STUDIES IN ORGANOBISMUTH CHEMISTRY

BY

MUSHTAQ ALI

A Thesis Submitted for the Degree of Doctor of Philosophy

The University of Aston in Birmingham

July 1990

<u>DECLARATION</u>

The work described herein was carried out at the University of Aston in Birmingham between October 1986 and October 1989. It has been done independently and submitted for no other degree.

Mushtaq Ali

July 1990

Professor W. R. McWhinnie

Summary

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Perturbations in the bismuth market resulted in Mining and Chemical Products Ltd., seeking further outlets in the market. Together with Manchem Ltd. they were anxious to evaluate the possibility of using bismuth compounds as a replacement for lead/calcium soaps in paint driers.

A range of new organobismuth compounds were synthesised of the type $RBiX_2$ and R_3BiX_2 (X= halogen, OOCR, dithiocarbamate). A variety of synthetic techniques were explored, including the use of mathematical reactions, phase-transfer catalysis and microwave energy. The preparation of a range of trivalent and pentavalent organobismuth carboxylates is reported and their infra-red , ^{13}C, ^{1}H nmr spectra. The compounds were evaluated as paint driers and in cases found to enhance paint drying to a greater degree than the standard driers, to which they were being compared. The drying times of paint films containing the organobismuth compounds are reported, together with a comparison of the drying times with the addition of bismuth *tris*-diethyldithiocarbamate, which may promote the cross-linking reaction that occur in paint films during the drying process.

Examples are reported to illustrate the great reductions in reaction times possible when using microwave energy. Reactions such as metallation of aromatic rings, ligand redistribution and synthesis were carried out in PTFE containers in a conventional domestic microwave oven.

An X-ray diffraction study of (phenylazophenyl-C,N')mercury(II) chloride has shown it to be dimeric via long Hg-Cl bridging interactions of 3.367A. Its crystal structure is reported, together with its ^{13}C nmr spectra and mass spectrum.

The Lewis acidity of compounds of the type $RBiX_2$ was investigated. The donor group being anchored to the organo group (R). The dithiocarbamates *bis*-(diethyldithiobarbamato)phenylbismuth(III) and [2-2-pyridyl)phenylbismuth(III) were synthesised, and their crystal structures, ^{14}N, ^{13}C nmr and infra-red spectra are reported. Both compounds are pseudo-pentagonal bipyramidal in geometry, with two long Bi-S bonds and two short Bi-S bonds. The reaction of $RBiBr_2$ (R= 2-(pyridyl) with various ligands is reported. The infra-red evidence suggesting that the coordination of extra ligands is accompanied by a reduction of the strength of the Bi-interaction.

Key words

Bismuth
Carboxylates
Lewis acidity
organobismuth
metallation

To my Parents, [illegible] d
all my Family

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CHAPTER ONE

INTRODUCTION

1.0 INTRODUCTION

1.1 GENERAL BACKGROUND

The origin of the word bismuth has not been clearly established. Various opinions have been offered, for example that it comes from the Arabian word *wis majaht* [1], or from the word *Bleiweiss* (white-lead). However the most popularly regarded theory is that it is of German origin. From the word *wismat* (later *wismuth*), which is a German miner's term *wis mat* meaning *weisse masse* (white metal or white mass). This was latinised to *bisemutum* in the sixteenth century by Bauer & Agricola[1a] However it was still confused with lead, antimony and tin for a further two hundred years.

Bismuth is situated in group 15, atomic number 83 and only one isotope is found in nature, ^{209}Bi ,atomic weight 208.980, electronic configuration [Xe] $4f^{14}\ 5d^{10}6s^2\ 6p^3$. Although it is an element that is frequently encountered , it is of low crustal abundance[2] (Table 1.1). Several minerals contain it as a major constituent.

Table 1.1 **CRUSTAL ABUNDANCE ^{209}Bi**

ppm	
0.07	Noddack and Noddack (1934)
0.20	Goldschmidt (1937)
0.009	Vinogradov (1962)
0.17	Taylor (1964)
0.008	Greenwood (1984)

It is a chalcophile (in common with all B subgroup metals), occurring in association with the chalcogens S, Se and Te rather than as oxides and silicates.

Although the size of an atom depends on its environment, for comparative purposes the radius of the bismuth atom [3] is given relative to its neighbours Arsenic and Antimony. (Table 1.2).

Table 1.2.

	As (pm)	Sb (pm)	Bi (pm)
From metal	125	145	153
Tetrahedral	118	136	146

1.2 Applications and market situation

Metallic bismuth is largely used in the preparation of fusible alloys e.g. with tin (including type metal). These alloys are used in fire prevention apparatus e.g. sprinklers etc. Bismuth has also been quite extensively used for pharmaceutical purposes [4]. In the 15th century bismuth compounds were recognised as having therapeutic properties. The French School of Bismuth Therapy was established in 1921. In fact one of the main markets for bismuth compouds was in the pharmaceutical industry in the treatment of gastric infections and as antacids in France and the United States.

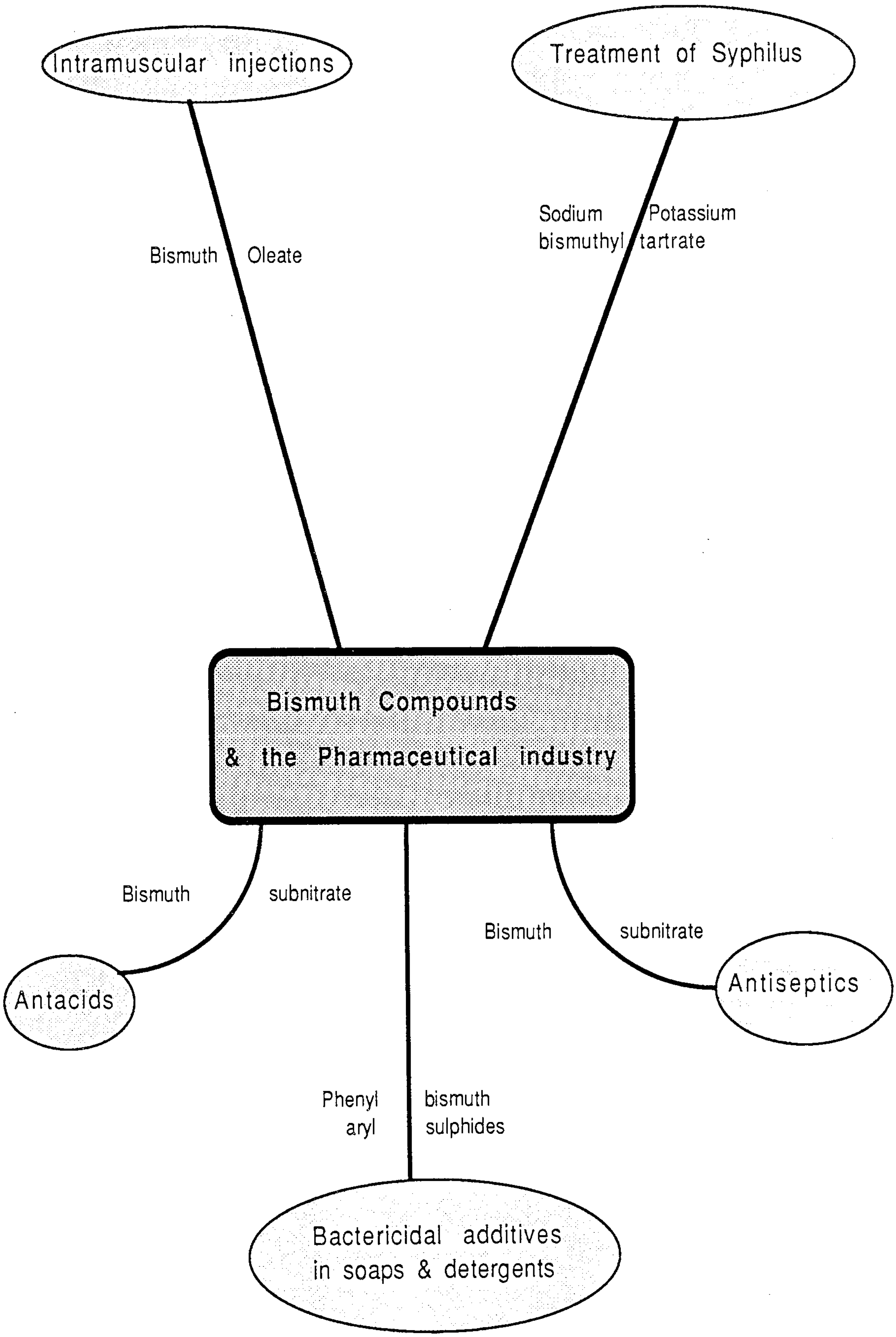


Fig 1.1a Bismuth Compounds and the Pharmaceutical Industry

There use as antacids was based on the reaction below.

$$Bi^{3+} + H_2O \longrightarrow BiO^{+} + 2H^{+}$$ .reaction 1

Basic bismuth salts containing the BiO^+ group (bismuthyl compounds), are obtained when normal bismuth salts are brought into contact with water. This reaction (reaction 1) may be reversed by larger quantities of acid (hence their use as antacids).

In fact the trade name for the antacid BiSoDoL originated from its bismuth (Bi) content, although the formulation no longer contains bismuth.

The cosmetics industry uses bismuth compounds. Bismuth oxychloride possesses an unusual mother of pearl like quality such that it forms the base compound in the manufacture of artificial pearls. Its properties give many cosmetics, including lipstick and eye-shadow nail-varnish, hair-sprays an attractive lustrous pearly sheen. Bismuth chelates[4a,4b] e.g. as produced by the addition of a coordination compound of bismuth with hydroxycarboxylic acid, have been reported as having excellent electrodeposition properties when added to alkaline copper cyanide plating baths. Other uses include catalysis, for example a Bi/Mo catalyst is used in the manufacture of $CH_2=CHCN$. It is also used in the rubber industry e.g. in binding agents. Recently bismuth compounds have been investigated for use as superconductors[4c]

The bismuth market is unstable and fluctuations have occurred frequently in the demand for bismuth[5] .

Table 1.3.

USE OF BISMUTH IN THE UNITED STATES (in tonnes)

PRODUCT	1973	1975
Fusible Alloys	423	182
Metallurgical Additives	377	189
Other Alloys	7	12
Pharmaceuticals & other Chemicals	507	251
Others	7	4
TOTAL	1318	638

Table 1.4.

JAPANESE BISMUTH MARKET (tonnes)

	1984	1985	1986	1987	1988
Production	588	641	631	546	528
Consumption	520	318	466	578	785
Imports	-	-	-	100	325
Exports	114	230	244	54	68
Stocks	62	136	63	77	78

U.K. import/export statistics are no longer published in a helpful form but it is estimated that U.K. consumption was at around 250 tonnes in 1989, much of which is exported in fusible alloy form.

Their are no commercially exploitable reserves of bismuth in the United Kingdom but Capper Pass Ltd and Mining & Chemical Products Ltd process imported ores, concentrates, bullions and scraps containing bismuth . MCP has been responsible for the refining of the processed bismuth to metallurgical and pharmaceutical grades. There is no longer any major production of bismuth chemicals in the U.K., May & Baker and Evans Medical having discontinued their activities several years ago. MCP is a major manufacturer of fusible alloys, most of which contain around 50% bismuth. They also produce tailor-made bismuth metal shapes and master alloys for the steel, foundry and aluminium industries.

Perturbations causing such instability as shown in tables 1.3 & 1.4 were of concern to MCP (a major Bi producer), and prompted them to seek an increase in the market. Discussions with Manchem Ltd (RTZ Northern Chemicals Division), who perform research in paint driers, inks, binders for rubber etc., led to the idea of exploring the possibility of bismuth compounds as paint driers. The advent of new driers was necessitated by presssure for the removal of lead drier compounds from paints for toxicological reasons [6].

Lead, for drier applications was used in the form of "soaps" (carboxylates)[7]. It was noted that, in some cases, mixtures of compounds were more effective than the sum of the individuals (e.g. a mixture of lead and calcium soaps). This implies that some synergism occurred and that, for example, anionic complexes may have been formed. The development of the current work was based on the observation that the organobismuth species RBi^{2+} was pseudo-isoelectronic with Pb^{2+} and the possibility of it being able to mimic the active lead species existed.

ORGANOBISMUTH CHEMISTRY

1.3 NOMENCLATURE OF ORGANOBISMUTH COMPOUNDS

The Table below illustrates the IUPAC nomenclature for organobismuth compounds.

Table 1.5

GROUP	EXAMPLE	
$-BiH_2$	$EtBiH_2$	Ethylbismuthine
$=BiH$	Me_2BiH	Dimethylbismuthine
$\equiv Bi$	Et_3Bi	Triethylbismuthine
$-BiX_2$	$CH_2 = CHCH_2BiBr_2$	Allyldibromobismuthine
$=BiX$	$(CH_2 = CHCH)_2BiBr_2$	Diallylbromobismuthine
$= Bi-Bi =$	$Et_2BiBiEt_2$	Tetraethyldibismuthine
$=Bi^-$	$Et_2Bi^- K^+$	Potassium diethylbismuthide
$\equiv BiX_2$	Ph_3BiCl_2	Triphenylbismuth dichloride
$\equiv BiX$	Ph_4BiN_3	Tetraphenylbismuth azide
$\equiv Bi =$	Ph_5Bi	Pentaphenylbismuth

1.4 CHEMISTRY OF ORGANOBISMUTH COMPOUNDS

With an electronic configuration of [Xe] $4f^{14}5d^{10}6s^{2}6p^{3}$, bismuth has all its lower energy orbitals completely filled. Thus the electrons left in the outer orbitals may paticipate in bonding. The participation of the two s electrons leads to two possible covalencies for bismuth +3 and +5. This consequently gives rise to two series of compounds, the trivalent (R_3Bi) and the pentavalent (R_5Bi) derivatives.

Bismuth exhibits coordination numbers of 3, 4, and 5. Triphenylbismuth, triphenylbismuth dichloride being good examples of coordination numbers 3 and 5

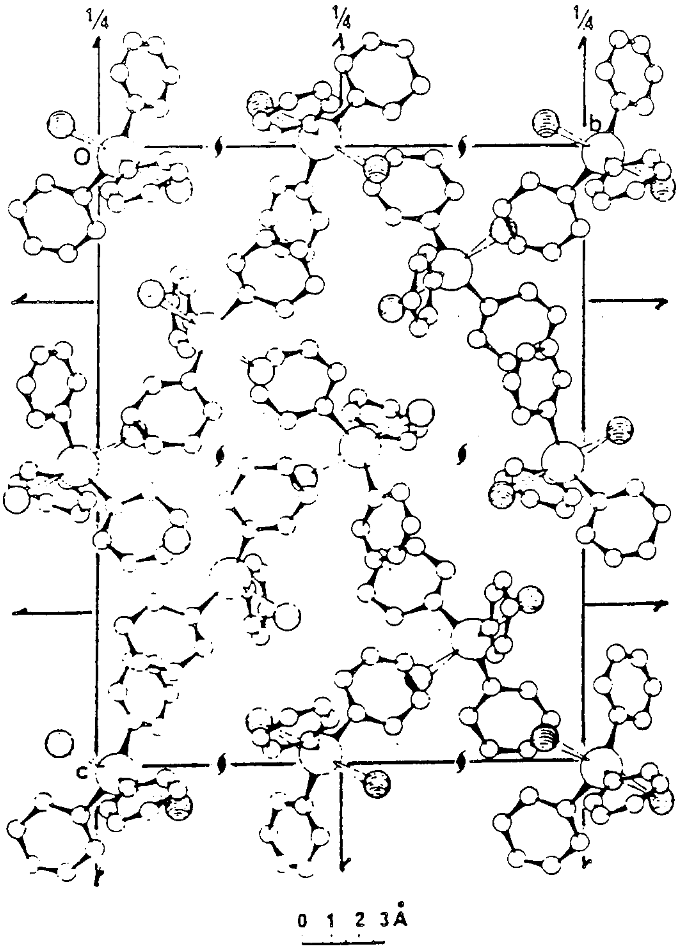


Figure 1.1b The crystal structure of triphenylbismuth dichloride as viewed along the a axis.

1.4.1 Primary and secondary bismuthines

Few bismuth derivatives fall in this category. Methyl and dimethylbismuthine being the classic examples, ($MeBiH_2$ and Me_2BiH).[8] They are not very stable, the methylbismuthine disproportionating to trimethylbismuthine and bismuthine at 45 °C. Both the methyl and dimethyl compounds decompose to trimethylbismuthine, bismuth and hydrogen at room temperature.

1.4.2 Tertiary bismuthines

These may be divided further into the :-

(i) Trialkylbismuthines

(ii) Triarylbismuthines

1.4.2.1 (i) Trialkylbismuthines

The majority of organobismuth derivatives in this category are spontaneously inflammable in the air [4a], due to the ease of formation of the oxycompounds R_3BiO and not to the ease of the splitting of the metal - carbon bond. However the bismuth - carbon bond in these compounds is fairly weak, and virtually all of their reactions involve the cleavage of a bismuth - carbon bond

Marquardt [8,9] reported that even at 0 °C the bismuth to carbon bond was cleaved by Cl_2 or Br_2 .

$$R_3Bi + X_2 \xrightarrow{0^\circ C} R_2BiX + RX$$

Reports [10] have been made of the bismuth to carbon bond remaining intact on reaction in this class of compounds, but very low temperatures were used, such as in the conversion of the *cis* isomer of triisopropenylbismuth to the *trans* conformation.

1.4.2.2 (ii) Triarylbismuth Compounds

These are comparatively stable and reports of a wide variety of reactions concerning these compounds have been made. They are readily converted to pentavalent derivatives of the type Ar_3BiX_2 where X is an electronegative group. The stability of this class in comparison with the trialkyl derivatives is perhaps exemplified by the fact that triphenylbismuth can be distilled without decomposition.

The action of strong mineral acids on triarylbismuth compounds was investigated by Michaelis[11] and co-workers and later by Challenger[12]. The authors reported that inorganic bismuth salts were formed.

$$Ar_3Bi + HX \longrightarrow 3ArH + BiX_3$$

The mechanism for this type of reaction has been investigated by Eaborn[12a] and Waters, using spectrophotometry to study reactions. They reported that the cleavage of the Ar-M bonds was by electrophilic attack at the Ar group by the H^+. This is well known in organotin chemistry. This electrophilic aromatic substitution is analagous to those in which Ar-H bonds are broken.

Challenger and coworkers[13] showed that trivalent organobismuth compounds of the type Ar_2BiX and $ArBiX_2$ were formed by the action of weak acids (or even halogens e.g Cl_2) on triarylbismuthines.

Gilman and Yale[14] studied the reaction of thiols and carboxylic acids on triarylbismuthines. Their findings showed that cleavage of the aryl groups resulted. The authors however offered no explanation for the anomalous behaviour of tri-α-naphthylbismuth, in which the aryl groups were not cleaved.

1.4.3 Formation of a Bismuth to Carbon Bond

1.4.3.1 (i) From Grignard Reagents

The use of Grignard reagents in the formation of a bismuth to carbon bond was first demonstrated by Pfeiffer[15] and Pietsch.

$$3RMgX + BiX_3 \longrightarrow R_3Bi + 3MgX_2$$

Since then, it has become the most widely accepted method.
Adaptations of the above method have been reported,[22] using organobismuth chlorides.

$$RBiCl_2 + 2R'MgX \longrightarrow RR'_2Bi + 2MgXCl$$

$$R_2BiCl + R'MgCl \longrightarrow R_2R'Bi + MgXCl$$

$$Ph_2BiCl + \sigma\text{-}ClC_6H_4MgBr \longrightarrow \sigma\text{-}ClC_6H_4BiPh_2$$

Doak and Freedman[23] in their 1982 review of organobismuth chemistry have reported the synthesis of $(\sigma\text{-}MeOC_6H_4)_3Bi$ by a Grignard reaction. Others[24] have prepared $(Me_3Si)_2CHBiCl_2$ via the Grignard reaction below.

$$(Me_3Si)_2CHMgCl + BiCl_3 \longrightarrow (Me_3Si)_2CHBiCl_2$$

1.4.3.2 (ii) Organozinc Compounds [25]

The use of organozinc compounds in the synthesis of trialkylbismuth compounds, is rare because the alkylzinc compounds, are spontaneously inflammable.

1.4.3.3 (iii) From Organomecury Compounds

Frankland and Duppa[28] reported the synthesis of triethylbismuth by heating a mixture of diethylmercury and powdered bismuth at 120-140 °C. The reaction of an organic mercurial with bismuth or with bismuth trihalides was used quite extensively until the popularity of the Grignard method superceded it. Triphenylbismuth has been made by a similar method [26-28] using diphenylmercury.

1.4.3.4 (iv) Using Group 1 Metals[29-31]

Synthetic procedures involving the use of group 1 metals were employed during the early stages of organobismuth chemistry. A bismuth-sodium or bismuth-potassium alloy was allowed to react with an alkyl or aryl halide.

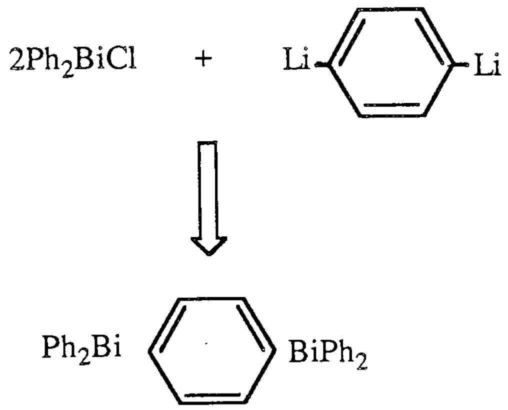
$$3RX + Bi + 3K \longrightarrow \underset{\substack{\text{triorgano-} \\ \text{bismuth compound}}}{R_3Bi} + 3KX$$

$$Ar_2BiNa + Ar'X \longrightarrow Ar_2Ar'Bi + NaX$$

$$Ph_2BiNa + PhX \longrightarrow Ph_3Bi + NaX$$

1.4.3.5 (v) From Organolithium Reagents

Gilman[32] reported the use of organolithium reagents, in organobismuth chemistry.



1.4.3.6 (vi) From Aluminium Alkyls

The preparation of triethylbismuthine, from the alkylation of a bismuth trihalide by $LiAlEt_4$ has been reported[33].

1.4.3.7 (vi) Halonium Salts

$$\begin{array}{c}\text{Diarylhalonium salt} + BiCl_3 + Bi\\ \big\downarrow\\ \text{Triarylbismuth compound}\end{array}$$

Example[34]

$$\begin{array}{c}[pClC_6H_4IPh]Cl + BiCl_3 + Bi\\ \big\downarrow\\ (p\text{-}ClC_6H_4)_3Bi + PhI\end{array}$$

Triphenylbismuthine[35] has been prepared by the action of phenylhalonium tetrachlorobismuthate on bismuth metal.

1.4.3.8 (vii) Diazo Compounds

Two basic methods incorporating diazo compounds have been used in the synthesis of organobismuth compounds.

(a) The formation of an aryldiazonium chloride - bismuth trichloride complex then reduction by treatment with a strong base[36-37] e.g. hydrazine.

$$(ArN_2Cl)_2.BiCl_3 + 4Cu \longrightarrow Ar_2BiCl + CuCl + 2N_2$$

$$Ar_2BiCl \xrightarrow{H_2NNH_2} Ar_3Bi$$

(b) The second method[38] involved the action of a diazonium salt on metallic bismuth. Krommes and Lorbeth[39] reported the reaction of organometallic - substituted diazoalkanes with a strongly basic phosphine $P(NMe_2)_3$.

Nesmeianov[40] and coworkers showed that the decompositon of aryldiazonium fluoroborates rather than double salts of diazonium compounds with a halide of the metal gave higher yields of the organometallic compound. They reported the synthesis of a variety of organometallic compounds of bismuth through the use of diazo compounds.

1.4.3.9 Organofluorosilanes

This route is not extensively used. Originally it was reported by Mueller and Dathe[41] for the preparation of triphenylbismuth. (equation below)

$$\begin{array}{c} Bi(OH)_3 + 3PhSiF_3 + 6NH_4F + 3HF \\ \Bigg\downarrow \\ Ph_3Bi + 3H_2O + 3(NH_4)_2SiF_6 \end{array}$$

1.4.3.10 Miscellaneous

(1) From bismuth oxides and bismuth halides.

Anischenko[42] and coworkers reported the synthesis of bismuth compounds containing, bismuth - oxygen bonds from the reaction of bismuth oxides and halides with carboxylic acids. (equation below)

$$Bi_2O_3 + 6RCOOH \longrightarrow 2Bi(OCOR)_3 + 3H_2O$$

$$BiBr_3 + 3TlOCOCH_3 \longrightarrow Bi(OCOCH_3)_3 + 3TlBr$$

(2) Alkyl radicals reacting with diazomethane and bismuth chloride[43]

(3) Reaction of alkyl radicals with bismuth mirrors [44-46]

1.5 The Strength of the bismuth - carbon bond

The strength of the metal - carbon bond affects the reactions compounds containing that bond will undergo and how readily they will proceed.

The equations[47,48] below relate electronegativities in the Pauling scale to the ionic character exhibited by a bond.

$$\% \text{ ionic character} = 100\,[1 - e^{-0.25\,(x_A - x_B)^2}] \quad \text{..............(1)}$$

$$\% \text{ ionic character} = 16(x_A - x_B) + 3.5(x_A - x_B)^2 \quad \text{................(2)}$$

where x_A and x_B are the electronegativities of the bonded atoms A and B

The table below lists comparative values for the electronegativity for Arsenic, Antimony and Bismuth , according to, Pauling[48], Sanderson[50] and Batsanov[50a].

		Pauling	Sanderson	Batsanov
As		2.0	3.9	2.19
Sb		1.8	3.4	2.06
Bi		1.9		2.14

Fig 1.1c **Table of electronegativities**

Mulliken[49] has also stated electronegativity values. Haissinsky[51] has filled some of the 'gaps' in Paulings tables of electronegativities.

Electronegativity of Bi(III) =1.8
"   "   " Bi(V) = >2.3   (values according to Haissinsky.)

Equation 1 shows that a covalent bond will be 50% or more ionic when the difference in the electronegativity (according to Pauling) is equivalent to or exceeds 1.7.

Using this relationship the metal - carbon bond ionic character for arsenic, antimony and bismuth have been calculated in the table below. (values for tin and sodium are given for comparative purposes.

Element	% ionic character
Arsenic	8.8
Antimony	15.0
Bismuth	12.9
Tin	12.9
Sodium	37.3

Table 1.6

Other factors however warrant consideration. For in the above comparison it has been assumed that in all cases the metal - carbon bond the carbon has constant electronegativity. In fact the electronegativity of the carbon may vary depending on the nature and number of the organic groups (R) or atoms attached.

A simplified example is the methyl group. The carbon is attached to three hydrogens considerably more electropositive than the carbon itself. (i.e. hydrogen releases electrons more readily than carbon.). Thus it follows that the methyl group is more electron-releasing than a hydrogen atom, because the three hydrogen atoms of the methyl group all contribute electrons to the carbon atom which in turn may release them to an attached group.

1.5.1 Bond Polarity Effects on Reactions

The polarity (degree of ionic character) influences the chemical reactivity of the compound. For example if a $C^{\delta-}$ -- $M^{\delta+}$ is exposed to water hydrolysis occurs resulting in the formation of a hydrocarbon and a metal hydroxide. However if the $C^{\delta-}$ -- $M^{\delta+}$ is less polar (e.g. in dimethylmercury) the reaction is slow and requires catalysis.

1.5.2 (i) Solvation Effects

The effect of coordinated solvent molecules on the distribution of electron density.Solvation tends to decrease bond polarity by a contribution of electrons from the electronegative donor atom of the solvent (e.g. the oxygen of ether) to the metal, but solvolytic dissociation into ion pairs is also possible. Thus the electronegativity of the metal in an organometallic compound is a major factor in the relative reactivities. In fact simplified, the greater the electronegativity the higher the reactivity of its organometallic compounds.

1.5.3 (ii) Substituent Effects.

Substituents on the carbon and metal atoms of the organometallic bond also exert an influence. e.g. negative atoms such as chlorine or oxygen attached to a metal atom of the C - M bond will withdraw electrons from the metal and bring about a corresponding shift of electronic charge in that bond. This has the effect of decreasing the polarity of the C-M bond and diminishing its reactivity towards ionic reagents. An Electro-positive substituent on the carbon atom would have the same effect. Electro-negative groups on the carbon atom or in the organic group increase the polarity of the C - M bond by withdrawing electrons from the carbon and shifting the bond electrons further from the metal.

1.5.4 Strength of the Bi-C bond - Bond Energies

$$D(M - R) = \Delta H^o/n \qquad \text{........ equation 1.4}$$

ΔH^o is the heat of formation, and D is the mean bond dissociation energy

The equation above (equation 1.4) gives the mean bond dissociation energy in compounds R_nM (M being an element of valency n and R an atom or group attached to it). Skinner[50b] has calculated the mean bond dissociation energies for compounds containing M-C bonds. The values decrease on descending group 15 for trialkyl and triaryl compounds.

Table 1.7

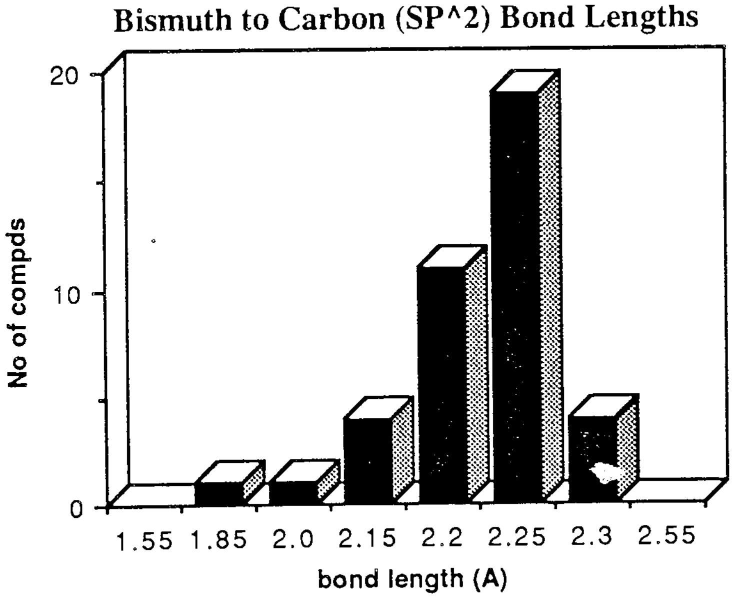
Mean Bond Dissociation Energy for the Molecules in the Gaseous State (at 25°C)

Compound	Bond	D(A-B) kcal/mole
Trimethylbismuthine	Bi-C	34.1
Triphenylbismuthine	Bi-C	42.2
Me_3Sb and Ph_3Sb	Sb-C	51.5 and 58.3

1.5.5 Strength of the Bismuth - Carbon Bond sp vs sp^2 vs sp^3

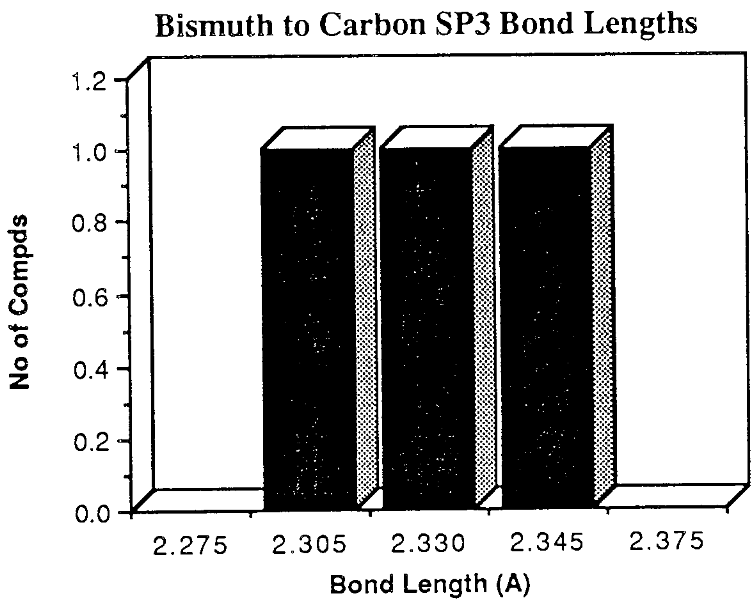
A survey (of the Cambridge crystallographic database) of bismuth-carbon bond lengths revealed a range of 1.999 - 2.316 A for Bi-C(sp^2), it is temptimg to equate bond length with bond strength within this series.

Figure 1.2



Mean Bond Length	2.227 (A)
Standard Deviation Sample	0.056
Standard Deviation Mean	0.009
Minimum Bond Length	1.999 (A)
Maximum Bond Length	2.316 (A)
No of Compounds Used	39
No Omitted	1

Figure 1.3



Mean	2.328 (A)
Standard Deviation (sample)	0.020
Standard Deviation (Mean)	0.012
Minimum Bond Length	2.307

Maximum Bond Length 2.347

All of the above statistics are after removal of compounds where the bond length was more than + or - 4.000 S.D. Sample from the mean.

1.5.6 Bismuth to Carbon (SP).

No crystal structures of compounds containing a bismuth to carbon(sp) bond were found at the time of compiling this survey.

1.6 Compounds of the Type $RBiX_2$

Since Pb^{2+} and RBi^{2+} are pseudo-isoelectronic, this section reviews the chemistry of organobismuth compounds of the type $RBiX_2$.

1.6.1 (a) Preparation

(i) Reaction between a tertiary bismuth compound and a bismuth trihalide.

$$R_3Bi + 2BiX_3 \longrightarrow 3RBiX_2$$

Yields by this method are good . If the molar ratio of the bismuth trihalide and tri-organobismuth compound is reversed di-organobismuth compounds (R_2BiX) are formed.

$$2R_3Bi + BiX_3 \longrightarrow 3R_2BiX$$

Literature reports[51] regarding compounds of the type $RBiCl_2$ have stated that they are extremely insoluble.

(ii) Reactions between a tertiary bismuth compound and an inorganic halide other than bismuth trichloride.Moedritzer et al[51a] have patented the use of redistribution reactions for the preparation of organobismuth compounds of the type $RBiX_2$.

(iii) Reaction between a di-organobismuth chloride and potassium iodide[16]

(iv) Reaction between a di-organobismuth halide and a halogen.

Challenger[51] prepared phenylbismuth dibromide by reacting diphenylbismuth bromide with bromine in chloroform.

1.6.2 (b) Reactions

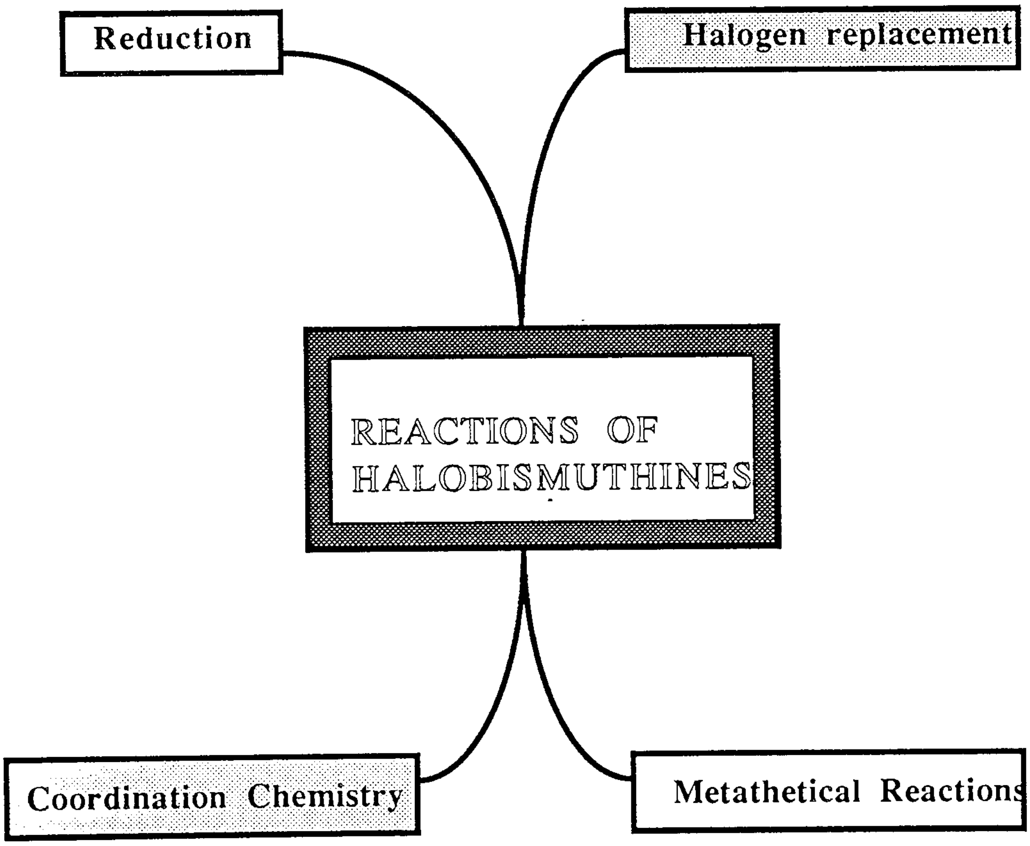


Figure 1.4 The various reactions of halobismuthines

Generally organobismuth(III) halides are reactive and unstable. Exposure to water or alcohol results in their decomposition, although Gilman and Yablunky[52] have reported several *ortho* - substituted compounds which show resistance to decomposition by moisture.

Challenger and Ridgway[53] reported that tertiary bismuthines may be synthesised from the reaction of halobismuthines with bases e.g. ammonia.

1.6.3 (i) Replacement of Halogen

The halobismuthines are capable of undergoing a wide range of metathetical reactions, with the alkali metals, silver, ammonium and lead salts.[54]

Wieber and Baudis[55] used the reaction below to replace the bromide in phenylbismuth dibromide by reacting it with a sodium ethanolate to yield phenyldiethoxybismuthine.

$$PhBiBr_2 + 2NaOC_2H_5 \longrightarrow PhBi(OEt)_2 + 2NaBr$$

Wieber and coworkers[56] have prepared a series of compounds of the type $RM(SR')_2$, where M was bismuth or antimony, and NaR' was sodium pyrimidine-2-thiolate or sodium 1-methylimidazole-2-thiolate, R was Me or Ph, using the same general reaction.

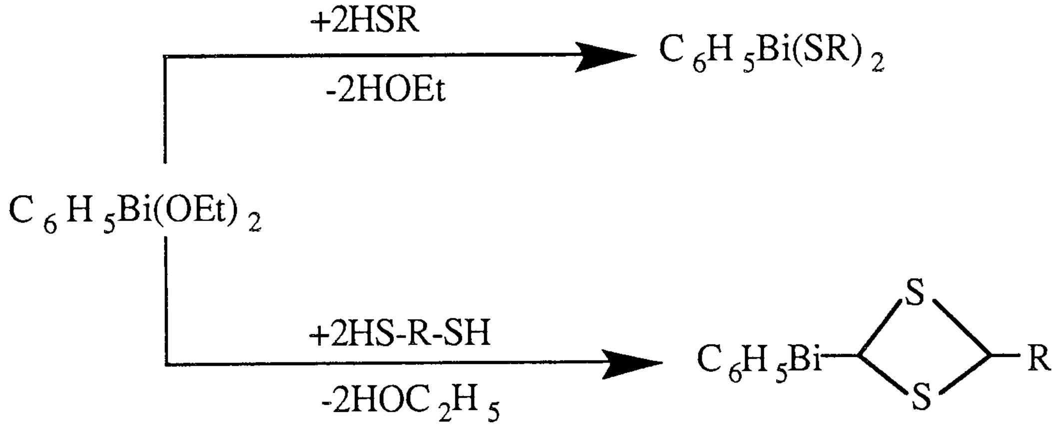
$$RBiBr_2 + 2NaSR' \longrightarrow RBi(SR')_2 + 2NaBr$$

The reaction of phenylbismuth dibromide with sodium dialkyldithiocarbamate in chloroform results in the formation of phenylbismuth bis(dialkyldithiocarbamates)[57]. Kupchik and Theisen[57] also attempted the synthesis of diphenylbismuth dialkyldithiocarbamates unsuccessfully. The formation of phenylbismuth bis(dialkyldithiocarbamates) illustrates the weakness of the Bi-C bond to cleavage. The presence of a strong band near 1500cm^{-1} in the infra-red spectrum was assigned to the C=N stretch of the dithiocarbamate ligand. The dihalides are converted to the hydroxides by the action of zinc bromide on salts of methylbismuth dibromide[8]. The action of ammonia on an alcoholic solution of methylbismuth dibromide salt resulted in the formation of an amorphous solid (CH_3BiO). The oxide was reported as being amphoteric and was readily oxidised by air.

1.6.4 (ii) Metathetical Reactions (not involving the replacement of halogens)

Wieber and Baudis[55] showed that phenyldiethoxybismuthine reacts with thiols and 1,2,ethanedithiol. Reaction scheme below.

Route 1



Route 2

2 3 4 5

R= C_2H_5 $CH_2C_6H_5$ C_6H_5

CH_2CH_2OH In route 1 R= between 2 & 5

In route 2 R= $-CH_2CH_2-$

Figure 1.5(a) Metathetical reactions of $RBiX_2$

The same authors reported that the phenyldiethoxybismuthine was susceptible to thermal degradation resulting in the formation of triphenylbismuth.

1.6.5 (iii) Coordination Chemistry $RBiX_2$

Pyridine adducts [57] $C_6H_5BiX_2.\ 2Py$ of the halobismuthines have been prepared from the action of pyridine on the halobismuthine. Faleschini [58] and coworkers have studied the molecular addition compounds of phenyldihalobismuthines with neutral bidentate ligands such as 2,2'-bipyridine and 1,10-phenanthroline. Products of the type $C_6H_5BiX_2.L$ (X=Cl, Br, I, and L = 1,10-phenanthroline or 2,2'-bipyridine) were formed. The adducts were studied using infra-red spectroscopy.

The action of carbon disuphide on methyldialkoxybismuthines results in the formation of xanthates[59].

$$MeBi(OR_2) + 2CS_2 \longrightarrow MeBi(S_2COR)_2$$

R= Me, Et, or Me_2CH

1.6.6 (iv) Reduction

Aryldihalobismuthines have been converted to triarylbismuthines by the action of hydrazine hydrate [31,52]. The reaction of bis(o-carbomethoxyphenyl)chlorobismuthine, is worthy of note as it has been reported[31] to be complicated by secondary reactions. Amberger[60] has reported the reduction of methyldichlorobismuthine by $LiAlH_4$. The reaction proceeds at low temperatures to yield trimethylbismuthine.

1.7 Comparison of Bismuth and Antimony Compounds.

1.7.1 General

In Group 15 the chemistry of nitrogen differs from the remaining group because of the absence of low energy d orbitals and its ability to readily form double bonds. Metallicity increases on descending the group and the strength of the covalent bond decreases. All of the elements form trivalent compounds (R_3M, RMX_2, R_2MX, and MX_3 R= organic group and X= inorganic group).

Antimony forms pentavalent compounds of the type MX_5, RMX_4, R_3MX_2, R_2MX_3 (R = organic group, X = halogen or other electronegative group). Bismuth forms compounds of the type R_3BiX_2 but not RMX_4 or R_2MX_3. In all of these compounds the central atom probably utilises sp^3d hybrid orbitals. X- ray crystallography has shown that trigonal bipyramidal is the preferred geometry with the electronegative groups situated apically.

1.7.2 Bismuth and Antimony compounds containing Nitrogen

The crystal structure[61] of $(C_6H_5)_3$Bi (MeOx)Cl (Ox=8-quinolinato) shows that the bismuth atom exists in a distorted octahedral coordination environment. The Bi-N bond is fairly weak, bond distance 2.71(2)A. The structure of the analogous antimony complex has not been reported. The work showed that the complexes Ph_3Bi(MeOx)X and Ph_3BiOxX (X=Cl, Br) octahedral coordination is maintained in non-polar solvents, and that polar solvents tend to break the Bi-N bond. In triphenylbismuth 8-hydroxyquinoline the molecule exists in a trigonal bipyramidal structure with three phenyl rings occupying equatorial positions and the bismuth atom in the plane of the the three carbon atoms (of the phenyl rings). the Bi-N bond distance of 2.807(10) is weaker than in $(C_6H_5)_3$Bi (MeOx)Cl.

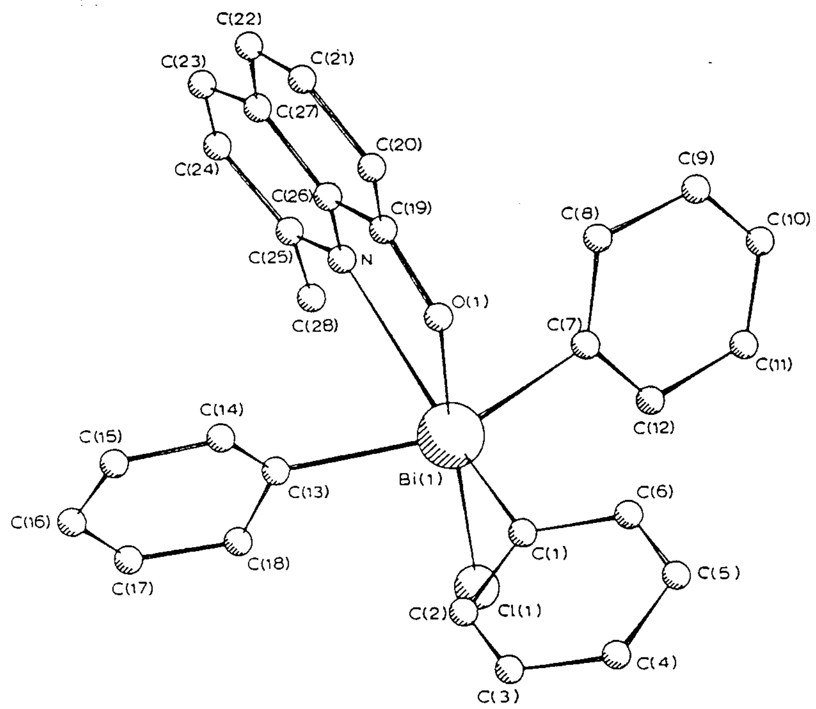


Figure 1.6 Crystal structure of chloro(2-methyl-8-quinolato) triphenylbismuth (v)

It is an interesting feature that the nitrogen atom in the quinoline structure is directed towards the central bismuth atom and that although the Bi-N bond length is weaker than in the previous example it still results in a large angular distortion between $\phi 1$ and $\phi 2$ (143^0). The 2-methyl-8-quinolate (X= Cl or Br) has a distorted octahedral geometry with Bi-O and Bi-N distances of 2.19 and 2.71 A respectively[62].

The amine substituted antimony(III) compound, $MeSb[N(SiMe_3)_2]$ is the product from a reaction between $SbCl_3$ and $Na[N(SiMe_3)_2]$ in benzene solution. Kolondra et al[63] showed that $MeSbCl_2[N(SiMe_3)_2]_2$ is trigonal bipyramidal having Sb-N distances of 1.9991 A. Preti et al[64] studied some antimony and bismuth trisdithiocarbamate and five monohalobisdithiocarbamate derivatives. The data for the complexes of antimony(III) and bismuth(III) with piperidinedithiocarbamate(Pipdtc), morpholinedithiocarbamate (Morphdtc) and thiomorpholinedithiocarbamate had a distorted octahedral stereochemistry, the distortion being due to the stereochemically active lone pair of electrons on the antimony and bismuth atoms. The authors stated that the central atom in the monohalobisdithiocarbamate derivative has a coordination number of five, and that it may adopt a trigonal bipyramidal form or, alternatively, that of a square based pyramid. A distorted square based pyramidal geometry was proposed on the basis of the reported π backdonation. The square based pyramidal structure represents a better arrangement for efficient π- backdbonding than the trigonal bipyramidal geometry.[65] .X-ray structures confirmed the structures proposed[66,67].

1.8 Bismuth(III) Halides (structural chemistry)

$BiCl_3$ will be discussed as this is the compound used later in the experimental work. $BiCl_3$ is reasonably pyramidal in the gas phase, but there was some controversey as to the solid state structure for some years. The large asymmetry parameter from ^{35}Cl nqr led to the postulation of an associated structure, but Raman data were interpreted in terms of discrete molecules. Its crystal strucure shows it to be associated. It consists of well defined $BiCl_3$ molecules (Bi-Cl distances 2.468, 2.513, 2.518 A).[68-69]. Though there is some tendency towards higher coordination, in the neighbourhood of the bismuth atom there are five more chlorine atoms (the Bi...Cl distances vary from 3.216 to 3.450 A).

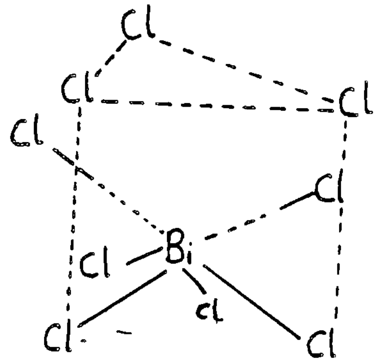


Figure 1.7 structure of Bismuth trichloride

It has a distorted 8-fold coordination. $BiCl_3$ is a Lewis acid with a coordination chemistry that is fairly well developed.

1.9 Compounds of the type R_3BiX_2

The best examples are probably the triarylbismuth dihalides. The addition of bromine or chlorine in stoichiometric quantities to an ice cold solution of the appropriate triarylbismuth compound in a solvent such as chloroform[12], petroleum ether, or carbon tetrachloride[13] being the common method of preparation. At the time of this survey no publications concerning the structure of triarylbismuth diiodide were found. However it is probably formed at -78^{0}C by the action of iodine on triphenylbismuth in an ethereal solution[13]. Triarylbismuth dichlorides and dibromides will undergo metathetical reactions with silver salts to produce compounds of the type Ar_3BiY_2 (where Y is an anionic group). This type of reaction has been used to prepare triphenylbismuth dicyanate[70-72] diacetate[70], dibenzoate[71], dinitrate[73,74]. Sodium, potassium and lead salts undergo metathetical reactions with triarylbismuth dichlorides and dibromides. Supniewski and Adams[73] used lead acetate to prepare a number of triarylbismuth dicetates. Whilst Goel and Prasad used sodium and potassium salts to prepare the triarylbismuth oxalate[75], Gilman and Yale[76] prepared a number of triarylbismuth dicarboxylates by this method. Ouchi et al[77] reported the preparation of a number of dicarboxylates by the reaction given below.

$$Ph_3BiBr_2 + 2RSCH_2CO_2H + 2Et_3N \longrightarrow Ph_3Bi(O_2CCH_2SR)_2 + 2EtNH^+Br^-$$

$R = Me, Et, Pr, Me_2CH, Bu, Ph, PhCH_2$

Ouchi et al[78] have prepared triphenylbismuth dibenzoate and propionate in a similar manner.

1.10 Present Work

The object of this work was to synthesise new organobismuth compounds, to investigate their Lewis acidity by reacting them with various nitrogen donor and other ligands, and to structurally characterise all new materials , using various physical techniques including NMR, FTIR, and X-ray crystallography. Compounds were assessed at Manchem Ltd for a variety of industrial uses including paint driers and rubber binding agents.Some compounds produced by Manchem Ltd were also examined.

CHAPTER TWO

GENERAL EXPERIMENTAL TECHNIQUES

2.0 General Experimental Techniques

2.1 General

Many organic bismuth compounds are susceptible to breakdown under normal conditions. During the synthesis and handling of organyl bismuth compounds care is required, therefore wherever the possibility of such a danger existed the experiment including the general handling of the reagents was performed under an inert atmosphere of dinitrogen gas or argon gas. For use in reactions these were passed over calcium chloride/silica gel and bubbled through liquid paraffin or sulphuric acid prior to use.

2.2 Chemicals

The starting materials used for the reactions were obtained from one of the sources below:- British Drug Houses (BDH), or Aldrich Chemical Company for most reagents and solvents. Mining and Chemical Products Ltd for bismuth metal as ingots, and powder (99.999% purity) and a variety of other inorganic bismuth compounds. Manchem Ltd for a variety of carboxylic acids.

2.3 Solvents

All the solvents were obtained from the sources given above in 2.2. Analytically pure solvents were used without further purification. Other solvents were purified and stored in clean dark coloured containers according to the methods given by Perin [79].

2.4 Physical Measurements and Techniques

2.4.1 Melting Points

Melting points of all solid compounds were determined using a Gallenkamp electrically heated melting point apparatus with a mercury thermometer. All readings were uncorrected.

2.4.2 Conductivity Measurements

Molar conductance of dilute solutions of the samples (10^{-3}M) was measured at room temperature using a standard Mullard conductivity bridge and immersion type bright platinum electrodes (type E 7591/B) with a cell constant of 1.46.

2.4.3 Flame Photometry

Flame Photometry was performed on solutions of samples using an Evans Electroselenium Ltd Model A flame photometer.

2.4.4 Infra-Red Spectroscopy

Infra-red spectra were recorded on a Perkin-Elmer FTIR 1710 spectrometer equipped with a Perkin-Elmer 3600 Data station. Samples were prepared as KBr discs and run between the range 4000 - 220 cm^{-1}. For more careful work in the 400- 220 cm^{-1} region, samples were prepared as polyethylene discs.

2.4.5 Elemental Analysis

Micro-elemental analyses for carbon, hydrogen and nitrogen were performed using a Carlo-Erba 1106 elemental analyser. Micro-elemental analyses for sulphur, halogens, and carbon, hydrogen and nitrogen were also performed by Elemental Microanalysis Ltd and Butterworth Laboratories Ltd.

2.4.6 Nuclear Magnetic Resonance Spectroscopy

NMR spectra (solution and solid state) were performed by the Aston University Dept of Chemical Engineering and Applied Chemistry , using a Bruker Spectrospin AC 300 MHz instrument.

2.4.7 Gel-Permeation Chromatography

Spectra were recorded on a Perkin-Elmer LC85B instrument using RI and ultra-violet detection.THF or Chloroform was used as the solvent and eluent. The spectra were recorded using an eluent flow rate of 1.0 cm^3 min^{-1}

2.4.8 Atomic Absorption Spectroscopy

The bismuth content of the compounds was determined by atomic absorption spectroscopy, using IL 151 and Perkin-Elmer 360 instruments. Details of the method are given in section 5.5

2.4.9 Drier Measurements

The drying time of paint formulations containing the bismuth compounds was measured with a 3-speed Beck-Koller drying recorder. The viscosity of the paint used was measured using an ICI Cone and Plate Viscometer.

2.4.10 Mass Spectra

Mass spectra were obtained at the University of Birmingham and via the SERC service at University College, Swansea .

2.4.11 X-Ray Measurements

The bismuth compounds were recrystallised from suitable solvents to obtain crystals of a suitable quality. Preliminary examination was performed by photographic methods. The cell parameters and reflection intensities were measured with graphite monochromated

Mo-K_{α} radiation for the crystals using an Enraf-Nonius CAD-4 diffractometer, operating in the ω-2θ scan mode. Three standard reflections were monitored at regular intervals of to check the stability of the system. Absorption corrections were applied.

The structures were solved by Patterson and Fourier difference synthesis methods, using reflections having $I > 2.5\alpha$ (I). The refinements were by least - squares, using anisotropic temperature factors for the heavier atoms. Hydrogen atoms were placed in calculated positions (C-H = 1.08 ^{0}A) " riding " on their respective carbon atoms for the subsequent

refinement of the structure. Refinement was terminated when all calculated shift/error ratios were < 0.1. Computations were performed on the University of Birmingham Honeywell Multics computer with the SHELX76, and SHELX86, program[80] and also at the University of Manchester Regional Computer Centre. Absorption corrections were applied using the DIFABS[81] program.

2.5 X-Ray crystallography background

X-ray analysis is based on the phenomenon of interference which occurs when X-rays pass through a crystalline substance. The resultant pattern from the interference provides information about the structure of the crystal. The theory was developed by Bragg.There is a simple relation derived from the wave theory of light, between the wavelength of the radiation, angle of radiation and the distance between successive lines on a grating. In crystals the structural units are arranged in a regular manner due to the repition of the unit cell. Interference and diffraction must therefore occur when radiation passes through the lattice, if the wavelegth of the radiation and the lattice constant (i.e. the distance between successive lattice planes are approximately equal). The crystal may act as a diffraction grating. Fig 2.10 shows that when a parallel beam of X-rays is incident on a crystal the X-rays are diffracted by reflection from the lattice planes. The two parallel rays S_1 and S_2 are incident at an angle θ and are reflected from adjacent lattice planes at this angle also. After leaving the crystal the two rays differ in the path by the amount BC + CD which S_2 travels further than S_1 . However an intense diffracted beam is only obtained if the rays

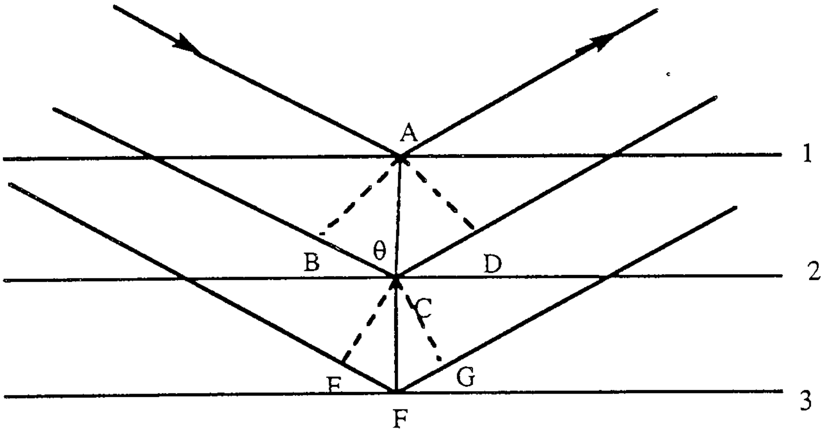


Fig 2.1 Reflection of X-rays from lattice planes of a crystal

reflected by the single lattice planes reinforce each other. The precondition being that the path difference of the rays must be integral multiples of the wavelength. In Fig 2.10 the path difference of the two neigbouring rays is BC + CD. Let us designate the distance between the two lattice planes by 'd'. Since BC = CD the path difference is 2BC, this being the integral wavelength:

$$\mathbf{2BC = 2d\sin\theta = n\lambda} \quad \text{.......... equation 2.1}$$

θ =the angle which the X-ray beam makes with the lattice plane.
λ = the wavelength of the X-ray radiation.

As can be seen from equation 2.1, interference may only occur if λ < or = 2d. For a given radiation e.g. monochromatic, interference may be produced by varying the angle θ.

2.6 Determining the structure

2.6.1 The rotating crystal method

This method uses a single crystal. The size of the crystal is such that not all of the radiation is absorbed. The crystal in the diffraction apparatus (Fig 2.2) is slowly rotated about a definite axis, so that the angle of incidence θ is continually varied (and single planes come
successively into the position reflecting the X-rays). These reflections flashing up briefly would be insufficient to either produce an image on a photographic plate or reflection data on a diffractometer, therefore the crystal is rotated many times. The main problem is, then

to determine the precise positions of the atoms within the unit cell. The data or reflection intensities are analysed by a number of ways, e.g. Fourier analysis. Although the electron density may vary quite irregularly from point to point within the unit cell, depending on the positions of the atoms, the variation throughout the crystal must be periodic, since the lattice is built up by repetion of the unit cell. Thus the electron density is a periodic function, $\rho(x)$, of distance, and may be represented as a sum of trigonometric functions known as a Fourier series.

$$\rho(x) = F_o + F_1 \cos(2\pi x/d' + \alpha_1) + F_2 \cos(4\pi x/d' + \alpha_2) + \ldots\ldots\ldots\ldots \text{equation 2.2}$$

$$\rho(x) = \Sigma F_n \cos(2n\pi x/d' + \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{equation 2.3}$$

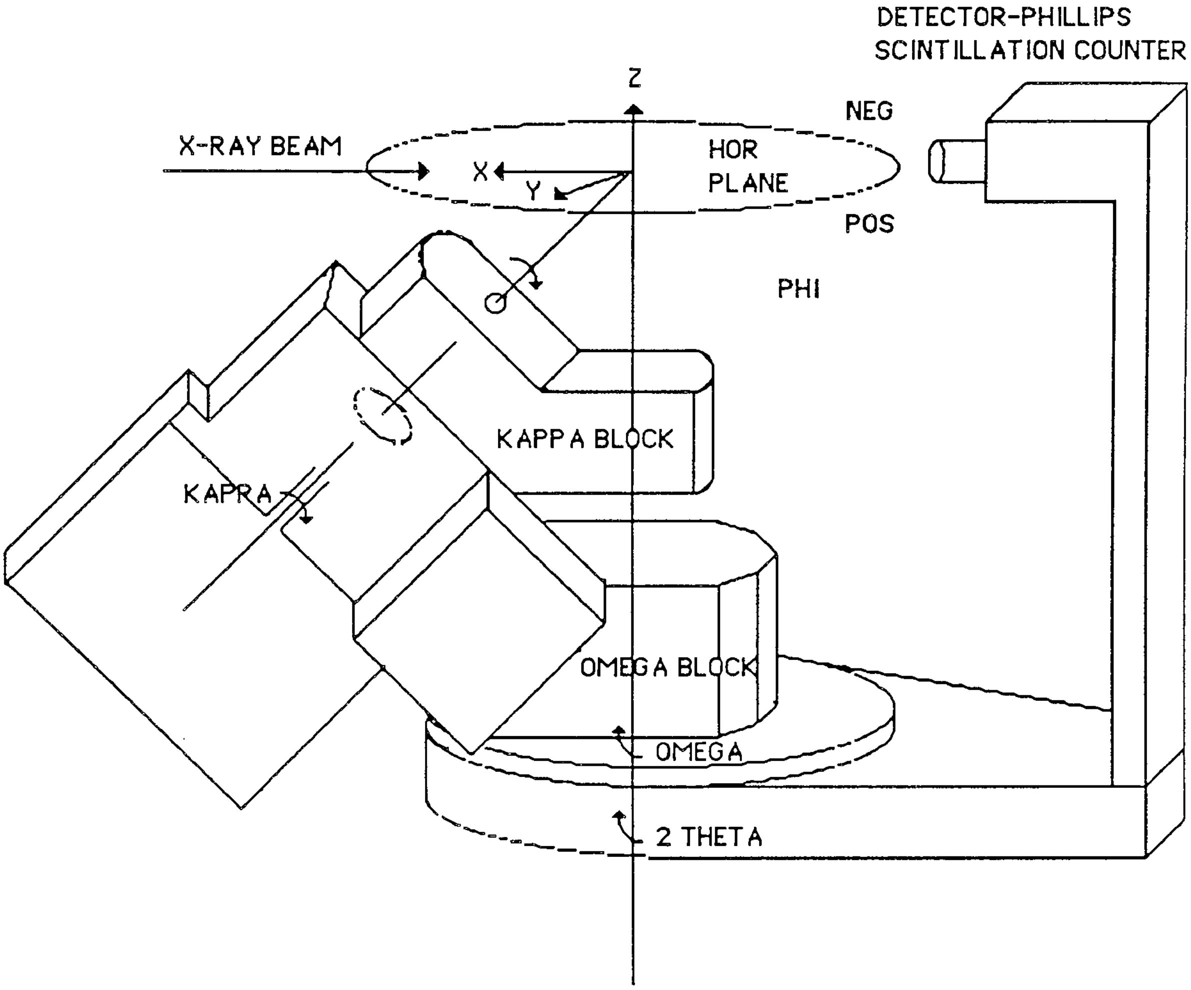
F= amplitude α= phase of each cosine term

d'= distance within which the periodic function repeats itself

Note: the equation above is given for one dimension only i.e. x

Thus if the F and α terms can be determined, it becomes possible to sum the series and so obtain a measure of the electron density at any point within the unit cell. The F terms can be determined from the intensities of the reflections or diffraction spots, but the phases of the diffracted waves are not directly observable. Various techniques have been devised to overcome this phase problem.

Figure 2.2 **Enraf-Nonius CAD-4 Diffractometer**



Graphite monochromated MoKα radiation generated via an Enraf-Nonius generator run at 50kV and 20mA

2.6.2 (a) Heavy atom technique

In this technique a single outstanding heavy atom in the structure gives sufficient information about the phases for the Fourier series to be summed.

2.6.3 (b) Patterson synthesis

In this method the squares of the amplitudes of the diffracted waves are used as coefficients and the phases not used at all.

Figures 2.3 and 2.4 illustrate the stages involved in collecting the data and determining the crystal structure respectively.

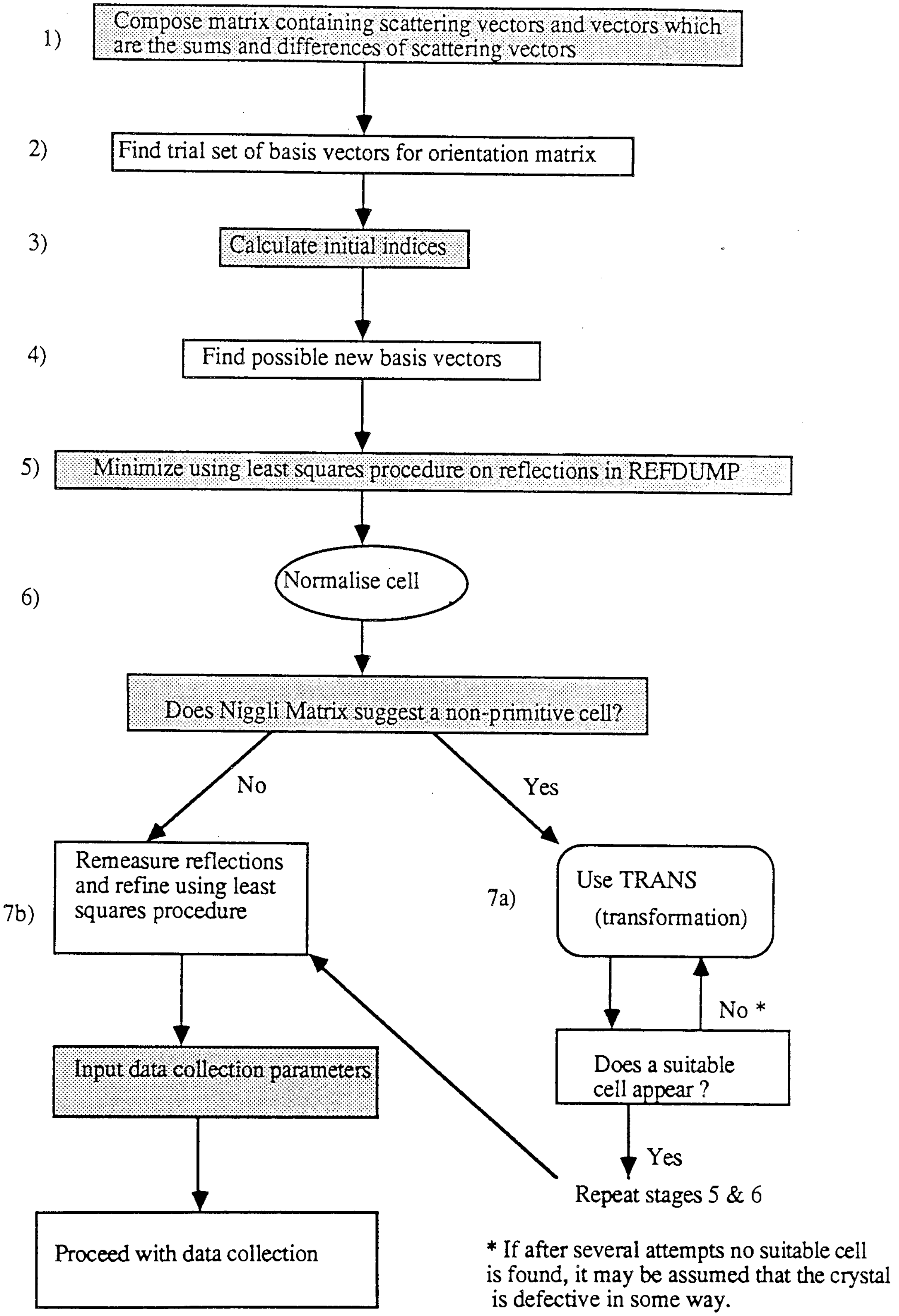
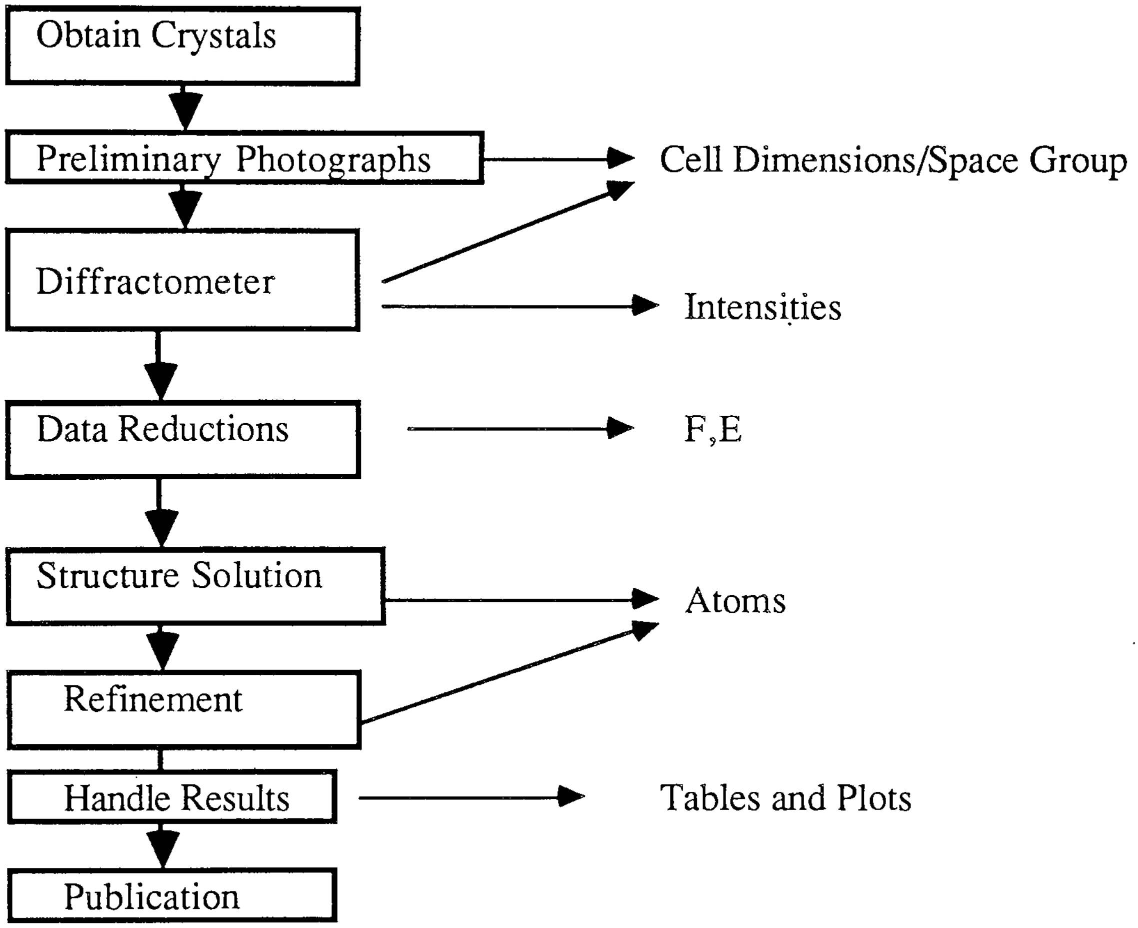


Figure 2.3 A flow diagram illustrating the stages involved in collecting unit cell data and intensity data using an Enraf-Nonius CAD-4 diffractometer

Figure 2.4 A flow diagram illustrating the stages in the determination of a crystal structure from initiation to completion



CHAPTER THREE

MICROWAVE ENERGY IN ORGANOMETALLIC CHEMISTRY

3.0 INTRODUCTION

Investigations of possible industrial applications of microwave energy began in the 1940's. The removal of organic sulphur from coal by microwave irradiation[82] and the use of microwaves in rubber vulcanisation[83] are examples. Recently there have been reports[84] that remarkable enhancements of the rates of some organic reactions could be achieved by performing the syntheses in Teflon containers in a simple domestic microwave oven. Gedye and coworkers achieved these enhancements by performing the reactions in sealed containers. This of course gives rise to the argument that the increased pressures play an important role in improving the reaction rates. However Mingos [85] has performed reactions involving the intercalation of compounds onto clays in open vessels, and still achieved improved reaction rates, by using microwave energy. Thus although increased pressure may help certain reactions it is by no means the chief factor for the enhanced reaction rates.

The field of microwave reactions was extended by the commercial production of a microwave reactor produced by the Australian Research Institute [86].

3.1 Theoretical Background

Microwaves are a constituent of the electromagnetic spectrum (Figure 3.1).

Microwave energy is a non-ionising radiation that causes molecular motion by migration of ions and rotation of dipoles, without causing changes in molecular structure.

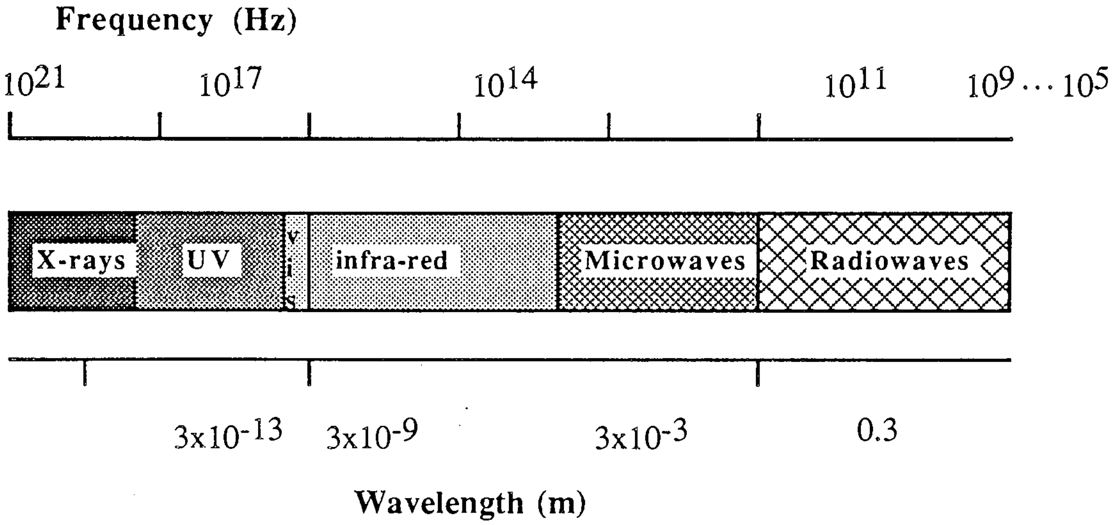


Figure 3.1 Microwaves in relation to the electromagnetic spectrum.

Generally a microwave system has an energy output in the range of 600 -700W.

3.1.1 Comparison of Conventional Heating with Microwave Heating

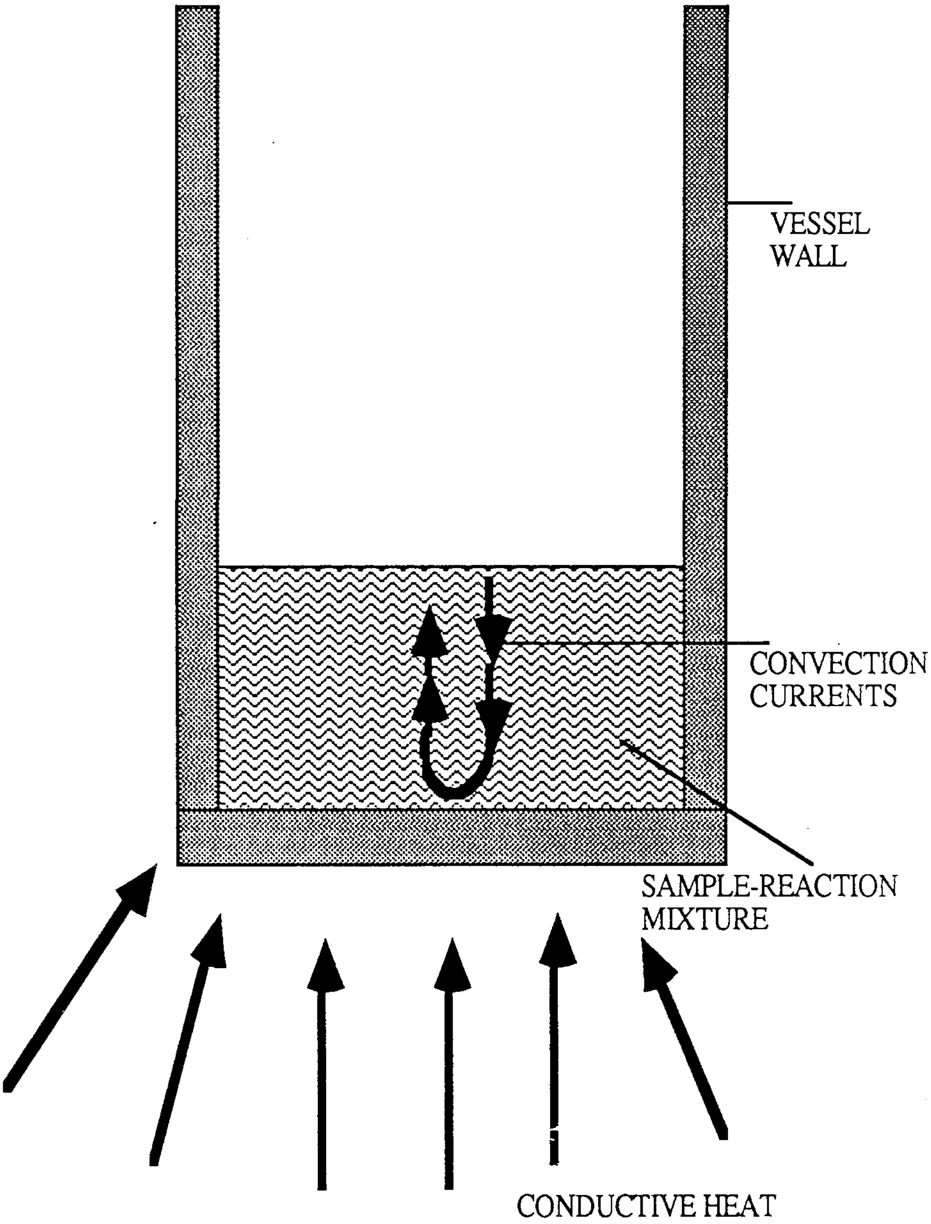
Figures 3.2 and 3.3 show schematic diagrams of the processes occurring when a sample is heated by conduction and by microwave energy respectively. The diagrams illustrate that in conductive heating the vessel must first be heated and subsequently the heat is transferred to the sample solution.This process is not instantaneous . The factors

which should be remembered are :-

(a) vaporisation of the liquid at the surface

(b) a thermal gradient must be established via convection currents

FIGURE 3.2 SAMPLE HEATING BY CONDUCTION

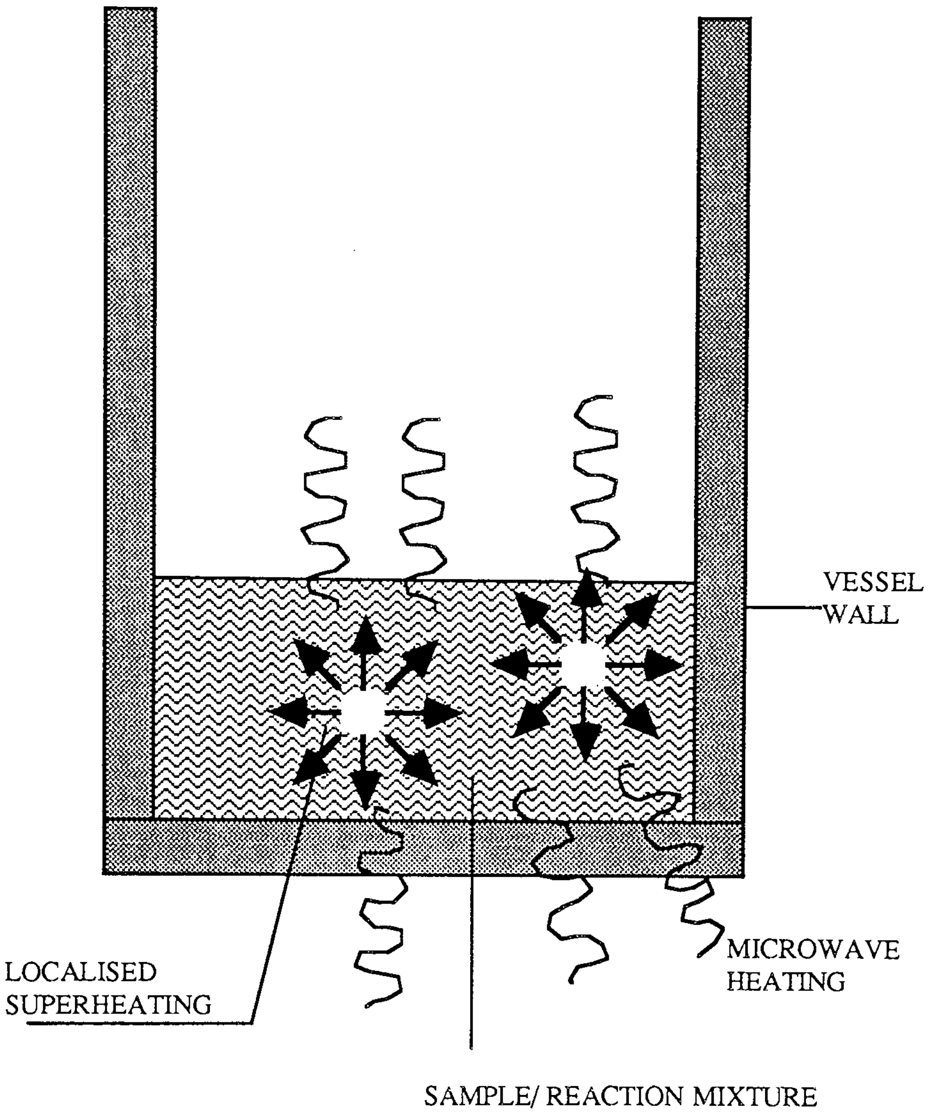


(c) only a small amount of the sample solution is at the same temperature as the external vessel wall.

In microwave heating, the entire solution volume is heated simultaneously, without heating the vessel, unlike in conductive heating where only a small proportion of the

FIGURE 3.3

Sample Heating by Microwave Energy



solution is above the boiling point of the solution. Thus in microwave heating the solution reaches its boiling point much faster. This rapid heating rate may also lead to superheating.

3.1.2 Heating Pattern of a Sample and Dielectric Loss

The ability of the sample to obstruct microwaves is given by its dielectric constant.The dissipation of the energy passing through the sample is given by the loss factor. Therefore the dissipation factor gives the rate at which microwave energy is absorbed by a particular sample.

Dissipation Factor **tan d** = Dielectric loss (sample) / Dielectric Constant of Sample

i.e. $\mathbf{\tan d = e''/e'}$

3.1.3 Microwave Energy Penetration

Penetration is regarded as zero for materials[87] which totally reflect microwaves e.g. metals. It is regarded as infinite for materials which are completely transparent to microwaves. A scale based on the factors given above exists for materials with penetration to varying degrees between the two extremes.

The greater the value for the dissipation factor for a sample the quicker microwaves are absorbed and dissipated into a sample ,thus the less the penetration of the microwave energy at a given frequency.

3.1.4 Mechanisms of Microwave Energy Absorption

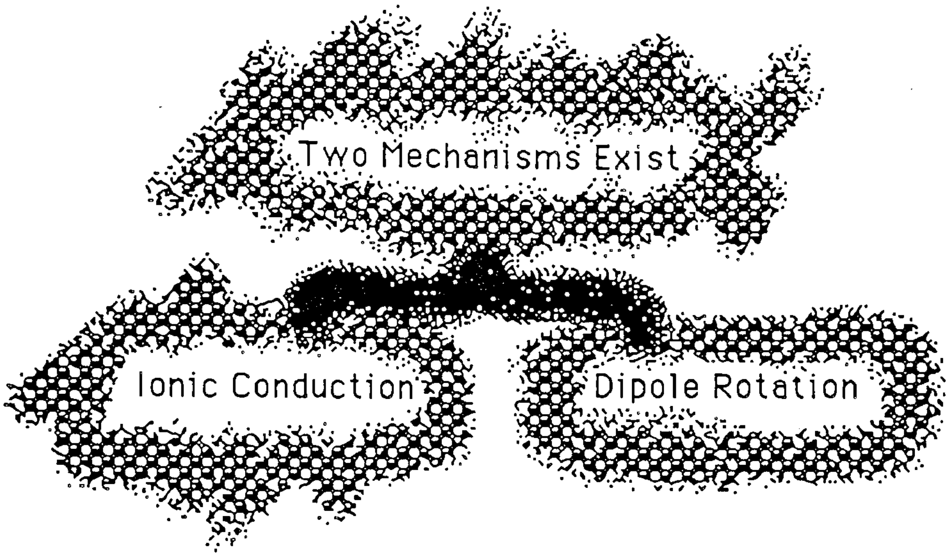


FIGURE 3.4

3.1.5 Ionic Conduction

This is the conductive (or electrophoretic) migration of dissolved ions in an applied electromagnetic field. Because of resistance to ion flow the flow of current (resulting from the ionic migration) results in a loss equivalent to I^2R (where I and R are the current and resistance respectively).This loss occurs as heat production.

The parameters affecting ionic conduction are :-

(a) Ion concentration

(b) Ion mobility

(c) Temperature of the solution

3.1.6 Dipole Rotation

This is the alignment of molecules in the sample (due to the electric field) that have a dipole, permanent or induced. As the electric field of the microwave energy increases it aligns the polarised molecules. On removing the field, the molecules return to a state of disorder via thermal agitation, in relaxation time t, and this results in thermal energy being released. This momentary alignment of the molecules and return to disorder is extremely fast. For example at 2450MHz this occurs 4.9 x 10^9 times per second.

The efficiency of sample heating by dipole rotation depends on the dielectric relaxation time of the sample, its viscosity, and temperature.

3.2 EXPERIMENTAL

Equipment used:

The work was carried out using a Sharp Carousel II R-84801 (650W), domestic microwave oven. The experiments were performed in 100 cm^3 Teflon bottles with screw caps supplied by the Savillex Corporation, Minnetonka, Minnesota 55345, USA.

Materials supplied by ICI were tested. The materials were used to construct screw cap vessels of the design in Figure 3.6 . These vessels were used for reactions and considered as replacements for the Savillex vessels.

3.2.1 Methods

3.2.2 Synthesis of (phenylazophenyl- C, N') mercury(II) acetate

To a solution of azobenzene (0.5 g, 2.75 mmol) in absolute ethanol (10cm^3), in a Savillex 100 cm^3 screw cap vessel, mercuric acetate (0.88 g , 2.75 mmol) was added.The vessel was sealed and placed in the microwave oven. It was then subjected to microwave energy irradiation in short bursts of 1 minute duration each, with 1 minute intervals between bursts, for a total microwave irradiation period of 30 minutes.

Yield = 45%

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

To a solution of (phenylazophenyl- C, N')mercury(II) acetate (0.67 g,1.34 mmol) prepared as above a solution of lithium chloride (0.11 g , 2.68 mmol) in isolation was added.

The sealed vessel containing the reaction mixture was placed in the microwave oven and irradiated for a further 7 minutes (ie 37 min total) , in a series of bursts of 1 minute on and 1 minute off. After allowing a short period for cooling the reaction mixture was filtered and washed with methanol, on slow evaporation of the solvent bright red needles of the compound were obtained.

Yield = 33%

3.2.4 Synthesis of 2-(2-Pyridyl)phenylmercury(II) acetate

To 2- phenylpyridine (2.0 g, 0.01 moles) in a Savillex 100 cm^3 screw cap vessel, mercuric acetate (4.1 g , 0.01 moles) in 10cm^3 of absolute ethanol was added.The vessel was sealed and placed in the microwave oven. It was then subjected to microwave energy irradiation in short bursts of 1 minute (with 1 minute intervals), for a total microwave irradiation period of 47 minutes.

3.2.5 Synthesis of 2-(2-Pyridyl)phenylmercury(II) chloride

To a solution of 2 -(2 - pyridyl)phenylmercury (II) acetate) (0.57 g, 1.2 mmol) in absolute ethanol (5 cm^3) (prepared as above) a solution of lithium chloride (0.10 g, 2.4 mmol) in was added.The sealed vessel containing the reaction mixture was placed in the microwave oven and irradiated for a further 7 minutes following above in-situ preparation) (ie 47 min total) , in a series of 1 minute bursts (with 1 minute intervals between each burst). After allowing a short period for cooling the reaction mixture was filtered and

washed with cold absolute ethanol.

Yield = 40%

3.2.6 Synthesis of Phenylbismuth(III) dichloride (isolated as bipy complex)

To a solution of triphenylbismuth (0.55 g,1.25 mmol), in propan-2-ol (5 cm^3) in a Savillex 120 cm^3 vessel was added a solution of bismuth trichloride (0.79 g, 2.5 mmol) in propan-2-ol (5 cm^3). The sealed vessel containing the reaction mixture was placed in the microwave oven and irradiated for 6 minutes, in a series of periodical bursts of1 minute on followed by 1 minute off. Then a slight excess of 2-2 bipyridyl in propan-2-ol was added. After allowing a short period for cooling the reaction mixture was filtered washed with hot propan-2-ol.

Yield = 46%

3.2.7 Synthesis of Phenylbismuth(III) dichloride (dimethylbipy complex)

Prepared as for bipyridyl complex except 4,4-dimethyl- 2,2 'bipyridyl ligand used.
Yield= 55%

3.2.8 Synthesis of Triphenylbismuth

To a solution of tetraphenyltin (0.6 g, 1.4 mmol), in a toluene/absolute ethanol (50:50) solvent mixture, was added a solution of bismuth trichloride (0.44 g, 1.4 mmol), in the above solvent mixture. The total solvent volume used was 12 cm^3. The sealed vessel containing the reaction mixture was placed in the microwave oven and irradiated for 6 minutes, in a series of bursts of 1 minute on, followed by 1 minute off. After allowing a short period for the reaction mixture to cool, an excess of hot ethanol was added. After filtration, the filtrate was boiled down. On setting aside white crystals appeared and were filtered. A mixture of the products was obtained which could not be separated into the individual components.

3.2.9 Attempted synthesis of (phenylazophenyl- C, N') bismuth (III) chloride

To a solution of (phenylazophenyl-C, N') mercury(II) chloride (1.0 g, 2.4 mmol), in absolute ethanol (6 cm^3) was added a solution of bismuth trichloride (0.75 g,2.4 mmol) in 6 cm^3 of the same solvent. The PEEK microwave vessel containing the reaction mixture was then placed in a microwave oven. The reaction mixture was subjected to 6 one minute bursts of microwave energy (1 minute on, 1 minute off). A product assumed to be (phenylazophenyl- C, N') bismuth (III) chloride was obtained, (see section 3.5).

3.2.10 Attempted synthesis of (phenylazophenyl- C, N') bismuth (III) bromide

To a solution of (phenylazophenyl- C, N') mercury(II) chloride (1.0 g, 2.4 mmol), in absolute ethanol (6 cm^3) was added a solution of bismuth tribromide (1.0 g, 2.4 mmol) in 6 cm^3 of the same solvent. The PEEK microwave vessel containing the reaction mixture was then placed in a microwave oven. The reaction mixture was subjected to periodical one minute bursts of microwave energy (1 minute intervals between bursts). (for preparation of bismuth tribromide see chapter 4 & 5). The starting materials were recovered unreacted.

3.2.11 Attempted synthesis of a Triphenylbismuth/ 7,7,8,8 tetracyanoquinodimethane (tcnq) complex

To a solution of tcnq (0.25 g, 1.2 mmol) in 5 cm^3 of a acetonitrile/toluene mixture (20:80), was added a solution of triphenylbismuth (0.53 g, 1.2 mmol) in 6 cm^3 of the same solvent mixture. The sealed PEEK vessel containing the reaction mixture was placed iinto the microwave oven and irradiated for 6 minutes, in a series of 1 minute bursts. After allowing the reaction mixture to cool, it was removed from the microwave vessel , heated, filtered and the filtrate allowed to evaporate slowly. The starting materials were recovered unreacted.

3.2.12 Attempted synthesis of a Triphenylbismuth/ 7,7,8,8 tetracyanoquinodimethane (tcnq) complex(by conventional heating)

To a hot solution of tcnq (0.5 g, 2.4 mmol) in 10 cm^3 of a acetonitrile/toluene mixture (50:50), was added a hot solution of triphenylbismuth (1.1 g, 2.4 mmol) in 10 cm^3 of the same solvent mixture. The mixture was refluxed under dinitrogen for 1.5 hours. Then it was filtered hot and the filtrate allowed to evaporate slowly. Again the starting materials were recovered unreacted.

3.2.13 Reaction of Azobenzene with bismuth(III) octanoate

To a solution of azobenzene (0.3 g, 1.65 mmol) in absolute ethanol (5 cm^3), was added a solution of bismuth trioctanoate (0.89 g, 1.65 mmol).The reaction mixture was sealed in a PEEK microwave vessel and placed in a microwave oven, and irradiated for 30 minutes, in a series of 1 minute bursts, with 1 minute intervals. After allowing the reaction mixture to cool, it was removed from the microwave vessel, heated and filtered. The filtrate was allowed to evaporate slowly over a period of five days. A mixture of products was obtained which could not be separated.

3.2.14 Reaction of Azobenzene with bismuth(III) octanoate by conventional heating

To a solution of azobenzene (1.5 g, 8.2 mmol) in absolute ethanol (25 cm^3), was added a solution of bismuth trioctanoate (4.5 g, 8.2 mmol) in absolute ethanol (25 cm^3). The reaction mixture was refluxed for 2 hours. Then filtered and washed three times with absolute ethanol. The products were not isolable.

3.2.15 Reaction of Azobenzene with bismuth(III) octanoate (by conventional heating)

Using excess azobenzene as the solvent.

Bismuth octanoate (4.5 g, 8.2 mmol) was added to excess azobenzene. The flask containing the mixture was placed in an oil bath. The mixture was heated until the azobenzene was molten. Then the mixture was kept within the temperature range of 95-110 °C , for 4 hours. The reactants were recovered unreacted.

3.2.16 Reaction of Azobenzene with bismuth(III) chloride (by conventional heating)

Using excess azobenzene as the solvent.

The reaction was performed as above. The bismuth(III) chloride was recovered as the oxychloride salt and no reaction with the azobenzene was observed.

3.2.17 Reaction of (phenylazophenyl- C, N') mercury chloride with silver perchlorate

To a solution of (phenylazophenyl- C, N') mercury chloride (0.5 g, 1.2 mmol) in

1,4 dioxan (30 cm^3), was added silver perchlorate (0.5 g, 2.4 mmol).The reaction mixture was stirred at room temperature for 7 days. The reaction solution was observed to darken in colour, and a precipitate formed. There appeared to be a breakdown of the silver salt occurring. No pure product was isolated.

It was at one time thought that a reaction between (phenylazophenyl- C, N') mercury chloride and the solvents used for NMR studies may have occurred during the recording of the spectrum. Thus this was investigatedwith chloroform and methanol.

3.2.18 Reaction of (phenylazophenyl- C, N') mercury chloride with chloroform

A sample of (phenylazophenyl- C, N') mercury chloride was dissolved in chloroform (ethanol free). The solution was heated for 15 minutes. On allowing to cool and evaporate crystals of a bright red compound having a melting point corresponding to the intial compound were isolated. No further compound was isolated.

3.2.19 Reaction of (phenylazophenyl- C, N') mercury chloride with methanol

A sample of (phenylazophenyl- C, N') mercury chloride was dissolved in methanol. The solution was heated for 15 minutes. On allowing to cool and evaporate crystals of a bright red compound having a melting point corresponding to the intial compound were isolated. No further compounds were isolated.

3.2.20 Reaction of (phenylazophenyl- C, N') mercury chloride with phenylbismuth(III) bis-diethyldithiocarbamate(by conventional heating)

To a solution of (phenylazophenyl- C, N') mercury chloride (2.0 g, 4.8 mmol) in absolute ethanol (35 cm^3), was added a solution of phenylbismuth(III) bis-diethyldithiocarbamate (2.80 g, 4.8 mmol) in absolute ethanol (20 cm^3).The reaction mixture was refluxed for 3 hours. Then filtered and washed three times with absolute ethanol. The starting reagents were identified by melting points and infra-red spectroscopy. Difficulty was encountered on attempting to find a suitable solvent to dissolve the bismuth compound for microwave work.

3.2.21 Reaction of (phenylazophenyl-C,N') mercury(II) chloride with triphenylbismuthdioctanoate

To a solution of (phenylazophenyl- C, N') mercury (II) chloride (0.25 g,1.4 mmol), in absolute ethanol (8 cm^3) was added a solution of triphenylbismuthdioctanoate (0.6 g, 1.4 mmol) in 10 cm^3 of the same solvent. The PEEK microwave vessel containing the reaction mixture was then placed in a microwave oven. The reaction mixture was subjected to one minute bursts of microwave energy (with 1 minute intervals between bursts) for a total duration of 5 minutes.

3.2.22 Reaction of (phenylazophenyl- C, N') mercury chloride with triphenylbismuthdioctanoate (by conventional heating)

To a solution of (phenylazophenyl- C, N') mercury chloride (2.0 g, 4.8 mmol) in absolute ethanol (35 cm^3), was added a solution of triphenylbismuthdioctanoate (2.1 g, 4.8 mmol) in absolute ethanol (15 cm^3).The reaction mixture was refluxed for 3 hours. Then filtered and washed three times with absolute ethanol. The starting reagents were identified by melting points and infra-red spectroscopy.

3.2.23 Preparation of bismuth *tris*- diethyldithiocarbamate

To a solution of bismuth trichloride (1.0 g, 3.7 mmol) in absolute ethanol (30 cm^3)was added a solution of sodium diethyldithiocarbamate (2.14 g, 11 mmol) in absolute ethanol (35 cm^3). On stirring a yellow precipitate of the product formed in near quantitative yield.

3.2.24 Reaction of (phenylazophenyl-C,N') mercury(II) chloride with *Tris*-diethyldithiocarbamatobismuth(III)

To a solution of (phenylazophenyl- C, N')mercury chloride (0.25 g, 0.6 mmol) in absolute ethanol/benzene (50:50) solvent mixture (5 cm^3), was added a solution of bismuth tris-diethyldithiocarbamate (0.39 g, 0.6 mmol)in the same solvent mixture such that the total solvent volume was 14 cm^3. The PEEK microwave vessel containing the reaction mixture was then placed in a microwave oven. The reaction mixture was subjected to one minute bursts of microwave energy (with 1 minute intervals between bursts) for a total duration of 18 minutes. The starting materials were recovered unreacted.

3.2.25 Attempted reaction of (phenylazophenyl- C, N') mercury (II) chloride with hydrogen sulphide

Hydrogen sulphide gas was bubbled through a solution of (phenylazophenyl- C, N') mercury chloride , (1.0 g, 2.4 mmol) in absolute ethanol (100 cm^3), at room temperature for 3 hours. The (phenylazophenyl-C,N') mercury chloride was recovered unreacted.

3.2.26 Synthesis of phenylbismuth(III) bis- diethyldithiocarbamate

To a solution of triphenylbismuth (0.50 g, 1.1 mmol) in absolute ethanol (5 cm^3), was added a solution of bismuth trichloride (0.72 g, 2.3 mmol) in the same solvent (6 cm^3) . The PEEK microwave vessel containing the reaction mixture was then placed in a microwave oven. The reaction mixture was subjected to periodical one minute bursts of microwave energy (with 1 minute intervals) for a total duration of 4 minutes. Then a solution of sodium diethyldithiocarbamate (0.77 g, 3.4 mmol) in absolute ethanol (15cm^3). The vessel was once again sealed and irradiated with microwaves for 3 minutes. After allowing the reaction mixture to cool, it was filtered and the crude product was recrystallised from absolute ethanol.

Yield = 53%

melting point = 77-78^oC

3.2.27 Reaction of Triphenylbismuth and versatic acid

To a solution of triphenylbismuth (0.5 g, 1.1 mmol), in absolute ethanol (5 cm^3)was added an excess of versatic acid. The reaction mixture was sealed in a Savillex vessel and placed in the microwave oven for 6 minutes. The microwave energy being used as in the previous experiments in 1 minute 'bursts'. The excess unreacted versatic acid was allowed to evaporate and the remaining solution was evaluated as a 'drier'.

Table 3.1 Elemental Analysis Results

Compound	**Experimental**				**Expected**			
	%C	%H	%N	%Bi	%C	%H	%N	%Bi
Phenylazophenyl-CN mecury(II)acetate	38.20	2.64	6.5	-	38.27	2.70	6.38	-
Phenylazophenyl-CN mecury(II)chloride	34.25	2.01	6.64	34.66	2.17	6.74		
bipy.BiPhCl_2	37.15	2.91	5.39	40.45	37.35	2.72	5.95	40.66
dimethylbipy.BiPhCl_2	39.85	3.32	5.17	38.56	39.53	3.71	5.23	38.25
Triphenylbismuth	48.70	4.6	-	46.10	49.10	3.41	-	47.50
Bi(S_2CNEt_2)$_3$	31.50	5.02	7.36	36.25	31.75	5.29	7.41	36.86
PhBi(S_2CNEt_2)$_2$	32.50	4.18	4.76	35.20	32.99	4.30	4.81	35.91
	S = 21.32				S = 21.99			

3.3 EVALUATION OF NEW MATERIALS FOR USE WITH MICROWAVES

Materials supplied by ICI were evaluated for work using microwave energy. The materials Victrex PES and Victrex PEEK were considered.

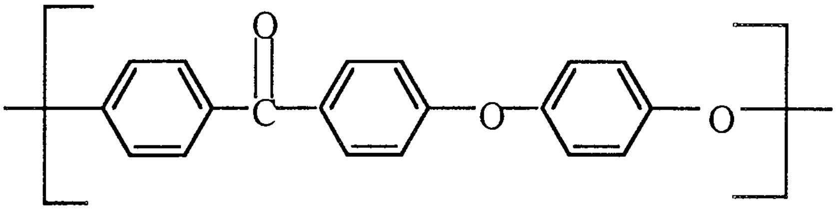
3.3.1 VICTREX PES

PES (Polyethersulphone) was found too difficult to machine and therefore was not considered further.

3.3.2 VICTREX PEEK

Victrex PEEK (polyetheretherketone), is a linear aromatic polymer which can be chemically described as a poly(aryletherketone), based on the repeating unit in

Figure 3.5



PEEK 450G was found to be easily machinable, and was used to manufacture vessels shown in Figure 3.6 for use in the microwave oven.

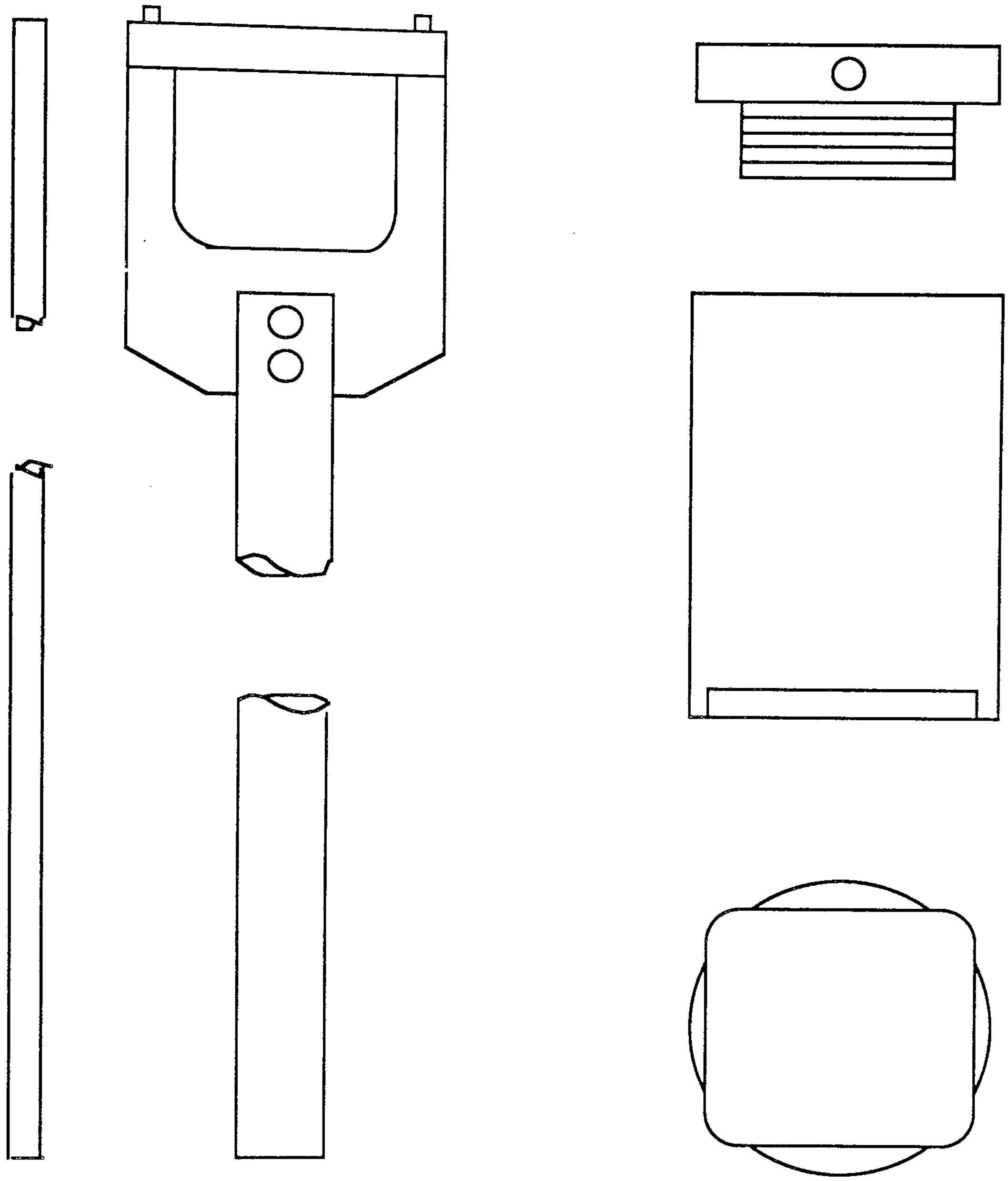
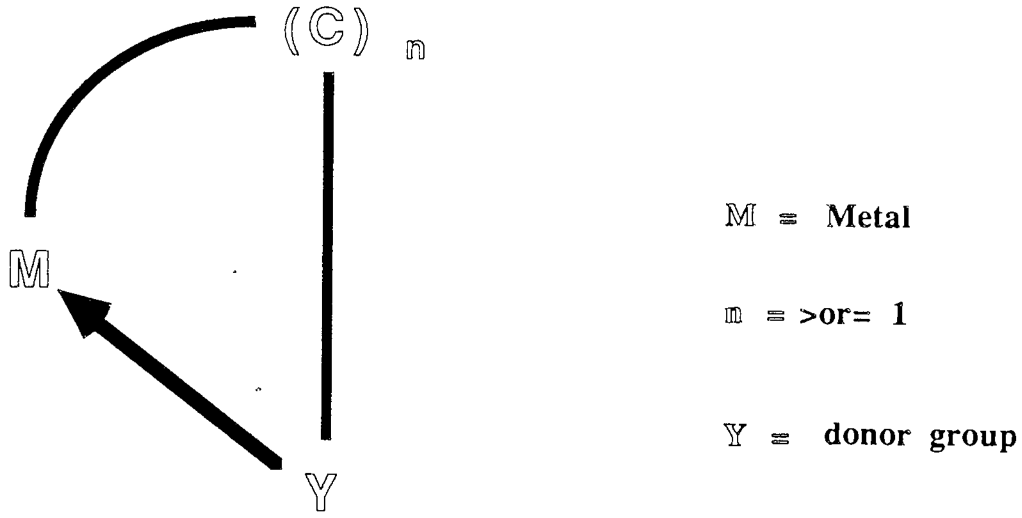


Figure 3.6 PEEK Vessel and Tools Design used in Microwave Experiments

3.4 The Bismuthation of Azobenzene

3.4.1 Introduction

Organometallic intramolecular coordination compounds, as the term indicates, are those which have at least one metal-carbon bond, and at least one ligand group forming an intramolecular coordination bond Figure 3.7 .



M ≡ Metal

m ≡ >or= 1

Y ≡ donor group

Figure 3.7 Diagram illustrating intramolecular coordination

Introduction of built in donors , for example, oxygen, nitrogen, phosphorus and sulphur, into the *ortho* - position of the aryl group in organometallic compounds has been shown to be a useful method of stabilizing organometallic compounds. The *ortho*--metallated complexes generally, form strain-free five - membered ring structures. There have been reports[88] of numerous organometallic intramolecular - coordination compounds having a five membered ring and five membered chelate ring structures.

The structures of some have been confirmed by X-ray diffraction studies and in cases crystal structures have been determined[88]. Azobenzene derivatives of transition metals have been known for a number of years. The most common method for their synthesis is from the reaction between azobenzene and a metal compound.[88,89,90,91].

The first reported metallation of azobenzene was by Kleiman and Dubeck[90] in 1963. The authors reported that azobenzene reacted with bis(cyclopentadienyl)- nickel to produce h-cyclopentadienyl - 2 - (2 - phenylazophenyl -C,N')nickel. McWhinnie et al [92] reported the first examples of compounds in which azobenzene was *ortho* - metallated by tellurium (IV) and tellurium (II). The crystal and molecular structure of the tellurium(II) derivative was given. This was one of the first compounds containing an intramolecular Te - N bond to be crystallographically characterised. The work was extended further by McWhinnie and Singh[93] . The authors reported derivatives of m-methoxybenzylideneaniline. Figure 3.8.

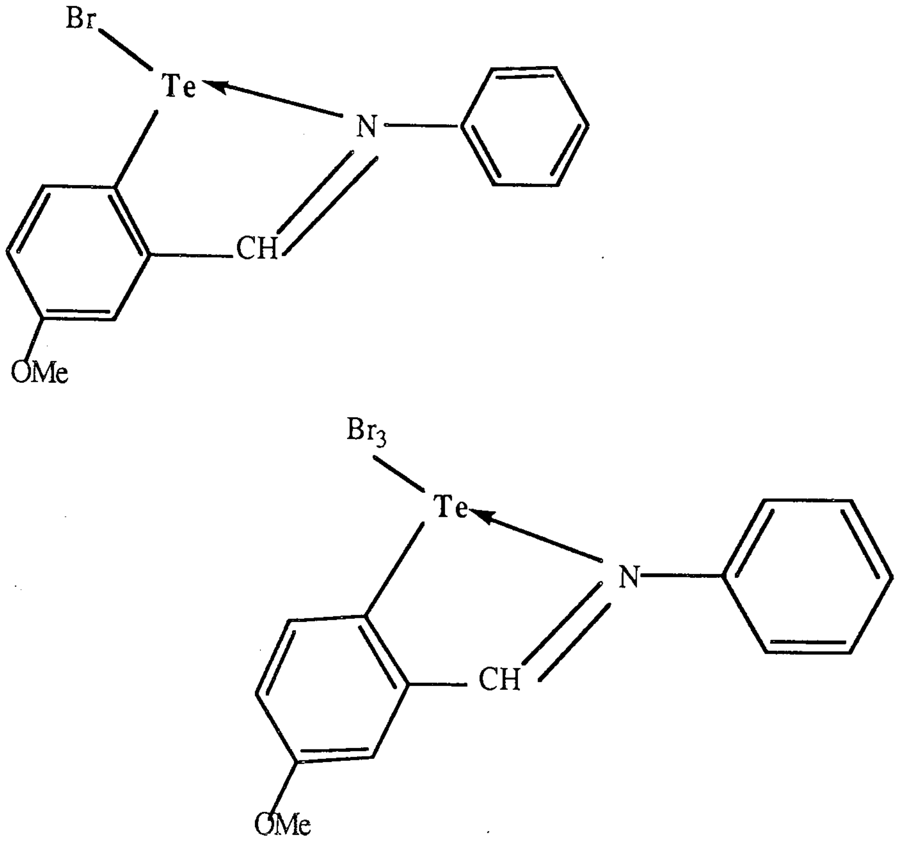


Figure 3.8 Tellurated derivatives of m-methoxybenzylideneaniline

Further work[94] in the same research group presented interesting observations as to the original synthesis of (2 - phenylazophenyl - C,N')tellurium(IV) trichloride[92]. Thus the original preparation method was re-investigated and the possibility of direct metallation of azobenzene with tellurium was considered. The crystal and molecular structures of (2- phenylazophenyl - C,N')tellurium (IV) trichloride were reported[94].

This work extends the investigations to bismuth. The bismuthation of azobenzene by replacement of mercury was first investigated. Figure 3.9

3.4.2 Mechanism of *ortho* - Metallation

The mechanism presumed from regiospecificity[90], is that the mercury is directed into an *ortho* position by coordinating to an azo nitrogen atom. This is followed subsequently by electrophilic substitution of the chloride.

3.4.3 *Ortho* - Bismuthation Of Azobenzene By Replacement Of Mercury

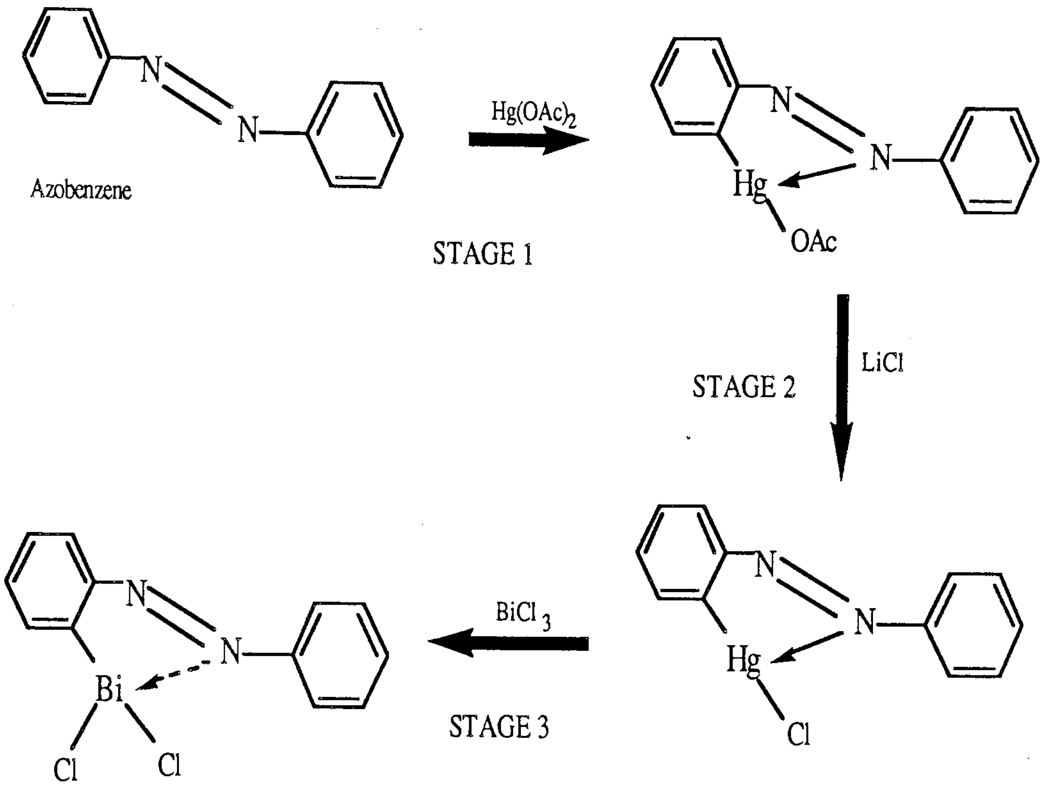


Figure 3.9 Reaction scheme for *ortho* - bismuthation of azobenzene

3.4.3 Direct *Ortho* - Bismuthation Of Azobenzene

The direct bismuthation of azobenzene was also investigated. Musa ^{95}, was unsuccessful in attempts to directly tellurate azobenzene. Ahmed ^{94}, showed that by using more forcing conditions (135-150^0) for the reaction of $TeCl_4$ with molten azobenzene, the tellurated product was formed in moderate yield.

Therefore the experimental conditions used by Ahmed were adopted for the reaction of azobenzene with bismuth halides.

3.4.4 By conventional methods[94,95]

Ortho-bismuthation of the azobenzene was attempted using conventional techniques (3.4.5).

3.4.5 Method

A modification of Roling's[91] synthesis was used. Bismuth trichloride was added to an excess of azobenzene. The excess azobenzene served as the solvent. The mixture was heated for 4 hours at temperatures > 135 °C. Afterwards the mixture was filtered. The purple-black residue and orange filtrate were separated and the residue was washed with methanol. The filtrate portions were kept separate, evaporation of the methanol resulted in the appearance of red needle crystals , which were thought to be (phenylazophenyl) bismuth (III) chloride.

3.4.6 By microwave energy

The unsuccessful attempt at the direct bismuthation of azobenzene by using the method of Ahmed, led to the investigation of whether even more extreme conditions may be required. Thus the use of microwave energy was explored.

3.4.7 Method

See section 3.2.15-16 .

3.5 RESULTS AND DISCUSSION

Although bismuth trichloride was used in the preparation of (phenylazophenyl) bismuth (III) chloride[96] (by reaction with azobenzene), RHgCl was obtained (R = phenylazophenyl). The NMR, IR and elemental microanalysis results of the product were all in agreement for the expected (phenylazophenyl) bismuth (III) chloride. Table 3.2 and (spectra) Figures 3.10,3.11 & 3.12 . Only the mass spectrum showed conclusively that the azobenzene had been mercurated and not bismuthated. The compound was not (phenylazophenyl) bismuth(III) chloride but in fact (phenylazophenyl)mercury(II) chloride. On checking with the suppliers of the bismuth trichloride used in the reaction (Mining and chemical products Ltd), it was discovered that it originated from an American company which also manufactured mercuric chloride. On investigation of the bismuth trichloride used it was discovered that it was contaminated with mercuric chloride.This preference of the azobenzene for mercury over bismuth was of interest and the crystal structure of the (phenylazophenyl)mercury(II) chloride was determined .

3.5.1 ^{13}C NMR Spectra

^{13}C NMR spectra were determined using a Jeol 300MHz Fourier transform multinuclear magnetic resonance instrument operating at 100.40MHz. (TMS as reference). The operating temperature was 293K and a pulse width of 6.0msec and a pulse delay of 0.281 seconds. 40000 scans were used with an acquisition time of 0.819 seconds. The ^{13}C NMR spectrum obtained is given together with a comparison of the peak positions with those of $(C_{12}H_9N_2)HgCl$ in DMSO-D6. Due to the decreased solubility in CH_3OD some of the peaks were not found. ^{13}C assignments were made by comparison with previous work[110].

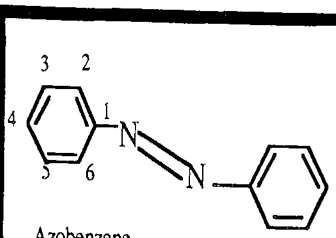
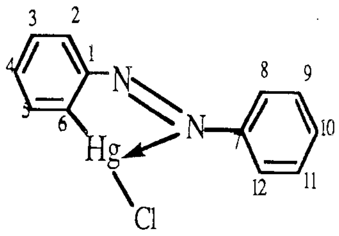
COMPOUND / PEAK	 Azobenzene		
C1	in DMSO-D6 151.8	in DMSO-D6 154.2	in CH3OD 155.624
C2	122.4	122.6	
C3	122.6	129.1	129.061
C4	131.3	131.7	131.987
C5		137.7	137.931
C6		143.1	
C7		150.9	151.872
C8		127.4	128.350
C9		129.5	129.601
C10		132.2	

Table 3.2 13C Spectra of $(C_{12}H_9N_2)HgCl$ and Azobenzene

3.6 The Crystal and Molecular Structure of (Phenylazophenyl-C,N')Mercury(II) chloride

The cell parameters and reflection intensities were measured with graphite monochromated Mo-K_α radiation from a bright red crystal 0.6 x 0.06 x 0.05 mm in size, using an Enraf - Nonius CAD-4 diffractometer, operating in the ω - 2θ scan mode. Three standard reflections were monitored at regular intervals to check the stability of the system. 2929 reflections ($\theta < 25^0$) were scanned of which 2055 were unique, and 1306 with $F > 5s$ (F) were used in the structure analysis. The atomic coordinates for mercury were located by Fourier difference synthesis. As not all of the hydrogen atoms could be located from the difference maps, the hydrogen atoms were placed in calculated positons (C-H 1.08 A^0), and were allowed to " ride " on their respective carbon atoms in the subsequent least-squares refinements. Non - hydrogen atoms were allowed to vibrate anisotropically. Unit weights were used and the refinements converged to give R = 0.0471 when all the shifts were < 0.02s. An empirical absorption correction was applied using DIFABS[81]. The structure of the complex and the atom numbering are shown in Figure 3.10 . The complex exists as a dimer [$Hg_2L_2Cl_2$]. The bond lengths and atomic coordinates are given in Table 3.4 and Table 3.5 respectively.

Table 3.3 Crystal Data for Phenylazophenyl-C,N')Mercury(II) chloride

Molecular weight	M = 417.3
Cell type	monoclinic
space group	$P2_1/c$
Cell Dimensions	a = 10.648(3) A^0
	b = 4.582(4) A^0
	c = 23.900(7) A^0
	b = 94.05(2)^0
Volume	1163 $A^{0\,3}$
Z	4
Cell Density D_c	2.38 g cm^{-3}
F(000)	768
m	13.70mm^{-1}

The mercury atom is bonded to a carbon and a chlorine atom, Hg-C(1), 2.01(2), Hg-Cl, 2.309(6) A^0. There are also the presence of secondary interactions to the nitrogen atom and two symmetry-related chlorine atoms. There is also another chlorine Cl' acting as a bridging atom. This bridging chlorine is located at the coordinate position corresponding to -x, 1-y, 1-z, and has a distance of 3.367(6)A^0 from the mercury atom. There is another weaker interaction with a chlorine atom located at x, 1+y, z, Hg...Cl" 3.632(5) A^0. The Hg-C primary bond distance lies within the range 1.922 -

2.228 A^0 and the value for the Hg-Cl primary bond length is within the range 2.239 - 3.289 A^0.

The ranges stated above were found from bond length searches of the Cambridge Crystallographic Database. The sum of the Pauling single-bond covalent radii for the bonds Hg-C and Hg-Cl are 2.01 and 2.43 A^0 respectively.The Hg...N(2) distance is 2.70(2) A^0. This is indicative of a rather weak interaction.

The distances for the title compound may be compared to the crystal structure of the related complex 2(2-pyridylphenyl)mercury(II) chloride. In this related complex the Hg-C, and Hg-Cl primary bond distances are 2.07 and 2.32A^0 respectively. There is a secondary Hg-Cl bond having a mean bond length of 3.43 A^0. In this structure there is also an Hg...Cl contact of intermediate length 3.184 A^0. As in the title compound, the Hg...N interactions are weak. The distances for the interactions being 2.627 and 2.673 A^0 for the two independent molecules.

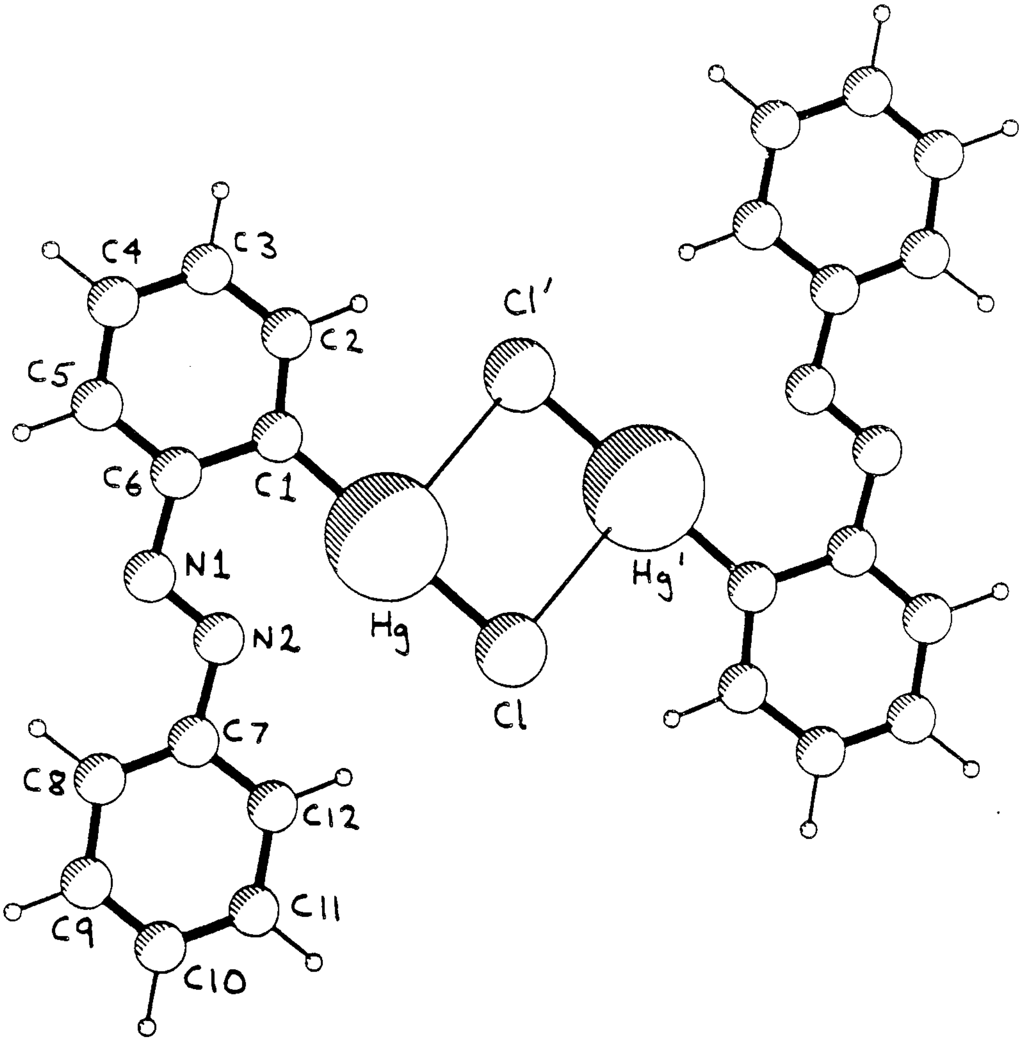


Figure 3.10 The crystal structure of phenylazophenyl-C,N'mercury(II)chloride

Hg(1) ---Cl(1)	2.309 (6)	C(4) ---C(5)	1.376 (27)
Hg(1) ---C(1)	2.014 (24)	C(5) ---C(6)	1.389 (25)
N(1) ---N(2)	1.245 (20)	C(7) ---C(8)	1.380 (27)
N(1) ---C(6)	1.414 (22)	C(7) ---C(12)	1.401 (27)
N(2) ---C(7)	1.408 (23)	C(8) ---C(9)	1.380 (29)
C(1) ---C(2)	1.370 (25)	C(9) ---C(10)	1.329 (29)
C(1) ---C(6)	1.465 (27)	C(10) ---C(11)	1.377 (27)
C(2) ---C(3)	1.380 (25)	C(11) ---C(12)	1.405 (27)
C(3) ---C(4)	1.346 (27)	Hg(1)....N(2)	2.701 (20)

Cl(1) -Hg(1) -C(1)	178.6 (5)	N(1) -C(6) -C(5)	116.0 (17)
N(2) -N(1) -C(6)	117.0 (16)	C(1) -C(6) -C(5)	119.8 (18)
N(1) -N(2) -C(7)	116.9 (17)	N(2) -C(7) -C(8)	125.9 (21)
Hg(1) -C(1) -C(2)	125.7 (16)	N(2) -C(7) -C(12)	114.0 (19)
Hg(1) -C(1) -C(6)	119.1 (13)	C(8) -C(7) -C(12)	120.1 (18)
C(2) -C(1) -C(6)	115.1 (20)	C(7) -C(8) -C(9)	119.4 (21)
C(1) -C(2) -C(3)	123.1 (19)	C(8) -C(9) -C(10)	122.2 (21)
C(2) -C(3) -C(4)	121.6 (19)	C(9) -C(10) -C(11)	119.4 (19)
C(3) -C(4) -C(5)	119.1 (19)	C(10) -C(11) -C(12)	121.2 (19)
C(4) -C(5) -C(6)	121.3 (19)	C(7) -C(12) -C(11)	117.6 (19)
N(1) -C(6) -C(1)	124.2 (17)		

Table 3.4 Bond lengths (Å) and bond angles(°) with e.s.d's in parentheses for (phenylazophenyl C N') mercury(II) chloride

Table 3.5 Fractional atomic coordinates (x10^4) with e.s.d.'s in parentheses.

	x	y	z
Hg(1)	-1469(1)	6785(2)	4481(1)
Cl(1)	-1665(5)	3656(14)	5228(2)
N(1)	-3279(13)	7580(30)	3317(7)
N(2)	-3512(15)	6244(39)	3752(7)
C(1)	-1260(16)	9461(45)	3826(10)
C(2)	-254(17)	11267(44)	3763(8)
C(3)	-132(17)	12941(45)	3289(9)
C(4)	-1015(20)	12927(51)	2858(9)
C(5)	-2057(17)	11173(46)	2887(8)
C(6)	-2198(16)	9382(43)	3347(8)
C(7)	-4559(14)	4360(40)	3715(10)
C(8)	-5253(18)	3580(57)	3228(9)
C(9)	-6233(19)	1625(55)	3255(10)
C(10)	-6556(18)	506(50)	3737(10)
C(11)	-5847(19)	1160(42)	4225(9)
C(12)	-4846(18)	3156(57)	4229(8)

Fractional atomic coordinates (x10^4) and isotropic temperature factors (Å^2 x10^3)

	x	y	z	Uiso
H(2)	480	11352	4098	57(19)
H(3)	690	14304	3266	57(19)
H(4)	-907	14276	2494	57(19)
H(5)	-2782	11185	2548	57(19)
H(8)	-5032	4516	2832	57(19)
H(9)	-6755	977	2871	57(19)
H(10)	-7368	-501	3746	57(19)
H(11)	-6061	104	4611	57(19)
H(12)	-4321	3794	4613	57(19)

	U11	U22	U33	U23	U13	U12
Hg(1)	51(1)	52(1)	50(1)	4(1)	3(1)	-5(1)
Cl(1)	56(3)	64(4)	65(3)	14(3)	6(2)	-7(3)
N(1)	38(8)	25(12)	65(10)	-1(7)	8(7)	-9(6)
N(2)	53(10)	52(13)	53(10)	-2(9)	15(8)	6(8)
C(1)	28(9)	36(11)	103(17)	-28(12)	22(10)	3(8)
C(2)	50(11)	48(15)	51(11)	-2(10)	-2(9)	-18(10)
C(3)	43(10)	29(12)	80(14)	18(11)	17(10)	15(9)
C(4)	77(14)	44(15)	52(12)	22(11)	20(11)	8(12)
C(5)	45(11)	53(16)	49(11)	10(10)	11(9)	0(10)
C(6)	41(9)	34(11)	50(11)	-13(9)	16(8)	2(8)
C(7)	17(8)	22(10)	106(17)	-8(11)	1(9)	1(7)
C(8)	54(12)	59(16)	66(13)	-4(14)	7(10)	-6(12)
C(9)	50(12)	52(15)	82(16)	-15(15)	-6(11)	-5(12)
C(10)	48(11)	47(13)	78(16)	-15(13)	10(11)	-21(11)
C(11)	61(12)	31(13)	64(13)	4(10)	15(10)	-6(9)
C(12)	58(12)	68(15)	50(11)	13(13)	16(9)	-1(13)

Table 3.5b Anisotropic temperature factors (A^{2} x 10^{3}) with e.s.d's in parentheses for phenylazophenyl C,N' mercury(II) chloride

The conformation of the organic ligand in the title compound can be described in terms of the angles which the phenyl rings make with the central group of coplanar atoms C(6)-N(1)-N(2)-C(7). These angles are virtually identical with mean planes of 9.7 and 8.0^0. Thus it can be seen that the Hg...N interaction has no apparent effect on the orientation of the C(1)-C(6) phenyl ring. When cosidering it as a whole, the non-hydrogen atoms of the ligand are coplanar to within ± 0.22 A^0. The mercury and chlorine atoms being displaced by 0.45 and 0.84 A^0 from the ligand mean plane.

The crystal and molecular structure of an analagous tellurium compound (2-phenylazophenyl-CN)tellurium(II) chloride has been determined by Cobbledick [92]et al. The Te....N distance reported [2.23(2) A], is shorter than that determined in the (2-phenylazophenyl-CN)mercury(II) compound. The compound was reported as being pseudo-trigonal bipyramidal. The stereochemical activity of the compound was attributed to the tellurium lone pairs. It had two discrete weakly interacting molecules in the asymmetric unit.

3.7 Mass Spectra

The mass spectrum of the (Phenylazophenyl-C,N')mercury(II) chloride showed a significant fragment of *m/e* = 799 (100%) having the correct isotopic distribution for $[(C_{12}H_9N_2)HgClHg(C_{12}H_9N_2)]^+$ Figure 3.11. This suggested that the material was not monomeric and this was confirmed from the crystallography. A possible fragmentation pattern for the compound is given in Figure 3.12

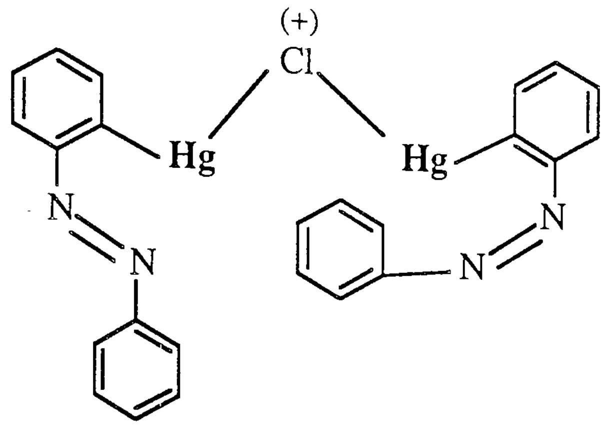
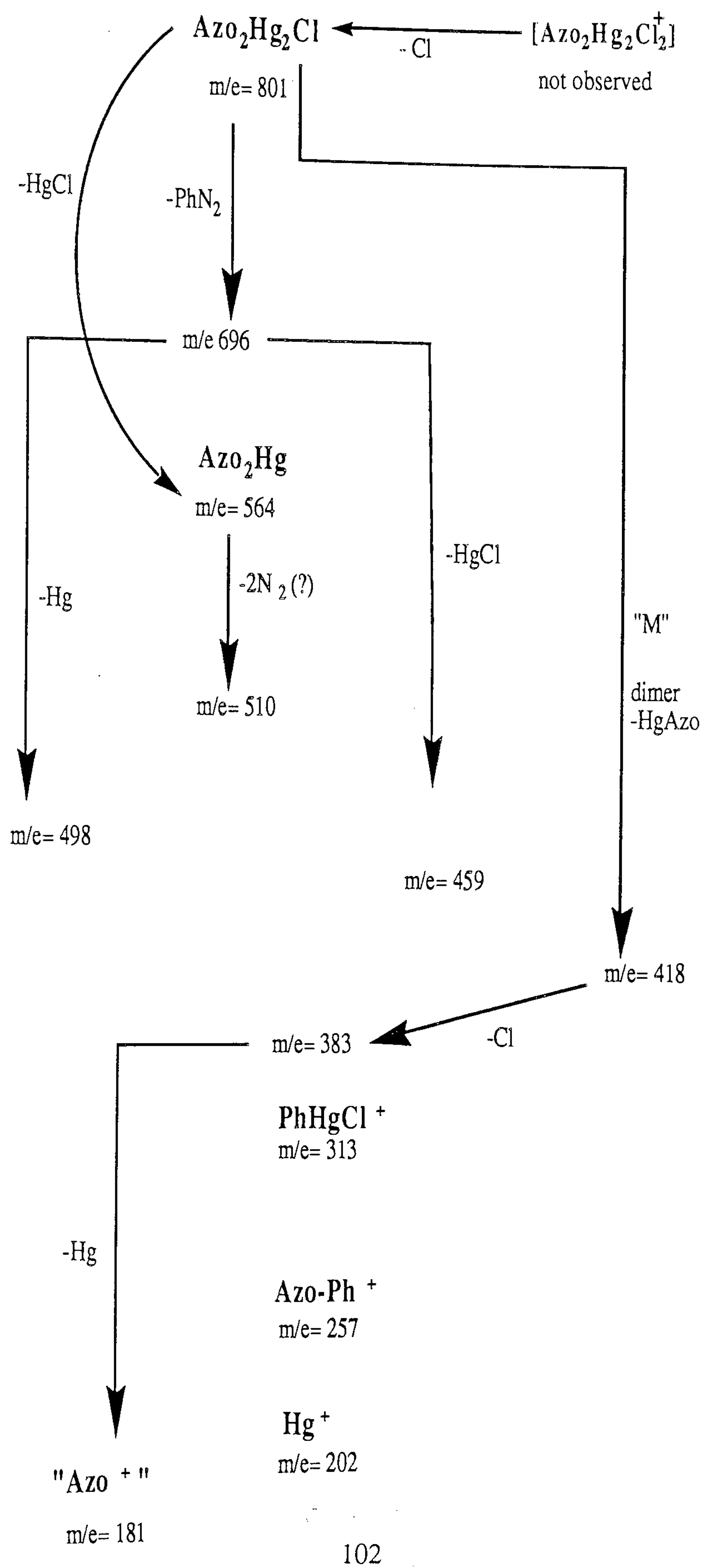


Figure 3.11 $[(C_{12}H_9N_2)HgClHg(C_{12}H_9N_2)]^+$

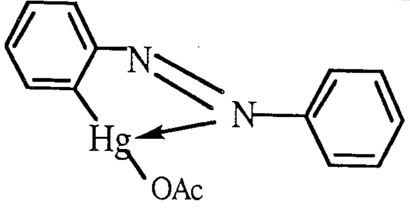
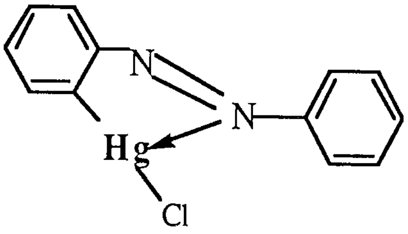
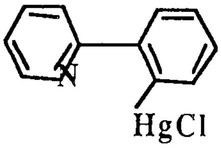
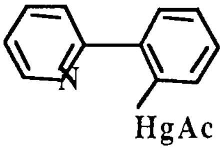
Figure 3. 11 Possible Fragmentation Pattern



3.8 MICROWAVE INVESTIGATIONS

The results[97] are summarised in Tables 3.6 and 3.7 for identical experiments conducted in the microwave and by conventional methods respectively.

Table 3.6. reaction times using microwave energy

Compound or Reaction	Time (mins)	Yield %
	30	45
	37	33
	47	--
	47	40
$[(Bipy)BiPhCl_2]_n$	6	46
$[(Me_2Bipy)BiPhCl_2]_n$	6	55
Preparation of Ph_3Bi from $Ph_4Sn + PhBiCl_2$	6	products un-isolable mixture
Azobenzene + bismuth(III) octanoate	30	" "
$PhBi(S_2CNEt_2)_2$	7	53

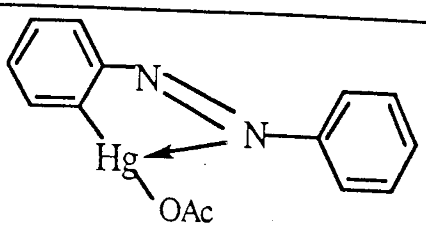
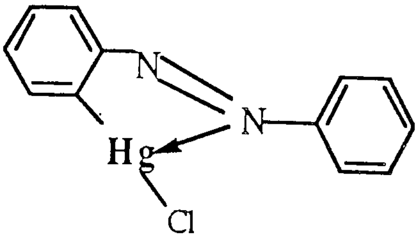
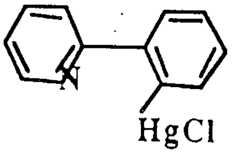
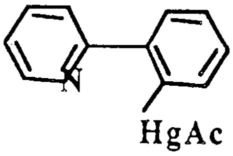
Compound or Reaction	Time Hours	Yield %
	12 - 18	45-50
	22	45
	24	36
	18 - 20	35
$[(Bipy)BiPhCl_2]_n$	3-4	30-68
$[(Me_2Bipy)BiPhCl_2]_n$	3-4	40-60
Preparation of Ph_3Bi from $Ph_4Sn + PhBiCl_2$	4	products un-isolable
Azobenzene + bismuth(III) octanoate	4	" "

Table 3.7 Reaction times using conventional heating

The material PEEK 450G does show promise although for solvent absorption does exist insome of the experiments. It has been pointed out that a polar solvent is required for the success of this method using microwave energy [99]. However strongly polar solvents are not recommended as the rate of microwave energy absorption has been noticed to be so great that a danger of the vessel exploding or deforming [97,98] becomes almost unavoidable. The data in Tables 3.6 and 3.7, clearly indicate that mercuration reactions proceed at a much faster rate under the conditions used in the microwave than when perfomed by conventional means. The relatively small scale of each microwave experiment may appear to be a disadvantage if large quantities of product are required, but the use of several vessels simultaneously for the reaction overcomes this problem. In extreme cases when many vessels are not available, several repetitions of the experiment would still represent a saving of time.Ligand redistribution reactions proceed extremely fast; for example $PhBiCl_2$ is generated in 6 minutes from triphenylbismuth and bismuth trichloride, as opposed to 3-4 hours [98] . Less successful was the reaction between tetraphenyltin and bismuth trichloride, to form triphenylbismuth; the problem was not at the microwave stage, but rather in the difficult separation of the products, Ph_2SnCl_2 and Ph_3Bi. Thus in this particular case the use of a microwave oven is not the preferred method of synthesis of either product. Other reactions [98] not concerning the use of bismuth compounds have been found to proceed well by the use of microwave energy. It was observed that sample size appears to affect the rate of a reaction when using this microwave oven method. Although this should only affect to a significant level if very large sample volumes are used. This probably occurs because the microwave penetration is affected. Thus the heating occurring below the microwave energy penetration depth is probably due to thermal conduction via molecular collisions. Some reactions were unsuccessful even by using microwave energy, if for example the direct bismuthation of azobenzene. However this method may well significantly improve yields and reaction times for other metals e.g. tellurium and warrants further investigation. The greater affinity of azobenzene for mercury than bismuth, is illustrated when a sample of bismuth trichloride, contaminated with mercuric chloride (manufactured by the same company) supplied by an American subsidiary of Mining and Chemical Products Ltd , was used. The resulting mercurated compound was characterised finally by mass spectroscopy, as elemental analysis and spectroscopic data fitted the expected bismuth analogue as well as the mercurated compound. In summary, the microwave oven is a useful addition to laboratory equipment, improving the efficiency of many syntheses.

CHAPTER FOUR

4.0 Introduction

Modern paint driers are essentially solutions of metallic soaps in hydrocarbon solvents, e.g.white spirit. These accelerate the drying process. An example is calcium and lead soaps, these give an acceptable and even drying rate. Some synergism exists as mixtures of soaps appear to be more effective than either of the individuals above. The presence of the two metals may also suggest the formation of an anionic complex of lead. It also appears that the lewis acidity of the metal ion or complex as well as the redox chemistry of the metal where reactions a & b are possible have a marked affect on the drying obtained.

reaction a ..... $ROOH + M^{(n-1)+} \rightarrow RO + M^{n+} + OH^-$

reaction b .... $ROOH + M^{n+} \rightarrow RO_2 + M^{(n-1)+} H^+$

It must be remembered that the active lead compounds are of the Pb^{2+} type. Bismuth is of a similar size. An organic group attached to bismuth produces a species RBi^{2+} which may mimic Pb^{2+}. The other point worthy of note is that organobismuth compounds are less toxic than lead. One of the objectives was thus to investigate monoorganobismuth(III) compounds, particularly carboxylates and related species. This was extended to the bismuth(v) area to include the triorganobismuth(v) carboxylates.

This area of bismuth chemistry is fairly neglected. Few literature publications are available, the work by Deacon[100] being the only publication relevant.

4.1 Experimental

Triphenylbismuth was prepared via a Grignard reaction. This compound was then used as a precursor in the synthesis of a variety of organbusmuth (III) and triorganobismuth compounds. These compounds were characterised and selected compounds were evaluated as driers in paints.

4.1.1 Synthesis of Triphenylbismuth

A Grignard method was used

$$C_6H_5Br + Mg \rightarrow C_6H_5MgBr$$

$$3C_6H_5MgBr + BiCl_3 \longrightarrow (C_6H_5)_3Bi + 3MgBrCl$$

Magnesium turnings were placed in a 2-litre round bottomed flask (3-necked), fitted with dinitrogen inlet and a reflux condenser, and were covered with dry ether. A small amount of bromobenzene (75 cm^3/ether (200 cm^3) mixture was added, together with a crystal of iodine. Once the reaction had initiated the bromobenzene/ether mixture was added at a rate which caused gentle refluxing of the reaction mixture.

On completion, a $BiCl_3$ (50 g, 0.16 moles)/ether (150 cm^3) mixture was added at a rate maintaining gentle reflux. The reaction mixture was then heated for a further 1—2 hours. When cool the reaction mixture was then poured slowly into 2 litres of ice and water with stirring. The ether layer was separated, the hydrolysis mixture extracted three times with 100 cm^3 portions of ether and the grey residue discarded. The ether portions were combined and on evaporation a yellow semi-solid remained, which upon cooling crystallised to a white solid. The crude triphenylbismuth was purified by recrystallisation from petroleum-ether (60°—80°C). The purity was assessed by melting point, elemental analysis, ir and nmr spectroscopy. A crystal was selected for crystallographic structure determination .

Melting point = 76.5°C—77°C. Lit. = 77.6°C Yield = 71%. Found: C, 48.7; H,4.60; Bi 46.1% $C_{18}H_{15}Bi$ requires C, 49.1; H, 3.41; Bi, 47.5%.

4.1.2 ^{13}C NMR of Triphenylbismuth

^{13}C nmr were recorded using a Bruker AC300 MHz Fourier Transform multinuclear magnetic resonance spectrometer ^{13}C resonances were observed within a spectral width of 17.24 KHz. Chemical shifts were referred to TMS. The Quat-D[101] pulse sequence was also used for locating quatenary carbon resonances.

TABLE 4.1

^{13}C NMR Peak Positions (in $CDCl_3$)

Peak Position	Assignment	Lit. Value [102]
137.49	Ortho	138.33
130.45	meta	131.26
127.7	para	128.52
155.14	ipso	-0.12

Due to the difference between the literature value and that experimentally determined for the positions of the peak for the ipso carbon, it was thought best to check the crystallographic structure.

4.1.3 Synthesis of Phenylbismuth Diacetate

The method[100]. used was based on the cleavage of the aryl groups from an arylbismuth(III) compound by a carboxylic acid.

e.g. $Ph_3Bi + 2Me\,COOH \rightarrow PhBi(OOC\,Me)_2 + 2PhH$

Experimental details were as described by Deacon[100] et al. % yield = 38%. MP = 183—185°C. Found C = 32.20%, H 2.90%, Bi 48.50%

$C_{10}H_{11}Bi\,O_4$ requires C = 29.70%, H 2.70%, Bi 50.98%

4.1.4 Reaction of Triphenylbismuth with Maleic Acid

To a refluxing solution of triphenylbismuth (1.0 g, 2.3 mmol) in dry diethyl ether (25 cm^3) was added a hot solution of maleic acid (0.3 g, 2.6 mmol) in dry ether (50· cm^3)· The reaction mixture was refluxed under dinitrogen for three hours. The reaction mixture was filtered hot to remove the white precipitate (product A) and the filtrate was stored under dinitrogen for 12 hours, after which a second white product (product B) was separated. Due to the low solubility of both compounds they could not be purified further.

Results

	Compound A	Compound B
Melting Point	>300°C	282—284°C
% Yield	(I)	(II)
Found (A)	C 32.2%	H 0.5%
$PhBi(Mal)_2$ requires	C 32.5%	H 2.10%
Found (B)	C 36.1%	H 1.0%
$Ph_2Bi)_2$ (OOCCH CHCOO) requires	C 35.5%	H 3.2%

Table 4.2

4.1.5 Attempted Reaction of Phenylbismuth diMaleate with Sodium Acetate

To a solution of Phenylbismuth di-monomaleate in a dmso/ethanol mixture (25 cm^3 of 4 : 3 mixture) was added a solution of sodium acetate (0.16 g, 2.2 mmol) in 15 cm^3 of the above solvent mixture. The reaction mixture was then refluxed for 3 hours. It was allowed to stand in a sealed vessel over a period of 4 weeks, whilst a precipitate developed.

The product was filtered and stored over calcium chloride subsequent analysis showed it to be an inorganic mixture. No further products were isolated.

4.1.6 Reaction of Phenylbismuth dichloride with Phthalic Acid

To a refluxing solution of phenylbismuth dichloride (0.01 moles) in dry acetone

(50 cm^3), Phthalic acid (1.67 g, 0.01 moles) in an ethanol/acetone (7 : 3) (25 cm^3) solvent mixture was added. The reaction mixture was refluxed under dinitrogen for two hours.

Two new products were isolated (referred to as I and II) Recrystallisation was not possible due to the low solubility of these compounds.

Elemental analysis

Found	C 44.80	H 7.30 (I)
	C 36.90	H 1.90 (II)

4.1.7 Synthesis of Phenylbismuth dichloride

To a solution of triphenylbismuth (1.0 g, 2.3 mmol) in dry ether (20 cm^3)was added a solution of bismuth trichloride (1.5 g, 4.6 mmol), in a dry ether (20 cm^3). The reaction mixture was gently refluxed under dinitrogen for three hours.

It was not possible to isolate the pure compound, however a white ppte formed on exposure to air or water, which was insoluble in organic solvents and was thought to be PhBiO. Due to the small quantities it was not possible to identify the product positively.

4.1.8 Synthesis of Phenylbismuth dichloride 2.2.Bipyridyl

(See section 3.2.7)

4.1.9 Reaction of Phenylbismuth dichloride with Potassium Acetate

Phenylbismuth dichloride(synthesised in-situ Section 4.1.7) (10 mmol) in acetone (50 cm^3) was heated to reflux. A white precipitate formed immediately and the reaction mixture was refluxed for a further 2 hours. The precipitate was filtered and stored over calcium chloride in a desiccator. Subsequent analysis of the product (elemental analysis, IR spectroscopy), revealed that it was largely inorganic.

4.1.10 Preparation of Potassium Octanoate

Potassium octanoate was prepared by the addition of potassium carbonate solid to a boiling solution of octanoic (2-ethyl hexanoic) acid in acetone until no carbon dioxide ($CO_2(g)$) was evolved i.e. effervescence ceased.

The product was a very viscous semi-solid clear in colour.

4.1.11 Reaction of Phenylbismuth dichloride with Potassium Octanoate

To a solution of triphenylbismuth (3.5 g, 8.0 mmol) in dry acetone (15 cm^3)

was added a solution of bismuth trichloride (5.0 g, 16 mmol) in dry acetone (20 cm^3). The reaction mixture was refluxed for 3 hours under dinitrogen. After that time a solution of potassium octanoate (4.4 g, 24 mmol)) in acetone (14 cm^3) was added. The reaction mixture was refluxed under dinitrogen for a further 3 hours.

The white precipitate was filtered off and identified as KCl. The filtrate was then stored under dinitrogen for a period of 2 days and any further KCl precipitate filtered off. The filtrate (acetone solution) was then centrifuged at 4 000 rpm for 10 mins, the acetone layer decanted. The acetone was removed by evaporation under reduced pressure. Dinitrogen gas was then bubbled through the liquid to remove any remaining traces of acetone. The viscous liquid product was then stored over calcium chloride in a desiccator. The product becomes a 'waxy' substance.

Elemental Analysis (Table 4.3)

Found	C 50.45%	H 7.99%	Bi 31.50%
Phenylbismuth octanoate requires	C 46.15%	H 6.1%	Bi 36.54%
Bismuth tris octanoate requires	C 45.14%	H 7.05%	Bi 32.76%

The ^{13}C nmr supported the bismuth tris octanoate structure; despite low carbon and high hydrogen figures.

4.1.12 Attempted Synthesis of Triphenylbismuth from Tetraphenyltin

$$3Ph_4Sn + 2BiCl_3 \rightarrow 3Ph_2SnCl_2 + 2Ph_3Bi$$

To a refluxing solution of tetraphenyltin (1.0 g, 2.4 mmol) in 100 cm^3 of a mixture of benzene and ethanol (50 : 50), $BiCl_3$ (0.6 g, 2 mmol) in 25 cm^3 of above solvent mixture was added. The reaction mixture was refluxed for 3 hours under dinitrogen.

The starting materials were recovered unreacted.

4.1.13 Attempted Synthesis of Phenylbismuth Thioacetate

To a solution of phenylbismuth dichloride (prepared as in section 4.1.8) was added potassium thioacetate (0.5 g, 3.5 mmol) in 25 cm^3 absolute ethanol. The reaction mixture was refluxed under dinitrogen for three hours. The potassium thioacetate was recovered unreacted.

The organobismuth (III) compounds were found to be only sparingly soluble and thus difficult to purify. It was decided to synthesize penta valent compounds, in order to obtain crystals of suitable quality for crystallography. Triphenylbismuth dichloride was selected as the precursor for the synthesis.

4.1.14 Synthesis of Triphenylbismuth dichloride

$$Ph_3Bi + SO_2Cl_2 \rightarrow Ph_3BiCl_2 + SO_2\uparrow$$

To a solution of triphenylbismuth (3.0 g, 6.82 x 10^{-3} moles) in petroleum ether (40—60) (40 cm^3), was added dropwise a solution of sulphuryl chloride (1.0 g

7.4 mmol) in petroleum ether (40-60) (20 cm^3) under dinitrogen, and the reaction mixture was stirred at room temperature for 30 minutes. The white product was filtered and washed with cold petroleum ether. (40—60°C). The crude product was recrystallised from benzene and stored in a desiccator in the dark.

Yield = 86.6% Mp = 146°C Lit = 142°C.

Found	C 40.40%	H 2.80%	Bi 39.90%
$C_6H_5BiCl_2$ requires	C 42.27%	H 2.94%	Bi 40.90%

4.1.15 13C NMR of Triphenylbismuth dichloride (wrt TMS)

Carbon	ppm	Assignment
C1	206.08	ipso
C2	135.14	ortho
C3	132.54	meta
C4	132.43	para

Table 4.3 13C nmr assignments for triphenylbismuth dichloride

4.1.16 Synthesis of Triphenylbismuth Carbonate

$$Ph_3BiCl_2 + K_2CO_3 \rightarrow Ph_3BiCO_3 + 2KCl \downarrow$$

To a solution of triphenylbismuth dichloride (6.0 g, 0.012 moles) in dry tetrahydrofuran (40 cm^3), a solution of potassium carbonate (1.62 g, 0.012 moles) in water (15 cm^3) was added. Dinitrogen was bubbled through the mixture.

The mixture was warmed whilst being stirred to temperature range between 40—45°C for 4 hours and then allowed to cool to room temperature with continued stirring.The reaction mixture was then filtered and the separated solid washed with tetrahydrofuran, followed by distilled water and finally twice with tetrahydrofuran. The white product was allowed to dry in a desiccator and stored in the dark.

Yield = 89%

Found	C 45.40%	H 3.08%	Bi 42.05%
$C_6H_5BiCO_3$ requires	C 45.60%	H 3.00%	Bi 41.80%

4.2 SYNTHESIS OF PENTAVALENT ORGANOBISMUTH CARBOXYLATES

4.2.1 Synthesis of Triphenylbismuth oxalate

$Ph_3BiCl_2 + 2\ NaOOC \rightarrow$ Products

To a solution of triphenylbismuth dichloride (1.0 g , 2.0 mmol) in benzene (100 cm^3) a solution of sodium oxalate (0.3 g, 4.0 mmol), in water (50 cm^3) was added. The reaction mixture was shaken on a Stuart flask shaker for 8 hours. Afterwards the benzene layer was separated and the aqueous layer extracted three times with 20 cm^3 portions of benzene. The benzene portions were combined and concentrated under reduced pressure. The addition of petroleum ether (40—60) caused the precipitation of the crude product. This was purified by recrystallisation from a benzene/petroleum ether solvent mixture (60 : 40).

Yield = very poor $\approx$ 10%

4.3 Synthesis of Organobismuth Carboxylates by Phase Transfer Catalysis

Conventional reflux methods were not successful in the preparation of triorganobismuth compounds. therefore, the use of phase transfer catalysis in their synthesis was investigated.

4.3.1 Introduction

One of the major developments in organic chemistry has been the use of phase transfer catalysis in the synthesis of a variety of compounds[103,104]. In this work the technique has been applied to organobismuth reactions.

These reactions are performed in an aqueous base/organic two phase solvent system, with the use of an ammonium or phosphonium salt as a catalyst. Crown ethers have also been used, but in solid-liquid systems. The technique usually allows reactions to be performed under relatively mild conditions.

4.3.2 Synthesis of Triphenylbismuth Carboxylates by Phase Transfer Catalysis

A Phase transfer method was used. Triphenylbismuth dichloride was reacted with a variety of metal carboxylates in the presence of a phase transfer catalyst.

$$Ph_3 BiCl_2 + 2MCOOR \rightarrow Ph_3Bi(OOCR)_2 + 2MCl \downarrow$$
$$R = [COOM, Me , C_6H_5, CH_3CH_2, CH_3 COSM]$$

The experimental procedure used was as described for the synthesis of Triphenylbismuth oxalate except for the following modifications :-

(i) A small quantity of But N E $t_3^+Br^-$ was added to the reaction mixture.

(ii) The length of reaction time was increased to 48 hours.

4.3.3 Synthesis of t-BuNEt$_3^\pm$ Br$^-$

Equal portions of Triethylamine and butyl bromide were mixed and heated for 15 minutes in a fume cupboard, or until a white precipitate is formed.

4.4 Results

Compound	Melting Point /°C
Triphenylbismuth oxalate	151
" " acetate	162—164
" " propionate	160—161
" " benzoate	165—166
" " thioacetate	—
" " octanoate	98—99

Table 4.4 Melting points of organobismuth carboxylates

Compound	Experimental			Calculated		
	%C	%H	%Bi	%C	%H	%Bi
Triphenylbismuth oxalate	-	-	-	-	-	-
" " diacetate	47.10	4.01	37.20	47.31	3.76	37.46
" " dipropionate	49.20	4.20	35.52	49.15	4.27	35.67
" " dibenzoate	56.10	3.70	30.53	56.30	3.76	30.65
" " dioctanoate (2-ethyl hexanoate)	56.01	4.19	28.50	56.20	4.13	28.79

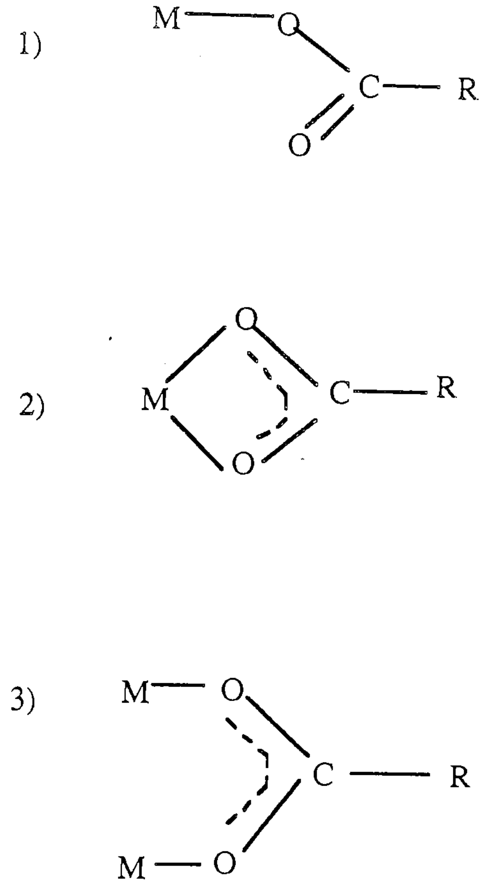
Table 4.4a Elemental Analysis results for organobismuth Carboxylates

4.4.1 Infra-Red Spectroscopy

The carboxylate ion may co-ordinate to a metal in a number of ways :-

Coordination modes between a metal and carboxylate ion

FIGURE 4.0



Deacon and Phillips[104a] studied the infra-red spectra of many carboxylates of which the crystal structures were already known and a set of rules for carboxylate complexes were derived:-

(1) The type of co-ordination can be predicted by examining the separation of the asymmetric and symmetric stretching modes of the carboxylate group.

(2) Unidentate complexes having the type of structure shown in diagram 1, exhibit Δ values for $[\gamma_a (CO_2^-) — \gamma_s (CO_2^-)]$ which are greater than the ionic complexes.

(3) Chelating or bidentate complexes (diagram 2) exhibit Δ values which are significantly smaller than those of the ionic complexes.

(4) Bridging complexes (diagram 3) exhibit Δ values greater than the chelating complexes and close to ionic values.

4.4.1.1 Infra-Red Data

Table 4.5 Infra-red data for Arylbismuth(III) compounds.

Compound	γcm^{-1}	
Assignment		
Ph_3Bi	1056	q
x sensitive modes for PhBi	449	y
	232	t
t mode approximates	well to γ (BiC)	
$PhBi(OOCMe)_2$	1550 (s)	γ asym [COO]
	1435 (s)	γ sym [COO^-]
$PhBi\ (OOCCHCHCOOH)_2$	3428	O—H stretch
	1585 (s)	γ asym[COO]
	1533 (s)	γ asym [COO]
	1436	
	1297	γ sym [COO]
	1261	γ sym [COO]
$(Ph_2Bi)_2\ (OOCCHCHCOO)$	1588	γ asym [COO]
	1483	γ asym [COO]
	1395	
	1363	γ sym [COO]

Phenylbismuth phthalate		
	(I)	1627
		1601
		1569
		1432
		1368
	(II)	1648
		1627
		1573
		1536
		1450
		1432

Table 4.6 infra-red data for Triarylbismuth compounds

Compound	γ (cm^{-1})	Assignment
Triphenylbismuth oxalate	1636	γ asym [COO^-]
	1380	γ asym [COO^-]
	1253	γ sym [COO^-]
Triphenylbismuth diacetate	1588	γ asym [COO^-]
	1572	γ asym [COO^-]
	1385	γ sym [COO^-]
	1331	γ sym [COO^-]
Triphenylbismuth dibenzoate	1600	γ asym [COO]
	1560	γ asym [COO]
	1491	
	1448	
	1351	γ sym [COO]
	1326	Shoulder
Triphenylbismuth dipropionate	1596	γ asym [COO]
	1377	
	1356	
	1269	
Triphenylbismuth dioctanoate		

4.4.2 NMR of Triphenylbismuth Carboxylates

4.4.2.1 Triphenylbismuth dipropionate ^{13}C NMR in $CDCl_3$ (wrt TMS)

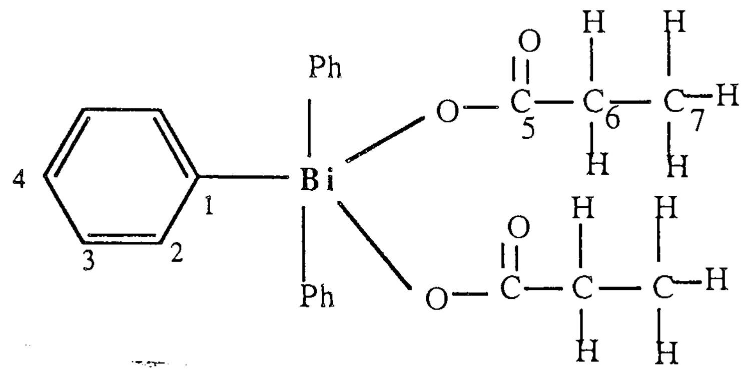


Figure 4.1 Triphenylbismuth dipropionate

C1	160.98
C2	133.91
C3	131.01
C4	130.53
C5	—
C6	28.75
C7	10.13

The ^{13}C nmr was recorded on a Bruker AC300 MHz Fourier-Transform multinuclear magnetic resonance spectrometer. ^{13}C resonances were observed at 438.57 Hz/cm with a spectral width of 16.67 KHz.

4.4.3 ^{1}H NMR (wrt TMS)

4.4.3.1 Triphenylbismuth dipropionate

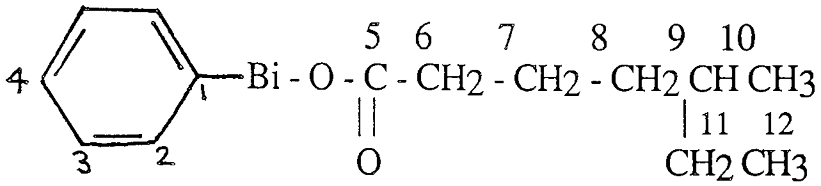
ppm Range	Multiplicity	Relative Integral	Assignment
8.10—8.20		6	Aromatic Ring
7.62—7.52	3 x triplet	9	
7.48—7.40	3 x triplet		
2.10—2.02	quadruplet	4	Ethyl Group
0.91—0.86	triplet	6	
	TOTAL	25	

Table 4.7 Proton NMR assigments for triphenylbismuth dipropionate

The total number of protons predicted from the relative integrals of the peaks agrees with the structure of the propionate.

Note: The presence of three triplet for the aromatic rings suggests that the phenyl rings may be inequivalent.

4.4.4 ^{13}C NMR of Triphenylbismuth di-octanoate in $CDCl_3$ wrt TMS



^{13}C assignments

	PPM		PPM
C1	161.73	C7	29.28
C2	134.13	C8	26.15
C3	130.64	C9	47.91
C4	130.28	C10	13.79
C5	182.67	C11	22.55
C6	32.64	C12	11.47

Table 4.8

4.4.5 NMR Investigation of Stability of Phenylbismuth dimonomaleate Complexes in dimethylsulphoxide

Deacon[100]. et al reported the instability of complexes of the type R Bi $(OOCR)_n$ in DMSO solutions. The authors studied the acetate complex and noted changes in the ^1H nmr spectra in DMSO solution when recorded at different times.

The ^1H nmr spectrum of the phenylbismuth di-mono-maleate was recorded in DMSO solution, at time intervals of 0 mins, 4 hours and 12 hours. No changes were observed.

4.5 STRUCTURAL CHEMISTRY OF ORGANOBISMUTH COMPOUNDS

The structural chemistry of organobismuth(III) carboxylates is limited. The structure of $[Ph_2Bi(O_2CCF_3)_2]$ complex has been reported[105] and of diphenylbismuth N-benzoylglycinate[106]. $Ph_2\,BiO_2\,CCH_2\,NHCO\,C_6H_5$
The same authors have reported the crystallographic structure of Bis [2-furoato (1) triphenylbismuth(V) $[\,Bi\,(C_5H_3O_3)_2\,(C_6H_5)_3\,]$.[107]

Attempts were made to determine crystallographic structures of some of the organobismuth carboxylates synthesised.

Crystallography

4.5.1 Crystal Structure Of Triphenylbismuth Oxalate

Unit Cell

Monoclinic P

$\alpha = 90.0440(10)$ β 90.1202(3) $\gamma = 89.9680(7)$

a = 9.2263(20) b 22.3969(5) c 17.2195(4)

The crystal suffered from x-ray degradation and thus the crystal structure could not be determined.

4.5.2 Crystal structure of Triphenylbismuth dipropionate

The crystals had surface imperfections and even on double recrystallisation the imperfections were enough to stop the structure from being determined.

4.5.3 Crystal Structure of Triphenylbismuth

Due to the presence of anomalous peaks in the ^{13}C nmr spectrum (section 4.1.2) of triphenylbismuth, it was thought to warrant a crystal structure determination. The original determination was reported by Ferguson[108] quite a long time ago and more accurate cell dimensions and bond lengths were sought. The crystal structure was determined and although initially a different unit cell was used it was found on applying a transformation the cell agreed with the literature report. Hence the structure was not refined further and is not reported here.

Characterisation of samples supplied by Manchem Ltd.

Some samples prepared by the Industrial sponsor Manchem Limited, were included in the characterisation studies. All of the samples were liquids or semi-solids. Of the samples provided (Table 4.9)

Octanoic acid
Versatic acid
Naplthenic acid
Bismuth octanoate
Bismuth versatate
Bismuth naplthenate

Table 4.9

The octanoates, and versatates were selected for characterisation. (Table 4.10)

	Elemental Analysis Experimental %C	 %H	 Expected %C	 H%
Bismuth Octanoate	50.80	8.30	45.14	7.05
Octanoic Acid	65.70	10.85	66.67	11.11
Versatic Acid	68.8	11.1	—	—
Bismuth Versatate	49.9	8.5	—	—

Table 4.10 Samples supplied by Manchem Ltd selected for characterisation

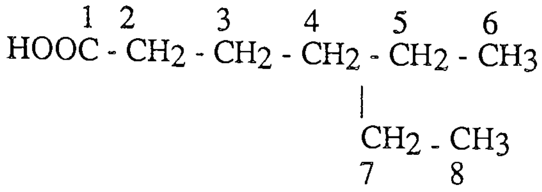
Gel permeation chromatography was performed on the octanoic acid and versatic acids provided. The octanoic acid was found to be of a satisfactory standard of purity. The chromatogram of versatic acid showed two major components. Thus the ^{13}C nmr of the versatic acid was expected to be complex. However the spectrum recorded was certainly not expected. (Figure 4.2). The presence of two sets of peaks (Figure 4.4) at 183—185ppm in the carboxylate carbon region may be due to some isomers.

Comparison of the γ_{asym} [COO$^-$] — γ_{sym} [COO$^-$] parameter (ΔV) for the bismuth octanoate indicates that the octanoate is interacting with the bismuth as a unidentate ligand as expected for bismuth carboxylates.

4.5.3.1 ^{13}C NMR

^{13}C nmr spectra for Octanoic acid, bismuth octanoate and versatic acids were recorded.

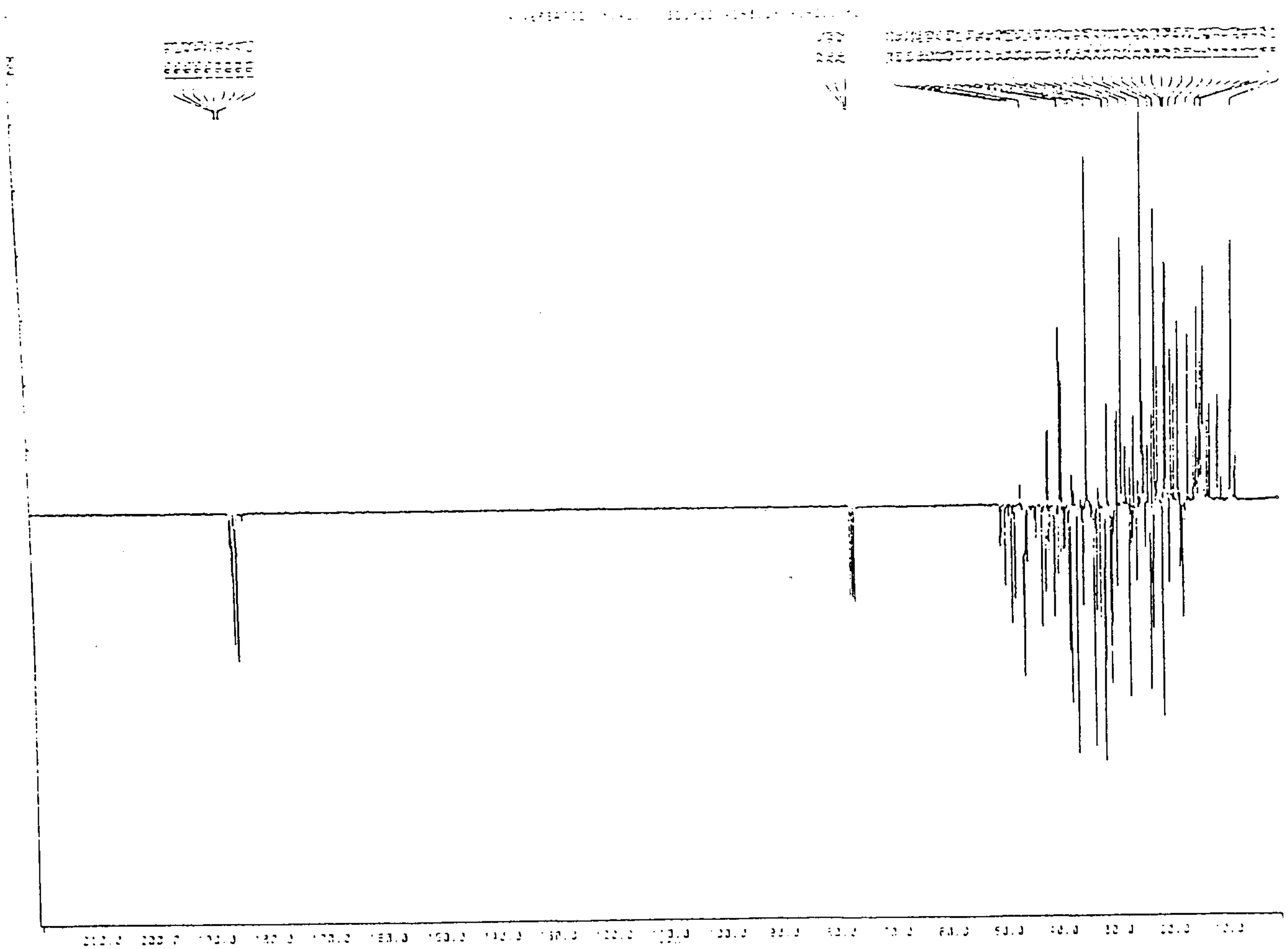
Peak Assignments



$$\begin{array}{l} \mathrm{HOO}\overset{1}{\mathrm{C}} - \overset{2}{\mathrm{CH_2}} - \overset{3}{\mathrm{CH_2}} - \overset{4}{\mathrm{CH_2}} - \overset{5}{\mathrm{CH_2}} - \overset{6}{\mathrm{CH_3}} \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\quad \underset{7}{\mathrm{CH_2}} - \underset{8}{\mathrm{CH_3}} \end{array}$$

	PPM		PPM
C1	183.04	**C7**	22.37
C2	31.22	**C8**	11.37
C3	29.29		
C4	24.92		
C5	46.93		
C6	13.53		

The ^{13}C nmr of versatic acid was not able to be interpreted and assignments were not made, for reasons which are apparent on examining the NMR spectrum (Figure 4.2-4).



^{13}C nmr spectrum of versatic acid

FIGURE 4.2

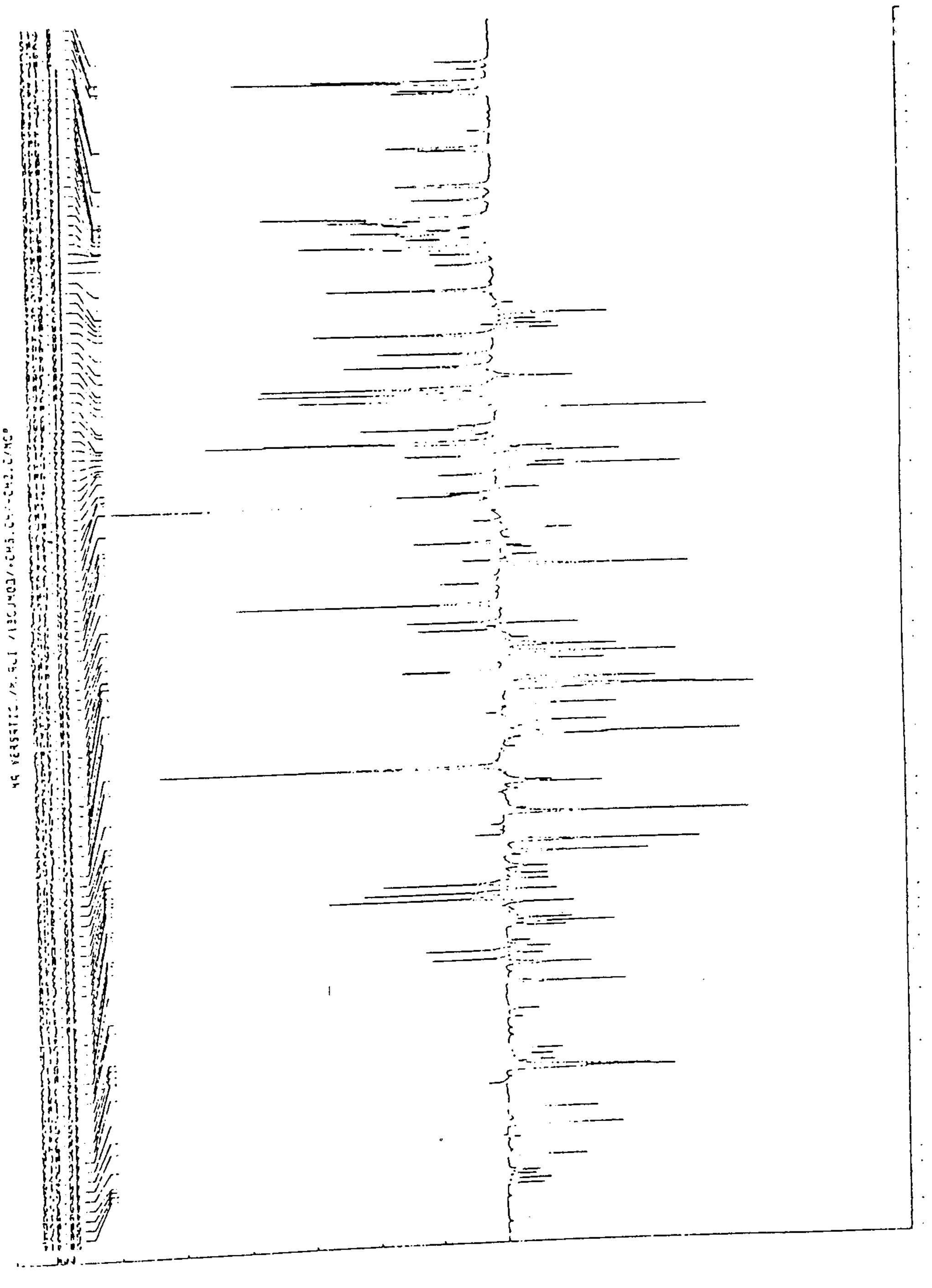
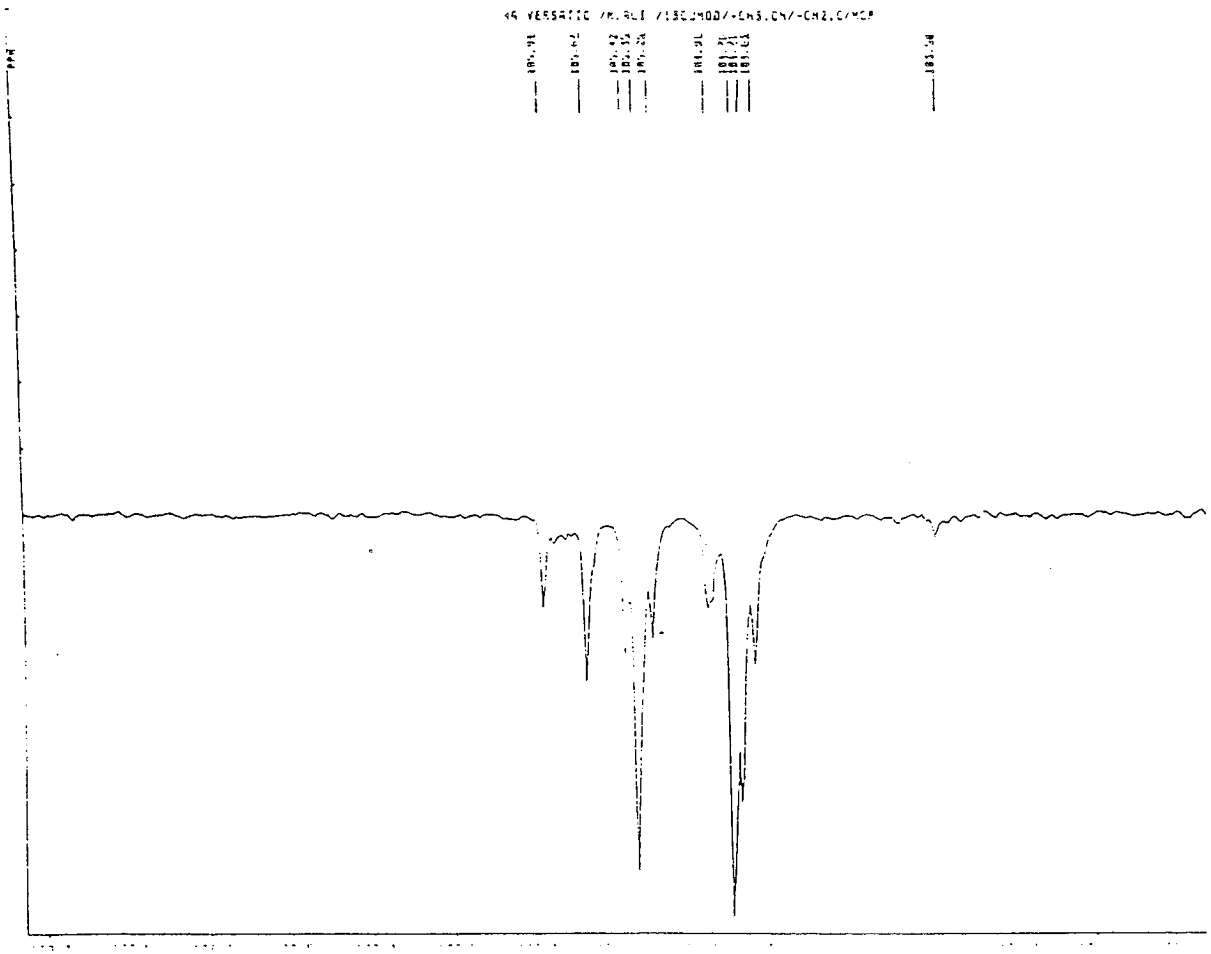
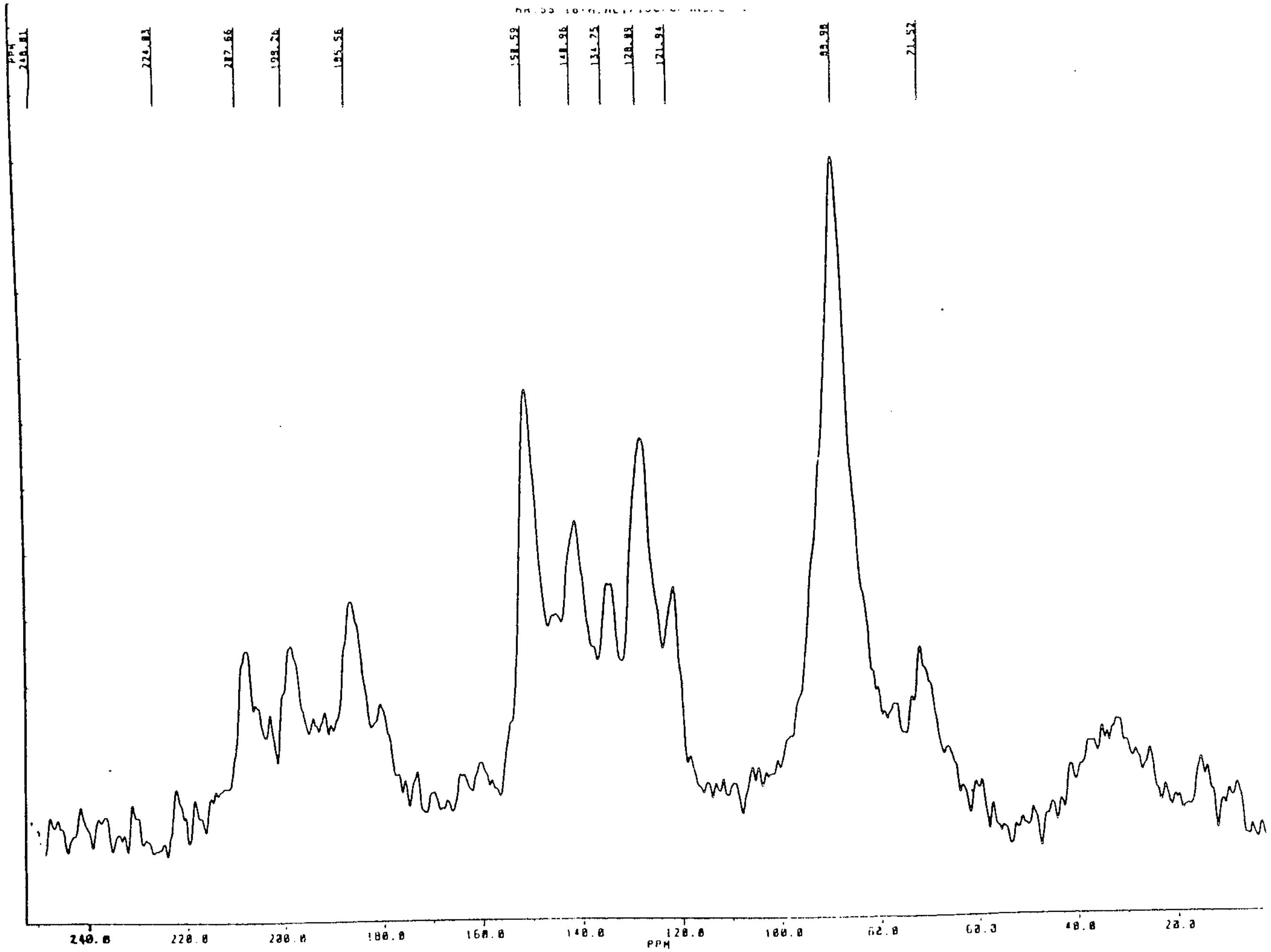


FIGURE 4.3

^{13}C nmr of versatic acid (expansion of 10-60ppm region)



^{13}C nmr of versatic acid (expansion of 160-180ppm region) FIGURE 4.4



Solid state ^{13}C nmr spectrum of $PhBiCl_2$.Bipy complex

FIGURE 4.5

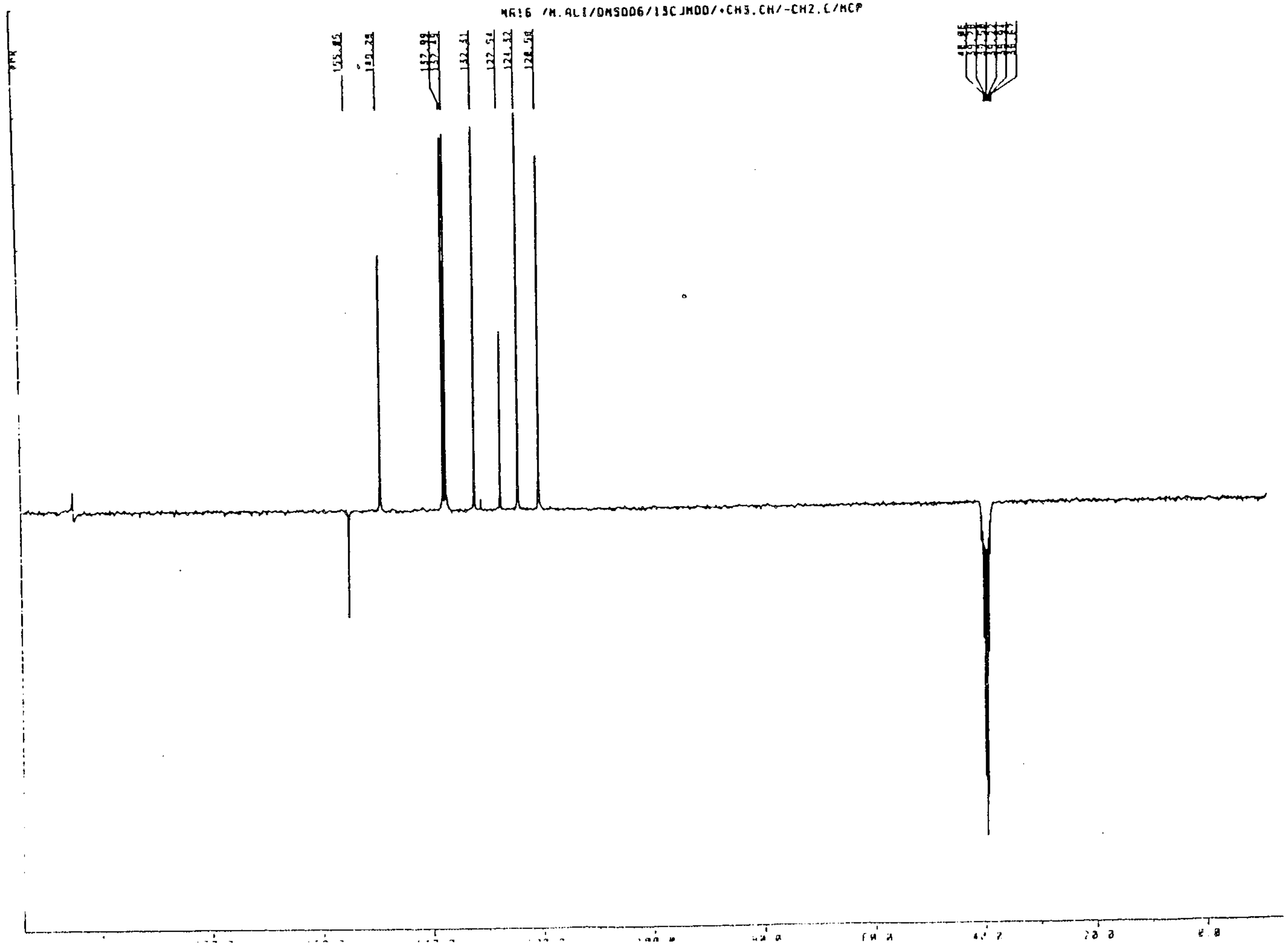


Figure 4.6 ^{13}C nmr spectrum of $PhBiCl_2$.bipy in DMSO-D6

Figure 4.7 ^{13}C (proton decoupled) NMR spectrum of phenylbismuth dimonomaleate

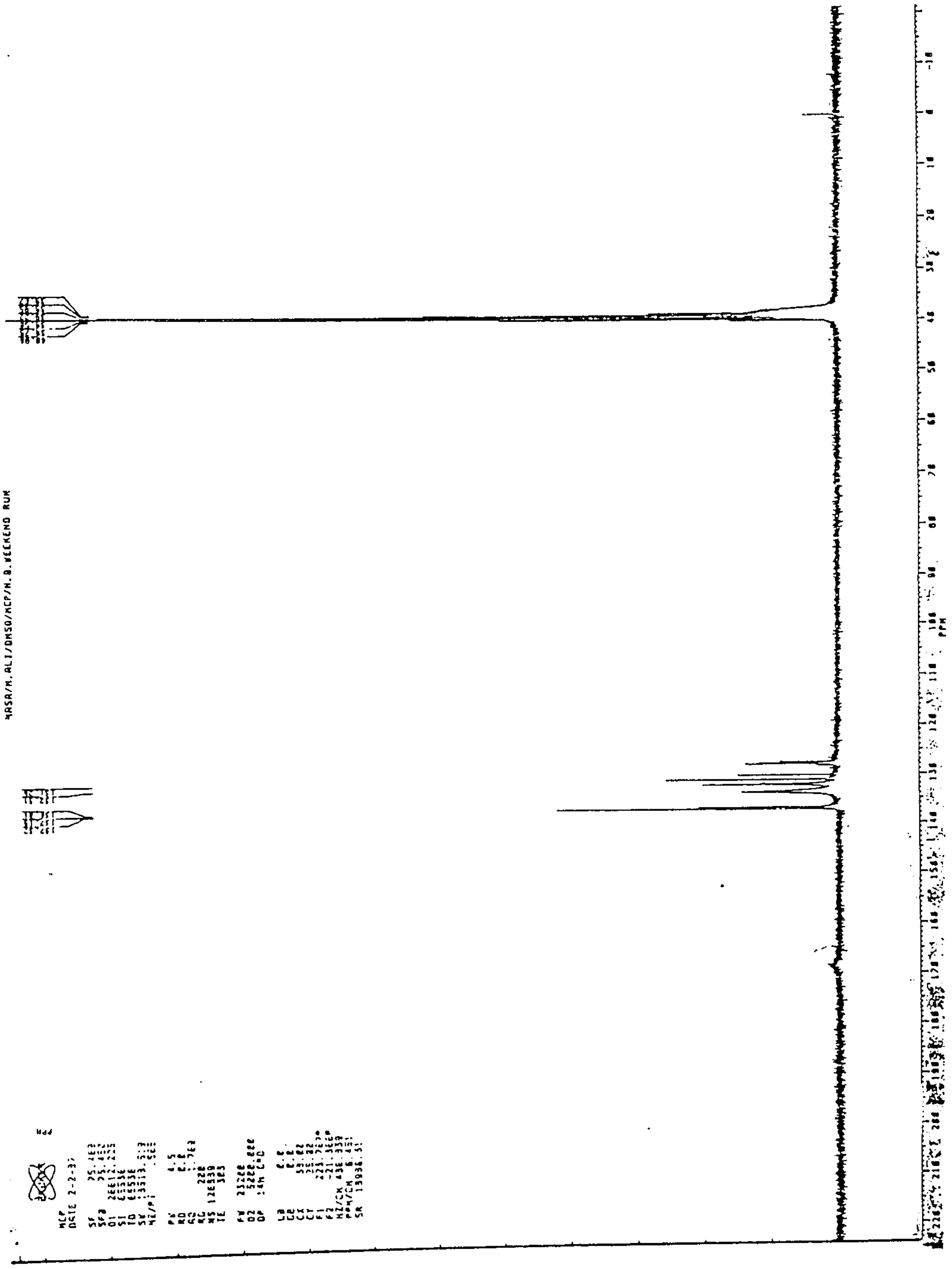


Figure 4.8 ^{13}C (proton decoupled) NMR expansion of phenylbismuth

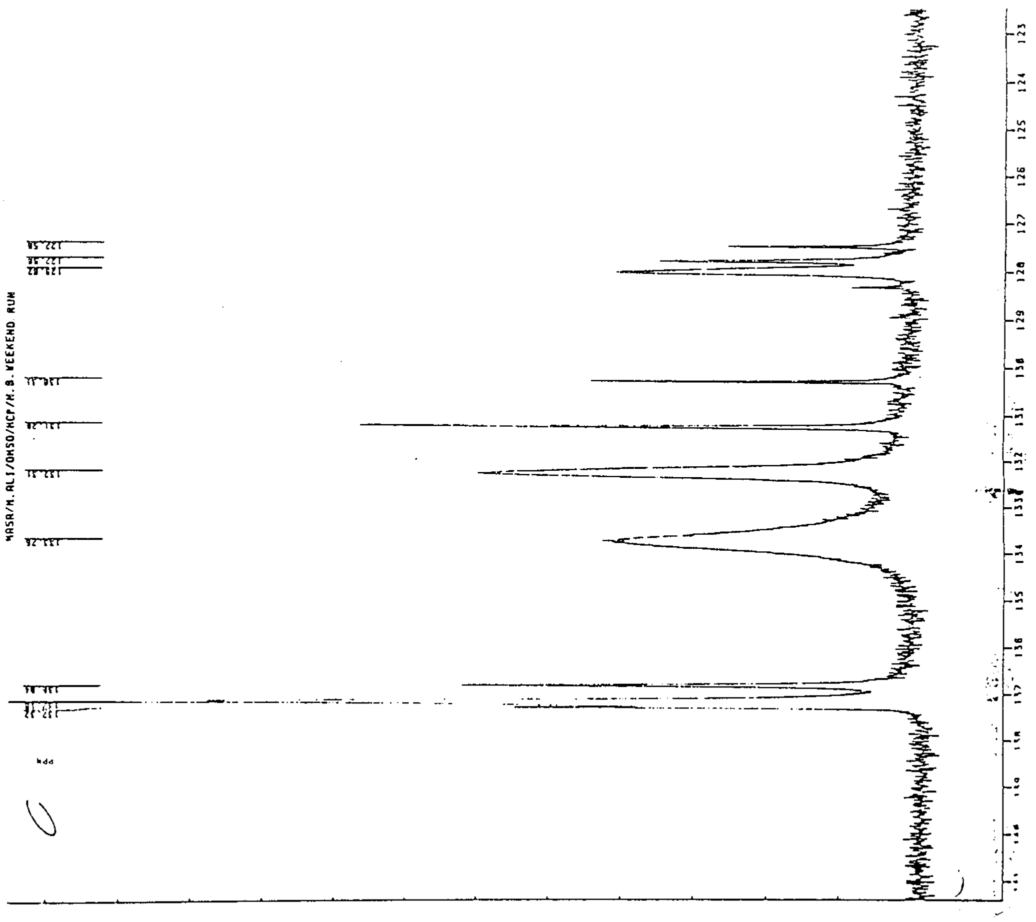
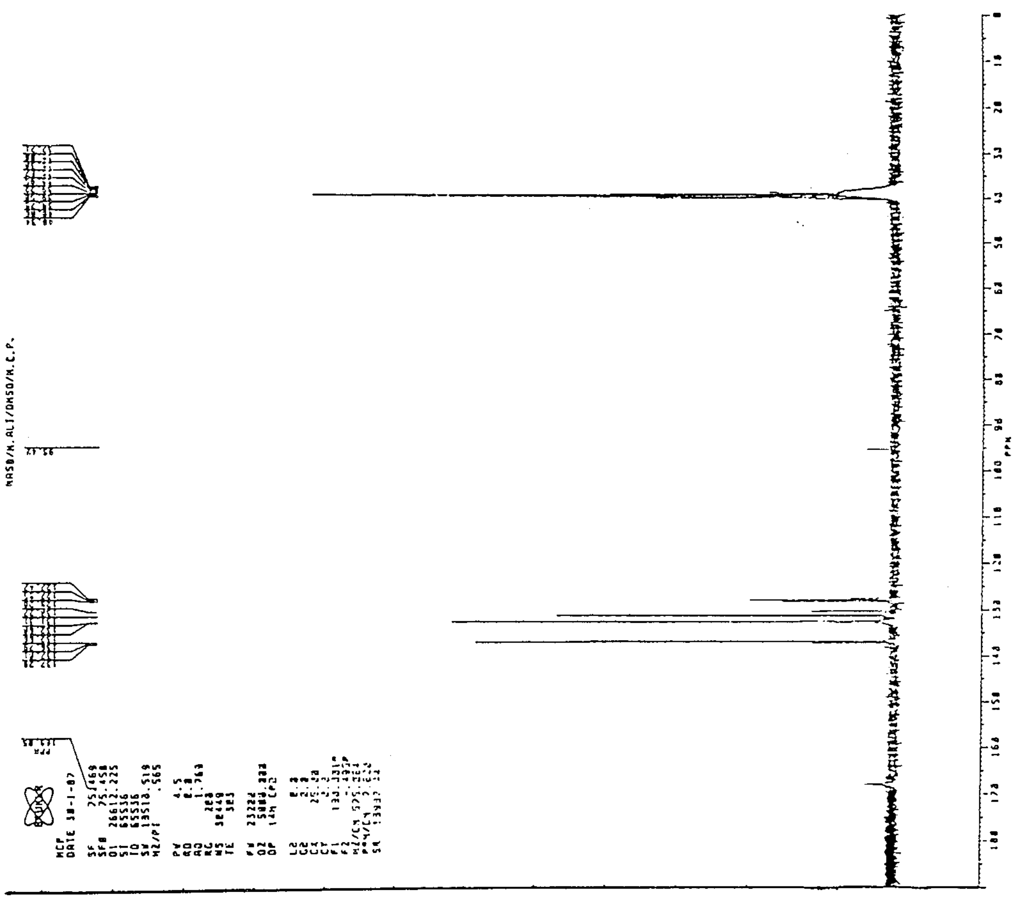


Figure 4.9) ^{13}C (proton decoupled) NMR spectrum of bridged monomaleate $(ph_2Bi)_2$ $(O_2CCH = CHCO_2)$



4.6 DISCUSSION

4.6.1 Arylbismuth(III) Carboxylates

There has been little work on these components and subsequently little is known about their chemistry.

The cleavage of Bi—C bonds of triphenylbismuth by a carboxylic acid (1), appears to be a successful method for the synthesis of these compounds to a satisfactory standard of purity. Initial purity was important since insolubility did not allow recrystallisation.

$$(1) \quad Ar_3Bi + n\,RCOOH \longrightarrow Ar_{3-n}\,Bi(OOCR)_n \quad n = 1 \text{ or } 2$$

An equilibrium appears to exist between the reactants and products. This would account for the relatively low yields obtained.

The use of a phase transfer catalysis method may improve the yields of these compounds. Infra-red data (Table 4.5) and m.pt. for the phenylbismuth diacetate prepared by this method were concordant with the literature[100]. values.

The reaction between maleic acid and triphenylbismuth resulted in two products. Analytical and spectroscopic data fit the structures $PhBi(OOCCHCH\,COOH)_2$ and the bridged mono-maleate structure $(Ph_2Bi)_2$ $(OOCCHCHCOO)$. As expected, the infra-red spectra of these compounds show the COO group vibrations and the consequent disappearance of the carbonyl absorption band characteristic of free carboxylic acids.

The γ_{sym} and γ_{asym} vibrations of the COO group for both maleates (Table overleaf) show the type of interactions involved in both complexes.

Compound	*$\Delta\gamma$ (cm^{-1})
Potassium maleate	157
PhBi $(OOCCHCHCOOH)_2$	280
$(Ph_2Bi)_2$ OOCCHCHCOO	156

*$\Delta\gamma$ = Separation between γ sym and γ asym

<u>Infra-red data for phenylbismuth diacetate</u>

The increase in separation for one of the organobismuth maleates substantiates the structure proposed, of the maleate behaving as a unidentate ligand towards the bismuth, whereas the second product is behaving as a bridging ligand. The possibility that the doublet COO peaks in the i.r. spectrum were due to the two carboxylate groupings being in different environments was considered, but appears not to be valid in these cases, as the analytical data support the proposed structures.

^1H nmr spectra were recorded in deutero dimethylsulphoxide solutions for both compounds. For the Phenylbismuth di-monomaleate the spectrum was recorded over two days. The complex spectrum obtained has been suggested by Deacon[100] to be due to the occurrence of a rearrangement reaction of the carboxylate.

$$\mathrm{PhBi\ (OOCCHCHCOOH)_2} \longrightarrow$$
$$\mathrm{(Ph_2Bi)_2(OOCCHCHCOO) + Bi(OOCCHCHCOOH)_3}$$

Note: Equation not balanced.

To investigate this a time dependent ^1H nmr study was performed. The maleate spectrum remained unchanged, and thus the complexity may be due to second order effects.

^{13}C nmr spectra (Figure 4.8,4.9) revealed the position of the ipso carbon. The spectra also gave information as to the shielding and electron release effects involved. The observed trend

COO ipso ortho meta para

<————————————————

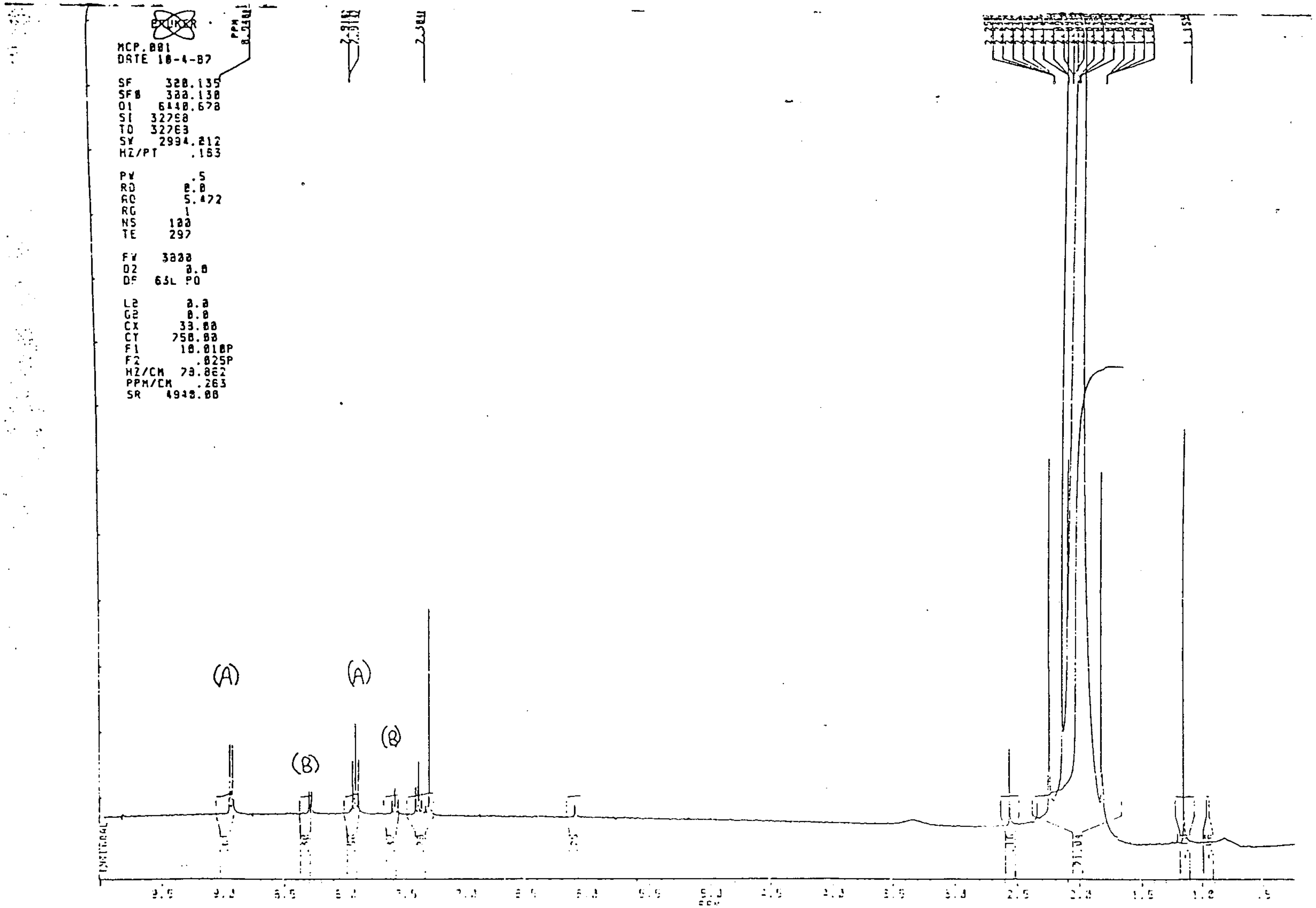
agrees with the trend expected because of the effects of the electron release from the bismuth to the phenyl ring. (Figure 4.8) illustrates quite neatly the diminishing quadrupolar effect of Bi on the neighbouring carbon atoms with distance. The ipso carbon giving the broadest resonance. This is probably due to scalar spin-spin relaxation.

4.6.2 Phenylbismuth dichloride

A survey of the published literature has only served to emphasize the uncertainty surrounding the nature and stability of this compound. Although it was readily prepared from triphenylbismuth and bismuth trichloride in ethereal solutions, the presence of slight traces of moisture caused hydrolysis, and resulted in the formation of a white precipitate, probably phenylbismuth oxide.[109] In prolonged exposure to air the white precipitate changed to a dark brown semi-solid, probably a polymeric compound.

^{1}H nmr studies (in deutero-acetone) resulted in a very complicated spectrum. (Figure 4.10). The spectrum was expected to consist of a doublet (downfield @ 8.8. wrt TMS cf Ph_3Bi) and two triplets due to the meta and para hydrogens of the phenyl ring, as reported by Smith and Waller.[110] The complexity of the spectrum may be explained by a disproportionation, hydrolysis or rearrangement reaction occurring in solution, producing Ph_3Bi, PhBiO or Ph_2BiCl. Integration of the spectrum shown the ratio doublet (A) : doublet (B) (Figure 4.10) is 2 : 1 suggesting that (A) may be due to the ortho phenyl ring proton of Ph_2BiCl whilst (B) may be due to the equivalent proton in $PhBiCl_2$ (or PhBiO), although the ratio does not hold for the triplets (C) and (D). The multiplet at $\sigma = 7.4$ may be due to second order effects.

Attempts at obtaining an infra-red spectrum of the compound (in acetone) were unsuccessful because of the extremely rapid rate of hydrolysis on exposure to air.



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MCP.001
DATE 10-4-87

SF     300.135
SFO    300.130
O1    6440.670
SI   32768
TD   32768
SW    2994.012
HZ/PT      .183

PW          .5
RD         0.0
AQ         5.472
RG         1
NS       100
TE       297

FW     3800
O2         0.0
DP    63L PO

LB         0.0
GB         0.0
CX        33.00
CY       750.00
F1        10.010P
F2          .025P
HZ/CM    78.962
PPM/CM     .263
SR      4940.00
```

Fig 4.10 Proton nmr spectrum of $PhBiCl_2$ in deuteroacetone

The observations throughout this work suggest that Phenylbismuth dichloride can only be formed in solution and is extremely unstable with regard to hydrolysis, in disagreement with Smith and Waller.[110]

4.6.3 Stabilisation of Phenylbismuth dichloride

Nitrogen donors were considered as a means of stabilising the phenylbismuth dichloride. The 2,2,bipyridyl ligand proved extremely successful. In fact much more so, than anticipated. The adduct was found to be sparingly soluble in nitromethane and dichloromethane. It was soluble in dimethylsulphoxide. Attempts at recrystallisation inorder to grow crystals of a suitable size for X-ray crystallographic studies, using a nitromethane/dmso solvent mixture resulted in the formation of platelets. The adduct appears to discolour on prolonged exposure to light or air. It also readily takes on a pink colourations, probably due to traces of iron in the solvent used.

The infra-red spectrum showed the presence of three new bands (300 cm^{-1} — 200 cm^{-1}) and these may be attributed to the Bi-phenyl ring, Bi-N and Bi-halide vibrations, as these are expected in this region. The spectrum in the 1600 cm^{-1} — 400 cm^{-1} was consistent with that of co-ordinated bipyridyl. The ring vibrations undergo slight modifications and shift from 1581 and 1547 cm^{-1} (free bipy) to higher frequencies in the adduct (1591 and 1566 cm^{-1}) as would be expected. The shift of the peak from 993 cm^{-1} (free ligand) to 1012 cm^{-1} (adduct) together with the corroborating shift of the band at 757 cm^{-1} (γ C—H) and shoulder at 738 cm^{-1} are diagnostic of co-ordination of bipyridyl to a metal. The latter is also split in the adduct and this could indicate two bipy units in molecular unit i.e. $[(bipy)BiPhCl_2]_n$ n>1. This is consistent with co-ordinated bipy spectra. The far infra-red region of the spectra on examination showed the presence of modes involving contribution from the bismuth-bipy bond vibrations. A band at 402 cm^{-1} (free bipy spectrum) was shifted to 411 cm^{-1} in the adduct spectrum. This band is probably due to ring deformation (ØCC). A new band appeared at 347 cm^{-1}.

Nmr spectra of the adduct in deutero dimethylsulphoxide shared the pyridine resonances as expected and the position of the phenyl ring carbon ipso (155.05 ppm) ortho, meta and para 179.28, 137.99, 137.49 ppm respectively (wrt TMS). ^{13}C CP MASNMR of the solid compound showed considerably broadening of the peaks and subsequently poorer resolutions, but in general the spectrum was in good agreement with that obtained in solution. If only one bipy and one Ph environment are seen, this suggests structure with some elements of symmetry. (Figure 4.5 and 4.6).

4.6.4 Triarylbismuth Compounds

Numerous triarylbismuth compounds were synthesised. The triphenylbismuth and triphenylbismuth carbonate prepared had physical properties in agreement with expectation.

4.6.5 Triarylbismuth Carboxylates

These compounds were prepared as described in section 4.3.2

The infra-red spectra of these compounds were found to be useful in providing information of the interaction of the carboxylate with the bismuth. (Section 4.4.1).

The region of interest is between 1700 and 1000 cm^{-1}

Triphenylbismuth Carboxylates	$\Delta\gamma(cm^{-1})$	$\Delta\gamma(cm^{-1})$ Na or K Salts
Oxalate	256	301
Acetate	203	115
Benzoate	209	138
Propionate	230	138
Octanoate	—	157

Table 4.11 Separation between γ asym [COO] and γ sym [COO] in triphenylbismuth carboxylates

The infra-red data indicate that the oxalate is interacting with the bismuth as a bidentate ligand* (Figure 4.11)

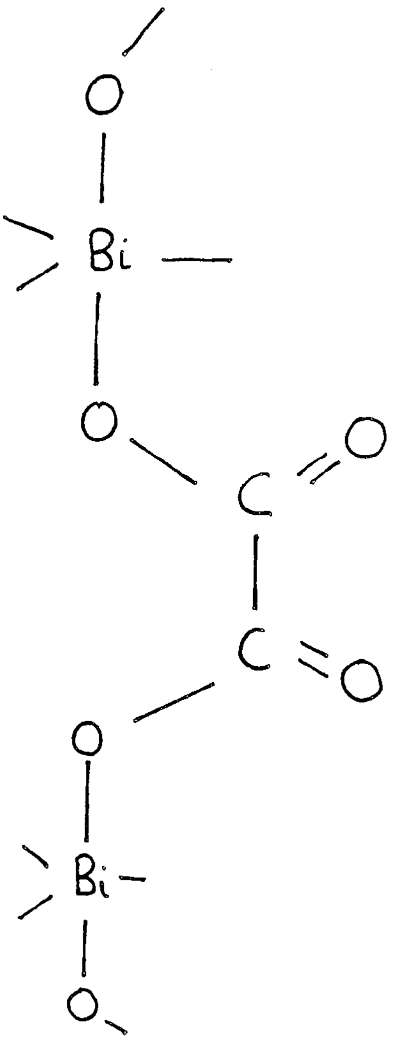


Figure.4 11 Triphenylbismuth Oxalate.

The acetate, benzoate, propionate all appear to act as unidentate ligands. The elemental analysis data also support the structures proposed.

4.6.6 X-ray Crystallography

(Section 4.5.1)

4.7 Bismuth Compounds as Driers

4.7.1 Introduction

Selected compounds were evaluated as driers.

4.7.1.1 Paints

Paints are generally highly complex systems consisting of binders, solvents, pigments and various additives. It is the binder which is responsible for the formation of the film, whether by simple solvent evaporation (e.g. nitrocellulose) or by various chemical processes.

4.7.1.2 Driers

The term 'drier' is used to designate chemical substances which promote the hardening of autoxidising resins or oils. Driers are usually metallic soaps of monocarboxylic acids dissolved in mineral spirits and are generally manufactured from acids containing 7—22 carbon atoms. The acid has little effect on the drier performance, its main function is to render the metal soluble in the medium, where it can promote oxidative drying. However, the acid does effect the physical properties of the drier, e.g. viscosity, solids content, colour. Although driers are only added at low levels, in some cases it is desirable to incorporate the least amount of solvent possible. This is best achieved by using driers with a high metal content.

4.7.1.3 Dry Time Measurement

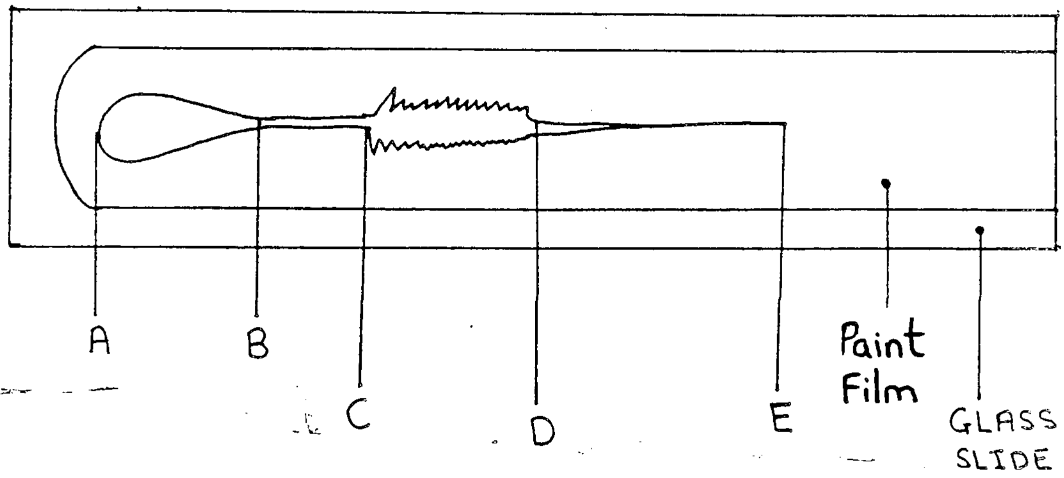
The time required for drying of a film of paint was recorded using a Beck-Koller drying time recorder. The recorder has six needles which traverse a fixed length over a pre-determined time.

4.8 Experimental

A 12" x 1" glass slide, was coated with the sample to be tested, with a 38μ or 76μ applicator cube. The needles were dropped onto the paint film, and the power switched on.

4.8.1 Interpretation of Needle Track

A typical needle tract obtained from a Beck-Koller recorder (Figure 4.12) consists of four stages.



A = Start of track

AB = Stage 1 B = End of stage 1

BC = Stage 2 C = End of stage 2 etc.

CD = Stage 3

DE = Stage 4

4.8.1.1 Stage 1

This is equivalent to the distance from point A to B. The length can be related to time in hours, since the speed of the needle traversing the entire glass slide distance is known. Between points AB, the paint is still fluid and flows back into the groove behind the needle.

Solvent evaporation occurs during this stage and the driers begin to promote the cross linking of the resin autoxidation.

The effect of the anti-skinning agent (in paint mixture) ensures that the reaction rate is slow initially, the solvent vapour immediately above the paint film also helps to slow the initial reaction rate. As the solvent is lost, the viscosity of the film increases.

The end of stage 1 is characterised by the tapering off of the 'peardrop' shape. The needle may also sink deeper. At this point the viscosity of the paint is such that it does not flow back behind the needle.

4.8.1.2 Stage 2

During this stage the remainder of the solvent evaporates and the primary driers begin to act on the surface of the paint film. The end of this stage is recognisable by the initial tearing of the surface skin of the paint.

4.8.1.3 Stage 3

During this stage the surface of the paint film forms a skin but the main body of the paint is still wet. Thus the needle pulls the skin away from the paint leaving the tell-tale tear marks. Sometimes stage 3 may manifest itself as 'picking' of the surface instead of tearing. During the latter part of stage 3 the effect of the auxilliary driers is recognisable as the skin no longer being pulled from the body of the paint.

4.8.1.4 Stage 4

The start of stage 4 is the end of 'tearing' (i.e. end of stage 3). During this stage the paint film hardens. The needle tract is seen as a faint single line, which gradually gets fainter, until the paint film becomes so hard that it is not marked. The end of this final stage that it is not marked by the needle is the end of this final stage.

4.9 Evaluation of Bismuth Compounds as Driers

4.9.1 Comparison of Drying Capability of Triphenylbismuth dioctanoate against Standard Driers Table 4.12

The bismuth driers tested were bismuth versatate, Manchem bismuth octanoate, Nuodex bismuth octanoate and triphenylbismuth dioctanoate. The other bismuth driers were included for comparison.

All of the above compounds were compared in P470 and 50W paints, against the standard driers EP9138 (Ca drier) and cozirc 69 (standard Co/Zirconium drier).

4.9.2 Experimental

The accelerated (50°C.) and non-accelerated properties of the bismuth and standard driers were evaluated with Beck-Koller drying time recorder under ambient conditions at film thicknesses of 38 and 76 microns. Each bismuth drier was added to the Synolac 50W and Sorbral P470 paint, such that the concentration levels were 0.1% bismuth 0.03% Co and 0.1% Ca. The standard driers were added at the levels normally used by Manchem Limited.

i.e. Cozirc 69	0.06% Co / 0.09 Zr / 0.2 Co
EP 9138	0.04% Co / 0.02 Li / 0.133 Co

4.10 Results and Discussion

4.10.1 Drying properties in 50W Paint

4.10.1.1 (a) Paints stored at ambient temperature and conditions for four days

At 38μ Film thickness	Figure 4 .13
At 76μ Film thickness	Figure 4..14

At 38μ film thickness, all the drier systems had comparable drying times. At 76μ the bismuth driers were faster than the standard driers.

Compound	Drying Time/hours
Bismuth Octanoate *	8.5
Bismuth versatate	9.0
Bismuth Octanoate **	12.0
EP9138	13.5
Cozirc 69	18.5
Triphenylbismuth dioctanoate	21.0

Table 4.12

* Prepared by Manchem Limited

** (Nuodex drier)

4.10.1.2 (b) Drier ability after storage

The paints containing the drier systems were stored at ambient conditions for eight months and then re-evaluated. All of the paints containing the bismuth driers, appeared to suffer adverse effects to a greater extent that the standard drier systems. The bismuth drier systems experienced a "loss of dry" (38μ film thickness). The standard drier systems dried faster after ageing (38μ film).

They produced a stage 4 drying time of 5 hours after aging compared to 7—9 hours for the bismuth systems. However when considering the drying efficiency at 76µ film levels the bismuth driers still achieved a better drying time, than the standard systems.

4.10.1.3 (c) Drier ability storage (accelerated)

This involved the storage of the paint systems for six weeks at 50°C., followed by six months at ambient conditions. At 38µ all of the bismuth driers evaluated required longer to dry the paint film than the standard drier. The bismuth systems requiring 7—13 hours compared to 6—7 hours for stage 4 drying in the standard systems . At 76µ film thickness only the bismuth versatate and bismuth octanoate (Manchem Limited) dried at a faster rate than the standard driers.

The bismuth systems achieving drying times of 12.5—13.5 hours compared to 14—15.5 hours for the standard systems.

4.10.2 Drying Properties in P470 Paint

The bismuth required upto 5.5 hours longer to dry the P470 paint system than the standard driers, when tested on 38µ film thickness, the same trend is true for the 76µ films. The bismuth driers experienced a greater "loss of dry" in the P470 paint system than in the Synolac 50W system.

Order of Efficiency in P470 Paint
Bismuth Octanoate (Manchem)
Bismuth Versatate
Bismuth Octanoate (Nuodex)
Triphenylbismuth dioctanoate

4.10.2.1 Evaluation of Bismuth Compounds as Driers in P470 Paint

A variety of bismuth compounds (Table 4.12) were tested as driers in P470 paint. Drying times of six slides per paint were measured under ambient conditions using a 76μ cube applicator.

Compound		% Bi
1	Bismuth Trioctanoate (MA32C)	32.7%
2	Bismuth octanoate (Manchem) (MA101)	25%
3	Triphenylbismuth dioctanoate (MA21)	28.8%
4	Triphenylbismuth oxalate (MA21A)	39.6%
5	Phenylbismuth versatate (MAPHVERS)	30% *
6	Bismuth versatate (MA102)	24%
7	Bismuth octanoate (Manchem)(MA100)	25%
8	Triphenylbismuth propionate (MA31A)	35.7%
9	Bismuth Naphthenate (MA103)	
10	Triphenylbismuth dichloride (Ph_3BiCl_2)	
* Estimated		

Table 4.13

Selected bismuth compounds were evaluated as driers in the presence of a known quantity of bismuth tris-diethyldithiocarbamate (DTC), in the P470 paint. 5 cm^3 of a 0.03 g / 250 cm^3 solution in Butanol/white spirit 50 : 50 ratio. (i.e. MA32CDTC, MA21DTC)

Compounds selected were numbers 1, 3 and 8.

All the compounds were compared against the standard driers CD44 and cozirc 69.

4.11 Results

4.11.1 Surface Drying

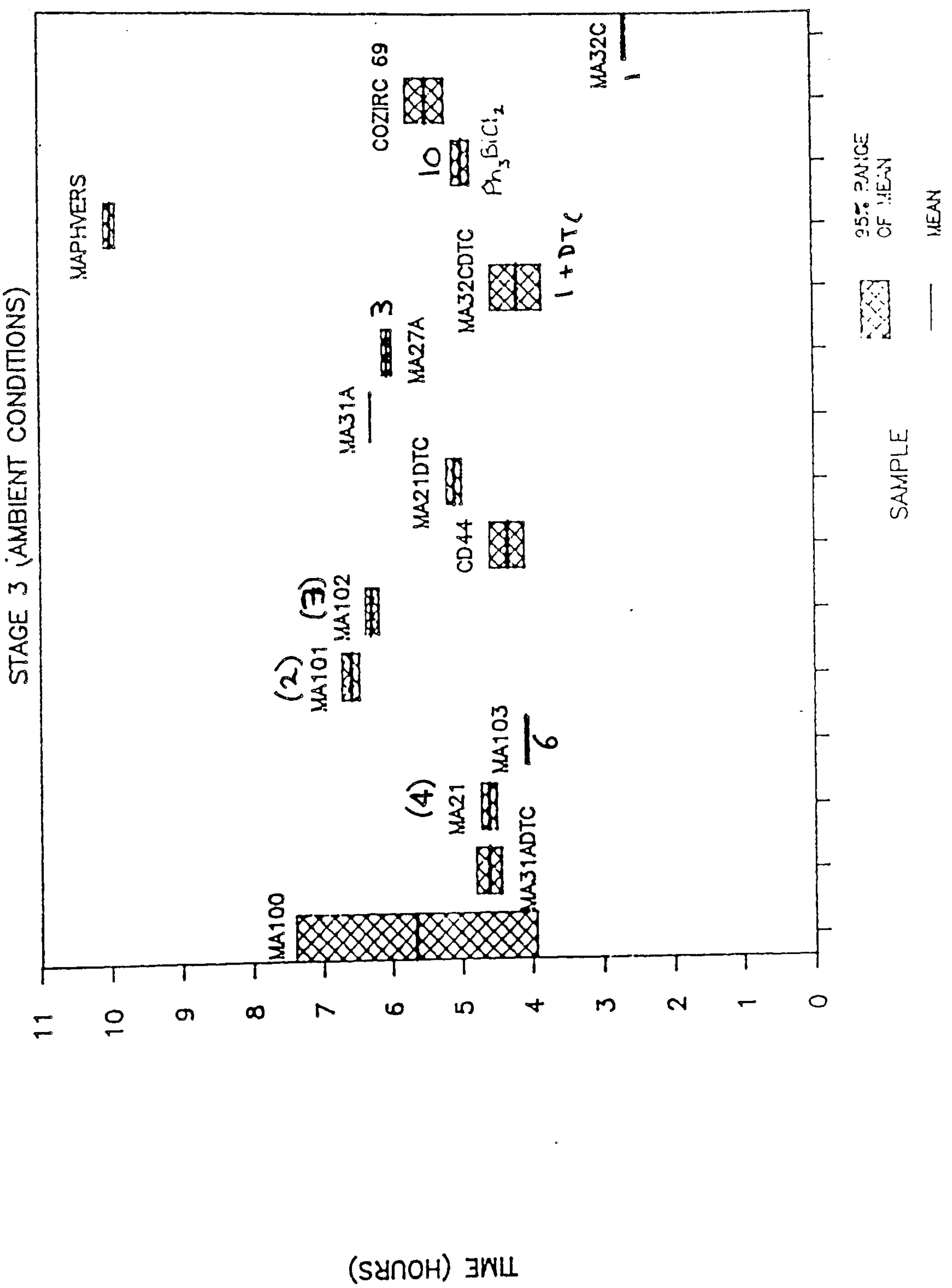


Figure 4.13 Stage 3 surface drying times

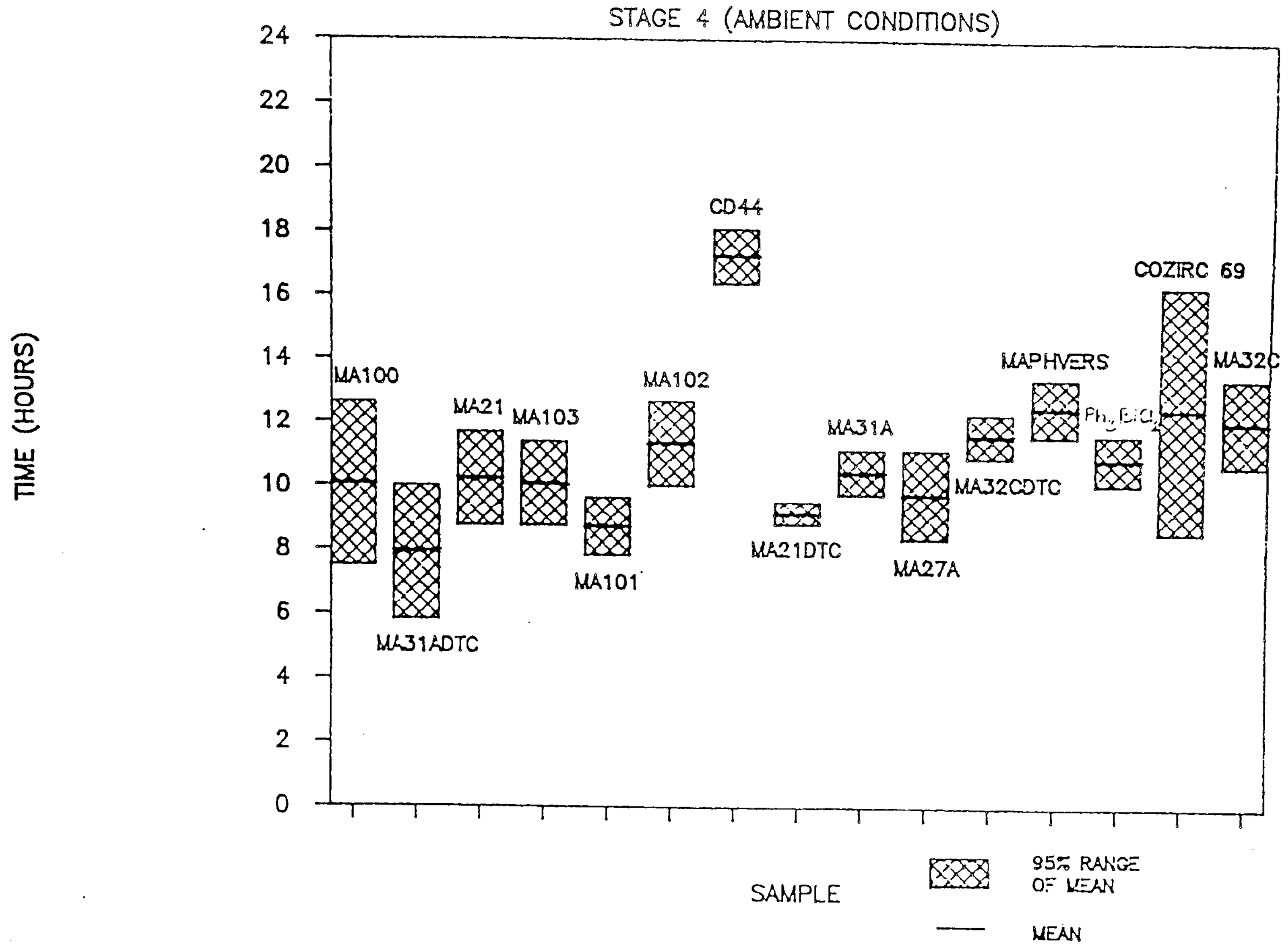


Figure 4.14 Stage 4 drying Times (See Fig 4.13 for codes)

Paint Formulation Details

Type of paint used =	P470	
Quantity of paint	100 g for each drier evaluation	
Drier Formulation	0.03%	Co
(% contained in 100 g of paint)	0.1%	Bi
	0.1%	Ca (Manonec 10% Ca Solution)
Controls	Cozirc 69	0.397 g added to 100 g of paint
	CD44	1.985 g added to
100 g		of paint

4.12 Discussion for drier evaluations

The paint with the best stage three drying time was that containing the bismuth tri-octanoate (2.6 hours). The paint containing the bismuth tri-octanoate + bismuth tris-diethyldithiocarbamate produced a stage 3 drying time of approximately 4.5 hours. The standard driers CE44 and Cozirc 69 gave drying times of 4.5 hours and 5.5. hours respectively.

Order of drying	
Bismuth tri-octanoate	Fastest
CD44	
	↓
Cozirc 69	
Bismuth versatate	Slowest

The paint with the best through drying (stage 4) time was the one containing triphenylbismuth dipropionate + bismuth tris-diethyldithiocarbamate. (A) (7.9 hours), whilst the paint containing the bismuth tri-octanoate (B) gave a stage 4 drying time of 12.1 hours. So where as drier (A) was far behind (B) at stage 3 there appears to be a dramatic change in drying after stage 3.

From (Figure 4.13 and 4.14) it can be seen that the paint with the best drying characteristics overall was that containing triphenylbismuth dipropionate with bismuth tris-diethyldithiocarbamate, although the majority of bismuth compounds produced faster drying times (stage 4) than the standard driers cozirc 69 and CD 44. The presence of the bismuth tris-diethyldithiocarbamate even in the small amounts used, enhanced the drying ability of the bismuth compounds. This may be due to the dithiocarbamate enhancing or stabilising the cross-linking reactions occurring during the drying of the paint.

CHAPTER FIVE

LEWIS ACIDITY OF ORGANOBISMUTH COMPOUNDS

5.0 Introduction

In 1923 the American Chemical Society published a monograph by G.N Lewis[111], in which Lewis reviewed and extensively elaborated the theory of the electron-pair bond, which he had first proposed in 1916. It was not until 1938[112] G.N. Lewis categorised substances capable of acting as ligands, bases, and the substances with which these react as acids. A Lewis acid was said to be an acceptor of an electron pair[113]. This could be a molecule e.g. BF_3 or a positive ion e.g. H^+, Cu^{2+}. Alternatively it could be regarded as a compound in which the central atom may use its d-orbitals e.g. $SnCl_4$, $TeCl_4$. A Lewis base is an electron pair donor. This may be a negative ion e.g. CN^-, OH^-, Cl^-.. etc, or molecules possessing one or two lone pairs of electrons e.g. NH_3, H_2O, PPh_3, or molecules containing multiple bonds between carbon atoms e.g. $CH_2=CH_2$, C_6H_6 etc. The drawback is that only qualitative predictions regarding complex formation can be made. The term complex is given to the product of a reaction involving a Lewis acid and Lewis base.

It is perhaps timely at this point to list the various ways complex formation may take place.

5.0.1 (a) Simple Complex Formation

$$R_nEX_{4-n} + xL \longrightarrow R_nEX_{4-n}xL$$

L= a neutral base E= metal

5.0.2 (b) Autocomplex Formation

Lewis acid and base centres are present in the same molecule. This gives rise to the possibility of complex formation by either intra or inter- molecular interactions between these centres. These interactions can be divided into two categories (i) Long range and (ii) short range. The first type has been called " secondary bonding " 114. It can be described by considering the example where a donor L is interacting with a metal E in a neighbouring molecule. Figure 5.1

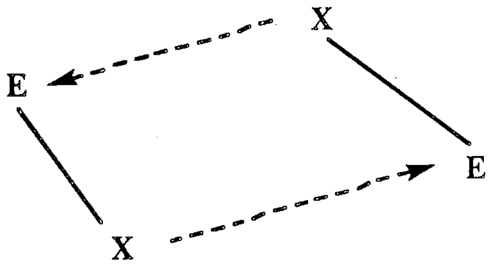


Figure 5.1 Secondary Bonding

One set of bonds is longer than the sum of the covalent radii of E and X , but is still shorter than the van der Waals distance. Lastly intramolecular complex formation is also possible, steric factors permitting. This is found when the organic group R also possesses a donor group L. Figure 5.2

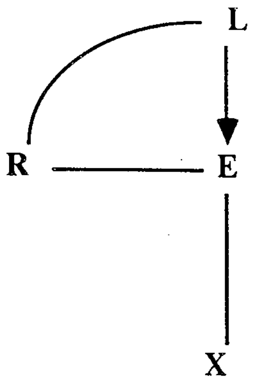


Figure 5.2 Intramolecular complex formation

As mentioned earlier the main drawback of the Lewis acid base theory is its lack of quantitative prediction regarding complex formation. If it were possible to make quantitative predictions and construct a scale of Lewis acid and Lewis base strengths, this would enable the prediction of the relative stabilities of complexes. (A possible scale of Lewis acidity using ^{125}Te Mössbauer spectroscpoy quantitative method was investigated by Davies et al [115]). For this to be the case a means of quantifying the strengths of different bases is by choosing a reference acid. If proton (H^+) is the reference acid then bases where N, O, or F is the donor atom are found to be stronger than those where sulphur or chlorine are the donor atoms. Thus acids containing Hg+, Cu^+ will form more strong complexes with sulphur ligands, but will be weaker acids than those forming strong complexes with nitrogen ligands. The definitions of hard and soft bases state that hard bases have high resistance to oxidation, high electronegativity, and low polarisability[116], whilst soft bases are those which have low electronegativity, are readily oxidised and a high polarisability. Considering the metals, soft metals ions are usually large and have a low charge (or possess valence shell electrons which are easily removed). They usually bond to soft ligands. Hard metal ions prefer hard ligands. Some ions however e.g. transition metal ions cannot be classified as either hard or soft and are called borderline acids.

The concept of symbiosis must be mentioned here as it important. A cation which is classified as borderline is made softer by the coordination of a soft ligand or hard ligand. Thus it is more likely to add soft or hard ligands respectively. Table 5.1 classifies some metal ions and ligands [117].

	Acids	Bases
Hard	H^+, Li^+,Na^+,K^+ Be^{2+}, $Be(CH_3)_2$, Mg^{2+},Ca^{2+}, Sr^{2+},Mn^{2+} Sc^{3+}, Gd^{3+}, Ga^{3+},Lu^{3+}, Ti^{4+}, Zr^{4+}, Fe^{3+}, Co^{3+}, BF_3, BCl_3, Al^{3+}, CO_2, Sn^{4+}, SO_3, HX(hydrogen bonding molecules)	NH_3, RNH_2 , H_2O, OH^-,O^{2-}, SO_4^{2-} , Cl^-
Borderline	Fe^{2+}, Ni^{2+}, Co^{2+},Cu^{2+} Pb^{2+}, Bi^{3+},	Py, N_2, SO_3^{2-},Br^-
Soft	Pd^{2+},Pt^{2+}, Cu^+, Ag^+,Hg^{2+}, Pt^{4+}	H^-, R^-, R_2S, RSH

Table 5.1 Classification of Hard and Soft Acids and Bases

It must be remembered that the hardness of acids and bases is thus affected by size, oxidation state, electronic structure and the nature of attached groups already present. There appears to be no literature available regarding the Lewis acidity of organobismuth compounds. Our objective was to expand this area of organobismuth chemistry. The Lewis acidity of these compounds was important for their possible use as driers, because the old Pb(II) drier systems were known to operate favourably when the Lewis acidity of the lead was saturated. Remembering that the idea was that the RBi^{2+} species being pseudo-isoelectronic may be able to mimic the Pb^{2+}species. Compounds of the type $RBiX_2$ were prepared and studied. $[RBi(III)(S_2CNEt_2)_2]$ is an example. The alkyl compound $[MeBi(III)(S_2CNEt_2)_2]$ has been well characterised and its crystal structure reported[117,118]. Although $[PhBi(III)(S_2CNEt_2)_2]$ had already been reported [119] in the literature, its crystal structure had not been determined. In the methyl compound the bismuth uses S-bridging within dimers to achieve a pentagonal bipyramidal geometry (Figure 5.3).

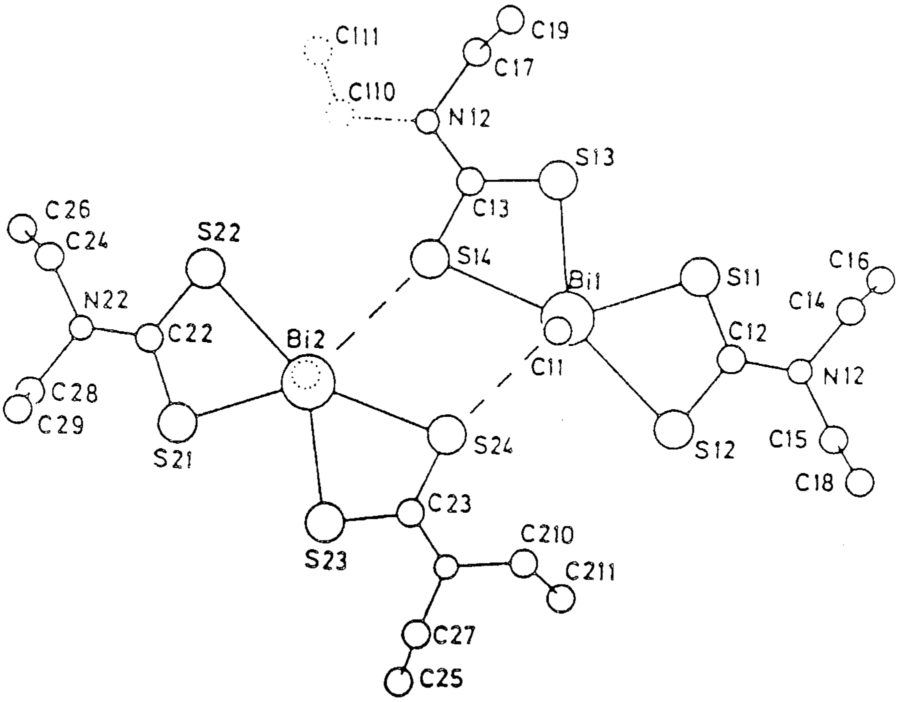


Figure 5.3 . Crystal structure of $[CH_3Bi(S_2CN(C_2H_5)_2]_2$

Of particular interest was the assessment as to whether the bismuth prefers donors containing sulphur or nitrogen. Examples of bismuth nitrogen coordination include; tris- (4-aza-1,7-dioxa-2,6-di-t-butylhepta-2,5-dien-1,4,7-triyl)bismuth(III) in which all three nitrogen atoms are coordinated to give a 9-coordinate complex [120]. Raston et al[121] showed that in $[Bi(III)(S_2CNEt_2)X_2(py)_3]$ where X= Cl or I the pyridines (py) are loosely coordinated to give a seven coordinate complex. In contrast tris-dithiocarbamato-complexes containing antimony give only " solvates" with 4,4'-bypyridyl. The same authors report in another publication [122] the reaction of $[Bi(III)(S_2CNEt_2)I_2]$ with 2,2'-bipyridyl (bipy) or 2,2';6', 2"-terpyridyl (terpy), resulted in the formation of dimeric $[(bipy)I(Et_2NCS_2)BiI_2Bi(S_2CNEt_2)I)bipy)]$ and monomeric $[(terpy)BiI_2(S_2CNEt_2)]$ respectively. This implies that there is some affinity between bismuth(III) centres for -N= ligands. We investigated whether this was also true for organobismuth(III) species. It was decided to 'anchor ' the nitrogen donor group to the organic group attached to the bismuth. i.e. to build the donor group into the R moeity. (Figure 5.2). Ortho-bismuthated 2-phenylpyridine was selected. By determining the crystal structures of both the [PhBi(III) $(S_2CN(C_2H_5)_2]_2$ and [2-py.C_6H_4Bi(III) $(S_2CN(C_2H_5)_2]_2$ compounds an assessment was made of the affinity of bismuth for -N= and S donors.

In order to obtain information on the Lewis acidity of organobismuth compounds of the type RBiX2, as mentioned previously the donor group was anchored to the organic moeity R, and the reactions of the resulting new organobismuth compounds with additional ligands Figure 5.4 , e.g. carboxylate, iodide and dithiocarbamate were studied.

5.1 Ortho-metallation

The method of ortho- metallation has been discussed in section 3.4.2 .

5.2 Experimental

5.2.1 Synthesis of 2-(2-Pyridyl)phenylbismuth(III) dibromide

A solution of bismuth tribromide (4.49 g , 10 mmol) in dry dioxane (20 cm^3) was added to a solution of 2-(2-Pyridyl)phenylmercury(II) chloride (for preparation see section 3.2.5) (4.0 g, 10 mmol) in dry dioxane (40 cm^3). The mixture was refluxed under dinitrogen for four hours resulting in the formation of a pale yellow compound. The solution was then filtered hot, and the precipitate was washed with absolute ethanol and recrystallised from acetonitrile.

Yield 76.0 % m.p.= 248-250 °C

Found C 26.0 % , H 1.60 % N 2.70 %

$C_{11}H_8BiBr_2N$ requires C 25.20 % H 1.55 % N 2.70 %

5.2.2 Synthesis of Bis-(diethyldithiocarbamato)[2-(2- pyridyl) phenyl bismuth(III)

A solution of 2-(2-pyridyl)phenylbismuth(III) dibromide (0.53 g, 1.0 mmol) in a dry acetonitrile (20 cm^3) was mixed with a solution of sodium diethyldithiocarbamate (0.38 g, 2.0 mmol) in dry acetonitrile (15 cm^3). The reaction mixture was then refluxed under dinitrogen for 3 hours. Afterwards it was filtered hot and set aside to cool. Pale yellow crystals formed and were filtered and stored in a desiccator.

Yield 88.0 % m.p.= 222-224 °C

Found C 37.80 % H 4.10 % N 6.15 %

$C_{21}H_{28}BiN_3S_4$ requires C 38.20 % H 4.25 % N 6.40 %

5.2.3 Reaction of 2-(2-pyridyl)phenylbismuth(III) dibromide with sodium propionate.

The method used was as for the preparation of the Bis-(diethyldithiocarbamato) [2-(2-pyridylphenyl]bismuth(III) except that sodium propionate was used, (in place of the sodium diethyldithiocarbamate) in dry acetonitrile.

Yield 84.0 % mp. > 250 °C

Found C 28.10 % H 2.35 % N 2.15 % Na 4.10 % (by atomic absorption).

$C_{14}H_{13}BiBr_2NNaO_2$ i.e. $Na(C_{11}H_8N)BiBr_2(OOCEt)$ requires C 27.10 % H 2.10 % N 2.30 % Na 3.70 %.

5.2.4 Reaction of 2-(2-pyridyl)phenylbismuth(III) dibromide with tetraethylammonium Iodide.

The experimental procedure used was as described above but using tetraethylammonium iodide. The crude product obtained was recystallised from nitromethane.

Yield 85.0 % mp. 155-157 °C

Found C 28.60 % H 3.90 % N 3.60 %

$C_{19}H_{28}BiBr_2IN_2$, i.e. $[Et_4N][(C_{11}H_8N)BiBr_2I]$ requires: C 29.2 % H 3.60 % N 3.60 % .

5.2.5 Synthesis of phenylbismuth(III) dimonomaleate

A solution of maleic acid (1.32 g, 11.5 mmol) in dry diethyl ether (30 cm^3) was added to a solution of triphenylbismuthine (2.5 g, 5.7 mmol) in dry diethyl ether (30 cm^3). The reaction mixture was refluxed under dry nitrogen for three hours. The solution was then filtered hot and the separated solid was dried under vacuum in a desiccator.

Yield = 26 % mp. > 300 °C

Found C 32.2 % H 1.50 %

$C_{14}H_{11}BiO_8$ requires: C 32.5 % H 2.10 %

Slow evaporation of the filtrate afforded a second product which was not able to be characterised fully.

Yield (See Chapter 4)

5.2.6 Synthesis of Bis-(diethyldithiocarbamato)phenylbismuth(III)

This compound was obtained from the reaction: sodium diethyldithiocarbamate (0.44 g, 2.0 mmol) in a dimethyl-sulphoxide/ nitromethane/ water (1:1:1) solution was added to a solution of phenylbismuth(III) dimonomaleate (1.0 g, 2.0 mmol), also in the above solvent mixture, to give a total volume of 100 cm^3. A small quantity of $[Et_4N]ClO_4$ was added and the mixture was refluxed under dinitrogen for five hours, then filtered hot. The filtrate was set aside to evaporate slowly to give a mixture of white and yellow crystals. The white crystals were separated and found to be triphenylbismuth.The yellow crystals were recrystallised from absolute ethanol. Crystals of a suitable quality for x-ray crystallography were grown by low temperature recrystallisation from absolute ethanol over a period of 4 weeks.

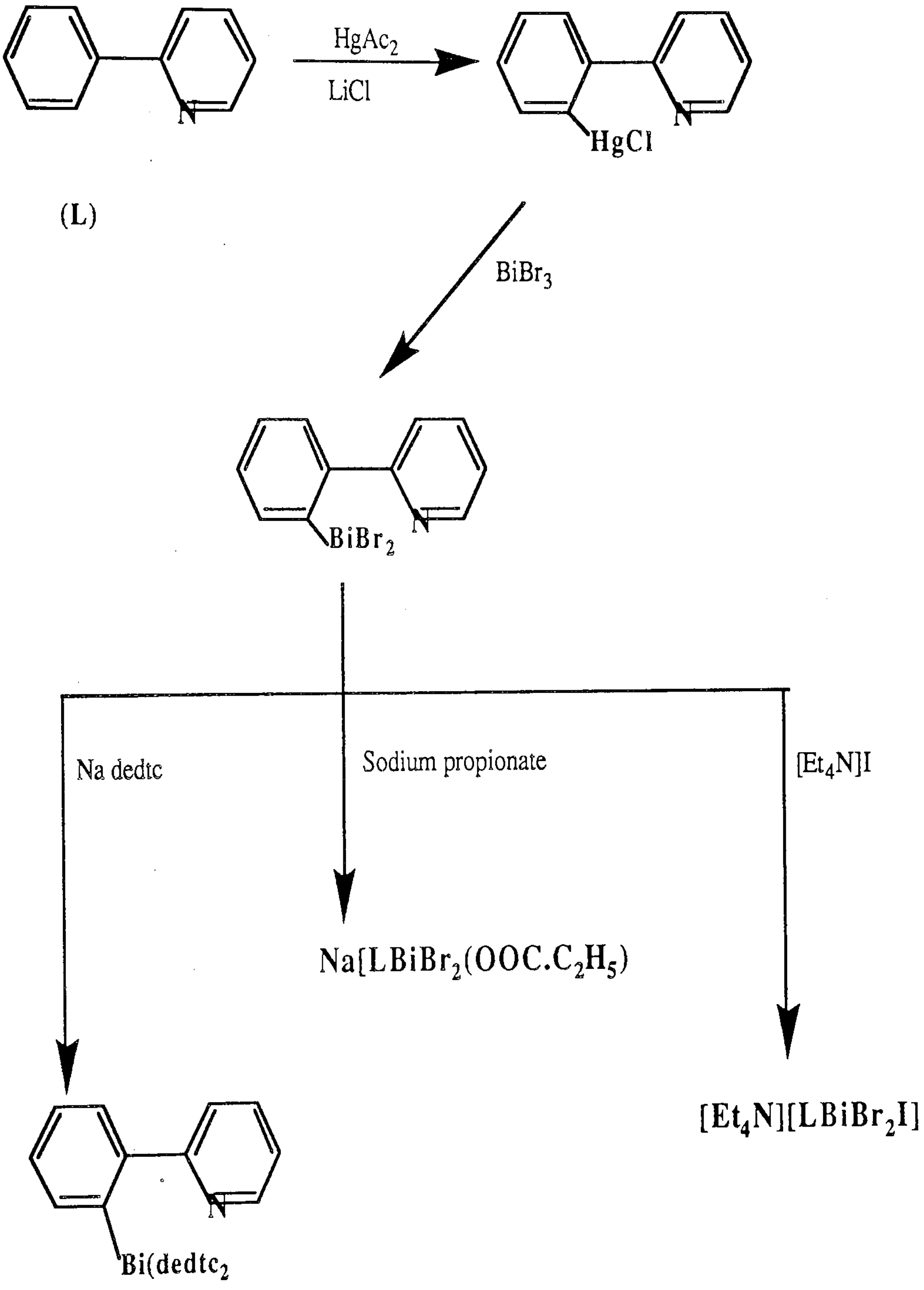


Figure 5.4 Reaction Scheme for Lewis acidity investigation

RESULTS AND DISCUSSION

5.3 Results

5.3.1 Infra-red spectroscopy

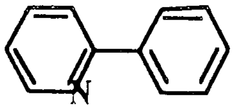
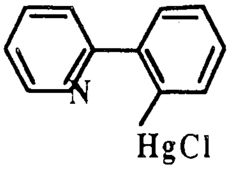
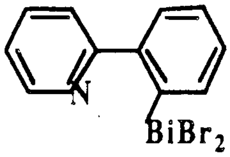
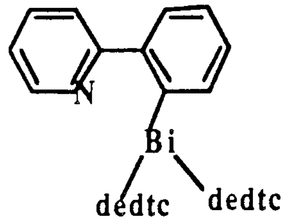
Compound	in - plane ring deformation	out of plane ring deformation
	604 cm^{-1}	405cm^{-1}
	625 cm^{-1}	420 cm^{-1}
	629 cm^{-1}	406 cm^{-1} 416 cm^{-1} doublet
	631 cm^{-1}	420 cm^{-1}
$Na[C_{11}H_8N)BiBr_2(OOCEt)]$	637 cm^{-1}	407 cm^{-1}

Table 5.2 Pyridine ring vibrational changes

Compound	Band Position (cm^{-1})	Δ V (v_{as} - v_s) (cm^{-1})
Potassium maleate	---	157
$PhBi(OOCCHCHCOOH)_2$	1533 v_{as}[COO] 1436 1297 v_{sym}[COO] 1261 v_{sym}[COO]	280
Sodium propionate	1561 v_{as}[COO] 1430 } v_s[COO] 1416 }	138
$Na[(C_{11}H_8N)BiBr_2(OOCEt)]$	1617 } v_{as}[COO] 1597 } 1431 v_{sym}[COO]	166

Table 5.3 Infra-red carboxylate stretching frequencies

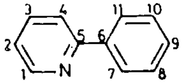
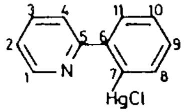
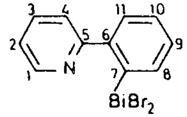
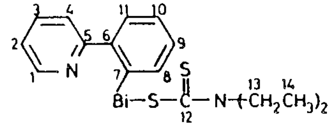
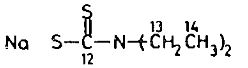
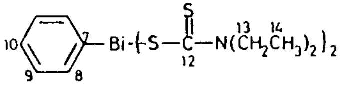
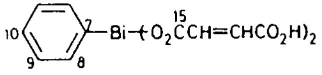
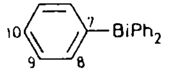
Compound	CN stretch (cm^{-1})
Phenylbismuth *bis*-diethyldithiocarbamate	1494
Sodium diethyldithiocarbamate	1477
Bis -Diethyldithiocarbamato-2-(2-pyridyl)phenylbismuth(III)	1481

Table 5.4 CN infra-red stretching frequencies

Compound	Resonance position (ppm)
Phenylbismuth *bis* -diethyldithiocarbamate (in $CDCl_3$)	198.96
Sodium diethyldithiocarbamate (in D_2O)	208.15
Bis-diethyldithiocarbamato-2(2-pyridyl)phenylbismuth(III)	201.22

Table 5.5 13C nmr peaks for C-S carbon (wrt TMS)

Table 5.5a ^{13}C N.m.r. data for organylbismuth compounds. Solvents are indicated and all chemical shifts are p.p.m. *vs.* $SiMe_4$ as internal standard

Compound	Solvent	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}
	$CDCl_3$	149.1	119.1	136.2	121.5	156.7	138.8	126.3		128.1		126.3			
	$CDCl_3$	149.1	120.9	138.3	123.4	155.9	141.3	147.9	137.8	128.2	129.2	127.1			
	$(CD_3)_2SO$	148.3	121.9	139.2	124.3	162.9	147.4	140.9	134.6	128.6	130.4				
	$(CD_3)_2SO$	147.2	121.2	139.6	123.7	160.6	146.7	141.5	133.2	128.2		127.6	201.2	47.7	12.0
 $Na\ S-\overset{S}{\underset{12}{\overset{\Vert}{C}}}-N\left(\overset{13}{C}H_2\overset{14}{C}H_3\right)_2$	D_2O												208.2	51.3	14.0
	$CDCl_3$								138.6	131.3	127.2		198.9	47.5	11.5
	$(CD_3)_2SO$							133.8	132.3	131.3	130.2		168.0 (C=O)		
	$CDCl_3$							155.0	137.5	130.5	127.7				

5.4 Discussion

The objective of this work was to obtain information on the Lewis acidity of the organylbismuth species $RBiX_2$. In order to achieve this objective it was decided to "anchor" the donor group to the organic moeity R. The resulting new organylbismuth compounds were then reacted with additional ligands such as dithiocarbamate, carboxylate and iodide (see Figure 5.4). Previous workers in the research group had used an *ortho* - metallation route to prepare a variety of interesting organyltellurium compounds[123] from 2-(2-pyridyl)phenylmercury(II) chloride. More recently Constable and Leese [124] have used the reagent as a route to obtaining transition metal complexes which may be viewed as analagoues to C,N bonded bipyridine compounds. It was decided to use this route by reacting the mercurated 2-phenylpyridine derivative with bismuth tri-bromide. The bromide was selected instead of the chloride because of its slower rate of hydrolysis. The reaction was successful and produced $(C_{11}H_8N)BiBr_2$.2-(2-pyridyl)phenylbismuth(III) bromide was found to be stable and isolable, in contrast to this phenylbismuth dichloride and dibromide, which are known in solution , had not to our knowledge been isolated as solids [125] . When it is considered that they have been isolated by complex formation [125] (for example as the bipyridyl complex, $PhBiBr_2$(bipy)), the implication arises that a bismuth - nitrogen coordinate bond has been formed. McWhinnie et al [126] showed that the base tri-2-pyridylamine (tripyam) may function as a bidentate or tripodal tridentate ligand to copper(II). In the same publication the authors reported that the 2-pyridyl out of plane ring deformation mode, ϕ (CC) near to 405 cm^{-1} in the infra-red region was very sensive to the coordination of the 2-pyridyl-group. By analogy with this work i.r data on $RBiBr_2$ (Table 5.2) suggest that the Bi-N interaction must at best be weak. Constable [127] et al have recently determined the structure of $(C_{11}H_8N)HgCl$ and shown that the Hg-N interaction is weak , it is included in the table for comparison. A feature of interest in the infra-red spectrum of $(C_{11}H_8N)BiBr_2$ (Table 5.2) is that there is the implication that two environments are present for the 2-pyridylphenyl-group in this compound, one weakly coordinated, the other uncoordinated. The compound thus is probably not monomeric in the solid state. There appears to be no evidence from ^{13}C nmr (Table 5.5a) for the presence of inequivalent organic groups in dmso solution.

The Lewis acidity of 2-(2-pyridyl)phenylbismuth(III) bromide was investigated by studying the reactions with (a) tetraethyl ammonium iodide Et_4NI (b) sodium diethyldithiocarbamate Nadedtc (c) sodium propionate NaOOCEt. For (a) and (c) acid - base reactions were observed. The product from the reaction with Et_4NI produced well formed crystals of $[Et_4N][C_{11}H_8N)BiBr_2I$. the crystals were of a suitable quality for x-ray crystallography and the following unit cell for the compound was determined:-

Unit cell for $[Et_4N][C_{11}H_8N)BiBr_2I$

a= 12.077(16), b=17.910(28), c=13.419(26) Å; $\alpha = 90.00(14)$ $\beta= 116.57(12)$, $\gamma= 90.00(12)$ °

Unfortunately the structure could not be determined because insufficient reflections were observed to resolve the structure.

^{14}N nmr spectroscopy of the compound in a dmso solution was used to confirm the presence of the cation. Two resonances were observed , a broad band at -45.4 ppm and a very sharp band at -310.2 ppm (both relative to aqueuos $NaNO_3$ as an external reference). The ^{14}N nucleus is quadrupolar having a spin of I=1,therefore the sharp resonance must be due to a species in which the nitrogen is in a highly symmetrical environment i.e. Et_4N^+ [128] . Thus the broad resonance is due to the low symmetry pyridyl nitrogen atom. This is confirmed by the fact that the pyridyl nitrogen in 2-phenylpyridine (in dmso) gives a resonance at -56.0 ppm. Although it appears that ^{14}N nmr would be very useful in studying these compounds, a comprehensive study could not be performed because of solubility problems encountered. Also the strongly coordinating solvent dmso, was a solvent of necessity rather than choice for this work. Hence we do not speculate as to the significance, if any, of the apparent deshielding of the pyridyl-nitrogen atom in the presence of the bismuth. It must be noted that from table 5.2 , that the ϕ (CC) vibration at 409 cm^{-1} implies that at best an extremely weak Bi-N interaction in the solid.

The reaction of sodium propionate with $(C_{11}H_8N)BiBr_2$ produced the compound $Na[(C_{11}H_8N)BiBr_2(OOCEt)]$. The compound appears to be an intractable solid with a high melting point. The infra-red spectroscopic data (Table 5.3) suggest that the propionate group is coordinated. The separation Δv, between the $v_{as}(COO)$ and $v_s(COO)$ frequencies is a good indication of the mode of coordination [129,130]. The value for $Na[(C_{11}H_8N)BiBr_2(OOCEt)]$ is 166 cm^{-1} . This implies that the carboxylate is symmetrically bridging or symmetrically bidentate, since the value found was close to that obtained for NaOOCEt i.e. 131 cm^{-1}. If the group was unsymmetrically bidentate or monodentate then the separation would be much greater. For example the monodentate acetato-complex tricyclohexyltin(IV) acetate[131] gives a $\Delta v = 361$ cm^{-1}, whilst $SnMe_2(OOCMe)_2$ [132] , which possesses an unsymmetrically bidentate acetato-groups, shows $\Delta v = 227$ cm^{-1}. The infra-red data also suggests that the 2-pyridyl-group to be either non- or very weakly coordinated.

The reaction of $(C_{11}H_8N)BiBr_2$ with I^- or $EtCOO^-$ resulted in the addition of the anionic group and, according to the infra-red data, a significant weakening of the Bi-N bond. In contrast to the two above reactions the reaction of $(C_{11}H_8N)BiBr_2$ with Nadedtc (dedtc = diethyldithiocarbamate) resulted in a substitution reaction to produce $(C_{11}H_8N)Bi(dedtc)_2$ in which the 2-pyridyl group interacts with bismuth at least as strongly as it interacts with mercury in $(C_{11}H_8N)HgCl$ (Table 5.2). This interaction is confirmed crystallographically in agreement with the ir prediction. Other workers in the research group had recently hoped to compare the competitive affinity of tellurium(IV) for S and N donors and to this end (2-phenylazophenyl-C,N')tellurium(IV) *tris*-diethyldithiocarbamate[133] with a view to comparing the structure to that of $PhTe(dedtc)_3$[134] , however it transpired that "$(C_{12}H_9N_2)Te(dedtc)_3$" was a charge transfer complex of the tellurium(II) compound and dithiuram sulphide. Since Bi(III) is pseudo-isoelectronic with Te(IV) and should be less likely to give reductive elimination of the disulphide, it was decided to compare the structures of $(C_{11}H_8N)Bi(dedtc)_2$ and $PhBi(dedtc)_2$. The latter compound was prepared via *bis*-monomaleate. The "substitution" reaction is not straightforward since <u>two</u> products were noted . The two products were (a) yellow crystals of $PhBi(dedtc)_2$ and (b) white crystals which proved to be triphenylbismuth. The identity of the triphenylbismuth was positively confirmed by x-ray crystallography, the parameters for the unit cell were in good agreement with an earlier determination by Ferguson[135] , and thus the details are not presented here. The presence of the two compounds in the end product may be explained by the occurrence of a disproportionation reaction of the *bis*-monomaleate simultaneously with the substituition reaction.

5.4.1 ^{13}C Nmr Spectroscopy

The assignments for the carbon attached to the sulphur are given in Table 5.5 . The assignments for the carbons of the 2-phenylpyridine were concordant with those developed for tellurated 2-phenylpyridines by Al-Salim et al [123] .

Doak and Freedman [102] reported that the resonance of the *ipso* carbon atoms of triphenylbismuth was at -0.12 ppm (wrt TMS). It was difficult to believe that this carbon should be so strongly shielded compared to similar atoms in organyltellurium[123] and analogous mercury compounds[136]. Consultation of the original paper [134] revealed that the authors made no assignment of the *ipso* resonance and that the figure of -0.12 was in fact the Taft constant. Therefore the positon of the *ipso* carbon was determined. The positon was determined by using longer delay times between pulses and also using the QUAT-D[101] pulse sequence on the Bruker instrument. The value is 155 ppm (wrt TMS). *Ipso* carbon resonances for other organobismuth compounds are also given in Table 5.6 . The resonances were found to be usually broad as would be expected, a consequence of the nuclear spin (9/2) of the 100 % abundant ^{209}Bi.

5.4.2 Structural Investigations Crystal structures of *Bis*(diethyldithiocarbamato)2-(2-pyridyl)-phenylbismuth(III) and *Bis* (diethyldithiocarbamato)phenylbismuth(III)

After preliminary studies by photographic methods, final cell dimensions and reflection intensities were measured with graphite monochromated Mo-Kα

radiation on a Enraf-Nonius CAD-4 diffractometer, operating in the $\omega - 2\theta$ scan mode. Three standard reflections were monitored at regular intervals to check the stability of the system. Empirical absorption corrections[81] (range of transmission factors applied for *Bis*(diethyldithiocarbamato) 2-(2-pyridyl)-phenylbismuth(III) (compound 1) and *Bis*(diethyldithiocarbamato)phenylbismuth(III) (compund 2) were 1.039-1.895 and 1.012-1.756 respectively. Details of the crystal and experimental parameters are given in Table . Both structures were solved by Patterson and Fourier methods. As it was not possible to distinguish all of the hydrogen positions in either structure, hydrogens were placed in calculated positions (C-H 1.08 A) and allowed to 'ride' on thier respective carbon atoms in the subsequent least-squares refinements. Anisotropic thermal parameters were used for all the non-hydrogen atoms. Atomic coordinates for compounds I and II are given in Tables 5.7 and 5.8 bond lengths and bond angles are in tables 5.9 and 5.10. Crystal parmaters are given in Table 5.11

Computations were carried out on the Birmingham University Honeywell computer with SHELXS-86[80] and SHELXS-76[80]. The structures were drawn using PLUTO[81b] at the University of Manchester Regional Computer Centre.

5.4.3 *Bis*(diethyldithiocarbamato)2-(2-pyridyl) phenyl bismuth(III) (Compound 1)

The structure is shown in figure 5.5, the coordination about the central bismuth atom can be considered as essentially pseudo-pentagonal bipyramidal, with the four sulphur atoms from the diethyldithiocarbamato groups and the pyridyl nitrogen making up the equatorial coordination and the phenyl carbon C(1) and the lone pair of electrons on the bismuth atom axial. The deviation from ideal pentagonal bipyramidal values is due to the constraints imposed on the system, by the bite of the 2-(2-pyridyl)phenyl and the diethyldithiocarbamato ligands. Apart from the N(1) - Bi - C(1) angle of 70.8° (ideal 90°, and S(2) - Bi - S(4), 156.7 ° (ideal 144 °), all angles at bismuth are within 10 ° of the theoretical values. The BiS_4 equatorial grouping is coplanar to within ±0.06 A with the nitrogen displaced by 0.067 A. The distance Bi - C(1) [2.263(7) A] is in good agreement with the sum of the Pauling covalent single bond radii for sp^2 hybridized carbon and bismuth [2.26 A][127,138] , and with the values found for triphenylbismuth [2.21 - 2.25(20 A][22]. The Bi - N distance is of particular note. At 2.553(6) A it is significantly longer than the sum of the covalent radii for Bi - N single bond (2.22 A) [137,138] , but is well within the van der Waals distance. This observation lends support to the interpretation of the infra-red data presented earlier (section 5.3). The distance lies at the lower end of the range reported for the same interaction in other bismuth compounds[121,122] which lie in the range 2.56-2.86 A. Similar short metal - nitrogen secondary interactions have been reported for a number of tellurium compounds incorporating the 2-(2-pyridyl)phenyl-group[123,139] . Then, as with this material, the metal-nitrogen interaction holds the 2-(2-pyridyl)phenyl ligand in a virtually planar geometry. In the present structure the relative twist of the mean planes is only 4.0(1)° and the ligand is planar to within ± 0.06 A, with the bismuth atom situated 0.18 A from the plane.

Although all four bismuth-sulphur distances are longer than the theoretical value for a covalent Bi-S single bond (2.55 A)[137,138] , they are comparable with previously reported Bi-S values and may be categorised similarly. Each dithiocarbamato-ligand can be considered to be linked to the cental bismuth atom *via* one short bismuth-sulphur bond and one long bond[140]. The two short Bi-S bonds [2.798(2) and

2.766(2) A] lie at the upper limit for this type of bond [2.595(5)-2.775(5) A] 4,27; the two long Bi-S bonds [2.878(2), 2.895(2) A] fall at the lower end of their range [2.886(4)-2.965(4) A] 4,27. The bond lengths and angles within each dithiocarbamato- ligand fall within the range of standard values. The S_2CNC_2 portion of each dithiocarbamato- group is essentially planar (± 0.04 A), with a dihedral angle between the mean plane for each ligand and the mean plane of the bismuth 2-(2-pyridyl)phenyl moeity of 88.5(1)° and 92.7(1)° The $Bi(S_2CNC_2)_2$ equatorial grouping is planar to within ± 0.13 A with N(1) displaced by 0.68 A. The closest intermolecular contacts involving the bismuth atom are with the molecule at 1-x, 1-y, -z, Bi.....Bi' and C(1) - Bi.....S(4)' are 155.6(2)° and 160.9(2)°. Bi' and S(4)' thus straddle the other apex of the pentagonal bipyramid (Figure 5.6). Any bonding interaction at this range must be considered extremely weak.

5.4.4 *Bis*(diethyldithiocarbamato)phenylbismuth(III) (CompoundII)

The structure is shown in Figure 5.7. Although the bismuth atom is only five coordinate, the coordination geometry is similar to that in compound I. The four sulphur atoms and the bismuth are coplanar to within ± 0.02 A. The fifth contact completing the equatorial pentagonal coordination is to S(4)' of the centrosymmetrically related molecule at 3.421(2) A and 0.58 A from the equatorial plane. The pertinent angles are S(1)-Bi....S(4)', 88.0(1) ° and S(4)-Bi...S(4)', 64.9(1)°. This interaction is similar to that found in *Bis* (diethyldithiocarbamato)methylbismuth(III)[4], where sulphur bridges between symmetrically related molecules link them into dimers with slightly shorter Bi....S distances of 3.27 and 3.36 A. As in compound I, the phenyl carbon, C(11) is apical with the Bi lone pair of electrons completing the pentagonal bipyramid. The Bi-C(11) bond length [2.241(10) A] is similar to the corresponding length in compound1. The pattern of Bi-S bond lengths, however, differs noticeably in the "long" bonds are longer and the "short" bonds are shorter. The difference between the means of the "long" and "short" bonds is 0.26 A compared with 0.11 A for (compound I). However, the relative orientations of the long and short bonds is similar in the two structures. As might be expected, the sulphur atoms, S(2) and S(3), involved in the short Bi-S bonds have longer S-C bonds [1.714(10) A and 1.740(8) A] than the other sulphur atoms, S(1) and S(4), [1.698(10) A and 1.703(9) A] . The S_2CNC_2 portions of both dithiocarbamato groups are planar to within ± 0.02 A. The dihedral angles between the bismuth-phenyl plane and the v planes are 89.4(2) ° and 103.3(2) °. The Bi($S_2CNC_2)_2$ grouping is planar to within ± 0.28 A.

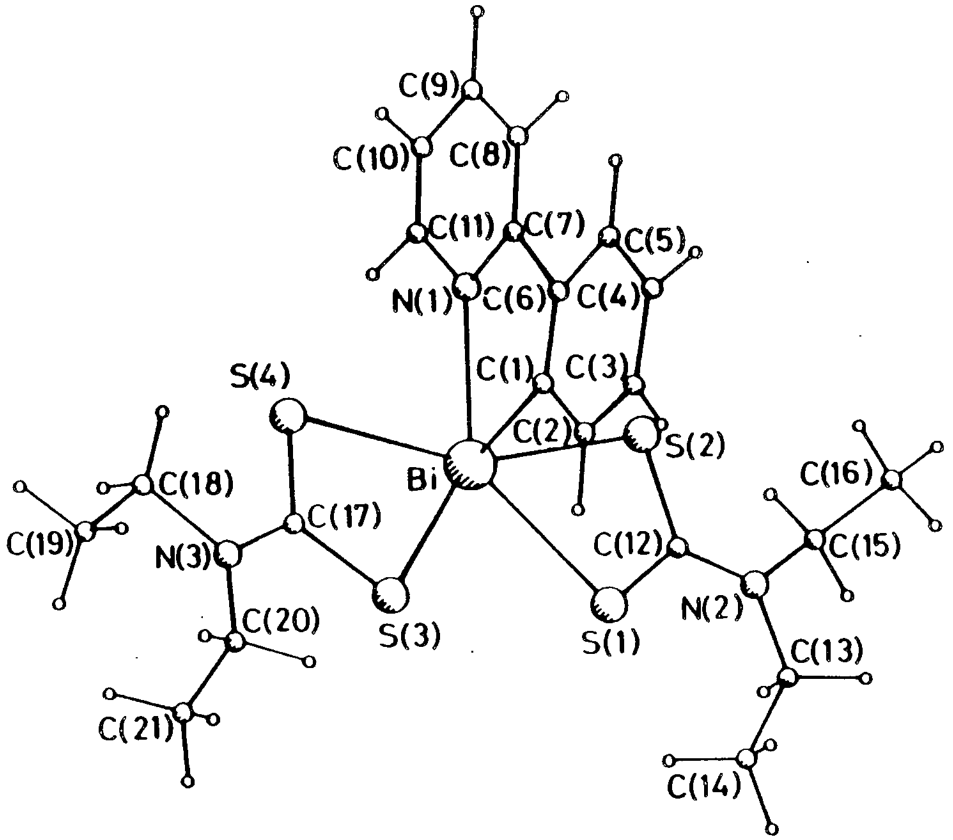


FIGURE 5.5 Molecular structure of bis(diethyldithiocarbamato)[2-(2′-pyridyl)phenyl]bismuth(III)

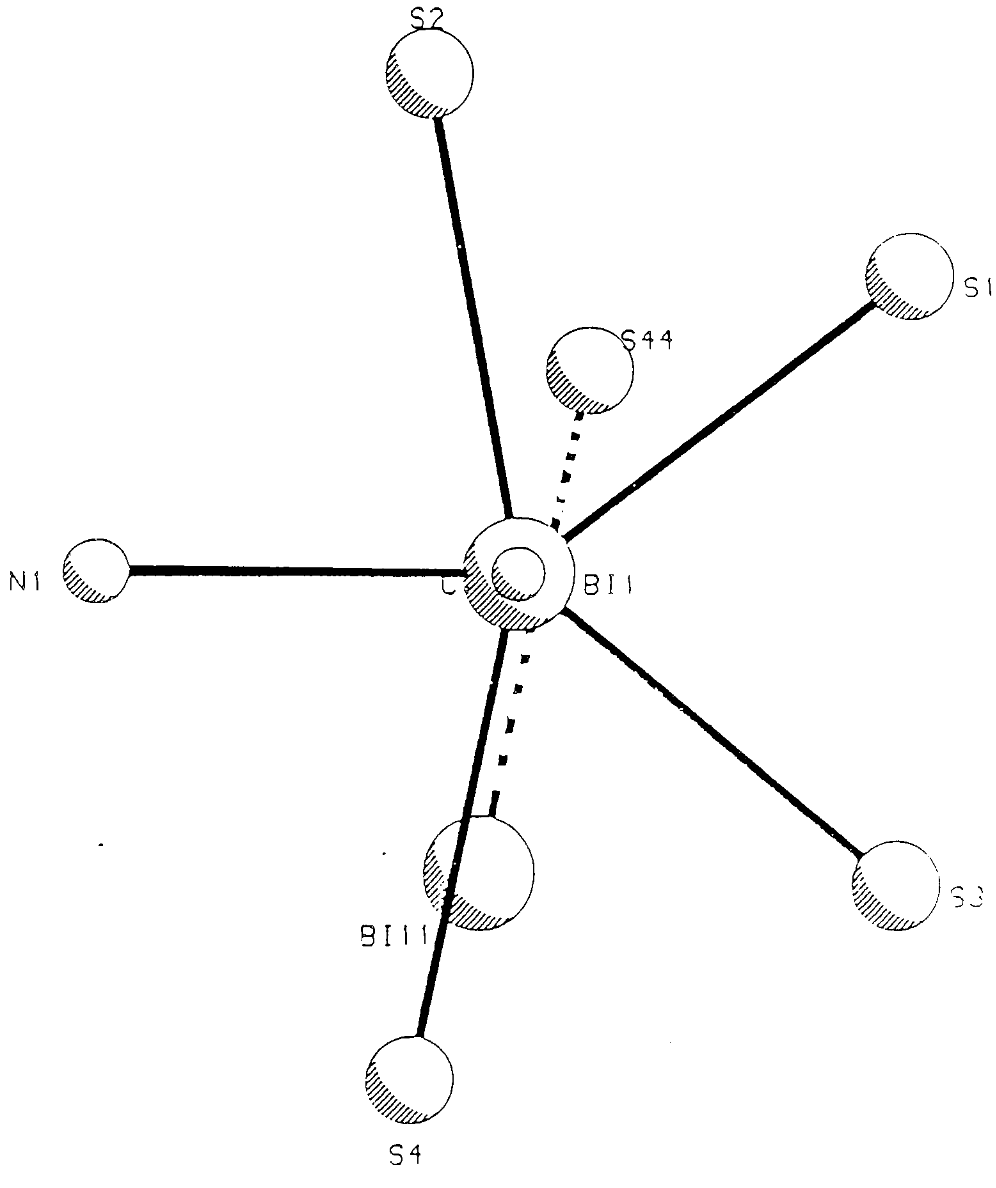


Figure 5.6 Intermolcular interations in compond I

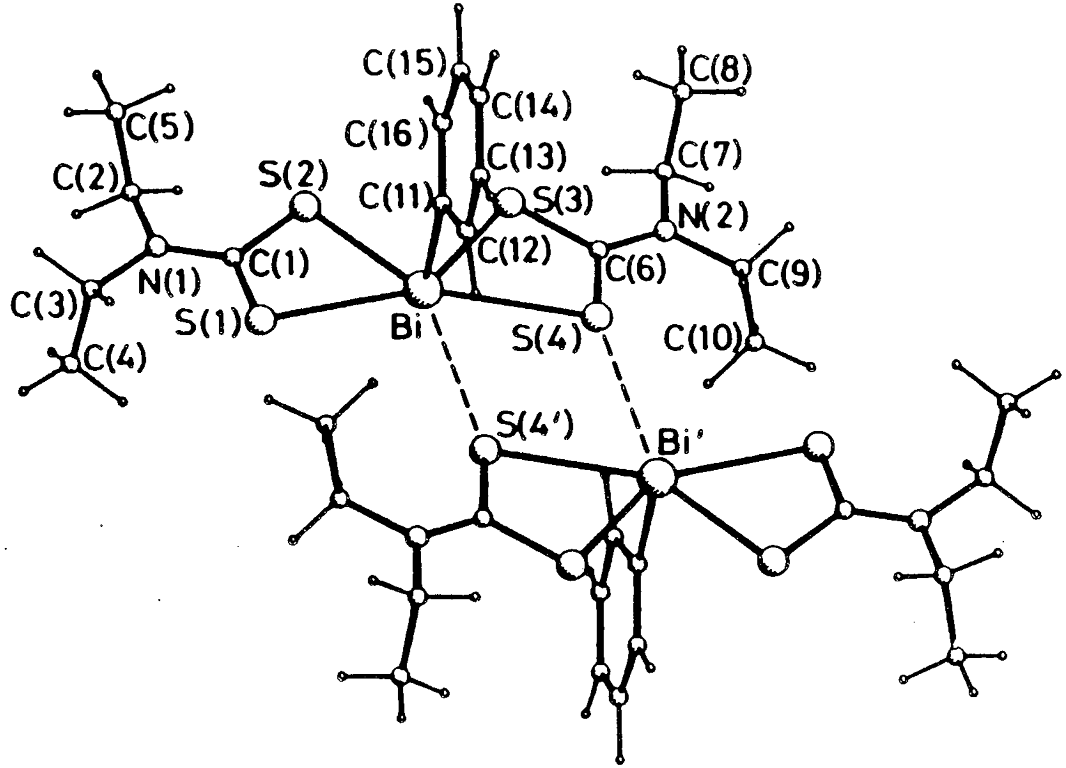


FIGURE 5.7 Molecular structure of bis(diethyldithiocarbamato)phenylbismuth(III) dimer

Table 5.7 Fractional atomic coordinates ($x10^4$, for Bi $x\ 10^5$) with e.s.d.'s in parentheses, for compound I.

	x	y	z
Bi	41062(2)	49682(2)	16594(2)
S(1)	2027(2)	3092(2)	2346(2)
S(2)	4549(2)	2659(2)	3078(2)
S(3)	2123(2)	6065(2)	714(2)
S(4)	4632(2)	7546(2)	471(2)
N(1)	5984(6)	5707(6)	2391(5)
N(2)	2635(7)	884(6)	3425(6)
N(3)	2612(7)	8452(6)	-360(6)
C(1)	3074(7)	5843(6)	3287(6)
C(2)	1654(7)	5932(8)	3714(7)
C(3)	1033(8)	6396(7)	4764(7)
C(4)	1843(8)	6718(8)	5371(7)
C(5)	3270(8)	6657(7)	4938(7)
C(6)	3909(7)	6209(6)	3882(6)
C(7)	5458(7)	6144(6)	3411(6)
C(8)	6356(9)	6518(9)	3947(7)
C(9)	7779(9)	6475(10)	3413(10)
C(10)	8287(8)	6053(9)	2348(9)
C(11)	7359(8)	5677(8)	1886(8)
C(12)	3031(7)	2101(7)	2991(6)
C(13)	1329(9)	353(9)	3385(8)
C(14)	1595(16)	-330(13)	2342(12)
C(15)	3422(10)	-3(9)	3973(9)
C(16)	2994(12)	49(10)	5241(9)
C(17)	3078(7)	7479(7)	212(6)
C(18)	3531(11)	9577(9)	-871(10)
C(19)	2856(17)	10757(12)	-1323(17)
C(20)	1281(10)	8367(10)	-571(9)
C(21)	1420(13)	7836(13)	-1650(11)

Fractional atomic coordinates (x10^4)
and isotropic temperature factors (A^2 x10^3)
for compound I.

	x	y	z	Uiso
H(2)	1013	5646	3247	51
H(3)	-86	6499	5091	51
H(4)	1356	7023	6200	51
H(5)	3902	6955	5409	51
H(8)	5943	6839	4776	51
H(9)	8489	5768	3818	51
H(10)	9393	6026	1903	51
H(11)	7752	5333	1065	51
H(13)	901	-327	4138	81
H(13A)	592	1134	3359	81
H(14)	627	-708	2333	150
H(14A)	2328	-1115	2364	150
H(14B)	2019	346	1585	150
H(15)	3262	-972	3832	81
H(15A)	4514	232	3603	81
H(16)	3614	-634	5612	150
H(16A)	1905	-192	5622	150
H(16B)	3158	1012	5393	150
H(18)	3932	9844	-231	81
H(18A)	4384	9283	-1570	81
H(19)	3615	11516	-1678	150
H(19A)	2007	11080	-637	150
H(19B)	2459	10520	-1976	150
H(20)	597	7749	130	81
H(20A)	828	9325	-615	81
H(21)	405	7800	-1753	150
H(21A)	1863	6873	-1617	150
H(21B)	2094	8449	-2361	150

Table 5.7 (contd)

Anisotropic temperature factors (A^{2} x10^{3},x 10^{4} for Bi) with e.s.d.'s in parentheses for compound I

	U11	U22	U33	U23	U13	U12
Bi	320(1)	323(2)	299(2)	-47(1)	-89(1)	-5(1)
S(1)	39(1)	38(1)	57(1)	-2(1)	-20(1)	-3(1)
S(2)	46(1)	45(1)	50(1)	2(1)	-24(1)	-4(1)
S(3)	39(1)	43(1)	51(1)	5(1)	-19(1)	-6(1)
S(4)	49(1)	40(1)	59(1)	4(1)	-25(1)	-9(1)
N(1)	35(3)	42(3)	43(3)	-8(3)	-11(2)	3(2)
N(2)	52(3)	37(3)	52(4)	2(3)	-19(3)	-8(3)
N(3)	51(3)	34(3)	59(4)	2(3)	-22(3)	6(3)
C(1)	39(3)	31(3)	36(3)	-4(3)	-10(3)	2(3)
C(2)	41(3)	48(4)	44(4)	-6(3)	-6(3)	-1(3)
C(3)	45(4)	41(4)	49(4)	-9(3)	-1(3)	1(3)
C(4)	55(4)	41(4)	43(4)	-10(3)	-3(3)	5(3)
C(5)	60(4)	31(4)	42(4)	-8(3)	-14(3)	3(3)
C(6)	43(3)	27(3)	35(3)	-1(3)	-10(3)	-4(3)
C(7)	47(3)	27(3)	38(4)	1(3)	-19(3)	-5(3)
C(8)	62(5)	55(5)	47(4)	-8(4)	-23(4)	-7(4)
C(9)	51(4)	69(6)	88(7)	-7(5)	-42(5)	3(4)
C(10)	31(3)	65(6)	80(6)	-5(5)	-18(4)	9(3)
C(11)	42(4)	43(4)	58(5)	-6(4)	-10(3)	3(3)
C(12)	39(3)	39(4)	38(4)	-8(3)	-10(3)	0(3)
C(13)	57(5)	55(5)	66(6)	-3(4)	-18(4)	-21(4)
C(14)	119(10)	75(8)	97(9)	-34(7)	-37(8)	-18(7)
C(15)	74(5)	42(5)	69(6)	13(4)	-33(5)	1(4)
C(16)	89(7)	55(6)	71(6)	9(5)	-33(6)	2(5)
C(17)	40(3)	39(4)	44(4)	-7(3)	-13(3)	1(3)
C(18)	75(6)	46(5)	78(7)	13(5)	-25(5)	-2(4)
C(19)	141(12)	51(6)	211(19)	37(9)	-115(14)	-15(7)
C(20)	61(5)	59(6)	79(7)	9(5)	-31(5)	5(4)
C(21)	92(8)	89(8)	101(9)	-11(7)	-63(7)	10(6)

Table 5.7 (contd)

Table 5.8 Fractional atomic coordinates ($\times 10^4$, for Bi $\times 10^5$) with e.s.d.'s in parentheses, for compound II.

	x	y	z
Bi	19059(2)	4297(4)	5661(2)
S(1)	2937(2)	-154(3)	2335(2)
S(2)	3747(2)	1206(4)	1138(2)
S(3)	2082(2)	1501(3)	-838(2)
S(4)	171(2)	413(3)	-928(1)
N(1)	4644(5)	1084(10)	2769(5)
N(2)	528(5)	1677(8)	-2183(5)
C(1)	3841(6)	723(11)	2137(6)
C(2)	5443(7)	1849(13)	2622(8)
C(3)	4777(7)	736(14)	3642(7)
C(4)	4450(9)	1897(19)	4088(9)
C(5)	6165(9)	882(19)	2492(11)
C(6)	873(6)	1250(10)	-1401(5)
C(7)	1142(8)	2383(12)	-2597(7)
C(8)	1563(12)	1353(16)	-3040(10)
C(9)	-493(7)	1510(11)	-2702(6)
C(10)	-1088(7)	2750(13)	-2612(8)
C(11)	2209(7)	-1772(11)	227(6)
C(12)	1629(11)	-2849(14)	296(8)
C(13)	1781(15)	-4199(15)	63(10)
C(14)	2479(15)	-4418(18)	-292(11)
C(15)	3016(12)	-3365(23)	-404(9)
C(16)	2885(8)	-2021(15)	-147(7)

Fractional atomic coordinates ($\times10^4$)
and isotropic temperature factors ($Å^2 \times10^3$)
for compound II.

	x	y	z	Uiso
H(2)	5164	2501	2070	74
H(2A)	5785	2512	3158	74
H(3)	4377	-214	3659	74
H(3A)	5530	551	3966	74
H(4)	4566	1590	4728	128
H(4A)	3695	2087	3772	128
H(4B)	4848	2853	4079	128
H(5)	67384	1484	2391	128
H(5A)	5833	216	1954	128
H(5B)	6453	228	3042	128
H(7)	717	3140	-3047	74
H(7A)	1716	2929	-2128	74
H(8)	2008	1904	-3332	128
H(8A)	995	806	-3513	128
H(8B)	1993	595	-2594	128
H(9)	-545	1411	-3351	74
H(9A)	-769	563	-2507	74
H(10)	-1826	2589	-2997	128
H(10A)	-818	3702	-2809	128
H(10B)	-1042	2854	-1965	128
H(12)	1078	-2641	568	132
H(13)	1337	-5055	145	132
H(14)	2582	-5478	-486	132
H(15)	3551	-3570	-695	132
H(16)	3320	-1157	-236	132

Table 5.8 (contd)

Anisotropic temperature factors (A^2 x10^3 ,x 10^4 for Bi) with e.s.d.'s in parentheses for compound II

	U11	U22	U33	U23	U13	U12
Bi	476(2)	470(2)	476(2)	-46(2)	157(1)	2(2)
S(1)	53(1)	64(2)	58(1)	0(1)	19(1)	-8(1)
S(2)	60(1)	103(2)	60(1)	9(2)	20(1)	-20(2)
S(3)	54(1)	78(2)	74(2)	19(1)	22(1)	-12(1)
S(4)	51(1)	66(1)	49(1)	1(1)	19(1)	-9(1)
N(1)	47(4)	71(6)	61(5)	-1(4)	9(3)	-4(4)
N(2)	68(4)	36(4)	55(4)	4(3)	28(3)	2(3)
C(1)	50(4)	56(6)	59(5)	0(5)	17(4)	-1(4)
C(2)	54(5)	72(8)	89(8)	0(7)	10(5)	-14(6)
C(3)	58(5)	87(8)	60(6)	-1(6)	3(5)	-9(6)
C(4)	82(8)	159(16)	95(10)	-38(10)	33(7)	-4(9)
C(5)	69(7)	142(15)	158(15)	-10(12)	59(9)	-14(9)
C(6)	48(4)	41(5)	54(5)	8(4)	20(4)	5(4)
C(7)	85(7)	55(6)	70(7)	25(5)	40(5)	11(6)
C(8)	169(14)	86(10)	140(13)	44(10)	123(12)	34(10)
C(9)	72(6)	57(6)	44(5)	2(5)	8(4)	-3(5)
C(10)	67(6)	71(8)	99(9)	27(7)	25(6)	12(6)
C(11)	71(6)	48(6)	58(6)	-3(5)	17(5)	23(5)
C(12)	148(12)	58(8)	77(8)	-9(7)	50(8)	-2(8)
C(13)	195(18)	53(8)	101(12)	13(8)	51(12)	18(10)
C(14)	164(17)	69(10)	86(10)	-9(9)	0(11)	58(11)
C(15)	117(12)	136(15)	85(10)	-22(11)	22(8)	67(12)
C(16)	79(7)	95(10)	76(8)	-11(7)	19(6)	35(7)

Table 5.8 (contd)

Bond lengths (A) and bond angles (°)
with e.s.d.'s in parentheses for compound I

Bi	---S(1)	2.798 (2)	N(3)	---C(20)	1.463 (11)
Bi	---S(2)	2.895 (2)	C(1)	---C(2)	1.367 (10)
Bi	---S(3)	2.766 (2)	C(1)	---C(6)	1.390 (10)
Bi	---S(4)	2.878 (2)	C(2)	---C(3)	1.402 (11)
Bi	---N(1)	2.553 (6)	C(3)	---C(4)	1.365 (12)
Bi	---C(1)	2.263 (7)	C(4)	---C(5)	1.372 (11)
S(1)	---C(12)	1.714 (7)	C(5)	---C(6)	1.404 (10)
S(2)	---C(12)	1.714 (7)	C(6)	---C(7)	1.489 (10)
S(3)	---C(17)	1.737 (7)	C(7)	---C(8)	1.389 (10)
S(4)	---C(17)	1.713 (7)	C(8)	---C(9)	1.381 (13)
N(1)	---C(7)	1.350 (9)	C(9)	---C(10)	1.390 (15)
N(1)	---C(11)	1.332 (9)	C(10)	---C(11)	1.351 (13)
N(2)	---C(12)	1.340 (10)	C(13)	---C(14)	1.515 (15)
N(2)	---C(13)	1.479 (10)	C(15)	---C(16)	1.512 (15)
N(2)	---C(15)	1.436 (10)	C(18)	---C(19)	1.507 (14)
N(3)	---C(17)	1.316 (10)	C(20)	---C(21)	1.493 (16)
N(3)	---C(18)	1.478 (11)			

Table 5.9

S(1)	-Bi	-S(2)	62.9 (1)
S(1)	-Bi	-S(3)	76.9 (1)
S(2)	-Bi	-S(3)	139.8 (1)
S(1)	-Bi	-S(4)	139.9 (1)
S(2)	-Bi	-S(4)	156.7 (1)
S(3)	-Bi	-S(4)	63.1 (1)
S(1)	-Bi	-N(1)	137.5 (1)
S(2)	-Bi	-N(1)	78.4 (1)
S(3)	-Bi	-N(1)	138.3 (1)
S(4)	-Bi	-N(1)	78.6 (1)
S(1)	-Bi	-C(1)	89.5 (2)
S(2)	-Bi	-C(1)	87.0 (2)
S(3)	-Bi	-C(1)	91.6 (2)
S(4)	-Bi	-C(1)	88.5 (2)
N(1)	-Bi	-C(1)	70.8 (2)
Bi	-S(1)	-C(12)	89.9 (2)
Bi	-S(2)	-C(12)	86.7 (3)
Bi	-S(3)	-C(17)	91.1 (2)
Bi	-S(4)	-C(17)	87.9 (3)
Bi	-N(1)	-C(7)	113.1 (4)
Bi	-N(1)	-C(11)	127.1 (5)
C(7)	-N(1)	-C(11)	119.8 (7)
C(12)	-N(2)	-C(13)	122.1 (7)
C(12)	-N(2)	-C(15)	123.3 (7)
C(13)	-N(2)	-C(15)	114.6 (7)
C(17)	-N(3)	-C(18)	117.9 (7)
C(17)	-N(3)	-C(20)	120.8 (7)
C(18)	-N(3)	-C(20)	121.1 (7)
Bi	-C(1)	-C(2)	120.6 (5)
Bi	-C(1)	-C(6)	118.6 (5)
C(2)	-C(1)	-C(6)	120.6 (7)
C(1)	-C(2)	-C(3)	119.6 (7)
C(2)	-C(3)	-C(4)	120.1 (7)
C(3)	-C(4)	-C(5)	120.6 (7)
C(4)	-C(5)	-C(6)	119.9 (7)
C(1)	-C(6)	-C(5)	119.0 (6)
C(1)	-C(6)	-C(7)	121.0 (6)
C(5)	-C(6)	-C(7)	120.0 (6)
N(1)	-C(7)	-C(6)	116.1 (6)
N(1)	-C(7)	-C(8)	119.8 (7)
C(6)	-C(7)	-C(8)	124.2 (7)
C(7)	-C(8)	-C(9)	119.6 (8)
C(8)	-C(9)	-C(10)	119.2 (8)
C(9)	-C(10)	-C(11)	118.2 (7)
N(1)	-C(11)	-C(10)	123.3 (8)
S(1)	-C(12)	-S(2)	120.2 (4)
S(1)	-C(12)	-N(2)	120.2 (5)
S(2)	-C(12)	-N(2)	119.7 (6)
N(2)	-C(13)	-C(14)	111.0 (8)
N(2)	-C(15)	-C(16)	112.4 (8)
S(3)	-C(17)	-S(4)	117.9 (4)
S(3)	-C(17)	-N(3)	120.2 (5)
S(4)	-C(17)	-N(3)	121.9 (6)
N(3)	-C(18)	-C(19)	115.6 (9)
N(3)	-C(20)	-C(21)	113.3 (9)

Table 5.9 (contd)

S(1)	-Bi	-S(2)	63.9 (1)	C(7)	-N(2)	-C(9)	115.7 (8)
S(1)	-Bi	-S(3)	144.0 (1)	S(1)	-C(1)	-S(2)	121.0 (5)
S(2)	-Bi	-S(3)	80.1 (1)	S(1)	-C(1)	-N(1)	120.6 (8)
S(1)	-Bi	-S(4)	152.5 (1)	S(2)	-C(1)	-N(1)	118.4 (7)
S(2)	-Bi	-S(4)	143.6 (1)	N(1)	-C(2)	-C(5)	112.5 (10)
S(3)	-Bi	-S(4)	63.5 (1)	N(1)	-C(3)	-C(4)	112.9 (11)
S(1)	-Bi	-C(11)	90.4 (3)	S(3)	-C(6)	-S(4)	118.8 (5)
S(2)	-Bi	-C(11)	94.6 (3)	S(3)	-C(6)	-N(2)	119.6 (7)
S(3)	-Bi	-C(11)	92.0 (3)	S(4)	-C(6)	-N(2)	121.6 (6)
S(4)	-Bi	-C(11)	88.1 (2)	N(2)	-C(7)	-C(8)	111.9 (9)
Bi	-S(1)	-C(1)	83.2 (3)	N(2)	-C(9)	-C(10)	111.9 (8)
Bi	-S(2)	-C(1)	91.2 (3)	Bi	-C(11)	-C(12)	119.0 (8)
Bi	-S(3)	-C(6)	92.8 (3)	Bi	-C(11)	-C(16)	121.1 (9)
Bi	-S(4)	-C(6)	84.8 (3)	C(12)	-C(11)	-C(16)	119.3 (11)
C(1)	-N(1)	-C(2)	122.2 (9)	C(11)	-C(12)	-C(13)	120.0 (15)
C(1)	-N(1)	-C(3)	122.0 (8)	C(12)	-C(13)	-C(14)	119.0 (17)
C(2)	-N(1)	-C(3)	115.8 (8)	C(13)	-C(14)	-C(15)	121.6 (15)
C(6)	-N(2)	-C(7)	121.5 (8)	C(14)	-C(15)	-C(16)	119.5 (16)
C(6)	-N(2)	-C(9)	122.8 (8)	C(11)	-C(16)	-C(15)	120.4 (16)

Table 5.9 (contd)

Bond lengths (A) and bond angles (°)
with e.s.d.'s in parentheses, for compound II.

Bi	---S(1)	2.926 (2)	N(2)	---C(7)	1.479 (12)
Bi	---S(2)	2.671 (2)	N(2)	---C(9)	1.480 (12)
Bi	---S(3)	2.676 (3)	C(2)	---C(5)	1.477 (17)
Bi	---S(4)	2.942 (2)	C(3)	---C(4)	1.500 (18)
Bi	---C(11)	2.241 (10)	C(7)	---C(8)	1.486 (17)
S(1)	---C(1)	1.698 (10)	C(9)	---C(10)	1.502 (15)
S(2)	---C(1)	1.714 (10)	C(11)	---C(12)	1.360 (16)
S(3)	---C(6)	1.740 (8)	C(11)	---C(16)	1.371 (15)
S(4)	---C(6)	1.703 (9)	C(12)	---C(13)	1.374 (19)
N(1)	---C(1)	1.351 (11)	C(13)	---C(14)	1.372 (25)
N(1)	---C(2)	1.476 (13)	C(14)	---C(15)	1.325 (24)
N(1)	---C(3)	1.463 (14)	C(15)	---C(16)	1.376 (21)
N(2)	---C(6)	1.315 (11)			

Table 5.10

Table 5.11 Crystal and experimental parameters

	(1)	(2)
Molecular Formula	$C_{21}H_{28}N_3S_4Bi$	$C_{16}H_{25}N_2S_4Bi$
M	659.7	582.6
Crystal size (mm)	1.00 x 0.35 x 0.25	0.32 x 0.25 x 0.03
a/Å	10.126 (1)	14.796 (7)
b/Å	10.447 (2)	9.437 (9)
c/Å	12.512 (8)	16.942 (8)
α/°	82.06 (4)	90
β/°	71.27 (4)	109.50 (5)
γ/°	86.92 (1)	90
U/Å^3	1241.4	2229.9
Space group	PT	P2$_1$/C
Z	2	4
Dc(gms/cm^3)	1765	1.735
F(000)	644	1128
M(Mo-Kα)mm^{-1}	7.412	8.240
Data collection range θ/° (Å = 0.71069 Å)	2-25	2-25
Unique data measured	5346	3916
Significant data [I > 2.5 θ(I)]	4063	3017
Least-squares weight K{w=[θ^2(f)+KF^2]$^{-1}$}	0.001	0.0001
Maximum Shift/Error in final least-squares cycle	0.06	0.48
Final Π	0.0297	0.0374
Final Π/w	0.0545	0.0496
Residential Election density/eÅ^{-3}	-1.2 to 1.8	-1.1 to 1.4

5.5 Determination of Bismuth Content of New Organylbismuth Compounds

5.5.1 Introduction

A number of spectrophotometric methods are mentioned in the literature [141,143] for the determination of bismuth. However they require large sample weights, and therefore they were not feasible for us, because of the small sample sizes being handled. Also none of the methods found were for the determination of bismuth in organometallic compounds. It was decided to develop an atomic absorption method, the advantages being, firstly a small sample weight is required, and also the low detection limits usually available with atomic absorption.

5.5.2 Theoretical Background

Atomic absorption spectroscopy is the study of the absorption of energy by atoms. It is based on the principle of absorption of electromagnetic radiation in the visible and ultraviolet regions of the spectrum by atoms resulting in changes in the electronic structure. Radiation characteristic of the particular element being analysed is passed through an atomic vapour of the sample. The sample is vaporised by aspirating a solution into a flame or evaporation from an electrically heated surface. When electromagnetic radiation characteristic of electronic transitions in the outer orbitals of atoms of a partcular element is passed through an atomic vapour of that element, the radiation at certain frequencies is attenuated.This absorbed radiation excites electrons from the ground state to various higher energy levels (excited states) and the degree of absorption is a quantitative measure of the concentration of ground state atoms in the vapour.

5.5.3 Experimental

Various acid mixtures were examined, for the digestion of the organylbismuth compounds. The use of beakers and hotplates for performing these digestions was found to be unsatisfactory at destroying the organic matter in these compounds. The apparatus below was designed and used for all subsequent determinations.

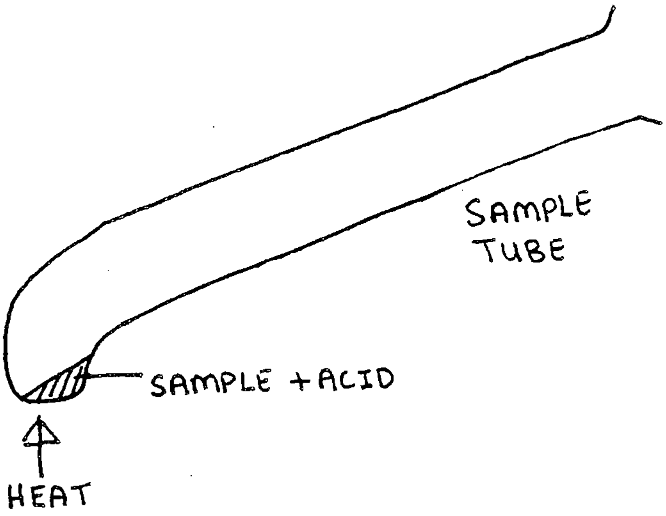


Figure 5.8 Quartz tube used for preparartion of samples for atomic absorption.

5.5.4 Procedure

To a known weight of sample (0.05-0.1g), concentrated sulphuric acid and concentrated nitric acid (3:2 ratio dropwise) were added carefully. The sample tube was then heated until all traces of the acid were removed. The procedure was repeated twice, then distilled water added with a few drops of nitric acid, to dissolve all traces of the bismuth metal or oxides. The sample was then filtered, diluted and atomic absorption using a bismuth lamp used to determine the percentage of bismuth in the sample.

5.5.5 Discussion

The method allowed the determination of bismuth at trace levels and only required a small sample for the analysis. It was found to give reproducible results, however, interferences by other metals may be a problem in some cases. The method was used to determine the bismuth content of all of the compounds where a figure has been given.

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