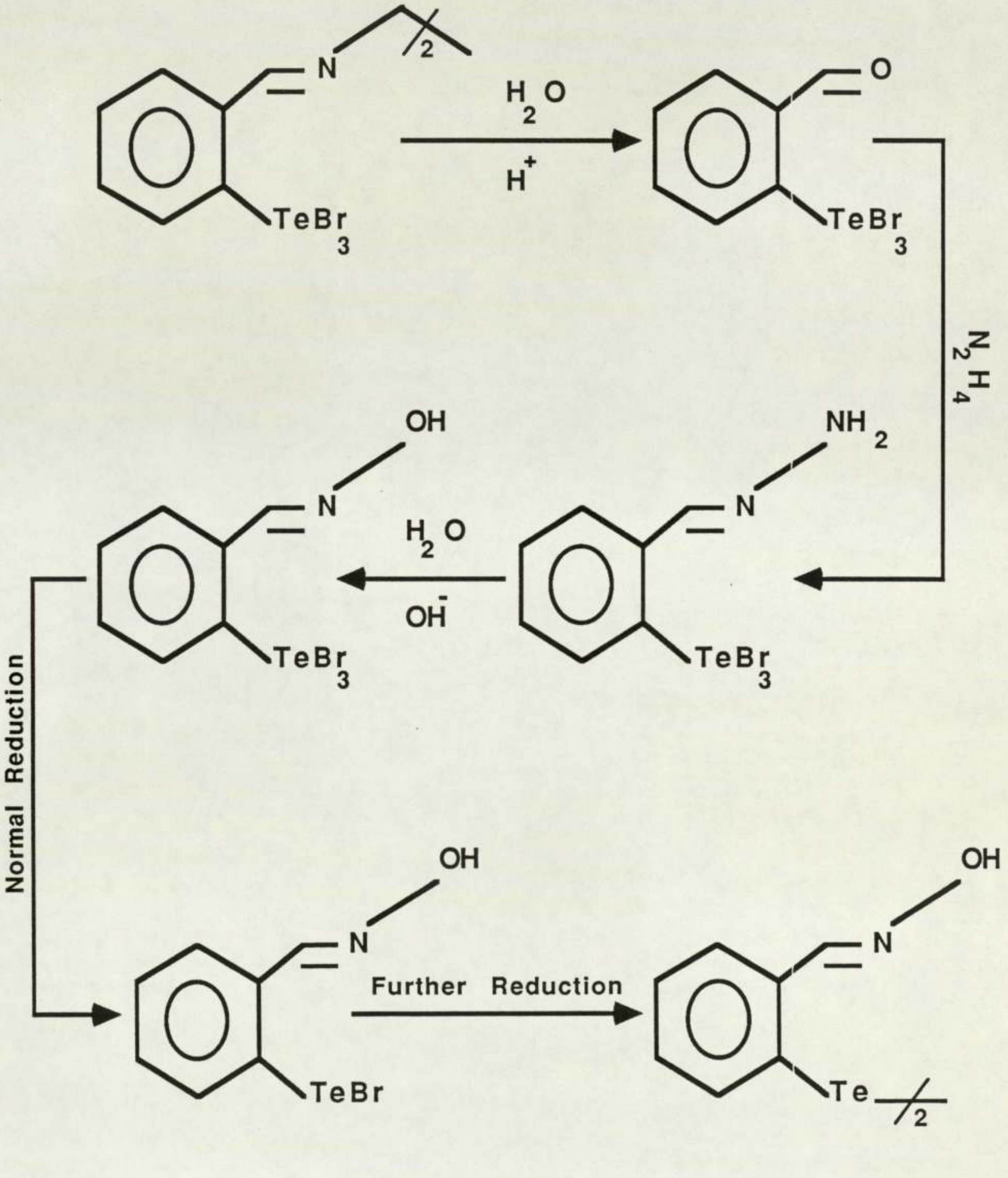


(v)



(xviii)

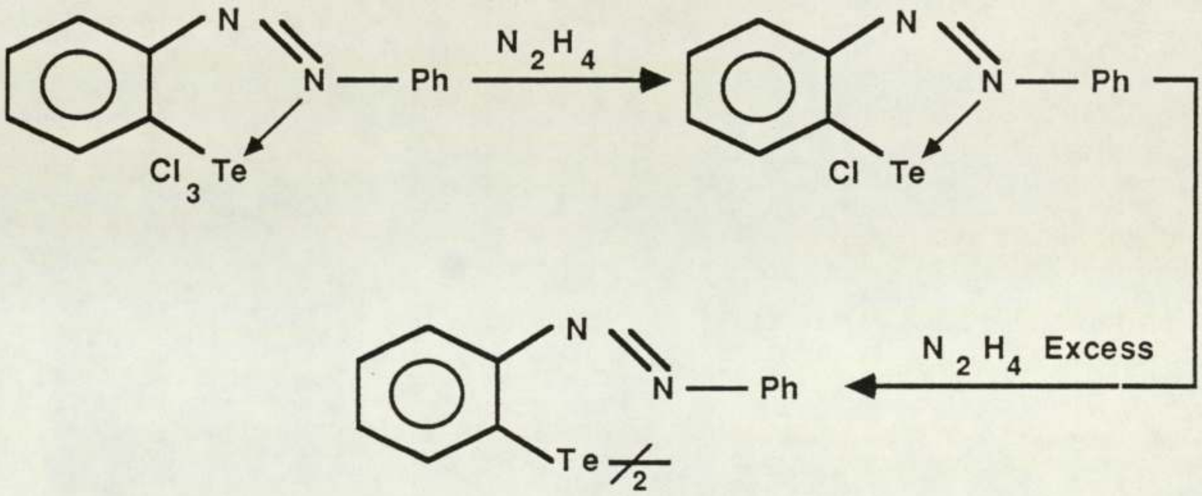
The reduction reaction mechanism of the tribromide compounds with hydrazine hydrate is not clear, but may be as follows:-



H_2O
H^+
TeBr₃
O
N_2H_4
NH₂
N
OH
H_2O
OH^-
Normal Reduction
Further Reduction
TeBr
Te
2

SCHEME 6.4

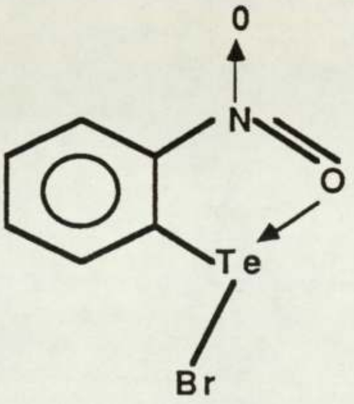
The observation by Bergman[214] that hydrazine reacts with aryltellurium trihalide to give diaryl ditelluride, led one of our colleagues in the laboratory to reduce $(C_{12}H_9N_2)TeCl_3$ as illustrated below (Scheme 6.5):-



SCHEME 6.5

No broken bond was yielded in this case, because of the strong interactions of (-N=N- 1.25°A) and (N-Ph 1.42°A)[182], while N is bonded to two alkyl carbons in compound (VII and IX) which is easier to break.

breaking the $=N-CH_2$ bond (Scheme 6.3). However the analytical data and the infra-red have confirmed the existance of compound (XIV) (page 218). This mono bromide compound could also be stabilised by the intramolecular interaction of Te<--N, similar to Cava's point[196], that the o-nitro group can serve as an efficient stabilising ligand (XIX).



(xix)

6.3.6 Complexes of Ligands L and L'

Interest in ligands containing a heavier group 6A donor atom, sulphur, selenium or tellurium and their coordination compounds has grown substantially in the last two decades.

Many mercury(II) compounds have been published in which the mercury ions show an affinity towards hard ligands as well as soft ligands. A mercuric phenyltellurol complex was prepared and the structure of its tetraphenylphosphonium salt was reported (Figure 6.15)[215].

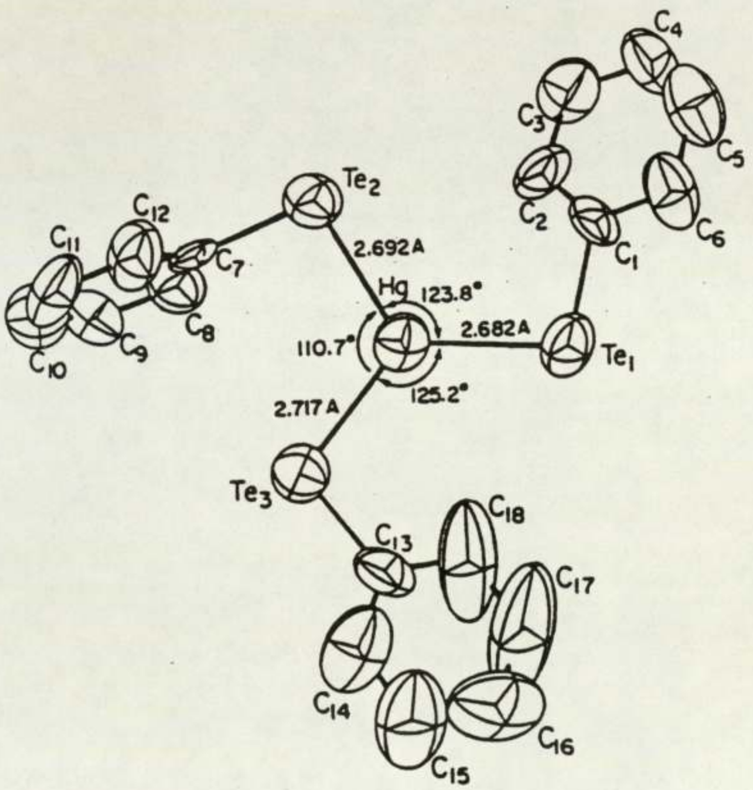


Figure 6.15 Molecular structure of $[Hg(TePh)_3]^-$.

Recently, some new bis-telluride ligands have been prepared within the tellurium group at Aston University. The Pd(II), Pt(II) and Hg(II) complexes of these new bis-telluride ligands have been investigated[190]. Also recently, the preparation of ligand(L') and its complex with mercury (II) chloride was the subject of a struture determination (Figure 6.16)[166].

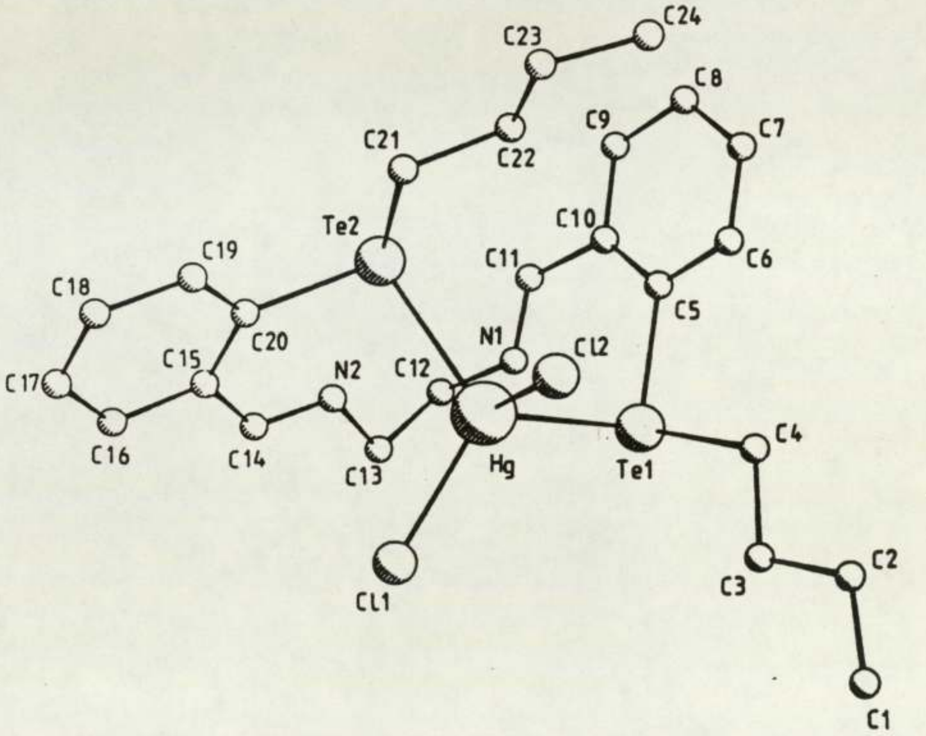
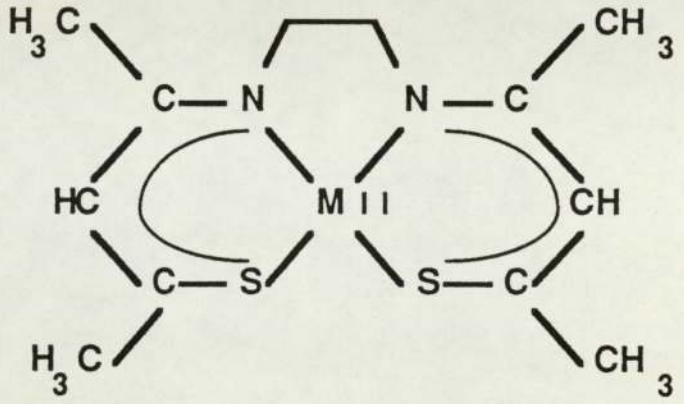


Figure 6.16 The molecular structure of $HgCl_2.L'$ complex.

In spite of the extensive investigation of the coordination chemistry of ligands containing group 6A with different transition elements[216], the use of organotellurium compounds with cadmium metal particularly has been paid little attention and remained very limited.

However, Blum[217] has synthesised a series of metal complexes containing a tetradentate Schiff base ligand (XX):-



(xx) M(II)= Ni , Cu , Co , Pd , Zn , Cd.

Coates[218] claimed that dimethyl telluride forms a complex with cadmium iodide, but no details were given. Although, cadmium complexes with $Te(E\ Et_3)_2$ (E= Ge, Sn) have been prepared and characterized (eq. 6.8)[219].

$$Cd(Ge(C_6F_6)_3)_2 + n\ Te(E\ Et_3)_2 \rightarrow Cd(Ge(C_6F_3)_2(Te(EEt_3)_2)_n \qquad \text{(eq. 6.8)}$$

$E = Ge, n=1$; $E = Sn, n=1,2$

In the present study a mercury(II) chloride complex with ligand(L) and cadmium(II) bromide complex with ligand(L') has been prepared.

Firstly the reaction of compound(VI) with mercury(II) chloride in a mixture of acetone and ethanol gave a 1:1 complex according to the elemental analysis (Table 6.10). The recrystallised new complex, from nitromethane gave pale-yellowish crystals. The molar conductivity of a solution of this complex (10^{-3}mol.l^{-1}) is 3.2 $ohm^{-1}cm^{2}mol^{-1}$ in nitromethane at room temperature. This low value suggests a strong mercury-ligand interaction and the non ionic character of the compound.

Since the molecular structure of complex $HgCl_2$.L' is available (Figure 6.16)[220] one should not expect big difference with complex $HgCl_2$.L. (Table 6.10).

The infra-red spectrum of complex $HgCl_2$.L showed a slight shift in the imine group ν(C=N) to a higher energy (1643 cm^{-1}) (Table 6.11). This band become less sharp due to the complexation with mercury. New bands which were weak and medium appeared in the fingerprint region. These changes are similar to those in complex $HgCl_2$.L', which

Complex	Elemental Analysis C% (req.)	 H% (req.)	 N% (req.)	Colour	M. Pt°C
Ligand (L)	48.4	5.61	4.50	yellow	-
	(48.9)	(5.50)	(4.53)	liquid	
$HgCl_2$.L	33.6	3.71	3.00	white	137
	(33.8)	(3.83)	(3.15)	yellow	
Ligand(L')*	47.4	5.50	4.60	yellow	83-85
	(47.7)	(5.30)	(4.64)		
$CdBr_2$ .L'	32.8	3.40	2.93	white	151-152
	(32.9)	(3.65)	(3.20)		

* reference[166]

Table 6.10 Analytical data for the complexes L and L'.

Complex	ν(C=N) cm^{-1}	$\Delta\nu$(C=N) cm^{-1}	ν(M-X) cm^{-1}	$\Omega^{(a)}$
Ligand (L)	1638			
$HgCl_2.L$	1643	+5	315	3.2 (CH_3NO_2)
Ligand (L')	1637			
$CdBr_2.L'H_2O$	1642	+5	305	4.1 (DMSO)

(a) molar conductivity ($ohm^{-1}cm^2mol^{-1}$) of 10^{-3}M solution.

Table 6.11 Infra-red and molar conductivities data for the complexes of L and L'.

were attributed to the rotation of half of the molecule along the alkyl C-C bond of the ethylene diimine group. The rotation, movement was explained in terms of necessity to bring both Te atoms within bonding distance to mercury[166]. This could be the same in $HgCl_2.L$ complex. A weak band at 315 cm^{-1} could be assigned as ν (Hg-Cl), which was at 312 cm^{-1} for the complex $HgCl_2.L'$[166].

The complexes of ligand (L') with Hg, Rh, Pd and Pt have been studied[166]. The reaction of the same ligand with $CdBr_2.4H_2O$ in a mixed solvent of ethanol and methanol resulted in a 1:1 white coloured complex. The elemental analysis, (Table 6.10) confirmed this composition. The molar conductivity measurement of a solution of this complex ($10^{-3}mol.l^{-1}$) is 4.1 $ohm^{-1}cm^2mol^{-1}$ in DMSO at room temperature. This value indicates that the compound is non ionic and the formula based on the elemental analysis is 1:1.

The infra-red spectrum of $CdBr_2.L'$ showed that the imine stretching vibration, ν(C=N) at 1642 cm^{-1} (Table 6.11) with a limited shift. A clear change in the fingerprint part was seen, with new medium and sharp bands. The medium band at 305 cm^{-1} could be assigned for ν(Cd-Br) which appears normally around 319 cm^{-1}[221].

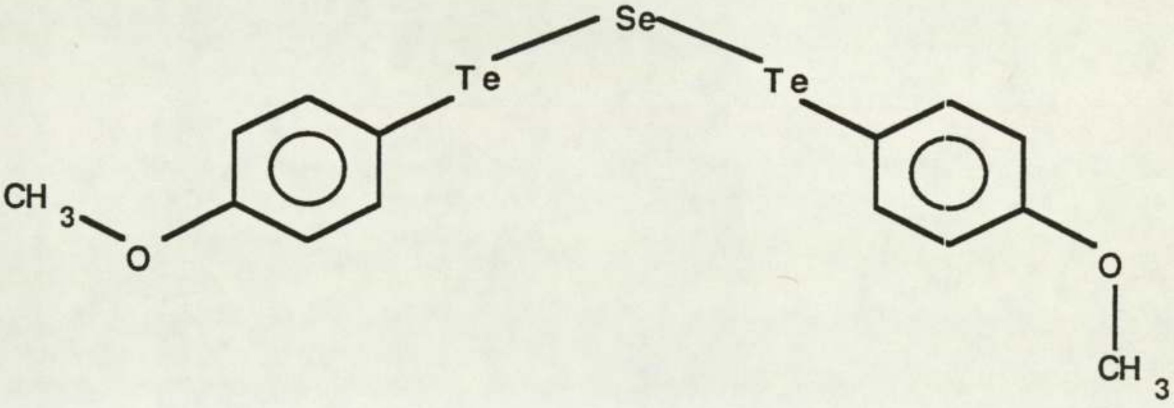
6.3.7 The Synthesis of a Tritelluride Compound

Only a limited number of triselenids and tritellurides are known. In general, they are difficult to obtain in good yield and in high purity. The infra-red spectra of related di- and triselenides and -tellurides do not vary appreciably.

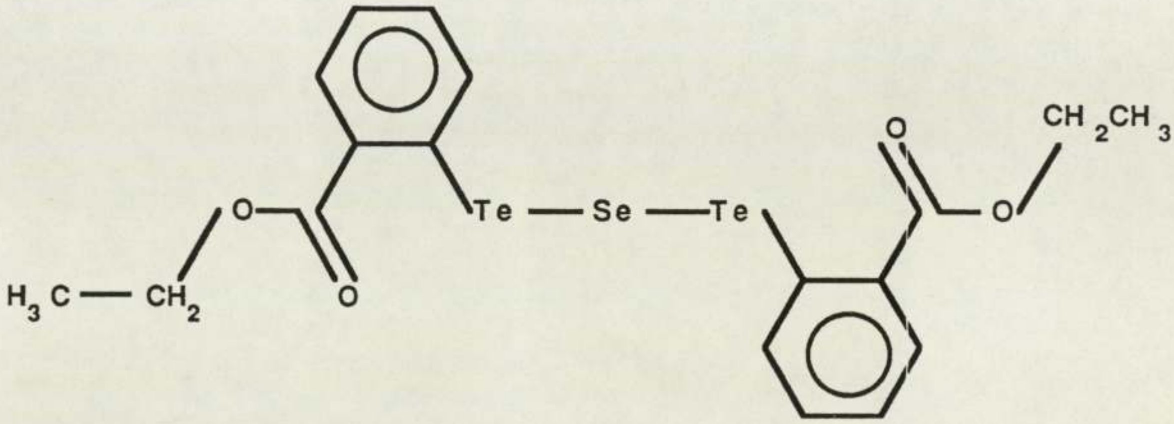
The first triselenides were reported by Levi and Baroni (equation 6.9)[147].

$$4C_2H_5SeH + SeOCl_2 \longrightarrow C_2H_5SeSeSeC_2H_5 + C_2H_5SeSeC_2H_5 + 2\,HCl + H_2O \qquad (eq.6.9)$$

Zingaro et. al.[222] have reported the molecular structures of bis(4-methoxybenzenetellurenyl)selenide (XXI) and bis-(2-ethylcarboxybenzenetellurenyl)selenide (XXII), with Te....O interaction (2.658°A).

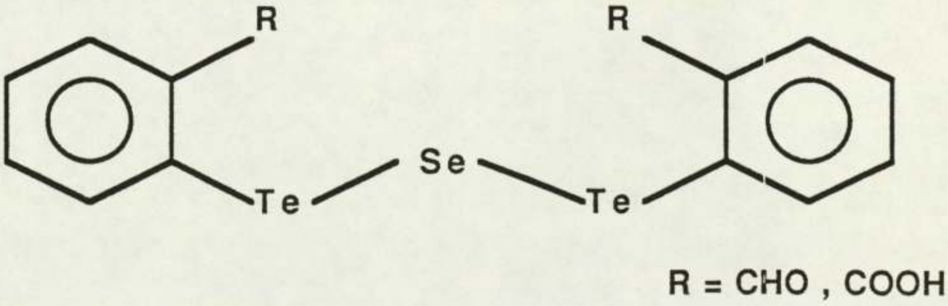


(xxi)



(xxii)

The preparation and N.M.R. study of $(ArTe)_2Se$ compounds (by reacting the ditellurides with SeO_2 in hot pyridine) has been reported (XXIII)[223].



(xxiii)

In 1985, Sladky et al[224] reported the molecular structure of $[(Me_3Si)_3C]_2Te_3$ (XXIV) which involves a Te-C bond. The preparation was as follows:-

$$\text{TsiLi} \xrightarrow{2\ \text{Te}} \text{TsiTeTeLi} \xrightarrow{H_2O/O_2} \underset{\text{red-black crystals (XXIV)}}{\text{TsiTeTeTeTsi}} \quad \text{(eq.6.10)}$$

Tsi = tris(trimethylsilyl)methyl-

At the time of reporting this compound (XXIV), a number of colleagues in the tellurium team (Aston University) were due to publish the synthesis and molecular structure of bis(2-(2-pridyl)phenyl tritelluride (XVIII) as a novel tri-telluride compound (Figure 6.17)[225].

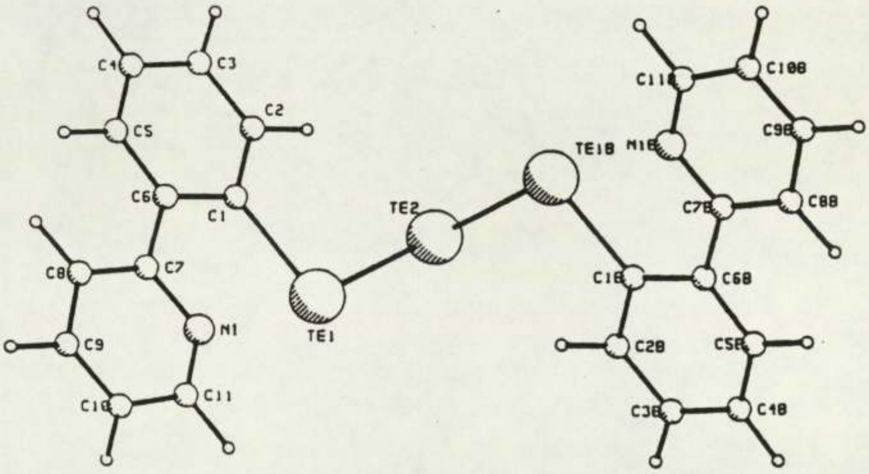


Figure 6.17 The molecular structure of bis[2-(2-pyridyl)-phenyl]tritelluride.

Very recently, the molecular structure of $[R_3P\text{-}Te\text{-}Te\text{-}Te\text{-}PR_3]^{2+}$ has been published[226]. The Te-Te bond length is of 2.71°A and weak P-Te of 2.50°A (Figure 6.18).

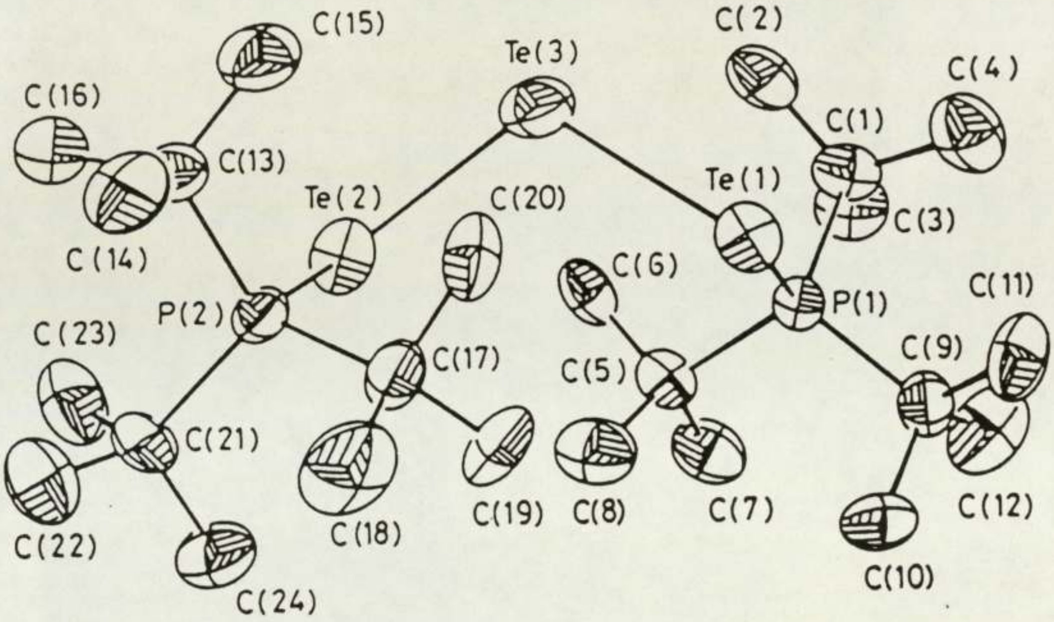
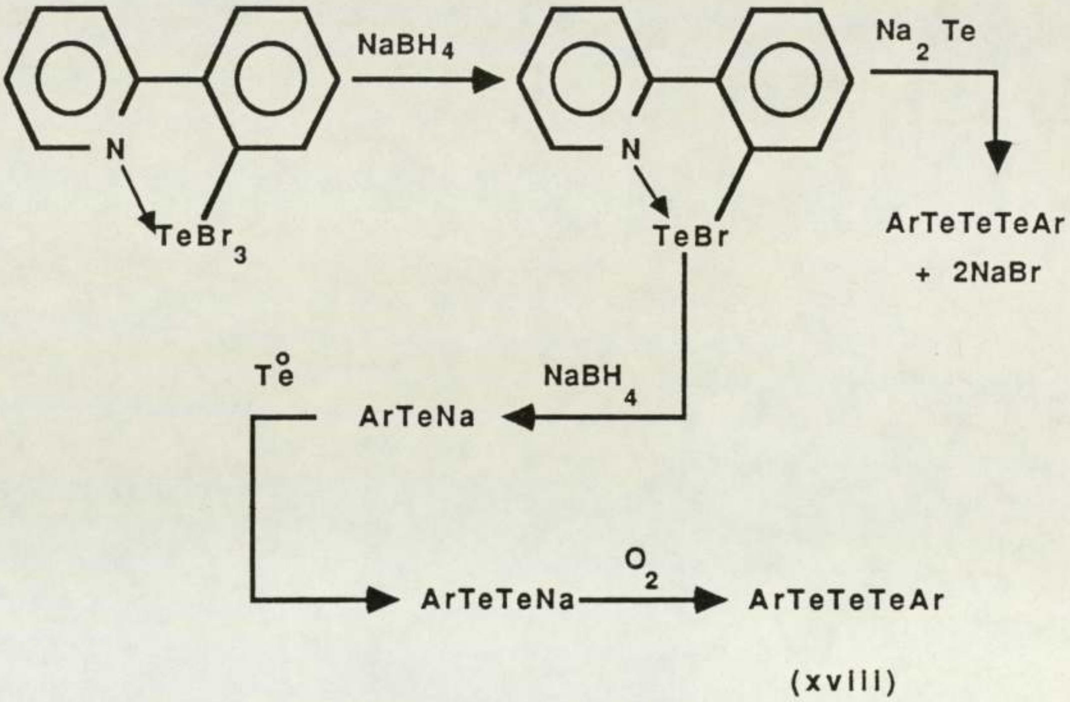


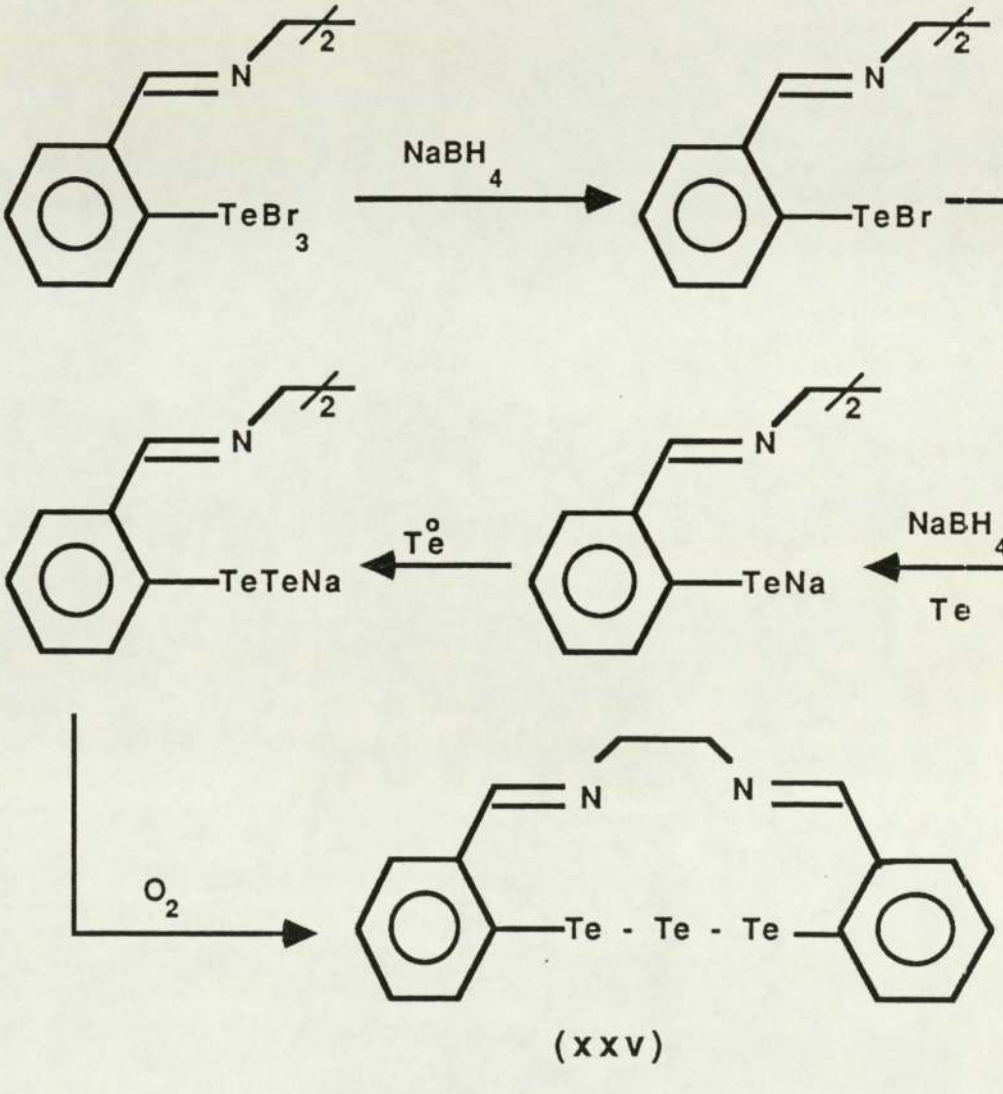
Figure 6.18 The molecular structure of $[R_3P\text{-}Te\text{-}Te\text{-}Te\text{-}PR_3]^{2+}$.

The preparation of <u>bis</u>(2-(2-pyridyl)phenyl)tritelluride was achieved by the reduction of 2-(2-pyridyl)phenyltellurium tribromide with $NaBH_4$ in ethanol solution. The suggested mechanism for this preparation is shown in Scheme (6.6)[166].



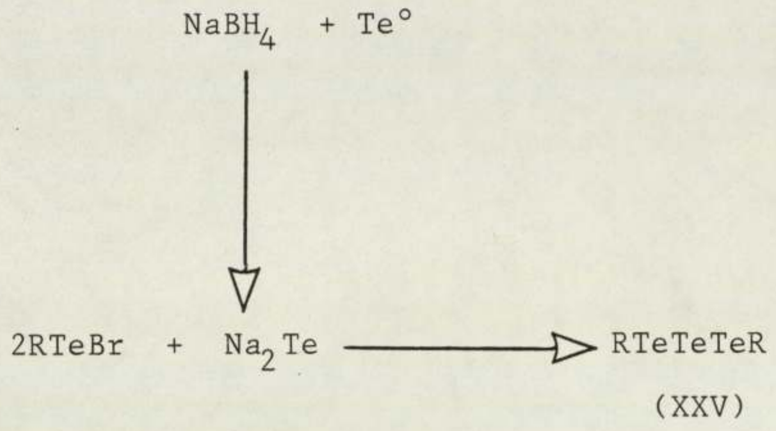
SCHEME 6.6

In the present work attempts were made to synthesise a cyclic maritelluride using ligands L and L'. The reduction of 1,6-bis-2-tribromotellurophenyl-2,5-diazahexa-1,5-diene(VII) with $NaBH_4$ and tellurium metal resulted in an orangish coloured compound. The elemental analysis of this material confirmed the formation of a new tritelluride compound. This tritelluride compound is either cyclic or polymeric. The lack of suitable crystals for crystal structure determination has prevented the final judgement from being made to date. However the use of sodium borohydride in this experiment gave no problem with the $C=N-CH_2$ group. This is in contrast to the reaction observed when using hydrazine hydrate. The possible mechanism for the synthesis is indicated in Scheme 6.7:-



SCHEME 6.7

An alternative mechanism for this reaction is as follows:-



$$\begin{tikzcd} NaBH_4 + Te^{\circ} \arrow[d] & \\ 2RTeBr + Na_2Te \arrow[r] & \underset{(XXV)}{RTeTeTeR} \end{tikzcd}$$

Scheme 6.8

The infra-red spectrum of the new tritelluride compound (XXV) is different from that of the starting material (the tribromide compound (VII)).

The ^{13}C N.M.R. spectrum of this tritelluride compound (Figure 6.19) shows some interesting features. The most interesting point is the resonance of the tellurated carbon (C1—131.99 ppm) (Table 6.12) with a shift of 6.37 ppm higherfield compared to the corresponding tribromide compound (Table 6.8). While (C-1) in compound (XXIII) is 120.4 ppm. The difference here could be related to the structure of this tritelluride compound (XXV). There is a clear shift of C7 (140.79 ppm) compared to the same carbon position in the tribromide compound (C7 —166.71 ppm). C8 and the rest of the

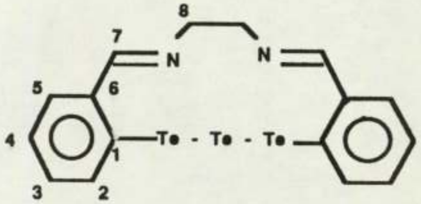
Compound	^{13}C - chemical shifts (ppm) relative to TMS							
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
	131.99	131.67	126.96	129.73	128.63	-	140.79	54.55

Table 6.12 ^{13}C N.M.R. data for the tritelluride compound (XXIV).

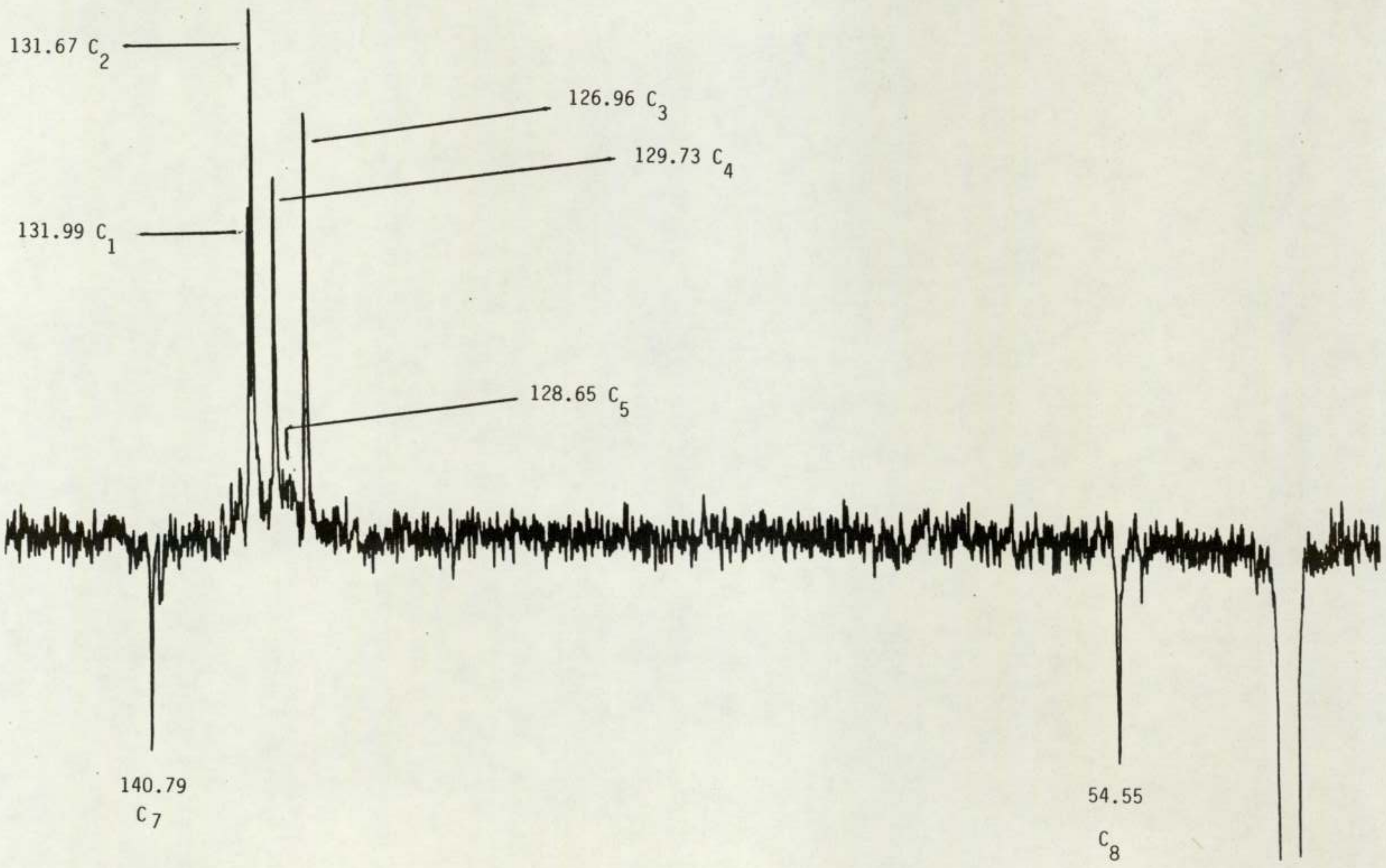


Figure 6.19 $^{13}C[^{1}H]$ NMR spectrum of compound (XXIV).

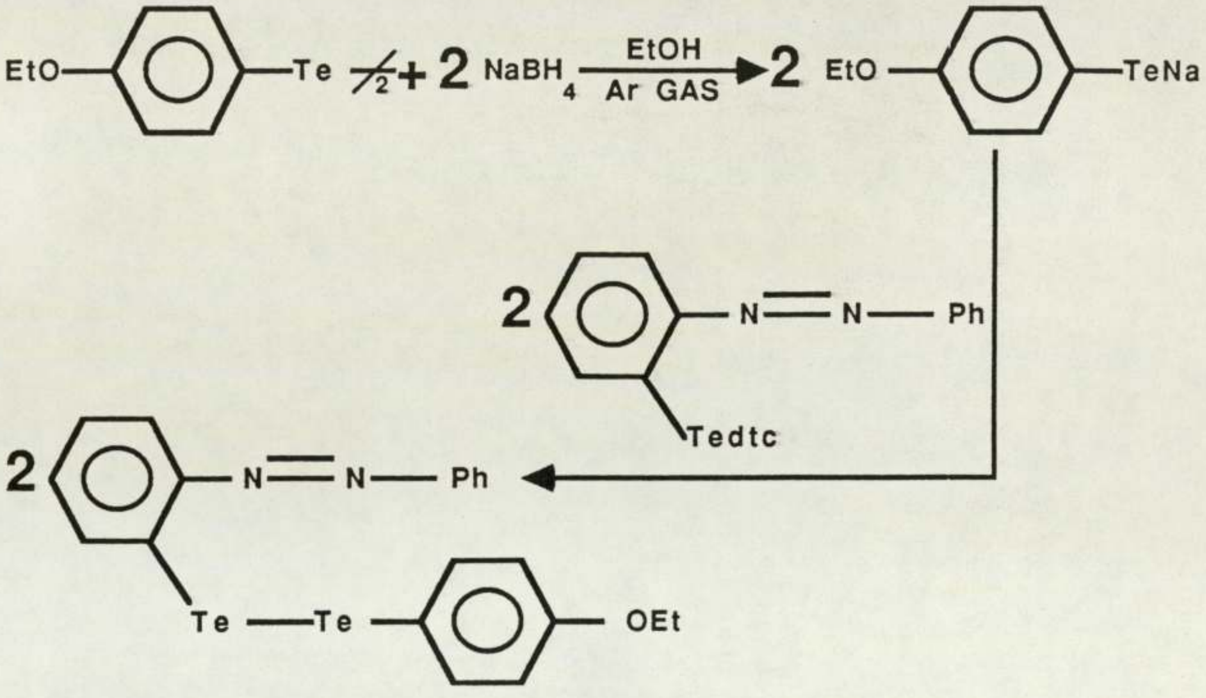
aromatic carbon values (Table 6.12) are close to that of the starting material (the tribromide compound) (Table 6.8).

6.3.8 Attempt to Synthesise an Unsymmetrical Ditelluride

To date no work has been published on solid unsymmetrical ditellurides. In 1975 Petragnani has synthesised a series of unsymmetrical selenotelluride compounds (equation 6.11) [227].

$$\mathrm{ArSeH} \xrightarrow[-C_2H_6]{\mathrm{EtMgBr}} \mathrm{ArSeMgBr} \xrightarrow{\mathrm{Ar'TeX}} \mathrm{ArSeTeAr'} \qquad \text{(eq. 6.11)}$$

An attempts have been made to prepare the first solid unsymmetrical ditelluride compound. Di(p-ethoxyphenyl)ditelluride was reacted with sodium borohydride and dimethyldithiocarbamato(2-phenylazophenyl-C,N')tellurium(II) in ethanol. This yielded a dark purple crystalline material. Elemental analysis of this material gave figures close to those for the unsymmetrical ditelluride. The expected mechanism for such reaction could be as follows:-



(xxvi)

SCHEME 6.9

There is a certain change on the infra-red spectrum of the resultant compound (expected to be the unsymmetrical ditelluride) from that of the starting materials. For example, the aliphatic region is very clear at ν(2979-2882 cm^{-1}). On searching for suitable crystal for crystallography, it has been found that this crystalline material is a mixture of the starting materials. Thus, the elemental analysis and infra-red gives no full evidence about the forming of this compound. However the subject needs further investigations to confirm the synthesis of the first unsymmetrical ditelluride compound.

REFERENCES

REFERENCES

1. H A Benesi and J H Hildebrand, J. Am. Chem. Soc., 1949, 71, 2703.
2. R S Mulliken, J. Am. Chem. Soc., 1950, 72, 600.
3. R S Mulliken, J. Am. Chem. Soc., 1952, 74, 811.
4. S H Hastings, J L Franklin, J C Schiller and F A Matesen, J. Am. Chem. Soc., 1953, 75, 2900.
5. N S Bayliss, Nature, 1949, 163, 764.
6. R S Mulliken, J. Am. Chem. Soc.,1950, 72, 4493.
7. R S Mulliken, Recl. Trav. Chim., Pays. Bas., 1956, 75, 845.
8. N S Ham, A L G Rees and A Walsh, Nature, 1952, 169, 110.
9. S D Ross, M Bassin and I Kuntz, J. Am. Chem. Soc., 1954, 76, 4176.
10. K G Cunningham, W Dawson and F S Spring, J. Chem. Soc., 1951, 2305.
11. J Weiss, J. Chem. Soc., 1942, 245.
12. W Brackman, Rec. Trav. Chim., 1949, 68, 147.
13. J N Murrell, Quart. Rev. Chem. Soc., 1961, 15, 191.
14. R E Gibson and O H Loeffler, J. Am. Chem. Soc., 1940, 62, 1324.
15. W R Burton and R E Richards, J. Chem. Soc., 1950, 1316.
16. H Kainer and W Otting, Chem. Ber., 1955, 1921.
17. R A Friedel, J. Phys. Chem., Ithaca, 1958, 62, 1341.
18. Y Matsunaga, J. Chem. Phys., 1964, 41, 1609.

19. H B Fridrich and W B Person, J. Chem. Phys., 1966, 44, 2161.

20. J Weiss, J. Chem. Soc., 1943, 462.

21. R Fostor, "Molecular Complexes", Vol. 1, Elek Science, London (1973).

22. C K Prout and J D Wright, Angew. Chem., 1968, 7, 659.

23. R Foster and T J Thomson, Trans. Farad. Soc., 1963, 59, 296.

24. F H Herbstein, "Perspectives in Structural Chemistry", Vol. IV, eds. J D Dunitz and J A IBers, Wiley, New York (1971).

25. L E Orgal and R S Mulliken, J. Am. Chem. Soc., 1957, 79, 4839.

26. M Tamers and R L Strong, in R Foster (ed.), "Molecular Association", Vol.2, Acedemic Press, London (1979).

27. J B Torrance, Acc. Chem. Res., 1979, 12, 79.

28. D S Acker and W R Hertler, J. Am. Chem. Soc., 1962, 84, 3370.

29. W Schienk, Ann., 1909, 368, 277.

30. L R Melby, Can. J. Chem., 1965, 1448.
C J Frichie, Acta Cryst., 1966, 20, 892.

31. F Gutmann and L E Lyons, "Organic Semiconductors", Wiley, New York (1967).

32. Z C Soos, Ann. Rev. Phys. Chem., 1974, 25, 121.

33. J G Andre, A Bieber AND F Gautier, Ann. Phys., 1967, 145.

34. I F Shchegolve, Phys. Status Solidi A, 1972, 12, 9.

35. R P Shibaeva and L O Atomyan, J. Struct. Chem., 1972, 13, 514.

36. F Wudl, D Wobschall and E J Hufnagel, J. Am. Chem. Soc., 1972, 94, 670.

37. L B Coleman, M J Cohen, D J Sandman, F G Yamagishi, A F Garito and A J Heeger, Solid State Commun., 1973, 12, 1125.

38. J B Torrance and B D Silverman, Phys. rev. B., 1977, 15, 788.

39. T J Kistenmacher, T E Phillips and D O Cowan, Acta. Aryst., 1974, B30, 763.

40. F Denoyer, R Comes, A F Garito and A J Heeger, Phys. Rev. Lett., 1975, 35, 445.

41. A J Epstein and J S Miller, Sci. Amer., 1979, 241, 52.

42. J B Torrance, B A Scott and F B Kaufman, Bull. Am. Phys. Soc., 1975, 20, 496.

43. J B Torrance and B D Silverman, Bull. Am. Phys. Soc., 1975, 20, 498.

44. E M Engler and V V Patel, J. Am. Chem. Soc., 1974, 96, 7376.

45. K Bechgaard, D O Cowam and A N Bloch. J. Chem. Soc., Chem. Comm., 1974, 937.

46. D Jerome A Mazaud M Ribault and K Bechgaard, J. Phys. Lett., 1980, 41, L95.

47. F Wudl, J. Am. Chem. Soc., 1981, 103, 7064.

48. L Alcacer, Ed."The Physics and Chemistry of Low Dimensional Solids", D Reidal Publishing Co., Holland (1980)

49. K Bechgaard, C S Jacobsen K Mortensen, H J Pedersen and N Thourp, Solid State commun., 1980, 33, 1119.

50. M Lamache, S Wuryanto and F Benhamou, Electrochimica Acta, 1985, 30, 817.

51. K Bechgaard, K Carneiro, F B Rasmussen and M Olsen, J. Am. Chem. Soc., 1981, 103, 2440.

52. D Jerome A Ribault and K Bechgaard, New. Sci., 1980, 104.

53. G C Hayward and P J Hendra, J. Chem. Soc.,A, 1969, 1760.

54. G Y Chao and J D McCullough, Acta. Cryst., 1961, 14, 940.

55. H Maddox and J D McCullough, Inorg. Chem., 1966, 5, 522.

56. N S Dance, W R McWhinnie, J Mallaki and Z Monsef-Mirzai, J. Organometal. Chem., 1980, 198, 131.

57. N Petragnani and G Schill, Chem. Ber., 1970, 103, 2271.

58. K G K De Silva, Z M Mirzai and W R McWhinnie, J. Chem. Soc., Dalton Trans, 1983, 2143.

59 N S Dance, PhD Thesis, university of Aston in Birmingham, 1976.

60. F H Musa, PhD Thesis, University of Aston in Birmingham, 1978.

61. J Mallaki, PhD Thesis, University of Aston in Birmingham, 1980.

62. F J Berry, E H Kustan and B C Smith, J. Chem. Soc., Dalton Trans, 1975, 1323.

63. K V Smith, J S Thayer and B J Zambransky, Inorg. Nucl. Chem. Lett., 1975, 11, 441.

64. C H W Jones, R Schultz, W R McWhinnie and N S Dance, Can. J. Chem., 1976, 54, 3234.

65. F J Berry and C H W Jones, Can. J. Chem., 1976, 54, 3737.

66. F J Berry and J Silver, J. Organometal. Chem., 1977, 129, 437.

67. H B Singh, W R McWhinnie, R F Ziolo and C H W Jones, J. Chem. Soc. Dalton Trans., 1984, 1267.

68. G M Bancroft and R H Platt, Inorg. Chem. Radiochem., 1972, 59, 15.

69a. W R Blackmore and S C Abrahams, Acta Crystal., 1955, 8, 317.

b. F H Cruse, R E Marsh and J D McCullough, Acta. Crystal., 1957, 10, 201.

c. G Llabres, O Dideberg and L Dupont, Acta. Crystal. Sect. B, 1972, 28, 2438.

70. F J Berry, C H W Jones, W R McWhinnie, "Bonding and Structure in Organotellurium Compounds Investigation by Mossbauer Spectroscopy", Presented at the "Forth International Conference on the Organic chemistry of Se and Te", University of Aston in BirmingHam, 25-29 July (1983).

71a. G D Christofferson and J D McCullough, Acta. Cryst., 1958, 11, 782.

b. G D Christofferson and R A Sparks and J D McCullough, Acta Cryst., 1958, 11, 782.

72. L Y Y Chan and F W B Einstein, J. C. S., D. Trans., 1972, 316.

73. W R McWhinnie and M G Patel, J. C. S., D. Trans., 1972, 109.

74. J D McCullough, C Knobler and R F Ziolo, Inorg. Chem., 1985, 24, 1814.

75. K V Smith and J S Thayer, Inorg chem., 1974, 13, 3021.

76. R F Ziolo, W H H Gunther, J. Organometal Chem, 1978, 146, 245.

77. J D McCullough, Inorg. Chem., 1973, 12, 2669.

78. J D McCullough, Inorg. Chem., 1975, 14, 1142.

79. H Matsuo, J. sci., Hiroshima Univ. Ser. A., 1958, 22, 51; 1958, 22, 281; Chem. Abs., 53, 9857b, 54, 4206h.

80. K J Irgolic and R A Zingaro, "Organometallic Reactions", Ed. E. I. Becker and M Tsutsui, Vol.2 (p. 136), Wiley, New York (1971).

81. V Z Latypova, Yu M Kargin and E G Kataev, J. General Chem., USSR, 1979, 49, 1588.

82. V Z Latypova, O G Yakovleva and Yu M Kargin, J. General Chem., USSR, 1980, 50, 462.

83. V Z Latypova, Zhuranal Obschei Khimii, 1984, 54, 848.

84a. Y Liftman and M Albeck, Electrochim. Acta., 1983, 28, 1835.

b. Y. Liftman and M Albeck, Electrochim. Acta., 1983, 28, 1841.

c. Y Liftman and M Albeck, Electrochim. Acta, 1984, 29, 91.

d. Y Liftman, M Albeck and J N E Goldschmidt, Electrochim. Acta., 1984, 29, 95.

85. H B Singh and W R McWhinnie, J. Organometal. Chem., 1984, 264, 305.

86. H B Singh, PhD Thesis, University of Aston in Birmingham, 1983.

87. D D Peerin, W L F Armargeo and D R Perrin, "Purification of Laboratory Chemicals", Pergamon Press, 1980.

88. F H Kruse, R W Sanftner anf J F Suttle, Analy. Chem., 1953, 500.

89. H C E McFarlane, J. Chem. Soc., Dalton Trans., 1973, 2416.

90. B Hetnarski and W Hofman, Bull. Acda. POL., 1969, 17(1), 1.

91. D P Rainville, R A Zingaro and J P Ferraris, Can. J. Chem., 1980, 58, 1133.

92. J B Torrance, J J Mayerle, V Y Lee and K Bechgaard, J. Am. Chem. Soc., 1979, 101, 4747.

93. J B Torrance, J E Vazquez, J J Mayerle and V Y Lee, Phys. Rev. Lett., 1981, 46, 253.

94. P H Reigar and G K Fraenkel, J. Chem. Phys., 1963, 39, 609; 1962, 37, 2759; D A Lowitz, ibid, 1967,4698.
95. J Bergman and L Engman, J. Am. Chem. Soc., 1981, 103, 2715.
96. S Cuthbertson and D D MacNicol, Tetrahedran Lett., 1975, 1893.
97. N N Magdesieva and V A Vdovin, Chem. Hetracyclo. Comp., 1972, 8, 24.
98. J Ferraris, D O Cowam, V Walatka and J Peristein, J. Am. Chem. Soc., 1973, 95, 948.
99. O H Le Blane. J. Chem. Phys., 1965, 42, 4307.
100. P M Chaikin, A F Garito and A J Heeger, J. Chem. Phys., 1973, 58, 2336.
101. F Wudl, Acc. Chem. Res., 1984, 17, 227.
102. J B Torrance, Ann. N. Y. Acad. Sci., 1978, 210, 313.
103. J B Torrance and Y Tomkiewicz, Bull. Am. Phys. Soc., 1976, 21, 313.
104. R C Wheland and J L Gillson, J. Am. Chem. Soc., 1976, 98, 3916.
105. R C Wheland, J. Am. Chem. Soc.,1976, 98, 3926.
106. H Kusakawa and K Akashi, Bull. Chem. Soc. Jpn., 1969, 42, 263.
107. H J Keller, "Chemistry and Physics of One-Dimensional Metals", Plenum Press, New York (1977).
108. K Y Abid and W R McWhinnie, J. Organometal. Chem., 1987, 330, 337.

109. R S Mulliken and W B Person, "Molecular Complexes", Wiley New York, 1969.

J Yarwwod, Ed.,"Spectroscopy and Structure of Molecular Complexes", Plenum, New York, 1973.

110. E M Engler, V V patel, J R Andersen, R R Schumaker and A A Fukushima, J. Am. Chem. Soc., 1978, 100, 3769.

111. J S Chappel, A N Bloch, W A Bryden, M Maxfield, T O Poehler and D O Cowan, J. Am. Chem. Soc., 1981, 103, 2442.

112. J Tanaka, M Tanaka, T Kawai, T Takabe and O Maki, Bull, Chem. Soc. Jpn., 1976, 49, 2358.

113. Y Iida, Bull. Chem. Soc. Jpn., 1969, 42, 71; 1969, 42, 637.

114. C A Heller, R A Zingaro and E A Meyers, Can. J. Chem., 1974, 52, 3814.

115. M Hillebrand, O Maior and V Em Sahini, Rev. Roum. Chem., 1970, 15, 149.

116. H Block, G Brahler, D Dauplaise and J Meinwald, Chem. Ber., 1981, 114, 2622.

117. D N Stamires and J J Turkevich, J. Am. Chem. Soc., 1963, 85, 2557.

118. G Cauquis and M Maurey, Mey; Bull. Soc. Chim. Fr., 1973, 291.

119. A Gioaba, V Em Sahini and E Volanschi, J. Chem. Soc., Perkin Trans, 1977, 2, 529.

120. B Lamotte and G Berthier, J. Chem. Phys, 1966, 63, 369.

H F Chiu and B C Gilbert, J. Chem. Soc., Perkin Trans, 1973, 2, 258.

121. K Yoshino, K Kaneto, S Inoue and K Tsukagoshi, Jpn. J. App. Phys., 1981, 22, L701.

122. K Yoshino, K Kohno, T Shiraishi, K Kaneto, S Inoue and K Tuskagoshi, Synthetic Metals, 1985, 10, 319.

123. R Sugimoto, K Yoshino, S Inoue and K Tsukagoshi, Jpn. J. App. Phys., 1985, 24, L425.

124. M Gazard, J P Montheard, M Champagne, J C Dubois, Fr Demande, FR 2,554, 133.

125. A D Baker, G H Armen, Y Guang-di, D Liotta, N Flannagan, C Barnnum, M Saindane, G Zima, J Grossman, J. Org. Chem., 1981, 46, 4127.

126. D Liotta, Acc. Chem. Res., 1984, 17, 28.

127. H D Smyth, Proc. Roy. Soc., (London), ser.A. 1922, 102, 28.

128. F P Lossing, A W Tickner and W A Bryce, J. Chem. Phys., 1951, 19, 1254.

129. J W Warren, Nature, 1950, 165, 810.

130. F P Colonna, G Distefano, V Galasso, K J Irgolic, C E King and G C Pappalardo, J. Organometal. Chem., 1978, 146, 235.

131. H M McConnel, B M Hoffman and R M Metzger, Proc. Natl. Acad. Sci., 1965. 53, 46.

132. A M Heyns and C W F Pistorius, Spectrochim. Acta., 1974, 30A, 99.

133. S A Bell, J C Lancaster and W R McWhinnie, Inorg. Nucl. Chem. Lett., 1971, 7, 405.

134. G L Cote and H W Thompson, Proc. Roy. Soc., 1951, 210A, 217.

135. H C Clerk and R J O'Brien, Inorg. Chem., 1963, 2(5), 1020.

136. A Z Al-Rubaie, W R McWhinnie, P. Granger and S Chapelle, J. Organometal. Chem., 1982, 234, 287.

137. D J Sandman, G P Hamill and W A Burke, Mol. Cryst. Liq. Crysy., 1982, 86, 79.

138. G Y Chao and J D McCullough, Acta. Cryst., 1962, 15, 887.

139. C Knobler, J D McCullough and H Hope, Inorg. Chem., 1970, 9, 797.

140. H Hope, C Knobler and J G McCullough, Inorg. Chem., 1973, 12, 2665.

141. F Einstein, J Trotter and C Williston, J. Chem. Soc. A., 1967, 2018.

142. C Knobler, J D McCullough, Inorg. Chem., 1972, 11, 3026.

143. P H Bird, V Kumar and B C Pant, Inorg. Chem. 1980, 19, 2487.

144. H Campsteyn, L Dupont, J Lamotte-Brasseur and M Vermeir, J. Heter. Chem., 1978, 15, 745.

145. E M Engler, V V Patel, J R Andersen, Y Tomkiewioz, R A Craven, B A Scott and S Etemad, Ann. N. Y. Acad. Sci., 1978, 313, 343.

146. B R Muth and A I Kiss, J. Org. Chem., 1956, 21, 576.

147. D L Klyman, W H H Gunther, "Organic Selenium Compounds", Wiley, New York, 1973.

148. V Kovocik, M Fedoronko and I Jezo, Org. Mass Spectrum., 1973, 7, 449.

149. E J Moriconi and A J Fritsch S. J., J. Org. Chem., 1965, 30, 1542.

150. D B Denney, D Z Denney, P J Hammond and Y F Hsu, J. Am. Chem. Soc., 1981, 103, 2340.

151. P Granger, S Chapelle, W R McWhinnie and A Al-Rubaie, J. Organometal. Chem., 1981, 220, 149.

152. P. Granger, S Chapelle and C Brevared, J. Mag. Reson., 1981, 42, 203.

153. H J Gysling, N Zumbulyadis and J A Robertson, J. Organometal. Chem., 1981, 209, C41.

154. W McFarlane, J. Chem. Soc. A, 1969, 670.

155. N Zumbulyadis and H J Gysling, J. Organometal. Chem., 1980, 192, 183.

156. E Shustorovich, Inorg. Chem., 1979, 18, 2108.

157. C Knobler, R F Ziolo, J. Organometal. Chem., 1979, 178, 423.

158. H Pritzkow, Inorg. Chem., 1979, 18, 311.

159. J D McCullough and C knobler, Inorg. Chem., 1976, 15, 2728.

160. N W Alcock and R M Countryman, J. Chem. Soc., Dalton Trans, 1977, 217.

161. K Lerstrup, D Talham, A Bloch, T Poeler and D Cowan, J. Chem. Soc., Chem. Commun., 1982, 336.

162. R T Mehdi and J D Miller, J. Chem. Soc., Dalton Trans., 1983, 1071

163. R D McCullough, G B kok, K A Lerstrup and D O Cowan, J. Am. Chem. Soc., 1987, 109, 4115.

164. F Wudl, G M Smith, E J Hu Nagel, J. Chem. Soc., Chem. Commun, 1970, 1453.

165a. F Wudl, E Aharon-Shalom, J. Am. Chem. Soc., 1982, 104, 1154.

b. M R Detty, B J Murray, J. Org. Chem., 1982, 47, 1148.

c. K Lerstrup, D O Cowan, T J Kistenmacher, J. Am. Chem. Soc., 1984, 106, 8303.

d. K Lerstrup, A Bailey, R D McCullough, M Mays, D O Cowen, Synth. Metals, 1986, 19, 647.

166. N. I Al-Salim, PhD Thesis, 1987, Aston University, in Birmingham.

167. B K Teo, F. Wudl, J H Marshall, A Kruger, J. Am. Chem. Soc., 1977, 99, 2349; 1977, 99, 4862.

168. A Y Girgis, Y S Sohn, A L Balch, Inorg. Chem. 1975, 14, 2327.

169. U T Mueller-Westerhoff, "Inorganic Compounds with Unusual Properties", R B King, Ed., Adv. Chem. Ser., 1976, 150, 31-45.

170. J J Mayerle, Inorg. Chem., 1977, 16, 916.

171. D R Rosseinsky and R E Malpas, J. Chem. Soc., D. T., 1979, 740.

172. J S Miller and A J Epstein, J. Coord. Chem., 1979, 8, 191.

173. J W Bray, H R Hart, L V Interrant, I S Jacobs, J S Kasper, P A Piacente and G D Watkins, Phys. Rev. Ser. B., 1977, 16, 1359.

174. A E Underhill and M M Ahmad, J. C. S. Chem. Commun., 1981, 67.

175. L Alcacer and H Novais, "Extended Linear chain Compounds", Vol. 3, Ed. J. S. Miller, Plenum Press, New York, 1983, pp 319-351.

176a. A Kobayashi, Y. Sasaki, H Kobayashi, A E Underhill and M M Ahmad, J. C. S. Chem. Commun., 1982, 390.

b. R Kato, T Mori, A Kobayashi, Y. Sasaki and H Kobayashi, Chem. Lett., 1984, 1.

c. M. Boussaue, L Valade, M F Bruniqual, P Cassoux, M Garbauskas, L Interrante and J Kasper, Nouv. J. Chim., 1984, 3.

d. L Valade, J P Legros, M Bousseau, P Gassoux, M Garbauskas and L V Interrante, J. Chem. Soc. D.T. 1985, 783.

e. R Kato, H Kobayashi, A Kokayashi and Y Sasaki, Chem. Lett., 1985, 131; 1985, 191; 1985;535.

177. S T Enoki, K Torium and H Inokuchi, Solid State Commun., 1982, 42, 557.

178. W B Heuer and B M Hoffman, J. C. S. Chem. Commun., 1986, 174.

179. U Geisor, H H Wang, L E Gerdom, M A Firestone, L M Sowa, J M Williams, M H Hhangbo, J. Am. Chem. Soc., 1985, 107, 8305.

180. U Geiser, H H Wang, K M Donega, B A Anderson, J M Williams, Inorg. Chem. Commun., 1986, 25, 401.

181. J L Pitte and M Renson, Bull. Soc. Chim. Belges, 1970, 79, 367.

182. M A K Ahmed, PhD Thesis, 1985, University of Aston in Birmingham.

183. G A Kalabin, V M Bzhezovskii, D F Kushanev and A Q Proidakov, J. Org. Chem., USSR, 1981, 17, 1009.

184. D F Ewing, Org. Mag. Res., 1979, 12, 499.

185. E G Paul and D M Grant, J. Am. Chem. Soc., 1963, 85, 1701.

186. L P Lindeman and J Q Adams, Anal. Chem., 1971, 43, 1245.

187. B E Mann. J. Chem. Soc., Perkin Trans.(II), 1972, 30.

188a. R B King and J C Cloyd, jun., J. Chem. Soc., Perkin Trans. (II), 1975, 938.

b. W E Hill, D N A Minaham, J G Taylor and C A McAulffe, J. Chem. Soc., Perkin Trans II, 1982, 327.

189. G Llabres, M Baiwir, L Christiaens, J Denoel, L. Laitem and J L Piette, Cand. J. Chem., 1978, 56, 2008.

190. H Pathirana, PhD Thesis, 1985, Aston University in Birmingham.

191. R K Chadha and J M Miller, Cand. J. Chem., 1982, 60, 596.

192. G A Olah and D J Donovan, J. Org. Chem., 1978, 43, 860.

193. R K Chadha and J M Miller, J. Chem. Soc., Dalton Trans., 1982, 117.

194. D H O'Brien, K J Irgolic and C K Huang in "Proceed Fourth Int. Conf. Org. Chem. of Selenuim and Tellurium, 1983, 468", F J Berry and W R McWhinnie (Eds)

195. M M Campus, E L Suranyl, H de Andrade and N Petragnani, Tetrahedran, 1964, 20, 2797.

196. P Wiriyachitra, S J Falcone and M P Cava, J. Org. Chem., 1979, 44, 3957.

197. N S Dance and W R McWhinnie, J. Chem. Soc., Dalton Trans., 1975, 43.

198. D Kobelt and E F Paulus, J Organometal. Chem., 1971, 27, C63.

199. C L Ralston, R J Secomb and A H White. J. C. S. Dalton, 1976, 2307.

200. T S Cameron, R B Amero and R E Cordes, Cryst. Struct. Comm., 1980, 9, 533, 539.

201. N W Alcock and W D Harrison, J. C. S. Dalton, 1982, 251.

202. J D Korp, I Bernal, J C Turley and G E Martin, Inorg. Chem., 1980, 19, 2556.

203. A Bondi, J. Phys. Chem., 1964, 68, 441.

204. F J Berry and A J Edwards, J. Chem. Soc., Dalton Trans, 1980, 2306.

205a. R Close, D Cagniant, G Le Coustumer, C G Andrieu and Y Mollier, J. Chem. Res.(S), 1978, 4.

b. J Lamotte, H Campsteyn, L Dupont and M Vermeive, Cryst. Struct. commun., 1977, 6, 749.

206. L Pauling , "The nature of the Chemical Bond" 3rd Ed., Cornell Univ. Press, Ithaca, New York, 1960.

207. B Buss and B Krebs, Angew Chem., Int. ed. Engl., 1970, 9, 463.

208. P M Baiwir, G Llabres O Dideberg and L Dupont, Acta Cryst., 1974, B 30, 139.

209. A Brown, PhD Thesis, 1980, University of Aston in Birmingham.

210. A A West, Unpublished data.

211. M V Lakshmikantham, M P Cava, M Albeck, L Engman and P Carrol, Tetrahedron Lett., 1981, 22, 4199.

212. G Van den Bossche, M R Spirlet, O Didberg and L Dupont, Acta Cryst., 1984, C40, 1011.

213. R A Zingaro, C Herrera and E A Meyers, J. Organometal. Chem., 1986, 306, C36-C40.

214. J Bergman, Tetrahedron, 1972, 28, 3323.

215. U. Behrens, K Hoffman and G. Klar, Chem. Ber., 1977, 110, 3672.

216a. D Coucouvanis, prog. Inorg. Chem., 1970, 11, 233; 1979, 26, 301.

b. E Diemann and A Muller, Coord. Chem. Rev., 1973, 10, 79.

c. R P Burns and C A McAuliffe. Adv. Inorg. Chem. Radioochem., 1979, 22, 303.

d. R A Walton, Coord. Chem. Rev., 1980, 31, 183.

e. I Omae, Coord. Chem. Rev., 1979, 28, 97.

217. P R Blum, R M C Wei and S C Cummings, Inorg. Chem., 1974, 13, 450.

218. G E Coates, J. Chem. Soc., 1951, 2003.

219. M N Brochkarev, V S Andreevichev and N S Vyazankin, Izv. Akad. Nank. SSSR, Ser. Khim., 1973, 702.

220. N Al Salim, T A Hamor and W R McWhinnie, J. Chem. Soc., Chem. Commun., 1986, 453.

221. K Nakamoto, Infrared and Raman Spectra, Fourth Ed., John Wiley and Sons, 1986.

222. N L M Dereu, R A Zingaro and E A Meyers, Cryst. Struct. Commun., 1981, 10, 1345; 1981, 10, 1353.

223. N L M Dereu, R A Zingaro, E A Meyers and M Renson, Organometallics, 1982, 1, 111

224. F Sladky, B Bildstein, C Rieker, A Gieren, H Betz and T Hubner, J. Chem. Soc., Chem. Commun., 1985, 1800.

225. T A Hamor, N Al Salim, A A west and W R McWhinnie, J. Organometal. Chem., 1986, 310, C5-C7.

226. N Kuhn, H Schumann and R Boese, J. Chem. Soc., Chem. Commun., 1987, 1257.

227. N Petragnani and L Torres, J. Organometal Chem., 1975, 92, 185.

Journal of Organometallic Chemistry, 330 (1987) 337–346
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Simple charge transfer complexes of some new and of some known heterocyclic compounds of selenium and tellurium

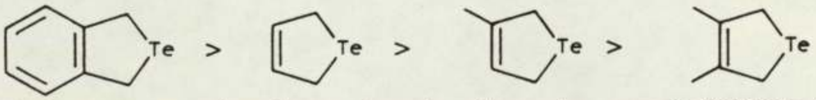
Khalid Y. Abid and William R. McWhinnie

Department of Molecular Sciences, Aston University, Aston Triangle, Birmingham B4 7ET (Great Britain)

(Received February 10th, 1987)

Abstract

Charge transfer (CT) complexes (1 : 1) of 2,5-dihydrotellurophene and the 3-methyl and 3,4-dimethyl compounds with TCNQ and tetrachlorobenzoquinone (TCB) are reported. The organotellurium compounds failed to give complexes with *p*-dinitrobenzene (DNB). The variation of solid state (disc) conductivity with temperature and as a function of methyl substituents is considered. The complexes show semi-conducting behaviour and a consideration of these data, together with IR and UV spectroscopic data, in comparison with those for 1,3-dihydro-2-tellurain-dene given the following order of donor power with respect to TCNQ:



With respect to a given donor, the order of acceptor power is TCNQ > TCB > DNB.

1,3-Dihydro-2-selenaindene forms a complex with TCNQ. The molecular ionisation potential of the selenaindene is 7.4 eV (by mass spectroscopy) and it has been shown that the compound may be electrochemically oxidized to materials such as $C_8H_8SePF_6$.

New quinoxalino-1-chalcogenacyclopentanes are reported; namely those derived from selenium, and for the 7,8-dimethyl series, those based on both selenium and tellurium. Their preparation and characterisation are described, and their chemistry shown to be strongly analogous to that of quinoxalino-1-telluracyclopentane. CT complexes of the new Se^{II} and Te^{II} compounds (1 : 1) are prepared with TCNQ which are believed to be strongly ionic.

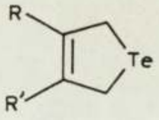
Introduction

Interest in molecular charge transfer (CT) complexes, particularly those such as the strongly conducting black polymorph of the complex of tetramethyltetraselena-

0022-328X/87/$03.50

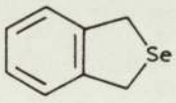
fulvalene · tetracyanoquindimethane (TMTSF · TCNQ) [1] and in the series $(TMTSF)_2X$ ($X = PF_6$, ClO_4 etc.) [2] which show superconductivity at low temperature (ClO_4) or low temperature and high pressure (PF_6), continues to be strong. We have been interested in CT complexes formed by more simple organic derivatives, particularly of tellurium and have suggested the use of ^{125}Te Mossbauer spectroscopy to measure the degree of charge transfer in such systems [3]. In addition we have found quite strong interactions between bis-tellurides and some alkyl halides [4] as well as between some tellurium(IV) compounds and organic halides [5]. We believe that a CT interaction may be the first step in some reactions of simple tellurides [6] and note that the suggestion that several "diorganyl selenium diiodides" may be CT complexes of a selenide with diiodine is long stablished [7].

This paper is an extension of two previous pieces of work [3,5] in which we consider the effects of methyl substituents on the properties of the CT complexes formed by the compounds **1–3**; we also extend our studies to selenium. Some of the heterocyclic compounds are reported for the first time.

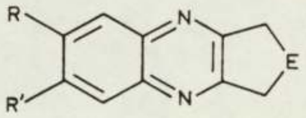


(**1**)

(R = R' = H ;
R = Me, R' = H ;
R = R' = Me)



(**2**)



(**3**)

(R = R' = H ; E = Se, Te ;
R = R' = Me ; E = Se , Te)

Experimental and Results

Preparations

2,5-Dihydrotellurophene [8], 3-methyl-2,5-dihydrotellurophene [8], 3,4-dimethyl-2,5-dihydrotellurophene [8], 1,3-dihydro-2,2-telluraindene [9] and 1,3-dihydro-2-selenaindene [10] were prepared by the indicated literature methods, as was 3,4-quinoxalino-1-tellurapentane [5]. 3,4-Quinoxalino-1-selenacyclopentane and the 1 : 1 complex with 2,3-bis(iodomethyl)quinoxaline were prepared using the conditions previously described for the tellurium compounds, substituting elemental selenium for tellurium [5].

1,1-Diiodo-7,8-dimethyl-3,4-quinoxalino-selenacyclopentane. 1,4-Dibromo-2,3-butanedione (1.20 g, 0.5 mmol) in warm benzene (20 cm^3) was added to a solution of 4,5-dimethyl-*o*-phenylenediamine (0.68 g, 0.5 mmol) in benzene (20 cm^3). The mixture was refluxed for 40 min and cooled to afford white crystals. Recrystallisation from ethanol gave pure 7,8-dimethyl-2,3-bis(bromomethyl)quinoxaline (m.p. 149–151° C), which (0.5 mmol) was then treated with sodium iodide (1.5 g, 20 mmol) and selenium powder (0.2 g, 5 mmol) in 2-methoxyethanol (50 cm^3) under gentle reflux for 2 h. After cooling, the mixture was treated with distilled water (100 cm^3) which caused additional precipitation. The crude material was separated, dried, and recrystallised from 2-methoxyethanol to give a deep violet solid, m.p. 168–169° C.

Replacement of sodium iodide by potassium iodide and reduction of the reflux period to 1 h gave a yellow product, which recrystallised slowly from acetone to give

Table 1

Analytical data for new compounds

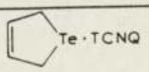
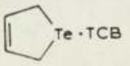
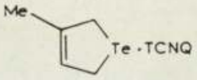
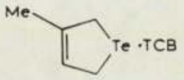
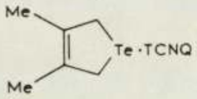
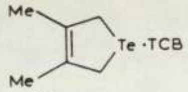
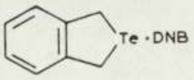
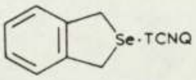
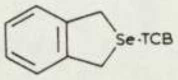
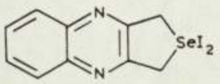
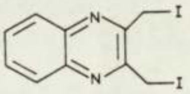
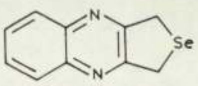
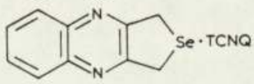
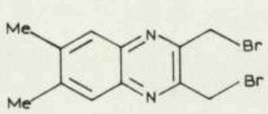
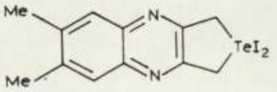
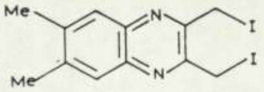
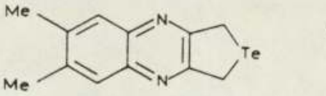
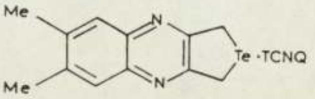
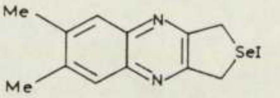
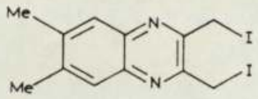
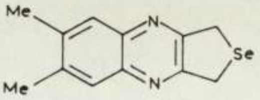
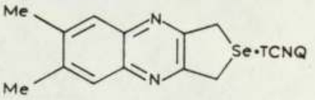
Compound		Colour (M.p. (°C))	Yield (%)	Analyses (Found (calc) (%))		
				C	H	N
	(1)	deep violet (102–104)	84	50.1 (49.8)	2.6 (2.6)	14.1 (14.5)
	(2)	dark brown (198–200)	78	28.5 (28.0)	1.45 (1.40)	33.6 [a] (33.1)
	(3)	red-black (92–95)	82	51.4 (51.0)	3.1 (3.0)	13.5 (14.0)
	(4)	deep brown (171–173)	80	28.2 (29.9)	2.3 (1.8)	31.6 [a] (32.1)
	(5)	black (83–85)	86	52.5 (52.2)	3.7 (3.4)	14.1 (13.5)
	(6)	brown-black (159–161)	76	32.0 (31.6)	2.7 (2.1)	31.9 [a] (31.2)
	(7)	black (108–110)	82	42.9 (42.0)	2.8 (3.0)	6.0 (7.0)
	(8)	blue-black (135–137)	85	62.2 (62.0)	3.3 (3.1)	14.0 (14.4)
	(9)	violet (197–199)	75	39.6 (39.0)	2.1 (1.8)	33.3 [a] (33.1)
	(10)	deep violet (138–140)	61	24.8 (24.5)	1.7 (1.6)	5.4 (5.7)
10 • 	(11)	yellow (145–147)	80	29.8 (29.8)	1.85 (1.90)	7.0 (6.9)
	(12)	pale-yellow (148–150)	62	50.4 (51.0)	3.3 (3.4)	11.4 (11.9)
	(13)	black (135–136)	80	59.7 (60.2)	2.5 (2.7)	18.2 (19.1)
	(14)	white (149–151)	75	41.8 (41.8)	3.50 (3.48)	8.5 (8.1)
 b	(15)	deep-violet (169–171)	53	25.7 (25.4)	1.6 (2.1)	4.1 (4.9)
15 •  b	(16)	yellow (164–165)	65	28.7 (28.7)	2.3 (2.3)	5.1 (5.5)

Table 1 (continued)

Compound		Colour (M.p. (°C))	Yield (%)	Analyses (Found (calc) (%))		
				C	H	N
 [b]	(17)	pale-yellow (167–169)	60	45.7 (46.2)	3.7 (3.8)	8.5 (8.9)
	(18)	black (164–166)	80	56.2 (55.8)	2.8 (3.1)	15.5 (16.2)
	(19)	deep violet (168–169)	54	28.2 (27.8)	2.0 (2.3)	4.9 (5.4)
19 · 	(20)	yellow (163–164)	70	33.5 (33.5)	2.7 (2.7)	6.1 (6.4)
	(21)	pale-yellow (169–171)	61	54.2 (54.8)	4.5 (4.6)	10.1 (10.6)
	(22)	black (144–146)	85	62.2 (61.7)	3.5 (3.4)	18.8 (18.0)

[a] % Cl. [b] Satisfactory tellurium analysis were obtained for these compounds.

yellow crystals (m.p. 163–164°C) of *1,1-diiodo-7,8-dimethyl-3,4-quinoxalino-selenacyclopentane: 7,8-dimethyl-2,3-bis(iodomethyl)quinoxaline (1 : 1) complex.*

The corresponding tellurium compounds were prepared by identical procedures but with elemental tellurium in place of selenium.

7,8-Dimethyl-3,4-quinoxalino-1-selenacyclopentane. Violet 1,1-diiodo-7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane (1.2 g, 2.3 mmol) in suspension in ethanol (75 cm^3) and water (15 cm^3) was treated dropwise with hydrazine hydrate (0.45 g, 9 mmol) in ethanol (15 cm^3). The reaction mixture was then warmed gently until all the violet crystals had reacted; it was then poured into distilled water (200 cm^3) and an ether extraction was carried out. The separated ethereal solution was dried over anhydrous Na_2SO_4 and the solvent then removed on a rotatory evaporator. The yellow powder obtained was treated with charcoal and ether to give yellow needles, m.p. 169–171°C. The tellurium compound was obtained similarly by reduction of $C_{12}H_{12}N_2I_2Te$.

Charge transfer complexes. A common procedure was adopted, and only one example of which is given as an illustration. In this, 7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane (0.26 g, 1 mmol) in acetonitrile (20 cm^3) was added to a solution of TCNQ (0.2 g, 1 mmol) in acetonitrile (30 cm^3). The mixture was stirred under reflux for 1 h, and its volume than reduced to 10 cm^3 to give black crystals (m.p. 144–146°C).

In this manner, compounds **1** were treated with TCNQ and also with chloranil (tetrachlorobenzoquinone, TCB) and with 1,4-dinitrobenzene (DNB). True complexes were obtained with TCNQ and TCB, but with DNB incorrect analytical data were obtained and careful examination of the products revealed mixtures of crystals of the individual components. Compounds **2** and **3** were treated with TCNQ only.

Analytical and other data for the new compounds are summarised in Table 1.

Physical measurements

Infra-red spectra were recorded for KBr discs (solids) or liquid film with a Perkin–Elmer 599B instrument. UV/VIS spectra were recorded for solutions in 1 cm pathway quartz cells with a Pye Unicam SP8-100 spectrophotometer. Nuclear magnetic resonance data were obtained at 60 MHz (proton) with a Perkin–Elmer RB12 instrument (TMS standard). ESR data were obtained with a JEOL-IX spectrometer using a manganese(II)/MgO standard. Mass spectra were obtained with an AE1 MS9 instrument; appearance potential measurements were obtained by varying the exciting voltage within the range 70–6 eV, argon being incorporated with the sample as a substance of known ionisation potential.

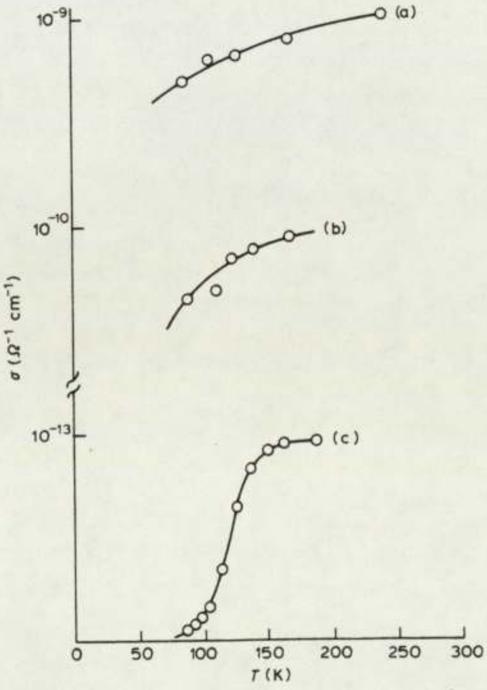
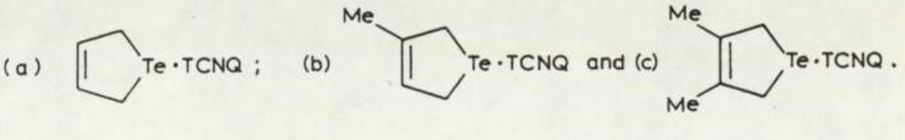


Fig. 1. Temperature dependence of the electrical conductivity of



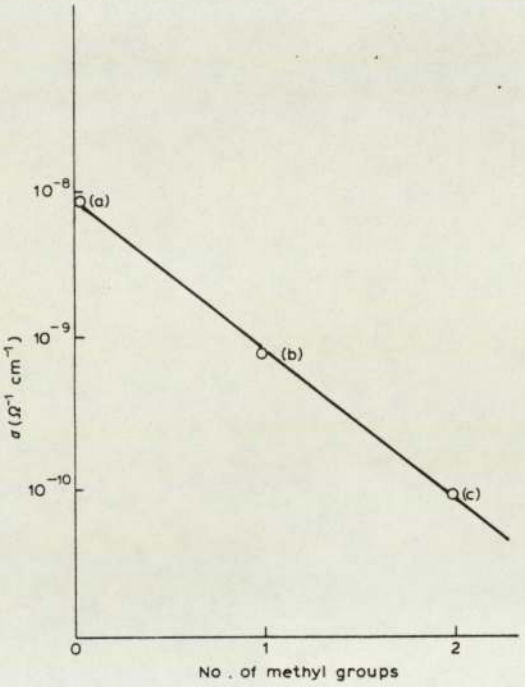


Fig. 2. The relationship between the conductivity and the number of methyl groups at 330 K,

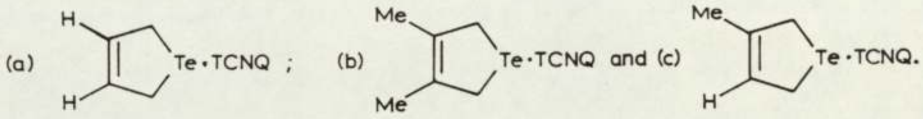


Table 2

Physical data for CT complexes of dihydrotellurophenes

Compound	Solid conductivity (350 K, Ω^{-1} cm^{-1})	ν(CN) (TCNQ), ν(CO) (TCB)	ESR (*g*-value)	UV-VIS λ_{max} (nm)
1	10^{-8}	2198, 2166	2.0026	656
2	10^{-8} (r.t.)	1682, 1694	2.0038	508
3	10^{-9}	2238, 2198, 2160	2.0040	654
4	10^{-11} (r.t.)	1682, 1693	–	506
5	10^{-10}	2236, 2197, 2158	2.0048	648
6	10^{-12} (r.t.)	1683, 1693	–	504
8	10^{-11} (r.t.)	2228, 2198	2.0041	623
9	10^{-13} (r.t.)	1684, 1696	–	–
13	10^{-13} (r.t.)	2132, 2158, 2196	2.0036	
18	10^{-13} (r.t.)	2132, 2182	2.0025	
22	10^{-14} (r.t.)	2146, 2188	2.0038	

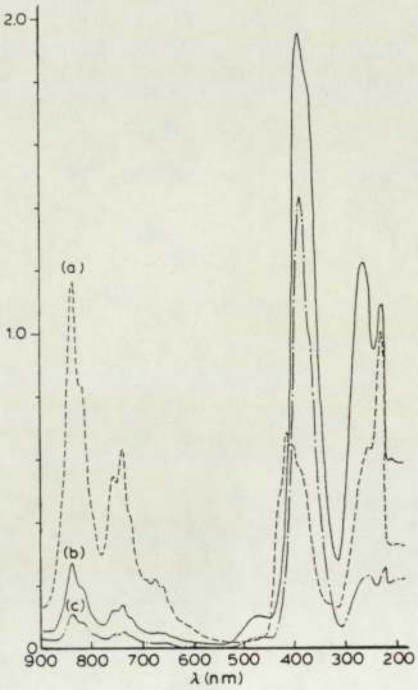
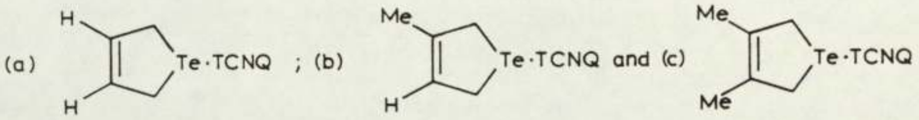


Fig. 3. Electronic spectra of the tellurophene complexes with TCNQ;



Solid state conductivity measurements were made on samples which had been pressed into discs of diameter 13 mm and thickness 0.6–1.0 mm. Silver paste was carefully applied to each side of the disc and thin gold wires were attached with a dab of silver paste. A two-pulse method was used. A solid state electrometer (Keithley A610C) and stabilised power supply (Kingshill model 305) were used. Facilities for variable temperature measurements were available. (We are most grateful to Mr. Basi of the Department of Electronic Engineering and Applied Physics for help with these measurements).

The variation of the solid state conductivity for compounds **1** with TCNQ is shown graphically in Fig. 1, and the variation of conductivity at a fixed temperature with the number of methyl substituents is shown in Fig. 2. Figure 3 shows the UV spectra for **1** · TCNQ in acetonitrile solution. Table 2 gathers together pertinant IR, ESR and UV data for **1** · TCNQ. Table 3 includes similar relevant physical data for the quinoxaline derivatives.

Electrochemical oxidation of 1,3-dihydro-2-selenaindene

It was recently reported [11] that 1,3-dihydro-2-telluraindene can be electrochemically oxidised to compounds such as $[C_8H_8Te]PF_6$, we decided to ascertain whether

Table 3

Spectroscopic data for new quinoxalino-1-chalcogenacyclopentane derivatives

Compound	UV-VIS λ (nm)	^{1}H NMR (δ (ppm) vs. TMS)
10	247, 270, 330	4.82 (CH_2, s, 4H) 7.7–8.4 (aromatic, m, 4H)
12	241, 318	4.74 (CH_2, s, 4H) 7.2–8.1 (aromatic, m, 4H)
14	255, 349	4.92 (CH_2, s, 4H) 2.52 (CH_3, s, 6H) 7.3–7.8 (aromatic, m, 2H)
15	243, 269, 331, 343	4.88 (CH_2, s, 4H) 2.52 (CH_3, s, 6H) 7.3–7.9 (aromatic, m, 2H)
17	246, 257, 333	4.58 (CH_2, s, 4H) 2.50 (CH_3, s, 6H) 7.3–7.6 (aromatic, m, 2H)
19	251, 267, 348	4.8 (CH_2, s, 4H) 2.57 (CH_3, s, 6H) 7.3–7.8 (aromatic, m, 2H)
21	248, 326, 338	4.68 (CH_2, s, 4H) 2.46 (CH_3, s, 6H) 7.3–7.7 (aromatic, m, 2H)

the selenium analogue behaved similarly. Thus recrystallised 1,3-dihydro-2-selenaindene (10 mmol) in pure dichloromethane (200 cm^3) containing tetra-n-butylammonium hexafluorophosphate (20 mmol) was electrolysed between two platinum electrodes with a spacing of ~ 1 cm at a constant current of 2 mA. A shiny deposit formed on the anode after a few minutes but the yield in all experiments was very low. The material analysed as $C_8H_8SePF_6$: Found: C, 29.2; H, 2.50%. $C_8H_8F_6PSe$ calc: C, 29.2; H, 2.43%. The melting point was 125° C and the infra-red spectrum confirmed the presence of ionic hexafluorophosphate (848 vs, 570s cm^{-1}). The molar conductivity in acetonitrile was 117 Ω^{-1} cm^2 mol^{-1}. No ESR signal was observed.

Discussion

2,5-Dihydrotellurophene derivatives

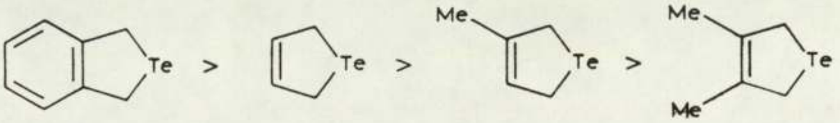
No complexes with DNB were isolable. With both TCNQ and DTB, complexes of 1 : 1 stoichiometry were obtained. The infra-red spectra of the DTB complexes were virtually the superposition of the spectra of the individual components and, (Table 2), there is no shift of ν(CO) with change of donor. This implies an extremely weak CT interaction, and this observation is in line with results previously obtained for the 1,3-dihydro-2-telluraindene · DTB complex [3]. The spectra of the TCNQ complexes are also virtually the sum of the component parts, but the ν(CN) region shows a little variation for the compounds **1**, **3** and **5** (Table 1). Thus **3** and **5** show a band at ~ 2235 cm^{-1} which is absent in **1**. Bands close to 2230 cm^{-1} can be attributed to neutral TCNQ and those near 2180 cm^{-1} to $TCNQ^{\cdot(-)}$ [12]. The infra-red data thus suggests that there is less radical ion character in the complexes of the methyl-substituted 2,5-dihydrotellurophenes. All these complexes give ESR signals in the solid state. Within experimental error the g values are the same, and close to 2.0023 (Table 2), thus the unpaired electron density detected is on TCNQ.

The electronic spectra (acetonitrile solutions) of compounds **1**, **3**, and **5** are shown in Fig. 3. The absorptions around 700–900 nm are attributable to $TCNQ^{\cdot(-)}$ and those at 380–420 nm to a combination of $TCNQ^{\cdot(-)}$ and TCNQ · **13**. The greater relative intensity in the 700–900 nm region for compound **1** is notable, and again implies greater radical ion character. Indeed, the acetonitrile solution of complex **1** is quite conducting (108 Ω^{-1} cm^2 mol^{-1}), in contrast to solutions of **2** and **3**, again implying a greater ionic character. Bands at 656 (**1**), 654 (**2**), and 648 nm (**3**) that are not attributable to the dihydrotelluraphene or to TCNQ are seen, and can be assigned to the CT (HOMO → LUMO) transition. If this assignment is correct, the band for the 2,5-dihydrotelluraphene complex is at marginally lower energy than those for compounds **3** and **5**.

The disc conductivities of the three TCNQ complexes were measured over a range of temperature. The values increase with temperature, initially quite steeply (80–150 K), then more gradually to the plateau values of 350 K given in Table 2. This behaviour is illustrated in Fig. 1, and Fig. 2 shows the variation of the plateau conductivity with the number of methyl substituents. The apparent linear relationship is regarded as fortuitous.

The low ionisation potentials of both 1,3-dihydro-2-telluraindene (**3**) and 1,3-dihydro-2-selenaindene (see below) are quite unlike those of acyclic tellurides [14]. Furthermore, the detailed behaviour with TCNQ is dependent upon the 3 and 4 substituent on the 2,5-dihydrotellurophene ring. (We regard the telluraindene as a special case of a substituted 2,5-dihydrotelluraphene.) If donation is from the double bond (π-system), this result is contrary to expectation and would favour our previous contention [3], supported by ^{125}Te Mossbauer measurements, that donation is from the tellurium p_z lone pair.

A complex (No. 7 in Table 1) of 1,3-dihydro-2-telluraindene with DNB was isolated. Thus a combination of data in this and earlier three papers suggests that the order of donor strength is:



and that of acceptor strength:

TCNQ > TCB > DNB.

1,3-Dihydro-2-selenaindene

This compound was synthesised for comparison of its behaviour with that of the tellurium analogue. Complexes with both TCNQ and TCB are formed (Nos. 8 and 9, Table 1).

The complexes with both TCNQ and TCB have low room temperature conductivities and the infra-red spectra imply that the selenium compound may be less ionic than the tellurium analogue. A value of 6.55 eV was found for the ionisation potential of 1,3-dihydro-2-telluraindene (**3**). The same mass spectroscopic method (Warren's extrapolated voltage difference method [15]) was used to determine a value of 7.4 eV for the selenium compound. The telluraindene may be electrochemically oxidised in acetonitrile in the presence of appropriate supporting electrolytes [11], and we have now shown that the selenium compound also behaves in this way: indeed, the parallel is so close that the discussion need not be repeated.

Quinoxaline derivatives

The preparation of the compounds **3** has been extended to compounds of selenium and the studies extended to consider the effect of 7,8-dimethyl substituents (compounds **12**, **17**, **21**, Table 1). The synthesis developed earlier [5] worked well, and it was noted that the interesting molecular complex of 1,1-diiodo-7,8-dimethyl-3,4-quinoxalino-1-telluracyclopentane and 2,3-bis(iodomethyl)quinoxaline is not unique, and has parallels in compounds **11**, **16** and **20** (Table 1). The new diiodides (**10**, **15**, **19**), 1 : 1 complexes (**11**, **16**, **20**), and quinoxalino-1-chalcogenacyclopentanes (**12**, **17**, **21**) were characterised by analysis, infra-red, UV and ^{1}H NMR spectroscopy, and mass spectroscopy. The data are consistent with those presented in our earlier paper [5], and some are presented in Tables 1, 2 and 3.

Compounds **12**, **17**, and **21** form complexes with TCNQ (**13**, **18**, **22**) which all have disappointing room temperature solid state conductivities (Table 2). However, the ν(CN) region of the infra-red spectrum shows no band above 2200 cm^{-1} and imply that the ground state is strongly ionic.

References

1 K. Bechgaard, D.O. Cowan, and A.N. Bloch, J. Chem. Soc., Chem. Commun., (1974) 937.
2 K. Bechgaard, C.B. Jacobsen, K. Hortensen, H.J. Pedersen, and N. Thourp, Solid State Commun., 33 (1980) 1119.
3 H.B. Singh, W.R. McWhinnie, R.F. Ziolo, and C.H.W. Jones, J. Chem. Soc., Dalton Trans., (1984) 1267.
4 K.G.K. De Silva, Z. Monsef-Mirzai, and W.R. McWhinnie, J. Chem. Soc., Dalton Trans., (1983) 2143.
5 H.B. Singh, W.R. McWhinnie, T.A. Hamor, and R.H. Jones, J. Chem. Soc., Dalton Trans., (1984) 23.
6 N.S. Dance, W.R. McWhinnie, J. Mallaki, and Z. Monsef-Mirzai, J. Organomet. Chem., 198 (1980) 131.
7 H. Maddox and J.D. McCullough, Inorg. Chem., 5 (1966) 522.
8 J. Bergman and L. Engman, J. Amer. Chem. Soc., 103 (1981) 2715.
9 S. Cuthbertson and D.D. MacNicol, Tetrahedron Lett., (1975) 1893.
10 N.N. Magdesieva and V.A. Vdovin, Chem. Heterocyc. Comp., 8 (1972) 24.
11 H.B. Singh and W.R. McWhinnie, J. Organomet. Chem., 264 (1984) 305.
12 J.S. Chappell, A.N. Bloch, W.A. Bryden, M. Maxfield, T.O. Poehler, and D.O. Cowan, J. Am. Chem. Soc., 103 (1981) 2442.
13 Y. Yumoto, R. Nishioka, and T. Tanaka, Bull. Chem. Soc. Japan, 53 (1980) 1251.
14 N.S. Dance, W.R. McWhinnie, and C.H.W. Jones, J. Organomet. Chem., 125 (1977) 291.
15 J.W. Warren, Nature, 165 (1950) 810.