NEW ASPECTS IN ORGANOTELLURIUM HALIDE CHEMISTRY.

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Master of Philosophy

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Summary

A literature review of the known chemistry of organotellurium fluorides and iodides is presented.

The synthesises of new organotellurium iodides (RTeI and $RTeI_3$), where R = 2-(2-pyridyl)phenyl- and 2-phenylazophenyl- have been reported. It is suggested on the basis of spectroscopic examination (NMR, Mass and Raman) that the oxidation state of tellurium in these "tri-iodides" species is (II).

Attempts to synthesise RTeF and $RTeF_3$ (R = 2-(2-pyridyl)phenyl- and 2-phenylazophenyl-) are reported. The NMR (^{19}F and ^{125}Te) and analytical data for these materials are reported and discussed.

A second crystalline modification (monoclinic) form of 2-(phenylazophenyl-C,N')tellurium(II) chloride, has been formed by recrystallisation from methanol. One molecule is present in the unit cell.

The crystal structure of 2-(2-pyridyl)phenyltellurium(II) chloride has been solved in which there are six molecules present within the unit cell. There is a short Te...N interaction, with a distance of 2.205(11) Å.

Two crystalline modifications of 2-(2-pyridyl)phenyltellurium(II) iodide are reported. One form of monoiodide is triclinic and has been formed by recrystallisation from acetonitrile-methanol. The second form (monoclinic) was formed when a sample of the corresponding triiodide was recystallised from acetonitrile-methanol.

To my parents.

In things pertaining to enthusiasm,
no man is sane who does not know how
to be insane on occasions.
(Henry Ward Beecher)

Acknowledgments

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CONTENTS

List of Tables.

List of Figures.

List of Spectra.

Spectrum Page

List of schemes.

Scheme Page

CHAPTER ONE

INTRODUCTION

Introduction

Tellurium was first isolated by the Austrian chemist F. J. Muller von Reichenstein in 1782. The first organic derivative of tellurium, Et_2Te, was prepared about 60 years later in 1840 by Wohler(1). Only a few isolated investigations were performed during the next 70 years.

Lederer enriched the knowledge in this area of chemistry through his fruitful work in the decade between 1910 and 1920. His synthetic efforts produced a large number of aromatic tellurium derivatives.

1.1 *Elemental Tellurium*

Tellurium(2) has the electron configuration of [Kr] $4d^{10}\,5s^2\,5p^4$, atomic number (Z) 52. The relative atomic mass of tellurium has been determined by Berzelius, to be 127.61. Tellurium is located in group 16 of the periodic classification between selenium which has an atomic number of 34 and polonium which has an atomic number of 84. As stated above tellurium has an even Z number, therefore tellurium will have many stable isotopes, as shown in table 1.

In addition to the isotopes listed in table 1, tellurium has in excess of twenty identified unstable isotopes. Of the eight stable isotopes two isotopes are of exceptional analytical importance, which are ^{125}Te and ^{123}Te. Both are spin $^1/_2$ nuclei and suitable for nuclear magnetic resonance (NMR), in addition, ^{125}Te is suitable for Mossbauer spectroscopy studies.

Table 1. Isotope of tellurium.

Isotope of tellurium	Abundance in %	uses
^{130}Te	34.46	-----
^{128}Te	31.72	-----
^{126}Te	18.72	-----
^{125}Te	7.01	NMR and Mossbauer spectroscopy
^{124}Te	4.63	-----
^{123}Te	0.89	NMR spectroscopy
^{122}Te	2.49	-----
^{120}Te	0.09	-----

The abundance of tellurium has been determined to be 2×10^{-7} per cent by weight in the earth's crust. Therefore tellurium is as rare as gold. Tellurium maybe enriched to 5×10^{-3} per cent by weight, by replacing the sulphur in sulphuric ore. There are a few known minerals that contain tellurium, for example nagyagite and sylvanite which are found in Hungary, but they do not form large deposits of elemental tellurium.

1.2 Extraction of Tellurium

Tellurium has been obtained as a by-product of the extraction processes of other ores. Tellurium is also obtained as a by-product of the electrolysis of copper and nickel during their refining process; from the waste product of the manufacturing of sulphuric acid; from the waste products of the smelting of lead and processes for recovering noble metals.

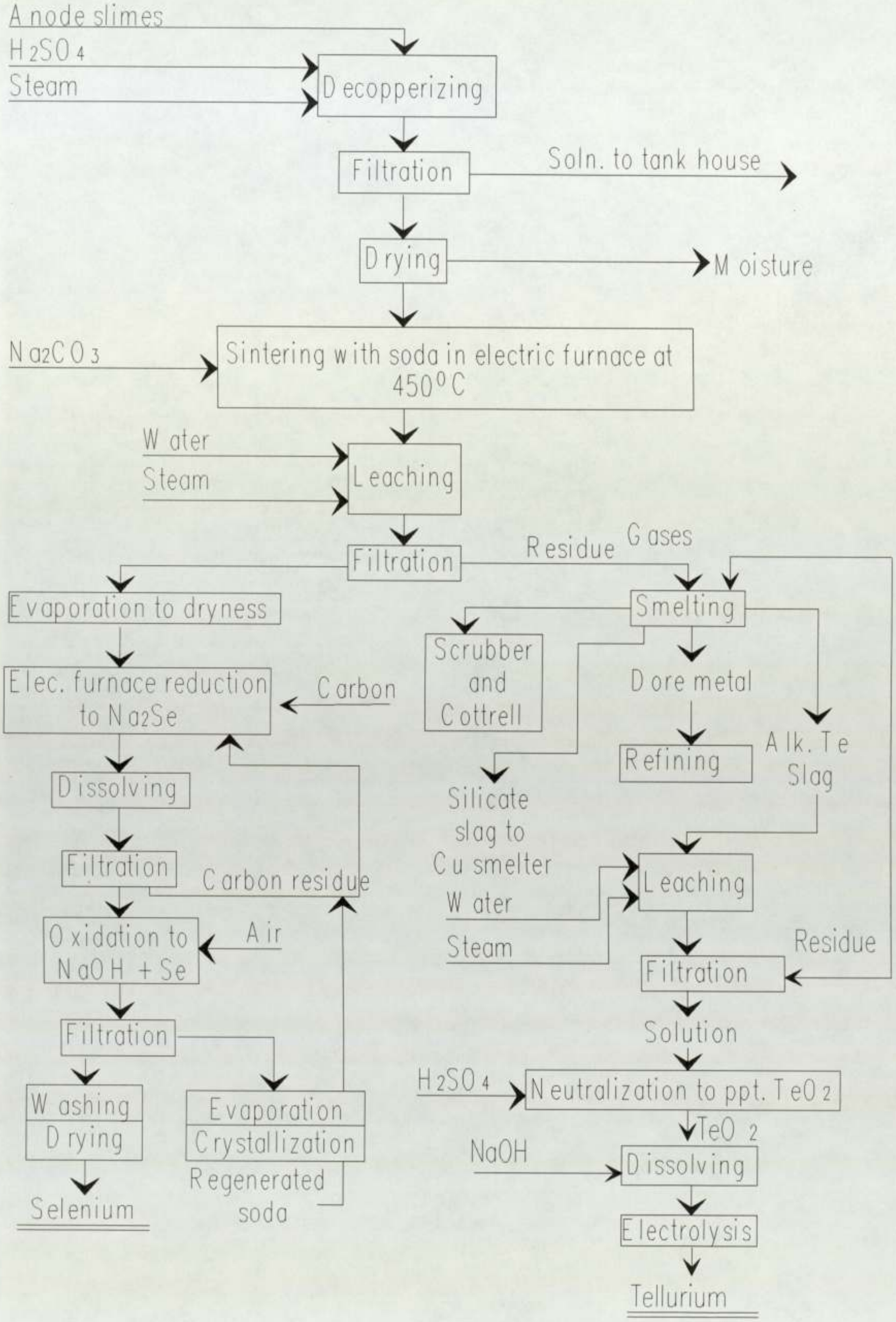
Tellurium is formed at the anode during the electrolysis of copper and lead. Tellurium is not formed pure, it is formed in a sludge, which can contain up to 8 per cent copper, silver, gold and the platinum group metals. Tellurium can be extracted from the sludge, by the method shown below (figure 1)$^{(3)}$.

As shown in figure 1, the sludge is roasted in an oxidizing atmosphere. The roasted sludge is melted with sodium carbonate or with a sodium nitrate - sodium hydroxide mixture, this converts the tellurium into sodium tellurite, which is a water soluble compound. Therefore the sodium tellurite can be extracted in solution, which is known as a melt.

The cooled melt precipitates tellurium dioxide upon neutralization with sulphuric acid. Sodium selenite remains in solution. Therefore the sodium selenite can be separated and then can be treated to form selenium, which is also shown in figure 1. The tellurium dioxide that is formed will dissolve in sodium hydroxide. The electrolysis of the solution will form crude tellurium.

This crude tellurium contains impurities such as selenium, copper, arsenic, antimony, bismuth and traces of other elements. The purification of the tellurium is achieved by employing several techniques which are given by Kraus and Chiu$^{(4)}$.

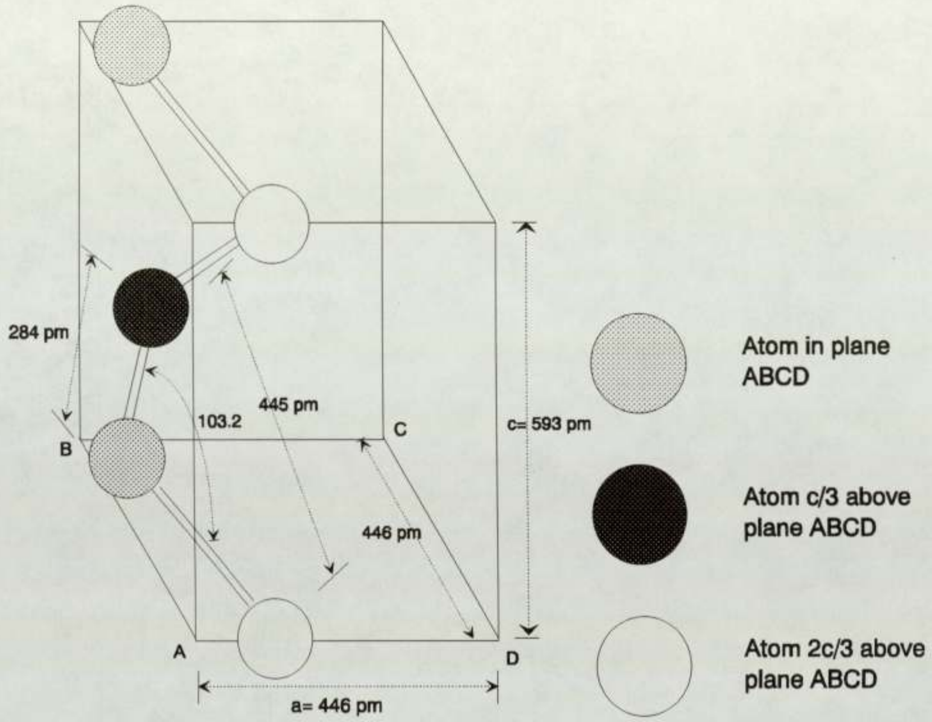
Figure 1. Production of crude tellurium.



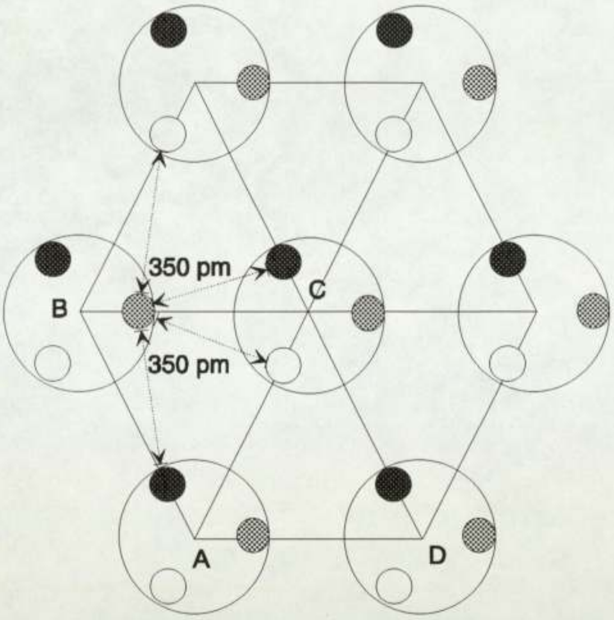
1.3 *Structure of Tellurium*

Unlike sulphur and selenium which can exist in several allotropic forms, only one crystalline and amorphous form of tellurium has been detected so far. The crystalline form of tellurium is composed of a network of spiral chains similar to those in hexagonal Selenium(5) (figure 2(a))

Figure 2.



a) The helical chain in crystalline tellurium shown in perspective.



b) Projection of the crystalline tellurium structure on a plane perpendicular to the c - axis.

The hexagonal unit cell contains three tellurium atoms. The atoms are arranged in a helix of three - fold symmetry as shown in figure 2(a), the prism edge serving as the screw axis. The fourth tellurium atom is positioned exactly above the first atom.

The helix has a radius 445 pm, which is taken from the perpendicular distance from the centre of each atom. The shortest distance between two atoms in the same helix is 284 pm, while the shortest distance between atoms in neighbouring helices(6) was found to be 446 pm.

Crystalline tellurium is a silver-white substance with a metallic luster. It melts at 449.8°C to a dark liquid and boils at 1390°C (7).

1.4 Tellurium Halides

Elemental tellurium combines with the halogens to produce tellurium halides, of the forms di-, tetra- and hexa-halides.

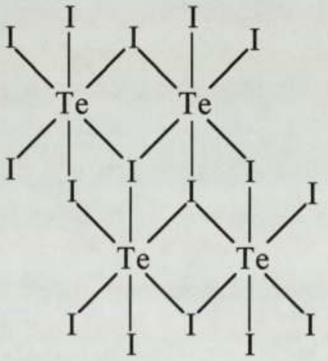
The halides of tellurium are more stable than those of sulfur and selenium. Dutton(8) lists more than one hundred simple and complex tellurium halides and their preparation method.

1.4.1 A) Tellurium Iodides

The only iodide that has been produced is the tetraiodide.

The formation of this compound is very simple, in that elemental tellurium will react with elemental iodine forming tellurium tetraiodide, through the iodination of tellurium. The structure of this compound is tetrameric(9) but is based on a stepped rather than on a cubic conformation, as shown below in figure 3.

Figure 3.



The structure of tellurium tetraiodide

1.4.2 B) Tellurium Bromides

There are two bromides - $TeBr_2$ and $TeBr_4$.

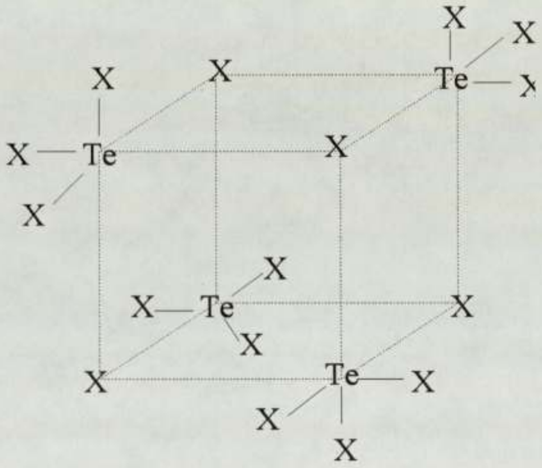
Tellurium dibromide

The dibromide is prepared by reducing tellurium tetrabromide in ether in the dark with $SnCl_2$ or tellurium powder. The compound that is formed is a brown colour, which is an unstable solid, therefore on warming or exposure to water the compound disproportionates readily to tellurium and tellurium tetrabromide.

Tellurium tetrabromide

The formation of this compound is achieved by the direct bromination of tellurium. The tellurium tetabromide hydrolyzes very slowly in the atmosphere. The structure(10) of this compound has been established to be cubic tetrameric structure, Te_4Br_{16}. Each tellurium atom is in a distorted octahedral environment as shown in figure 4.

Figure 4.



The structure of tellurium tetrachloride or tetrabromide.

Where X = Br (or Cl see next section).

1.4.3 C) Tellurium Chlorides

There are two chlorides - $TeCl_2$ and $TeCl_4$.

Tellurium dichloride

The compound is prepared by passing dichlorodifluoromethane over molten tellurium. The compound is a black solid in appearance, which will disproportionate in ether or dioxane to give tellurium and tellurium tetrachloride.

Tellurium tetrachloride

The compound is prepared by heating elemental tellurium with elemental chlorine(11), or by the chlorination of heated tellurium or its dioxide with SCl_2, $SeOCl_2$, CCl_4 and ICl.

Tellurium tetrachloride is white, crystalline, hygroscopic, and deliquescent in moist air with partial hydrolysis. The structure(10) of this compound has been found to be the same as tellurium tetrabromide and it is shown is figure 4.

1.4.4 D) Tellurium Fluorides

There are two fluorides - TeF_4, and TeF_6, while TeF_2 is not known.

Tellurium tetrafluoride

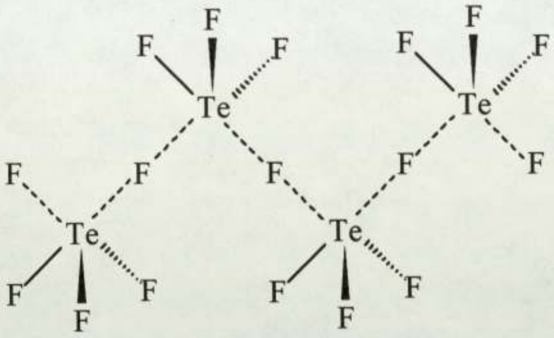
Tellurium tetrafluoride is prepared(12), by heating elemental tellurium with tellurium hexafluoride or tellurium dioxide with selenium hexafluoride, as shown in equation 1.

$$\begin{aligned} &Te + 2TeF_6 \rightarrow 3TeF_4 \\ &TeO_2 + 2SeF_6 \rightarrow TeF_4 + 2SeOF_2 \end{aligned} \qquad (1)$$

The formation takes place in a fused alumina tube, since the fluorides attack glass, silica and metals. Tellurium tetrafluoride forms white needles with a sublimation point of 120°C, a melting point of 129.6°C and which decompose above 194°C. It is very hygroscopic and readily hydrolyzed.

The tellurium tetrafluoride(28) is monomeric in the gas phase, but in the solid state the structure of the compound is best described as being a polymeric zig-zag structure as shown below in figure 5. As can been seen in figure 5, tellurium has an Ψ-octahedral environment via two bridging and three terminal fluorine atoms.

Figure 5.



The structure of tellurium tetrafluoride.

Tellurium hexafluoride

Tellurium hexafluoride is colourless, highly toxic gas with an unpleasant odour. It is prepared from the elements at 150°C(12), and purified by fractional distillation at low temperature. Some properties of the gas have been given in table 2.

Table 2. Physical properties of tellurium hexafluoride.

Property	Values
Melting point	-37.8°C
Sublimation point	-38.9°C
Critical temperature	83.25°C
Heat of formation	-1316.7 kJ/mole
Heat of fusion	~ 7.94 kJ/mole
Heat of sublimation	28 kJ/mole
Density at -37°C	3.025 g/cm^3

Tellurium hexafluoride reacts with tellurium below 200°C giving a lower fluoride. Tellurium hexafluoride hydrolyzes with water slowly but more readily than selenium hexafluoride. It is a weak Lewis acid, forming alkali fluorotellurate salts.

Ditellurium decafluoride oxide

Ditellurium decafluoride oxide is a stable, colourless, volatile liquid. Some physical properties of the liquid have been given in table 3.

It is prepared by passing elemental fluorine over a tellurium-calcium fluoride mixture(12), or by passing a mixture of fluorine and oxygen over a mixture of tellurium and tellurium dioxide at 50-60°C giving a 40-50% yield. The structure configuration indicated by infrared spectrum is $F_5TeOTeF_5$. The compound attacks glass slowly, reacts vigorously with sodium and violently with potassium. On the other hand, it is inert to water, acids, dilute alkalis, copper, mercury, nickel, iron, sulphur and selenium.

Table 3. Physical properties of ditellurium decafluoride oxide.

Property	Values
Boiling point	59°C
Melting point	-33.8°C
Density	2.88 g/cm3

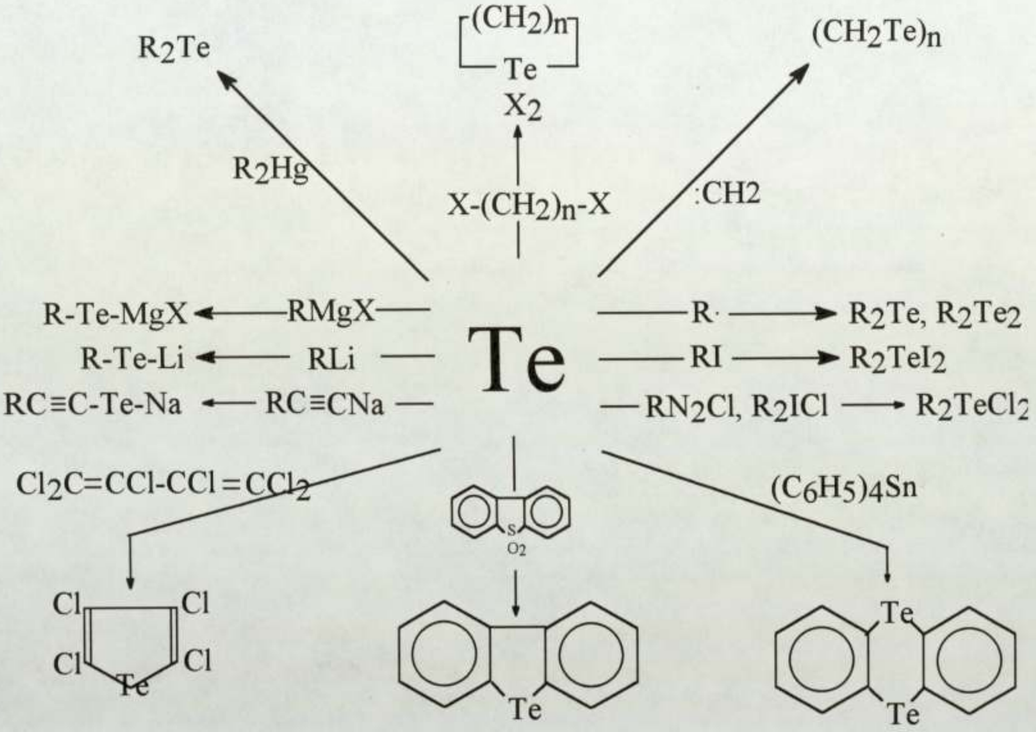
1.5 Methods for the Introduction of Tellurium into Organic Molecules

Elemental tellurium can be used directly in the formation of a few organic tellurium compounds. Organic tellurium compounds can be synthesized by using inorganic tellurium compounds as starting materials. The most common inorganic starting materials are tellurium tetrahalides and alkali metal tellurites.

1.5.1 A) Elemental Tellurium

The reactions summarized in figure 6 will form at least one carbon - tellurium bond, by using elemental tellurium as a starting material.

Figure 6. The synthesis of organic tellurium compounds from elemental tellurium.

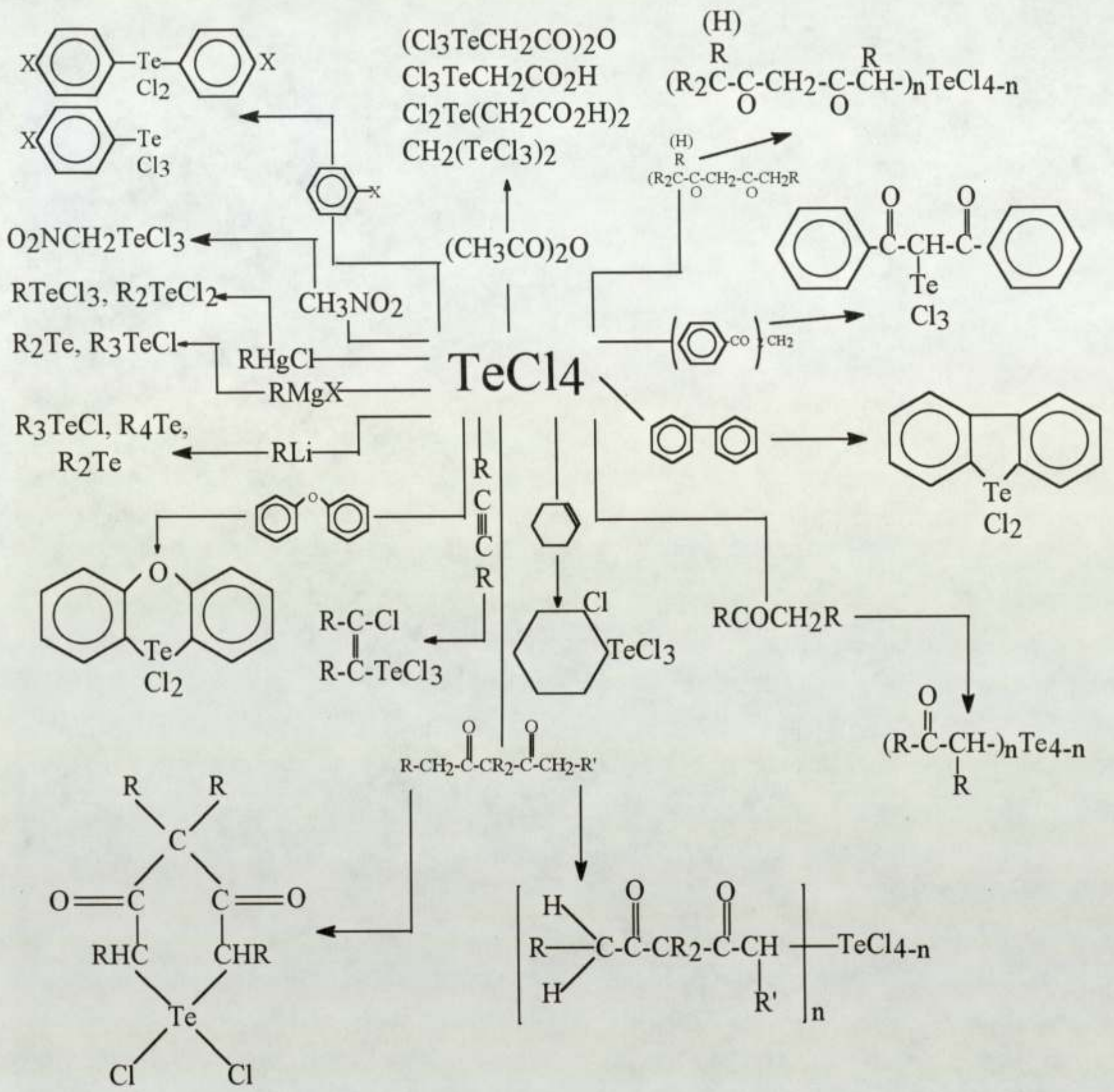


1.5.2 B) Tellurium Halides

Among the tellurium tetrahalides the tetrachloride is used almost exclusively over the other tetrahalides. Tellurium tetrabromide and tetraiodide have been used, but only in a limited number of reactions. The tellurium tetra- and hexa- fluorides have not yet been employed in the synthesis of organic tellurium compounds. This is because tellurium tetrafluoride is polymeric and the hexafluoride is thermally unstable.

As tellurium tetrachloride has been used almost exclusively, the reactions between tellurium tetrachloride and organic reagents, which proceed during the formation of at least one carbon - tellurium bond, have been summarized in figure 7.

Figure 7. Organic tellurium compounds from tellurium tetrachloride.



The methods and conditions for the reaction that have been summarized in Fig 6 and 7 can been found in the following references$^{(2, 13)}$.

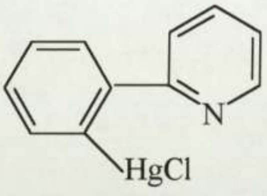
The next sub-heading in this introduction will describe the reaction pathway that was taken to produce the carbon-tellurium bond in this thesis.

1.5.3 Reaction of Tellurium Halides with Aryl Mercury Chlorides

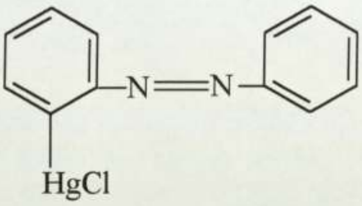
Aryl mercury chlorides, which can be prepared from mercuric chloride and diazonium salts, can be employed to form carbon-tellurium bonds when a direct condensation between tellurium tetrachloride and an aromatic compound is not possible. Equimolar quantities of the aryl mercury chloride and tellurium tetrachloride in dioxane give aryl tellurium trichloride(13, 14, 15, 16), in yields ranging from 60-90 per cent, as shown in equation 2,

$$RHgCl + TeCl_4 \rightarrow RTeCl_3 + HgCl_2 \qquad (2)$$

where the aryl mercury chlorides in the equation (2) above can be;



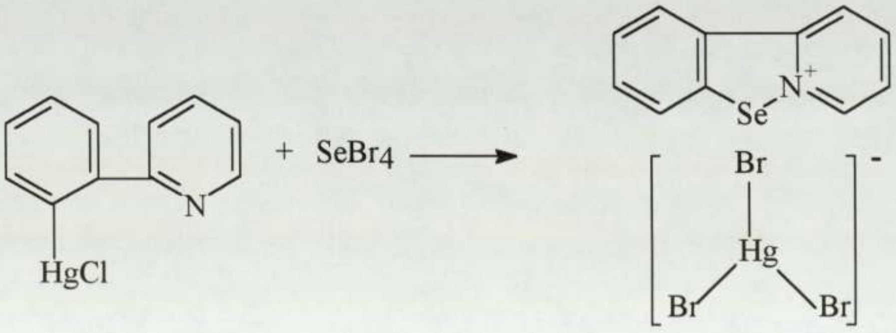
or



(These are the two aryl mercury chlorides used for this research).

Tellurium tetrabromide can also be used in the above reaction forming aryl tellurium tetrabromide(17).

Aryl mercury chlorides can also be reacted with the selenium tetrachloride or tetrabromide, this reaction has been carried out by Mbogo(18). The reaction was carried out in the same way as above, in that the reactants were refluxed in dioxane. The products from these reactions were not pure. They were mixtures, containing intermediates of the *trans*-metallation process. The end product that was isolated was 2-(2-pyridyl)phenylselenium(II) tribromomercurate, which can be seen in equation (3) below.



(3)

1.6 Tellurium - Fluorine Chemistry

The first inorganic compounds that were made with the elements tellurium and fluorine have been described in the section "Tellurium Halides". The compounds were established in 1933 by Yost and Claussen(19).

The first organotellurium fluoride compound was reported in 1946, by Emeleus and Heal(20). Work on the formation of these compounds was carried out during World War II. Much attention was given to organometallic - fluorine chemistry at this time, due to its potential to produce poisonous gases. Since the war very little has been done in the organotellurium fluorine field.

Surprisingly this area of chemistry has received very little attention, therefore this research has been carried out to try to remedy this situation.

1.7 The Formation of Tellurium - Fluorine Containing Compounds using Metallic Fluorides as Starting Materials

Many reactions of the tellurium hexafluoride have been done in this field, but not with tellurium tetrafluoride.

1.7.1 Tellurium Hexafluoride Chemistry

Tellurium hexafluoride will react with water or ROH(21); or TeX_6 will react with anhydrous HF(22) to produce TeF_nX_{6-n} compounds, where X is OH or OMe, as shown in equations (4 and 5).

$$TeF_6 + xROH \rightarrow TeF_{6-x}(OR)_x + xHF \qquad (4)$$

$$Te(OH)_6 + nHF \leftrightarrow Te(OH)_{6-n}F_n + nH_2O \qquad (5)$$

Other highly substituted alkoxy species of TeF_nX_{6-n} have also been prepared, which are presented in the Table 4 below.

Table 4. Substituted alkoxy species of TeF_nX_{6-n}.

TeF_nX_{6-n}, where X is	Reference no.	N =
$MeOCH_2CH_2$	21	1 - 4
$EtOCH_2CH_2$	23	3 - 4
$ClCH_2CH_2$	21	1 - 3
$BrCH_2CH_2$	21	1 - 4
CF_3CH_2	21	2 - 3
$NCCH_2CH_2$	23	3 - 4

The products stated in Table 4, are produced as a mixture which can not be separated by fractional distillation due to their similar physical properties. The products were analyzed and identified using ^{19}F NMR.

Tellurium hexafluoride will also react with Me_3SiX(24) (where X = N_3 or NMe_2) to give all members of the series TeF_nX_{6-n} (n = 1 - 5) except *mer*-TeF_3X_3. The reaction was carried out in a NMR tube and the species were identified using ^{19}F NMR spectroscopy.

N-trimethylsilyaminotellurium pentafluoride(25) is prepared by reacting tellurium hexafluoride with $(R_3Si)_2NH$ (where R = methyl group) at liquid nitrogen temperature, then allowed to warm up to room temperature and then stirred for another 12 hours. Aminotellurium pentafluoride, which is prepared by reacting N-trimethylsilyaminotellurium pentafluoride with a small excess of anhydrous hydrogen fluoride and then cooled to dry-ice temperatures, as shown in equation (6).

$$\begin{aligned} &(R_3Si)_2NH + TeF_6 \rightarrow R_3SiF + R_3SiNHTeF_5 \\ &R_3SiNHTeF_5 + HF \rightarrow R_3SiF + H_2NTeF_5 \end{aligned} \qquad (6)$$

Where $R_3SiNHTeF_5$ = N-trimethylsilyaminotellurium pentafluoride

H_2NTeF_5 = aminotellurium pentafluoride

1.7.2 Xenon Difluoride

Di-pentafluoroethantellurium [$(C_2F_5)_2Te$]$^{(26)}$ was stirred with xenon difluoride and SO_2ClF at -45°C, for 30 minutes and then allowed to warm up to room temperature. Once the reaction was complete, analysis of the product showed a mixture of di-pentafluorethantellurium difluoride and other compounds, as shown in equation (7) below.

$$(C_2F_5)_2Te \xrightarrow{XeF_2} (C_2F_5)_2TeF_2 + \text{Mixture} \qquad (7)$$

Mixture = Xe, SO_2ClF, C_2F_6, C_2F_5Cl, SO_2F_5 and $(C_2F_5)_2Te$

Organotellurium trifluoride can also be synthesized by using xenon difluoride and SO_2F_2 as shown below in equation (8).

$$(C_2F_5)_2Te_2 \xrightarrow{XeF_2} (C_2F_5)TeF_3 \qquad (8)$$

Equation (8) shows that di-pentafluorethantellurium [$(C_2F_5)_2Te$]$^{(26)}$ will react with the XeF_2 and SO_2F_2 stated above at -45°C to form the organotellurium trifluoride.

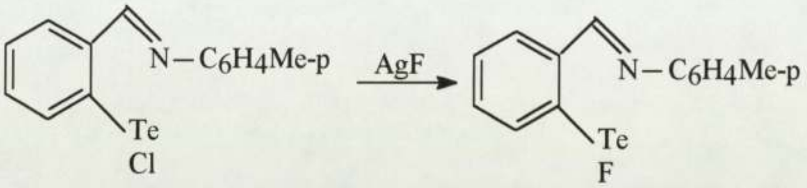
1.8 The Formation of Tellurium - Fluorine Containing Compound using Organotellurium Halides as Starting Materials

As stated above only a few organotellurium fluorine compounds have been made.

An organotellurium halide [where the halide is usually the chloride, bromide or iodide] is reacted with a suitable reagent to exchange the halide for a fluoride. The formation of these compounds are carried out under a wide range of conditions.

1.8.1 a) Organotellurium(II) Halide

The reaction of [2-(p-tolyiminomethyl)phenyl]tellurium(II) chloride or bromide(27) with a silver(I) fluoride in HPLC-grade acetone, will produce the fluoride as shown below in equation (9). The reaction was carried out in a stirred flask at room temperature.

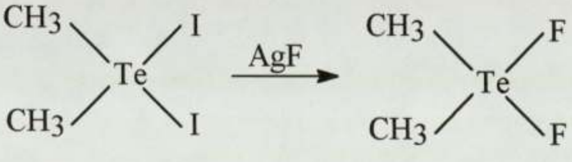


(9)

1.8.1 b) Organotellurium(II) Dihalide

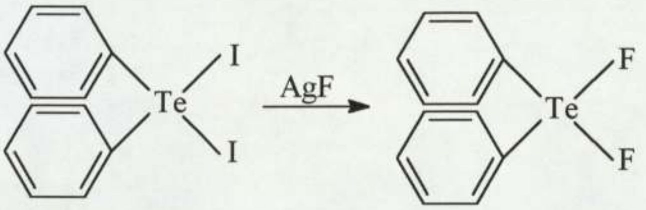
The organotellurium(II) difluoride was formed using the same reagent as in the mono-fluoride. The reaction conditions that were used to form the organyltellurium(IV) difluoride were more harsh than the organyltellurium(II) fluoride. The reactant was dissolved in sodium dried toluene and refluxed with an excess of silver(I) fluoride.

The formation of dimethyltellurium difluoride has been carried out by Emeleus and Heal(20), in the same way as stated above. The reactant that was used was dimethyltellurium diiodide which gave dimethyltellurium difluoride, as shown in equation (10) below.



(10)

The formation of diphenyltellurium difluoride has been carried out by Berry, Kustan, Roshani and Smith(29), again in the same way as stated above. The reactant that was used was diphenyltellurium dichloride which gave diphenyltellurium difluoride, as shown in the equation (11) below.

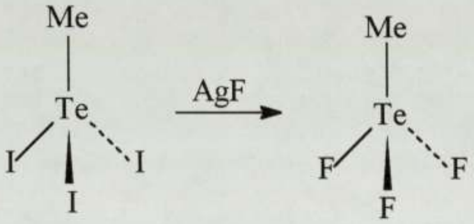


(11)

1.8.3 c) Organotellurium(IV) Trihalide

In the past attempts to form organyltellurium trifluorides, have resulted in mixtures rather than pure products.

The reaction of methyltellurium triiodide with silver(I) fluoride was carried out by Emeleus and Heal(20) [as shown in equation (12) below], in the same way as for the preparation of organotellurium difluoride. The reactants were refluxed in toluene, with an excess of the silver salt. The product was not pure, in fact it was an oil, which did not form crystals.



(12)

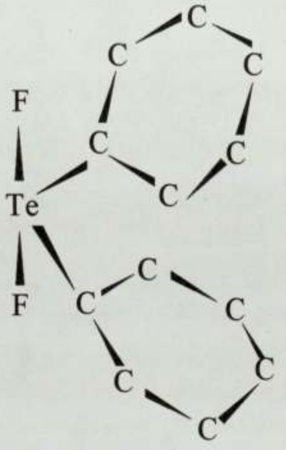
1.9 The Structure of Tellurium - Fluorine Containing Compounds

The first structure that was determined for these types of compounds was for tellurium tetrafluoride. The structure has already been detailed in the section "Tellurium Halides".

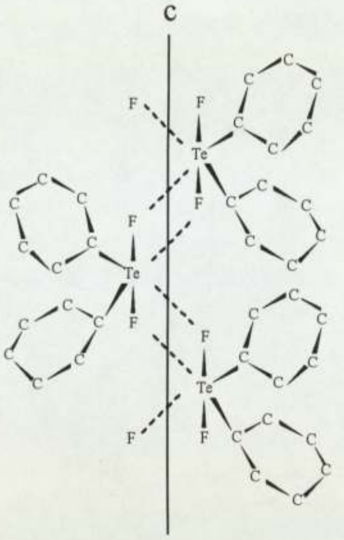
The structure for diphenyltellurium difluoride has been reported by Berry and Edwards(30). Analysis of the results showed that diphenyltellurium difluoride adopted a distorted Ψ-trigonal-bipyramidal arrangement, shown in Figure 8(a), in which the fluorine atoms occupy axial positions with the F-Te-F bond angle (173°) which is close to the theoretical value of 180°. The angle between the equatorial phenyl groups is 96.9° (theoretical, 120°) and may due to repulsion of the aromatic groups by the tellurium lone pair according to simple valence-shell electron-pair repulsion theory.

There are two long bridging contacts from tellurium to fluorine which lie either side of the tellurium lone pair. These weak contacts are known as secondary Te---F interactions, also these secondary Te---F interactions effectively link the units into chains parallel to the c-axis, see figure 8(B).

Figure 8.



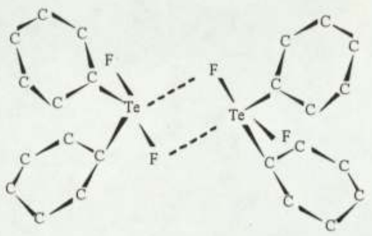
(a) Structure of diphenyltellurium difluoride.



(b) Showing the weak intermolecular interactions.

Another structure which has been reported in the series R_2TeF_2, is for bis(pentafluorophenyl)tellurium difluoride(31). The structure appears to be a molecular solid in which pairs of crystallographically independent molecules are mutually linked by secondary Te---F interactions. Each of the two independent molecules displays the approximate Ψ-trigonal-bipyramidal geometry as stated above for the diphenyltellurium difluoride. In bis(pentafluorophenyl)tellurium difluoride each tellurium atom has only one secondary Te---F interactions to a fluorine on an adjacent molecule (figure 9), whereas in diphenyltellurium difluoride each tellurium atom has two such interactions.

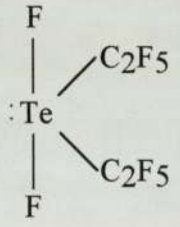
Figure 9



Molecular structure of bis(pentafluorophenyl)tellurium difluoride with the secondary interactions.

Structures have also been determined for the alkyl series of bis(perfluoroalkyl)tellurium difluoride for example bis(perfluoroethyl)tellurium difluoride(26). The structure of bis(perfluoroethyl)tellurium difluoride is similar to that of the aryl series, in that the two fluorine atoms are in the axial position, the other conformation of the structure is Ψ-trigonal-bipyramidal, see figure 10. The structure also has some very weak intermolecular interactions.

Figure 10.



Molecular structure of bis(perfluoroethyl)tellurium difluoride.

The table 5, below shows the tellurium --- fluoride bond lenghts of organyltellurium fluoride compounds.

Table 5. Tellurium --- fluoride bond lenghts of organyltellurium fluoride compounds.

Compound	Bond	Lenght, Å	Reference
$(Ph)_2TeF_2$	Te - F	2.006	30
$(C_6F_5)_2TeF_2$	Te - F (1)	1.990	31
	Te - F (2)	1.932	
$C_2H_5TeF_3$	Te - F(1)	2.190	26
	Te - F (2)	1.874	
	Te - F (3)	1.870	

The covalent radii of tellurium and fluorine are 1.37 and 0.72 Å respectively, giving the bond lenght of 2.09 Å. When comparing the sum of covalent radii with the found bonds lenghts it was noted that $(Ph)_2TeF_2$ and $(C_6H_5)_2TeF_2$ are very similar to the calculated valve, but on the other hand $(C_2F_5)TeF_3$ were found to have short bonds than expected.

1.10 Tellurium - iodine Chemistry

The first inorganic compounds that were made with the elements tellurium and iodine have been mentioned in the section "Tellurium Halides".

When comparing tellurium - iodine inorganic compounds with the other tellurium halides, it was noted that only the tetraiodide was known. This was surprising since other tellurium dihalides were known.

The first organotellurium iodide, dimethyltellurium diiodide was reported in 1883 by Demarcay(32). This area of chemistry has received a little more attention, than the organotellurium fluoride field.

1.11 Formation of Tellurium - iodine Containing Compounds.

It was noted that mention of the organotellurium mono-, tri- and tetra- iodides were uncommon in the literature. It appeared that organotellurium diiodides dominated the literature.

1.11.1 Organotellurium monoiodides

A series of organotellurium monoiodides have been made, see table 6.

The triorganotellurium monoiodides listed in table 6 were synthesised in a two step reaction. The first step was the reduction of an diorganotellurium diiodide (R_2TeI_2) to an diorganotelluride (R_2Te). The second step is the oxidative addition of R'I, see equation 13

Table 6. Triorganotellurium monoiodides compounds.

Compound	Reference
$(CH_3)_3TeI$	33
$(n\text{-}C_3H_7)_3TeI$	34
$(n\text{-}C_4H_9)_2CH_3TeI$	35
$(CH_3)_2C_6H_5TeI$	34
$(CH_3)_2C_2H_5TeI$	34

$$R_2TeI_2 \xrightarrow{\text{Reduction}/K_2SO_3+NaCO_3} R_2Te \xrightarrow{\text{Oxidation}/R'I} R_2R'TeI \qquad (13)$$

Where R $= CH_3$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$

R' $= CH_3$, C_2H_5, $n\text{-}C_3H_7$, C_6H_5

The formation of bis(diethyldithiocarbamato)iodomethyltellurium(IV)$^{(36)}$, see equation 14, which applied that a solution of $Te(Etdtc)_2$ [where Etdtc = diethyldithiocarbamato] in dichloromethane was added to an excess of iodomethane.

The reaction rate was considered to be slow, judging from the slow colour change from red to yellow.

$$\mathrm{Te(Etdtc)_2 + MeI \xrightarrow{CH_2Cl_2} MeTeI(Etdtc)_2} \qquad (14)$$

Bis[2-((dimethylamino)methyl)phenyl]tellurium monoiodide (2-$NMe_2CH_2C_6H_4TeI$) was obtained as a minor side product when the formation of bis[2-((dimethylamino)methyl)phenyl]telluride(37) was carried out. The synthesis involved the addition of iodomethane, therefore it is apparent that iodomethane must be the reagent responsible for the iodination of both the organotellurium compounds.

Another reagent used in the formation of monoiodide was dimethyltellurium diiodide, which has been used in the formation of iododimethyl(N,N-diethylmonothiocarbamato)-tellurium(IV)(38), see equation 15.

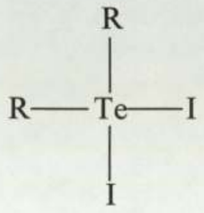
$$\mathrm{[Me_2SCONEt]^- Na^+ + (CH_3)_2TeI_2 \rightarrow Me_2TeI(SCONEt_2)} \qquad (15)$$

A solution of the sodium salt of N,N-dimethylmonocarbamato and dimethyltellurium diiodide, are stirred in the solvent dichloromethane. The reaction to occured in a few minutes, judged by the change in colour. A rapid change in colour indicated a fast reaction.

1.11.2 Diorganotellurium diiodides

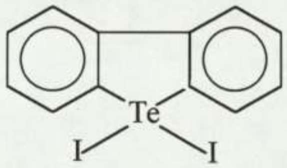
Two different classes of compounds have been reported in the literature.

The first class is R_2TeI_2, where two organic groups are attached to the tellurium atom, see below.



$\mathrm{R_2TeI_2}$

The second class is, $RTeI_2$, where the compounds is a heterocycle with tellurium as the heterocycle atom, for example dibenzotellurophene(39).



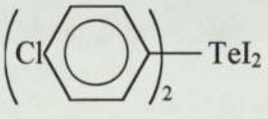
Giving rise to tellurium(IV) in both cases.

1.11.3 R_2TeI_2

A few compounds have been synthesised, where there are two organic group attached to the tellurium atom.

The first compound reported was dimethyltellurium diiodide(32), which had the general formula (R_2TeI_2). A sample of derivatives have been made, see table 7.

Table 7. Organotellurium diiodide compounds.

Compound	Reference
$(CH_3)_2TeI_2$	32
$(C_2H_5)_2TeI_2$	40
$(n\text{-}C_3H_7)_2TeI_2$	34
$(n\text{-}C_4H_9)_2TeI_2$	35
$(n\text{-}C_5H_{11})_2TeI_2$	34
$(Ph)_2TeI_2$	41
	42

The synthesis of the following compounds dimethyltellurium diiodide(32), diethyltellurium diiodide(40), dipropyltellurium diiodide(34), dibutyltellurium diiodide(35), dipentyltellurium diiodide(34) and di-p-chlorodiphenyltellurium diiodide(42) were carried out in a similar fashion, which was by mixing a solution of the components in carbon tetrachloride, see equations 16.

$$2RI + Te \xrightarrow{CCl_4} R_2TeI_2 \qquad (16)$$

Where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, Cl-C_6H_5

Vernon(43) showed that dimethyltellurium diiodide exists in two isomeric forms, α and β. Vernon also showed that two isomeric forms also existed in dimethyltellurium dichloride(43) and dibromide(43). These isomers could be prepared separately. The α-isomer was made by the method stated by Demarcay(32), and the β-isomer was produced by taking the α-form and carrying out the synthesis stated in equation 17.

$$\underset{\alpha-form}{Me_2TeI_2} \xrightarrow{AgO_2} \underset{\alpha-form}{Me_2Te(OH)_2} \xrightarrow{evap.} \underset{\beta-form}{Me_2Te(OH)_2} \xrightarrow{HI} \underset{\beta-form}{Me_2TeI_2} \qquad (17)$$

Vernon also noticed that the α- and β- forms were very different in chemical and physical properties. The molecular structure of the α- and β- forms are discussed later in the introduction.

The preparation of the diphenyltellurium diiodide(41) was carried out using diphenyltellurium oxide and a slight excess of hydriodic acid, see equation 18.

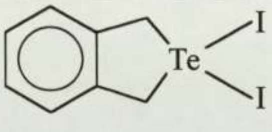
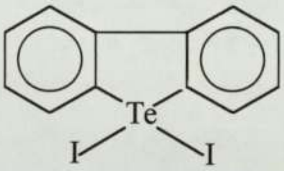
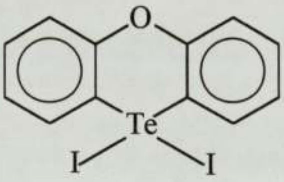
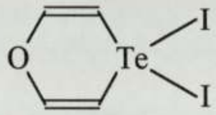
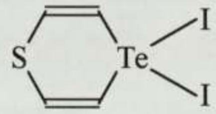
$$Ph_2TeO + HI \xrightarrow{methanol} Ph_2TeI_2 \qquad (18)$$

Giving deep orange/red crystals. When the crystals were recrystallised from hot toluene a mixture of deep orange/red crystals and carmine/red crystals resulted. The crystals were identified to be the α- (carmine/red crystals) and β- (deep orange/red crystals) forms of diphenyltellurium diiodide. The molecular structure of the α- and β-forms are described later in the introduction.

1.11.4 $RTeI_2$

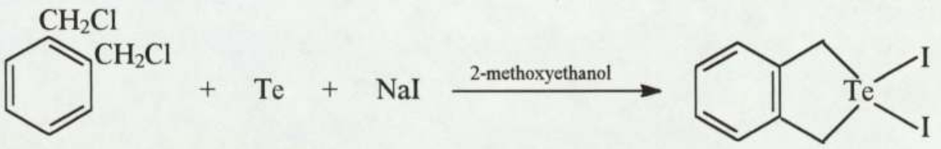
A number of compounds have been synthesised, where the tellurium atom is the heterocyclic atom, as in table 8.

Table 8. Heterocyclic tellurium compounds.

Compound	Reference
	44
	39
	45
	46
	47

Three iodination reagents were used to form the above compounds in table 7. These reagents were sodium iodide, potassium iodide and iodine.

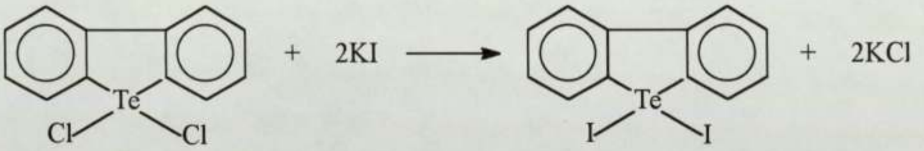
The formation of 1,1-diiodo-3,4-benzo-1-telluracyclopentane(44), was carried with gentle heating and stirring of elemental tellurium, α,α'-dichloroxylene and sodium iodide in 2-methoxyethanol, see equation 19.



(19)

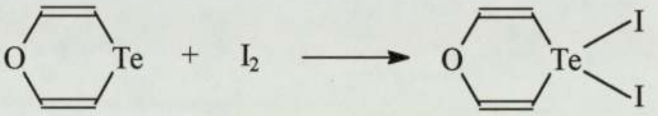
Analysis of the compound 1,1-diiodo-3,4-benzo-1-telluracyclopentane(44), showed two isomeric forms, α- and β- forms.

Dibenzotellurophene diiodide(39) was prepared by grinding dibenzotellurophene dichloride with a two-fold excess of potassium iodide under methylethyl ketone, see equation 20.

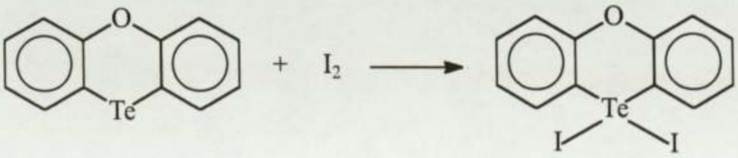


(20)

Synthesis of phenoxatellurin-10,10-diiodide(45), 1-oxa-4-telluracyclohexane-4,4-diiodide(46) and 1-thio-4-telluracyclohexane-4,4-diiodide(47) were synthesised using iodine as the iodinating reagent. All three syntheses were carried out in methylene chloride. The molar ratio of iodine to starting material was 1:1. The reaction mixture was only stirred, see equations 21 to 23.



(21)



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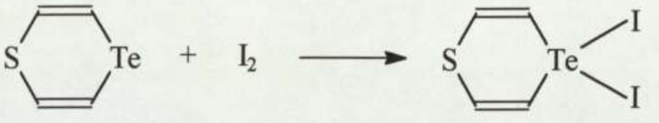
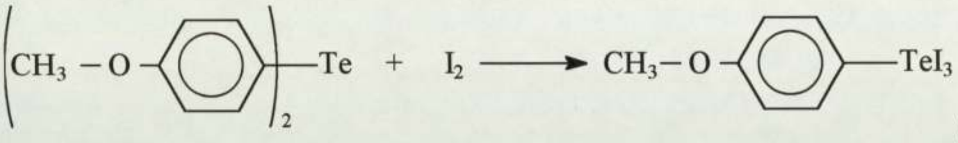


(23)

1.11.5 Organotellurium triiodides

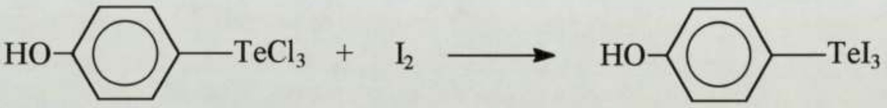
Only a few organotellurium triiodides have been produced to date.

Petragnani synthesised p-methoxyphenyltellurium triiodide(48) by reacting p-methoxyphenyltelluride with iodine in carbon tetrachloride, see equation 24.



(24)

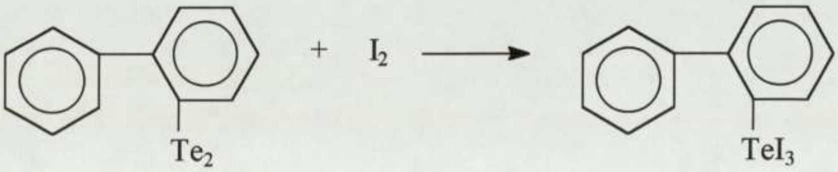
Petragnani also prepared p-hydroxyphenyltellurium triiodide(48) in 1960 from the corresponding trichloride in methanol with excess aqueous potassium iodide, see equation 25.



(25)

Organotellurium triiodides were found to be soluble in organic solvents, but p-hydroxyphenyltellurium triiodide was found to be soluble in water, by Petragnani.

McCullough and Knobler prepared 2-biphenyltellurium triiodide(49). The synthesis involved the reaction of 2-biphenyltellurium trichloride to produce (2-biphenylyl)ditelluride then, iodide is added to this compound, see equation 26. The reaction was carried out in chloroform and carbon tetrachloride.



(26)

α- and β- forms of phenyltellurium(IV) triiodide$^{(41)}$ were prepared by Alcock and Harrison. Diphenylditellurium was treated with a 5 % stoicheiometric excess of iodine in chloroform, see equation 27.

$$Ph_2Te_2 + 3I_2 \xrightarrow{ChCl_3} 2PhTeI_3 \qquad (27)$$

1.11.6 Diorganotellurium "tetraiodide",

Organotellurium tetraiodides are very uncommon in the literature. Only four have been synthesised to date, see table 9.

Table 9. Organotellurium tetraiodides compounds.

Compound	Reference
$(CH_3)_2TeI_4$	34
$(C_2H_5)_2TeI_4$	33
$(n\text{-}C_3H_7)_2TeI_4$	34
$(n\text{-}C_4H_9)_2TeI_4$	34

A reaction with the organotellurium diiodide and iodine produced the organotellurium tetraiodides in table 9, see equation 28.

$$R_2TeI_2 + I_2 \rightarrow R_2TeI_4 \qquad (28)$$

Where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9

Propyltellurium tetraiodide is unstable and will decompose at room temperature, whereas the other tetraiodides are stable.

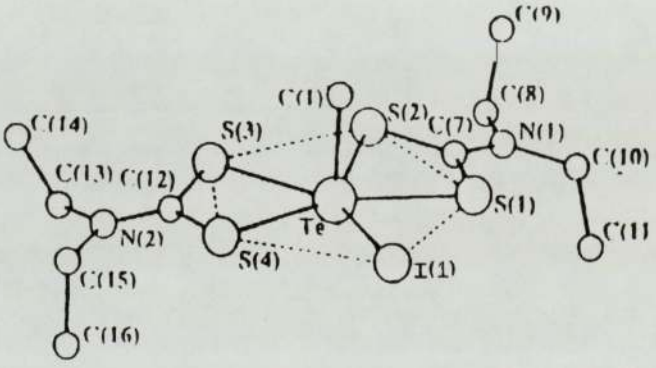
1.12 The structures of tellurium - iodine compounds.

1.12.1 Organotellurium monoiodide

The molecular structure of bis(diethyldithiocarbamato) iodomethyltellurium(IV)(36) is shown in figure 11.

It can be seen from the figure 11, that the tellurium atom is co-ordinated to four sulphur atoms, one methyl carbon and an iodine atom. The iodine atom and the four sulphur atoms are arranged in a pentagonal plane about the tellurium atom, whilst the methyl group is perpendicular to the plane, and a sterically active lone pair electron pair, on the opposite side of the plane. This gives rise to an overall seven - co-ordinated pseudo ψ- pentagonal - bipyramidal environment about the tellurium atom.

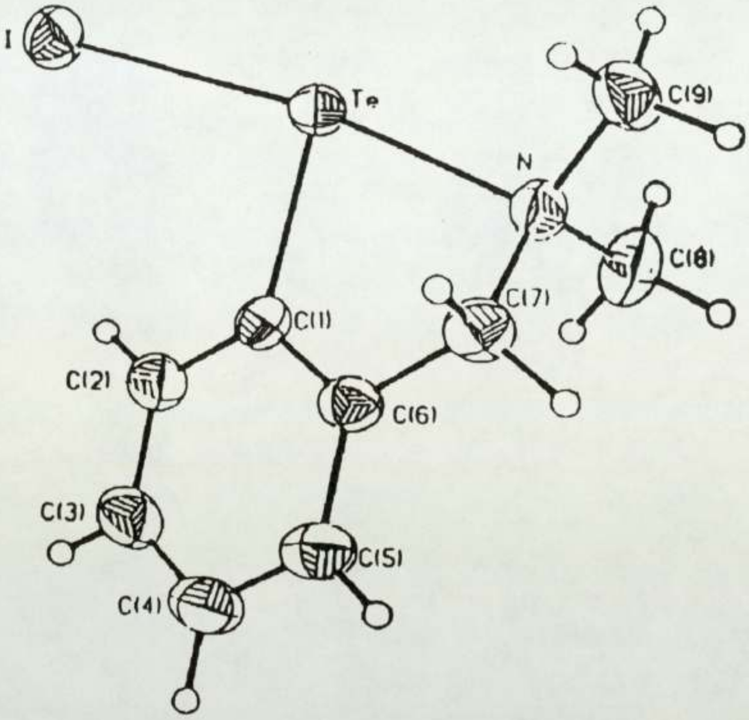
Figure 11.



Crystal structure of bis(diethyldithiocarbamato) iodomethyltellurium(IV).

Bis[2-((dimethylamino)methyl)phenyl]telluride monoiodide(37) is represented by the molecular structure shown in figure 12.

Figure 12.



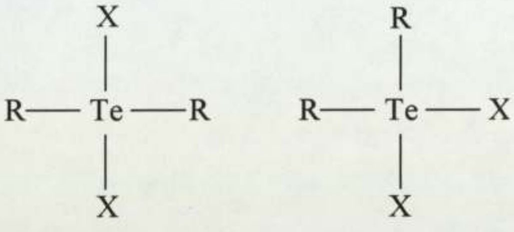
Crystal structure of Bis[2-((dimethylamino)methyl)phenyl]telluride monoiodide.

A typical T - shape geometry around the tellurium atom was found, with strong hypervalent tellurium --- nitrogen interaction (See section 1.10). The tellurium atom is bonded to a carbon atom from the phenyl group, an iodine atom and also has a tellurium --- nitrogen interaction, which gives rise to a three co-ordinated tellurium atom. The tellurium --- nitrogen separation is well within the sum of van der Waal's radii for nitrogen and tellurium. Where the tellurium - nitrogen bond length is 2.366(4) Å for the molecule and is comparable to 2.11 Å, which is the sum of the covalent radii, 1.37 Å for tellurium and 0.72 Å for nitrogen.

1.12.2 Diorganotellurium diiodides

Many organotellurium diiodides show two isomeric forms as suggested by Vernon(43, 40) the α- and β- forms, see figure 13.

Figure 13. Two isomeric forms of organotellurium diiodides.



$$\begin{array}{ccc} & X & \\ & | & \\ R- & Te & -R \\ & | & \\ & X & \end{array} \qquad \begin{array}{ccc} & R & \\ & | & \\ R- & Te & -X \\ & | & \\ & X & \end{array}$$

α- or trans form β- or cis forms

Where R = organic group

X = iodine

Simpler isomeric forms exist for the dichloride(43) and dibromide(43).

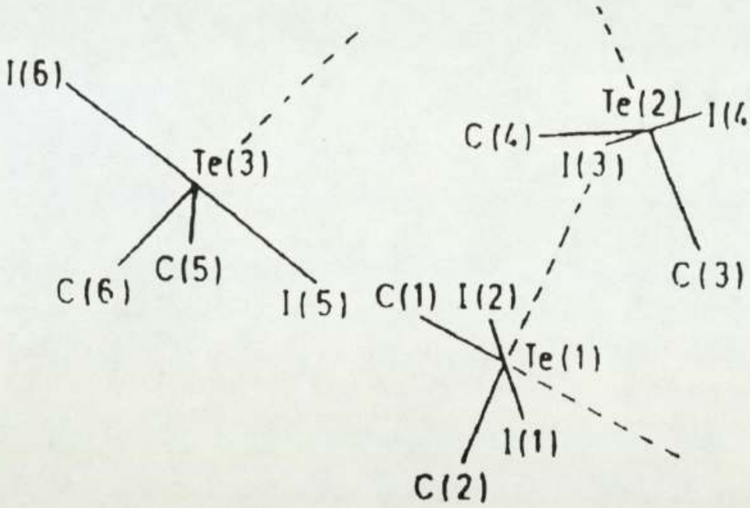
The simplest compound to show this phenomenon is dimethyltellurium diiodide. Initial chemical work on the compound suggested that the compound existed in α- and β- forms of a square - planar structure(43). Further chemistry on dimethyltellurium diiodide by Drew(49a) suggested that the α- form had a covalent structure and the β- form an ionic structure.

The molecular structure of α-dimethyltellurium diiodide(50) has been determined by Chan and Einstein. The structure of β- dimethyltellurium diiodide(51) was determined by Einstein, Trotter and Williston.

α-Dimethyltellurium diiodide

The molecular structure shows three independent dimethyltellurium diiodide molecules in an asymmetric unit, see figure 14.

Figure 14.



A section of the stereo-view of α-dimethyltellurium diiodide, showing the labelling within the asymmetric unit.

The tellurium atom has a distorted ψ-octahedral environment in each molecule. The environment is formed by two *trans*-tellurium iodide bonds, two *cis*-tellurium carbon bonds and two weak interactions between tellurium and iodine. These weak intermolecular tellurium --- iodine interactions form a sheet structure, where the sheets are stacked on top of each other which result in a polymer structure of tellurium --- iodine linkages.

If one considers the structure of dimethyltellurium diiodide in the gaseous state, it may be suggested that the independent molecule will have a ψ-trigonal bipyramidal structure in which the lone pair of electrons on the tellurium atom and the methyl-group are in a distorted plane and the iodine atoms are at the axial positions. In the solid state the structure was found to be octahedral with varying regularity for the tellurium atom. The partial donation and acceptance of electrons of the tellurium atoms and neighbouring iodine atom, results in weak intermolecular interactions.

When comparing the molecular structure of dimethyltellurium diiodide with dimethyltellurium dichloride it was noticed that the dimethyltellurium diiodide has a more regular octahedral geometry. The contribution of the differences in electronegativity between the iodine and chlorine atoms, results in two main consequences. Firstly the chlorine atom does not donate a lone pair of electrons to the tellurium atom and secondly, the tellurium --- chlorine sigma bond polarity leads to a more positive tellurium atom with correspondingly decreased lone - pair donor power to the tellurium --- iodine sigma bond.

β-Dimethyltellurium diiodide

Analysis of the crystal structure of β-dimethyltellurium diiodide(51) provided evidence for the ionic form $[Me_3Te]^+$ $[MeTeI_4]^-$, where the cation $[Me_3Te]^+$ has a trigonal pyramidal structure, with the non - bonding electron - pair, presumably completing a ψ-tetrahedral configuration. The anion $[MeTeI_4]^-$, is a square pyramid, with the tellurium and iodine atoms with in the base, the methyl group at the apex and the lone pair of electrons probably occupying the sixth position of an octahedron around tellurium. It was also shown that presence of the iodine atoms results in steric interaction, therefore the square - planer configuration shown by the iodine atoms is slightly distorted.

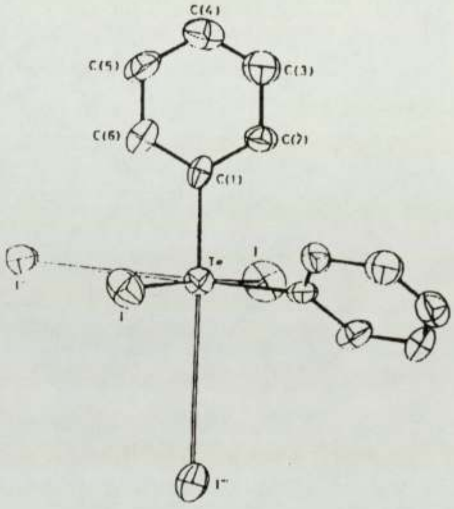
Weak bridge - bonding between the ions results in short interactions. Three interactions were made between the cation $[Me_3Te]^+$ and three neighbouring anions $[MeTeI_4]^-$ via the iodine atoms. These three interactions complete the distorted octahedral environment around the tellurium atom.

The fourth short interionic tellurium --- iodine interaction occurs between the anion $[MeTeI_4]^-$ and the tellurium on the cation $[Me_3Te]^+$, which completes an octahedral environment around the tellurium atom, with the anion $[MeTeI_4]^-$ being joined by two such interaction to form centrosymmetrical dimers.

Diphenyltellurium(IV) diiodide(41) also shows two isomers, α- and β- forms, therefore considering the two isomeric forms of dimethyltellurium diiodide(50, 51), where one is covalent and the other is ionic, one would expected that the α- and β- structures of diphenyltellurium diiodide, would give similar results. The structures were examined by Alcock and Harrison(41).

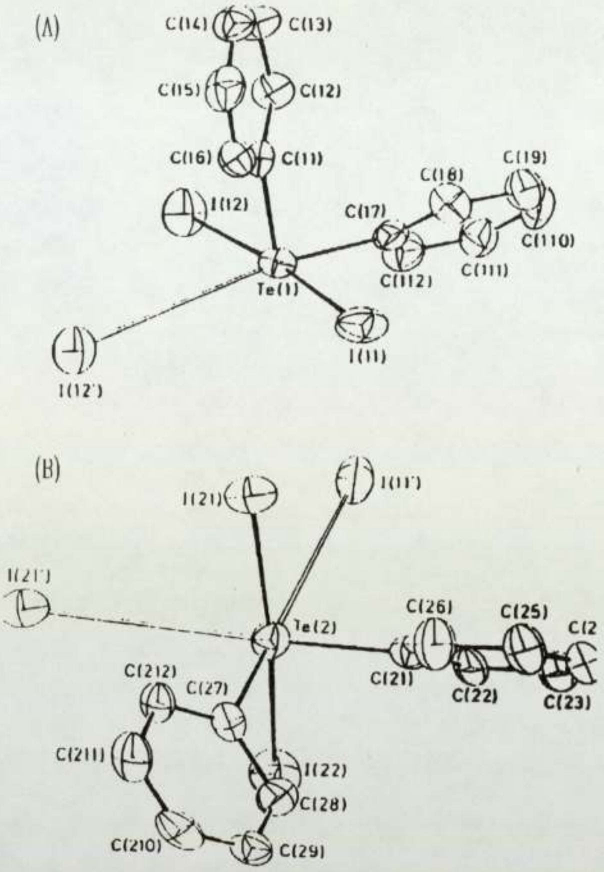
The isomers of diphenyltellurium(IV) diiodide are shown in figures 15 and 16.

Figure 15.



Crystal structure of α-diphenyltellurium(IV) diiodide.

Figure 16.



Crystal structure of β-diphenyltellurium(IV) diiodide.

As shown in figure 16, the β- form that was expected to be ionic was not.

Both the α- and β- form have a primary geometry of pseudo - trigonal bipyramidal, with axial iodine atoms. Two independent molecules were found in the β- form with variable tellurium --- iodine bonds, in that one having longer bonds than the other, while the value in the α- form falls in the middle of this range. The short bond between the iodine and tellurium in the β- form is not involved in any secondary bonding.

The main difference between the α- and β- forms of diphenyltellurium(IV) diiodide lies in the packing and the secondary bonding pattern.

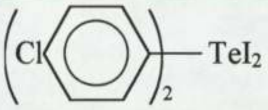
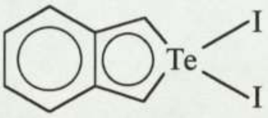
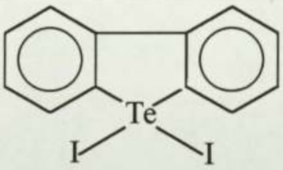
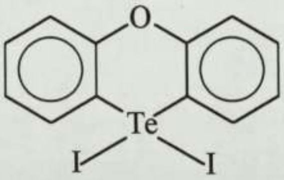
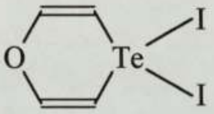
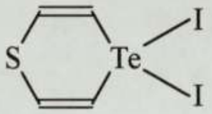
The α- form has two secondary bonds completing an irregular octahedron about each tellurium atom, which also link the molecules into a three dimensional network.

The β- form, which has two similar independent molecules contained in the structure. Both molecules have an octahedral geometry around tellurium. The first molecules also has two secondary bonds about the tellurium atom but in the second molecule there is only one secondary because there is only one vacant position on the tellurium. Which also resulted in a three dimensional network, but the packing is very complex.

Structures are also known for the diphenyltellurium difluoride(30) (See section 1.9), the diphenyltellurium dichloride(52) and the diphenyltellurium dibromide(53). All the compounds show very similar primary geometry, in each case supplemented by secondary bonds, producing either octahedral or square - pyramidal co-ordination. A general decrease in the strength of the secondary bonds is observed, following the series fluorine to iodine, except for diphenyltellurium dibromide.

Structures of diorganotellurium diiodides have been reported in the literature, see table 10.

Table 10. Reported Structures of diorganotellurium diiodides.

Compound	Reference
	42
	54
	39
	45
	46
	55

All the compounds given in table 10, exhibit secondary bonding, with the exception of 4,4-di-iodo-1-thia-telluracyclohexane$^{(54)}$, where the tellurium atom has a distorted pentagonal bipyramidal geometry. The tellurium atom in all the compounds is bonded to four primary and two secondary bonds, which give rise to a distorted octahedral geometry around the tellurium atom. However in di-p-chlorodiphenyltellurium diiodide the tellurium --- iodine secondary bonds are very weak and the iodine --- iodine bonds are of more importance. The chlorine atom which is substituted in the para- position of the phenyl group in this compound produces a very significant change of structure compared to the unsubstituted compounds. The molecular structure of di-p-chlorodiphenyltellurium diiodide has one notably short iodine --- iodine interaction and two longer interctions. It is not clear at present why this change occurs, when the chlorine is substituting in the para position. A suggestion could be that there is an inductive effect by the chloride atom, withdrawing electrons from the tellurium diiodide system. From the literature, is was apparent that there were significantly shorter secondary bonds in R_2TeX_2 when the organc group (R) was alkyl compared to aryl group. This is due to electron - inductive effects.

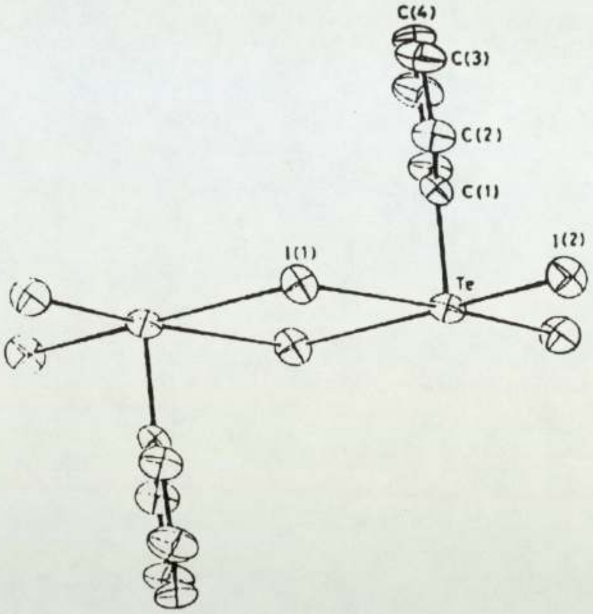
1.12.3 Organotellurium triiodides

The crystal structures of α- and β- forms of phenyltellurium triiodide(41), have been determined by Alcock and Harrison in 1984.

Both the α- and β- structures are dimers, see figure 17 and 18.

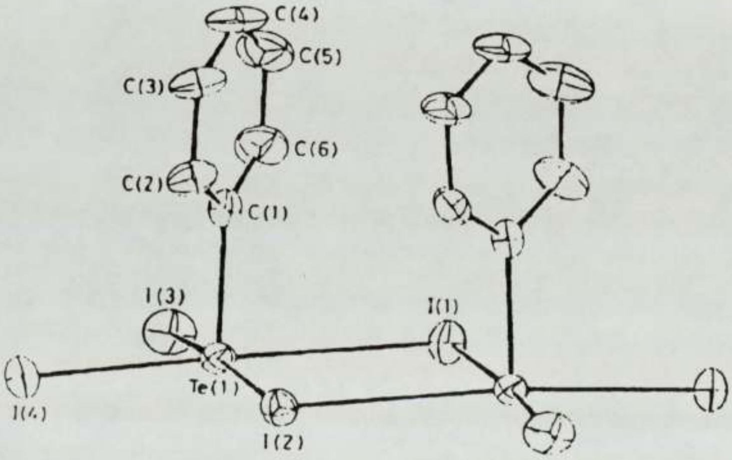
It can be seen form figures 17 and 18, that the α- form has the phenyl groups on opposite sides of the of the Te_2I_6 plane, and the β- form has the phenyl groups on the same side of the Te_2I_6 plane. The tellurium atom has square pyramdal geometry, in both cases. Alcock and Rrison noticed that the tellurium atom was slightly above the I_4 plane, towards the carbon atom in the phenyl group. This may be due to the effect of the iodine atoms.

Figure 17.



Crystal structure of α- phenyltellurium triiodide.

Figure 18.



Crystal structure of β- phenyltellurium triiodide.

From the literature it was noted that the same co-ordination is adopted by the compounds phenyltellurium trichloride(56) and phenyltellurium tribromide(57) and phenyltellurium triiodide. Phenyltellurium trichloride tends to give a polymeric form and the tribromide was either polymeric or dimeric. The triioidide in the other hand was only found to be dimeric. However if the organic group attached to the tellurium is bulky enough then the structure would be monomeric, for example (4-methoxylphenyl)tellurium triiodide(58). Dimeric structures are therefore preferred as the halogen size increases.

The tellurium atom has a square - pyramidal or *pseudo* - octahedral geometry. Which will prohibit the formation of secondary bonding by the tellurium atom because the vacant position where secondary bonding occurs is occupied by the lone pair of electrons on the tellurium.

Secondary bonding occurs in both dimers with iodine --- iodine interactions. The α- form has interactions between bridge and terminal iodine atoms, whilst the β-form links the terminal iodine atoms of the two molecules. Therefore both forms show near linear tellurium - iodine --- iodine bonding in the same plane.

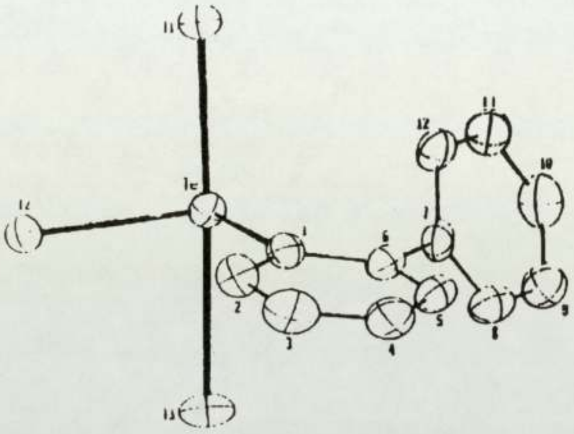
McCullough and Knobler reported three crystal structures of the 2-biphenyltellurium trihalide series, which are 2-biphenyltellurium tribromide(59), α- 2-biphenyltellurium triiodide(49) and β- 2-phenyltellurium triiodide(60).

The configuration around the tellurium atom for 2-phenyltellurium tribromide was found to be trigonal bipyramidal with two halogen atoms in the axial position. The third halogen atom, the carbon atom from the phenyl group and the lone pair of electrons are in equatorial positions. McCullough did not find any secondary bonding in the tribromide.

Comparing the structures of α- and β- biphenyltellurium triiodide with the tribromide, the configuration of the tellurium atom is essentially the same. However intermolecular and secondary bonding play a very important role in the crystal structures of the triiodides.

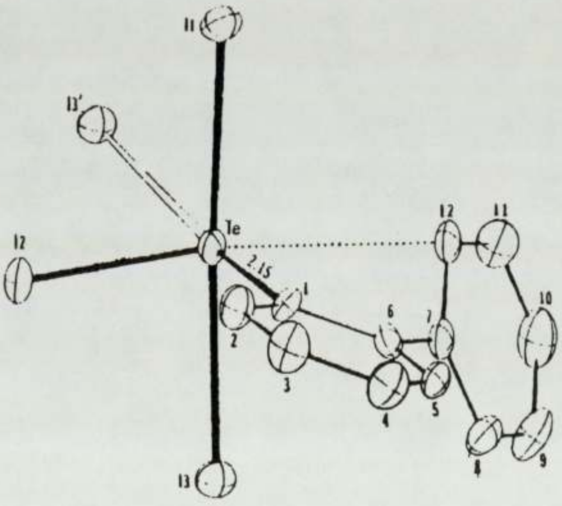
The crystals structures of the two isomers of 2-biphenyltellurium triiodide are very similar, see figure 19 and 20.

Figure 19.



Crystal structure of α-biphenyltellurium triiodide.

Figure 20.

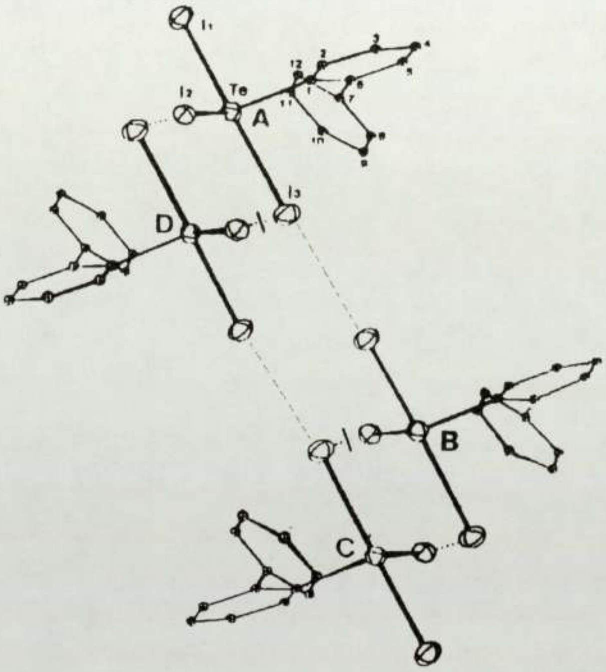


Crystal structure of β-biphenyltellurium triiodide.

The main differences between the two structures occur in the intermolecular bonds between heavy atoms.

α- Biphenyltellurium triiodide forms one strong intermolecular bond and one weak intermolecular bond. Both interactions are between iodine atoms of one molecule and the iodine atoms of another, see figure 21.

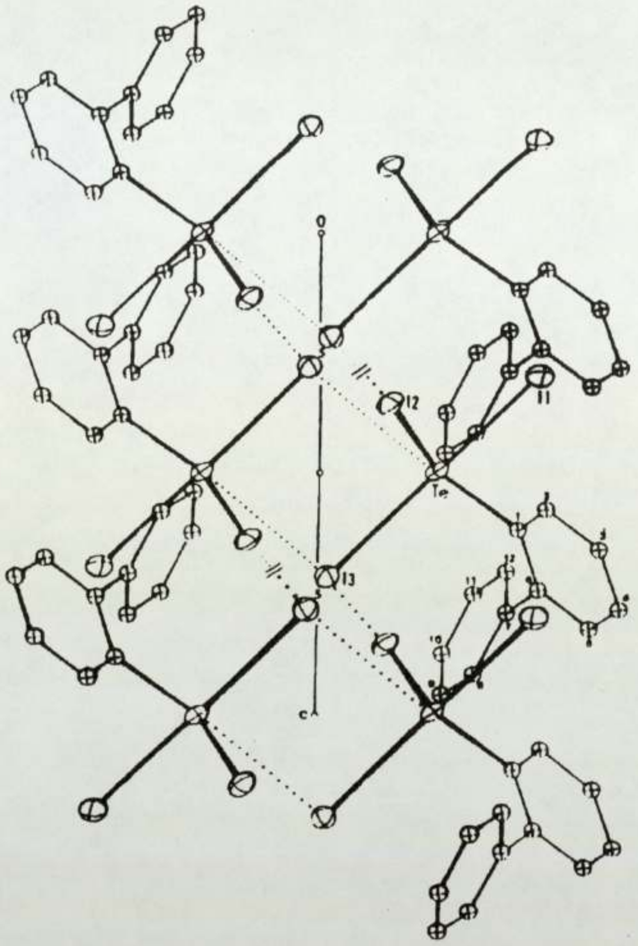
Figure 21.



Packing arrangement of α-biphenyltellurium triiodide.

The β- structure also forms strong intermolecular bonds between the iodide atoms, but unlike the α-structure the weak intermolecular bonds oscillate between iodine and tellurium, see figure 22.

Figure 22.



Packing arrangement of β-biphenyltellurium triiodide.

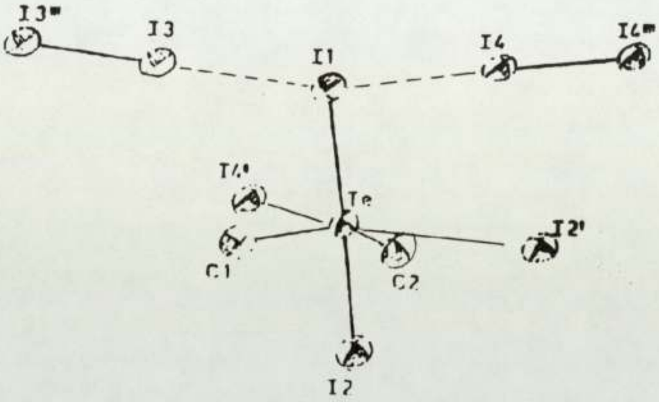
1.12.4 Organotellurium tetraiodides

The crystal structure of dimethyltellurium tetraiodide(61) was determined by Pritzkow in 1974.

The molecular formula of dimethyltellurium tetraiodide, suggests that the tellurium atom is in the oxidation state of plus six. Smith and Thayer(62) have carried out a spectroscopic study of dimethyltellurium tetraiodide. They suggested from the analysis of their results that a weakly bound adduct of dimethyltellurium diiodide and iodine must be present. They also suggested that the iodine molecules are weakly bound to the central tellurium.

Pritzkow found the molecular structure of dimethyltellurium tetraiodide to disagree with Smith and Thayer. The structure can be seen in figure 23.

Figure 23.



Crystal structure of dimethyltellurium tetraiodide.

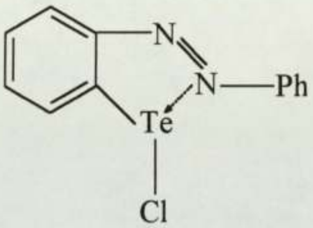
The crystal structure of dimethyltellurium diiodide shows iodine molecules to bonded to the iodine atoms of the tellurium - iodine bonds and not the central tellurium atom as suggested by Smith and Thayer(62).

The co-ordination around the tellurium atom can be described as distorted octahedron, formed by two *trans* tellurium --- iodine bonds, a tellurium --- carbon bond and two weak intermolecular tellurium --- iodine bonds.

1.10 Inter- and Intra-molecular Co-ordination Bonds in Organotellurium Halides Compounds

This section of the introduction deals with the Lewis acidic behaviour of the tellurium atom in the organotellurium halide compounds that have been formed in the past. Therefore the compounds that have been mentioned in this section will have chlorine and bromine as the halide atom, hence it would be a good opportunity to introduce a fluorine atom into the molecule, just to see if inter or intra co-ordination occurs.

Inter- and intra- molecular interactions may arise in organotellurium compounds when the compound contains centres of Lewis acidity and basicity in the same molecule. For example; (2-Phenylazophenyl-C,N')tellurium(II) chloride



[Ph = Phenyl]

Where, Te = Centre of Lewis acidity

N = Centre of Lewis basicity

1.10.1 a) Order of Lewis Acidity in Organotellurium Compounds

The Lewis acidity of tellurium becomes less as more organic groups are attached to the metal.

Therefore tellurium(IV) compounds with more organic groups attached will make the tellurium less acidic and show the order,

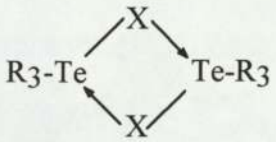
$RTeX_3 > R_2TeX_2 > R_3TeX$ [R = Organic group, X = halide]

Also the same effect can be seen in tellurium(II) compounds.

$RTeX > R_2Te$

1.10.2 b) Short - Range Intermolecular Co-ordination

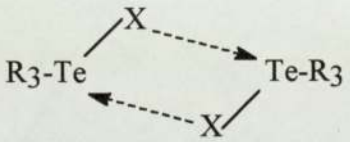
Short - range intermolecular co-ordination is found in organotellurium(II) monohalides and ocurrs when a halogen bridge two Lewis acidic centres.



[X = halide]

1.10.3 c) Long - Range Intermolecular Co-ordination

Long - range intermolecular co-ordination can be shown as;

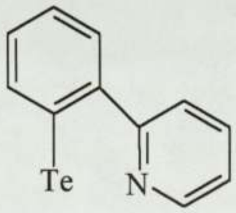


[X = halide]

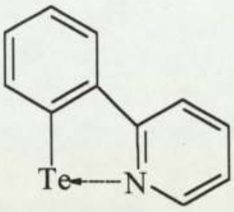
As shown above that, Te-----X bonds are much longer than the sum of covalent radii of tellurium and X, but shorter than the van der Waal distance. This is also known as Secondary bonding.

1.10.4 d) Intramolecular Co-ordination

Intramolecular co-ordination occurs when it is sterically feasible for the acidic and basic centres to interact within the molecule. The co-ordination may only be formed when the organic group attached to the tellurium atom has a donor group in it, for example; 2-(2-pyridyl)phenyltellurium(II) chloride.



The molecule shown above may undergo intramolecular co-ordination because the aryl- group has a basic functional group in the ortho- position to the tellurium. Therefore, co-ordination will occur between the tellurium and the nitrogen atom, as shown below.



CHAPTER TWO

GENERAL EXPERIMENTAL TECHNIQUES

Physical measurements / Chemical techiques

2.1 *Chemicals and Solvents*

Most chemicals used were obtained from the Aldrich Chemical Company. Tellurium power, tellurium tetrachloride and tellurium tetrabromide were used as sources of tellurium. Common solvents were supplied by the Department of Chemical Engineering and Applied Chemistry and were dried where necessary by storing over molecular sieves. Analytically grade solvents were used without further purification.

2.2 *Elemental Analysis*

Mirco-elemental analysis for carbon, hydrogen and nitrogen were carried out by Medac Ltd, Department of Chemistry, Brunel University.

2.3 *Melting points*

A Gallenkamp electrically heated melting point apparatus with a mercury thermometer was used to determine all melting points.

2.4 *Infra-red Spectroscopy*

Infra-red spectra were recorded on a Bio rad Fts 40A. Spectra for the range 4000-500cm^{-1} were recorded using KBr discs. For some compounds the low wavenuber region (500-200cm^{-1}) was recorded using polyethylene discs. To get the best spectra for the low frequency, a very high concentrated Nujol solution was used, and 256 scans were taken at 1 cm^{-1} resolution.

2.5 Nuclear Magnetic Resonance Spectroscopy

NMR spectra (^{1}H, ^{13}C, ^{19}F and ^{125}Te solution) were recorded within the Department of Chemical Engineering and Applied Chemistry using a Bruker AC-300 instrument at 300.13, 75.47, 282.4 and 94.71 MHz respectively. Tetramethylsilane was used as the internal reference for ^{1}H and ^{13}C. ^{125}Te solution data were collected using *bis*(p-ethoxyphenyl)ditelluride as the reference. ^{19}F solution data were collected using sodium fluoride and trifluoroacetic acid as references.

2.6 Mass Spectroscopy

Electron impact mass spectra of some compounds were recorded via V. G. Zabspec spectrometer. Fast atom Bombardment mass spectra of some compounds were recorded by a V. G. Prospec spectrometer. The mass spectroscopy was carried out at the Departement of Chemistry, Birmingham University.

2.7 Ultra-Violet and Visible spectroscopy

Ultra-violet and visible measurements were carried out on a Perkin Elmer model Lambda 12 spectrophotometer using 1cm quartz cells.

2.8 Raman Spectroscopy

Raman spectra were recorded at Brunel University using a Perkin Elmer FT-Raman 1700X instrument and using a NdYag laser operating at 1064nm and an InGaAs NIR detector cooled to 77K. Spectra were obtained from solids as powders pressed into cup sample holders.

2.9 X-ray Photoelectron spectroscopy

X-ray photoelectron spectroscopy was carried out on a Fisons VG Escalab 200D Spectrometer using a Mg Kα source and a 20 or 50eV analyser. The dwell time was 50 or 100 ms, with 2 to 8 scans. The data collection was carried out at the Department of Electronic Engineering and Applied Physics, Aston University.

2.10 X-ray Crystallography

Suitable crystals for X-ray crystallography technique were obtained by recrystallisation from high purity solvents. Accurate cell dimensions and reflection intensities were measured with a graphite-monochromated Mo-Kα radiation on a Rigaku R-AXIS II area detector diffractometer.

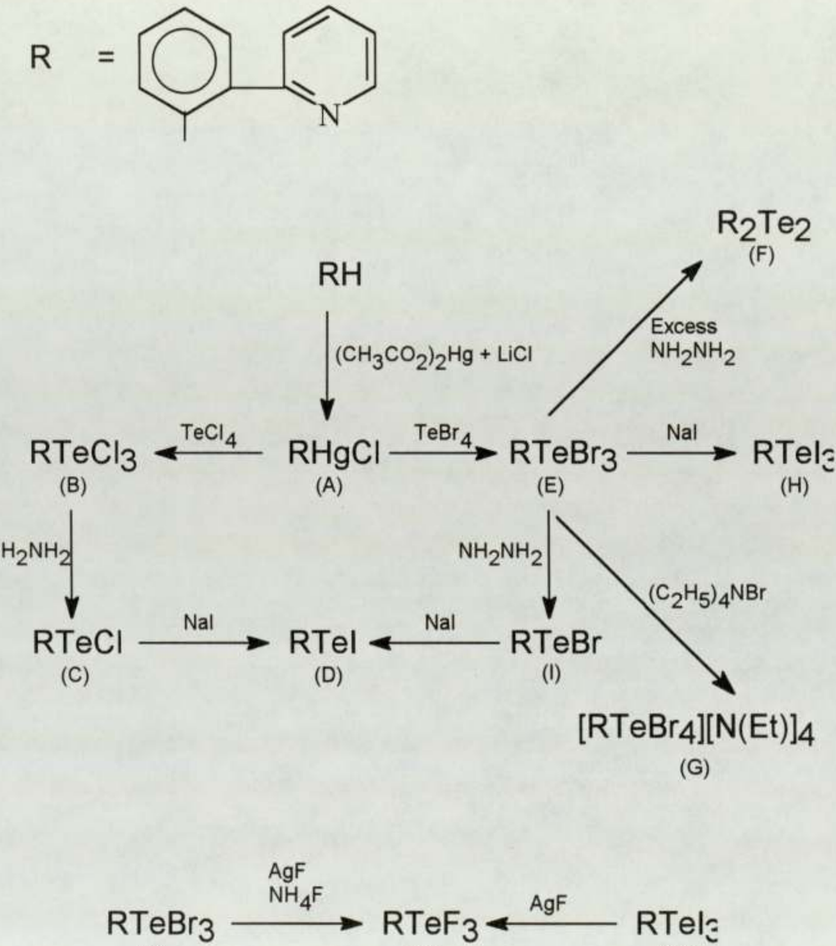
CHAPTER THREE

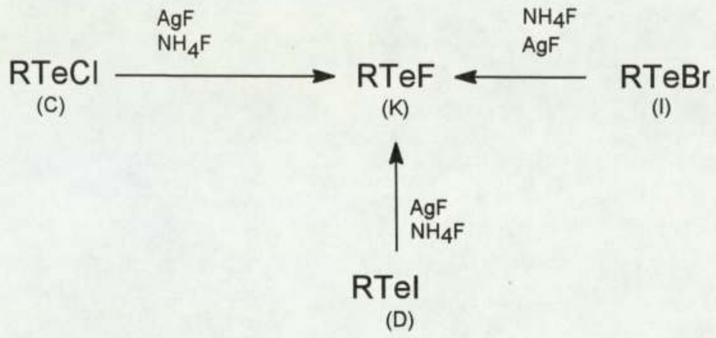
EXPERIMENTAL METHODS AND RESULTS INVOLVING THE 2-(PRYIDYL)PHENYLTELLURIUM HALIDE SERIES

Experimental Methods and Results involving the 2-pyridylphenyl- series

Scheme (1) summarised below shows the synthesis and inter conversion within the 2-(2-pyridyl)phenyl series.

Scheme (1) for the inter conversion within the 2-(2-pyridyl)phenyl series.





Methodology within the 2-(2-pyridyl)phenyl series.

3.1 Synthesis of 2-(2-pyridyl)phenylmercury(II) chloride

2-Phenylpyridine (7.8g, 50 mmol) and mercury(II) acetate (15.9g, 50 mmol) were mixed in absolute ethanol (100 cm^3) and refluxed for 24 hours, after which lithium chloride (4.4g) in absolute ethanol (100 cm^3) was added with vigorous stirring; the thick mixture was heated for a further 15 mins. The reaction mixture was poured into distilled water (300 cm^3) and filtered. The filtrate was left to stand at room temperature whereupon a white crystalline compound formed which was filtered off, washed with cold methanol, and oven dried at 60 °C.

Yield 91.6 %, m.p. 137 - 139 °C (Lit m.p. 138 - 140 °C).

3.2 Synthesis of 2-(2-pyridyl)phenyltellurium(IV) trichloride

2-(2-pyridyl)phenylmercury(II) chloride (3.9g, 10 mmol) was suspended in sodium dried 1,4-dioxane (20 cm^3). Tellurium tetrachloride (2.69g, 10 mmol) in sodium dried 1,4-dioxane (15 cm^3) was added to the stirring mixture under dinitrogen. Before addition of the tellurium tetrachloride the refluxing apparartus were flushed out with dinitrogen. Then mixture was refluxed under dinitrogen for 2 hours during which time a creamy yellow compound precipitated. The hot mixture was filtered and the creamy yellow product washed with dry ethanol and recrystallised from acetonitrile - methanol (1:1) to give creamy yellow product.

m.p. over 225 °C.

The preparation of 2-(2-pyridyl)phenyltellurium(IV) trichloride was repeated twice thereafter.

On the first occasion the mixture was refluxed for 20 minutes, after which a creamy yellow product had precipitated. The product was recovered in the same manner as above resulting in a creamy yellow product.

m.p. over 240 °C.

On the second occasion the reactants were refluxed for two hours. This time when the tellurium tetrachloride was added in small amounts to the refluxing mixture at five minutes intervals. The rest of the experiment was carried out as above.

3.3 *Synthesis of 2-(2-pyridyl)phenyltellurium(II) chloride*

2-(2-Pyridyl)phenyltellurium(IV) trichloride (0.78g, 0.2 mmol) was suspended in absolute ethanol. Hydrazine hydrate (0.1g, 2 mmol) in ethanol (5 cm^3), was added to the stirring mixture under dinitrogen. After the solid dissolved completely the solution was refluxed for 15 minutes and set aside to cool to room temperature. The yellow crystals which were deposited were filtered off and washed with ethanol.

Yield 46 %, m.p. 128 - 130°C, CHN see table 11.

3.4 *Synthesis of Tellurium tetrabromide*

Tellurium (5g, 3.9 mmol) powder was placed into a flask, then bromine liquid (19.4 cm^3, 3.9 mmol) was added very slowly to the tellurium powder. This was then sealed, with an outlet placed into water, so that any excess bromine gas was able to dissolve in the water. This was then left for 24 to 48 hours, whereupon a yellow compound was precipitated.

Yield 80 %, m.p. over 260 °C thermometer limit (Lit m.p. 368 °C).

3.5 *Synthesis of 2-(2-pyridyl)phenyltellurium(IV) tribromide*

A solution of 2-(2-pyridyl)phenylmercury(II) chloride (3.9g, 10 mmol) in sodium dried 1,4-dioxane (20 cm^3) was added to a solution tellurium tetrabromide (4.47g, 10 mmol) in sodium dried 1,4-dioxane (15 cm^3). The tellurium tetrabromide and 2-(2-pyridyl)phenylmercury(IV) tribromide were kept apart as the apparatus was purged with dinitrogen. The tellurium tetrabromide was then added into the refluxing mixture. The mixture was refluxed under dinitrogen for 2 hours during which time a yellow compound precipitated. The hot mixture was filtered and the yellow product washed with pure ethanol and re crystallised from acetonitrile - methanol which is a 1:1 mixture to give yellow crystals.

Yield 75.8 %, m.p. 285 - 286 °C (Lit m.p. 283 - 285 °C).

3.6 *Synthesis of Bis [2-(2-pyridyl)phenyl] ditelluride*

2-(2-Pyridyl)phenyltellurium(IV) tribromide (1.04g, 2 mmol) was dissolved in acetonitrile - ethanol (2:1) (30 cm^3) and treated with excess hydrazine hydrate (0.6g, 12 mmol) in ethanol (10 cm^3) and then refluxed for 20 min. The precipitate formed was filtered off and recrystallised from benzene to give yellow - orange crystals.

Yield 64%, m.p. 148 - 151 °C (Lit m.p. 150 - 152 °C), CHN see table 11.

3.7 Attempted synthesis of tetraethylammonium 2-(2-pyridyl)phenyltetrabromotellurte(IV)

A solution of 2-(2-pyridyl)phenyltellurium(IV) tribromide (0.78g, 1.5 mmol) in ethanol (30 cm^3), was added to a solution of tetraethyl ammonium bromide (0.32g, 1.5 mmol) in ethanol (30 cm^3) and the mixture was refluxed for 3 hours. After refluxing, the mixture was allowed to cool. A white solid precipitated which was filtered and washed with cold ethanol and dried. Its melting point was determined which suggest that it was tetraethyl ammonium bromide. The solvent was removed from the filtrate, leaving a yellow compound, which was later found to be unreacted 2-(2-pyridyl)phenyltellurium(IV) tribromide.

m.p. of yellow compound 282 - 284°C.

m.p. of white compound 283°C (decomposition).

3.8 Synthesis of 2-(2-pyridyl)phenyltellurium(IV) triiodide

Sodium iodide (4.5g, 30 mmol) in AR-grade acetone (40 cm^3) was poured into a solution of 2-(2-pyridyl)phenyltellurium(II) tribromide (2.66g, 5 mmol) in AR-grade acetone (100 cm^3). The solution was stirred for 40 minutes at room temperature a colour change ocurred from a yellow to a cloudy dark purple solution. The cloudy solution was left to stand at room temperature for 40 minutes after which it became clear with settlement of a precipitate of sodium bromide.

The dark purple solution was filtered and the acetone removed using a rotatory evaporator leaving a dark purple substance. Dichloromethane was used to extract the dark purple substance from the excess sodium iodide which was left as a precipitate. The dichloromethane was then removed using the rotatory evaporator.

Yield 82%, m.p. above 230°C. CHN see table 11.

Job's method was carried out with 2-(2-pyridyl)phenyltellurium(IV) triiodide ($1x10^{-4}$ M) and iodine ($1x10^{-4}$ M) to distinguish if a charged transfer complex between the two materials occurred. No clear results were obtained for the analysis. This was due to the over lapping of the observed peaks.

3.9 Synthesis of 2-(2-pyridyl)phenyltellurium(II) bromide

2-(2-Pyridyl)phenyltellurium(IV) tribromide (1.04g, 2 mmol) was suspended in absolute ethanol. Hydrazine hydrate (0.1g, 2 mmol) in ethanol (5 cm^3) was added to the stirred mixture under dinitrogen. The solid dissolved and the solution was refluxed for 15 minutes, after which it was set aside to cool to room temperature. Yellow crystals formed which were filtered and washed with ethanol.

Yield 62 %, m.p. 177 - 179°C (Lit. m.p. 178 - 180°C), CHN see table 11.

3.10 Synthesis of 2-(2-pyridyl)phenyltellurium(II) iodide

Sodium iodide (1.5g, 10 mmol) in AR-grade acetone (40 cm^3) was poured into a solution of 2-(2-pyridyl)phenyltellurium(II) chloride (1.64g, 5 mmol) in AR-grade acetone (100 cm^3). The solution was stirred for 40 minutes at room temperature and a colour change ocurred from a yellow to a cloudy orange solution. The cloudy solution was left to stand at room temperature for 40 minutes, after which it became clear with a precipitate of sodium chloride.

The orange solution was filtered and the acetone removed using a rotatory evaporator leaving a orange substance. Dichloromethane was used to extract the orange substance from the excess sodium iodide which was left as a precipitate. The dichloromethane was then removed using the rotatory evaporator. The an orange compound was recrystallised using acetonitrile - methanol (1:1).

Yield 92%, m.p. 162 - 164°C, CHN see table 11.

The same experiment was repeated with a different halide, 2-(2-pyridyl)phenyltellurium(II) bromide (1.87g, 5 mmol). An orange compound was formed and recrystallised using acetonitrile - methanol (1:1).

Yield 82%, m.p. 161 - 163°C.

Job's method was carried out with 2-(2-pyridyl)phenyltellurium(II) iodide ($1x10^{-4}$ Mol) and iodine ($1x10^{-4}$ Mol) to distinguish if a charged transfer complex between the two materials occurred. No clear results were obtained for the analysis. This was due to the over-lapping of the observed peaks.

3.11 Attempted synthesis of 2-(2-pyridyl)phenyltellurium(IV) trifluoride

2-(2-Pyridyl)phenyltellurium(IV) triiodide (0.66g, 1 mmol) in AR-grade acetone (40 cm^3) was poured into a suspension of silver(I) fluoride (1.1g, 9mmol) in AR-grade acetone (40 cm^3). The mixture was stirred in the dark at room temperature for 2 hours. Then the mixture was allowed to stand for another 24 hours in the dark. After which the mixture was filtered leaving silver (I) fluoride residue and a red filtrate. The acetone (ca. 70 cm^3) was removed from the red solution using a rotatory evaporator; the remaining solution was stored overnight in a refrigerator at +5°C, whereupon a dark purple compound was formed, which was filtered off, and washed with hexane and dried.

m.p. above 230°C.

The attempted preparation of 2-(2-pyridyl)phenyltellurium(IV) trifluoride was then repeated again. This time the solution of 2-(2-

pyridyl)phenyltellurium(IV) triiodide (0.66g, 1 mmol) and silver(I) fluoride (1.1g, 9mmol)) in AR-grade acetone (50 cm^3)was stirred in the dark for about 1 week. The work-up was carried out in as the above method.

m.p. above 235°C.

Two experiments were carried out with 2-(2-pyridyl)phenyltellurium(IV) tribromide (0.52g, 1 mmol) in AR-grade acetone (40 cm^3). One stirring for 2 hours and the other for 1 week. A yellow solution resulted. When stored overnight in a refrigerator, yellow compounds were formed in both cases.

m.p. above 228°C.

Another experiment was carried out with 2-(2-pyridyl)phenyltellurium(IV) tribromide (1.56g, 3 mmol) and ammonium fluoride(1g, 72mmol), as the fluorinating reagent. The work-up was carried out as in the above method, whereupon a yellow compound was formed.

m.p. of the yellow compound 285 - 287°C.

A solution of 2-(2-pyridyl)phenyltellurium(IV) triiodide (0.66g, 1 mmol) in sodium dried toluene (50 cm^3), was added to a refluxing suspension of silver fluoride (1.1g, 9 mmol) in sodium dried toluene (50 cm^3) under dry dinitrogen. When all the 2-(2-pyridyl)phenyltellurium(IV) triiodide was added, was refluxed for 2 hours, after which the reaction mixture was filtered. The solvent was removed on a rotatory evaporator and the product recystallised from benzene. Leaving a dark purple compound.

m.p. above 235°C.

The same experimental method was carried out with 2-(2-pyridyl)phenyltellurium(IV) tribromide (0.52g, 1 mmol), resulting in a yellow compound which was recrystallised from benzene.

m.p. above 238°C.

3.12 Attempted synthesis of 2-(2-pyridyl)phenyltellurium(II) fluoride

2-(2-Pyridyl)phenyltellurium(II) bromide (0.5g, 1.5 mmol) in acetone (20 cm^3) was poured into a suspension of silver(I) fluoride (0.6g. 4.5 mmol) in AR-grade acetone (20 cm^3). The suspension was stirred in the dark at room temperature for two hours following by standing for another 24 hours in the dark. The mixture was filtered and the filtrate was concentrated on the rotatory evaporator; the concentrated solution was stored overnight in a refridgerator at +5°C, whereupon a yellow compound was formed, which was then filtered and washed with hexane and dried.

m.p. 175 - 178°C.

The formation of 2-(2-pyridyl)phenyltellurium(II) fluoride was then repeated once more. This time the suspension of 2-(2-pyridyl)phenyltellurium(II) bromide (0.54g, 1.5 mmol) and silver(I) fluoride (0.6g. 4.5 mmol) in AR-grade acetone (40 cm^3) was stirred in the dark for 1 week. Product recovery was as above.

m.p. 174 - 176°C.

The experiment was repeated on two further occasions, with 2-(2-pyridyl)phenyltellurium(II) chloride (0.48g, 1.5 mmol) and 2-(2-pyridyl)phenyltellurium(II) iodide (0.61g, 1.5 mmol), following the method above.

2-(2-Pyridyl)phenyltellurium(II) chloride gave a yellow product, which was recrystallised from acetonitrile - methanol (1:1).

m.p. 129 - 131°C.

2-(2-Pyridyl)phenyltellurium(II) iodide gave an orange product, which was recrystallised from acetonitrile - methanol (1:1).

m.p. 163 - 165°C.

Another series of experiments was carried out with 2-(2-pyridyl)phenyltellurium(IV) chloride (0.48g, 1.5 mmol), 2-(2-pyridyl)phenyltellurium(II) bromide (0.54g, 1.5 mmol), 2-(2-pyridyl)phenyltellurium(II) iodide (0.61g, 1.5 mmol) and ammonium fluoride (excess eg, 0.8g, 20mmol), as the fluorinating reagent. The work-up was carried out as in the above method.

2-(2-Pyridyl)phenyltellurium(II) chloride gave an yellow product which was recrystallised from ethanol.

m.p. 128 - 129°C.

2-(2-Pyridyl)phenyltellurium(II) bromide gave a yellow product which was recystallised from acetonitrile and methanol (1:1).

m.p. 176 - 178°C.

2-(2-Pyridyl)phenyltellurium(II) iodide gave an orange product which was recrystallised from acetonitrile and methanol (1:1).

m.p. 161 - 163°C.

A solution of 2-(2-pyridyl)phenyltellurium(II) bromide (0.54g, 1.5 mmol) in sodium dried toluene (30 cm^3), was added slowly to a refluxing solution of silver fluoride (0.45g, 4.5 mmol) in sodium dried toluene (30 cm^3) under dry dinitrogen. When all the 2-(2-pyridyl)phenyltellurium(II) bromide was added, the mixture to refluxed for a further 2 hours, after which the reaction mixture was filtered, giving a yellow solution and a black ppt. The solvent was removed by rotatory evaporation and the resulting yellow product, was recystallised from benzene.

m.p. 175 - 177°C, CHN see below.

(C 38.7% H 2.41% N 4.01%) found, (C 44.0% H 2.66% H 4.66%) Calculated.

The experiment was repeated on two further occasions, with different halides, 2-(2-pyridyl)phenyltellurium(II) chloride (0.48g, 1.5 mmol) and 2-(2-pyridyl)phenyltellurium(II) iodide (0.61g, 1.5 mmol), following the method above.

2-(2-Pyridyl)phenyltellurium(II) chloride gave a yellow product which was recrystallised from acetonitrile-methanol (1:1).

m.p. 130 - 132°C.

2-(2-Pyridyl)phenyltellurium(II) iodide gave a yellow/orange product which was recrystallised from benzene.

m.p. 158 - 162°C, CHN see below.

(C 47.6% H 4.07% N 4.28%) found, (C 44.0% H 2.66% H 4.66%) Calculated.

A further experiments were carried out on 2-(2-pyridyl)phenyltellurium(II) iodide and silver fluoride, this time different molar quantity and conditions were used, see below.

2-(2-pyridyl)phenyltellurium(II) iodide (1g, 2.4 mmol) and silver fluoride (3g, 24 mmol) were refluxed as above, but for a total of three hours, this resulted in a yellow/orange compound (m.p. 157 - 160°C).

The yellow/orange compound was chromatographed on silica (50g) and eluted with dichloromethane giving a yellow solution, which was reduced to give a yellow compound (product 1). Futher elution with methanol removed the yellow band at the top of the column, giving a yellow solution which was reduced to give a yellow compound (product 2).

Product 1 m.p. over 220°C.

Product 2 m.p. 157 - 158°C, CHN see below.

(C 39.9% H 3.30% N 3.52%) found, (C 44.0% H 2.66% H 4.66%) Calculated.

3.13 Polymorphism

2-(2-pyridyl)phenyltellurium(IV) triiodide was recrystallised using acetonitrile - methanol (1:1), and crystal were grown by slow evaporation giving the monoclinic crystal polymorph of RTeI.

m.p. of monoclinic crystal 192-194°C. CHN see table 11.

A solution of 2-(2-pyridyl)phenyltellurium(II) iodide in acetonitrile - methanol (1:1) was allowed to evaporate slowly, affording crystals. Which were the triclinic crystal polymorph of RTeI.

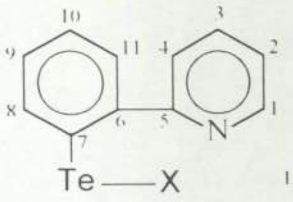
Table 11.

Analytical data for organotellurium compounds; R = 2-(2-pyridyl)phenyl.

Reaction No.	Compound	Colour	Found (%)			Calculated (%)		
			C	H	N	C	H	N
3.3	RTeCl	Yellow	40.8	2.57	4.34	41.7	2.54	4.42
3.6	R_2Te_2	Yellow /Orange	45.6	2.79	4.79	46.9	2.86	4.97
3.8	$RTeI_3$	Orange / red	20.0	1.24	2.15	19.9	1.22	2.11
3.9	RTeBr	Yellow	36.8	2.14	3.84	36.5	2.20	3.85
3.10	RTeI	Red	31.9	2.00	3.31	32.3	1.94	3.43
3.13	RTeI	Orange	33.4	2.24	6.24	32.3	1.94	3.43

Table 12.

^{13}C NMR data for organotellurium compounds; R 2-(2-pyridyl)phenyl.



^{13}C Chemical shifts (p.p.m.) relative to $SiMe_4$.

Reaction No.	Compound	C 1	C 2	C 3	C 4	C 5	C 6	C 7	C 8	C 9	C 10	C 11	Other
3.5	$RTeBr_3$	141.8	120.3	137.8	121.8	152.0	132.2	129.5		130.0	125.4	125.2	
3.8	$RTeI_3$	142.3	121.0	138.5	122.7			134.9	134.9	131.4	127.1	126.0	
3.10	RTeI	141.4	121.6	140.5	124.3	154.7	132.1	125.4	137.2	129.9	126.7	124.4	
3.13	RTeI	142.3	120.6	138.5	123.0	152.7	134.1	122.5	138.2	131.3	127.5	125.9	
3.12	RTeF (RTeBr)	145.2	121.2	138.5	122.5				133.4	131.2	126.8	126.2	

Reaction No.	Compound	C 1	C 2	C 3	C 4	C 5	C 6	C 7	C 8	C 9	C 10	C 11	Other
3.12	RTeF	145.6	120.9	142.8	123.7				137.8	131.8	126.0	125.5	+
	(RTeI 1)	146.8	120.6						139.3	130.7		125.9	
3.12	RTeF												
	(RTeI 2)	142.2	121.1	138.4	122.6				133.1	131.0	126.7	126.1	+
	Product 1									130.8	126.9		
3.12	RTeF												
	(RTeI 2)	147.9	120.3	138.1	123.5				137.8	129.9	128.8	127.0	+
	Product 2												

(***) = Starting material used in the reaction

Table 13.

Low frequency FTIR data for Organyltellurium compounds; R 2-(2-pyridyl)phenyl.

Reaction No.	Compound	ν(TeF)		ν(TeF)		ν(TeC)	ν(TeC)		ν(TeCl)	ν(TeBr)	ν(TeBr)	ν(TeBr)	ν(TeI)	ν(TeI)
3.3	RTeCl				379s	285m	263m	240m	218s		179w			
3.5	$RTeBr_3$				375s	279m	261m	239m		189s	172m			
3.9	RTeBr				377s	282m	259m	245m			174w	168w		
3.10	RTeI		416m		374s	274m		237s					161m	153s
3.12	RTeF (RTeI 1)	421m		406m	377s	283s	265s			193s	170s			
3.12	RTeF (RTeI 1 product 2)	420m		408m	377s	283m	265m	251m		195m	171w			

(***) = Starting material used in the reaction

Table 14.

^{125}Te NMR data for organotellurium compounds; R = 2-(2-pyridyl)phenyl.

Reaction No.	Compound	Peak (ppm) vs. Dimethyltelluride	Coupling constant (JTeF)
3.5	RTeBr3	775.1	
3.10	RTeI	679.2	
3.12	RTeF (RTeBr)	868.9	
3.12	RTeF (RTeI)	1181.5 1164.9	1568.75
3.12	RTeF (RTeI) (Product 2)	869.2	

(***) = Starting material used in the reaction

Table 15.

^{19}F NMR data for organotellurium compounds; R = 2-(2-pyridyl)phenyl.

Reaction No.	Compound	Peak (ppm) vs. Sodium fluoride	Coupling constant (JFTe)
3.12	RTeF (RTeI 1)	-85.1	1523
3.12	RTeF (RTeI) (Product 2)	-43.3 -41.4	

(***) = Starting material used in the reaction

Table 16.

Bromine XPS data for organotellurium compounds; R' = Phenylazophenyl.

Compound	Peaks (eV)	See spectrum
	Br1	
RTeBr	79.6	1

Table 17.

Tellurium XPS data for organotellurium compounds; R' = Phenylazophenyl.

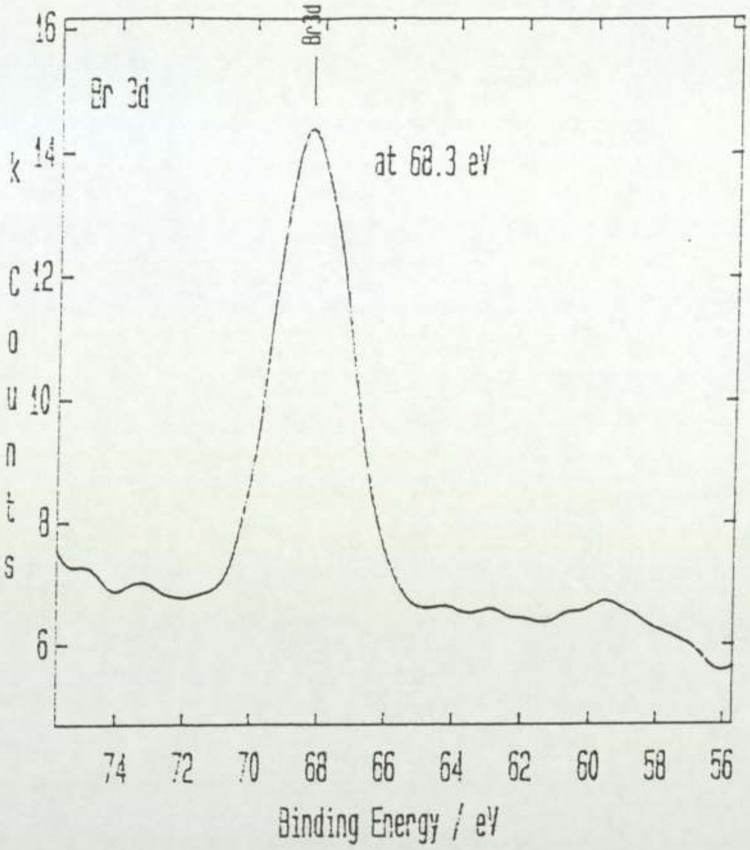
Compound	Peaks (eV)			See spectrum
	Te1	Te2	Te3	
RTeBr	573.2	574.3	576.5	2
RTeI	573.2	574.3		3

Table 18.

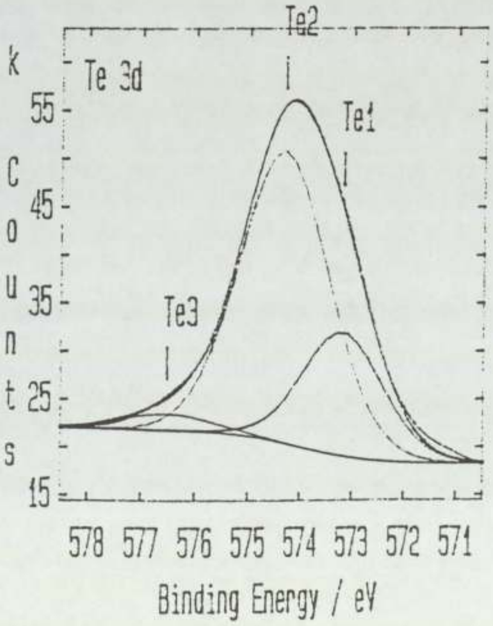
Iodine XPS data for organotellurium compounds; R' = Phenylazophenyl.

Compound	Peaks (eV)		See spectrum
	I1	I2	
RTeI	618.1	619.2	4

Spectrum 1. Bromine XPS data on the 2-(2-pyridyl)phenyltellurium(II) bromide.



Spectrum 2. Tellurium XPS data on the 2-(2-pyridyl)phenyltellurium(II) bromide.



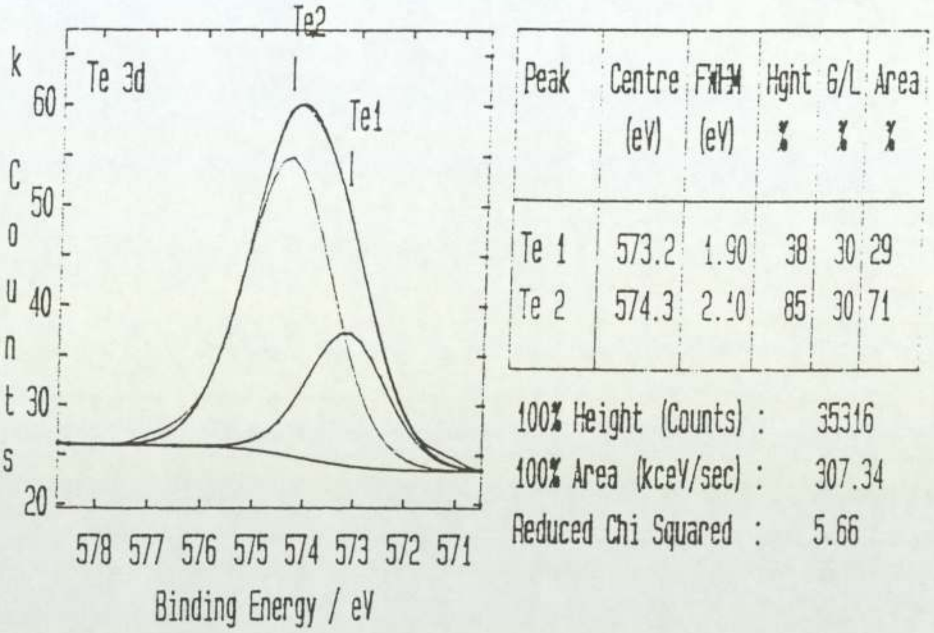
Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
Te 1	573.2	1.90	36	30	27
Te 2	574.3	2.10	85	30	69
Te 3	576.5	2.10	5	30	4

100% Height (Counts) : 35897

100% Area (kceV/sec) : 481.03

Reduced Chi Squared : 5.17

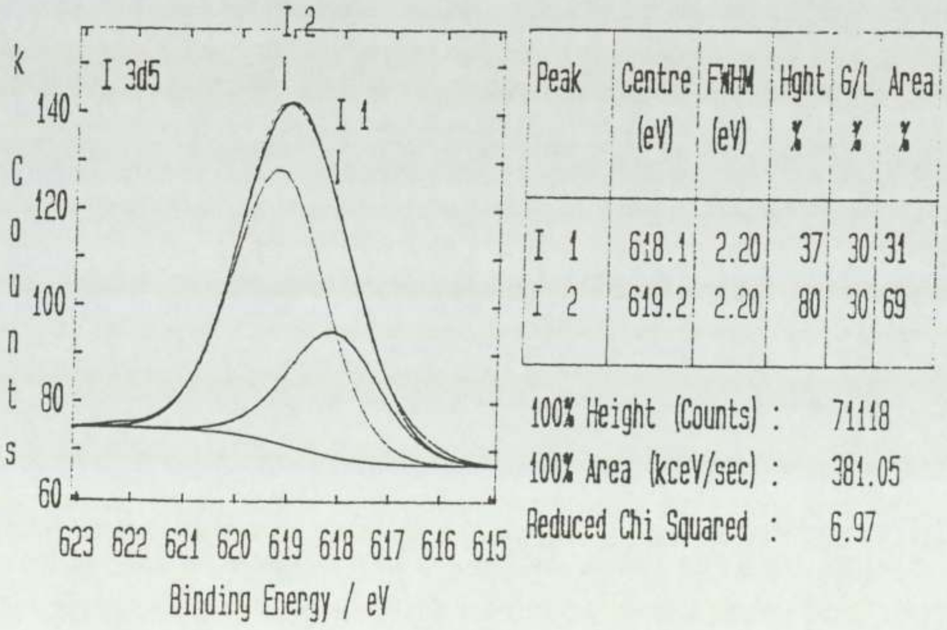
Spectrum 3. Tellurium XPS data on the 2-(2-pyridyl)phenyltellurium(II) iodide.



Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
Te 1	573.2	1.90	38	30	29
Te 2	574.3	2.10	85	30	71

100% Height (Counts) : 35316
100% Area (kceV/sec) : 307.34
Reduced Chi Squared : 5.66

Spectrum 4. Iodine XPS data on the 2-(2-pyridyl)phenyltellurium(II) iodide.



Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
I 1	618.1	2.20	37	30	31
I 2	619.2	2.20	80	30	69

100% Height (Counts) : 71118
100% Area (kceV/sec) : 381.05
Reduced Chi Squared : 6.97

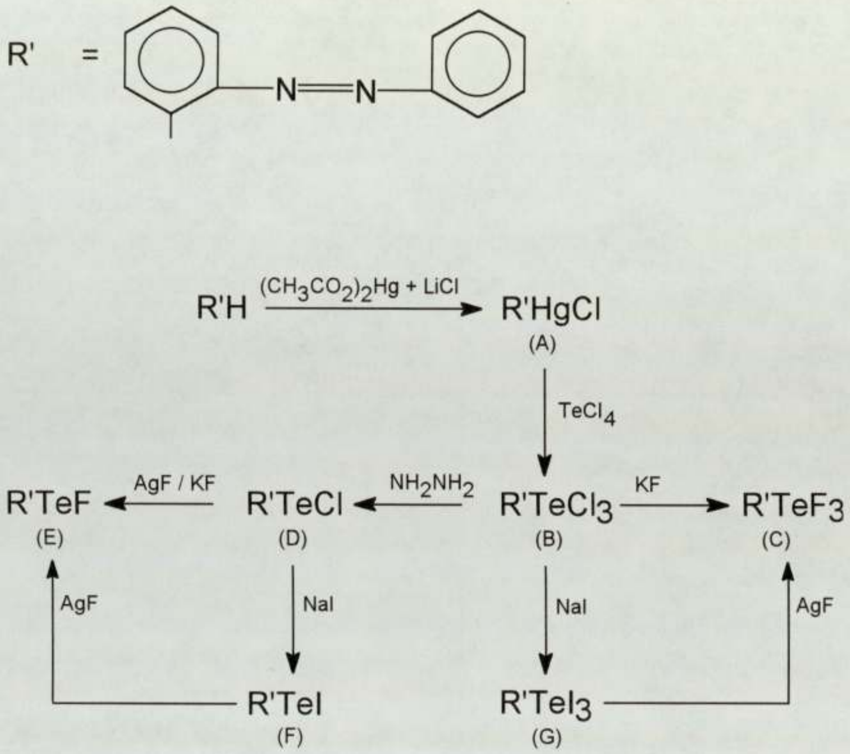
CHAPTER FOUR

EXPERIMENTAL METHODS AND RESULTS INVOLVING THE (PHENYLAZOPHENYL-C,N')TELLURIUM HALIDE SERIES

Experimental methods and results for the azobenzene series of compounds

Scheme (2) summarised below shows the synthesis and inter conversion within the 2- phenylazophenyl series. The analytical data for the compounds are given in table 2.

Scheme (2) for attempted inter-conversions within the 2 - phenylazophenyl series.



Methodology within the 2-phenylazophenyl series.

4.1 Synthesis of (phenylazophenyl-C,N')mercury(II) chloride

Azobenzene (10.0g, 55 mmol) and Mercury(II) acetate (18.0g, 56 mmol) were mixed in AR-grade methanol (125 cm^3) and refluxed for 22 hours.

At the end of the refluxing period, the reaction mixture was allowed to cool to room temperature and then lithium chloride (5.0g 120 mmol) dissolved in hot methanol was added and the resulting thick mixture stirred for about 10 min, whereupon it was poured into water (500 cm^3). The resulting precipitate was filtered and the filtrate extracted with ether until the extracts were colourless. The ether was evaporated and the resulting residue added to the filtered precipitate to give the reaction solid, which contained mercurials and the starting material, azobenzene.

The solid was extracted with four 100 cm^3 portions of xylene. The extracts were chromatographed on activated alumina (100g, pH = neutral) and eluted with xylene giving azobenzene, which was recrystallised from xylene, m.p. 65 -67°C (Lit. m.p. 68°C). Further elution with benzene removed the major band at the top of the column (a few very minor bands were noted but discarded) which gave a yellow/orange solution. Removal of the solution gave a yellow/orange compound with white crystals, which was found to be a mixture of 2-chloromercuriazobenzene and $HgCl_2 \cdot (dioxane)_2$ complex.

The 2-chloromercuriazobenzene was separated from the mixture by preferential dissolution of the latter in nitromethane. The yellow/orange solid was found to be pure 2-chloromercuriazobenzene, which was recrystallized from nitromethane to give an orange product.

Yield 33%, m.p. 198 - 200°C (Lit. m.p. 202 - 204°C).

4.2 *Synthesis of (2-phenylazophenyl-C,N')tellurium(IV) trichloride*

(2-Phenylazophenyl-C,N')mercury(II) chloride (3.2g 7.5 mmol) and tellurium tetrachloride (2.0g 7.5 mmol) were refluxed in sodium dried 1,4-dioxane (20 cm^3) for 6 hours under dry nitrogen. On cooling the 2:1 addition compound of dioxane and mercury(II) chloride separated as white plates which were removed by filtration. The filtrate was concentrated on the rotatory evaporator and nitromethane (20 cm^3) was added. Evaporation was carried out to dryness and the residue was recrystallised from nitromethane to give orange crystals.

Yield 88%, m.p. 236 - 237°C (Lit. m.p. 244 - 245°C).

4.3 Attempted synthesis of (2-phenylazophenyl-C,N')tellurium(IV) trifluoride

Potassium fluoride (0.4g, 7 mmol) in AR-grade acetone (40 cm^3) was poured into a solution of (2-phenylazophenyl-C,N')tellurium(IV) trichloride (1g, 2.5 mmol) in AR-grade acetone. The solution was stirred at room temperature for 1 week. The solution was filtered and the acetone was removed by rotatory evaporation, then dichloromethane was used to extract an orange/red substance, from the excess potassium fluoride. The orange/red produc was recovered from the dichloromethane by rotatory evaporation and recrystalised from nitromethane. Resulting to form an orange crystals.

m.p. 237 - 238°C.

4.4 Synthesis of (2-phenylazophenyl-C,N')tellurium(II) chloride

(2-Phenylazophenyl-C,N')tellurium(IV) trichloride (3.5g, 8.5 mmol) was dissolved in methanol (50 cm^3) and heated under reflux. A solution of hydrazine hydrate (0.5g, 1.5 mmol) in methanol (50 cm^3) was added slowly to the refluxing solution. The solution was filtered and cooled to afford brown crystals.

Yield 80%, m.p. 82-83°C (Lit m.p. 80°C), CHN see table 19.

4.5 Attempted synthesises of (2-phenylazophenyl-C,N')tellurium(II) fluoride

(2-Phenylazophenyl-C,N')tellurium(II) chloride (0.5 g, 1.5 mmol) in AR-grade acetone (40 cm^3) was poured into a suspension of silver(I) fluoride (0.63 g, 5 mmol) in AR-grade acetone (40 cm^3). The suspension was stirred in the dark at room temperature for two hours. The mixture on further standing for another 24 hours in the dark, became clear with settlement of a precipitate. The solution was filtered and acetone was removed on the rotatory evaporator, whereupon a brown compound was formed, which was then recrystallized from nitromethane.

m.p. 81 - 82°C.

The formation of (2-phenylazophenyl-C,N')tellurium(II) fluoride was then repeated once more. This time the suspension of (2-phenylazophenyl-C,N')tellurium(II) chloride and silver(I) fluoride in AR-grade acetone was stirred in the dark for about 1 week. The rest of the formation of 2-(2-pyridyl)phenyltellurium(IV) fluoride was carried out as in the above method.

m.p. 80 - 81°C.

A solution of (2-phenylazophenyl-C,N')tellurium(II) chloride (0.5 g, 1.5 mmol) in sodium dried toluene (50 cm^3), was added slowly to a refluxing solution of silver fluoride (6.3g, 0.5 mmol) in sodium dried toluene (50 cm^3) under dry nitrogen. When all (2-phenylazophenyl-C,N')tellurium(II) chloride was added, the mixture was left to reflux for a further 2 hours, after which the reaction mixture was filtered. The solvent was removed on a rotatory evaporator resulting in a brown compound. The brown compound was recrystallised from nitromethane.

m.p. 80 -81°C.

Potassium fluoride (0.4g, 7 mmol) in AR-grade acetone (40 cm^3) was poured into a solution of (2-phenylazophenyl-C,N')tellurium(II) chloride (0.5 g, 1.5 mmol) in AR-grade acetone (40 cm^3). The solution was stirred at room temperature for 1 week. The solution was filtered and acetone was removed on a rotatory evaporator, then dichloromethane was used to extract a brown substance, from the excess potassium fluoride. The extraction solvent was removed on the rotatory evaporator. Resuling in a brown compound which was then recrystalised from nitromethane.

m.p. 78 - 80°C.

4.6 Synthesis of (2-phenylazophenyl-C,N')tellurium(II) iodide

Sodium iodide (0.9g, 6 mmol) in AR-grade acetone (40 cm^3) was poured into a solution of (2-phenylazophenyl-C,N')tellurium(II) chloride (1g, 3 mmol) in AR-grade acetone (100 cm^3). On stirring for 40 minutes at room temperature a colour change was noticed from a dark orange to a cloudy blood red solution.

The blood red solution was filtered and the acetone removed using a rotatory evaporation leaving a dark red substance. Dichloromethane was then used to separate the dark red substance from the excess sodium iodide. The dichloromethane was then removed using the rotatory evaporator. Leaving a dark red compound which was recrystallised from nitromethane.

Yield 87%, m.p. 150 - 152°C, CHN see table 19.

Job's analysis was carried out with (2-phenylazophenyl-C,N')tellurium(II) iodide ($1x10^{-4}$ Mol) and iodine ($1x10^{-4}$ Mol), no clear results were obtained for the analysis. This was due to the strong intense observed for the phenylazophenyl group.

4.7 Attempted synthesis of (2-phenylazophenyl-C,N')tellurium(II) fluoride

(2-Phenylazophenyl-C,N')tellurium(II) iodide (0.5g, 1.1 mmol) in AR-grade acetone (40 cm^3) was poured into a suspension of silver(I) fluoride (0.63g, 5 mmol) in AR-grade acetone (40 cm^3). The suspension was stirred in the dark at room temperature for two hours. The suspension on further standing for another 24 hours in the dark, became clear with settlement of the suspension. The solution was filtered and the acetone was removed on the rotatory evaporator, resulting in an dark red compound, which was then recrystallized from nitromethane.

m.p. 152 - 153°C.

The synthesis of (2-phenylazophenyl-C,N')tellurium(II) fluoride was then repeated once more. This time the suspension of (2-phenylazophenyl-C,N')tellurium(II) iodide and silver(I) fluoride in AR-grade acetone was stirred in the dark for about 1 week. The above method was then followed.

m.p. 148 - 150°C.

4.8 Synthesis of (2-phenylazophenyl-C,N')tellurium(II) fluoride

A solution of (2-phenylazophenyl-C,N')tellurium(II) iodide (1g, 2.3 mmol) in sodium dried toluene (50 cm^3), was added slowly to a refluxing solution of silver fluoride (2g, 15 mmol) in sodium dried toluene (50 cm^3) under dry dinitrogen. When all (2-phenylazophenyl-C,N')tellurium(II) iodide was added, the mixture was left to reflux for a further 2 hours, after which the reaction mixture was filtered. The solvent was removed on a rotatory evaporator, giving an orange oil.

CHN see table 19.

4.9 Synthesis of (2-phenylazophenyl-C,N')tellurium(IV) triiodide

Sodium iodide (2.25g, 15 mmol) in AR-grade acetone (40 cm^3) was poured into a solution of (2-phenylazophenyl-C,N')tellurium(IV) trichloride (1g, 2.4 mmol) in AR-grade acetone (100 cm^3). On stirring for 40 minutes at room temperature a colour change occured from an orange to a cloudy deep blood red solution. The cloudy solution was left to stand at room temperature for 40 minutes, leaving a clear solution and a precipitate of sodium chloride.

The deep blood red solution was filtered and the acetone removed using a rotatory evaporator leaving a dark red/purple substance. Then dichloromethane was used to separate the dark red/purple substance from the excess sodium iodide which was precipitated. The dichloromethane was then removed using the rotatory evaporator. This resulted in the formation of a dark red/purple compound which was recrystallised using nitromethane.

Yield 88%, m.p. 102 - 105°C, CHN see table 19.

Job's analysis was carried out with (2-phenylazophenyl-C,N')tellurium(IV) iodide (1x10^{-4} Mol) and iodine (1x10^{-4} Mol), no clear results were obtained for the analysis. This was due to the strong intense observed for the phenylazophenyl group.

4.10 Attempted synthesis of (2-phenylazophenyl-C,N')tellurium(IV) trifluoride

(2-Phenylazophenyl-C,N')tellurium(IV) triiodide (1g, 1.5 mmol) in AR-grade acetone (40 cm^3) was poured into a suspension of silver(I) fluoride (0.63g, 5 mmol) in AR-grade acetone (40 cm^3). The suspension was stirred in the dark at room temperature for two hours. The suspension on further standing for another 24 hours in the dark, became clear with settlement of the suspension. The solution was filtered and the acetone was removed on the rotatory evaporator, leaving a dark red/purple compound, which was then recrystallized from nitromethane.

m.p. 102 - 105°C.

The formation of (2-phenylazophenyl-C,N')tellurium(IV) trifluoride was then repeated once more. This time the suspension of (2-phenylazophenyl-C,N')tellurium(IV) triiodide and silver(I) fluoride in AR-grade acetone was stirred in the dark for about 1 week. The above method was then followed.

m.p. 99 - 101°C.

Potassium fluoride (0.26g, 4.5 mmol) in AR-grade acetone (40 cm^3) was poured into a solution of (2-phenylazophenyl-C,N')tellurium(IV) triiodide (1g, 1.5 mmol) in AR-grade acetone (40 cm^3). The solution was stirred at room temperature for 1 week. The solution was filtered and acetone was removed on a rotatory evaporator, then dichloromethane was used to extract a blood red substance,from the excess potassium fluoride. The extraction fraction were ten reduced on the rotatory evaporator. This resulted in a red/purple compound was formed, this was then filtered off, and recrystalised from nitromethane.

m.p. 101 - 103°C.

4.11 *Synthesis of (2-phenylazophenyl-C,N')tellurium(II) fluoride*

A solution of (2-phenylazophenyl-C,N')tellurium(IV) triiodide (1g, 1.5 mmol) in sodium dried toluene (50 cm^3), was added slowly to a refluxing solution of silver fluoride (0.63g, 5 mmol) in sodium dried toluene (50 cm^3) under dry dinitrogen. When all (2-phenylazophenyl-C,N')tellurium(IV) triiodide was added, the mixture was left to reflux for a further 2 hours, after which the reaction mixture was filtered. The solvent was remove on a rotatory evaporator, resulting in an orange oil.

CHN see table 19.

Table 19.

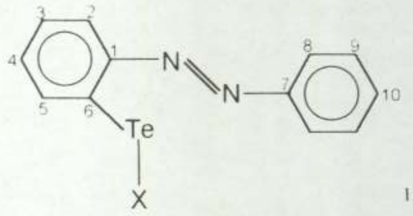
Analytical data for organotellurium compounds; R' = Phenylazophenyl

Reaction	Compound	Colour	Found (%)			Calculated (%)		
No.			C	H	N	C	H	N
4.4	RTeCl	Brown	41.7	2.72	7.97	41.8	2.63	8.14
4.6	R’TeI	dark red	33.4	2.24	6.24	33.1	2.08	6.43
4.8	R’TeF	orange oil	44.0	2.97	8.16	44.0	2.77	8.55
4.9	R’TeI$_3$	red/purple	22.3	1.56	4.15	20.9	1.32	4.06
4.11	R’TeF (R’TeF$_3$)	orange oil	43.3	3.17	8.43	44.0	2.77	8.55

(***) = Starting material used in the reaction.

Table 20.

^{13}C NMR data for organotellurium compounds; R' azobenzene



^{13}C Chemical shifts (p.p.m.) relative to $SiMe_4$.

Reaction No.	Compound	C 1	C 2	C 3	C 4	C 5	C 6	C 7	C 8	C 9	C 10
4.4	R'TeCl	155.3	122.3	129.8	131.3	134.4	139.1	148.8		130.3	132.6
4.6	R'TeI	155.1	122.8	129.9	131.4	139.4		148.1	127.7	131.2	132.9
4.8	R'TeF	155.0	121.7	129.7	131.3	133.5	143.2	149.6		130.8	132.4
4.9	R'TeI$_3$		122.9	129.9	131.4	139.3				131.3	132.8
4.11	R'TeF (R'TeF$_3$)	155.6	122.4	129.9	131.9	133.7		150.0	128.8	130.0	132.5

(***) = Starting material used in the reaction.

Table 21.

^{125}Te NMR data for organotellurium compounds; R' = Phenylazophenyl

Reaction No.	Compound	Peak (ppm) vs. dimethyltelluride	Coupling constant (J_{TeF}) in Hz
4.6	R'TeI	857.5	
4.8	R'TeF	1238.2 1223.1	1145
4.11	R'TeF ($RTeF_3$)	1243.9 1230.8	1250

(***) = Starting material used in the reaction.

^{125}Te NMR was carried out on R'TeI_3. On analysis of the NMR, no peaks were found. Therefore a small experiment was carried out, in that molar quatity of R'TeI and I_2 were mixed in solution (acetone). The mixture was placed into a NMR tube and the mixture was analysied for ^{125}Te. This experiment resulted in giving no NMR peak, even losing the NMR signal for the monoiodide.

Table 22.

^{19}F NMR data for organotellurium compounds; R' = Phenylazophenyl

Reaction No.	Compound	Peak (ppm) vs. sodium fluoride	Coupling constant (J_{FTe}) in Hz
4.8	R'TeF	-47.52	
4.11	R'TeF (R'TeF_3)	-47.44	

(***) = Starting material used in the reaction.

Table 23.

Chlorine XPS data for organotellurium compounds; R' = Phenylazophenyl

Compound	Peaks (eV) Cl1	See spectrum
R'TeCl	198.1	5

Table 24.

Tellurium XPS data for organotellurium compounds; R' = Phenylazophenyl

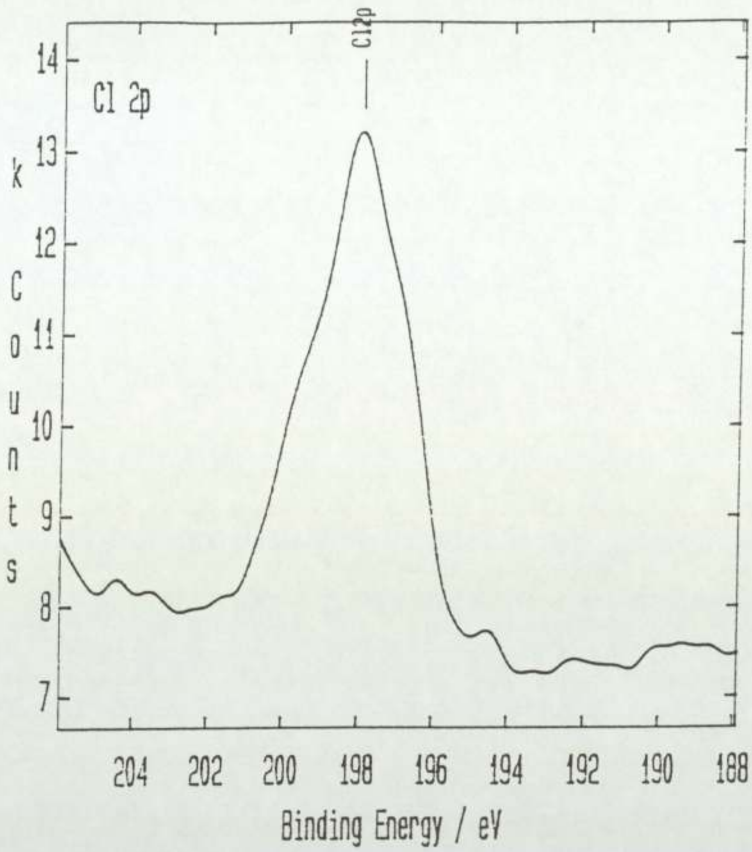
Compound	Peaks (eV)			See spectrum
	Te1	Te2	Te3	
R'TeCl	573.3	574.5	576.6	6
R'TeI	573.3	574.5	576.6	7
R'TeI$_3$	573.3	574.5	576.6	8

Table 25.

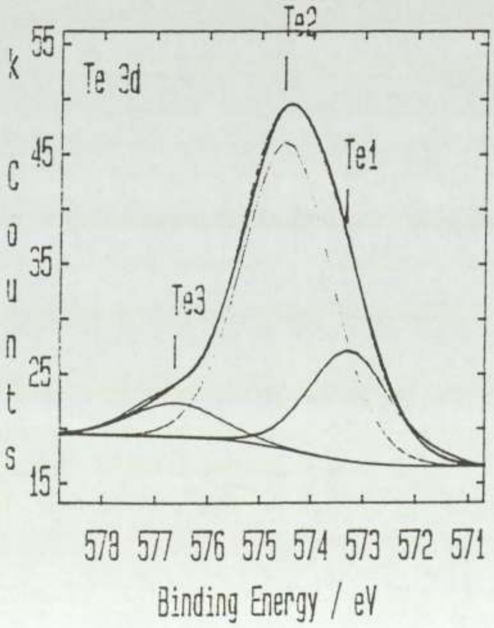
Iodine XPS data for organotellurium compounds; R' = Phenylazophenyl

Compound	Peaks (eV)		See spectrum
	I1	I2	
R'TeI	618.1	619.2	9
R'TeI$_3$	618.1	619.2	10

Spectrum 5. Chlorine XPS data on the (2-phenylazophenyl-C,N')tellurium(II) chloride.



Spectrum 6. Tellurium XPS data on the (2-phenylazophenyl-C,N')tellurium(II) chloride.



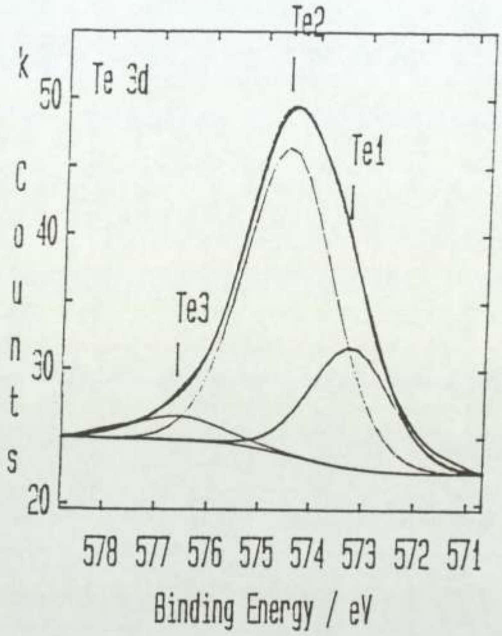
Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
Te 1	573.3	1.85	32	30	23
Te 2	574.5	2.05	89	30	70
Te 3	576.6	2.05	10	30	8

100% Height (Counts) : 31577

100% Area (kceV/sec) : 430.91

Reduced Chi Squared : 5.23

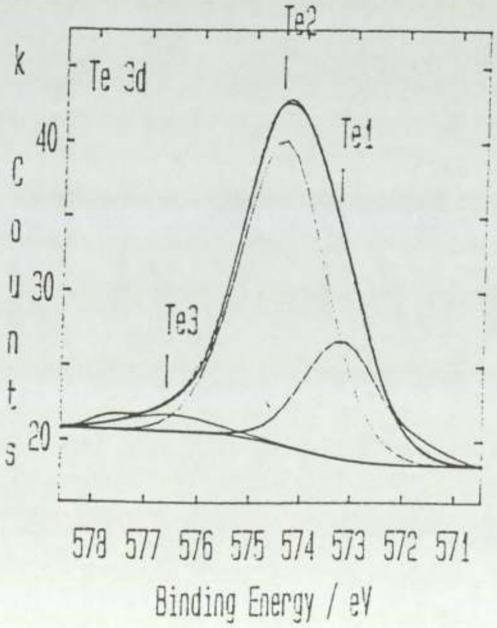
Spectrum 7. Tellurium XPS data on the (2-phenylazophenyl-C,N')tellurium(II) iodide.



Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
Te 1	573.3	1.88	35	30	25
Te 2	574.5	2.08	88	30	70
Te 3	576.6	2.08	7	30	6

100% Height (Counts) : 25819
100% Area (kceV/sec) : 235.40
Reduced Chi Squared : 3.06

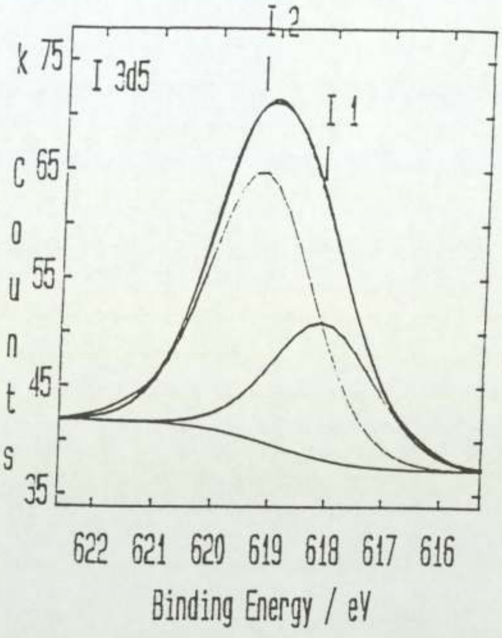
Spectrum 8. Tellurium XPS data on the (2-phenylazophenyl-C,N')tellurium(IV) triiodide.



Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
Te 1	573.3	1.83	35	30	25
Te 2	574.4	2.02	89	30	71
Te 3	576.6	2.02	5	30	4

100% Height (Counts) : 23027
100% Area (kceV/sec) : 302.92
Reduced Chi Squared : 5.08

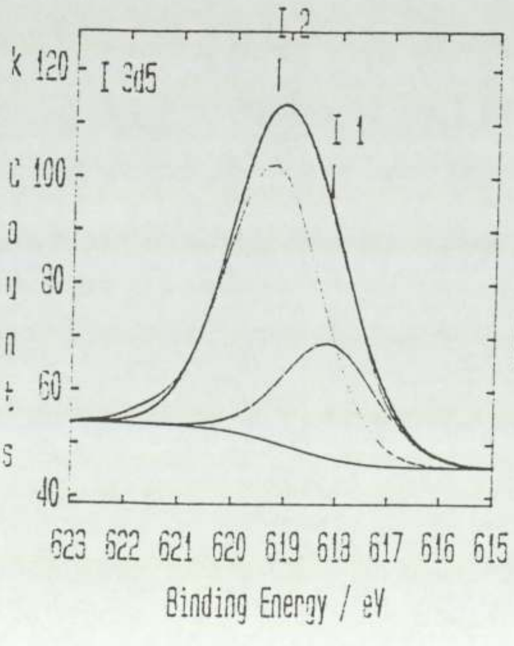
Spectrum 9. Iodine XPS data on the (2-phenylazophenyl-C,N')tellurium(II) iodide.



Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
I 1	618.1	2.20	40	30	34
I 2	619.2	2.20	79	30	66

100% Height (Counts) : 31486
100% Area (kceV/sec) : 286.08
Reduced Chi Squared : 2.39

Spectrum 10. Iodine XPS data on the (2-phenylazophenyl-C,N')tellurium(IV) triiodide.



Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
I 1	618.1	2.20	34	30	29
I 2	619.2	2.20	82	30	71

100% Height (Counts) : 63792
100% Area (kceV/sec) : 565.01
Reduced Chi Squared : 10.82

Table 26.

Mass spectral data for (2-Phenylazophenyl-C,N')tellurium(II) iodide

Relative to ^{130}Te, ^{14}N, ^{12}C, ^{1}H, ^{127}I

Species	m/e	Rel. Int.
$[C_6H_5]^+$	77	47
$[C_6H_5]_2^+$	152	39
$[C_6H_5Te]^+$	206	13
$[C_{18}H_{13}N_2]^+$	257	62
$[(C_6H_5)_2Te]^+$	282	27
$[C_{12}H_9N_2Te]^+$	311	100
$[(C_{12}H_9N_2)_2Te]^+$	492	11

Table 27.

Mass spectral data for (2-Phenylazophenyl-C,N')tellurium(IV) triiodide

Relative to ^{130}Te, ^{14}N, ^{12}C, ^{1}H, ^{127}I

Species	m/e	Rel. Int.
$[C_6H_5]^+$	77	47
I^+	127	20
$[C_6H_5]_2^+$	152	39
$[C_6H_5Te]^+$	206	13
$[C_{18}H_{13}N_2]^+$	257	62
$[(C_6H_5)_2Te]^+$	282	27
$[C_{12}H_9N_2Te]^+$	311	100
$[C_{18}H_{14}N_2Te]^+$	390	9
$[(C_{12}H_9N_2)_2Te]^+$	492	11

CHAPTER FIVE

DISCUSSION

Discussion.

The syntheses of the following starting materials, 2-(2-pyridyl)phenylmercury(II) chloride(17), 2-(2-pyridyl)phenyltellurium(IV) trichloride(17), 2-(2-pyridyl)phenyltellurium(II) chloride(17), 2-(2-pyridyl)phenyltellurium(IV) tribromide(17), 2-(2-pyridyl)phenyltellurium(II) bromide(17), *bis*[2-(2-pyridyl)phenyl] ditelluride(17) (phenylazophenyl-C,N')mercury(II) chloride(63), (2-phenylazophenyl-C,N')tellurium(IV) trichloride(64) and (2-phenylazophenyl-C,N')tellurium(II) chloride(64) were successfully accomplished as determined by their melting points and FTIR analysis.

Synthesis of 2-(2-pyridyl)phenyltellurium(II) iodide (RTeI) and phenylazophenyl(C,N')tellurium(II) iodide (R'TeI) by metathesis involving sodium iodide and the corresponding chloride (or bromide in the case of RTeI) worked well. The crystal structure of RTeI was found to be triclinic (see chapter six). The formation of $RTeI_3$ and $R'TeI_3$ where also achieved from the reaction of an organyltellurium(IV) trichloride/tribromide with an excess of sodium iodide. However, when these triiodide materials were recrystallised the monoiodide was obtained; interestingly, in the case of recrystallisation of $RTeI_3$ it is the monoclinic form of RTeI that is formed (see chapter six). Tris-dialkyldithiocarbamato - derivatives of phenylazophenyl(C,N')tellurium compounds(65) also show a similar behaviour, in that the tellurium(IV) compounds exist as tellurium(II) charge transfer complexes.

The analytical data (see table 11 and 19) for the organyltellurium iodides were in agreement with the calculated values. ^{13}C NMR spectra (see table 12 and 20) of the iodides supported the purity of the materials.

RTeI (δ = 1135 ppm *vs* Me_2Te) and R'TeI (δ = 1313 ppm *vs* Me_2Te) gave ^{125}Te NMR spectra which were consistent with those expected for tellurium(II) compounds(65). Interestingly, no ^{125}Te resonance were seen for either $RTeI_3$ and $R'TeI_3$ when the materials were scanned. Therefore an experiment was carried out, in which a molar quantity of organyltellurium(II) monoiodide and diiodine were mixed in acetone. The mixture was scanned for a ^{125}Te resonance, and surprisingly the tellurium resonance which was previously seen for the monoiodide, was lost. A possible explanation for the loss in signal may be due to the presence of a charge transfer complex, within which a degree of paramagnetism is present when organotellurium(II) monoiodide and diiodine are mixed, (see below).

$$RTeI + I_2 \leftrightarrow RTeI.I_2$$

Where R = phenylazophenyl or pyridylphenyl

The triiodides may also exhibited this phenomenon; forming a charge transfer complex of monoiodide and diiodine, which might explain why the materials did not give an NMR signal. An alternative explanation is that the triiodides contain the $[I_3]^-$ ion, if this is the case the triiodides should give a ^{125}Te resonance because there is no degree of paramagnetism. If this is so, the NMR observations are puzzling.

The colours of the organotellurium iodides were noted. The monoiodides ranged from red to dark red and the triiodides ranged from dark red/purple to dark purple/almost black. McCullough(60) suggested that the intermolecular or secondary bonding which takes place in the compound (2-biphenylyltellurium triiodide), is responsible for the colour of the compound. McCullough suggested that Te-I and Te---I bonds tend to produce colours of orange and red, (just like the monoiodides in this thesis) and the I---I interaction gives the dark purple/black colour, (just like as for triiodides). Therefore the colour of the triiodides supports the existence of a charge transfer complexes, in that the diiodine (in the complex) is secondary bonded to the iodine atom bonded to the tellurium (see below).

RTe-I-----I-I

Where ----- = Secondary bond

Mass spectroscopic data (see table 26 and 27) were collected. Similarities were found between the two compounds R'TeI and R'TeI$_3$. The only parent ion seen was for R'TeI at m/e = 438 (^{130}Te). Other major peaks in both spectra corresponded to R'$_2$Te$^+$, R'Te$^+$, (dibenzotellurophene)$^+$ and $C_6H_4Te^+$ fragments. In addition, a significant feature at m/e = 257 corresponded to $C_{18}H_{13}N_2$, which is a fragment derived from R$_2$'Te$^+$. The presence of this peak suggests that considerable thermolysis of the materials had occurred prior to passage to the vapour phase. One significant difference between the two spectra was the presence of a peak at m/e = 127 in the R'TeI$_3$ spectrum (60% of base peak, m/e = 311, R'Te$^+$), which is attributed to I^+ arising from loosely bound I_2. This questions the formation of a true organotellurium(IV) triiodide.

Raman data were obtained for R'TeI and R'TeI$_3$ (R' = phenylazophenyl-) and also for RTeI (R = 2-(2-pyridyl)phenyl-). The azobenzene derivatives fluoresced but gave spectra which were dominated by an intense shift at $\Delta\nu = 1355$ cm^{-1} ν(N=N). The spectral data were compared with there obtained by Greaves$^{(66)}$, for the related compound 2-phenylazophenyl(C,N')tellurium(II) chloride$^{(66)}$, which also showed a similar intense shift of 1375 cm^{-1} ν(N=N). The region above 200 cm^{-1} strongly suggested that the same molecular component (phenylazophenyl-group) was present in both materials, thereby providing further support for the view that the triiodide is a charge transfer complex of the monoiodide and diiodine. Unfortunately no data could be obtained below 200 cm^{-1} and hence no confident assignment of ν(Te-I) can be offered for RTeI.

Many attempts were made to form the organotellurium monofluoride or trifluoride. The methods followed were reported by Maslakov(27), and other methods reported in chapters 3 and 4. Melting points, FTIR and ^{19}F NMR analysis of the products showed that no reaction had taken place.

The attempted synthesises of RTeF and R'TeF, followed the method suggested by Emeleus and Heal(20), in which organyltellurium (tri)monohalide and silver fluoride were refluxed in toluene, showed some positive results.

The reaction mixture arising from the reaction of RTeI and AgF (in toluene) gave a promising ^{19}F NMR spectrum (see table 15) with a fluorine reasonance at -85.1 ppm vs. sodium fluoride, which suggested that a reaction had taken place. Satellites were seen in the spectrum and the coupling constant, J_{FTe}, was found to be 1523 Hz. The ^{125}Te NMR (see table 14) showed a doublet, at $\delta = 1172$ ppm vs. dimethyltellurium which is consistent for tellurium (II) compounds(65). A coupling constant J_{TeF} of 1568 Hz was acceptable when compared with the one found in the ^{19}F NMR (above). Satellites and doublets were seen in the ^{125}Te and ^{19}F spectra because the fluorine atom, with a spin of a half, couples with the tellurium which also has a spin of a half. Unfortunately the analytical data (see table 11) for this compound gave a empirical formula of $C_{13}H_{13}N$, which showed that the compound produced was not pure.

Reaction of R'TeI with silver(I) fluoride following Emeleus and Heal(20) method gave an orange oil analysing as the monofluoride; interestingly the same product was obtained from $R'TeI_3$ providing further support for the view that the triiodide is a charge transfer complex of the monoiodide and diiodine, because one would expect the formation of the trifluoride.

The analytical data (see table 19) obtained for the oils were found to be in reasonable agreement with the calculated values for 2-phenylazophenyl(C,N')tellurium fluoride. ^{19}F NMR (see table 22) of the oils, gave a resonance at -47.52 ppm for the reaction of R'TeI and -47.44 ppm for the reaction of $R'TeI_3$ with respect to sodium fluoride. Satellites were not seen in the spectra either because the samples was not pulsed for long enough, or the NMR solutions scanned contained a weak concentration of the ^{125}Te atoms (which is only approximately 7.01% abundance) bonded to the ^{19}F atom. ^{125}Te NMR (see table 21) of the oils showed a doublet at 1230 ppm for the reaction of R'TeI and 1237ppm for the reaction of $R'TeI_3$ with respect to dimethyltellurium. The spectra of the oils were both consistent for tellurium (II) compounds(65).

The orange oils were believed to be 2-phenylazophenyl(C,N')tellurium(II) fluoride.

An X-ray photoelectron (XPS) study was initiated on RTeBr, RTeI, R'TeCl, R'TeI and $R'TeI_3$ (where R = 2-(2-pyridyl)phenyl- and R' 2-phenylazophenyl-). Binding energy data can be seen on pages 92 and 108 corresponding 2-pyridylphenyl- compounds and phenylazophenyl- compounds respectively. XPS analysis was carried out on the above compounds to see if there was a relationship between the binding energy of tellurium - halide bond, where the halide increases in mass. Unfortunately no relationship was seen for the 2-(2-pyridyl)phenyltellurium halide series and for the 2-phenylazophenyl(C,N')tellurium(II) halide series.

One peak was resolved for chlorine in (2-phenylazophenyl-C,N')tellurium(II) chloride with a binding energy of 198.1 eV. One peak was resolved for bromine in 2-(2-pyridyl)phenyltellurium(II) bromide with a binding energy of 79.6 eV.

However caution is clearly needed during analysis since two peaks were resolved for the iodine region with the binding energies 618.1 and 619.2 eV for both the monoiodides and the triiodide. The explanation is in the tellurium region of the XPS spectrum where the data (table 17 and 24) indicate that there are two minor components at 573.2 and 576.5 eV for all of the compounds analysed which correspond to Te(IV) and Te(0) respectively. The binding energies of 573.2 and 576.5 eV were comparable with the binding energies of tellurium oxide (573.2 eV)(67) and tellurium (576.5 eV)(68). The problems encountered arose from radiation damage of the samples(69), and can be explained by the appearance of extra iodine peaks. Hence the XPS is rather inconclusive and the main conclusion that can be drawn is that the major tellurium peak seen all in the spectrums, corresponds to tellurium in oxidation state (II). To that extent, the balance of evidence is that a formulation of a triiodide based on tellurium(IV) may be excluded.

CHAPTER SIX

CRYSTALLOGRAPHY

Crystallography

Experimental and Results

Crystallographic analysis of 2-(2-pyridyl)phenyltellurium(II) chloride

Yellow crystals of 2-(2-pyridyl)phenyltellurium(II) chloride were obtained from the slow evaporation of a methanol solution at 5°C. A suitable crystal was mounted on a Rigaku R-AXIS II area detector diffractometer and the data were collected using MoK_α radiation. The crystal structure was determined(70) by Patterson and Fourier methods and refined(71) by least squares with anisotropic thermal parameters for tellurium and chloride, isotropic parameters for carbon and nitrogen atoms. Hydrogen atoms were placed in calculated positions riding on their respective bonded atoms. Details of the data collection are given in table 28. The calculations were terminated when all the shift/e.s.d. ratios were <0.1 and R = 0.0726 (3 540 reflections) for the compound.

Atomic co-ordinates are given in table 29. Selected geometrical parameters are listed in table 30. Hydrogen atom co-ordinates, anisotropic thermal parameters and a full list of bond lenghts and angles have been deposited with the Cambridge Crystallographic Data Centre. Figure 24 gives a PLUTO(72) plot of one molecule of 2-(2-pyridyl)phenyltellurium(II) chloride, showing the atom numbering.

Table. 28. Crystallographic and experimental data for 2-(2-pyridyl)phenyltellurium(II) chloride.

Formula	C11H8ClNTe
Molecular weight	317.2
Crystal size mm	0.4 x 0.3 x 0.2
Space group	P1
System	triclinic
a, Å	12.024(5)
b, Å	13.366(5)
c, Å	11.111(5)
α, deg	102.87(3)
β, deg	109.83(3)
γ, deg	77.46(3)
υ, Å^3	1618
Z	6
Dcalc, g cm^{-3}	1.953
μ(MoKα), mm^{-1}	2.96
λ, Å	0.71069
Temperature, °C	25
No. of unique data [$I>\sigma(I)$]	5825
Observed Data [$I>3.5\sigma(I)$]	3540
Scan range max, θ_{max}	27.5
R	0.0726
Residual electron densities ranges, e Å^{-3}	1.1 to -1.2

Table 29. Atomic coordinates (x 10^4) and isotropic diplacement parameters (A^2 x 10^3) for $C_{11}H_8ClNTe$. For the Te and Cl atoms U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U/U(eq)
Te(A)	-2(2)	29(2)	-50(2)	77(1)
Te(B)	-2307(2)	-2215(1)	-2458(2)	72(1)
Te(C)	1132(2)	-3519(2)	-1169(2)	79(1)
Te(D)	-1312(2)	-5633(1)	-3760(2)	75(1)
Te(E)	-4389(2)	-4327(2)	-5397(2)	79(1) *
Te(E')	-6811(36)	-1357(27)	-8403(38)	60(9) **
Te(F)	3030(2)	859(2)	1514(2)	78(1) *
Te(F')	5829(42)	3550(32)	4859(44)	73(9) **
Cl(A)	127(8)	562(8)	2391(8)	88(2)
Cl(B)	-2454(10)	-2038(7)	-158(8)	95(3)
Cl(C)	1378(12)	-3773(8)	-3445(9)	107(4)
Cl(D)	-1377(8)	-5890(6)	-6215(7)	78(2)
Cl(E)	-4376(9)	-4512(7)	-3085(8)	91(3)
Cl(F)	3330(8)	-538(6)	-435(8)	81(2)
N(1A)	-294(25)	-87(20)	-2138(27)	74(7)
C(1A)	-1296(35)	1279(27)	-631(37)	88(10)
C(2A)	-1861(30)	1977(23)	222(33)	75(8)
C(3A)	-2742(37)	2796(30)	-223(40)	98(11)
C(4A)	-3069(42)	2871(34)	-1565(44)	108(12)
C(5A)	-2573(35)	2161(26)	-2358(38)	88(10)
C(6A)	-1658(28)	1346(22)	-1901(30)	67(7)
C(7A)	-1149(31)	590(23)	-2764(32)	75(8)
C(8A)	-1305(37)	598(30)	-4051(38)	94(10)
C(9A)	-716(32)	-212(25)	-4779(35)	80(9)
C(10A)	105(38)	-908(30)	-4136(40)	99(11)
C(11A)	345(35)	-866(28)	-2786(37)	89(10)
N(1B)	-2429(26)	-2129(21)	-4460(28)	76(7)
C(1B)	-3535(28)	-873(22)	-2861(29)	64(7)
C(2B)	-4023(33)	-229(26)	-1961(36)	84(9)
C(3B)	-4875(33)	665(26)	-2310(36)	85(9)
C(4B)	-5183(40)	892(32)	-3549(42)	101(11)
C(5B)	-4638(39)	251(30)	-4474(42)	99(11)
C(6B)	-3801(31)	-678(23)	-4122(31)	73(8)
C(7B)	-3258(26)	-1356(20)	-5063(27)	59(6)
C(8B)	-3443(35)	-1258(28)	-6311(35)	87(10)
C(9B)	-2880(46)	-1994(36)	-7003(52)	119(14)
C(10B)	-2028(39)	-2783(32)	-6543(35)	103(12)
C(11B)	-1794(36)	-2833(27)	-5284(32)	87(10)
N(1C)	1239(29)	-3533(22)	826(31)	86(8)
C(1C)	2322(30)	-4831(23)	-724(31)	72(8)
C(2C)	2918(31)	-5548(25)	-1551(36)	82(9)
C(3C)	3681(38)	-6427(30)	-1123(42)	98(11)
C(4C)	3957(39)	-6633(31)	143(40)	106(12)
C(5C)	3413(35)	-5973(28)	936(38)	93(11)
C(6C)	2602(32)	-5073(25)	549(34)	78(9)

C(7C)	2013(34)	-4360(26)	1407(32)	81(9)
C(8C)	2194(45)	-4520(35)	2712(37)	112(13)
C(9C)	1532(45)	-3671(36)	3338(53)	128(16)
C(10C)	723(46)	-2903(37)	2831(52)	133(16)
C(11C)	630(34)	-2798(26)	1526(34)	82(9)
N(1D)	-864(32)	-5645(25)	-1677(33)	93(9)
C(1D)	-15(28)	-6941(22)	-3414(30)	67(7)
C(2D)	457(31)	-7610(23)	-4356(33)	75(8)
C(3D)	1310(30)	-8409(24)	-3933(33)	77(8)
C(4D)	1734(34)	-8628(27)	-2744(36)	88(9)
C(5D)	1330(32)	-7990(25)	-1803(35)	79(8)
C(6D)	416(29)	-7128(22)	-2119(30)	69(8)
C(7D)	-84(28)	-6444(22)	-1170(30)	66(7)
C(8D)	286(31)	-6536(24)	145(31)	75(8)
C(9D)	-249(36)	-5765(28)	950(40)	91(10)
C(10D)	-1063(34)	-5009(27)	435(32)	85(9)
C(11D)	-1400(35)	-4918(28)	-832(32)	89(10)
N(1E)	-4692(25)	-3924(20)	-7300(26)	74(7)
C(1E)	-5562(40)	-2935(33)	-5391(44)	103(12)
C(2E)	-5946(34)	-2436(26)	-4317(36)	85(9)
C(3E)	-6786(40)	-1484(32)	-4456(46)	109(13)
C(4E)	-7137(46)	-1088(38)	-5615(48)	119(14)
C(5E)	-6737(39)	-1628(31)	-6701(43)	101(12)
C(6E)	-5964(32)	-2513(25)	-6542(34)	78(8)
C(7E)	-5469(33)	-3061(26)	-7559(35)	83(9)
C(8E)	-5749(38)	-2731(30)	-8806(38)	98(11)
C(9E)	-5257(46)	-3326(37)	-9732(48)	132(16)
C(10E)	-4469(38)	-4172(29)	-9448(40)	96(11)
C(11E)	-4222(35)	-4475(27)	-8260(35)	85(9)
N(1F)	3165(26)	2176(20)	3208(27)	80(7)
C(1F)	4787(27)	1162(20)	2059(28)	66(7)
C(2F)	5649(29)	585(23)	1500(31)	71(7)
C(3F)	6820(35)	849(25)	1954(33)	88(9)
C(4F)	7126(34)	1696(25)	2985(34)	94(10)
C(5F)	6256(29)	2244(23)	3470(32)	75(8)
C(6F)	5137(29)	1975(22)	3100(31)	72(7)
C(7F)	4230(27)	2496(21)	3711(28)	66(7)
C(8F)	4417(33)	3298(26)	4753(35)	86(9)
C(9F)	3475(32)	3820(25)	5235(35)	83(9)
C(10F)	2331(38)	3473(28)	4566(38)	93(10)
C(11F)	2247(33)	2627(25)	3644(33)	82(9)

* Site occupancy 0.95

** Site occupancy 0.05; refined isotropically

Table 30. Bond lengths (Å) and selected angles (deg) with e.s.d.s in parentheses.

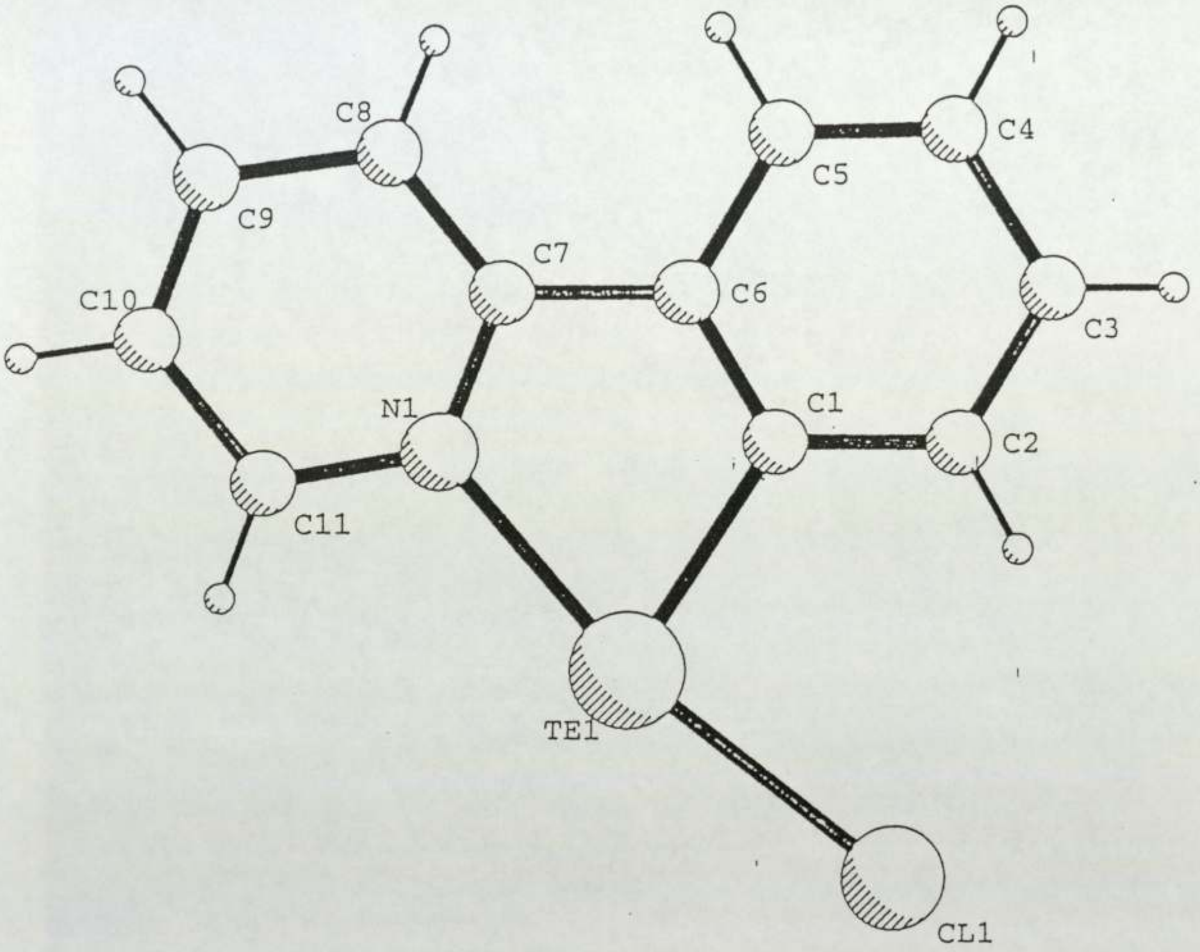
Te - X	2.606(11)
Te...N(1)	2.205(11)
Te - C(1)	2.077(7)
C(1) - C(2)	1.402(8)
C(2) - C(3)	1.405(13)
C(3) - C(4)	1.394(17)
C(4) - C(5)	1.370(20)
C(5) - C(6)	1.404(17)
C(6) - C(1)	1.401(12)
C(6) - C(7)	1.440(5)
C(7) - C(8)	1.405(16)
C(8) - C(9)	1.389(16)
C(9) - C(10)	1.352(19)
C(10) - C(11)	1.382(18)
C(11) - N(1)	1.379(16)
N(1) - C(7)	1.354(13)

N(1)...Te - X	168.2(5)
N(1)...Te - C(1)	75.7(4)
C(1) - Te - X	92.9(4)

where X = Cl[a]

[a] Averaged values; e.s.d.'s in mean values calculated from $[\sum (x - x_i)^2 / \{n(n-1)\}]^{1/2}$

Figure 24. Crystal structure of 2-(2-pyridyl)phenyltellurium(II) chloride



Crystallographic analysis of 2-(2-pyridyl)phenyltellurium(II) iodide, (modification 1).

Synthesis of 2-(2-pyridyl)phenyltellurium(II) iodide by metathesis of 2-(2-pyridyl)phenyltellurium(II) bromide or chloride with sodium iodide, (see chapter 3.10), was used for crystallographic analysis.

Orange crystals of 2-(2-pyridyl)phenyltellurium(II) iodide were obtained from slow evaporation of a dichloromethane solution at 5°C. A suitable crystal was mounted on a Rigaku R-AXIS II area detector diffractometer and the data were collected using MoK_{α} radiation. The crystal structure was determined(70) by Patterson and Fourier methods and refined(71) by least squares with anisotropic thermal parameters for tellurium and chloride, isotropic parameters for carbon and nitrogen atoms. Hydrogen atoms were placed in calculated positions riding on their respective bonded atoms. Details of the data collection are given in table 31. The calculations were terminated when all the shift/e.s.d. ratios were <0.1 and R = 0.0569 (7 064 reflections) for the compound.

Atomic co-ordinates are given in table 32. Selected geometrical parameters are listed in table 33. Hydrogen atom co-ordinates, anisotropic thermal parameters and full list of bonds lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. Fig. 24 gives a PLUTO(72) plot of one molecule of 2-(2-pyridyl)phenyltellurium(II) chloride, showing the atom numbering, which also represents the iodide molecule, the only visible difference being ca. 0.3 Å longer tellurium - halogen bond in that molecule.

Table 31. Crystallographic and experimental data for 2-(2-pyridyl)phenyltellurium(II) iodide(modification 1).

Formula	C11H8INTe
Molecular weight	408.7
Crystal size mm	0.2 x 0.2 x 0.15
Space group	P1
System	triclinic
a, Å	12.227(2)
b, Å	13.395(2)
c, Å	11.628(2)
α, deg	103.34(1)
β, deg	108.13(2)
γ, deg	78.42(1)
υ, Å^3	1744
Z	6
Dcalc, g cm^{-3}	2.335
μ(MoKα), mm^{-1}	5.17
λ, Å	0.71069
Temperature, °C	25
No. of unique data [$I>\sigma(I)$]	8662
Observed Data [$I>3.5\sigma(I)$]	7064
Scan range max, θ_{max}	25
R	0.0569
Residual electron densities ranges, e Å^{-3}	0.63 to -0.98

Table 32. Atomic coordinates (x 10^4) and isotropic diplacement parameters (A^2 x 10^3). for $C_{11}H_8INTe$ (triclinic). For the Te and I atoms U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U/U(eq)
Te(A)	-76(2)	-38(1)	-292(2)	62(1)
Te(B)	-2349(2)	-2236(1)	-2676(1)	58(1)
Te(C)	1196(2)	-3570(1)	-906(2)	65(1)
Te(D)	-1170(2)	-5754(1)	-3518(2)	63(1)
Te(E)	-4395(2)	-4414(2)	-5308(2)	56(1) *
Te(E′)	-6779(9)	-1376(8)	-8383(9)	57(3) **
Te(F)	2977(2)	729(2)	1418(2)	59(1) *
Te(F′)	5836(10)	3492(9)	4921(10)	65(3) **
I(A)	153(2)	239(2)	2365(2)	76(1)
I(B)	-2384(2)	-2133(2)	-154(2)	89(1)
I(C)	1309(2)	-3663(2)	-3387(2)	103(1)
I(D)	-1313(2)	-5933(2)	-6162(2)	78(1)
I(E)	-4389(2)	-4671(2)	-2868(2)	81(1)
I(F)	3261(2)	-888(2)	-688(2)	79(1)
N(1A)	-454(19)	-30(17)	-2302(20)	65(6)
C(1A)	-1378(19)	1185(18)	-593(20)	49(5)
C(2A)	-1916(24)	1829(23)	257(27)	81(8)
C(3A)	-2760(28)	2656(26)	-8(31)	94(10)
C(4A)	-3067(28)	2836(26)	-1190(28)	87(9)
C(5A)	-2672(24)	2249(22)	-2047(27)	73(8)
C(6A)	-1802(22)	1380(19)	-1821(23)	60(6)
C(7A)	-1256(20)	739(18)	-2732(20)	53(6)
C(8A)	-1535(25)	751(23)	-3988(26)	77(8)
C(9A)	-963(27)	53(24)	-4704(29)	85(9)
C(10A)	-98(27)	-731(25)	-4204(29)	86(9)
C(11A)	154(29)	-742(25)	-3025(29)	86(9)
N(1B)	-2531(19)	-2060(17)	-4633(19)	63(6)
C(1B)	-3487(20)	-911(18)	-2906(20)	50(6)
C(2B)	-4064(23)	-233(21)	-2055(24)	62(7)
C(3B)	-4856(27)	600(25)	-2297(29)	84(9)
C(4B)	-5143(28)	882(26)	-3456(28)	86(9)
C(5B)	-4679(25)	288(24)	-4358(29)	79(9)
C(6B)	-3898(20)	-657(19)	-4142(21)	53(6)
C(7B)	-3356(20)	-1311(19)	-5029(21)	54(6)
C(8B)	-3579(32)	-1198(29)	-6286(33)	105(11)
C(9B)	-2936(25)	-1896(23)	-7029(29)	82(9)
C(10B)	-2209(26)	-2724(24)	-6587(28)	85(8)
C(11B)	-1976(24)	-2810(22)	-5364(24)	68(7)
N(1C)	1437(19)	-3702(17)	1056(20)	64(6)
C(1C)	2400(19)	-4953(18)	-584(20)	49(5)
C(2C)	2855(29)	-5550(27)	-1521(32)	90(10)
C(3C)	3670(32)	-6479(29)	-1261(35)	102(11)
C(4C)	3922(36)	-6662(32)	-102(35)	112(12)
C(5C)	3423(25)	-6089(23)	728(28)	75(8)
C(6C)	2647(21)	-5204(19)	561(22)	58(6)

C(7C)	2061(24)	-4506(22)	1461(25)	68(7)
C(8C)	2326(23)	-4754(21)	2583(23)	65(7)
C(9C)	1826(32)	-4078(29)	3385(36)	108(11)
C(10C)	1047(25)	-3301(23)	3040(27)	78(8)
C(11C)	800(30)	-3003(28)	1837(29)	91(10)
N(1D)	-767(18)	-5791(17)	-1516(19)	60(5)
C(1D)	137(22)	-7061(20)	-3242(23)	60(7)
C(2D)	546(18)	-7688(17)	-4234(21)	52(6)
C(3D)	1424(24)	-8504(23)	-3917(27)	77(8)
C(4D)	1842(26)	-8658(23)	-2759(27)	79(8)
C(5D)	1362(24)	-8103(22)	-1799(27)	73(8)
C(6D)	528(21)	-7258(19)	-2102(22)	57(6)
C(7D)	67(25)	-6565(23)	-1120(27)	75(8)
C(8D)	379(24)	-6730(22)	92(25)	73(8)
C(9D)	-148(25)	-6017(22)	898(27)	76(8)
C(10D)	-917(23)	-5215(22)	563(25)	71(7)
C(11D)	-1205(29)	-5078(27)	-668(29)	89(10)
N(1E)	-4628(17)	-4045(16)	-7207(18)	54(5)
C(1E)	-5510(21)	-3008(18)	-5281(21)	52(6)
C(2E)	-5972(22)	-2489(20)	-4296(23)	62(7)
C(3E)	-6732(27)	-1536(25)	-4387(29)	85(9)
C(4E)	-7158(27)	-1172(25)	-5535(28)	87(9)
C(5E)	-6587(25)	-1687(23)	-6464(28)	74(8)
C(6E)	-5863(22)	-2615(20)	-6364(23)	62(7)
C(7E)	-5441(21)	-3164(19)	-7402(22)	55(6)
C(8E)	-5655(28)	-2871(25)	-8527(28)	83(9)
C(9E)	-5220(26)	-3450(24)	-9457(28)	81(8)
C(10E)	-4423(25)	-4320(22)	-9245(26)	72(8)
C(11E)	-4243(21)	-4636(21)	-8120(22)	62(7)
N(1F)	3038(18)	2037(16)	3063(18)	67(6)
C(1F)	4694(20)	1081(18)	1986(21)	59(6)
C(2F)	5532(25)	534(23)	1424(27)	78(8)
C(3F)	6667(26)	821(23)	1891(26)	75(8)
C(4F)	6932(26)	1588(22)	2824(26)	75(8)
C(5F)	6104(22)	2097(21)	3430(24)	71(7)
C(6F)	5002(20)	1838(18)	2998(20)	56(6)
C(7F)	4086(20)	2392(18)	3602(21)	59(6)
C(8F)	4271(22)	3185(19)	4632(22)	64(6)
C(9F)	3252(21)	3649(20)	5034(23)	62(7)
C(10F)	2236(29)	3346(25)	4483(28)	88(9)
C(11F)	2109(27)	2546(23)	3466(27)	80(8)

* Site occupancy 0.83

** Site occupancy 0.17; refined isotropically

Table 33. Bond lengths (Å) and selected angles (deg) with e.s.d.s in parentheses

Te - X	2.937(11)
Te...N(1)	2.260(10)
Te - C(1)	2.095(18)
C(1) - C(2)	1.405(9)
C(2) - C(3)	1.402(17)
C(3) - C(4)	1.367(17)
C(4) - C(5)	1.365(25)
C(5) - C(6)	1.397(13)
C(6) - C(1)	1.393(19)
C(6) - C(7)	1.465(10)
C(7) - C(8)	1.395(12)
C(8) - C(9)	1.380(17)
C(9) - C(10)	1.352(19)
C(10) - C(11)	1.397(21)
C(11) - N(1)	1.372(16)
N(1) - C(7)	1.342(16)

N(1)...Te - X	170.5(4)
N(1)...Te - C(1)	75.7(5)
C(1) - Te - X	95.2(3)

where X = I[a]

[a] Averaged values; e.s.d.'s in mean values calculated from $[\sum(x - x_i)^2 / \{n(n-1)\}]^{1/2}$

Crystallographic analysis of 2-(2-pyridyl)phenyltellurium(II) iodide, (modification 2).

Metathesis of 2-(2-pyridyl)phenyltellurium(IV) tribromide with sodium iodide followed by recrystallisation of the product from acetonitrile - methanol giving light purple crystals of 2-(2-pyridyl)phenyltellurium(II) iodide. A suitable crystal was mounted on a Rigaku R-AXIS II area detector diffractometer and the data were collected using MoK$_\alpha$ radiation. The crystal structure was determined(70) by direct methods and refined(71) by least squares with anisotropic parameters for all non - hydrogen atoms. Hydrogen atoms were placed in calculated positions riding on their respective bonded atoms. Details of the data collection are given in table 34. The calculation were terminated when all the shift/e.s.d. ratios were <0.1 and R = 0.0408 (1 977 reflections) for the compound.

Atomic co-ordinates are given in table 35. Selected geometrical parameters are listed in table 36. Hydrogen atom co-ordinates, anisotropic thermal parameters and full list of bonds lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. Fig. 24 gives a PLUTO(72) plot of one molecule of 2-(2-pyridyl)phenyltellurium(II) chloride, showing the atom numbering, which also represents the iodide molecule, the only visible difference being ca. 0.3 Å longer tellurium - halogen bond in that molecule.

Table 34. Crystallographic and experimental data for 2-(2-pyridyl)phenyltellurium(II) iodide (modification 2).

Formula	C11H8INTe
Molecular weight	408.7
Crystal size mm	0.15 x 0.08 x 0.05
Space group	$P2_1/c$
System	monoclinic
a, Å	8.319(2)
b, Å	19.644(4)
c, Å	7.822(2)
β, deg	114.79(2)
υ, $Å^3$	1160
Z	4
Dcalc, g cm^{-3}	2.339
μ(MoKα), mm^{-1}	5.18
λ, Å	0.71069
Temperature, °C	25
No. of unique data [I>σ(I)]	1977
Observed Data [I>σ(I)]	1977
Scan range max, θ_{max}	25
R	0.0408
Residual electron densities ranges, e $Å^{-3}$	0.56 to -0.87

Table 35. Atomic coordinates (x 10^4) and equivalent isotropic diplacement parameters (A^2 x 10^3) for $C_{11}H_8INTe$ (monoclinic). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Te(1)	2554(1)	2036(1)	705(1)	43(1)
I(1)	3570(1)	605(1)	1001(1)	68(1)
N(1)	1457(7)	3107(3)	-15(7)	44(1)
C(1)	-39(8)	1894(3)	-1397(8)	40(1)
C(2)	-831(9)	1259(4)	-1963(9)	52(2)
C(3)	-2522(10)	1222(4)	-3394(10)	64(2)
C(4)	-3423(10)	1815(5)	-4236(10)	66(2)
C(5)	-2656(10)	2435(4)	-3646(10)	58(2)
C(6)	-962(8)	2492(3)	-2205(9)	46(2)
C(7)	-115(9)	3152(3)	-1507(9)	46(2)
C(8)	-768(11)	3795(4)	-2230(12)	66(2)
C(9)	206(13)	4361(4)	-1454(14)	75(2)
C(10)	1819(13)	4302(4)	102(13)	72(2)
C(11)	2408(11)	3671(4)	790(11)	57(2)

Table 36. Bond lengths (Å) and selected angles (deg) with e.s.d.s in parentheses

Te - X	2.917(1)
Te...N(1)	2.268(5)
Te - C(1)	2.112(6)
C(1) - C(2)	1.392(9)
C(2) - C(3)	1.384(10)
C(3) - C(4)	1.391(11)
C(4) - C(5)	1.363(11)
C(5) - C(6)	1.392(9)
C(6) - C(1)	1.401(9)
C(6) - C(7)	1.467(9)
C(7) - C(8)	1.397(9)
C(8) - C(9)	1.361(11)
C(9) - C(10)	1.388(13)
C(10) - C(11)	1.359(10)
C(11) - N(1)	1.353(8)
N(1) - C(7)	1.342(8)

N(1)...Te - X	170.7(1)
N(1)...Te - C(1)	75.9(2)
C(1) - Te - X	95.8(2)

where X = I

e.s.d.'s in mean values calculated from $[\sum(x - x_i)^2 / \{n(n-1)\}]^{1/2}$

Crystallographic analysis of phenylazophenyl(C,N')tellurium(II) chloride

Brown crystals of phenylazophenyl(C,N')tellurium(II) chloride were obtained from slow evaporation of a methanol solution at 5°C. A suitable crystal was mounted on a Rigaku R-AXIS II area detector diffractometer and the data were collected using MoK_α radiation. The structure was determined(73) by direct methods and refined(71) by least-squares using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed in calculated positions riding on their respective bonded atoms. Details of the data collection are given in table 37. Final R = 0.0641, residual electron density within the range -0.9 to +0.8 $eÅ^{-3}$. For 1380 observed reflection $[I>2\sigma(I)]$, R = 0.0579.

Atomic co-ordinates are given in table 38. Selected geometrical parameters are listed in table 39. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, full set of bond lengths and angles, and hydrogen atom co-ordinates. Fig. 25 gives a ORTEP(74) plot of one molecule of phenylazophenyl(C,N')tellurium(II) chloride, showing the atom numbering.

Bonds lengths and angles, see table 40, anisotropic diplacement parameters, see table 41 and hydrogen coordinates and isotropic displacement parameters, see table 42.

Table 37. Crystallographic and experimental data for phenylazophenyl(C,N') tellurium(II) chloride

Formula	C12H9ClN2Te
Molecular weight	344.26
Crystal size mm	0.2 x 0.15 x 0.15
Space group	I2/a
System	monoclinic
a, Å	20.217(10)
b, Å	4.0880(9)
c, Å	28.863(14)
β, deg	102.840(11)
υ, $Å^3$	2326(2)
Z	8
Dcalc, g cm^{-3}	1.966
μ(MoKα), mm^{-1}	2.759
λ, Å	0.71069
Temperature, °C	25
No. of unique data [I>σ(I)]	1573
Observed Data [I>2σ(I)]	1380
Scan range max, θ_{max}	3 to 25
R	0.0579
Residual electron densities ranges, e $Å^{-3}$	-0.9 to +0.8

Table 38. Atomic coordinates (x 10^4) and equivalent isotropic diplacement parameters (A^2 x 10^3) for $C_{12}H_9ClN_2Te$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Te(1)	2613(1)	10577(2)	-1774(1)	46(1)
Cl(1)	3495(1)	8373(7)	-2192(1)	63(1)
N(1)	2336(4)	12242(18)	-810(2)	50(2)
N(2)	2044(3)	12327(18)	-1251(2)	43(2)
C(1)	3250(5)	9861(21)	-1118(3)	44(2)
C(2)	3886(4)	8395(24)	-1019(3)	53(2)
C(3)	4242(5)	8067(30)	-562(3)	64(3)
C(4)	3970(6)	9190(31)	-187(4)	74(4)
C(5)	3348(6)	10535(27)	-261(4)	61(3)
C(6)	2983(5)	10889(23)	-733(3)	52(2)
C(7)	1369(5)	13701(23)	-1367(3)	46(2)
C(8)	1114(6)	15545(22)	-1038(4)	55(2)
C(9)	463(5)	16743(27)	-1177(4)	61(3)
C(10)	79(6)	16160(27)	-1618(4)	59(3)
C(11)	329(6)	14373(25)	-1935(4)	57(3)
C(12)	983(5)	13133(25)	-1820(3)	51(2)

Table 39. Bond lengths (Å) and selected angles (deg) with e.s.d.s in parentheses

	Present analysis	Previous work(79)	
		Molecule A	Molecule B
Te - C	2.061(9)	2.04(2)	2.20(3)
Te - N(2)	2.210(7)	2.23(2)	2.19(2)
Te - Cl	2.533(3)	2.552(8)	2.549(8)
C(6) - N(1)	1.391(12)	1.43(3)	1.35(3)
N(1) - N(2)	1.280(9)	1.25(2)	1.28(2)
N(2) - C(7)	1.444(11)	1.45(3)	1.45(3)

Cl - Te - N	165.9(2)	167.6(6)	165.7(6)
Cl - Te - C(1)	91.4(3)	94.8(7)	89.0(8)
C(1) - Te - N(2)	74.5(3)	72.8(9)	76.8(9)

Table 40. Bond lengths (Å) and angles (deg) for $C_{12}H_9ClN_2Te$.

Te(1)-C(1)	2.061(9)
Te(1)-N(2)	2.210(7)
Te(1)-Cl(1)	2.533(3)
N(1)-N(2)	1.280(9)
N(1)-C(6)	1.391(12)
N(2)-C(7)	1.444(11)
C(1)-C(2)	1.391(13)
C(1)-C(6)	1.404(12)
C(2)-C(3)	1.361(13)
C(3)-C(4)	1.39(2)
C(4)-C(5)	1.35(2)
C(5)-C(6)	1.405(14)
C(7)-C(12)	1.386(12)
C(7)-C(8)	1.396(12)
C(8)-C(9)	1.38(2)
C(9)-C(10)	1.356(14)
C(10)-C(11)	1.35(2)
C(11)-C(12)	1.386(14)
C(1)-Te(1)-N(2)	74.5(3)
C(1)-Te(1)-Cl(1)	91.4(3)
N(2)-Te(1)-Cl(1)	165.9(2)
N(2)-N(1)-C(6)	112.3(7)
N(1)-N(2)-C(7)	116.4(6)
N(1)-N(2)-Te(1)	118.4(5)
C(7)-N(2)-Te(1)	125.2(5)
C(2)-C(1)-C(6)	117.8(9)
C(2)-C(1)-Te(1)	127.7(7)
C(6)-C(1)-Te(1)	114.4(7)
C(3)-C(2)-C(1)	120.5(9)
C(2)-C(3)-C(4)	120.3(10)
C(5)-C(4)-C(3)	121.8(10)
C(4)-C(5)-C(6)	117.8(10)
N(1)-C(6)-C(5)	118.0(8)
N(1)-C(6)-C(1)	120.4(8)
C(5)-C(6)-C(1)	121.7(9)
C(12)-C(7)-C(8)	121.1(9)
C(12)-C(7)-N(2)	117.3(8)
C(8)-C(7)-N(2)	121.6(8)
C(7)-C(8)-C(9)	117.9(10)
C(10)-C(9)-C(8)	121.4(9)
C(9)-C(10)-C(11)	120.5(11)
C(12)-C(11)-C(10)	121.0(10)
C(7)-C(12)-C(11)	118.1(8)

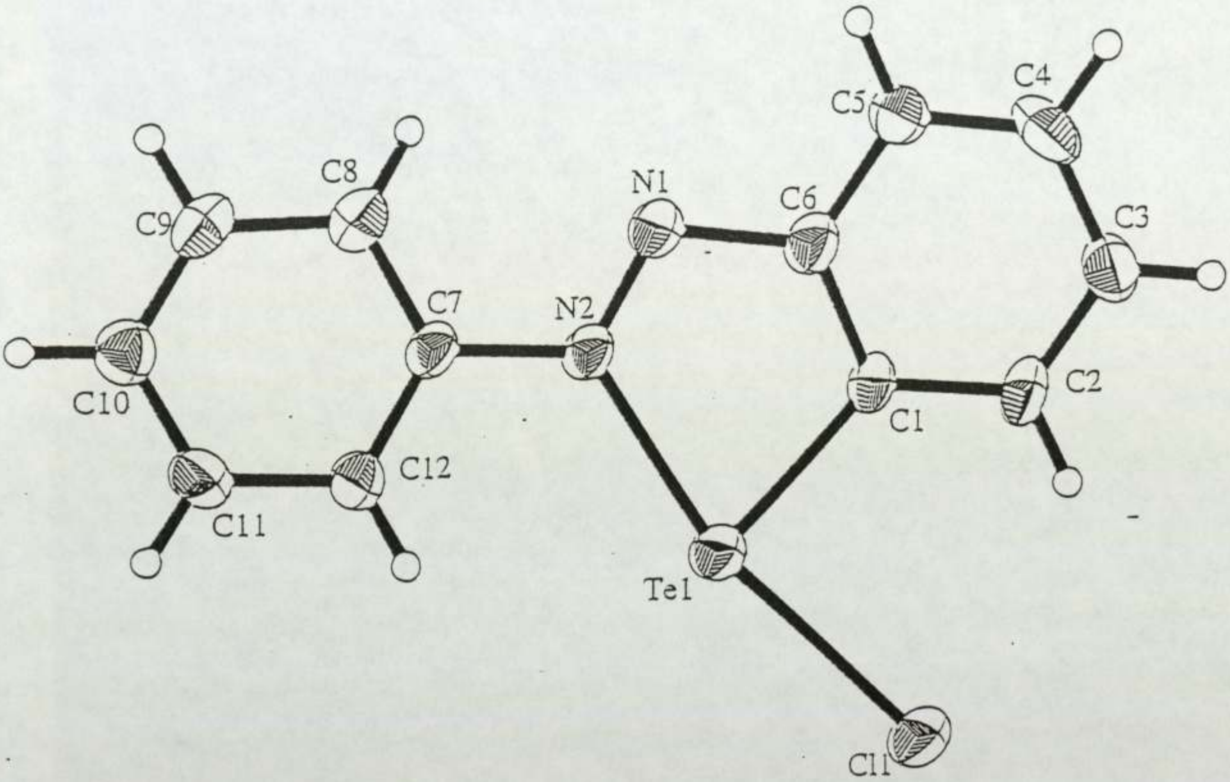
Table 41. Anisotropic displacement parameters ($A^2 \times 10^3$) for $C_{12}H_9ClN_2Te$.

	U11	U22	U33	U23	U13	U12
Te(1)	40(1)	53(1)	48(1)	-2(1)	14(1)	-1(1)
Cl(1)	51(2)	81(2)	60(1)	-8(1)	23(1)	0(1)
N(1)	40(5)	60(6)	52(4)	-1(3)	16(3)	-2(4)
N(2)	34(4)	51(5)	49(4)	-1(3)	16(3)	-4(3)
C(1)	26(5)	51(5)	57(6)	3(4)	17(4)	-4(4)
C(2)	35(5)	56(6)	72(6)	12(4)	22(4)	9(4)
C(3)	44(6)	90(8)	58(6)	16(5)	7(4)	5(5)
C(4)	57(8)	112(11)	44(6)	21(5)	-6(5)	-11(6)
C(5)	38(7)	99(9)	48(6)	0(5)	13(4)	-7(5)
C(6)	40(6)	59(7)	58(6)	-2(4)	16(4)	1(4)
C(7)	40(6)	54(6)	49(5)	5(4)	20(4)	3(4)
C(8)	53(7)	52(6)	63(7)	-5(4)	19(5)	3(5)
C(9)	61(7)	57(7)	72(7)	-4(5)	30(5)	13(5)
C(10)	47(7)	68(7)	62(6)	4(5)	13(5)	0(5)
C(11)	51(7)	68(7)	49(6)	-3(4)	3(5)	-3(5)
C(12)	42(6)	62(6)	50(5)	2(4)	13(4)	0(4)

Table 42. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($A^2 \times 10^3$) for $C_{12}H_9ClN_2Te$.

	x	y	z	U(eq)
H(2)	4071(4)	7633(24)	-1266(3)	63
H(3)	4667(5)	7088(30)	-499(3)	77
H(4)	4226(6)	9004(31)	122(4)	88
H(5)	3166(6)	11209(27)	-8(4)	73
H(8)	1376(6)	15952(22)	-736(4)	66
H(9)	284(5)	17978(27)	-964(4)	73
H(10)	-359(6)	16993(27)	-1703(4)	71
H(11)	58(6)	13972(25)	-2235(4)	69
H(12)	1158(5)	11952(25)	-2041(3)	62

Figure 25. Crystal structure of (phenylazophenyl-C,N')tellurium chloride.



Discussion

2-(2-Pyridyl)phenyltellurium(II) halide

2-(2-pyridyl)phenyltellurium(II) chloride (triclinic) and the 2-(2-pyridyl)phenyltellurium(II) iodide (triclinic) forms are very similar in terms of crystal structure. The only difference in the structures is the tellurium - halogen bond length, where the tellurium - iodide bond length is 0.3 Å longer than the tellurium - chloride bond length. Each structure has six independent molecules in the unit cell. The bond lengths and selected angles, averaged over the six molecules, are listed in table 30 (chloride) and 33 (iodide).

The 2-(2-pyridyl)phenyl group is both cases are essentially planar, with the rms atomic deviations ranging from 0.022 to 0.045 Å in the chloride and 0.025 to 0.040 Å in the iodide. The dihedral angles between the pyridyl and phenyl rings are all less than 3.6° in both the triclinic structures. However the estimated standard deviations for these angles are relatively large, in the order of 2°. E.s.d.'s in bond lengths and angles are also relatively large, with an average of 0.05 Å for C-C and C-N, 0.03 Å for Te-N and Te-C, 0.01 Å for Te-Cl and 1 - 5° for bond angles, in the chloride structure. The same values in the iodide structure are somewhat smaller, 0.04 - 0.03 Å for C-C and C-N, 0.02 for Te-N and Te-C, 0.003 Å for Te-I and 1 - 4° for bond angles.

2-(2-Pyridyl)phenyltellurium(II) iodide (monoclinic) form yielded more accurate parameters (see table 36). The 2-(2-pyridyl)phenyl group is again near-planar, rms atomic deviation 0.046 Å, and phenyl-pyridyl interplanar angle 5.2(4)°.

The tellurium atom is bonded to an aromatic carbon atom and to a halogen atom. The Te-Cl distance is 2.34 - 2.60 Å, which is at the upper end of the range, for this bond given by Allen *et al*(75). The bond length was compared with the Te-Cl bond length found in 1-chloro-1-hydro-N-*p*-toly-1-telluraisoindole(76) which is 2.568 Å, and was found to agree with that found for 2-(2-pyridyl)phenyltellurium(II) chloride. The Te-I distance of 2.937 Å (triclinic) and 2.917 Å (monoclinic) were in good agreement when the distances were compared with those found by Allen *et al* in 1-iodo-1-hydro-N-p-toly-1-tellurasioindole(77) where the Te-I distance was 2.926 Å.

The Te-C bond distance of 2.077 Å for the chloride, 2.095 Å for the triclinic iodide and 2.112 Å for the monoclinic iodide were slightly shorter than the bond distance given by Allen *et al.* for 1-chloro-1-hydro-N-*p*-toly-1-telluraisoindole(76) which is 2.098 Å and for 1-iodo-1-hydro-N-p-toly-1-tellurasioindole(77).

The Te-N distances of 2.205(11) Å for the chloride, 2.260(10) Å for the triclinic iodide and 2.268(5) Å for the monoclinic iodide are typical, when compared with $(RTeCl)_2R'HgCl$(78) where R = 2-(2-pyridyl)phenyl- and R' = p - ethoxyphenyl-, 1-chloro-1-hydro-N-*p*-toly-1-telluraisoindole(76) and 1-iodo-1-hydro-N-p-toly-1-tellurasioindole(77) in which the halide atoms are bonded *trans*- to the nitrogen. This interaction has the effect of holding the organic ligand in planar configuration.

Further inspection of the Te-N distance, however, appears to indicate a slight trend for these distances to increase as the atomic number of the *trans* halogen increases. Thus the Te-N distance is 2.205 Å for the chloride, 2.236 Å for the bromide(78), 2.260 Å for the triclinic iodide and 2.268 Å for the monoclinic iodide. Not entirely consistent with this tend is the Te-N distance of 2.236 Å in the chloride in its 2:1 inclusion complex with p-ethoxyphenylmercury(II) chloride(78).

In both the chloride and the triclinic form of the iodide, the two molecules, E and F, are affected by disorder, where 5% of the molecules in the chloride and 17% of the molecules in the triclinic iodide are rotated by 180° about a line perpendicular to the plane of the molecule, and passing through the mid-point of the C6-C7 inter-ring bond. The disordered tellurium atoms [Te(E') and Te(F')] show up clearly in difference maps. The corresponding halogen atoms do not appear to be affected by this disorder. However, disorder of the halogens may be concealed, since the probable positions of the halogen (E') and (F') coincide closely with the major halogen sites (F) and (E), respectively. Thus the distance Te(E')-Cl(F) and Te(F')-Cl(E) are 2.78(4) and 3.08(4) Å, while Te(E')-I(F) and Te(F')-I(E) are 2.919(10) and 3.161(11) Å. The relevant angles, halogen-Te'-N', (where N' coincides with C5) are all close to 180°.

The crystal structure of the bromide(78), 2-(2-pyridyl)phenyltellurium(II) bromide is isomorphous and exhibits a similar disorder (A different choice of unit cell axes was made for the bromide. Application of the matrix /00-1/100/010/ transforms the cells quoted above for the title compounds to that of the bromide given in ref. (78)). 6% Of the molecules are affected by disorder, which is midway to that shown by the chloride and the iodide. It is noteworthy that the minor component of Te-halogen bond length [mean 2.93 Å (chloride), 3.04 Å (iodide)] are closer to the values measured for the major component [2.606 Å (chloride), 2.937 Å (iodide)] in the iodide than in the chloride structure. The situation in the bromide structure(77) is again intermediate. This feature may account for the differing degrees of disorder in the three structures (An alternative, but crystallographically equivalent, interpretation of the disorder, is that only the RTe residues are affected by disorder, while the halogen atoms are in fixed positions.).

The distance for Te-Cl (2.606 Å), Te-N (2.077 Å) and Te-N (2.205 Å) for the chloride were in good agreement when compared with the distance found in the 2-(2-pyridyl)phenyltellurium(II) chloride 2:1 inclusion complex compound(78), in which the distances for Te-Cl, Te-N and Te-N are 2.558(1), 2.080(25) and 2.236(11) Å respectively. Also similar values were found for the iodide; the Te-Br bond length is as expected(75), an intermediate length of 2.707(11) Å.

The closest Te...halogen intermolecular separations are 3.92(1) Å for the chloride and 4.145(3) for the iodide, which both corresponds closely to normal van der Waals interactions.

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

The original structural determination of phenylazophenyl(C,N')tellurenyl chloride(79) was carried out on crystals grown by slow evaporation of a chloroform solution. The crystals were triclinic, whereas, by contrast those obtained from methanol were actually monoclinic. Similar triclinic/monoclinic polymorphism has also been observed for 2-(2-pyridyl)phenyltellurenyl iodide.

The present crystal structure only contained one independent molecule in the unit cell, whereas the previous crystal(79) structure showed two independent molecules in the unit cell.

The nine - atom moiety Te, N(1), N(2), C(1)-C(6), is essentially planar, rms deviation of 0.019 Å, with the C(7)-C(12) phenyl ring rotated by 15(1)° about the N(2)-C(7) bond. The dihedral angle between this phenyl ring and the five - member chelate ring is 16.7(4) °, compared to 13.6 and 24.4° for the corresponding angle in the two independent molecules of the earlier determination.

Selected bond distances and angles for the two structures are compared in Table 39. On comparing the two structures it was noticed that the bond distances and angles were generally in agreement; however, where there is a large difference between corresponding parameters in the two independent molecules of the previous analysis, the present values tend to be intermediate, between the two extremes. For example the Te-C has a bond length of 2.061(9) Å for the present work and when compared with the earlier study, the Te-C bond has a length of 2.04(2) and 2.20(3) Å. It can be seen that the bond length is in between both of the values. These values for the Te-C bond are comparable with the mean length for Te-C(aromatic) of 2.116 Å given by Allen et al.(75), and 2.077(7) Å in 2-(2-pyridyl)phenyltellurium(II) chloride (see table 30). The Te...N distance of 2.210(7) is comparable with the distances found for 2-(2-pyridyl)phenyltellurium(II) chloride and iodides, which are in the range of 2.205 - 2.268 Å and are typical of such interactions when the atom bonded to the tellurium *trans* to the nitrogen is a halogen. The Te-Cl bond length, 2.533(3) Å falls within the range 2.34 - 2.60 Å given by Allen et al.(75)

There are no abnormally short intermolecular contact distances. The closest Te...Cl non-bonded contact is 3.682 Å , which may indicate a weak secondary interaction. The corresponding Cl...Te-C angle is 145.7°.

CHAPTER SEVEN

CONCLUSION

Conclusion

One method for the synthesis of the organotellurium monoiodides is presented. The metathesis with the organotellurium monobromide or monochloride (where the organic group is 2-(2-pyridyl)phenyl and 2-phenylazophenyl) with sodium iodide leads directly to the organotellurium monoiodide. The compounds that are formed are stable in air and the crystal structure of 2-(2-pyridyl)phenyltellurium(II) iodide was found to be triclinic. During mass spectroscopy analysis, the parent ion of (2-phenylazophenyl-C,N')tellurium(II) iodide was observed, but only in very weak concentration, which may imply that the central tellurium is released as an initial step during the fragmentation process.

A method for the synthesis of the related organotellurium triiodides is also presented. Metathesis with the organotellurium tribromide or trichloride (where the organic group is 2-(2-pyridyl)phenyl and 2-phenylazophenyl) with sodium iodide, leads directly to the organotellurium triiodide. The compounds formed failed to give a ^{125}Te NMR resonance. The existence of a charge transfer complex with a degree of paramagnetism was suggested for the triiodide. Evidence for this suggestion was collected from examination of the organotellurium monoiodide and diiodide under ^{125}Te NMR in which the monoiodide resonance was lost hence showing that a charge transfer complex was possibly formed. During mass spectroscopy analysis, the parent ion of (2-phenylazophenyl-C,N')tellurium(II) iodide was observed, but only in very weak concentration just like the monoiodide. This also implies that the central tellurium is released as an initial step during the fragmentation process. The main difference between the mass spectrum of the monoiodide and the triiodide was the presence of a peak corresponding to I^+ which could arise from loosely bound diiodine in the "triiodide". This gives further weight to the concept of charge transfer complex formation. Recrystallisation of the triiodide gave the corresponding monoiodide, with a monoclinic crystal structure in the case of the 2-(2-pyridyl)phenyltellurium(IV) triiodide. This gives more evidence that the so called "triiodide" is a charge transfer complex, since the loss of diiodine by reductive elimination during recrystallisation seem unlikely.

Attempts to form 2-(2-pyridyl)phenyltellurium(IV) trifluoride and (2-phenylazophenyl-C,N')tellurium(IV) trifluoride have, to date failed.

Attempts to form 2-(2-pyridyl)phenyltellurium(II) fluoride as a pure solid failed, although the existence of the compound in solution was confirmed by NMR spectroscopy.

The synthesis of (2-phenylazophenyl-C,N')tellurium(II) fluoride is presented, and is *via* the metathesis of either (2-phenylazophenyl-C,N')tellurium (IV) triiodide or (II) iodide with silver fluoride. Both produced the same compound which was shown to be the monofluoride, giving further proof that the triiodide is a charge transfer complex since one would expect the triiodide to produce the trifluoride and not the monofluoride.

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