Studies on heterocyclic derivatives of mercury, silicon and group V elements

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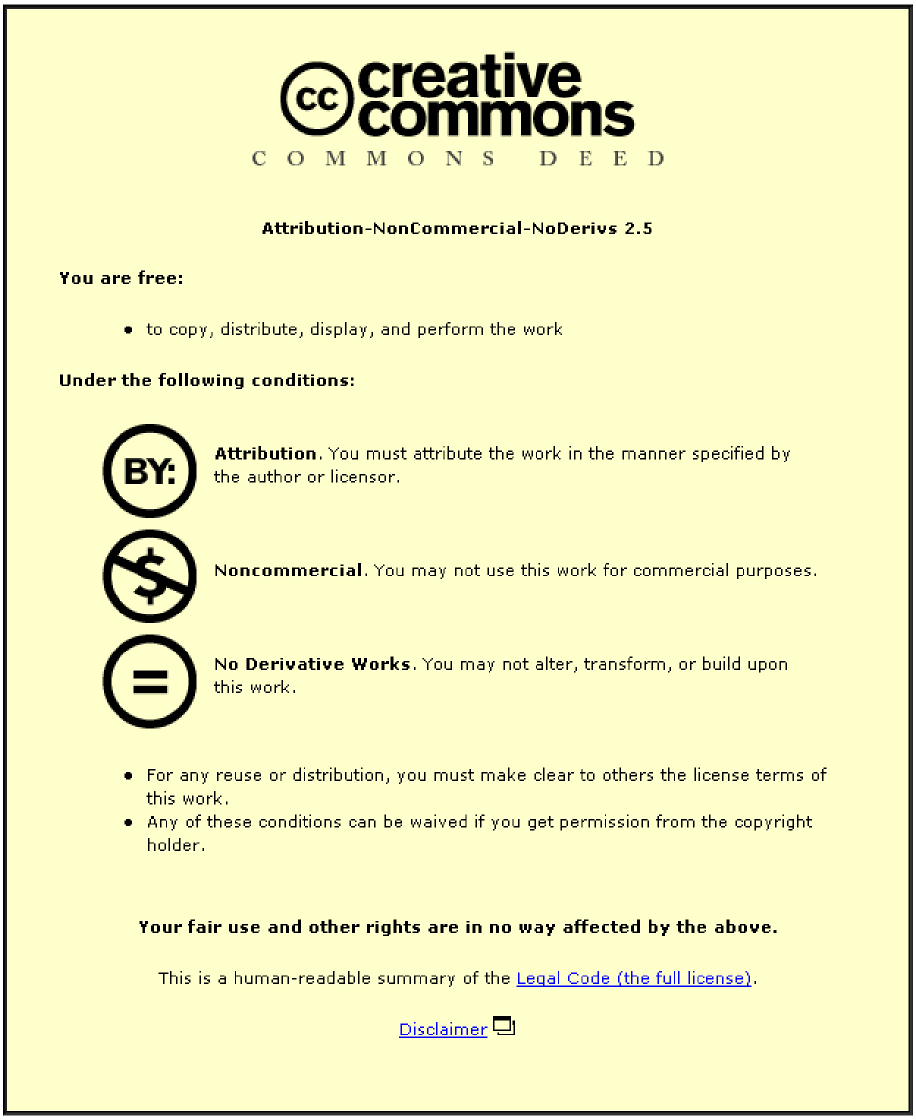

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Studies on Heterocyclic Derivatives of Mercury, Silicon and Group V Elements

by

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A Doctoral Thesis submitted in partial fulfilment of the requirement for the award of Doctor of Philosophy of the Loughborough University of Technology.

September 1985.

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To:

Lutphy and Farah

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Acknowledgements

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Summary

Several substituted phenylene- and biphenylene-mercurials have been prepared and their degree of polymerization checked using mass spectrometry; in all cases only the trimeric species were obtained. The chemistry of some of these organomercurials was thoroughly investigated and also a complete X-ray structural analysis of the orthorhombic form of biphenylenemercury carried out.

The direct syntheses and chemical study of perfluoro- and perchloro-distibatriptycenes are described: both compounds formed hemi-solvates with a variety of organic solvents. The step-wise synthesis, starting from 1,2-dibromotetrafluorobenzene, of eight fully-fluorinated 1,6-disubstituted triptycenes containing Group IV and Group V elements has been successfully accomplished and in each case the intermediate tris(2-bromotetrafluorophenyl) compounds isolated and characterized. Very few 1,6-disubstituted triptycenes were known previously.

Tris(2-chlorophenyl) derivatives of the Group V elements were synthesised in very high yield by reacting 2-chlorophenyllithium, stabilised by tetramethylethylene diamine, with MCl_3 where M = P, As, Sb and Bi. Many unsuccessful attempts were made to convert these $M(2\text{-}C\ell C_6H_4)_3$ derivatives into the hydrogen analogues of the 1,6-disubstituted triptycenes mentioned above.

Publications

1 - Substituted Phenylene-and Biphenylene-Mercurials.
N.A.A. AL-Jabar and A.G. Massey, J. Organomet. Chem., 275 (1984), 9.

2 - Dodecafluoro- and Dodecachloro-5, 10-o-Benzenostibanthrene.
N.A.A. AL-Jabar and A.G. Massey, J. Organomet. Chem., 276 (1984) 331.

3 - The Synthesis of Perfluoro-1,6-Disubstituted Triptycenes Containing Group IV and Group V Elements.
N.A.A. AL-Jabar and A.G. Massey, J. Organomet. Chem., 187 (1985) 57.

4 - The Synthesis of 2-Chlorophenyl Derivatives of Group V.
N.A.A. AL-Jabar and A.G. Massey, J. Organomet. Chem., 288 (1985) 145.

5 - a - 2,2'-Biphenylenemercury,
b - 2-Chlorophenyllithium,
N.A.A. AL-Jabar and A.G. Massey, Organometallic Synthesis., Vol. 3, Edited by J.J. Eisch and R.B. King, Academic Press (in the press).
c - Dodecafluoro-1,6-distibatriptycene (Dodecafluoro-5, 10-o-Benzenostibanthrene, $Sb_2(C_6F_4)_3$.
N.A.A. AL-Jabar, T.K. Mistry and A.G. Massey, Organometallic Synthesis., Vol.3, Edited by J.J. Eisch and R.B. King, Academic Press (in the press).

6 - The Synthesis of 1,6-Distibatriptycene (5,10-o-Benzenostibanthrene), $Sb_2(C_6H_4)_3$,
N.A.A. AL-Jabar, D. Bowen and A.G. Massey, J. Organomet. Chem., (in the press).

Chapter 1

An Introduction to the Synthesis of Organomercury Compounds

An enormous number of organomercury compounds have been prepared, largely in the earlier stages of the development of organometallic chemistry and to a great extent in the hope of finding substances of pharmacological value. Organomercury compounds are thermally stable at room temperature and have such a low order of reactivity that they are unaffected by air and water. They can thus be prepared and used under conditions that would be unthinkable with the more reactive organometallics of, say, lithium, magnesium or aluminium. Although organomercurials found increasing utility in the synthesis of other organometallic compounds, their low chemical reactivity towards organic substrates has rather limited their use as general synthetic agents compared with Grignard and organolithium reagents. However, the ready availability of these compounds, their ability to accommodate essentially all important organic functional groups, and their remarkable chemical and thermal stability have made them attractive as synthetic intermediates; see Chapter [2] for examples discovered in this work.

Organomercurials are most commonly prepared from the corresponding organolithium or organomagnesium compounds and mercuric salts, especially the halides. A wide range of organic groups may be transferred including primary, secondary or tertiary alkyl, alicyclic or polycyclic systems, alkenyl and aryl as well as certain functionally-substituted organic groups(1):

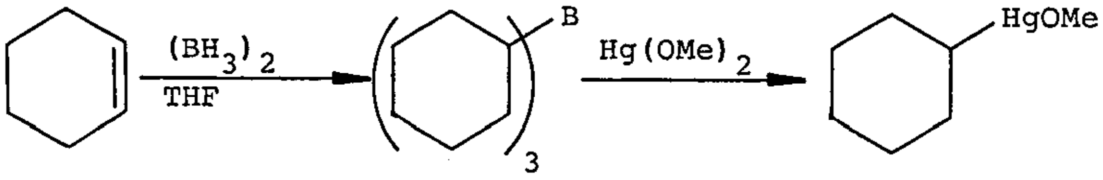
e.g. $2C_6H_5SO_2CH_2Li + HgX_2 \longrightarrow (C_6H_5SO_2CH_2)_2Hg$ Ref.1

$2C_6F_5MgBr + HgC\ell_2 \longrightarrow (C_6F_5)_2Hg$ Ref.2

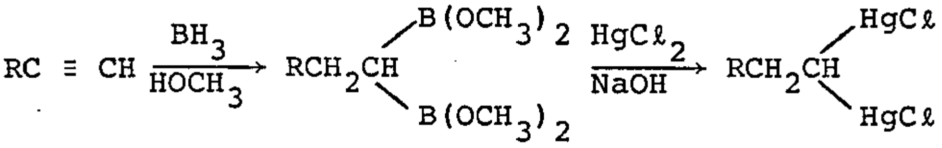
The mercuration of organoboranes offers a very valuable method for the synthesis of organomercurials containing a variety of functional groups(3). For example, primary trialkylboranes undergo a rapid and quantitative reaction with mercuric acetate at room temperature to give the corresponding alkylmercury acetates(4):

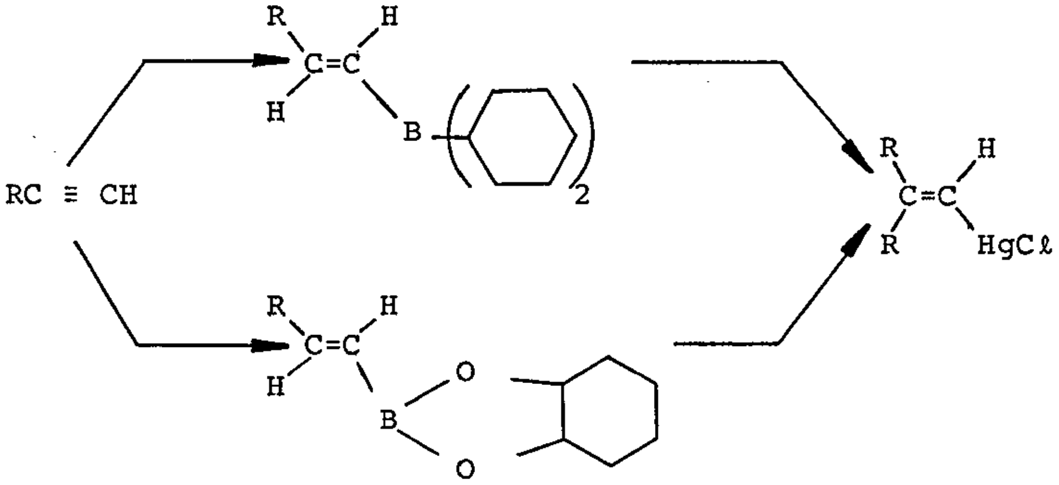
$$(RCH_2CH_2)_3B + 3Hg(OAc)_2 \longrightarrow 3RCH_2CH_2HgOAc$$

and secondary alkylmercury compounds are readily obtained from olefins via hydroboration followed by mercuration using mercury alkoxides(5):



Further increasing the potential of this method of synthesis, it has been found that the hydroboration-mercuration of alkynes can be controlled to give either alkylidenebis(mercuric chlorides)(6) or vinylmercury chlorides(7,8):

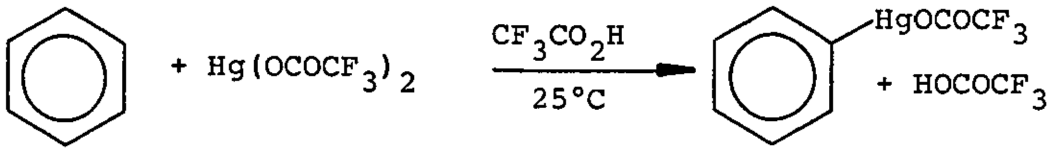




A variety of other organometal compounds have been used over the years for the formation of organomercurials including those of zinc, aluminium, the Group IVB metals, arsenic, antimony and bismuth(1). For example, the ease of cleavage of organic groups from tin and other IVB compounds by mercuric salts is aryl-metal>alkyl-metal(1):

$$\text{aryl} - \text{Sn(alkyl)}_3 + \text{HgX}_2 \longrightarrow \text{aryl} - \text{HgX} + \text{XSn(alkyl)}_3$$

Probably the most important route to arylmercurials is the direct mercuration of aromatic compounds. It generally exhibits the characteristics of a typical electrophilic aromatic substitution reaction and is facilitated by highly ionic mercury salts and by electron-donating groups on the aromatic ring$^{(3)}$:



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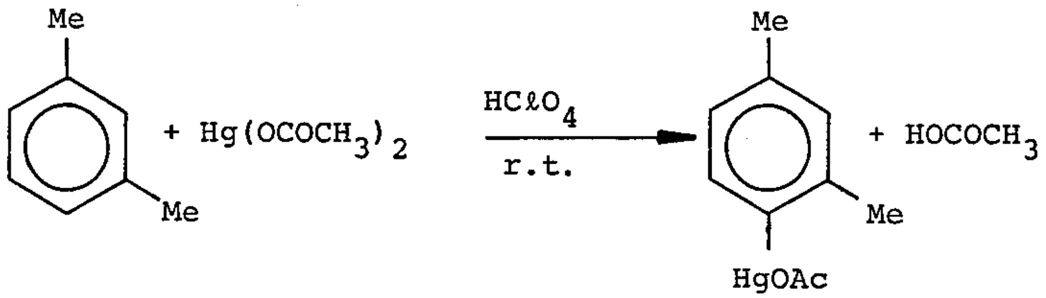
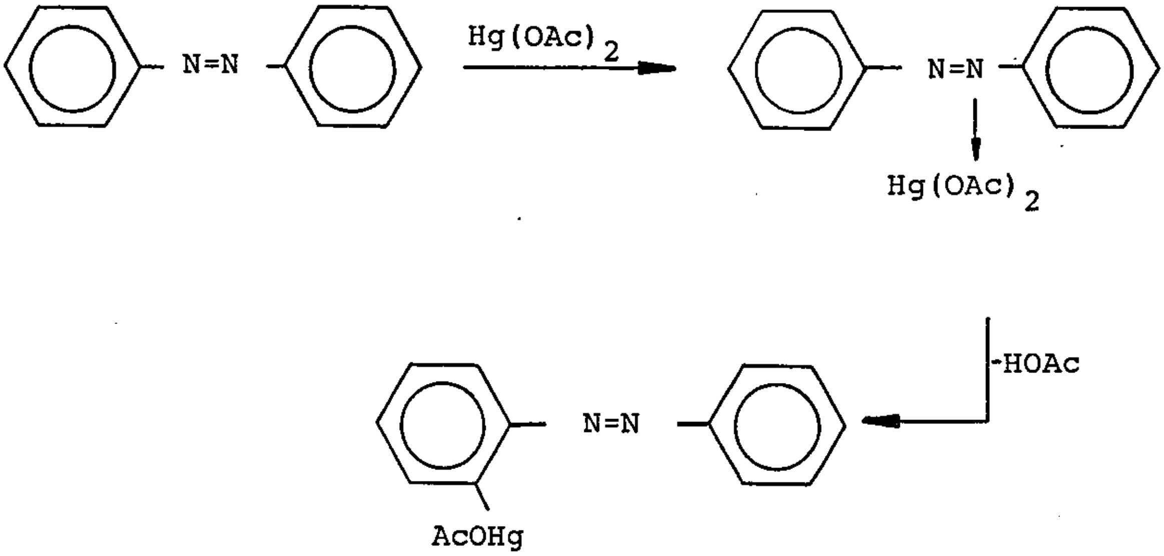


Ref.10

As a preparative method, mercuration of aromatics suffers from both the lack of selectivity and the formation of a mixture of all possible isomeric monomercurated compounds; additionally, the reaction is reversible and hence sometimes an isomer can transform into a more thermodynamically stable one if long reaction times are used, as in the mercuration of toluene$^{(11)}$.

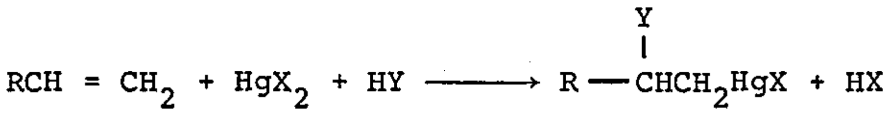
For phenols and primary or secondary aromatic amines, initial reactions can occur at the OH or NH groups to give oxygen-mercury and nitrogen-mercury species; subsequent rearrangement then leads to ring substitution, particularly at low pH(1). Prior complexation by azo and related groups directs the mercury species to the ortho site(12,13):



The mercurating agent can be mercuric oxide or salts such as mercuric sulphate, nitrate or perchlorate but the most useful is the acetate, since the liberated weak acetic acid does not decompose the resulting organomercury salt even at high temperatures(14). A modern development has been the use of molten mercuric trifluoroacetate(15,16); with this reagent even mercuration of the highly deactivated polychlorobenzenes (such as tetrachloronitrobenzenes) can be achieved at 220°C(17):

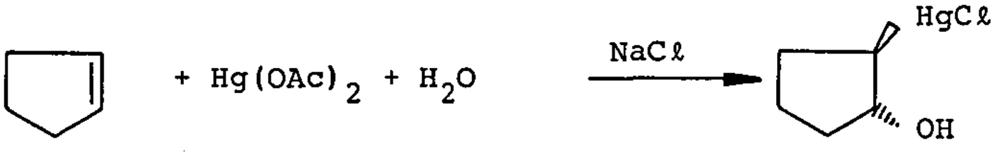
$$C_6HC\ell_4NO_2 + Hg(O_2CCF_3)_2 \longrightarrow (O_2NC_6C\ell_4)_2Hg + 2CF_3CO_2H.$$

The reaction of mercury salts with alkenes in the presence of a nucleophile HY can lead to very valuable β-substituted organomercurials(3):



$$RCH = CH_2 + HgX_2 + HY \longrightarrow R-\overset{\displaystyle Y}{\overset{|}{C}}HCH_2HgX + HX$$

The term solvomercuration applies to the situation where the nucleophile is actually part of the solvent system; other general terms are used such as oxymercuration(18) for addition of OH, aminomercuration(19) for addition of amines and alkoxymercuration(20) for addition of OR,



$$H_2C = CH_2 + Hg(OAc)_2 + EtOCH_2CH_2OH \longrightarrow EtO(CH_2)_2O(CH_2)_2HgC\ell$$

$$cis - MeCH = CHMe + HgC\ell + MeNH_2 \longrightarrow Me_2NMe(CH_2)_2MeHgC\ell$$

The reaction generally involves a trans-Markownikoff addition(3); however, with certain strained alkenes such as norbornene(21) and trans-cycloctene and - nonene(22) cis-addition occurs. Mercuric acetate is the most frequently employed in this reaction while for more electrophilic salts like $Hg(NO_3)_2$ and $Hg(C\ell O_4)_2$, additional base has to be present to remove the liberated acids and to drive the reaction completely to the right. The use of mercuric chloride is limited because of the ease of protonolysis of the solvomercuration products by $HC\ell$, but aminomercuration can be achieved with this salt if sufficient amine is added to act both as the base and the nucleophile. Salts of carboxylic acids other than acetic acid have also been used including the trifluoroacetate and tartarate(1). The nucleophiles can be the solvent for example, water, alcohols, carboxylic acids, and amines, or non-participating solvents may be employed including DMF, THF and $CH_2C\ell_2$(1). Less frequently carbon nucleophiles, such as anisole(23) or β-dicarbonyl(24) compounds, have been used:

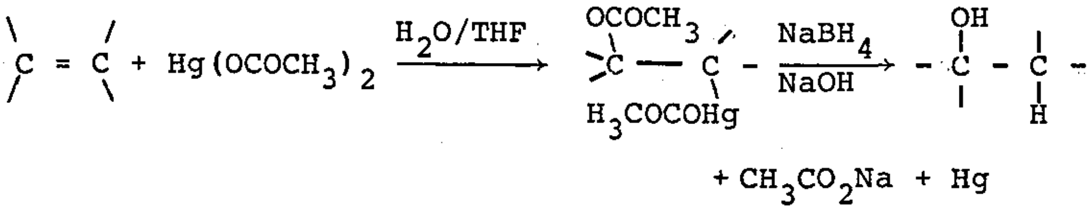
$$CH_2 = CH_2 + Hg(OAc)_2 + PhOMe \longrightarrow p - MeOC_6H_4(CH_2)_2HgOAc$$

$$CH_2 = CH_2 + Hg(OAc)_2 + MeCOCH_2CO_2Et \longrightarrow MeCOCH(CH_2)_2HgOAc$$

When more than one nucleophile is present, all could become involved in the reaction to extents dependent on their relative nucleophilicity and concentration, as in the peroxymercuration of alkenes using mercuric acetate which can lead to acetate-containing products(25):

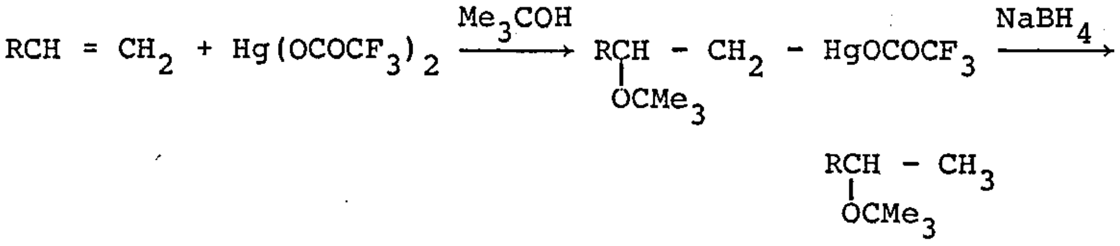
$$RCH=CH_2 + Hg(OAc)_2 + Bu^tO_2H \xrightarrow{CH_2C\ell_2} RCH(OAc)CH_2HgOAc + RCH(O_2Bu^t)CH_2HgOAc$$

The solvomercuration reactions have proved useful for the preparation of organic compounds when employed in conjunction with a demercuration step, often without isolation of the intermediate organomercurial. Thus the product of alkene oxymercuration can be demercurated to give alcohols by treatment with alkaline sodium tetrahydroborate(26):



$$>C=C< + Hg(OCOCH_3)_2 \xrightarrow{H_2O/THF} >\underset{H_3COCOHg}{\overset{OCOCH_3}{C}}-C< \xrightarrow[NaOH]{NaBH_4} -\overset{OH}{\underset{|}{C}}-\underset{H}{C}- + CH_3CO_2Na + Hg$$

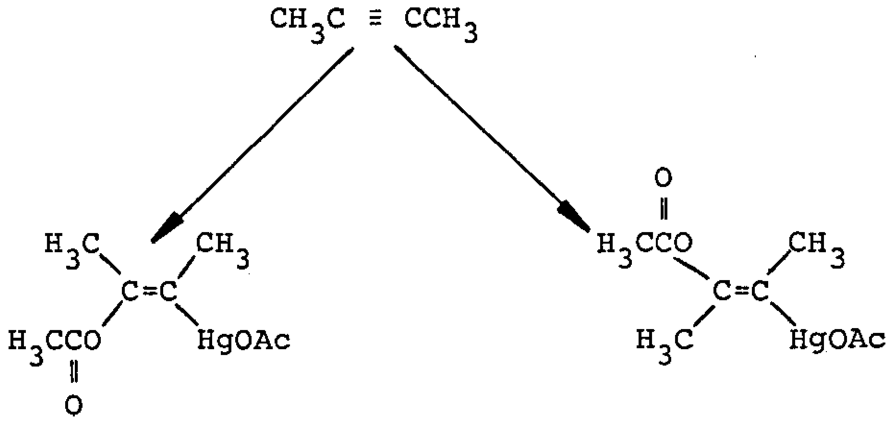
If the above reaction is carried out in alcohol rather than water, ethers are generally formed provided that the alcohol is reasonably nucleophilic. Ether formation is favoured by the use of mercuric trifluoroacetate and this reagent allows the preparation even of t-butyl ethers(27):



$$RCH=CH_2 + Hg(OCOCF_3)_2 \xrightarrow{Me_3COH} \underset{OCMe_3}{RCH}-CH_2-HgOCOCF_3 \xrightarrow{NaBH_4} \underset{OCMe_3}{RCH}-CH_3$$

The reaction has also been extended to the synthesis of peroxides, amines, amides, esters and lactones(3).

Alkyne addition reactions also lead to organomercurials; thus mercuric acetate readily reacts with alkynes in acetic acid to give β-(acetoxy)vinylmercurials and depending upon reaction conditions either the trans or the cis addition product(3) occurs:



The diazo method of synthesizing aromatic compounds of mercury consists in the decomposition of the double salts of aryldiazonium halides and mercuric halides by means of copper powder in acetone, ethyl acetate, alcohol or water(28):

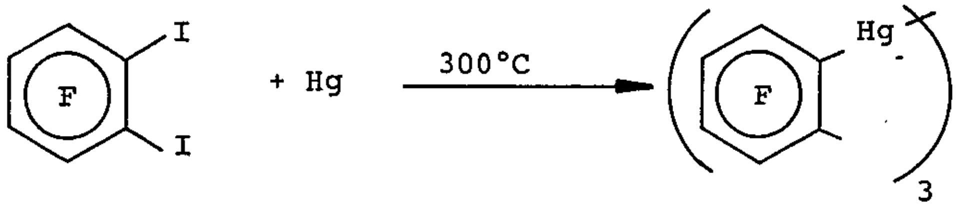
$$ArN_2X.HgX_2 + 2Cu \longrightarrow ArHgX + 2CuX + N_2.$$

With excess copper in the presence of aqueous ammonia the diarylmercury compounds are produced(28):

$$2ArN_2X.HgX_2 + 6Cu + 6NH_3 \longrightarrow Ar_2Hg + 6CuX.NH_3 + N_2$$

The method is useful for introducing mercury into a specific location and is reasonably high yielding, and hence has some advantages over aromatic mercuration if the starting amine is available. In addition, most functional groups are stable to the reaction conditions; however, for compounds having strong electron-withdrawing groups such as NO_2, COOH or SO_3H, lower temperatures in the decomposition step, and vigorous stirring have been advised(1).

The direct synthesis of organomercurials from organic halides and metallic mercury is rather limited(28); however, methyl, benzyl, methylene and allyl iodides react directly with mercury, particularly when catalysed by sun-light(29). Alkyl bromides react only with difficulty and, as might be expected, the chlorides generally do not react at all; even with iodides reactions usually do not proceed very readily(28) and high temperatures are often required as in the reaction of aryliodides with mercury:



Ref. (30)

Sodium amalgams are considerably more reactive towards both alkyl and aryl halides and a wide range of diorganomercurials has been obtained(28):

$$2RX + \text{"}Na_2Hg\text{"} \longrightarrow R_2Hg + 2NaX$$

The starting organic halides in this relatively simple method are usually bromides or iodides, but unfortunately the yields are often very low. The sodium amalgam is generally used in at least 100% excess over the theoretical amount; for alkyl halides the reaction may be carried out with dilute liquid amalgams but more concentrated amalgam is needed for the formation of arylmercury derivatives. o-Dihaloaromatic compounds react with sodium amalgam giving polymeric mercurials; for example, treatment of o-dibromobenzene with sodium amalgam in ether gives o-phenylenemercury trimer(31,32):

$$C_6H_4Br_2 \xrightarrow[\text{ether}]{\text{Na/Hg}} (C_6H_4Hg)_3$$

This type of reaction has been studied in some depth during this work and the details are discussed in Chapter 2.

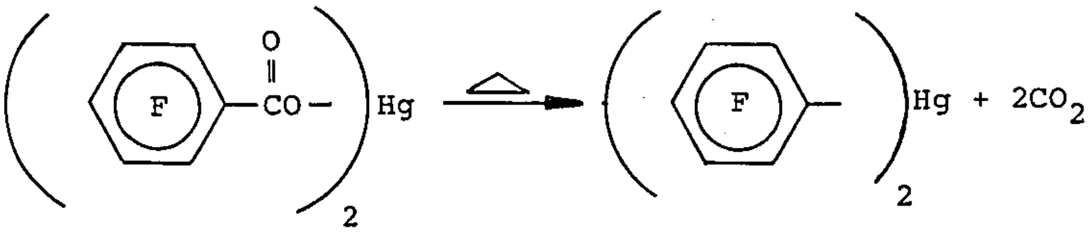
Other metal amalgams may also be used for the synthesis of organomercurials, as in the reaction of bromopentafluorobenzene with lithium amalgam which gives bis(pentafluorophenyl)mercury in good yield(33):

$$C_6F_5Br \xrightarrow[\text{ether}]{\text{Li/Hg}} (C_6F_5)_2Hg$$

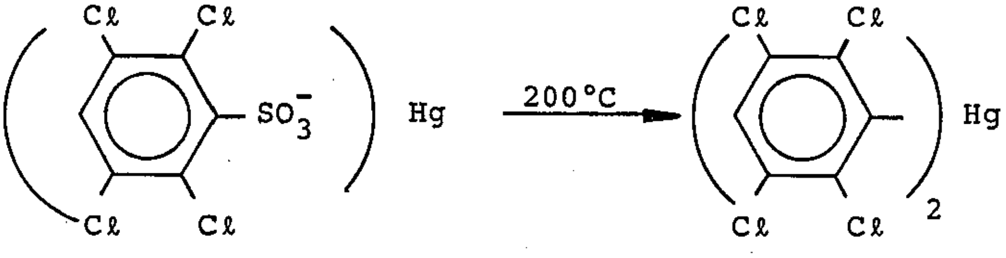
but this amalgam is much more difficult to prepare than that of sodium and hence is used less often.

The bis(perfluoroalkyl)mercury derivatives have been prepared from iodoperfluoroalkanes, using amalgams of Ag, Cu, Zn and Cd(34,35), of which the latter is best since the reactions proceed smoothly and rapidly at room temperature; silver amalgam requires heating to 80°C, copper amalgam to 160 - 180°C whereas zinc amalgam requires over 4 days reaction time at room temperature.

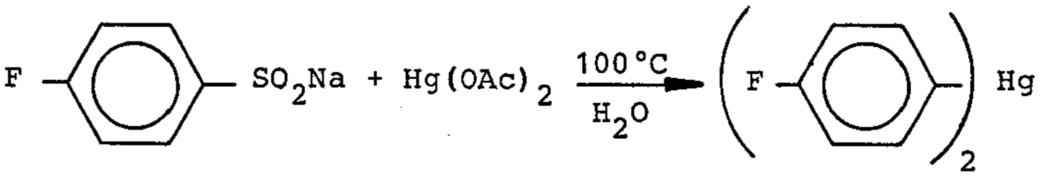
Thermal decarboxylation of the mercuric salts of arene carboxylates provides an alternate method for the synthesis of some arylmercurials, but appears limited to aryls containing strongly electron-withdrawing groups(36):



The photochemical or peroxide-initiated decomposition of many aliphatic and aromatic mercuric carboxylates proceeds under much milder conditions and often provides excellent yields of the corresponding organomercury carboxylates(3). As an extension of this decarboxylation technique it has been found that thermal decomposition of sulphonates may also be used for the preparation of polychloroaryl - and polyfluoroaryl-mercurials(37,38,39):



The name 'Peters reaction'(40,1) has been given to the thermal reaction between a mercuric salt and sulphinic acids or, in a subsequent improvement, their salts; it is used for the synthesis of a wide variety of aromatic, aliphatic and heteroaromatic mercury compounds:



As with the other thermal elimination reactions, the presence of electronegative substituents renders the reaction easier, as shown by the room temperature reactions of polyfluoroaryl systems(41):

$$YC_6F_4SO_2Li + HgX_2 \xrightarrow{H_2O;r.t.} YC_6F_4HgX + SO_2 + LiX$$

X = Cℓ,Br or AcO; Y = F,o-,m- or p-H

A variety of organomercury compounds has been prepared by electrochemical synthesis(1) using both cathodic and anodic processes. Reactions at mercury anodes have involved other metallo-organics such as Grignard reagents and complex organometallic anions:

$$\mathrm{Na}\left[\mathrm{MeA\ell C\ell_3}\right] \xrightarrow[\text{1.2V-216h}]{\text{Hg anode}} \mathrm{Me_2Hg}$$

while in the cathodic processes organic halides or unsaturated compounds such as alkenes and ketones have been employed(1):

$$\mathrm{CH_2 = CHCOMe} \xrightarrow{\text{Hg cathode}} \mathrm{Hg(CH_2CH_2COMe)_2}$$

The more important and general methods of obtaining symmetric diorganomercury compounds are those using organolithium and Grignard compounds, or mercuration. However, additional methods for preparing symmetric organomercurials are symmetrization and reductive disproportionation of organomercury salts, RHgX(1). The symmetrization reaction is, in fact, an equilibrium between the organomercury salt and the symmetrization products:

$$\mathrm{2RHgX + 2L} \rightleftharpoons \mathrm{R_2Hg + HgX_2.L_2}$$

The reaction can be forced completely in the direction of formation of the R_2Hg derivative by the removal of HgX_2 as a complex with the ligand, L. A number of complexing reagents have been used including both anionic and neutral ligands, typical ones being alkali metal iodides, cyanides, thiocyanates and thiosulphates; iodides are particularly useful for diarylmercurials(1) and coordinate strongly to mercury(II) removing it as HgI_4^{2-} species(42):

$$2C_6F_5HgC\ell + 4NaI \longrightarrow (C_6F_5)_2Hg + Na_2HgI_4 + 2NaC\ell$$

Ammonia is a mild and effective reagent for the symmetrization of the addition products obtained from mercuric salts and unsaturated aliphatic compounds(43):

$$2C\ell CH = CHHgC\ell + 2NH_3 \longrightarrow (C\ell CH = CH)_2Hg + (NH_3)_2HgC\ell_2$$

and can also be used successfully for the symmetrization of trans-oxymercuration products which, in aqueous or alcoholic solutions solvolyse under the influence of most of the usual symmetrizing agents such as KI, NaCN and $Na_2S_2O_3$; for example(28):

$$ROC_2H_4HgC\ell + 4KI + 2H_2O \longrightarrow C_2H_4 + K_2HgI_4 + ROH + 2KOH + HC\ell$$

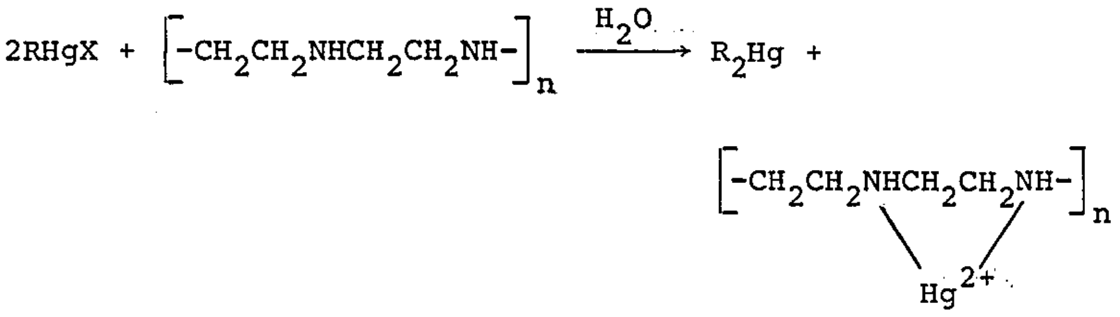
Triphenylphosphine has been found to be particularly effective as a symmetrization agent(44):

$$2(PhN_2C_6H_4)HgC\ell + 2Ph_3P \longrightarrow (PhN_2C_6H_4)_2Hg + (Ph_3P)_2HgC\ell_2$$

The rate of symmetrization of organomercury salts, RHgX, by tertiary phosphines(45,46) decreases in the sequence for X = I > Br > Cℓ and in the solvent order MeOH > Me_2O > THF > PhH; with these reagents, arylmercury salts are more readily symmetrized than alkyl ones. Phenylmercury chloride gives a 1:1 complex with triphenylphosphine and as a result does not symmetrize(47); on the other hand, the following reaction takes place when phenylmercuric acetate is heated for 30 minutes in benzene with tributylphosphine(48):

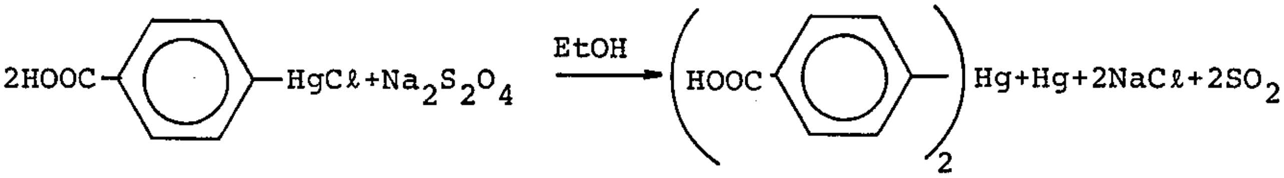
$$C_6H_5HgOCOCH_3 + (n\text{-}C_4H_9)_3P \longrightarrow Hg + (C_6H_5)_2Hg + (CH_3CO)_2O + (n\text{-}C_4H_9)_3PO$$

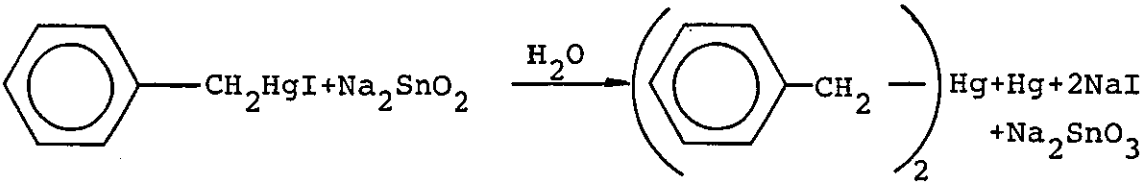
Alkylmercury salts, as well as arylmercury halides, hydroxides and acetates, are conveniently converted to the corresponding diorganomercurials by treatment with polyethyleneimine [Dow PEI-6 (Molecular weight 600)] in the presence of water(49):



$$2RHgX + [-CH_2CH_2NHCH_2CH_2NH-]_n \xrightarrow{H_2O} R_2Hg + [-CH_2CH_2NHCH_2CH_2NH-]_n \cdot Hg^{2+}$$

Various reagents can be used for the reductive disproportionation of organomercury salts, for example, sodium dithionite(50) and sodium stannite(51):





Metal systems, such as magnesium(52), zinc(53), copper-pyridine(54) and cadmium amalgam(55) have all been employed successfully in symmetrization processes, for example:

$$2BuHgOAc \xrightarrow[BF_3.Et_2O]{Zn} Bu_2Hg + Hg$$

The production of symmetric organomercurials in the electrolysis of some organomercury salts is also an example of reductive disproportionation(56):

$$\mathrm{NCCH_2HgC\ell} \xrightarrow[\mathrm{DMF,H_2O,NaOAc}]{\mathrm{Electrolysis}} \mathrm{(NCCH_2)_2Hg}$$

A number of symmetrization processes which give rise to heterocyclic organomercurials has been studied in this research and the results are presented in Chapter 2.

Chapter 2

Some New Studies of Substituted Phenylene- and Biphenylene-Mercurials

Experimental.

All reactions were carried out in oven-dried glass-ware under an atmosphere of dry, oxygen-free nitrogen using two double-surface liquid nitrogen traps connected in series as shown in Figure 2.1. The sealed reaction tubes were made from pyrex glass and thoroughly baked out under vacuum with a free flame before use. The apparatus used for sublimation under vacuum is shown in Figure 2.2.

The solvents such as diethylether, hexane, and petrol ethers, were all sodium-dried; tetrahydrofuran was dried over potassium hydroxide and distilled under nitrogen immediately before use. Tetramethylethylene diamine was dried over calcium hydride and then over molecular sieves.

n-Butyllithium was obtained commercially as a solution in hexane and standardized prior to use by the method of Gilman(1). The substituted dibromobenzenes and 2,2'-diiodo-4,4'-dimethylbiphenyl were prepared using standard procedures; 1,2-dimethoxy-4,5-dibromobenzene (4,5-dibromoveratrole) was purchased from Lancaster syntheses and used without purification.

The infrared spectra were recorded on a Perkin Elmer 457 grating spectrophotometer (4000-250 cm^{-1}) using liquid parafin (nujol) and hexachlorobutadiene (HCBD) mulls.

Analyses were performed by Mr. M. Hart, Microanalytical Department of Manchester University. Mass

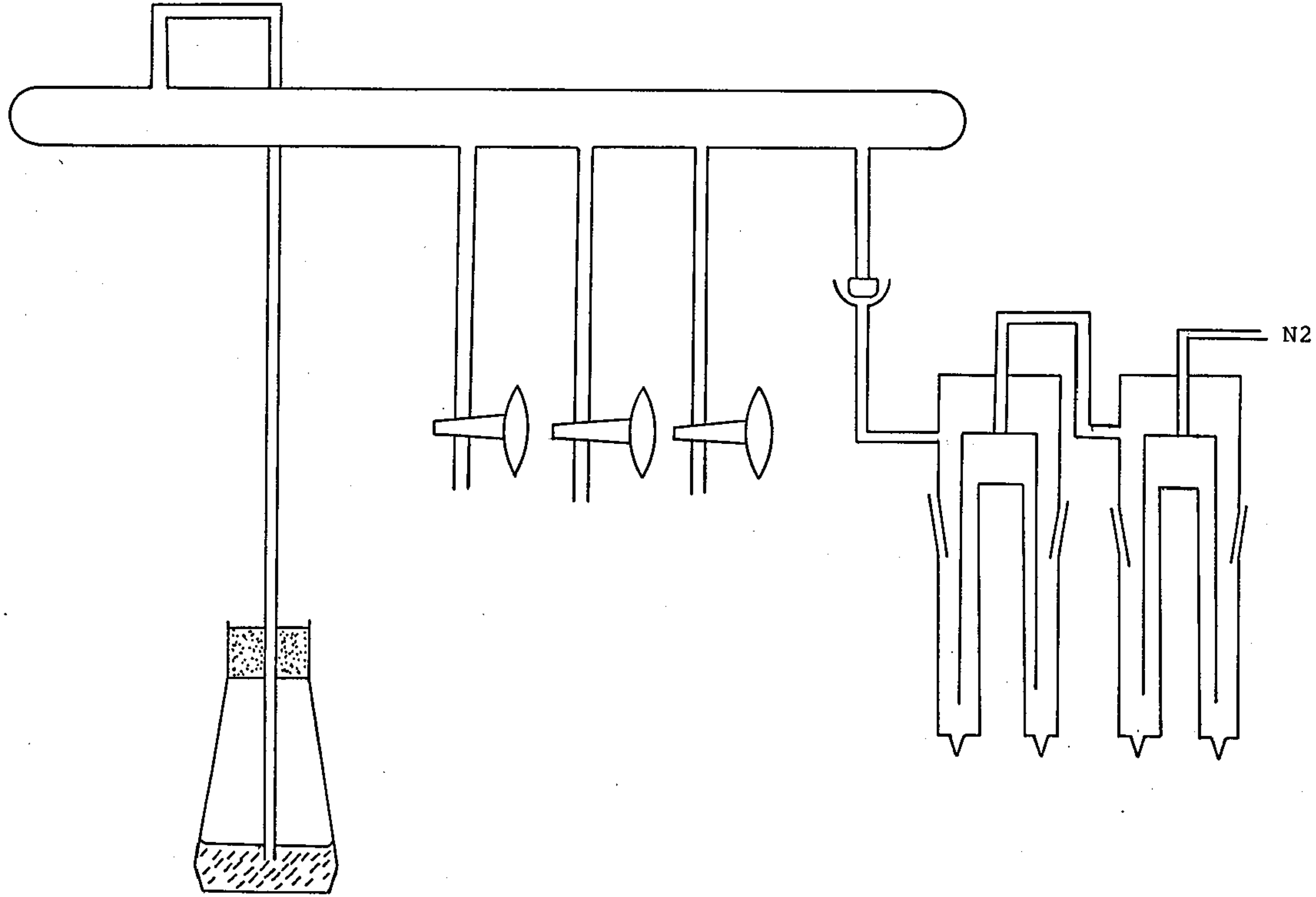


Figure 2.1: Apparatus for handling air sensitive compounds.

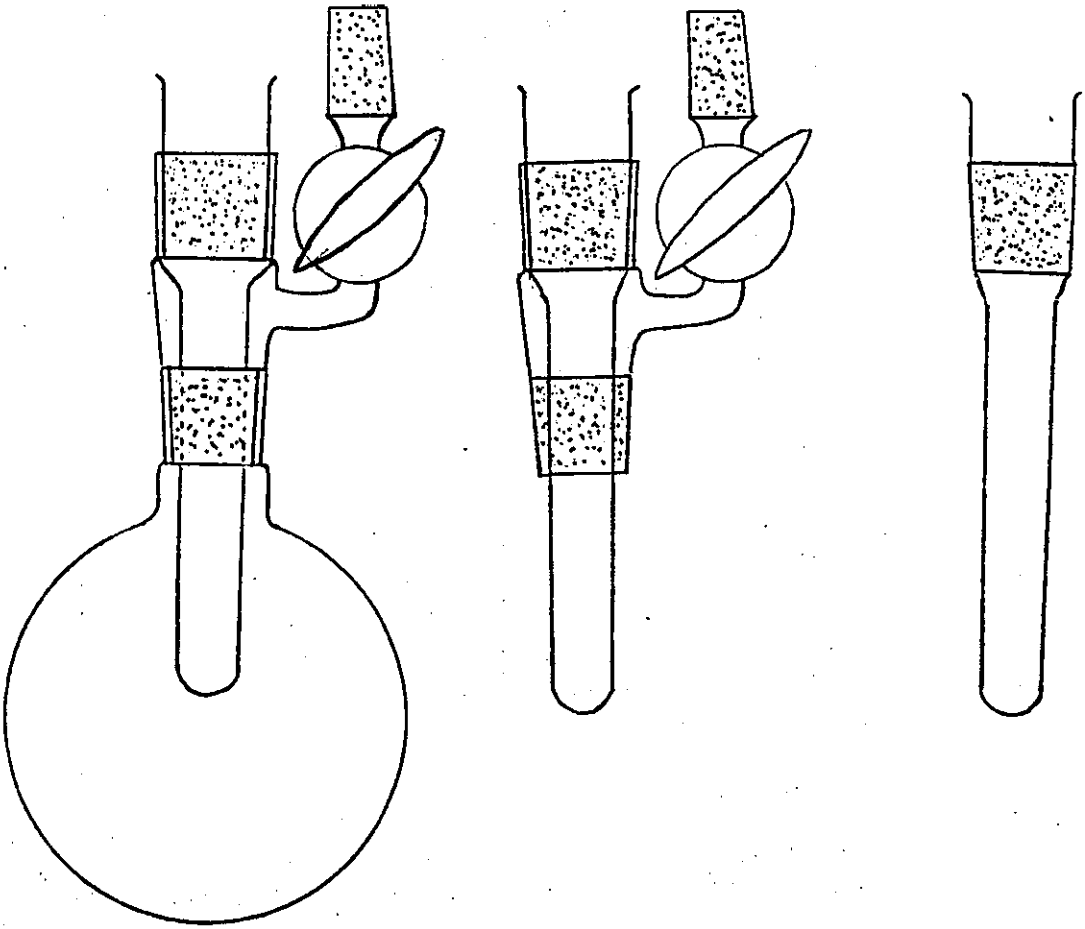


Figure 2.2: Apparatus used for sublimation under vacuum. The cold finger was cooled with either solid CO_2 or liquid N_2.

spectra were recorded on A.E.I. MS80 spectrometer by Mr. John Greenfield of this Department and Mr. Peter Cook of Queen Mary College, London.

Preparation of o-phenylenemercury trimer.

A solution of 4.78 gm (20 mmole) of 1,2-dibromobenzene in 50 mℓ of dry tetrahydrofuran was vigorously stirred at room temperature with an excess of 2% sodium amalgam (2 gm Na, 100 gm Hg). An exothermic reaction occurred which faded over about half an hour; stirring was continued for a further two hours. Water was then added until no more precipitate formed and the supernatant liquid separated from mercury and the precipitate, the latter being washed again with water after removal of the mercury. The precipitate was boiled with chloroform and filtered leaving a white solid which was then extracted with hot dimethylformamide to give o-phenylenemercury; yield 2%. The analytical sample was recrystallized from the same solvent and dried in an oven at 75°C, m.p.338-340°C with decomposition (lit.(2) 324-327°C), (Found: C,26.1; H,1.5%. $C_{18}H_{12}Hg_3$ calcd.: C,26.0; H,1.45%).

The chloroform solution, after removal of the solvent under reduced pressure gave o-terphenylenemercury dimer, m.p. 294-296°C (lit.(3) 292-293), (Found: C,50.6; H,2.7%. $C_{36}H_{24}Hg_2$ calcd.: C,50.4; H,2.8%).

Preparation of o-terphenylenemercury dimer.

A solution of 1,2-dibromobenzene (9.5 gm; 40 mmole) in 1,2-dimethoxyethane (100 mℓ) was stirred with sodium amalgam which was prepared from 4.3 gm Na and 200 gm Hg; after about half an hour the flask became hot and an exothermic reaction started. The mixture was left stirring for a further two hours, then the monoglyme solution was decanted and the remaining mercury and solid boiled with 150 mℓ of chloroform before being filtered. The chloroform and 1,2-dimethoxyethane solutions were combined together and the solvents removed under reduced pressure to give a mixture of solid and oil, which was then boiled again with chloroform and filtered. On addition of a little acetone to the hot filt rate, yellow crystals of o-terphenylenemercury dimer separated out; yield 3%. The analytical sample was recrystallized from chloroform and dried in an oven at 70°C, m.p. 294-296°C (lit.(3) 292-293°C), (Found: C,50.45; H,3.1%. $C_{36}H_{24}Hg_2$ calcd.: C,50.4; H,2.8%).

Solvates of o-terphenylenemercury dimer.

o-Terphenylenemercury dimer formed solvates with dimer: solvent ratios of 1:0.5; 1:1; 1:1.5 and 1:2 when recrystallized from a whole variety of solvents; in fact, no common solvent was found which did not form a solvate. Table 2.1 gives the analytical data for

TABLE 2.1

Micro-Analysis Results (%) for Fifteen Solvates of Terphenylenemercury Dimer (T).

Solvent used	T:Solvent ratio	Analysis. Found (calcd.) (%)		
		C	H	N (or Cℓ)
Cyclohexane	1:0.5	52.0,52.2 (52.0)	3.3,3.2 (3.4)	
Cyclohexanone	1:0.5	51.9(51.65)	3.3(3.2)	
Mesitylene	1:0.5	53.15,52.7, 53.3(53.0)	3.4,3.3, 3.1(3.3)	
p-Xylene		53.3(52.7)	3.0(3.2)	
m-Xylene	1:1	55.6,54.6 (54.9)	3.6,3.5 (3.5)	
o-Xylene	1:1	54.9(55.05)	3.5(3.55)	
Toluene	1:1	54.4(54.2)	3.4(3.4)	
Ethylbenzene	1:1	55.25(54.9)	3.5(3.5)	
Chlorobenzene	1:1	52.6(52.0)	3.0(3.0)	3.9(3.65)

contd...

TABLE 2.1 (Contd)

Solvent used	T:Solvent ratio	Analysis. Found (calcd.) (%)		
		C	H	N (or Cℓ)
Dimethylformamide	1:1	50.3(50.3)	3.5(3.4)	1.6(1.5)
Diethylformamide	1:1	51.0(51.35)	3.6(3.7)	1.5(1.5)
2-Picoline	1:1	53.2(53.1)	3.3(3.3)	1.4(1.5)
Pyridine	1:1.5	54.2,53.3	3.2,3.3	2.2,1.9
		54.1(53.5)	3.1(3.2)	2.2(2.15)
Acetone	1:1.5	Analysed gravimetrically		
Chloroform	1:2	Analysed gravimetrically		

these solvates; the chloroform and acetone solvates of dimer were not stable enough for carrying carbon and hydrogen analyses at Manchester University because of decomposition occurring in the post, but they were analysed gravimetrically as follows:

Solvent	Dimer:solventratio	Weight Loss.Found(calcd.)(%)
Chloroform	1:2	21.89, 21.93 (21.77)
Acetone	1:1.5	8.9 , 8.87 (9.21)

Preparation of 3,4-dibromotoluene.

The successive stages in the preparation of 3,4-dibromotoluene are described below.

p-Acetotoluidide and m-bromo-p-acetotoluidide: a solution of p-acetotoluidide in glacial acetic acid was prepared by boiling 107 gm of p-toluidine with 400 mℓ of glacial acetic acid in a 1 litre three-necked, round-bottomed flask provided with a reflux condenser and a mechanical stirrer. After two hours the solution was left to cool to about 45° whilst stirring the solution vigorously, then 51 mℓ of bromine were added from a separatory funnel at such a rate that the temperature remained at 50-55°. The stirring was continued for a further 30 minutes after all the bromine had been added, then the reaction mixture was poured into a well-stirred mixture of 1 kilo of crushed ice and 1 kilo of water to which

14 gm of sodium bisulphite had been added. The crystalline 3-bromo-4-acetaminotoluene was filtered and dried in the air (250 gm).

3-Bromo-4-aminotoluene hydrochloride: the dried 3-bromo-4-acetaminotoluene and 250 mℓ of ethanol were placed into a round-bottomed flask and the mixture refluxed on a water bath until the solid had dissolved completely. Concentrated hydrochloric acid (250 mℓ) was introduced through the condenser, refluxing being continued for a further three hours. The mixture was cooled, the crystals filtered off and washed with a little chilled ethanol to give 150 gm of the hydrochloride.

3-Bromo-4-aminotoluene: the hydrochloride was suspended in 400 mℓ of water and a solution of 70 gm of sodium hydroxide in 350 mℓ of water added with stirring; the free base separated as a dark heavy oil. After cooling, the mixture was transferred to a separatory funnel to run off the crude 3-bromo-4-aminotoluene (125 gm).

3,4-Dibromotoluene: a mixture of 50 gm of 3-bromo-4-aminotoluene and 175 mℓ of hydrobromic acid was cooled to 0.5° before a solution of 30 gm of sodium nitrite in 60 mℓ of water was added, the temperature being maintained below 10° by the addition of ice. The resulting 3-bromotolyldiazonium solution was added to a boiling solution of 30 gm of cuprous bromide in 40 mℓ of 48% hydrobromic acid contained in a 2.5 litre round-bottomed flask, and steam distilled to give 21.5 gm of 3,4-dibromotoluene 123-124°C at 19 mm Hg.

Preparation of 4-methylphenylenemercury.

(i) A solution of 3,4-dibromotoluene (5 gm; 20 mmole) in dry tetrahydrofuran (50 mℓ) was reacted with sodium amalgam (2 gm Na, 100 mℓ Hg). After about 20 minutes an exothermic reaction began and stirring was continued for a further two hours. The solvent was allowed to evaporate off in a fume-cupboard and the remaining solid separated from mercury. The 4-methylphenylenemercury was extracted from this solid using boiling DMF; recrystallization from the same solvent followed by drying in an oven at 100° gave the analytical sample which melted at 305-306°C (Found: C,29.4, 28.8; H,2.0, 2.05%. $C_{21}H_{18}Hg_3$ calcd.: C,28.9; H,2.1%).

(ii) The reaction of 3,4-dibromotoluene with sodium amalgam in dry 1,2-dimethoxyethane as a solvent also gave 4-methylphenylenemercury and not the corresponding methyl-substituted terphenylenemercury dimer as had been hoped.

(iii) Similarly 3-bromo-4-fluorotoluene (3.78 gm; 20 mmole) in 60-80°C petroleum ether (50 mℓ) was stirred with sodium amalgam (2 gm Na; 100 gm Hg). After evaporation of the solvent and removal of the mercury, the remaining solid was boiled with DMF; on filtration and cooling the solution fine crystals of 4-methylphenylenemercury separated out and were analysed using mass spectrometry.

Preparation of 2,3-dibromotoluene(4).

2-Methyl-6-nitro-bromobenzene:- a mixture of 76 gm of 2-methyl-6-nitroaniline in 175 mℓ of hydrobromic acid (sp.gr.1.48) was reacted with sodium nitrite (35 gm) in 70 mℓ of water at 0.5°C; the resulting diazonium salt was treated with a boiled solution of cuprous bromide (40 gm) in 40 mℓ hydrobromic acid and the resulting mixture steam distilled to give 2-methyl-6-nitrobromobenzene (54 gm).

2-Bromo-3-methylaniline:- iron filings (28 gm) and 20 mℓ of water were placed in a 1 litre three-necked flask equipped with a mechanical stirrer and reflux condenser; the mixture was heated on a boiling water bath and when it became hot the bath removed. While stirring vigorously, 10 gm of melted 2-methyl-6-nitrobromobenzene was added followed by 10 mℓ of concentrated hydrochloric acid when a vigorous reaction occurred immediately. When the reaction had subsided a further 44 gm of melted 2-methyl-6-nitrobromobenzene was added all at once and after 10 minutes, 350 mℓ of concentrated hydrochloric acid was poured in. Heating on a water bath with stirring was continued for one hour, after which time a solution of 5 gm sodium hydroxide in 10 mℓ of water was added and the reaction mixture filtered whilst still hot; most of the 2-bromo-3-methylaniline separated from the aqueous layer. The iron residues were boiled with 50 mℓ of benzene filtered and the benzene extracts combined with the 2-bromo-3-methylaniline before being dried over anhydrous magnesium sulphate. The benzene was removed under reduced pressure to give 22.7 gm of the amine.

2,3-Dibromotoluene:- a mixture of 2-bromo-3-methylaniline and 75 mℓ of hydrobromic acid was treated with a solution of sodium nitrite (8.75 gm) in water (17.3 mℓ) at o.5°C and the resulting diazonium salt reacted with boiling solution of cuprous bromide (10 gm) in hydrobromic acid (10 mℓ); the resulting 2,3-dibromotoluene was isolated by steam distillation of the reaction mixture (yield 10 gm), m.p. 28°C.

Preparation of 3-methylphenylenemercury.

(i) A solution of 2,3-dibromotoluene (5 gm; 20 mmole) in tetrahydrofuran (50 mℓ) was allowed to react with sodium amalgam (2 gm Na; 100 gm Hg); after about one hour an exothermic reaction occurred and the mixture was left stirring for a further hour. The solvent was evaporated and the remaining solid, after separation from the mercury, was extracted with boiling DMF when filtration and cooling of the solution gave 3-methylphenylenemercury (yield 2%), m.p. 323-325°C (Found: C,28.8; H,2.0%. $C_{21}H_{18}Hg_3$ calcd.: C,28.9; H,2.1%).

(ii) When 2,3-dibromotoluene was treated with sodium amalgam in dry 1,2-dimethoxyethane 3-methylphenylenemercury was again obtained as the only isolable product.

Thermal decomposition of 3-methylphenylenemercury.

3-Methylphenylenemercury heated at 320°C in a sealed, evacuated tube to give metallic mercury together with a mixture of a liquid and some colourless crystals. Mass spectral analysis of the ether-soluble material showed that the main component of the liquid was dimethyldiphenyl and that the relatively-involatile crystals were bis(methylphenyl)mercury.

Reaction of a mixture of 1,2-dibromobenzene and 3,4-dibromotoluene with sodium amalgam.

A solution of a mixture of 1,2-dibromobenzene (20 mmole) and 3,4-dibromotoluene (20 mmole) in tetrahydrofuran (50 mℓ) was reacted with sodium amalgam (2 gm Na; 100 gm Hg) for two hours. The product was extracted with DMF and had a mass spectrum showing the parent ion clusters of $(C_6H_4)_3Hg_3$; $(C_6H_4)_2(C_6H_3CH_3)Hg_3$; $(C_6H_4)(C_6H_3CH_3)_2Hg_3$; $(C_6H_3CH_3)_3Hg_3$.

Preparation of 1,2-dibromo-4,5-dimethylbenzene(5).

5-Bromo-4-acetamido-o-xylene:- 3,4-dimethylaniline (70 gm) was refluxed with 300 mℓ of glacial acetic acid for two hours when crystals of acetamido-o-xylene separated as the mixture was allowed to cool to 0°C; bromine (32 gm) dissolved in glacial acetic acid (180 mℓ) was then added gradually when a yellow precipitate of 5-bromo-4-acetamido-o-xylene was formed (40.4 gm).

5-Bromo-4-amino-o-xylene:- bromoacetamido-o-xylene (27.2 gm) was hydrolysed by boiling it gently with a mixture of concentrated sulphuric acid (400 mℓ) and water (400 mℓ), for three hours. The resulting bromo-o-xylidine was filtered and recrystallized from 40-60°C petroleum ether (yield 16.4 gm).

1,2-Dibromo-4,5-dimethylbenzene:- bromoamino-o-xylene (10 gm) was dissolved in dilute hydrobromic acid (80 mℓ of acid, s.p. gr. 1.48, and 350 mℓ of water) and diazotized with 10% solution of sodium nitrite; the resulting diazo-solution was added gradually to a solution of cuprous bromide (34 gm) in hydrobromic acid (108 mℓ) held at 90°C. The product was isolated by distillation with steam and extraction with ether. 1,2-Dibromo-4,5-dimethylbenzene (11 gm) was recrystallized from alcohol as white crystals, m.p. 88°C.

Preparation of 4,5-dimethylphenylenemercury.

Treatment of 1,2-dibromo-4,5-dimethylbenzene (5.32 gm; 20 mmole) in tetrahydrofuran (50 mℓ) with sodium amalgam (2 gm Na; 100 gm Hg) for two hours gave 4,5-dimethylphenylenemercury which was extracted by DMF in the usual manner; yield 1%. The analytical sample did not melt below 320°C (Found: C,32.2; H,2.5%. $C_{24}H_{24}Hg_3$ calcd.: C,31.5; H,2.6%).

Preparation of tetramethylphenylenemercury.

Sodium amalgam (2%) and 1,2-dibromotetramethylbenzene (5.84 gm; 20 mmole) were reacted together in refluxing decalin. The product proved highly insoluble even in such solvents as boiling DMF, dimethylsulphoxide or nitrobenzene. The analytical sample was refluxed with two portions of nitrobenzene, washed twice with boiling acetone and dried at room temperature in a vacuum, m.p. > 320°C (Found: C,36.0; H,3.5%. $C_{30}H_{36}Hg_3$ calcd.: C,36.1; H,3.6%). Although the compound did not melt below 320°C, close observation showed that the decomposition apparently occurred between 290 and 300°C in the air; decomposition in a sealed evacuated tube at 300°C gave free mercury.

Two very minor by-products, octamethylbiphenylene (Found: C,90.0; H,9.1%. $C_{20}H_{24}$ calcd.: C,90.8; H,9.15%; mol. wt. 264 from mass spectrum) and bis(tetramethylphenyl)-mercury, were found in the reaction mixture. The latter is probably formed due to the presence of some 1-bromo-3,4,5,6-tetramethylbenzene in the starting material.

Reactions of dihaloaromatic compounds with sodium amalgam.

The following, less-successful reactions were also carried out between 2% of sodium amalgam and the following dihaloaromatic compounds:

(i) 2,3-Dibromoethylbenzene.

2,3-Dibromoethylbenzene (5.28 gm; 20 mmole) was treated with sodium amalgam in tetrahydrofuran. After stirring for three hours, the product was extracted with hot DMF as a mixture of oils; no attempts were made to identify them.

(ii) 1,2-Dibromotetramethylbenzene.

1,2-Dibromotetramethylbenzene (5.84 gm; 20 mmole) was stirred with sodium amalgam in tetrahydrofuran for three hours. Octamethylbiphenylene was the only isolable product from the reaction and was extracted with DMF before being resrystallized from acetone, m.p. 240°C (Lit.(6) 240-242°C); mol. wt. 264 from the mass spectrum.

(iii) 2,3-Dibromonaphthalene.

Although, 2,3-dibromonaphthalene (5.72 gm, 20 mmole) was stirred with sodium amalgam in tetrahydrofuran for four hours, no reaction could be detected and the most of the starting materials were recovered unchanged.

(iv) 2-Bromochlorobenzene.

2-Bromochlorobenzene (3.82 gm; 20 mmole) and sodium amalgam were stirred together in 50 mℓ of tetrahydrofuran for two hours. The resulting mixture was treated with boiling DMF to give o-phenylenemercury trimer in very poor yield; the mercurial was identified from both its melting point and infrared spectrum.

(v) 3-Bromo-4-chloroanisole.

On reacting 3-brom-4-chloranisole (4.44 gm; 20 mmole) with sodium amalgam in tetrahydrofuran, the resulting product was a mixture of unidentified oils.

(vi) 3-Bromo-4-chlorotoluene.

Similarly, the reaction of 3-bromo-4-chlorotoluene with sodium amalgam failed to give any mercury-containing product.

(vii) 1,2-Diiodotetramethylbenzene.

1,2-Diiodotetramethylbenzene (3.82 gm; 20 mmole), on stirring with sodium amalgam in tetrahydrofuran, gave only octamethylbiphenylene after extraction of the reaction mixture with DMF; the yellow crystals were identified by their mass spectrum; yield 1%. No mercury-containing product was present.

Decarboxylation of mercuric tetrachlorophthalate.

Mercuric tetrachlorophthalate was cautiously heated in a continuously-evacuated tube using a free flame; considerable eruption of the solid occurred during the evolution of carbon dioxide. When no more gas was evolved the residue was fractionally sublimed to give mercury, $C_6C\ell_6$ (containing a minute trace of decachlorobiphenyl), bis(pentachlorophenyl)mercury (major product ; identified from its mass spectrum and by a comparison of its infrared spectrum with that of an authentic sample) and a solid of very low volatility which had properties similar to those of tetrachlorophenylenemercury described below.

Reaction of 1,2-diiodotetrachlorobenzene with mercury.

(i) Approximately 1.5 gm of 1,2-diiodotetrachlorobenzene were heated with an excess of mercury in a sealed, evacuated tube at 260°C for 24 hours; by arranging a slight thermal gradient in the furnace most of the HgI_2 by-product sublimed away from the off-white solid at the hotter, bottom end of the tube. The remainder of the mercuric iodide was removed by opening the tube and subjecting the solid product to gentle warming under high vacuum (ca.10^{-4} mm Hg) with a free flame; when all the yellow-to-red iodide had been removed further fractional sublimation produced a trace of white, volatile solid (shown to be bis(pentachlorophenyl)mercury using mass spectrometry) and a much less volatile, pale yellow component which proved to be bis(tetrachloroiodophenyl)mercury, m.p. > 330°C (Found: C,16.7; H,0.0; Cℓ, 32.4; I,28.9%. $C_{12}C\ell_8I_2Hg$ calcd.: C,16.3; H,0.0; Cℓ,32.15; I,28.8%). A mass spectrum verified that the compound was $(C_6C\ell_4I)_2Hg$ with a barely-detectable presence of $C_6C\ell_4IHgC_6C\ell_5$.

(ii) When the reaction was repeated but with a heating time of four days the product was tetrachlorophenylenemercury, purified by subliming away the excess mercury and the HgI_2 by-product; m.p. > 330°C (Found: C,17.3; H,0.0; Cℓ,34.0%. $C_{18}C\ell_{12}Hg_3$ calcd.: C,17.4; H,0.0; Cℓ,34.2%); the compound sublimes on strong heating in a good vacuum.

The mercurial can be extracted from the reaction products by boiling with 5 aliquots of 50 mℓ of DMF; on concentrating down the extracts, tetrachlorophenylenemercury separated as an extremely finely-divided solid which had to be centrifuged from the mother liquor. The analytical sample was washed three times with acetone and dried for 20 minutes on a vacuum line (Found: C,18.5; H,0.35; N,0.6; Cℓ,34.6%. $C_{18}C\ell_{12}Hg_3 \cdot 0.5$ DMF calcd.: C,18.3; H,0.3; N,0.55; Cℓ,32.2%). A sample washed with acetone and air-dried at room temperature for two days gave similar analyses (Found: C,18.1; H,0.2; N,0.5%).

Reaction of a mixture of 1,2-diiodotetrafluorobenzene and 1,2-diiodotetrachlorobenzene with mercury.

A mixture of 1,2-diiodotetrafluorobenzene and 1,2-diiodotetrachlorobenzene was heated with mercury at 260°C for four days. On opening the tube and removing the excess mercury and HgI_2, the remaining solid had a mass spectrum showing the parent ion clusters of $(C_6F_4Hg)_3$, $(C_6F_4)_2(C_6C\ell_4)Hg_3$, $(C_6F_4)(C_6C\ell_4)_2Hg_3$ (see Figure 2.6 on page 74).

Preparation of biphenylenemercury trimer.

A hexane solution of n-butyllithium (45 mℓ; 74 mmole) was placed in a 500 mℓ three-necked flask fitted with a mechanical stirrer, a reflux condenser and a nitrogen inlet. Addition of dry tetramethylethylene diamine (11 mℓ; 74 mmole) gave a yellow-orange mixture from which some crystals were deposited (probably solid LiBu. TMEDA). After the addition of solid biphenyl (5.4 gm; 36 mmole) the mixture was refluxed (ca. 69°) for about one and a half hours when a reddish-brown solution was formed; the flask was cooled in ice before a solution of mercuric chloride (9.8 gm; 36 mmole) in 200 mℓ of 1:1 tetrahydrofuran-ether was added slowly with stirring. A grey precipitate deposited immediately and stirring was continued for about half an hour at room temperature after the addition had been completed. The mixture was filtered and the solid, after being washed well with methanol, was extracted by boiling with three 50 mℓ aliquots of nitrobenzene. The hot aliquots were combined, filtered, boiled down to small bulk and allowed to cool to room temperature when colourless crystals of biphenylenemercury separated. The melting point at this stage is usually about 338°C but after recrystallization from toluene rises to 358-360°C (Lit.(7) 338°C); yield 3.7 gm (29%) (Found: C,40.7, 40.9; H,2.3, 2.2%. $C_{36}H_{24}Hg_3$ calcd.: C,40.9; H,2.3%).

Reaction of 2,2'-dilithiobiphenyl with excess of mercuric chloride.

2,2'-Dilithiobiphenyl was prepared as described above (from 35 mmole of biphenyl, 74 mmole of n-butyllithium and 74 mmole of tetramethylethylene diamine), cooled in an ice bath, then stirred with a solution of mercuric chloride (19.6 gm; 72 mmole) in 400 mℓ of 1:1 ether-tetrahydrofuran for one hour. The mixture was filtered leaving a grey solid which was washed with hot chloroform, the filtrate and the washing being combined together before the solvents were removed under reduced pressure to give a white solid. On boiling with acetone and filtration, the filtrate gave fine, white crystals of a $HgC\ell_2$-TMEDA complex m.p. 162-164°C (Found: C,18.8; H,4.0; N,6.9%. $C_6H_{16}C\ell_2N_2Hg$ calcd.: C,18.6; H,4.1; N,7.2%).

The remaining white solid, after being boiled with acetone, was recrystallized from chloroform giving a white powder which started to sublime above 240°C without melting and was identified as $C_{12}H_9HgC\ell$ from the mass spectrum. The grey solid from the reaction mixture was extracted with nitrobenzene to give biphenylenemercury, identified from its melting point and infrared spectrum. None of the expected $C_{12}H_8(HgC\ell)_2$ could be detected among the products.

Preparation of perfluorobiphenylenemercury.

n-Butyllithium (18 mℓ; 20 mmole) was added to a solution of 2,2'-dibromooctafluorobiphenyl (4.56 gm; 10 mmole) in ether (100 mℓ) at -78° and stirred for half an hour. Mercuric chloride (2.71 gm; 10 mmole) was added and the mixture stirred at room temperature for one hour. The ether solution was filtered off, the solvent removed and the mercurial, m.p. > 330°C (Lit.$^{(8)}$ > 380°C), extracted with carbon tetrachloride (yield 64%)(Found: C,28.6, 30.0; H,0.0; F,28.5, 31.4%. $C_{36}F_{24}Hg_3$ calcd.: C,29.0; H,0.0; F,30.6%).

Preparation of 2,2'-diiodo-4,4'-dimethylbiphenyl$^{(9)}$.

2,2'-Dinitro-4,4'-dimethylbiphenyl:- a mixture of 45.5 gm of 4-chloro-3-nitrotoluene and 75 gm of clean, dry sand was placed in a 250 mℓ flask equipped with a mechanical stirrer and heated in an oil bath to 215-225°C. Then 50 gm of copper bronze was added during 40 minutes, the temperature being maintained at 215-225°C for a further 90 minutes with continuous stirring. The hot mixture was poured into a beaker containing 125 gm of sand and stirred until small lumps were formed. The lumps were crushed by powdering in a mortar from which 2,2'-dinitro-4,4'-dimethylbiphenyl was extracted by boiling with three portions of 400 mℓ alcohol, the yield was 19 gm.

2,2'-Diamino-4,4'-dimethylbiphenyl:- the finely-powdered 2,2'-dinito-4,4'-dimethylbiphenyl (19 gm) was heated on a water bath with tin (100 gm) and concentrated hydrochloric acid (200 mℓ) until a clear solution was obtained. The solution was treated with excess of caustic soda and the 2,2'-diamino-4,4'-dimethylbiphenyl extracted with ether; yield 13 gm.

4,4'-Dimethylbiphenyleneiodonium iodide:- to a solution of 8.7 gm of 2,2'-diamino-4,4'-dimethylbiphenyl in 42 mℓ of concentrated hydrochloric acid and 42 mℓ of water at 5°C, a solution of 5.9 gm of sodium nitrite in 20 mℓ of water was added slowly with stirring. After 15 minutes a solution of 20.7 gm of potassium iodide in 50 mℓ of ice water was poured in slowly with manual stirring. A thick, black paste separated at once; the mixture was allowed to stand at room temperature for three hours and then with excess of sodium bisulfite overnight. The resulting yellow-green solid was filtered off, washed well with bisulfite solution, water and, finally, with cold methanol; yield 13 gm.

2,2'-Diiodo-4,4'-dimethylbiphenyl:- 4,4'-dimethylbiphenyleneiodoniumiodide (13 gm) was heated in an oil bath at 215-220°C for 30 minutes. The residue was extracted with ether and the extracts percolated through a short column of chromatographic alumina to remove coloured impurities; evaporation of the solvent, followed by recrystallization from ethanol, gave 2,2'-diiodo-4,4'-dimethylbiphenyl; yield 3.9 gm.

Preparation of 4,4'-dimethylbiphenylenemercury.

A solution of 2,2'-diiodo-4,4'-dimethylbiphenyl (3.9 gm; 8 mmole) in 50 mℓ ether was stirred with a solution of n-butyllithium (15 mℓ; 18.5 mmole) in 20 mℓ of ether at room temperature. After 3 hours, the resulting red-brown solution was cooled in an ice bath and treated with a solution of mercuric chloride (2,29 gm; 8.5 mmole) in ether (150 mℓ) and the stirring continued for a further two hours. After removal of the solvent under vacuum the mercurial extracted with hot DMF and recrystallized; the analytical sample was dried in an oven at 100°C; m.p. 316-318°C with decomposition (Found: C,43.8; H,3.5%. $C_{42}H_{36}Hg_3$ calcd.: C,44.1; H,3.2%).

The yields in some of the following reactions of organomercury compounds have not been calculated since these reactions were carried out on a small scale; the yields are quoted as q-quantitative, g-good and p-poor.

Some reactions of o-phenylenemercury trimer.

(i) Selenium.

o-Phenylenemercury (0.5 gm) and selenium (0.5 gm) were heated to 250°C for twelve hours in a sealed tube; metallic mercury could be seen in the tube after this time. After cooling and opening the tube, the contents were extracted with 40-60°C petroleum ether to give 50 mg of a solid shown to be $Se_2(C_6H_4)_2$ by the parent ion cluster centred at 130 m.u. in the mass spectrum.

A "mixed" reaction in which selenium was heated with o-phenylenemercury and o-perfluorophenylenemercury gave a product showing $Se_2(C_6F_4)_2^+$, $Se_2(C_6H_4)_2^+$ and $Se_2(C_6H_4)(C_6F_4)^+$ ions in its mass spectrum (see Figure 2.6 on page 74); no attempt was made to separate the components of the mixture.

(ii) Sulphur.

A similar synthesis occurred when o-phenylenemercury was heated with an excess of sulphur to 250°C in a sealed tube for twelve hours; the product (50 mg) was extracted with 40-60°C petroleum ether and identified as $S_2(C_6H_4)_2$ mass spectrometrically.

(iii) Mercuric chloride.

o-Phenylenemercury (0.210 gm; 0.253 mmole) was reacted with mercuric chloride (0.206 gm; 0.759 mmole) in boiling DMF (60 mℓ) for one hour. On cooling the solution, o-phenylenebis(mercury chloride) was deposited as a white solid (yield q), m.p. 322-324°C (Lit.(2) 322-323°C).

(iv) Mercuric bromide.

A mixture of o-phenylenemercury (0.215 gm; 0.259 mmole) and mercuric bromide (0.280 gm; 0.777 mmole) in DMF (60 mℓ) was refluxed for one hour. The solution was left to cool giving o-phenylenebis(mercury bromide) which was recrystallized from DMF, m.p. 318-320°C (Found: C,12.2; H,0.6; Br,24.7%. $C_6H_4Hg_2Br_2$ calcd.: C,11.3; H,0.6; Br,25.2), yield q.

Reaction of o-phenylenebis(mercury bromide) with sodium iodide.

o-Phenylenebis(mercury bromide) (0.4 gm) was dissolved in 100 mℓ of DMF and 20 mℓ of ethanol was added; the resulting solution was refluxed with an excess of sodium iodide in ethanol for half an hour. A white precipitate formed which was identified as o-phenylenemercury trimer from its infrared spectrum (yield g).

Attempted symmetrization of o-phenylenebis(mercury bromide) by heating.

A sample of o-phenylenebis(mercury bromide) was heated in a sublimer under vacuum to 220°C using an oil bath for one hour. The compound did not lose $HgBr_2$ and the starting material was recovered unchanged.

Some typical reactions of biphenylenemercury trimer.

(i) Mercuric chloride.

Biphenylenemercury (0.4614 gm; 0.436 mmole) and mercuric chloride (0.359 gm; 1.325 mmole) were reacted together in boiling mesitylene (40 mℓ) for 20 minutes, then allowed to cool when the white solid which formed was filtered and recrystallized from chloroform to give 2,2'-biphenylenebis(mercury chloride) m.p. 250-252°C, (Lit.(10) 246-247.5°C, (Found: C,23.15; H,1.1; Cℓ,11.2%. $C_{12}H_8Hg_2C\ell_2$ calcd.: C,23.1; H,1.3; Cℓ,11.4%), yield q.

(ii) Mercuric bromide.

Biphenylenemercury (0.209 gm; 0.197 mmole) was reacted with mercuric bromide (0.215 gm; 0.596 mmole) in boiling mesitylene (40 mℓ) for 20 minutes; on cooling the white solid was filtered and recrystallized from chloroform to give 2,2'-biphenylenebis(mercury bromide) (yield q), m.p. 198°C, (Found: C,20.4; H,0.95; Br,23.1%. $C_{12}H_8Hg_2Br_2$ calcd.: C,20.2; H,1.1; Br,22.4%).

(iii) Mercuric iodide.

Similarly, biphenylenemercury (0.349 gm; 0.333 mmole) was reacted with mercuric iodide (0.450 gm; 0.999 mmole) in mesitylene (40 mℓ) to give 2,2'-biphenylenebis(mercury iodide) (yield g); this was recrystallized from chloroform, m.p. 197°C, (Lit.(11) 198°C), (Found: C,17.7; H,0.9; I,28.6%. $C_{12}H_8Hg_2I_2$ calcd.: C,17.85; H,1.0; I,31.4%).

(iv) Mercurous chloride.

A mixture of biphenylenemercury (0.301 gm; 0.284 mmole) and mercurous chloride (0.210 gm; 0.852 mmole) in mesitylene was refluxed for three hours. Mercury was deposited at the bottom of the flask leaving a clear solution; on filtration and cooling this solution gave 2,2'-bisphenylenebis(mercury chloride) m.p. 250-252°C which was recrystallized from chloroform (Found: C,22.8; H,1.2%. $C_{12}H_8Hg_2C\ell_2$ calcd.: C,23.1; H,1.3%), yield g.

(v) Mercuric acetate.

Biphenylenemercury (0.253 gm; 0.242 mmole) and mercuric acetate 6.229 gm; 0.719 mmole) were reacted together in boiling methanol until a clear solution was obtained. The solution was boiled to small bulk and allowed to crystallize, when needle crystals were formed; filtration, washing the sample with distilled water and drying in an oven at 70°C gave the analytical sample of

2,2'-biphenylenebis(mercury acetate), m.p. 225-226°C, (Found: C,28.5; H,1.9%. $C_{16}H_{14}O_4Hg_2$ calcd.: C.28.6; H,2.1%), yield p.

(vi) Glacial acetic acid.

Biphenylenemercury (0.2 gm) was boiled with glacial acetic acid (20 mℓ) for 1.5 hours and the solution filtered; the glacial acetic acid was evaporated to leave a brown, hard wax. Washing with a little cold chloroform removed the brown colour leaving a white solid which had the same infrared spectrum as the 2,2'-biphenylenebis(mercury acetate), yield p.

Reaction of 2,2'-biphenylenebis(mercury bromide) with sodium iodide.

Solutions of 2,2'-biphenylenebis(mercury bromide) (0.2 gm) and excess of sodium iodide in aqueous ethanol (150 mℓ) were mixed and allowed to react under reflux for about 20 minutes. The precipitate was allowed to settle from the solution and the ethanolic layer was decanted; the precipitate was washed with water, decanted each time and left to dry in an oven at 70°C to give biphenylenemercury trimer (yield g), identified by its infrared spectrum.

Symmetrization of 2,2'biphenylenebis(mercury bromide) by heating.

Approximately 0.2 gm of 2,2'-biphenylenebis(mercury bromide) was heated in a sublimer by an oil bath to 200°C whilst continuously pumping on the vacuum line for one hour. A white sublimate formed from about 170°C which was presumably $HgBr_2$ since the product at the bottom of the sublimer was pure biphenylenemercury trimer (yield g) as indicated by its infrared spectrum and melting point.

Symmetrization of 2,2'-biphenylenebis(mercury iodide) by heating.

In a similar way, 2,2'-biphenylenebis(mercury iodide) was heated to 200°C on vacuum line for one hour when red HgI_2 was formed. The white product remaining had the same infrared spectrum as pure biphenylenemercury trimer (yield g).

Reaction of 2,2'-biphenylenebis(mercury acetate) with hydrochloric acid.

Concentrated hydrochloric acid was added dropwise to a solution of 2,2'-biphenylenebis(mercury acetate) (0.2 gm) in boiling methanol; immediately a white precipitate began to form and an excess of acid was added before water was used to dilute the methanol and cause complete precipitation. The precipitate was washed well with water and dried in an oven to give a product having an infrared spectrum and melting point identical to that of 2,2'-biphenylenebis(mercury chloride), yield g.

Reaction of o-phenylenebis(mercury chloride) and 2,2'-biphenelenebis(mercury chloride) with sodium iodide.

A mixture of o-phenylenebis(mercury chloride) and 2,2'-biphenylenebis(mercury chloride) in 140 mℓ of DMF/ethanol (1:6) was refluxed with an excess of sodium iodide in ethanol for one hour. The resulting white solid was washed with water and dried in the oven (yield g); it had a mass spectrum showing parent ion clusters of $(C_6H_4Hg)_3$, $(C_{12}H_8Hg)_3$ as well as the "mixed" species $(C_6H_4)_2(C_{12}H_8)Hg_3$.

Some reactions of o-terphenylenemercury dimer.

(i) Mercuric chloride.

A solution of o-terphenylenemercury dimer (0.312 gm; 0.346 mmole) in mesitylene (20 mℓ) was refluxed with mercuric chloride (0.187 gm; 0.692 mmole) for 20 minutes; on cooling and filtration the white solid gave 1,2-bis(chloromercuri-phenyl)benzene recrystallized from chloroform (yield g) m.p. 250°C (Found.: C,29.8; H,1.5%. $C_{18}H_{12}Hg_2C\ell_2$ calcd.: C,30.9, H,1.7%.

(ii) Mercuric bromide.

A mixture of o-terphenylenemercury dimer (0.295 gm; 0.345 mmole) and mercuric bromide (0.248 gm; 0.690 mmole) in mesitylene (20 mℓ) was refluxed for 20 minutes. On cooling, the resulting white product was filtered off and recrystallized from chloroform to give 1,2-bis-(bromomercuri-phenyl)benzene (yield q) m.p. 202-204°C, (Found: C,26.8; H,1.4; Br,21.4%. $C_{18}H_{12}Hg_2Br_2$ calcd.: C,27.4; H,1.5; Br,20.3%).

(iii) Mercuric iodide.

Reaction of o-terphenylenemercury dimer (0.311 gm; 0.363 mmole) and mercuric iodide (0.329 gm; 0.726 mmole) in mesitylene under reflux for 15 minutes gave 1,2-bis-(iodomercuri-phenyl)benzene. The analytical sample was first boiled with 40-60°C petroleum ether and then recrystallized from chloroform (yield g), m.p. 230°C (Found: C,23.9; H,1.4%. $C_{18}H_{12}Hg_2I_2$ calcd.: C,24.5; H,1.4%).

Reaction of 1,2-bis(chloromercuri-phenyl)benzene with sodium iodide.

Solutions of 1,2-bis(chloromercuri-phenyl)benzene (0.5 gm) and an excess of sodium iodide in ethanol (150 mℓ) were heated for half an hour; a white precipitate was formed which allowed to settle. The ethanolic layer was decanted and the white solid, o-terphenylenemercury dimer, was washed with water, dried in the oven and then recrystallized from chloroform (yield g), m.p. 294-296°C (Found: C,50.45; H,3.1%. $C_{36}H_{24}Hg_2$ calcd.: C,50.4; H,2.8%).

Infrared absorptions are quoted in cm^{-1} for mulls in nujol, using CsI optics (s - strong, m - medium, w - weak, sh - shoulder, d - doublet and br - broad).

$(C_6H_4Hg)_3$: 1259w, 1088m, 1021m, 866m, 745s, 679w, 422s, 325s, 289m.

$(C_{18}H_{12}Hg)_2$: 1158m, 1108w, 1072w, 1005w, 940w, 778 , 770s d, 745s, 733s, 725w sh, 617w, 568w, 542w, 458s, 382w, 345w.

$(4\text{-}CH_3C_6H_3Hg)_3$: 1568m, 1439m, 1365w, 1200m, 1085m, 872w, 797s, 716m; 570w, 510w, 492w, 414s, 387w, 293m, 275w.

$(3\text{-}CH_3C_6H_3Hg)_3$: 1130w, 1025w, 955w, 885w, 760s, 715m, 705w, 498w, 420w, 300w, 270s.

$[4,5\text{-}(CH_3)_2C_6H_2Hg]_3$: 1224w, 1150w, 1100w, 1015w; 868m, 720s, 640w, 430m.

$[4,5\text{-}(CH_3O)_2C_6H_2Hg]_3$: 1543m, 1330w, 1285s; 1260m, 1232s, 1195s, 1167s, 1106s, 858w, 838m, 764s, 718s, 400s br.

$[(CH_3)_4C_6Hg]_3$: 2970m, 2955m, 2930m, 2870sh; 1445w br, 1388m.

$(C_6C\ell_4I)_2Hg$: 1322m sh, 1311s, 1283m, 1157w, 351w, 820w, 645m, 596w, 322w.

$(C_6C\ell_4Hg)_3$: 1327m, 1310m, 1279m, 1160m, 1147m, 1066m, 844m, 825m, 640m, 350m.

$(C_6C\ell_4Hg)_3$. 0.5 DMF : 1659m, 1652sh, 1635sh br, 1326m, 1311m, 1287sh, 1282m, 1160m, 1151m, 844m, 831m br, 657w, 643m, 585w, 348m.

$(C_{12}H_8Hg)_3$: 1255w, 1157w, 1109w, 1005w, 785m, 780m d, 751s, 734 , 738s d, 621w, 536w, 452m sh, 446s, 428w, 361w, 320w.

$(C_{12}F_8Hg)_3$: 1623m; 1605m, 1590m, 1493s, 1462s, 1445s, 1403m sh, 1374w, 1364w, 1302s, 1282m, 1269m, 1127w, 1104s sh, 1101s, 1063s, 1029m sh, 1017s, 934m, 815m, 799m, 775w, 708m, 640w.

$\left[4,4'\text{-}(CH_3)_2C_{12}H_6Hg\right]_3$: 1587w, 1258w, 1134m sh, 1035w, 1002m, 884m, 835m, 830m, 817s, 811s, 722m, 563m, 549w, 472m, 415s, 353w, 327w, 298w.

$C_{12}H_8(HgC\ell)_2$: 1415w; 1281w, 1240w, 1156w, 1027m, 998s, 948w, 879w, 770w sh, 766m, 755 , 749sd, 728s, 720w sh, 662w, 617s, 550m, 532w, 440s, 432w sh, 369m, 329s, 315s sh.

$C_{12}H_8(HgBr)_2$: 1154w, 1041w, 1023m, 999s, 940w, 768 , 762m d, 752w sh, 745s, 729 , 722s d, 690w, 661w, 615w, 550w, 460w, 445w sh, 431m.

$C_{12}H_8(HgI)_2$: 1570w, 1412w, 1282w, 1159w, 1042w, 1021m, 999s, 950 , 945w d, 775s, 757w sh, 748s, 734w, 728w, 615w, 550w, 446w, 432m.

$C_{12}H_8(HgO_2CCH_3)_2$: 1580s br, 1328 , 1315s d, 1030w, 1010w, 925w, 777m, 750s, 732m, 720m, 690s, 608w, 445m, 290m.

$C_{18}H_{12}(HgC\ell)_2$: 1156w, 1022w, 1002 , 999m d, 941w, 874w, 779s, 769m sh, 753 , 748s d, 730s, 620w, 612w, 562m, 540w, 445s, 340m sh, 327m, 304w, 290w.

$C_{18}H_{12}(HgBr)_2$: 1157w, 1022w, 1000 , 998w d, 942w, 772s, 758w sh, 750 , 744s d, 726s, 718w sh, 618w, 612w, 560w, 540w, 441s.

$C_{18}H_{12}(HgI)_2$: 1208w, 1155w, 1024w, 1001 , 998m d, 940w, 870w, 778m sh, 772s, 750 , 744s d, 728s, 665w, 614w, 560m, 540w, 443s, 436m sh.

$C_6H_4(HgC\ell)_2$: 1268w, 1120w, 1032m, 970w, 775s, 739m sh, 701w, 652w, 442s, 349 , 330s d, 229m sh.

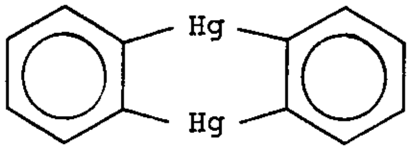
$C_6H_4(HgBr)_2$: 1440s, 1400w, 1250s, 1025w, 1016s, 1006w sh, 950w, 874w, 764 , 755s d, 720w sh, 635w, 422s, 316w, 298s.

Discussion.

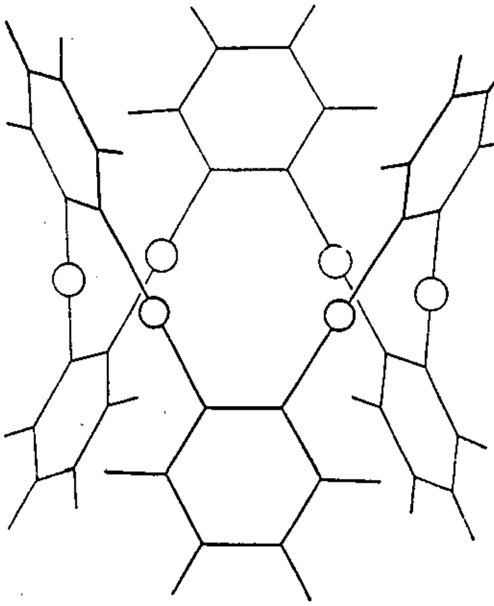
The synthesis of organomercury compounds by reaction of sodium amalgam with alkyl and aryl halides is one of the oldest methods, having been discovered by Frankland(12) early in the history of organometallic chemistry:

$$2RX + \text{"}Na_2Hg\text{"} \longrightarrow R_2Hg + 2NaX$$

ortho-Substituted dihalo-aromatic compounds have since been found to react with sodium amalgam to give heterocyclic compounds which are polymeric; for example, ortho-phenylenemercury was first prepared in 1930 by Vecchiotti(13) who treated 1,2-dibromobenzene with sodium amalgam in a petroleum ether/ethyl acetate mixed solvent and suggested the dimeric structure:



Some years later Wittig and Bickelhaupt(2) determined the molecular weight of the compound in solution which suggested that the molecule was hexameric. The agreement between the observed molecular weight and that calculated for the hexamer, though excellent, must have been fortuitous. The compound is not very soluble and the actual errors in the determination must have been considerable. ortho-Phenylenemercury adopts two crystal forms, one orthorhombic the other monoclinic. Grdenic(14) studied the latter using two-dimensional X-ray crystallographic techniques. Via a Patterson projection he only obtained the position of the mercury atoms but deduced the hexameric structure shown in I.



(I)

Although the hexamer is theoretically possible on steric grounds, when both crystal forms were subjected to a full, three-dimensional X-ray structure determination they were found to contain only trimeric molecules of ortho-phenylenemercury(15,16); furthermore the fluoro analogue, tetrafluorophenylenemercury, is also trimeric(17,18). This work shows that both the molecular weight determination by Wittig and the preliminary X-ray data of Grdenic are in error. Unfortunately the hexameric structure is still quoted as correct in research papers, reviews and even student text-books. To further substantiate the trimeric formulation, a number of substituted ortho-phenylenemercurials have been studied in this Thesis. We repeated the preparation of ortho-phenylenemercury using tetrahydrofuran or diethylether as a solvent and after purification by several recrystallizations the compound gave a melting-decomposition point of 338-340°C, while the reported melting point in the literature is 325-326°C. This lower value can probably be assumed to be due to the presence of ortho-terphenylenemercury dimer in the ortho-phenylenemercury trimer, since some of the dimer is often formed during the preparation. The two compounds can be separated quite easily by washing the mixture with refluxing chloroform in which the dimer is very soluble; the infrared spectrum of pure ortho-phenylenemercury trimer is shown in Figure 2.3. When the amalgam reaction is carried out in 1,2-dimethoxyethane, the main product is ortho-terphenylenemercury dimer(3,11).

Following the same procedure, a variety of substituted phenylenemercurials was prepared in this work because we hoped that, by changing the electronic and/or steric properties of the phenylene groups some phenylenemercurials, at least, could exist in the

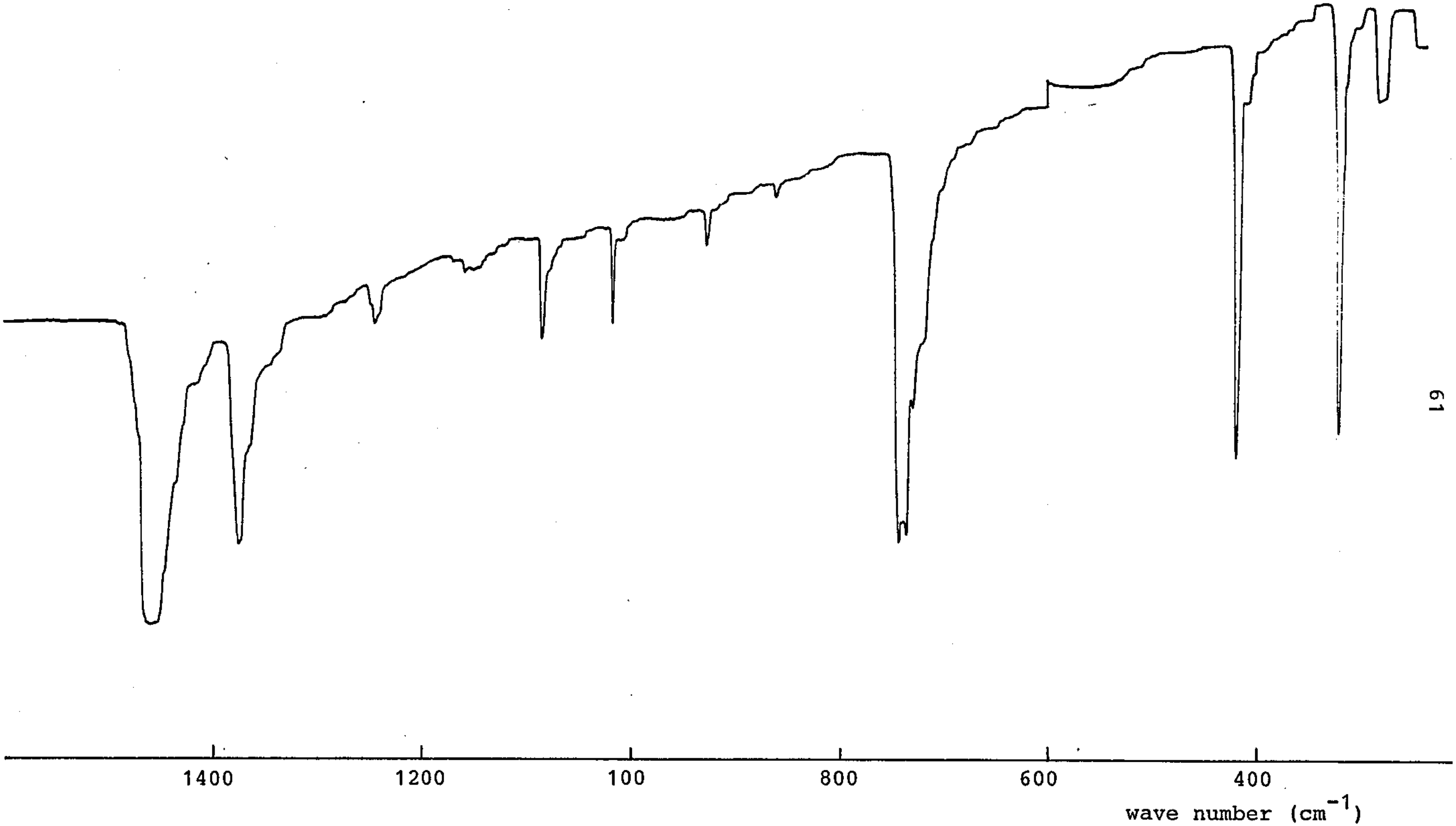
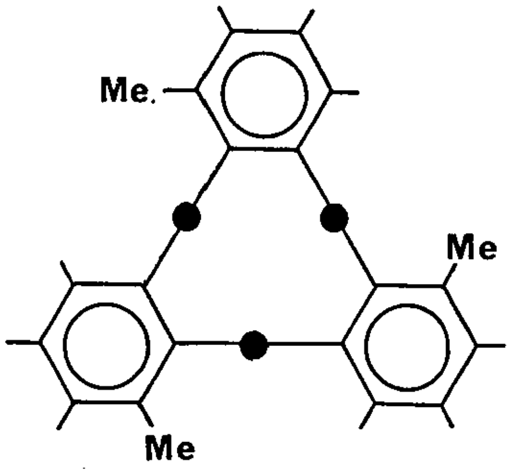


Figure 2.3: Infrared Spectrum of Ortho-phenylenemercury Trimer.

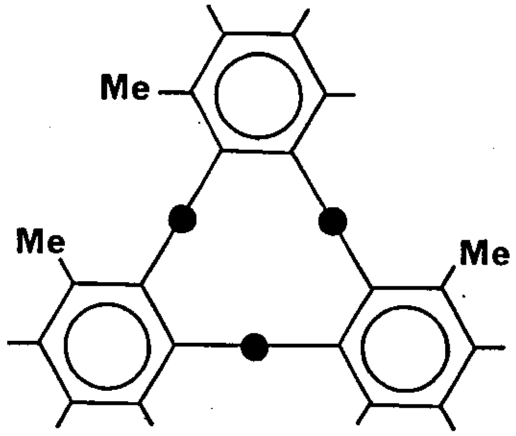
hexameric form (or even as the tetramer which appears just as feasible structurally). However, when their degree of polymerization was checked mass spectrometrically, in all cases only the trimers were found to be obtained. The methyl- and methoxy-phenylenemercurials (II-V) were prepared by vigorously stirring sodium amalgam with the corresponding 1,2-dibromobenzene derivatives in a suitable solvent (usually tetrahydrofuran) but the yields of the mercurials were always very low, typically being about 1% based on the dibromobenzene used.

Monomethylphenylenemercury trimers can exist in two isomeric forms IIa, IIb and IIIa, IIIb, depending on the relative positions of the three methyl groups. Presumably mixtures of the isomers were formed during the preparation of II and III but the very low solubility of these mercurials in all solvents hampered the isolation of the individual isomers when chromotography was attempted. Notwithstanding the isomeric mixtures presumably present, samples II and III were found to melt sharply.

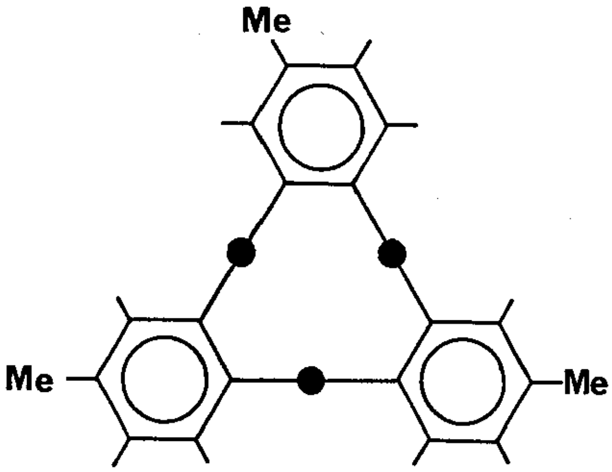
Tetramethylphenylenemercury was insoluble in all solvents tried and the only way found to purify it was to remove any impurities by extracting them with several aliquots of boiling nitrobenzene. Tetramethylphenylenemercury proved too involatile for a mass spectrum to be obtained but it could be made to sublime in high vacuum (ca. 10^{-4} mm Hg) on careful heating with a free



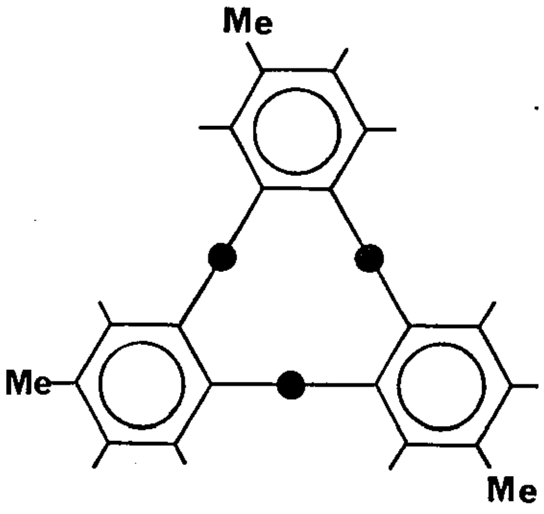
IIa



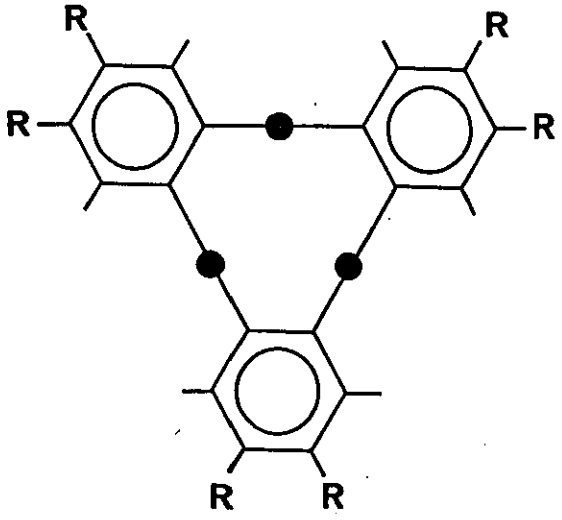
II b



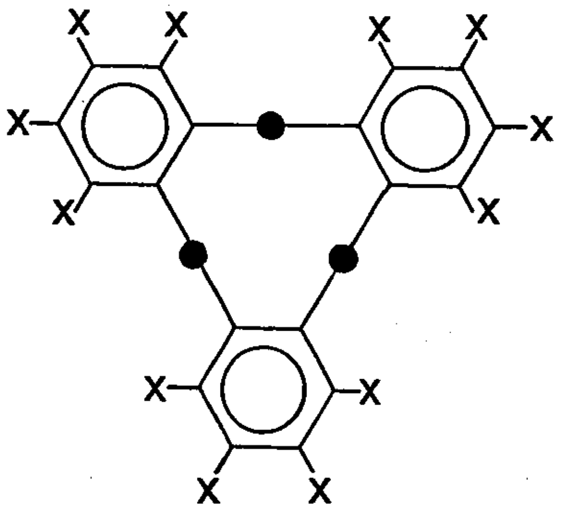
III a



III b



(IV, R = Me;
V, R = OMe)



(VI, X = Me
VII, X = Cl)

flame, the volatility being similar to that of tetrachlorophenylenemercury (shown to be trimeric by mass spectrometry).

When 1,2-dibromobenzene reacts with sodium amalgam in 1,2-dimethoxyethane solvent fair yields of terphenylenemercury dimer, $(C_{18}H_{12}Hg)_2$, are produced(3,11); no methyl-substituted terphenylenemercurials could be detected when 2,3-dibromotoluene or 3,4-dibromotoluene were treated with sodium amalgam in 1,2-dimethoxyethane. The mass spectra of II-V all show a mass cut-off at peaks representing the parent ion clusters, even at high gain there was no evidence of the corresponding tetrameric or hexameric mercurials. Apart from Hg^+, in each case the molecular ion was the only other intense mercury-containing species and the base peak was due to the methyl- or methoxy-substituted phenylene ion. Typically, III showed a parent ion cluster in its mass spectrum centred at 872 mass units, corresponding to the molecular weight of the trimer species $(C_6MeH_3)_3Hg_3^+$; other ions of reasonable intensities were $(C_6MeH_3)(C_6H_3)_2^+$, $(C_6MeH_3)_2(C_6H_3)^+$, Hg^+, $(C_6MeH_3)(C_6H_3)^+$, $(C_6MeH_3)_2^+$, $C_6MeH_3^+$ and $C_6MeH_4^+$ (Table 2.2, Figure 2.4), while Table 2.3 lists the important ions in the mass spectrum of compound II. Since all the mass spectra closely resemble that of o-phenylenemercury, now known from crystallographic studies to be trimeric, we are led to the conclusion that these methyl- and methoxy-substituted phenylenemercurials

Table 2.2: Partial Mass Spectrum of 4-Methylphenylenemercury Trimer.

m/e	Ion	Relative Abundance
872	$(C_6MeH_3Hg)_3^+$	10.0
380	$(C_6MeH_3)_2Hg^+$	2.0
270	$(C_6MeH_3)_3^+$	1.9
255	$(C_6MeH_3)_2(C_6H_3)^+$	8.4
240	$(C_6MeH_3)(C_6H_3)_2^+$	5.6
202	Hg^+	18.9
180	$(C_6MeH_3)_2^+$	56.6
165	$(C_6MeH_3)(C_6H_3)^+$	21.6
91	$C_6MeH_4^+$	100
90	$C_6MeH_3^+$	37.2
89	$C_6MeH_2^+$	43.0
65	$C_5H_5^+$	21.0
63	$C_5H_3^+$	18.6
51	$C_4H_3^+$	5.6
50	$C_4H_2^+$	2.3
38	$C_3H_2^+$	13.3
29	$C_2H_5^+$	61.3

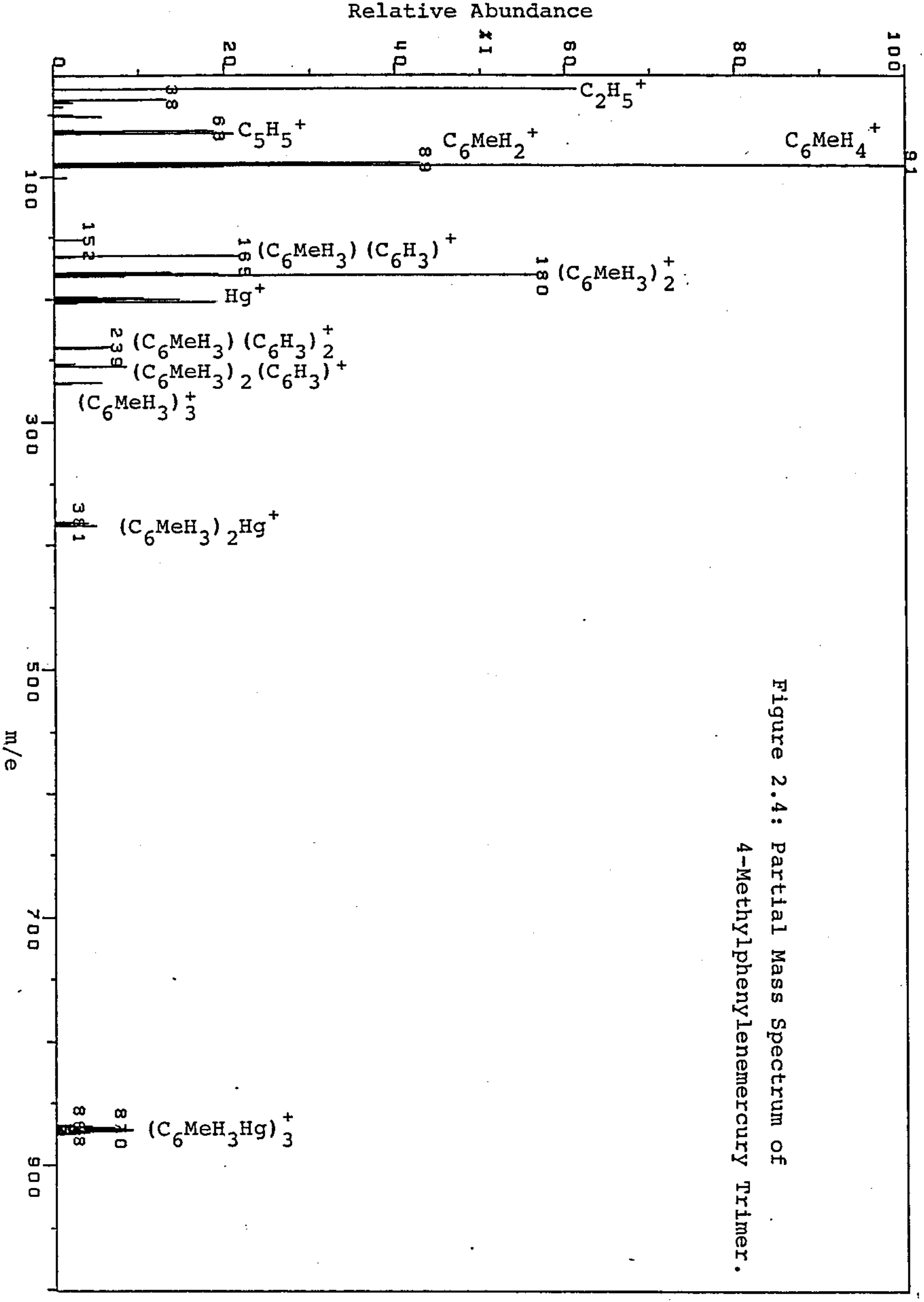


Figure 2.4: Partial Mass Spectrum of 4-Methylphenylenemercury Trimer.

Table 2.3: Partial Mass Spectrum of 3-Methylphenylenemercury Trimer.

m/e	Ion	Relative Abundance
872	$(C_6MeH_3Hg)_3^+$	10.5
380	$(C_6MeH_3)_2Hg^+$	2.1
290	$C_6MeH_3Hg^+$	1.7
270	$(C_6MeH_3)_3^+$	1.7
255	$(C_6MeH_3)_2(C_6H_3)^+$	6.6
240	$(C_6MeH_3)(C_6H_3)_2^+$	7.0
202	Hg^+	20.7
180	$(C_6MeH_3)_2^+$	41.4
165	$(C_6MeH_3)(C_6H_3)^+$	22.1
91	$C_6MeH_4^+$	100
90	$C_6MeH_3^+$	49.8
89	$C_6MeH_2^+$	53.6
65	$C_5H_5^+$	21.4
63	$C_5H_3^+$	25.6
51	$C_4H_3^+$	11.2
50	$C_4H_2^+$	6.3

also exist only in the trimeric forms shown in II-V. Fragments containing one or more mercury atoms are seen as complex patterns in the mass spectrum owing to the large number of naturally occurring isotopes of mercury, as shown below.

Mass No.	% Natural Abundance
196	0.14
198	10.02
199	16.84
200	23.13
201	13.22
202	29.80
204	6.85

As the pattern is unique to the number of Hg and C atoms it enables rapid and accurate identification of the various clusters. The calculated intensities for Hg^+, Hg_2^+ and Hg_3^+ ions are shown in Figure 2.5.

The reaction of a mixture of 1,2-dibromobenzene and 3,4-dibromotoluene with sodium amalgam in tetrahydrofuran, gave a product showing $(C_6H_4Hg)_3^+$, $(C_6H_4)_2$-$(C_6MeH_3)Hg_3^+$, $(C_6H_4)(C_6MeH_3)_2Hg_3^+$ and $(C_6MeH_3Hg)_3^+$ ions in its mass spectrum. Again, because of poor solubility it was found impossible to separate the "mixed" species.

Thermal decomposition of II at 320°C in a sealed, evacuated tube yielded metallic mercury together with a mixture of a liquid and some colourless crystals.

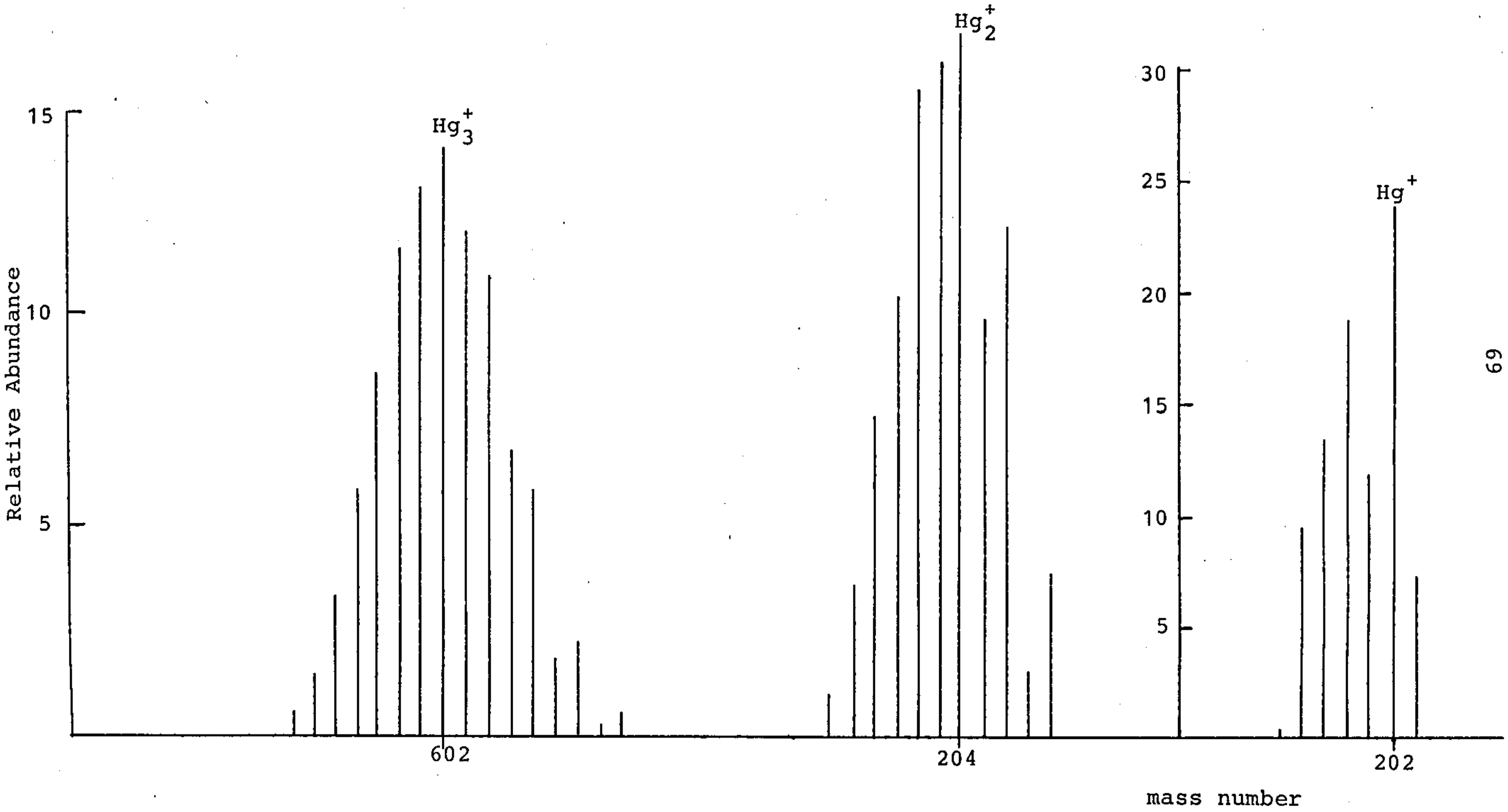
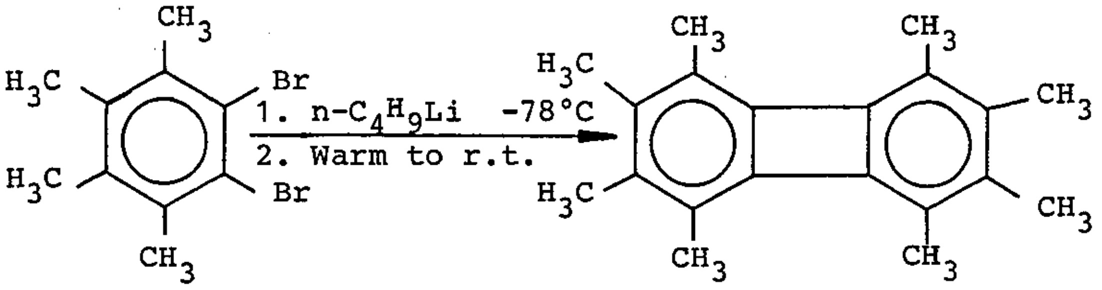


Figure 2.5: The calculated intensities for Hg_3^+, Hg_2^+, Hg^+ ions.

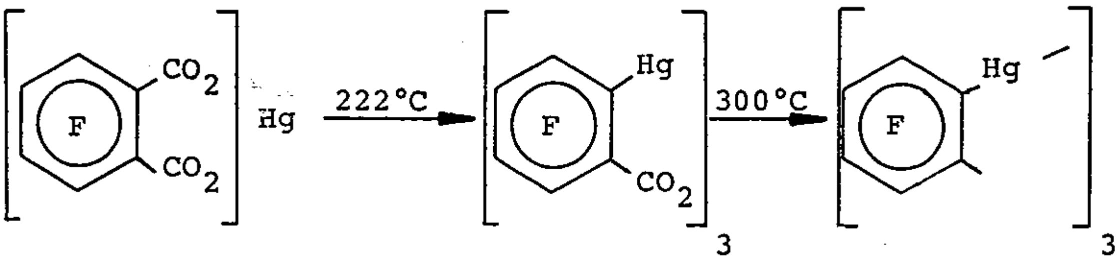
Mass spectral analysis of the ether-soluble material showed that the main component of the liquid was a dimethyldiphenyl and that the relatively involatile crystals were bis(methylphenyl)mercury. This may be compared to the thermal decomposition of o-phenylenemercury(11) trimer in a sealed, evacuated tube at 320°C which gave a complex mixture of compounds, three of which mass spectral analysis showed were triphenylene, diphenylmercury and phenylbiphenylmercury.

Substituted 1-bromo-2-chlorobenzenes invariably failed to give any mercury-containing products and even 2-bromochlorobenzene itselfgave only trace quantities of o-phenylenemercury trimer. This shows that the amalgam reaction does not work when chlorine is one of the halogens on the benzene ring. Repeated failures attended our efforts to make "naphthalenemercury" using 2,3-dibromonaphthalene and either sodium or potassium amalgam; similarly the attempted preparation of ethylphenylemercury from 2,3-dibromoethylbenzene with sodium amalgam failed. There appears to be no obvious reason why these two attempted syntheses did not work. Treatment of 1,2-diiodo- and 1,2-dibromotetramethylbenzene with sodium amalgam in tetrahydrofuran gave only octamethylbiphenylene in very low yield; this latter compound had previously been prepared in a good yield(6) when n-butyllithium was added to a solution of 1,2-dibromotetramethylbenzene in tetrahydrofuran at -78°C.



To make tetramethylphenylenemercury the very forcing conditions of refluxing the amalgam and 1,2-$Br_2Me_4C_6$ in decalin have to be used.

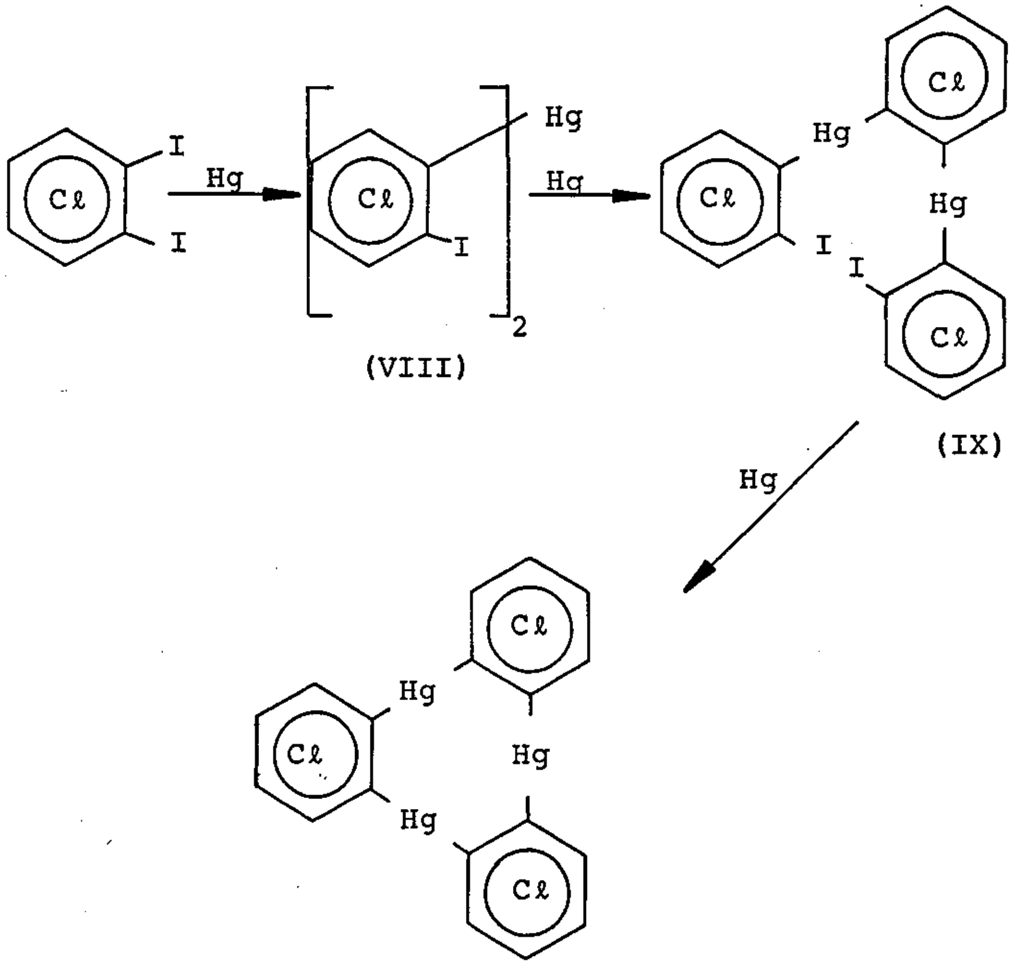
Perfluorophenylenemercury trimer is best made by decarboxylation of mercuric tetrafluorophthalate$^{(17)}$, which occurs in two stages:



However, when decarboxylation of mercuric tetrachlorophthalate was attempted, by heating it carefully under vacuum, chlorine-migration reactions occur to give mainly bis(pentachlorophenyl)mercury and some hexachlorobenzene; only tiny amounts of tetrachlorophenylenemercury can be sublimed from the involatile decarboxylation debris on strong heating with a free flame. A much more convenient synthesis of tetrachlorophenylenemercury is to heat together mercury and 1,2-diiodotetrachlorobenzene in a sealed, evacuated tube at 260-300°C for about four days. The yield is virtually quantitative as shown by the fact that an off-white, analytical sample could be obtained simply by carefully subliming away the HgI_2 by-product and excess mercury. Tetrachlorophenylenemercury is highly insoluble in the common organic solvents and is only very slightly soluble in boiling nitrobenzene or dimethylformamide; it separates from the latter, on cooling, in such a finely-divided state that the suspension has to be centrifuged to force the solid to settle. Unlike $(C_6F_4Hg)_3$, which exhibits solvates containing one, two and three molecules of solvent(18), tetrachlorophenylenemercury forms a solvate containing only half a mole of dimethylformamide (DMF). The broad carbonyl band of DMF (maximum intensity at 1690 cm^{-1}) shifts by only 31 wavenumbers to 1659 cm^{-1} in the solvate; the band centred at 1080 cm^{-1} and the sharp peak at 457 cm^{-1} which occur in the spectrum of free DMF are essentially unchanged in the solvate, strongly suggesting that the DMF is not coordinated to the mercury.

A similar "direct synthesis" in which a mixture of 1,2-$I_2C_6F_4$ and 1,2-$I_2C_6C\ell_4$ was heated with mercury gave the two expected products $(C_6F_4Hg)_3$ and $(C_6C\ell_4Hg)_3$ as well as the "mixed" species $(C_6C\ell_4)(C_6F_4)_2Hg_3$ and $(C_6C\ell_4)_2(C_6F_4)Hg_3$. All four components gave molecular ion clusters in the mass spectrum, those of the latter two mixed species occurring at around 1112 and 1178 mass units, respectively (see Figure 2.6).

If the reaction between 1,2-diiodotetrachlorobenzene and mercury was stopped after only one day then bis(2-iodotetrachlorophenyl)mercury (VIII), occurred in large amounts among the products, and it could be obtained free of tetrachlorophenylenemercury by fractional vacuum sublimation. Presumably this compound is an intermediate in the formation of tetrachlorophenylenemercury:



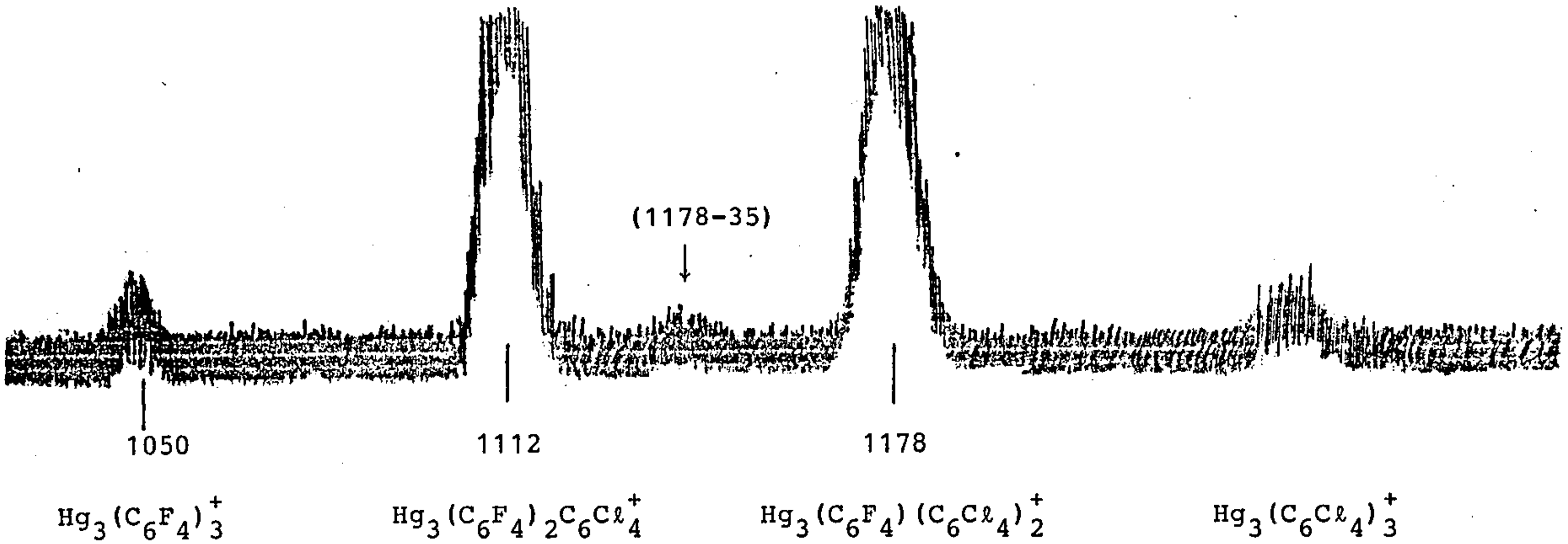
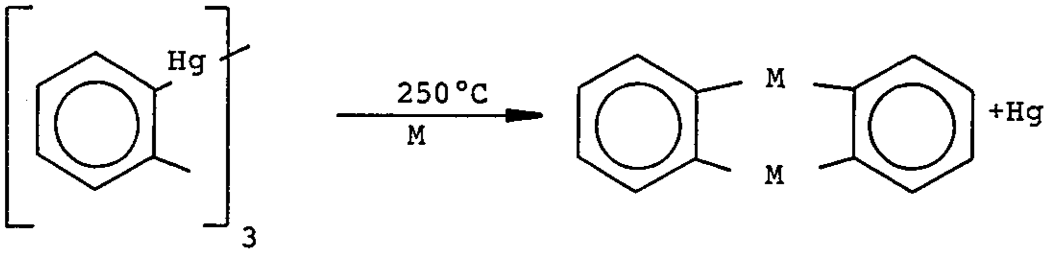


Figure 2.6: Parent Ions of Products Arising from the Reaction of Mercury with a Mixture of 1,2-$I_2C_6F_4$ and 1,2-$I_2C_6C\ell_4$

We have not, as yet, been able to obtain evidence for the occurrence of intermediate IX which, once formed, may well react rapidly with more mercury to give tetrachlorophenylenemercury.

The reaction between o-phenylenemercury and finely powdered tellurium metal at 250°C was found to yield telluranthrene(19). In order to investigate if o-phenylenemercury would be useful in small-scale synthesis of other heterocyclic systems, it was heated with selenium to 250°C in a sealed tube. The product, extracted with 40-60°C petroleum ether, was essentially pure selenanthrene, $Se_2(C_6H_4)_2$, as determined mass spectroscopically; in a similar manner sulphur gave thianthrene $S_2(C_6H_4)_2$:



M = Se,S

A "mixed" reaction in which selenium was heated with $(C_6F_4Hg)_3$ and $(C_6H_4Hg)_3$, gave a product showing $Se_2(C_6F_4)_2^+$, $Se_2(C_6H_4)_2^+$ and $Se_2(C_6H_4)(C_6F_4)^+$ ions in its mass spectrum (Figure 2.7). Since the experiment

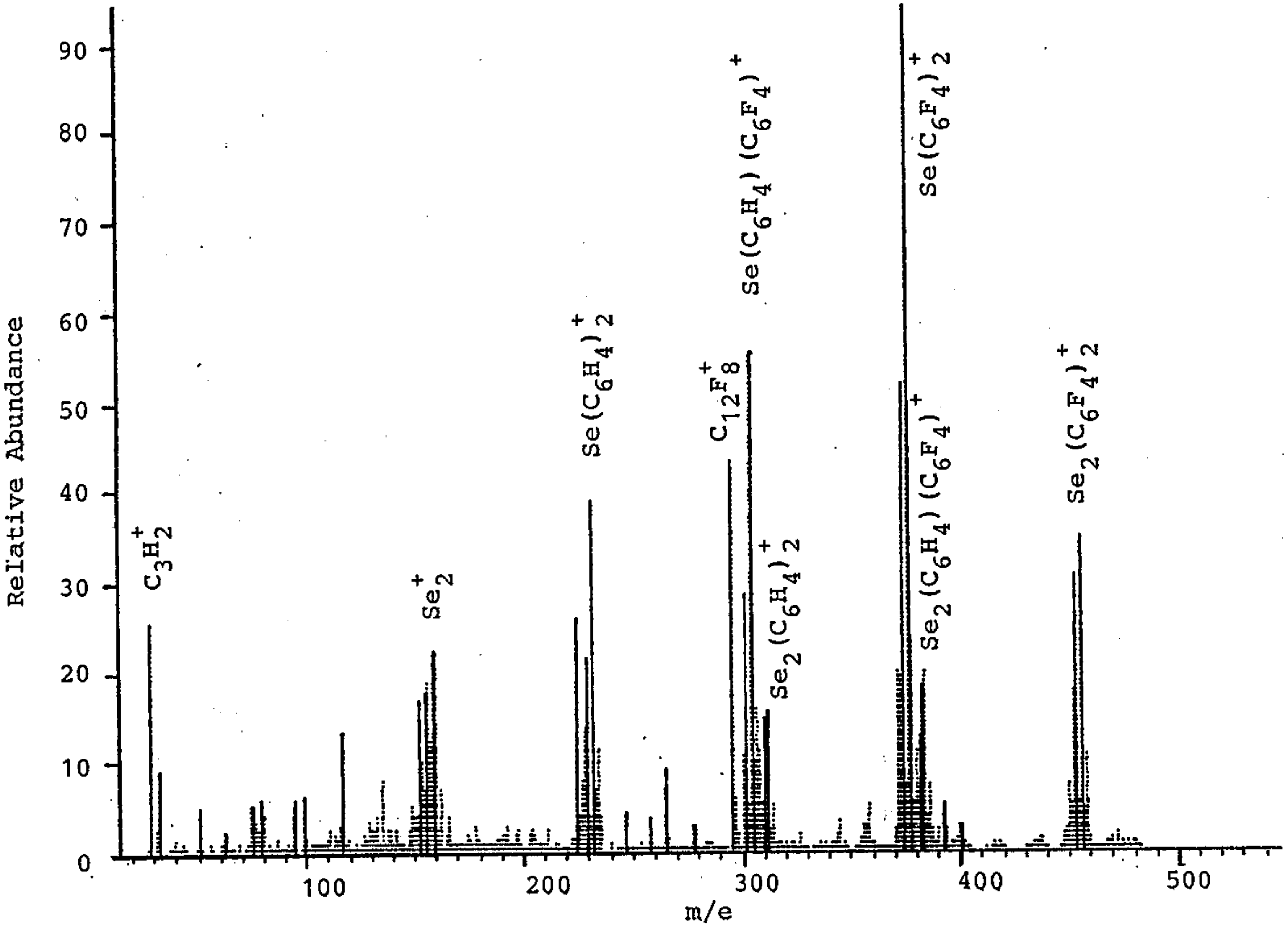


Figure 2.7: Partial Mass Spectrum showing the Parent Ions of Products Arising from the Reaction of Selenium with $(C_6H_4Hg)_3$ and $(C_6F_4Hg)_3$

was carried out to determine only the feasibility of the reaction no attempt was made to isolate the components of the mixture; no doubt TLC on alumina would have proved a simple method for separation.

In the infrared spectra of substituted benzene derivatives, intense absorption bands are found in the region of 950-650 cm^{-1} due to the C-H out-of-plane deformation vibrations. These vibrations are highly characteristic of the substitution type and afford the best method for identification and characterization of benzene derivatives. The regions of characteristic absorption for different substitution types are summarized in Table 2.4(20). In agreement with the assignments in Table 2.4, the C-H out-of-plane bending vibration of o-phenylenemercury occurs at 745 cm^{-1}, while in 3-methyl-, 4-methyl- and 4,5-dimethylphenylenemercury the bands appear at 760, 797 and 868 cm^{-1}, respectively. It should be pointed out, that in polysubstituted compounds, the intensity of the band decreases sharply, limiting the possibilities of characterization of the mode and degree of substitution(21); for example, with tetramethylphenylenemercury no infrared absorption occurred except in the 3000 and 1400 cm^{-1} region as shown in Figure 2.8. Assignment of structure based upon these out-of-plane bending vibrations is most reliable for alkyl substituted aromatic compounds or for molecules without certain polar groups(22).

Table 2.4: C-H Out-of-Plane Bending Vibrations for Benzenoid Derivatives (all bands are normally strong).

Benzene	671 cm^{-1}
Monosubstitutedbenzene	770-730
1,2-Disubstitutedbenzene	770-735
1,3-Disubstitutedbenzene	810-750
1,4-Disubstitutedbenzene	833-810
1,2,3-Trisubstitutedbenzene	780-760
1,2,4-Trisubstitutedbenzene	825-805
1,3,5-Trisubstitutedbenzene	865-810
1,2,3,4-Tetrasubstitutedbenzene	810-800
1,2,3,5-Tetrasubstitutedbenzene	850-840
1,2,4,5-Tetrasubstitutedbenzene	870-855
Pentasubstitutedbenzene	870

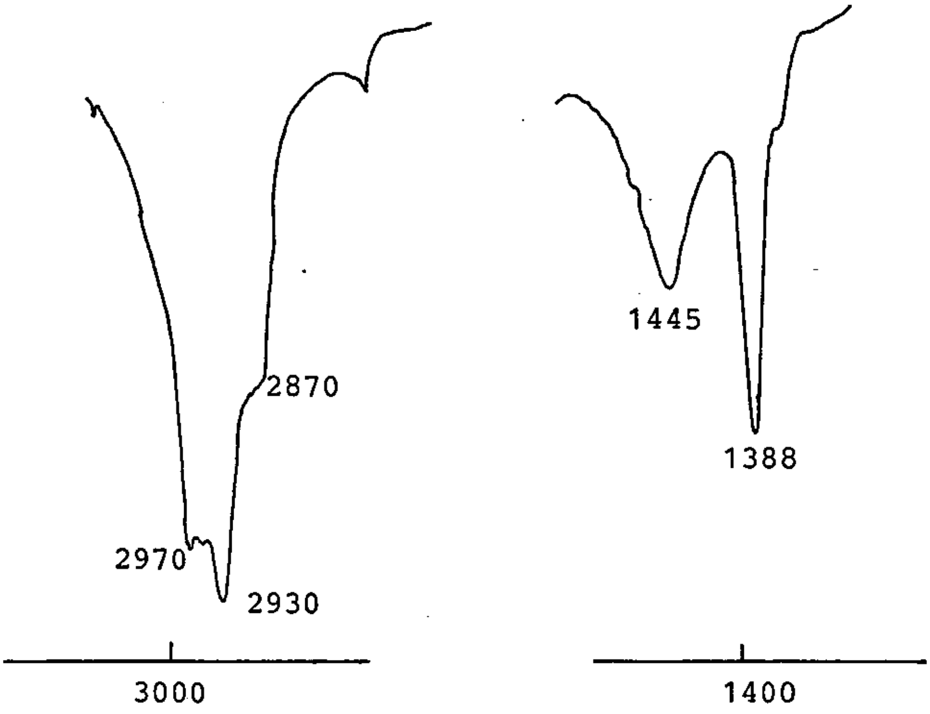


Figure 2.8: The Infrared Spectrum of Tetramethylphenylenemercury.

The absorptions at 2970, 2955, 2930, 2870 cm^{-1} are due to the C-H stretching vibrations, while the bands 1445 and 1388 cm^{-1} are due to asymmetric and symmetric C-H bending vibrations for the methyl groups respectively.

Substitution with polar groups often shifts these bands beyond the ranges given in the correlation (Table 2.4); for example, in the 4,5-dimethoxyphenylenemercury spectrum the out-of-plane absorption occurs at 838 and 764 cm^{-1}.

The C-H stretching mode is also characteristic in the methyl- and methoxy-phenylenemercury compounds when their infrared spectra are recorded in HCBD mulls; for example, in 4-methylphenylenemercury the aromatic C-H stretching frequency occurs at 3008 cm^{-1} whilst the asymmetric and symmetric C-H stretches of the methyl groups are at 1908 and 2855 cm^{-1}, respectively.

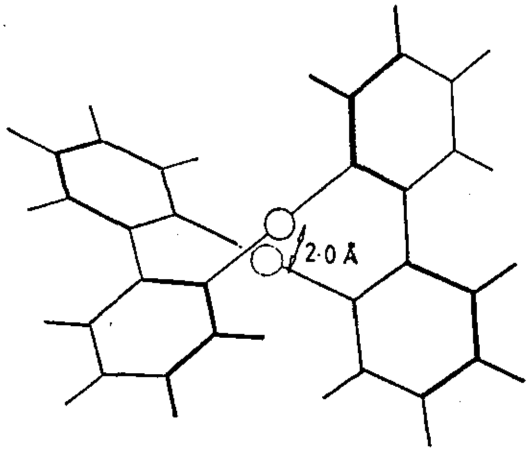
Biphenylenemercury, $(C_6H_4C_6H_4Hg)_n$, has been synthesized by the reaction of 2,2'-dilithiobiphenyl with mercuric chloride in ether solvents. It has a reported melting point of about 338°C and has been stated by Wittig to be tetrameric(7). The 2,2'-dilithiobiphenyl may be prepared either by the lithium-iodine exchange reaction using 2,2'-diiodobiphenyl(7) or by the direct metalation of biphenyl(23):

$$2,2'\text{-}I_2C_{12}H_8 + Li \longrightarrow 2,2'\text{-}Li_2C_{12}H_8 \xrightarrow{HgC\ell_2} (HgC_{12}H_8)_n$$

$$C_{12}H_{10} + LiBu.TMEDA \longrightarrow 2,2'\text{-}LiC_{12}H_8 \xrightarrow{HgC\ell_2} (HgC_{12}H_8)_n$$

(TMEDA = tetramethylethylene diamine)

The mass spectrum of biphenylenemercury, however, showed the molecule was probably trimeric(11), a fact later verified by X-ray diffraction studies on the triclinic crystal modification(24). In this work, biphenylenemercury has been made by direct metalation of biphenyl and has a melting point of 338°C after the first crystallization of the compound from the reaction mixture. The melting point at this stage is identical to that quoted by both Wittig(7) and Neugebauer(23), but when the compound is purified by several recrystallizations, it has a melting point of 358-360°C. Thus there is some doubt as to whether our sample of biphenylenemercury, which melted at 358-360°C, is a trimer, tetramer or hexamer. In order to prove the true extent of its oligomerization, the mass spectrum was repeated many times on different samples, and in all cases the samples had a mass cut-off at a cluster of isotopomeric ions centred at 1056 mass units, which represents the parent ion of the trimer; no peaks corresponding to the ion $(C_6H_4)_8^+$, which would probably be a strong fragment ion of the tetramer, could be distinguished even at high gain. Hence as the parent ion of the tetramer was absent, as was its probable principal fragment ion, the biphenylenemercury would appear to be pure trimer. However, in the mass spectrum of biphenylenemercury there is a group of peaks of almost equal intensity to the parent trimer ion which represent the isotopomeric species in the ion $(C_{12}H_8Hg)_2^{+}$; we have, therefore, to consider the possibility that biphenylenemercury can exist also as a dimer. Assuming that the C-Hg-C bond angle in a phenylenemercurial will be typically about 180°(25) then it can be shown by consultation of scale Dreiding models that the two mercury atoms in a dimer (XI) would approach to within about 2.0 Å of each other.



(XI)

This is considerably less than twice the van der Waals radius for mercury (ca. 3.1 Å) and suggests that the dimer molecule would be unstable sterically. Table 2.5 and Figure 2.9 give the details of the mass spectrum of biphenylenemercury. Like-wise, there is a strong peak in the mass spectrum of perfluorobiphenylenemercury representing the ionized "dimer", $(C_{12}F_8Hg_2)^{+}$, as well as weak peaks due to $(C_{12}F_8Hg)_2^{2+}$. However, in this spectrum there is also a broad metastable peak at about 662 mass units corresponding to the transition:

Table 2.5: Partial Mass Spectrum of Biphenylenemercury Trimer (only the most intense peak is recorded for isotopomeric clusters of peaks).

m/e	Ion	Relative Abundance
1062	$(C_{12}H_8Hg)_3^+$	21.8
704	$(C_{12}H_8Hg)_2^+$	3.5
456	$(C_{12}H_8)_3^+$	3.5
304	$(C_{12}H_8)_2^+$	11.2
303	$C_{24}H_{15}^+$	23.9
302	$C_{24}H_{14}^+$	18.3
289	$C_{23}H_{13}^+$	2.1
202	Hg^+	6.3
152	$C_{12}H_8^+$	100
77	$C_6H_5^+$	2.8
76	$C_6H_4^+$	5.6

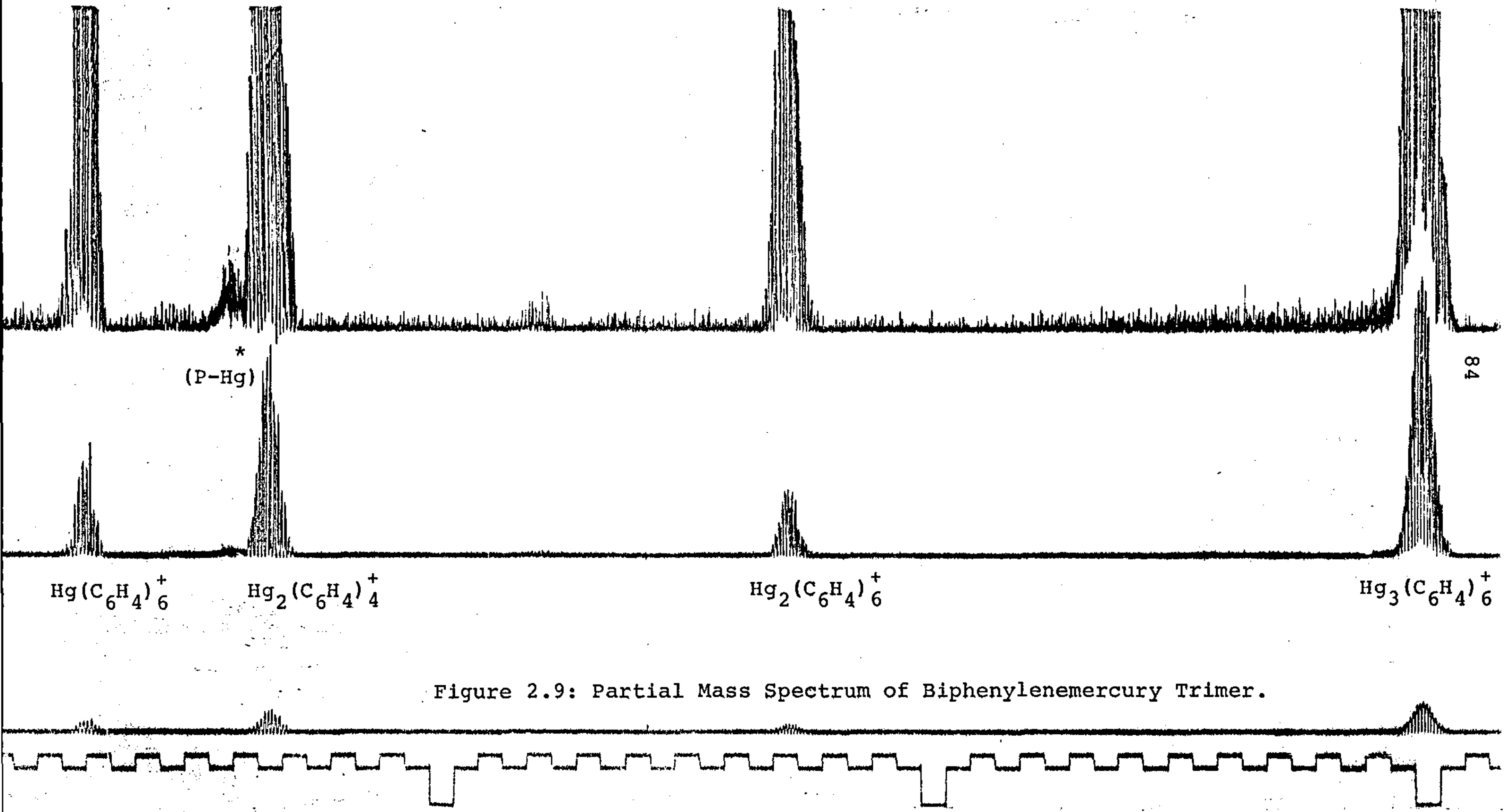


Figure 2.9: Partial Mass Spectrum of Biphenylenemercury Trimer.

$$(C_{12}F_8Hg)_3^+ \longrightarrow C_{12}F_8Hg + (C_{12}F_8Hg)_2^+$$

(Obs. 557-664, calcd. 662.3 m.u.)

Showing that most, if not all, of the "dimer" ions arise via fragmentation and not via molecular ionization of a dimer impurity.

More interestingly, the mass spectra of some samples of perfluorobiphenylenemercury show a group of peaks, visible only at high gain, corresponding to the tetramer (1992 m.u., see Figure 2.10). Thus trace amounts of tetramer must be present in those samples of perfluorobiphenylenemercury.

Biphenylenemercury is too insoluble in all solvents tried to carry out ^{13}C and ^{1}H NMR searches for the presence of either tetramer or dimer within the trimer samples. Hence it was decided to solve the structure of the high-melting sample of biphenylenemercury by X-ray diffraction studies. Two different crystal modifications have been identified and, by using measurements with symmetry properties to define the number of molecules per unit cell, it proved possible to calculate the molecular weight in each form: monoclinic (from p-xylene), MW 1056.1; orthorhombic (from toluene), MW 1053.2 compared with the calculated molecular weight for the trimer of 1058.2. Finally, as further proof, the single-crystal X-ray structure analysis of orthorhombic biphenylenemercury was used

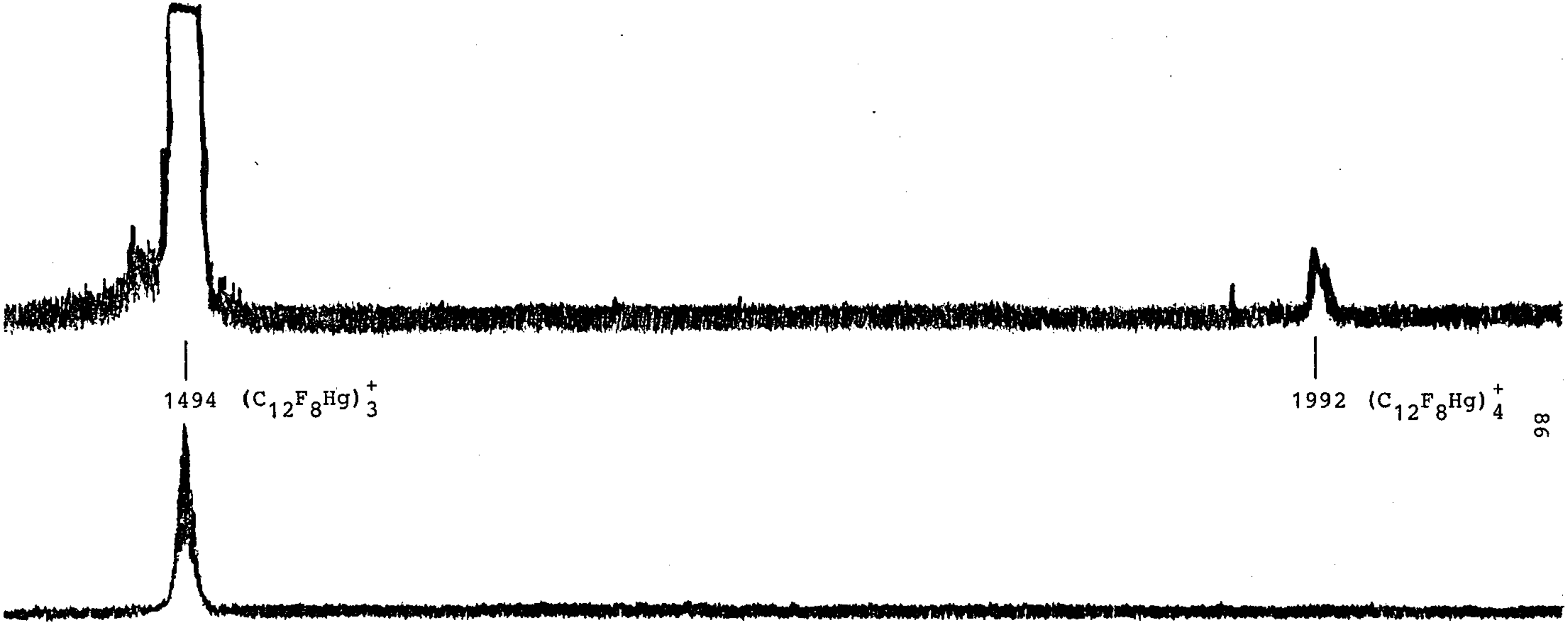
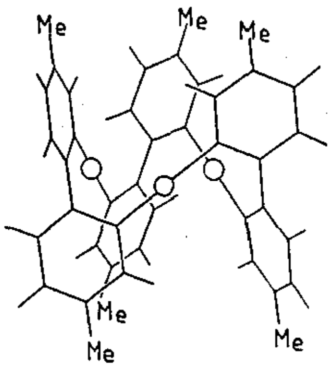


Figure 2.10: Partial Mass Spectrum Showing the Parent Ions of Perfluorobiphenylenemercury Trimer and Tetramer.

to confirm the trimeric nature of this compound (see Chapter 3).

The new compound 4,4'-dimethylbiphenylenemercury was prepared from the reaction of mercuric chloride and 2,2'-diiodo-4,4'-dimethylbiphenyl, lithiated with two moles of n-butyllithium. Like the parent biphenylenemercury, this molecule also shows only a molecular ion representing the trimeric species (XII) in its mass spectrum, as shown in Table 2.6.



(XII)

Octafluorobiphenylenemercury was prepared from the reaction of 2,2'-dilithiooctafluorobiphenyl and mercuric chloride in ether at -78°C. It is much more soluble than $(C_{12}H_8Hg)_3$ and shows four intense groups of peaks in its ^{19}F NMR spectrum at 120.6, 136.2, 154.2 and 154.9 ppm (relative to internal $CFC\ell_3$); these correspond to the F(3), F(6), F(5) and F(4) fluorine atoms of the trimer molecule (see Figure 2.11). Tiny impurity peaks just observable above the background

Table 2.6: Partial Mass Spectrum of 4,4'-Dimethylbiphenylenemercury Trimer (only the most intense peak is recorded for isotopomeric clusters of peaks).

m/e	Ion	Relative Abundance
1138	$(C_{14}H_{12}Hg)_3^+$	10.5
760	$(C_{14}H_{12}Hg)_2^+$	2.2
562	$(C_{14}H_{12})_2Hg^+$	3.7
360	$(C_{14}H_{12})_2^+$	9.0
359	$C_{28}H_{23}^+$	19.5
345	$C_{27}H_{21}^+$	13.5
344	$C_{27}H_{20}$	17.2
270	$C_{21}H_{18}$	3.7
202	Hg^+	12.0
180	$C_{14}H_{12}^+$	100
165	$C_{13}Hg^+$	53.3
90	$C_7H_6^+$	4.5

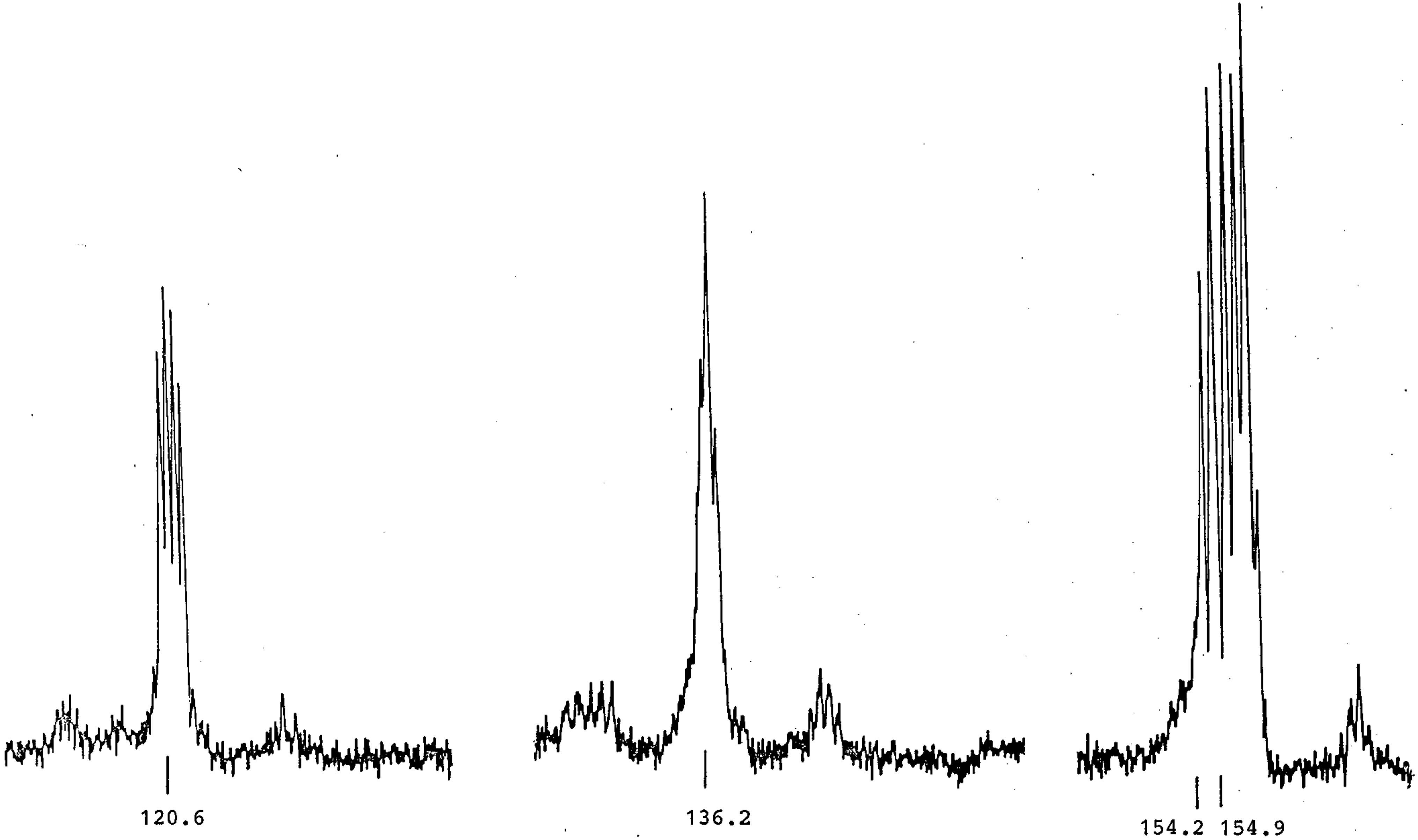
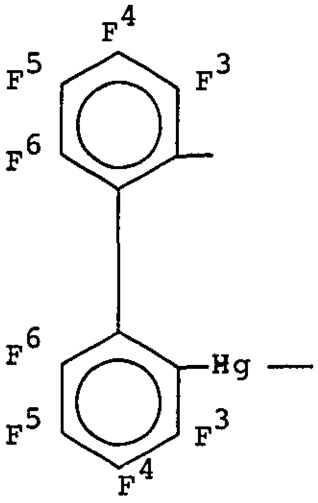


Figure 2.11: 19F NMP Spectrum of Octafluorobiphenylenemercury
(ppm relative to $CFCl_3$)



noise may be connected with the presence of the small amount of tetramer shown up by the mass spectrum.

Two peaks of almost equal intensities are present at 804 and 820 cm^{-1} in the infrared spectrum of perfluorobiphenylenemercury; this is the region where "Hg - C_6H_4" vibration peaks might be expected to occur; Figure 2.12. At face value this spectrum could be taken as being indicative of about equal amounts of two perfluorobiphenylenemercury species (trimer and tetramer) being present in the sample. The very weak peaks corresponding to the tetramer in the mass spectrum could then be attributed to the low relative volatility of the tetrameric species. However, the infrared spectrum of bis(perfluorobiphenylene)silane, $(C_{12}F_8)_2Si$, also shows two similar peaks of about equal intensity (at 884 and 864 cm^{-1}) attributable to "Si - C_6F_4" vibrations(26). In view of this, and the lack of other

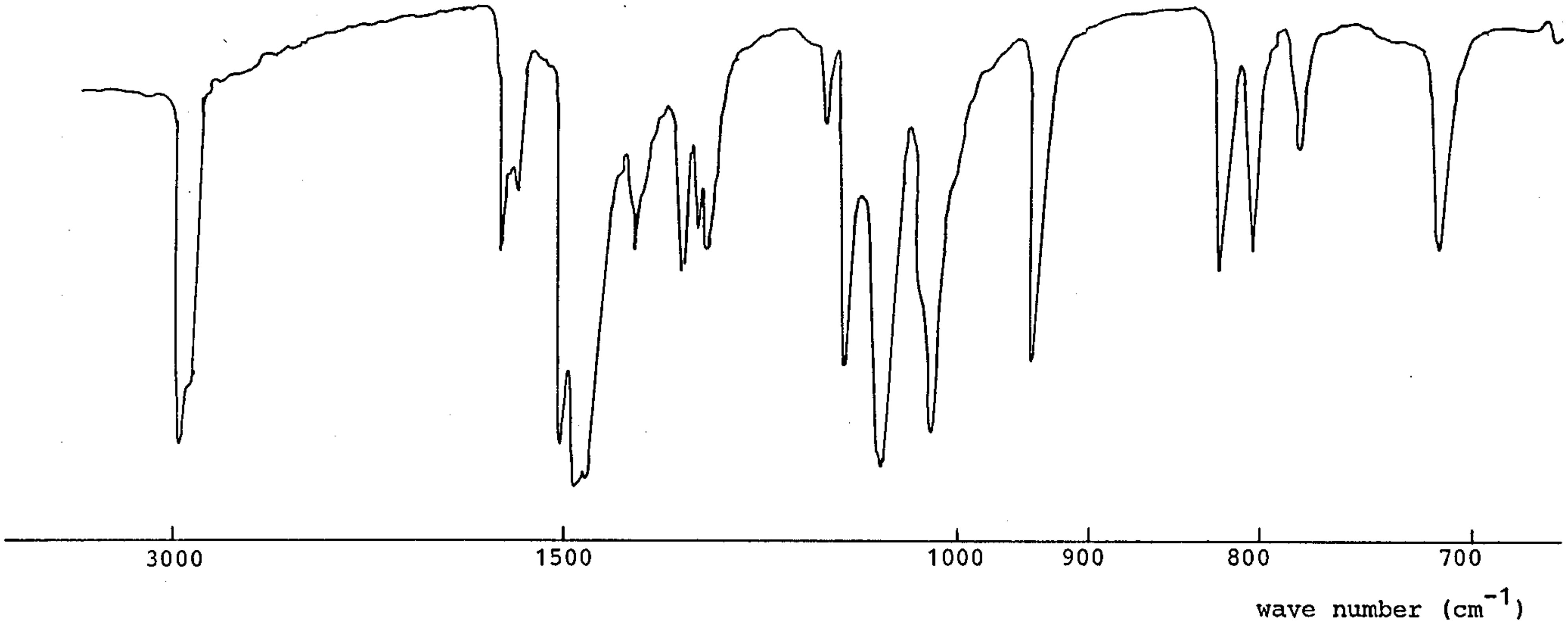


Figure 2.12: Infrared Spectrum of Perfluorobiphenylenemercury.

evidence to suggest the presence of appreciable amounts of tetramer in perfluorobiphenylenemercury samples, we assume the two "Hg - C_6F_4" peaks to be due to other effects within the samples of the trimer. Similarly in biphenylenemercury the "X-sensitive" peak at 447 cm^{-1} is found to be slightly split in several samples even though the rest of the spectrum remains unchanged (Figure 2.13). This behaviour is assumed to be associated with the different crystalline forms adopted by biphenylenemercury trimer.

In an attempt to prepare 2,2'-biphenylenebis(mercury chloride), $C_{12}H_8(HgC\ell)_2$, (which might be considered an intermediate in the formation of biphenylenemercury trimer) two moles of mercuric chloride were reacted with one mole of 2,2'-dilithiobiphenyl, prepared from the metalation of biphenyl by the n-butyllithium/TMEDA complex. The reaction products were biphenylenemercury, a white solid soluble in chloroform which sublimes above 240°C without melting (identified as 2-chloromercuribiphenyl $C_{12}H_9HgC\ell$ from the mass spectrum) and excess mercuric chloride recovered as its 1:1 $HgC\ell_2$.TMEDA complex. However, no $C_{12}H_8(HgC\ell)_2$ could be detected.

On the other hand, this compound and its bromo and iodo analogues can readily be prepared by reaction of biphenylenemercury with the appropriate mercuric halides in boiling mesitylene for half an hour:

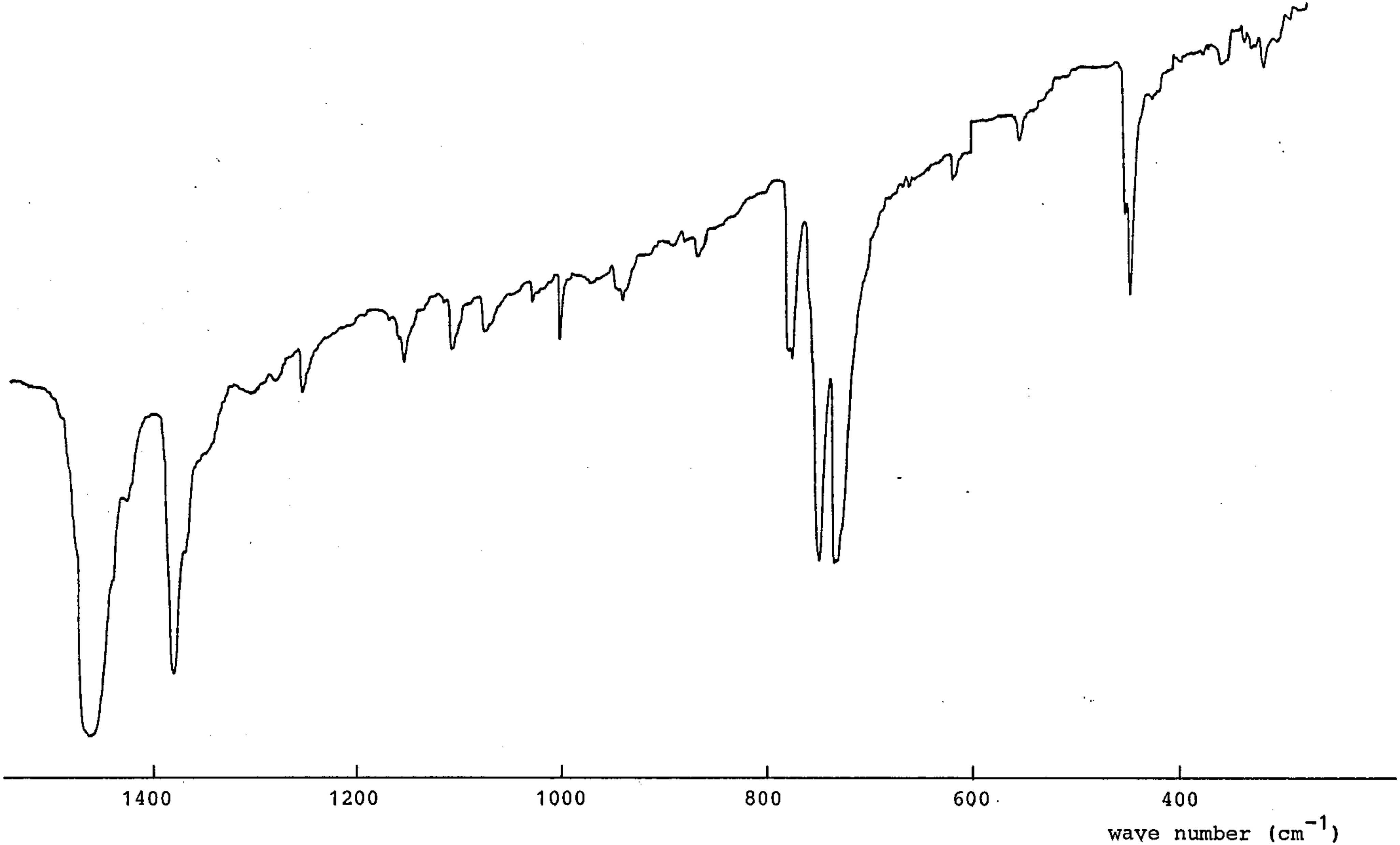
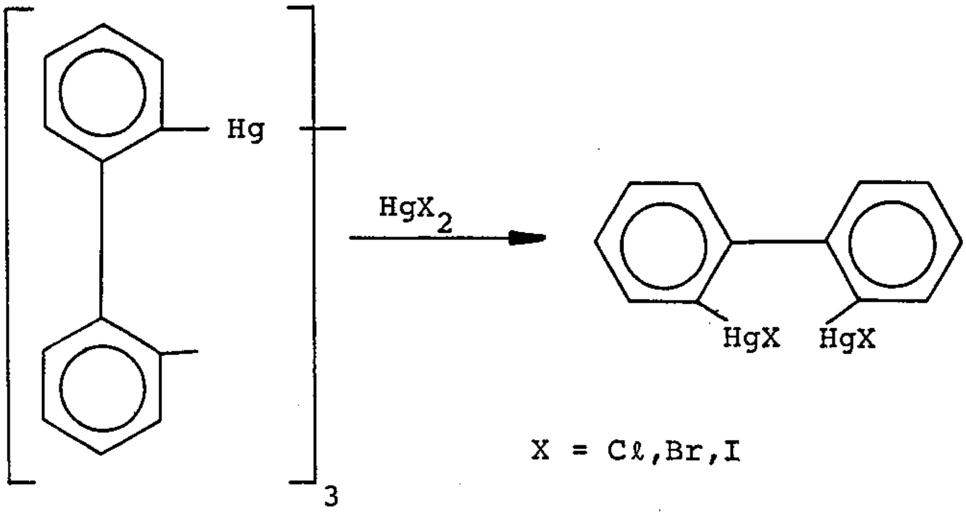
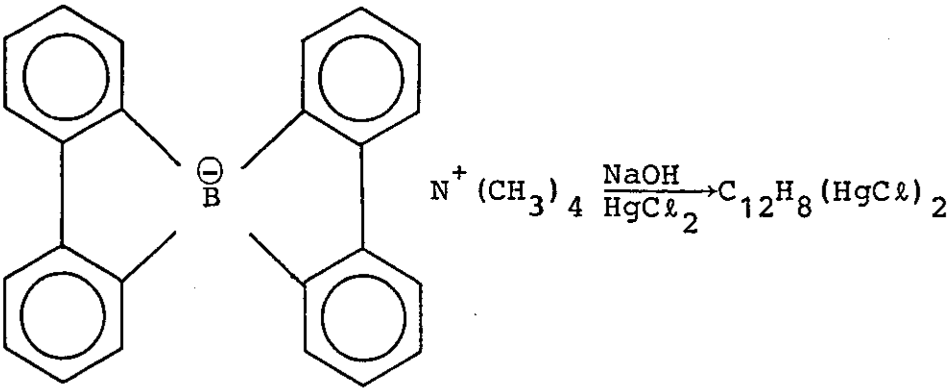


Figure 2.13: Infrared Spectrum of Biphenylenemercury Trimer.



Wittig had previously prepared 2,2'-biphenylenebis(mercury chloride) by treatment of tetramethylammonium bis-2,2'-biphenyleneborate with alkali in acetone and then boiling the solution with $HgCl_2$(10):



While the 2,2'-biphenylenebis(mercury iodide) has been reported in the literature(11) as a by-product in the formation of biphenylenemercury from 2,2'-diiodobiphenyl, lithium metal and mercuric chloride presumably due to a chlorine-iodine exchange occurring between the Hg - Cℓ bonds in the intermediate, $C_{12}H_8(HgCl)_2$, and lithium iodide, the latter remaining from the *in situ* preparation of 2,2'-dilithiobiphenyl.

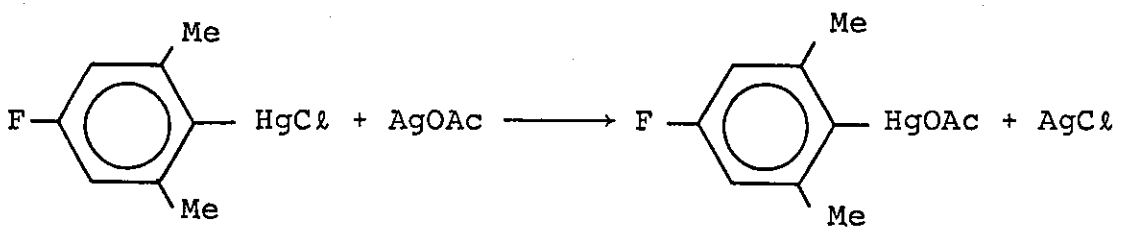
Biphenylenemercury is also cleaved by mercurous chloride in hot mesitylene giving again 2,2'-biphenylenebis(mercury chloride), and metallic mercury. 2,2'-Biphenylenebis(mercury acetate) may be prepared from the reaction of biphenylenemercury with either boiling glacial acetic acid or mercuric acetate in refluxing methanol. Some of the major preparative methods of organomercurials involve mercuric acetate, for example, oxymercuration and mercuration which naturally leads to the formation of organomercury(II) acetates. Thus, methods have been devised to transform these acetates into other salts, in particular the halides. Treatment with aqueous solutions of alkali metal halides results in the desired exchange(27):

$$\mathrm{RHgOAc} + \mathrm{MX} \longrightarrow \mathrm{RHgX}$$

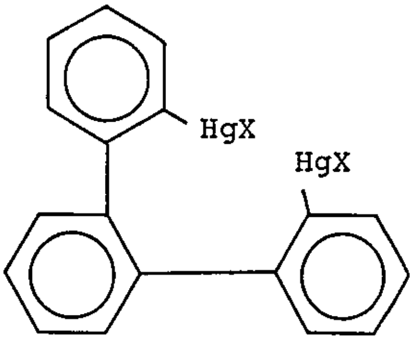
but as an excess of the metal halide may cause symmetrization(27), in this work the 2,2'-biphenylenebis(mercury acetate) was treated with concentrated hydrochloric acid in boiling methanol when the corresponding organomercury(II) chloride was obtained:

$$\mathrm{C_{12}H_8(HgOAc)_2} + \mathrm{2HC\ell} \xrightarrow{\text{methanol}} \mathrm{C_{12}H_8(HgC\ell)_2} + \mathrm{2HOAc}$$

Although not attempted in this work it is well known that transformation of organomercury(II) chlorides to acetates, nitrates, sulphates or perchlorates may be accomplished using silver salts(28):

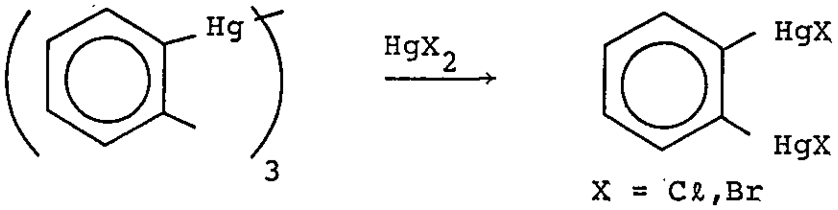


Treatment of o-terphenylenemercury dimer with mercuric halides in 1:2 ratio in boiling mesitylene similarly gave the 1,2-bis(halomercuri-phenyl)benzenes:



X = Cℓ,Br,I

The use of mesitylene in these reactions was simply to obtain a sufficiently high reflux temperature, in a relatively simple solvent, to cause the reactions to occur reasonably rapidly. However, since o-phenylenemercury trimer is highly insoluble in the common organic solvents but is slightly soluble in boiling dimethylformamide, the desymmetrization reactions using mercuric chloride and bromide could be carried out smoothly in this solvent with a reaction time of only about one hour:



X = Cℓ,Br

This is to compare with a reaction time of 8 hours required to make the above chloride in acetone$^{(2)}$.

Symmetrization reactions of 2,2'-biphenylenebis-(mercury halides) to biphenylenemercury trimer and 1,2-bis(halomercuri-phenyl)benzene to o-terphenylene-mercury dimer have been achieved using sodium iodide in refluxing aqueous ethanol, while symmetrization of the less-soluble o-phenylenebis(mercury halide) to o-phenylenemercury trimer was carried out with sodium iodide in a boiling mixture of ethanol/dimethylformamide. Heating 2,2'-biphenylenebis(mercury bromide) or -bis(mercury iodide) under vacuum to 200°C also caused symmetrization and gave mercuric halide as sublimate and left a residue of pure biphenylenemercury trimer. By contrast, o-phenylenebis(mercury bromide) did not appear to undergo substantial rearrangement on heating under vacuum up to 220°C. We attempted these symmetrizations mainly to check that the phenylene- and biphenylene-mercurials produced were trimeric; we had hoped that making them in a different manner might have formed other oligomers. Spectroscopic studies showed that only $(C_6H_4Hg)_3$ and $(C_{12}H_8Hg)_3$ were obtained in all cases.

Reaction of a mixture of o-phenylenebis(mercury chloride) and 2,2'-biphenylenebis(mercury chloride) with sodium iodide in a mixture of ethanol/dimethylformamide gave a product showing $(C_{12}H_8Hg)_2^+$, $(C_6H_4Hg)_3^+$,

$C_{12}H_8Hg(C_6H_4Hg)_2^+$ and $(C_{12}H_8Hg)_3^+$ ions in its mass spectrum (Figure 2.14); models have shown that the mixed phenylene-biphenylene species should be stable since it has linear C-Hg-C bonds as required by the sp hybridisation at mercury (XIII). No attempt was made to isolate the pure compound but this could probably have been done using TLC.

The vibrational frequencies of mercury-X bonds (X = Cℓ,Br,I,OAc) of arylmercury compounds are listed below(27,29):

Bond	ν(Hg-X) (cm^{-1})
Hg-Cℓ	331-322
Hg-Br	ca.210
Hg-I	160
Hg-OAc	304

In agreement with the above listing of Hg-X vibrations the infrared spectra of $C_{18}H_{12}(HgC\ell)_2$, $C_{12}H_8(HgC\ell)_2$ and $C_6H_4(HgC\ell)_2$ all show strong absorption at 327, 329 and 330 cm^{-1}, respectively, for the Hg-Cℓ bond vibration; the corresponding Hg-X frequencies in the bromides and iodides lay outside the range of our spectrometer. The band at 290 cm^{-1} in $C_{12}H_8(HgOAc)_2$ is presumably due to the Hg-OAc vibration.

There are certain substances formed by combining one stable compound with another without the existence of any chemical bonds between the two components; this

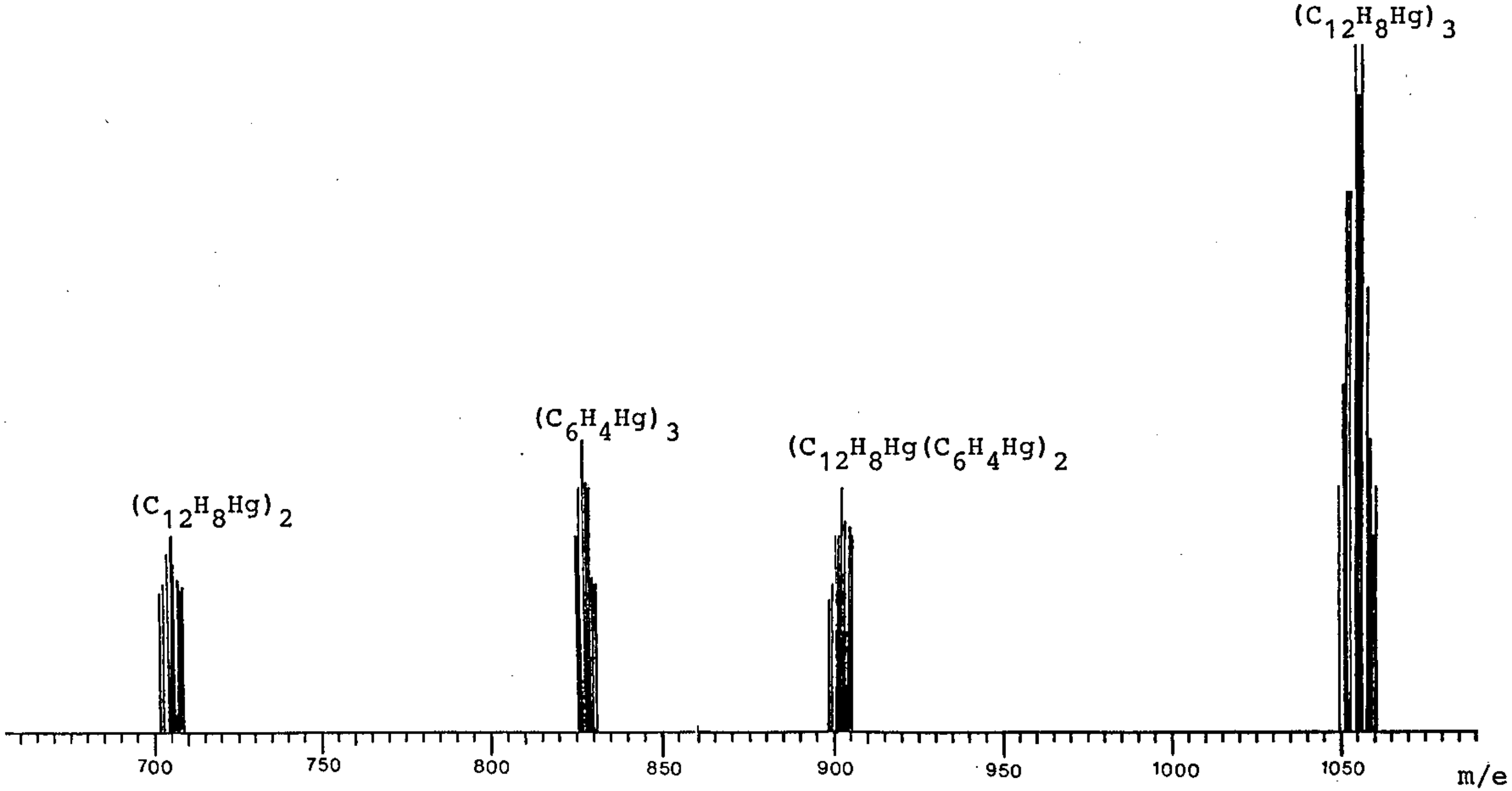
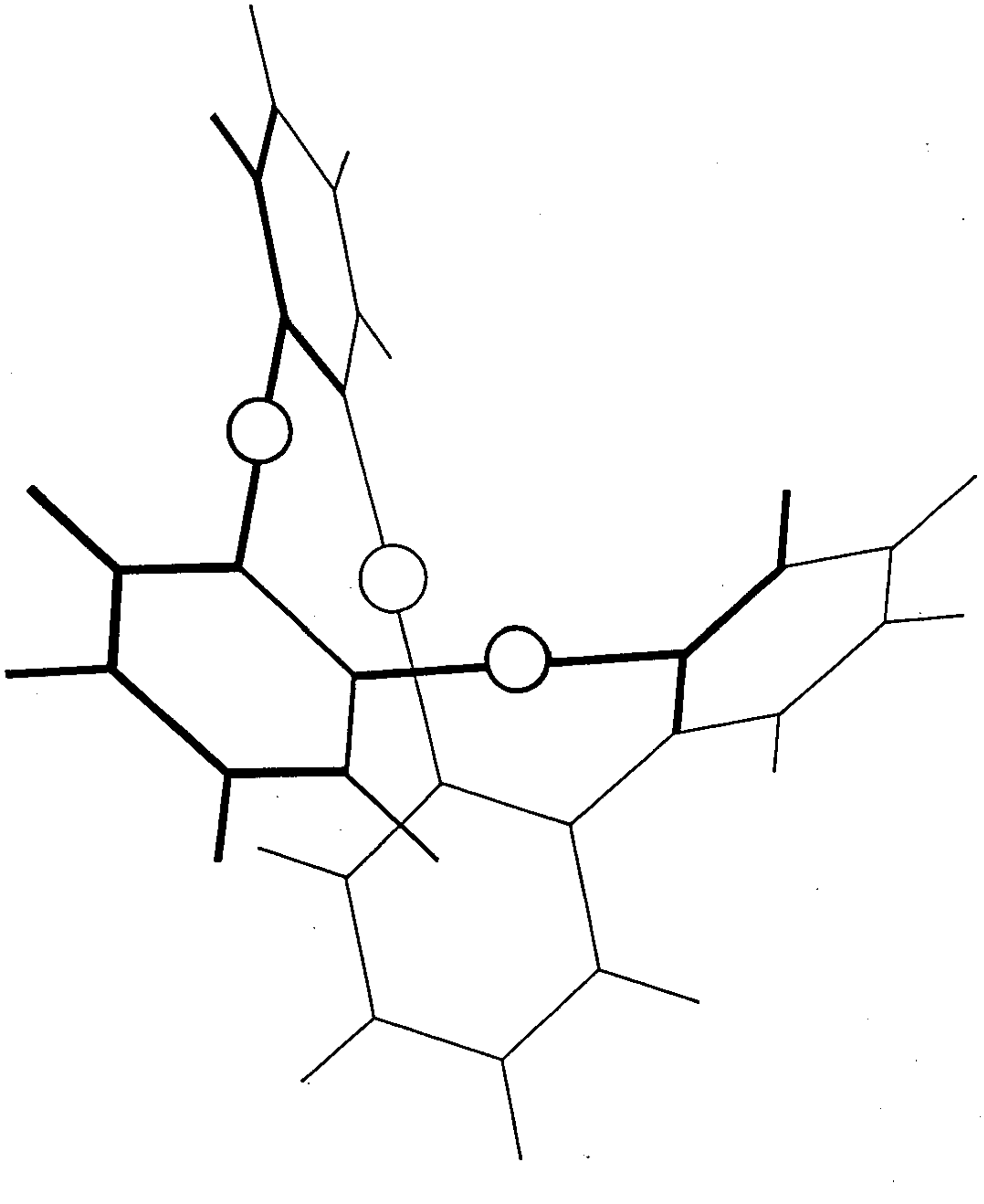
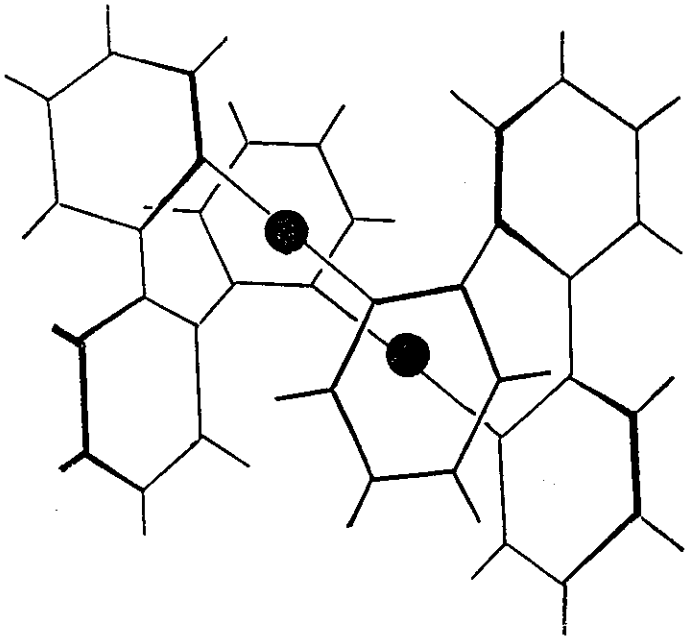


Figure 2.14: Partial Mass Spectrum of Products from the Mixed Symmetrization of $C_6H_4(HgC\ell)_2$ and $C_{12}H_8HgC\ell$ using Sodium Iodide in Ethanol/DMF Solvents.



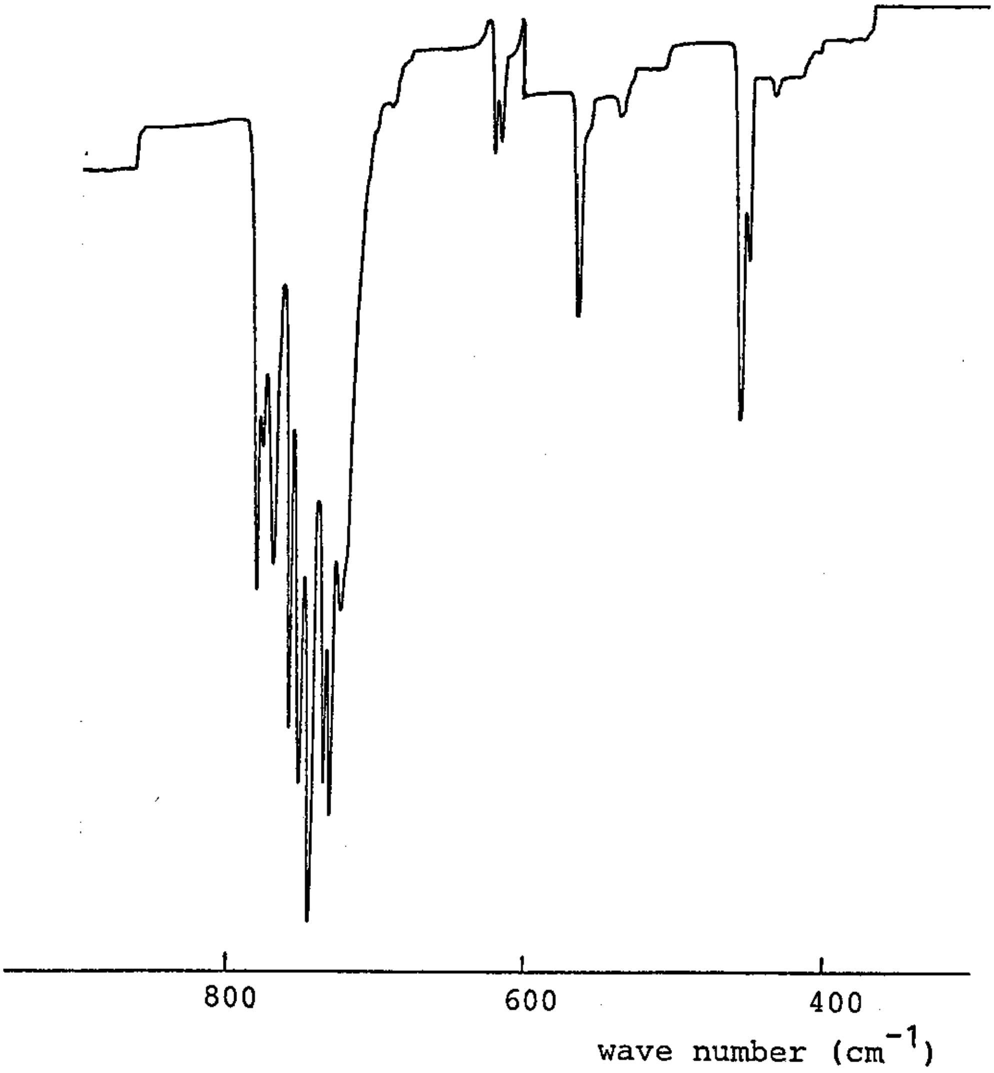
(XIII)

occurs when one of the compounds can crystallize in a very open structure containing cavities, holes, or channels in which molecules of the other can be trapped. Those compounds in which the host lattice contains cavities like cages are called clathrate compounds(30). Thus o-terphenylenemercury dimer (XIV) when recrystallized from a whole range of solvents gave



(XIV)

solvates with three different dimer : solvent ratios as shown in Table 2.1, page 26 . The dimer-chloroform and dimer-acetone solvates were not stable enough for carrying carbon and hydrogen analyses in the usual way (due to decomposition occurring in the post) but their constitution was confirmed by thermogravimetric methods (see page 28). In all the dimer complexes the solvent came off below 278-282°C and often could be seen as a condensate on the wall of the melting point capillary tubes; this left the dimer as a white solid melting at 294-296°C. The infrared spectrum of o-terphenylenemercury dimer is shown in Figure 2.15 and it can be seen that the region 800-600 cm^{-1} is very different from that in the spectrum of its solvate with m-xylene; the latter shows many more bands in this region and also splitting of the ("Hg-C") band at 450 cm^{-1}, as shown below. The splitting is probably due to a slight change in molecular geometry expected when extra molecules are co-crystallized.



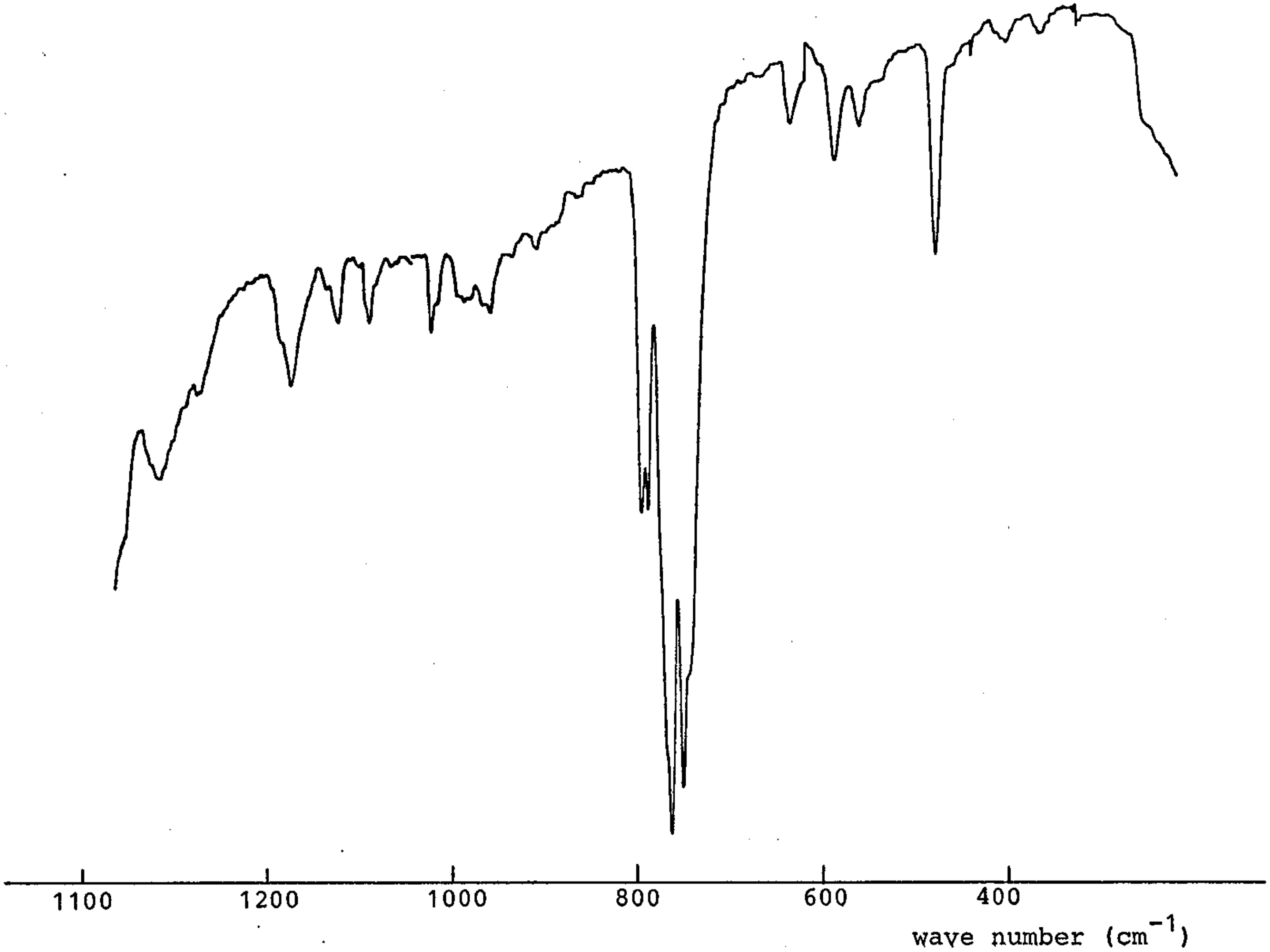
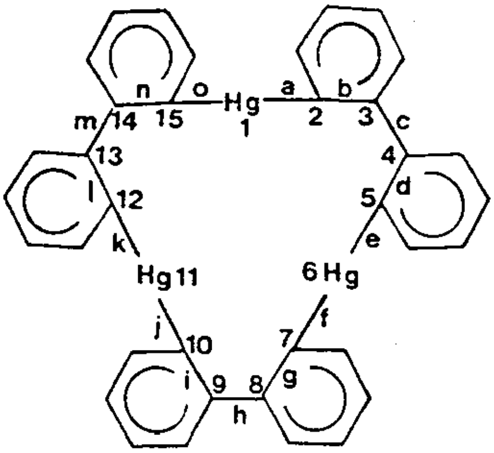


Figure 2.15: Infrared Spectrum of Ortho-terphenylenemercury Dimer.

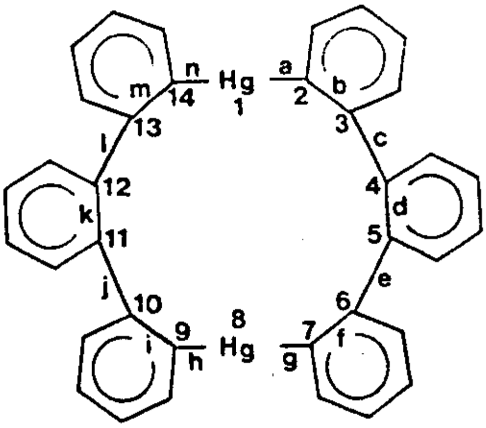
It is a peculiar fact that we have been unable to find any organic solvent which does not form a solvate (weak or strong) with o-terphenylenemercury dimer. No other hydrogen-substituted organomercurial reacts in this way although $(C_6F_4Hg)_3$ was found to form some solvates(18). The X-ray structure of one of these(18) confirmed that there was no solvent-mercury interaction so we may assume that in the dimer cases also, the compounds are best called simply "solvates" and not "complexes". It is assumed that the actual solvent: dimer ratio depends to a great extent on the size of the solvent molecule being incorporated into the o-terphenylenemercury dimer lattice since the smaller molecules have the higher ratios. In contrast, phenylenemercury trimer and biphenylenemercury trimer did not form any solvates when recrystallized from a whole range of solvents and this is possibly due to there being no room for packing other molecules in their crystal lattices.

Note on Nomenclature.

We have contacted the Editor of the Journal of the Chemical Society to ask for guidance concerning the names of these polyphenylene cyclic mercurials; they have suggested the following nomenclature for biphenylenemercury trimer and terphenylenemercury dimer.



Hexabenzo[b,d,g,i,ℓ,n][1,6,11] trimercuracyclopentadecene



Hexabenzo[b,d,f,i,k,m][1,8] dimercuracyclotetradecene

Chapter 3

X-ray Crystallography

Summary

The basic practical and theoretical aspects of single crystal X-ray structural analysis are outlined, and the complete structural analysis of orthorhombic o-biphenylenemercury is given.

3.1 INTRODUCTION.

The primary aim of a crystal structure analysis by X-ray diffraction is to obtain a detailed picture of the contents of the crystal at the atomic level, as if one had viewed it through an extremely powerful microscope. Once this information is available, and the position of the individual atoms are known, one can calculate interatomic distances, bond angles and other features of the molecular geometry that are of interest. The analysis of a crystal structure may be summarised as comprising three stages:

(i) Experimental measurement of both the unit cell dimensions and the intensities of a large fraction of the diffracted beams from the crystal; these intensities depend only on the nature of the atoms present and their relative position within the unit cell.

(ii) The deduction of an atomic arrangement: a "trial structure". The intensities of the diffracted maxima corresponding to the atomic arrangement can then be calculated and compared with those observed.

(iii) Modification (refinement) of this trial structure until the agreement between the calculated and observed intensities is within the limit of error of the observation. A simplified flow chart for the determination of a crystal structure is shown in Figure (3.1) and in what follows most of these steps will be explained briefly.

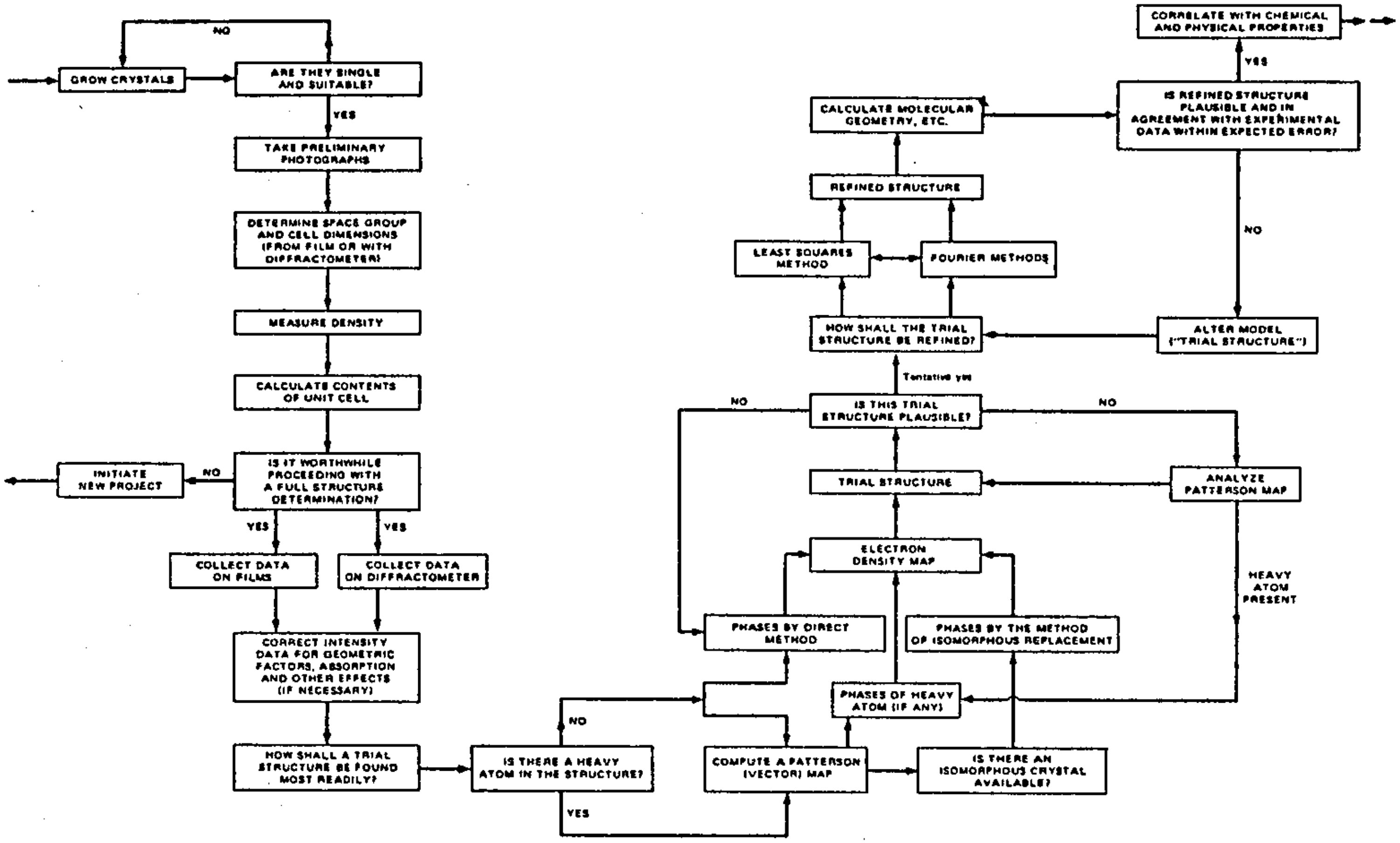


Fig. 3.1: The course of a structure determination by single crystal X-ray diffraction (after ref. 1)

3.2 GROWING CRYSTALS.

The process of crystallization is one of ordering, wherein randomly arranged molecules in the solution take up regular positions in the solid state. Three important methods for growing crystals are in general use:

(a) Crystallization by evaporation of solvent: in which a saturated, or nearly saturated, solution is allowed to stand under conditions where the solvent evaporates slowly.

(b) Crystallization by vapour diffusion: in this method a solution of the substance in solvent S_1 is contained in a tube. A second solvent, S_2, is chosen which produces with S_1 a mixed solvent in which the solute is less soluble than in S_1 alone; both the solution in S_1 and solvent S_2 are contained in open tubes within a closed beaker. Slow diffusion of solvent S_2 into solution S_1 will cause crystallization which under favourable conditions can result in the growth of relatively large single crystals.

(c) Crystallization by solute diffusion: this method depends on the difference in solvent density to maintain the initial separation between solvents S_1 and S_2. The solute must always be dissolved in the solvent in which it is the more soluble. Crystals appear at the interface between S_1 and S_2 and grow as the solvents slowly mix by diffusion.

3.3 SELECTION AND ORIENTATION OF A CRYSTAL.

The crystal whose structure is to be determined must be a single crystal, not cracked or a conglomerate. This may be usually checked by examining it under a polarizing microscope. When the crystal is rotated about an axis normal to the polarizing material, the crystal should either appear dark in all positions or appear dark once every 90°. Crystals which are not single will always reveal themselves by displaying both dark and light regions at the same time. This is a relatively crude method and the final evidence of the internal structure of the crystal can only be furnished by the diffraction pattern; if the crystal is single the reflections which appear should be single spots without tails connecting them. If the crystal is too large it will not be fully bathed by the X-ray beam and so it may be cut into smaller pieces with a razor blade; grinding the crystal into a spherical shape ensures that the path length of X-radiation through the crystal is the same in all directions but this time-consuming and difficult technique is relatively little used.

The choice of a suitable size for a crystal specimen depends on a number of factors such as absorption and the apparatus for diffraction data collection. For example, in the diffractometer it is possible to obtain a plateau of uniform intensity of dimensions 0.5 × 0.5 mm in the primary beam of the X-rays and in single crystal work the size of the crystal should not exceed these dimensions in order that all parts of the crystal receive the same intensity of the X-rays. The optimum size for the crystal is usually about $2/\mu$ (i.e. 0.2 - 0.3 mm), where μ is the linear absorption coefficient.

Once a crystal has been chosen then it may be attached to a glass fibre with nail varnish, glue or some other suitably similar material. If for some reason, the crystal is unstable in air it may be put into a fine glass capillary which is then sealed after the appropriate atmosphere has been introduced. For example, the presence of mother liquor is often essential for crystals containing solvent of crystallization to combat efflorescence. The fibre, or capillary, is fixed onto a brass pin by glue and this pin is then placed on a goniometer head so the crystal can be rotated and centred in the X-ray beam. Alignment is performed by rotation of the mounted crystal on its goniometer head and adjusting both the arcs for tilt, and the sledges for centring at the focal point of the arcs. This ensures that the crystal is perpendicular to the X-ray beam during a complete rotation. Deviations from alignment on the horizontal arc cause the layer lines on the exposed photographic film to be curved, whereas misalignment on the vertical arc causes them to be tilted. Suitable adjustments can be made after studying oscillation trial diffraction photographs.

3.4 MEASUREMENT OF THE DENSITY.

The density of a crystal can usually be measured by mixing together two miscible liquids (one more dense, one less dense than the crystal) until a composition is formed in which the crystal will neither sink nor float. The density of the liquid mixture is then equal to that of the crystal.

3.5 METHODS OF DATA COLLECTION.

The intensities of the diffracted beams are measured by intercepting the beams with some device that is sensitive to X-rays. The measurement may be done either photographically or electronically using a scintillation counter. This latter method is now the most widely used in automatic diffractometers. In the diffractometer technique the angular settings of the crystal and detector are obtained in advance with a computer. In fact, the entire instrument may be controlled by a computer and the whole data collection done automatically. The instrument is then called an automatic X-ray diffractometer. The result of the collection of X-ray diffraction data is relative intensities, I, for each reflection with indices h, k, ℓ together with scattering angle 2θ for each reflection.

The most important quantity derived from the intensities is the structure factor amplitude $|F_{hk\ell}|$, which is related to the observed intensities:

$$|F_{hk\ell}| \propto \sqrt{I} .$$

These structure factor amplitudes, together with the phases of each reflection are the quantities which will be used in the calculation of the electron density maps from which the positions of the various atoms may be determined. A general expression for the intensity is of the following form:

$$I = k|F|^2(Lp)(T_v)(Abs),$$

where k is some initially unknown factor,

L is the Lorentz factor,

$L = \sin\theta/\sin 2\theta \sqrt{\sin^2\theta - \sin^2\mu}$, ($\mu$ being the equi-inclination setting angle),

p is the polarization factor such that

$$p = \frac{1 + \cos^2 2\theta}{2}$$

T_v is a correction factor for thermal vibrations,

Abs is the absorption factor.

The structure factor $F_{hk\ell}$ is the resultant of the j waves scattered in the direction hkℓ by the j^{th} atoms in the unit cell. Each of these waves has an amplitude proportional to f_j, the scattering factor of the atom, and a phase angle α. The structure factor $F_{hk\ell}$ is composed of two terms A and B, these terms correspond to the amplitude and the phase of each reflection thus,

$$|F_{hk\ell}| = \left(A^2_{hk\ell} + B^2_{hk\ell}\right)^{1/2}, \quad \text{where}$$

$$\left.\begin{aligned} A_{hk\ell} &= \sum_{j=1}^{N} f_j \cos 2\pi\left(hx_j + ky_j + \ell z_j\right) \\ B_{hk\ell} &= \sum_{j=1}^{N} f_j \sin 2\pi\left(hx_j + ky_j + \ell z_j\right) \end{aligned}\right\}$$

, N being the number of atoms in the unit cell,

and the phase angle is given by:

$$\alpha = \tan^{-1}\left(\frac{B_{hk\ell}}{A_{hk\ell}}\right) .$$

For structures which have centre of symmetry at the origin of the unit cell, the phase angle is either 0° or 180°. The structure factor may also be written as a complex number,

$$F_{hk\ell} = A_{hk\ell} + iB_{hk\ell}$$

where $i = \sqrt{-1}$.

Also it can be expressed in terms of the electron density $\rho(x,y,z)$ at a point (x,y,z) in the unit cell as follows:

$$F_{hk\ell} = \int_V \rho(x,y,z) \exp\left[2\pi i(hx + ky + \ell z)\right] dV,$$

where V is the volume of a unit cell, the above expression can be rewritten in the following terms:

$$\rho(x,y,z) = \frac{1}{V} \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{\ell=-\infty}^{+\infty} F_{hk\ell} \exp\left[-2\pi i(hx + ky + \ell z)\right].$$

3.6 THE PHASE PROBLEM.

Experimentally, we can obtain only the structure amplitude $|F|$ and not the phase angle and, therefore, we must derive α, either from the values of A and B that are computed from the trial structure or by purely analytical methods. The problem of getting the phase angle is called the "phase problem". There are several ways of solving this problem, some of them will be explained briefly:

(i) The indirect method: this method involves the Patterson function

$$P(U,V,W) = \frac{1}{V} \sum_h \sum_k \sum_\ell |F|^2 \cos 2\pi (hU + kV + \ell W).$$

All the terms in this equation are known:

V is the volume of the unit cell,

P(U,V,W) is the value of the function at the point (U,V,W) and so a three dimensional map can be plotted by this Fourier synthesis.

Peaks in the map correspond to all interatomic vectors. Thus a peak at the point U,V,W in a Patterson map indicates that there exist in the crystal atoms at X_1, Y_1, Z_1 and X_2, Y_2, Z_2 such that,

$$U = X_1 - X_2 ,$$

$$V = Y_1 - Y_2 ,$$

$$W = Z_1 - Z_2 .$$

For a molecule containing N atoms in a unit cell, the Patterson map will contain N^2 peaks corresponding to the N possible vectors which can be drawn from each of the N atoms; of these there will be N vectors of zero length from each atom to itself and will be concentrated as a very large peak at the origin and the remaining $N^2 - N$ will be distributed throughout the unit cell. One disadvantage of this method is that when the unit cell contains more than a few atoms there will be a very large number of peaks which will overlap so that the structure cannot be resolved.

(ii) Heavy-atom method for solving structure: since the unit of P is $(\text{electron density})^2$, it has been found that structures in which one or a few atoms have atomic numbers considerably greater than those of the other atoms present, are usually more readily solved than those in which all the atoms are nearly alike. The reason for this behaviour is that it is possible to locate the heavy atoms in the unit cell by a method which does not require a prior knowledge of the phases. This is due to the fact that when a heavy atom is present the phase angle derived for the whole structure will not be far from those derived from the heavy atoms alone. Once the heavy atoms have been found they usually will serve as a phasing model from which the other atomic positions can be developed. The heavy atom method is a straightforward method for solving structures and, because of this, if the molecule of interest does not contain heavy atoms then one can prepare a derivative containing a heavy atom like bromine or iodine before the structure is attempted. Heavy atoms can be located by the analysis of a Patterson map. One drawback of the heavy atom method is that lighter atoms cannot be located with high precision; the reason for this is that when heavy atoms are present in the structure they will dominate the scattering and the comparison of $|F_o|$ and $|F_c|$ becomes relatively insensitive to the positions of the light atoms. Thus the uncertainty in the light atoms positions increases and the bond lengths measurements become less reliable; in extreme cases the light atoms may not be found at all.

(iii) Probability method: the basis for the probability method was described by Sayre$^{(2)}$ in 1952. It can be shown that under certain conditions

$$F_{hk\ell} = \phi_{hk\ell} \sum_{h'} \sum_{k'} \sum_{\ell'} F_{h'k'\ell'} \cdot F_{h-h',k-k',\ell-\ell'}$$

where ϕ is a scaler factor. The above equation implies that the structure factor $F_{hk\ell}$ is determined by the sum of products of all the pairs of structure factors whose indices add to give $hk\ell$. The above equation may appear rather useless since to determine one F it is necessary to know the magnitude and the phase of all others. However, it has been shown that for strong reflections the series must tend to one direction (+ or -), thus,

$$S(F_{hk\ell}) \sim S(F_{h'k'\ell'}) \cdot S(F_{h-h',k-k',\ell-\ell'})$$

or

$$S(F_{hk\ell}) \cdot S(F_{h'k'\ell'}) \cdot S(F_{h-h',k-k',\ell-\ell'}) \sim +1.$$

Where S means "sign of" and ∿ means it is probably equal to. The above equation is the basis for most of the current direct methods of phasing.

3.7 REFINEMENT.

After approximate positions have been determined for most, if not all, of the atoms then refinement of the structure can be started. In this process the atomic parameters are varied systematically so as to give the best possible agreement of the observed structure factor amplitudes with those calculated for the proposed structure. Since most crystal structure problems involve many parameters, several successive refinement cycles are usually needed before the structure converges to the stage at which shifts in the atomic parameters from cycle to cycle are negligible with respect to the expected experimental errors. There are two refinement techniques, one involving Fourier synthesis and the other a least-squares process; they are nearly equivalent but differ considerably in manipulative details. One measure of the correctness of the structure is the so-called discrepancy index, R, defined as:

$$R = \frac{\sum|F_o| - \sum|F_c|}{\sum|F_o|}$$

The lower the value of R, the greater the confidence that can be placed on the calculated structure. Very roughly it may be said that a trial structure with an R value around 0.35 is quite "hopeful" and for an R below 0.25 the structure is probably correct except for small (0.1 Å) atomic shifts and changes in thermal parameters. At present, R values between 3% and 8% are often quoted for the most reliably determined structures.

3.8 THERMAL FACTOR.

The effect of the thermal motion of the atoms is to spread the electron cloud over a larger volume and thus to cause the scattering power, which is proportional to sin θ/λ, of the real atom to fall off more rapidly than that of a theoretically stationary atom. The change in the scattering power can be given by the following expression:

$$f = f_o \exp\left[-B(\sin^2\theta/\lambda)\right], \quad \text{where}$$

$$B = 8\pi^2 \bar{U}^2 ,$$

and $|\bar{U}^2|$ is the mean square amplitude of the atomic vibration; if we assume the vibration to be isotropic then the above expression will become

$$f = f_o \exp\left[-B_{iso}(\sin^2\theta/\lambda)\right] .$$

However, it is clear that the approximation of isotropic motion is a poor one for atoms in most crystals, and it is fair to consider the motion as being anisotropic (ellipsoidal, for example) in which case the exponent in the above expression will become

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$$

3.9 MEASUREMENT OF THE UNIT CELL DIMENSIONS.

In an orthorhombic crystal the relationships between the direct and reciprocal dimensions are as follows:

$$a^* = \frac{1}{a} ,$$

$$b^* = \frac{1}{b} ,$$

$$c^* = \frac{1}{c} ,$$

$$v^* = \frac{1}{v} = a^*b^*c^* ,$$

$$\alpha = \beta = \gamma = \alpha^* = \beta^* = \gamma^* = 90° .$$

In a monoclinic system the above relations become:

$$a^* = \frac{1}{a\sin\beta} ,$$

$$b^* = \frac{1}{b} ,$$

$$c^* = \frac{1}{c\sin\beta} \quad ,$$

$$v^* = \frac{1}{v} = a^*b^*c^* \sin\beta^* \quad ,$$

$$\alpha = \gamma \ , \quad \alpha^* = \gamma^* = 90° \ , \quad \beta^* = 180° - \beta .$$

To measure the cell dimensions, two diffraction photographs must be taken of the crystal, one oscillation and one zero-layer Weissenberg. The former photograph is obtained as the crystal is oscillated through a small angle (about 20^{0}); the Weissenberg photograph is recorded as the crystal is oscillated through an angle of about 200^{0}; only the zero-layer reflections are selected by positioning a metal screen, with a slit in it, between the film and the crystal. The film-holder moves back and forth along the axis of rotation so that the spots are separated on the film, making indexing of the zero-layer reflections easier. Reflections from higher layers can also be selected by suitably positioning the screen. The crystal symmetry type (space group) can be deduced from the systematic absences on the zero- and first-layer Weissenberg photographs. The cell dimension, say b, that is parallel to the rotation axis, can be calculated from the oscillation photograph using the following relationship:

$$b = \frac{n\lambda}{\sin(\tan^{-1} \frac{y_n}{D})}$$

where b is the direct lattice parameter in Å , n is the index number of the layer line,

y_n is the separation in mm of the layer line ± n,

D is the camera diameter in mm,

λ is the wavelength of the X-ray used in Å.

In practice, b is measured for each layer-line pair by measuring the perpendicular distances for the layer pair ±1, ±2, ±3, ±4, etc. and then applying the above relationship to derive the value of b. In a monoclinic cell the angle β^* can be calculated by measuring the horizontal distance between the axial row, a^* and c^* from the zero Weissenberg photograph and then applying the relationship $\beta^* = 180 - \beta$, where β^* is twice the horizontal distance in mm. The other two dimensions are measured from the zero-layer Weissenberg photograph as reciprocal parameters.

$$\frac{1}{(a^* \text{ or } c^*)} = \frac{n\lambda}{2\sin\left(\frac{Y_n}{\sqrt{5}}\right)}$$

a^* or c^* are the reciprocal lattice parameters in Å^{-1},

Y_n is the separation in mm of the ±nth spots on the axial row,

λ is the wavelength of the X-rays used in Å.

$\sqrt{5}$ is the camera constant.

3.10 CALCULATION OF THE MOLECULAR GEOMETRY.

It is possible to calculate features of the molecular geometry if one knows the cell dimensions $(a,b,c,\alpha,\beta,\gamma)$, the fractional atomic coordinates (x,y,z for each atom) and the space group. For example, the distance between two points (x_1,y_1,z_1) and (x_2,y_2,z_2) is:

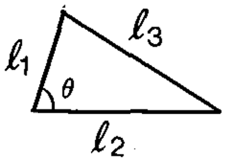
$$\ell^2 = \Big[(x_1-x_2)a\Big]^2 + \Big[(y_1-y_2)b\Big]^2 + \Big[(z_1-z_2)c\Big]^2$$

$$- \Big[2ab(\cos\gamma)(x_1-x_2)(y_1-y_2)\Big] - \Big[2ac(\cos\beta)(x_1-x_2)(z_1-z_2)\Big]$$

$$- \Big[2bc(\cos\alpha)(y_1-y_2)(z_1-z_2)\Big] .$$

If the length of three bonds ℓ_1, ℓ_2, ℓ_3 are known then the angle may be calculated with the law of cosines:

$$\cos\theta = \frac{\ell_1^2 + \ell_2^2 - \ell_3^2}{2\ell_1\ell_2} .$$



3.11 STANDARD DEVIATIONS IN BOND LENGTHS AND BOND ANGLES.

The general equation for an error in a function f, related to n uncorrelated variables $x_1,x_2,\ldots,x_a$ and derived by calculation from them, is$^{(3)}$

$$\sigma_f = \sqrt{\sum_{j=1}^{n}\left(\frac{\partial f}{\partial x_j}\right)^2 \sigma_j^2}$$

where σ_j is the standard deviation in x_j. Applying this equation to the bond lengths and bond angles in triclinic crystals will result in the following expression for standard deviation in bond lengths and bond angles:

$$\sigma_\ell = \sqrt{(\sigma x_1^2+\sigma x_2^2)\left[\frac{(x_1-x_2)a + (y_1-y_2)b\cos\gamma + (z_1-z_2)c\cos\beta}{\ell}\right]^2}$$

$$+\sqrt{(\sigma y_1^2+\sigma y_2^2)\left[\frac{(y_1-y_2)b + (x_1-x_2)a\cos\gamma + (z_1-z_2)c\cos\alpha}{\ell}\right]^2}$$

$$+\sqrt{(\sigma z_1^2+\sigma z_2^2\left[\frac{(z_1-z_2)c + (x_1-x_2)a\cos\beta + (y_1-y_2)b\cos\alpha}{\ell}\right]^2} ,$$

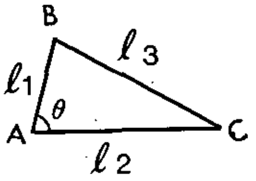
where σx_1, σx_2 are the standard deviations of atoms 1 and 2 in the x-direction with similar meaning for σy_1, σy_2, σz_1, σz_2; ℓ is the bond length.

In orthorhombic crystals $\alpha = \beta = \gamma = 90°$ and the above expression becomes:

$$\sigma_\ell = \sqrt{(\sigma x_1^2+\sigma x_2^2)\left[\frac{\Delta xa}{\ell}\right]^2 + (\sigma y_1^2+\sigma y_2^2)\left[\frac{\Delta yb}{\ell}\right]^2 + (\sigma z_1^2+\sigma z_2^2)\frac{\Delta zc}{\ell}} .$$

Similarly the expression

$$\sigma\theta = \sqrt{\sigma_B^2/\ell_1^2 + \sigma_A^2\ell_3^2 / (\ell_1^2\ell_2^2) + \sigma_C^2/\ell_2^2} ,$$



gives the standard deviation in the bond angle, where σ_A σ_B σ_C are the standard deviation in the positions of atoms A, B, C.

3.12 THE CRYSTAL AND MOLECULAR STRUCTURE OF BIPHENYLENEMERCURY.

Biphenylenemercury was prepared as described in Chapter 1. The crystal was grown by allowing a saturated toluene solution of biphenylenemercury to stand at room temperature for about six months. It was found experimentally that biphenylenemercury can take two crystallographic forms, one monoclinic and the other orthorhombic.

The unit cell dimensions for the monoclinic form are:

$a = 19.21$ Å $b = 15.12$ Å $c = 20.30$ Å .

The absences are:

$hk\ell$ when $h+k$ is odd

$ho\ell$ when ℓ is odd

oko when k is odd

and the space group is C2/c or C_c.

During the course of the study it proved impossible to find a suitable single crystal in the monoclinic form whereas orthorhombic crystals were relatively easy to obtain; therefore it was decided to attempt a full structure determination of the orthorhombic form.

3.13 CRYSTAL DATA.

Formula: $(C_6H_4C_6H_4H_g)_3$

Space group Pbca No.61

Absences:

hoℓ when ℓ = odd

okℓ when k = odd

hoo when h = odd

oko when k = odd

hko when h = odd

M_r = 1058.3 , a = 26.857 Å , b = 11.458 Å , c = 19.110 Å ,

D_x = 2.386g cm^{-3}, D_m = 2.398g cm^{-3} , U = 5880 $Å^3$, Z = 8 ,

F(000) = 3840 , Radiation MoKα , λ = 0.7107 Å ,

μ = 153.44 cm^{-1}, Crystal size (0.38 × 0.13 × 0.08) mm.

3.14 INTENSITY DATA COLLECTION.

Reflections were measured on a Stoe automatic Weissenberg diffractometer equipped with a graphite monochromator; rotation was about the crystallographic c axis. Lattice parameters were initially obtained from oscillation and Weissenberg photographs and the diffractometer was used to refine them. Accurate lattice parameters and crystal alignment are essential in diffractometer work since it is necessary to predict the exact position of each reflection before its intensity can be measured. The setting angles ω, 2θ (where ω is the angle of rotation of the crystal and 2θ is the angle of the counter from the horizontal plane containing the crystal) were calculated from the lattice parameters and each reflection was scanned with variable ω (2.5°- 25°). A standard reflection was measured every 50 reflections to check that there was no significant change in the intensity. The total number of reflections measured was 5123 of which 1898 had $I > 3\sigma(I)$. Lorentz and polarization effects were corrected but absorption effects were ignored. The intensity data were automatically punched onto a paper tape by the diffractometer counting unit and the results were read and stored in the main University computer on a single file. The structure was solved for the heavy atoms using EEES(3) and then the carbon atoms were located from the subsequent difference map. Least-squares refinement based on the minimization of $\sum w\Delta F^2$ (allowing anisotropic motion of the mercury atoms but not the light atoms) resulted in a final R value of 0.053 and $R_w = 0.0451$.

In the final refinement, $w = 2.2372/(\sigma^2(F) + 0.00015F^2)$, $\Delta/\sigma \leqslant 0.003$, $\Delta\rho$ max = 0.6520e $\mathring{A}^{-3}$ and $\Delta\rho$ min = -0.4187e $\mathring{A}^{-3}$. Analytical atomic scattering factors used for carbon and mercury were taken from "International Tables for X-ray Crystallography", Volume 4. Crystallographic calculations were performed using the SHELX(4) suite of programs as implemented at the University of Loughborough and molecular drawings were obtained using ORTEP. The bond angles and bond lengths were calculated using X-RAY72(5) at the Manchester University Computer Centre.

3.15 DISCUSSION.

When Wittig and Herwig(6) first prepared biphenylenemercury they assigned, without any supporting evidence, the monomeric structure shown in Figure 3.2I. Shortly afterwards Wittig described an ebullioscopic molecular weight determination(7) carried out in tetralin which suggested that the molecule was tetrameric with the possible structure shown in Figure 3.2II. However, when biphenylenemercury was subjected to mass spectral analysis(8,9) the spectrum showed a mass cut-off at m/e ≅ 1058 corresponding to the trimer with the presumed structure shown in Figure 3.2III. Further evidence for the trimeric nature of biphenylenemercury was demonstrated by an X-ray diffraction study on a triclinic crystal of biphenylenemercury(10) grown from 1,2-dibromobenzene. All the samples of biphenylenemercury which we grew from a variety of other solvents were found to be orthorhombic and, having a higher melting point than the literature value for this compound, could conceivably be the tetrameric form of the molecule since Dreiding models showed that the tetramer is sterically possible. From the unit cell dimensions and density measurements, the molecular weight of biphenylenemercury can be calculated using the following relationship:

$$nM = DVN \times 10^{-24}$$

where n is the number of molecules in the unit cell, M is the molecular weight,

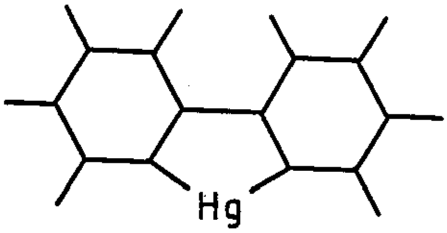
D is the density (2.386 $gm.cm^{-3}$),

V is the volume (5880 $Å^3$),

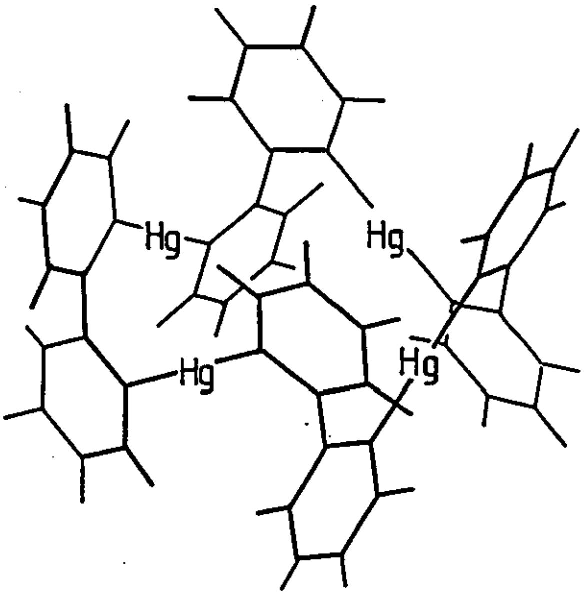
N is Avogadro's number.

On applying the above relationship to our orthorhombic crystals we get M = 2112.5 for n = 4 and M = 1056.25 for n = 8 (the calculated molecular weight for trimer is 1058.2). Thus it was evident that the molecule could be either trimeric or hexameric, but not tetrameric. The X-ray data described in the Experimental Section show that the orthorhombic crystals of biphenylenemercury contain trimeric molecules as found previously for the triclinic form. Since only trimeric biphenylenemercury molecules have been found by X-ray work the possibility of the dimer we thought might be present from the mass spectrum (page 84) can now be dismissed.

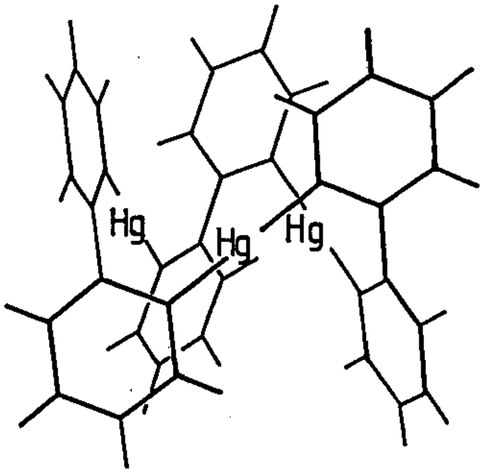
Final atomic coordinates appear in Table 3.1 and bond lengths and bond angles are given in Tables 3.2 and 3.3. Table 3.4 shows the intermolecular distances; Table 3.5 gives the angles between the various planes and Table 3.6 gives the equivalent isotropic thermal parameters. Figure 3.3 presents an ORTEP drawing of the biphenylenemercury structure together with the numbering scheme employed, Figure 3.4 shows the unit cell contents of biphenylenemercury projected onto the



[I]



[II]



[III]

Figure 3.2

c axis. (Least-square planes of biphenylenemercury are listed in Appendix 1 while the observed and calculated structure factors are listed in Appendix 2 at the end of this thesis). The carbon-mercury bond lengths are within the normal values found for organomercurials; for example 2.09 Å in diphenylmercury(11), 2.10 Å in bis(pentafluorophenyl) mercury(12) and 2.07 - 2.13 Å in tribenzo [b,e,h][1,4,7] trimercuronin(13). The sum of the covalent radii for mercury (1.34 Å) and carbon (0.77 Å) suggests that typical values for the Hg-C lengths should be about 2.11 Å. As expected(14,15,16) for an organomercurial in which the mercury atom is presumably sp hybridized the C-Hg-C bond angles are close to the sp value of 180°. There were no abnormal intermolecular contacts. The Hg-Hg distances, in Å, within the heterocyclic ring are 3.46(1-3), 3.48(2-3) and 3.64(1-2). The van der Waals radius for mercury was originally thought to be 1.50 Å(17); however, a value of 1.55 Å has been estimated from the critical volume of the metal(18) and 1.75 Å was suggested from the Hg-Hg contacts in $(Et_4N)_2 Hg_3 MC\ell_{10}$ (M = Pt or Pd)(19).

A recent survey(20) also indicated that the original value of 1.50 Å suggested by Grdenic is significantly underestimated and provided evidence that the van der Waals radius for mercury is probably about 1.75 Å. Even with this higher value of 1.75 Å there will be little or no Hg-Hg strain within the heterocyclic ring of the trimer. The idealized molecule of biphenylenemercury trimer has no centre of symmetry; it has, however, a three-fold principal axis (Figure 3.4) and three horizontal two-fold rotation axes (through the mid points of C6 - C7, and Hg2; C18 - C19, and Hg1; C30 - C31 and Hg3; Figure 3.3). As there are no horizontal or vertical planes of symmetry the point group in D_3 and the molecule should be chiral. In agreement with this it is possible to make two Dreiding models which are mirror images of each other and yet are not superimposable as shown in Figure 3.5. It has been suggested that another isomer(10) of biphenylenemercury trimer can be derived from the chiral form of hexa-o-phenylene, in which one of the three biphenylene groups would lie above the plane of the three mercury atoms, the second below it, while one ring of the third biphenylene group would be above and the other below the plane of mercury atoms, Figure 3.6. Attempts to make this isomer from Dreiding models suggest that the molecules will be very strained and may be incapable of existence.

Finally, it ought to be mentioned that it is probably not possible to get a better value for R for this compound because of some of the problems which arise from the use of X-ray diffraction with mercury compounds. For example, the location of the light atoms may be difficult to fix due to the relatively large scattering by mercury atoms; in addition, "ripple" near mercury atoms may make it difficult to obtain the mercury-carbon bond lengths with any great accuracy.

TABLE 3.1: Final positional parameters ×10^4 with their estimated standard deviations in parentheses

atom	X/a	Y/b	Z/c
Hg(1)	1804.3(0.4)	4590.0(1)	9566.3(0.5)
Hg(2)	1857.1(0.4)	7754(0.9)	9691.8(0.6)
Hg(3)	0730.0(0.3)	6248(0.9)	9678.3(0.5)
C(1)	1244(8)	3948(21)	8939(11)
C(2)	1314(9)	3858(26)	8211(14)
C(3)	0955(11)	3452(27)	7774(14)
C(4)	0497(10)	3042(25)	8052(14)
C(5)	0414(8)	3078(21)	8773(11)
C(6)	0791(8)	3599(21)	3199(11)
C(7)	0698(8)	3630(23)	9983(11)
C(8)	9589(8)	2702(21)	10366(12)
C(9)	0508(10)	2726(26)	11068(15)
C(10)	0530(10)	3811(29)	11394(14)
C(11)	0592(11)	4848(28)	11008(16)
C(12)	0685(8)	4727(19)	10298(11)
C(13)	0771(8)	7755(20)	9087(11)
C(14)	0695(9)	7706(24)	8341(13)
C(15)	0690(9)	8791(28)	8003(13)
C(16)	0695(10)	9849(28)	8326(14)
C(17)	0748(9)	9926(23)	9070(13)
C(18)	0803(8)	8802(24)	9451(11)
C(19)	0907(8)	8845(22)	10229(11)
C(20)	0537(9)	9321(23)	10649(13)
C(21)	0667(9)	9256(22)	11375(12)
C(22)	1096(11)	8719(29)	11622(14)
C(23)	1436(10)	8273(24)	11170(13)
C(24)	1342(8)	8331(20)	10433(12)
C(25)	2336(9)	7111(22)	8928(13)
C(26)	2295(9)	7399(26)	8213(14)
C(27)	2608(10)	6946(27)	7686(14)
C(28)	2963(10)	6128(30)	7963(15)

continued......

TABLE 3.1: Continued.

C(29)	3017(9)	5798(23)	8657(14)
C(30)	2696(10)	6279(26)	9149(14)
C(31)	2742(11)	5970(28)	9908(15)
C(32)	3146(9)	6468(25)	10281(14)
C(33)	3134(10)	6185(28)	10987(15)
C(34)	2778(11)	5590(28)	11292(15)
C(35)	2387(10)	5066(28)	10938(16)
C(36)	2380(9)	5199(26)	10242(14)

TABLE 3.2: Bond lengths (Å) with their estimated standard deviations in parentheses

Hg(1)	-	C(1)	2.06(2)
Hg(1)	-	C(36)	2.13(3)
Hg(2)	-	C(24)	2.08(2)
Hg(2)	-	C(25)	2.08(3)
Hg(3)	-	C(12)	2.11(2)
Hg(3)	-	C(13)	2.07(2)
C(1)	-	C(2)	1.40(3)
C(1)	-	C(6)	1.37(3)
C(2)	-	C(3)	1.36(4)
C(3)	-	C(4)	1.42(4)
C(4)	-	C(5)	1.40(3)
C(5)	-	C(6)	1.42(3)
C(6)	-	C(7)	1.53(3)
C(7)	-	C(8)	1.32(3)
C(7)	-	C(12)	1.39(3)
C(8)	-	C(9)	1.36(3)
C(9)	-	C(10)	1.39(4)
C(10)	-	C(11)	1.41(4)
C(11)	-	C(12)	1.38(4)
C(13)	-	C(14)	1.44(3)
C(13)	-	C(18)	1.39(3)
C(14)	-	C(15)	1.40(4)
C(15)	-	C(16)	1.36(4)
C(16)	-	C(17)	1.43(3)
C(17)	-	C(18)	1.48(3)
C(18)	-	C(19)	1.51(3)
C(19)	-	C(20)	1.39(3)
C(19)	-	C(24)	1.36(3)
C(20)	-	C(21)	1.43(3)
C(21)	-	C(22)	1.34(4)
C(22)	-	C(23)	1.35(4)
C(23)	-	C(24)	1.43(3)

continued......

TABLE 3.2: Continued.

C(23)	-	C(24)	1.43(3)
C(25)	-	C(26)	1.41(3)
C(26)	-	C(27)	1.41(4)
C(27)	-	C(28)	1.44(4)
C(28)	-	C(29)	1.38(4)
C(29)	-	C(30)	1.39(4)
C(30)	-	C(25)	1.42(4)
C(30)	-	C(31)	1.50(4)
C(31)	-	C(32)	1.41(4)
C(31)	-	C(36)	1.46(4)
C(32)	-	C(33)	1.39(4)
C(33)	-	C(34)	1.31(4)
C(35)	-	C(36)	1.34(4)

TABLE 3.3: Bond angles (°) with their estimated standard deviations in parentheses

C(1) - Hg(1) - C(36)	177.8(10)
C(24) - Hg(2) - C(25)	176.4(9)
C(12) - Hg(3) - C(13)	178.9(8)
Hg(1) - C(1) - C(2)	120.2(16)
Hg(1) - C(1) - C(6)	123.1(16)
C(2) - C(1) - C(6)	116.6(21)
C(1) - C(2) - C(3)	122.5(24)
C(2) - C(3) - C(4)	119.9(25)
C(3) - C(4) - C(5)	119.8(24)
C(4) - C(5) - C(6)	117.1(21)
C(1) - C(6) - C(5)	123.6(20)
C(1) - C(6) - C(7)	119.2(19)
C(5) - C(6) - C(7)	116.7(19)
C(6) - C(7) - C(8)	124.2(22)
C(6) - C(7) - C(12)	116.8(21)
C(8) - C(7) - C(12)	118.6(20)
C(7) - C(8) - C(9)	124.4(24)
C(8) - C(9) - C(10)	116.8(26)
C(9) - C(10) - C(11)	121.7(26)
C(10) - C(11) - C(12)	116.5(27)
Hg(3) - C(12) - C(7)	120.0(15)
Hg(3) - C(12) - C(11)	118.3(19)
C(7) - C(12) - C(11)	121.3(22)
C(14) - C(13) - C(18)	122.6(21)
Hg(3) - C(13) - C(14)	120.0(17)
Hg(3) - C(13) - C(18)	116.8(15)
C(13) - C(14) - C(15)	115.0(23)
C(14) - C(15) - C(16)	125.3(24)
C(15) - C(16) - C(17)	120.3(26)
C(16) - C(17) - C(18)	116.2(23)
C(13) - C(18) - C(17)	119.8(19)
C(13) - C(18) - C(19)	122.1(22)

continued......

TABLE 3.3: Continued.

C(17) - C(18) - C(19)	118.0(22)
C(18) - C(19) - C(20)	116.8(20)
C(18) - C(19) - C(24)	115.0(20)
C(20) - C(19) - C(24)	128.0(21)
C(19) - C(20) - C(21)	111.4(22)
C(20) - C(21) - C(22)	123.6(23)
C(21) - C(22) - C(23)	120.6(24)
C(22) - C(23) - C(24)	119.3(24)
Hg(2) - C(24) - C(19)	120.6(16)
Hg(2) - C(24) - C(23)	122.4(17)
C(19) - C(24) - C(23)	118.8(21)
Hg(2) - C(25) - C(26)	123.3(17)
Hg(2) - C(25) - C(30)	116.7(18)
C(26) - C(25) - C(30)	119.8(22)
C(25) - C(26) - C(27)	124.0(24)
C(26) - C(27) - C(28)	111.8(24)
C(27) - C(28) - C(29)	126.8(26)
C(28) - C(29) - C(30)	118.3(25)
C(25) - C(30) - C(29)	119.1(24)
C(25) - C(30) - C(31)	120.1(24)
C(29) - C(30) - C(31)	120.7(25)
C(30) - C(31) - C(32)	117.0(25)
C(30) - C(31) - C(36)	120.7(25)
C(32) - C(31) - C(36)	122.2(25)
C(31) - C(32) - C(33)	112.1(24)
C(32) - C(33) - C(34)	124.8(27)
C(33) - C(34) - C(35)	124.1(28)
C(34) - C(35) - C(36)	116.4(28)
Hg(1) - C(36) - C(31)	114.6(19)
Hg(1) - C(36) - C(35)	125.1(21)
C(31) - C(36) - C(35)	119.6(26)

TABLE 3.4: Contact distances [< 3.9 Å] with their e.s.d in parentheses

C(11) - C(5)	3.62(4)	Hg(2) - C(31)	3.86(3)
C(13) - C(9)	3.49(3)	Hg(2) - C(36)	3.62(3)
C(14) - C(9)	3.46(3)	Hg(3) - C(9)	3.80(3)
C(16) - C(29)	3.68(4)	C(7) - Hg(3)	3.89(2)
C(17) - C(29)	3.55(3)	C(8) - Hg(3)	3.74(2)
C(17) - C(20)	3.60(3)	C(32) - Hg(1)	3.83(3)
C(23) - C(24)	3.40(4)		
C(23) - C(33)	3.55(4)		
C(32) - C(8)	3.68(3)		

TABLE 3.5: Angles between ring planes in biphenylenemercury with their estimated standard deviations in parentheses (see figure 3.3 for ring number)

Ring Numbers	Angle (°)
2 and 1	61.3(3.3)
3 and 1	68.9(3.1)
3 and 2	17.5(3.5)
4 and 1	50.4(2.3)
4 and 2	68.4(2.7)
4 and 3	61.5(2.5)
5 and 1	65.3(2.1)
5 and 2	53.5(2.6)
5 and 3	50.4(2.4)
5 and 4	17.2(2.3)
6 and 1	19.1(3.5)
6 and 2	53.5(3.1)
6 and 3	55.8(3.7)
6 and 4	62.8(3.0)
6 and 5	74.3(2.9)

TABLE 3.6: Isotropic thermal parameters ($\mathring{A}^2$) with their estimated standard deviations in parentheses

$Beq = \frac{1}{3} \sum_i B_{ii}$ for Hg atoms

$Beq = 8\pi^2 U$ for carbon atoms

Hg(1)	4.23(1)	C(18)	2.9(5)
Hg(2)	4.26(1)	C(19)	2.8(5)
Hg(3)	3.72(1)	C(20)	5.2(8)
C(1)	3.4(6)	C(21)	4.1(6)
C(2)	4.9(7)	C(22)	6.4(9)
C(3)	7.2(10)	C(23)	4.6(9)
C(4)	6.0(9)	C(24)	3.9(6)
C(5)	3.5(6)	C(25)	3.9(6)
C(6)	3.4(6)	C(26)	5.5(8)
C(7)	2.6(5)	C(27)	6.1(9)
C(8)	4.0(6)	C(28)	6.6(9)
C(9)	4.5(7)	C(29)	4.6(7)
C(10)	4.9(7)	C(30)	4.9(7)
C(11)	5.9(9)	C(31)	5.4(8)
C(12)	2.8(4)	C(32)	5.9(8)
C(13)	3.2(5)	C(33)	6.4(9)
C(14)	4.8(7)	C(34)	6.3(9)
C(15)	5.1(7)	C(35)	6.0(9)
C(16)	5.5(8)	C(36)	5.0(7)
C(17)	4.4(7)		

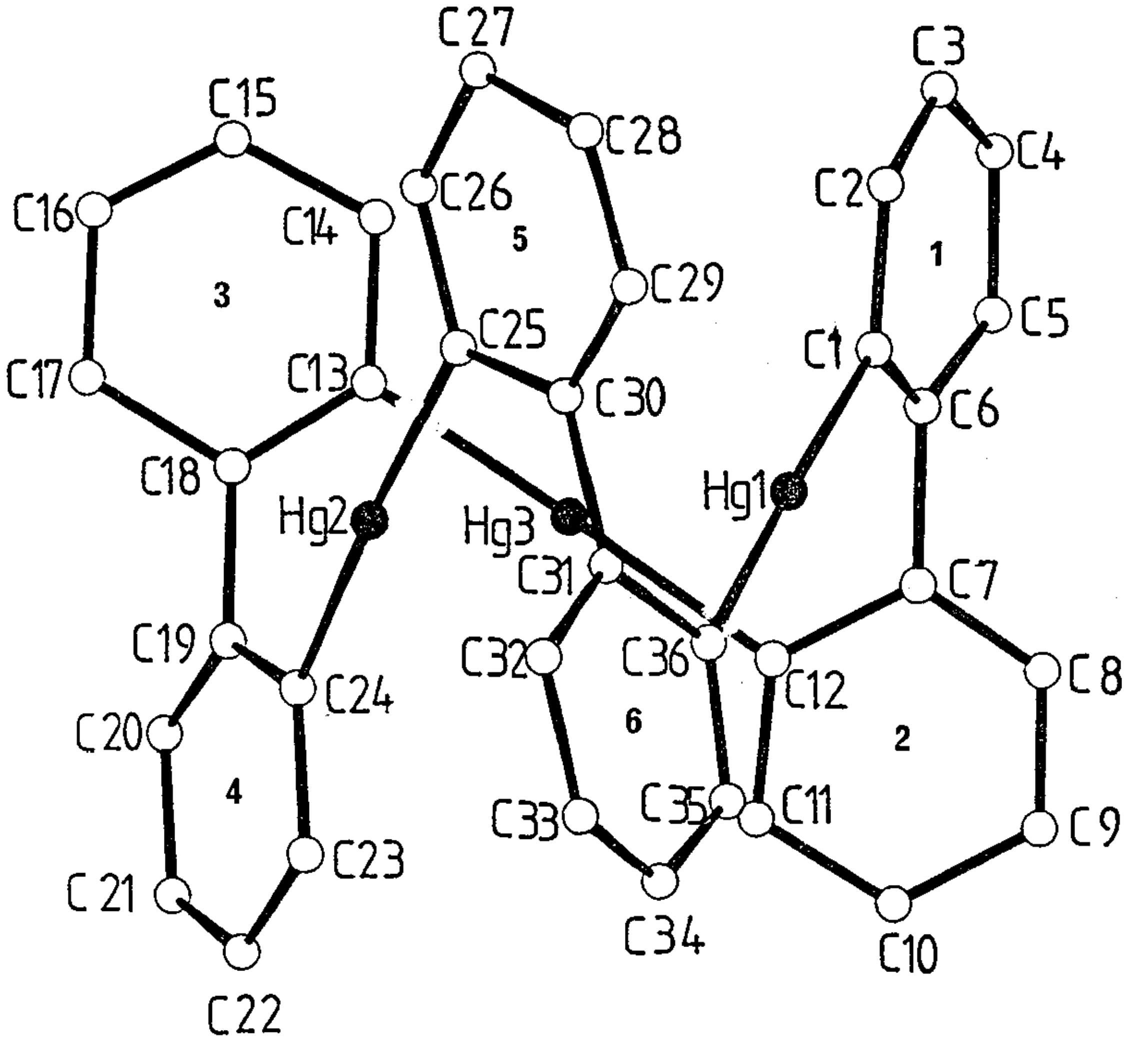


Figure 3.3: Numbering employed for biphenylenemercury.

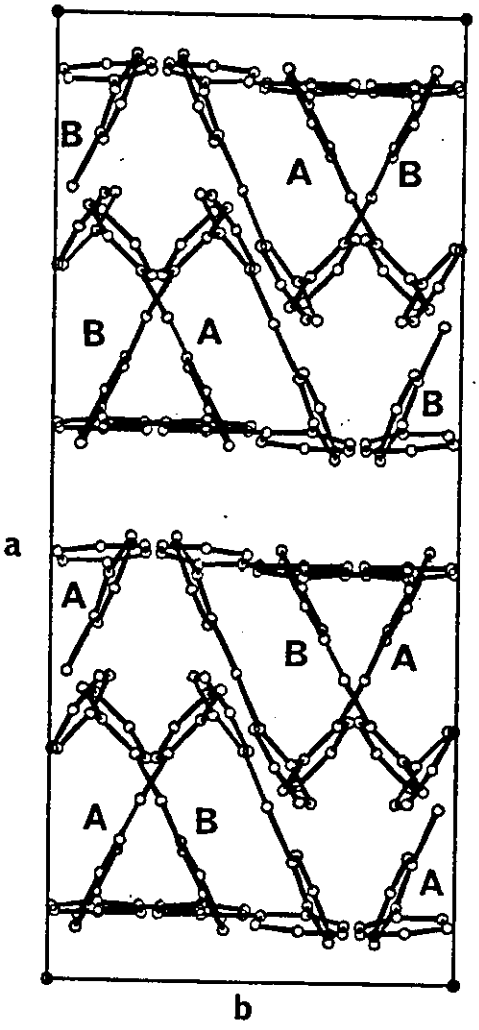


Figure 3.4: Unit cell contents in biphenylenemercury projected onto c axis. The two enantiomers are labelled A and B for clarity.

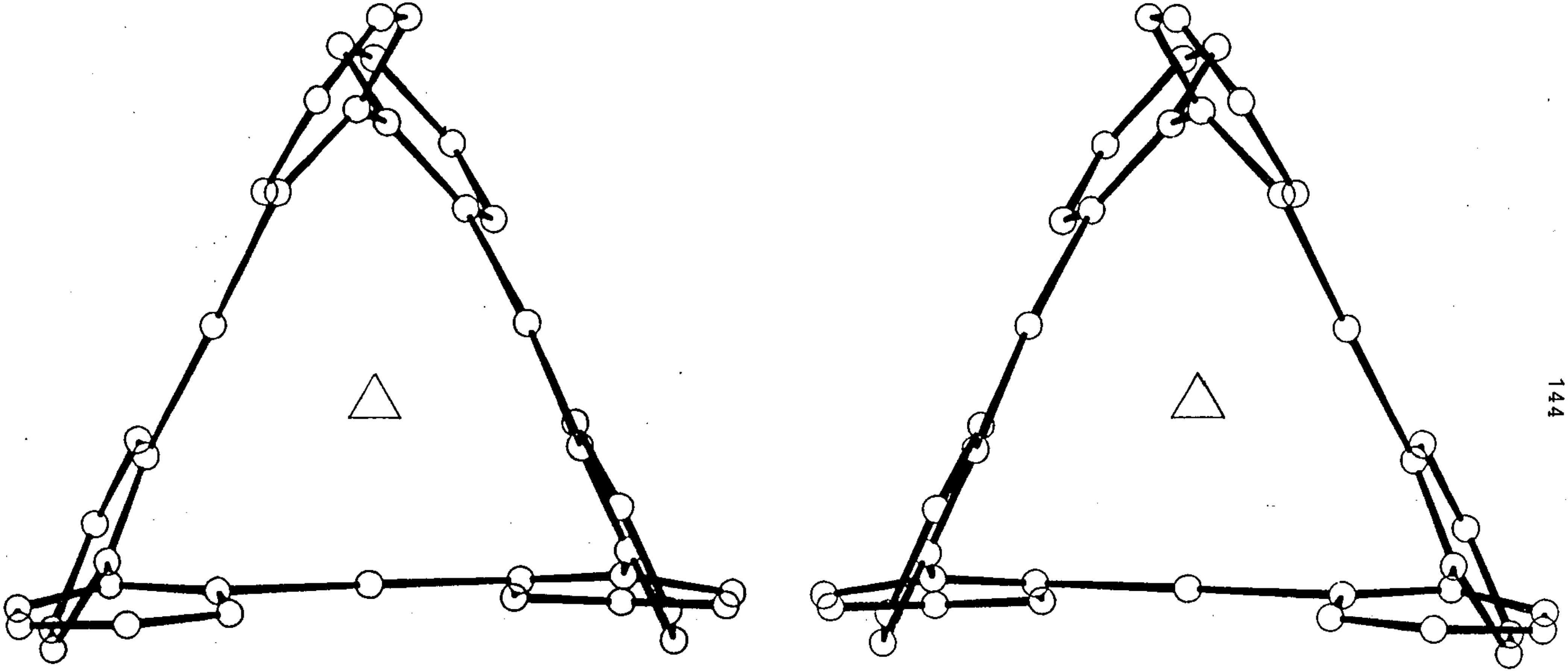


Figure 3.5a: Top views of the two biphenylenemercury enantiomers. showing the three-fold principal axes.

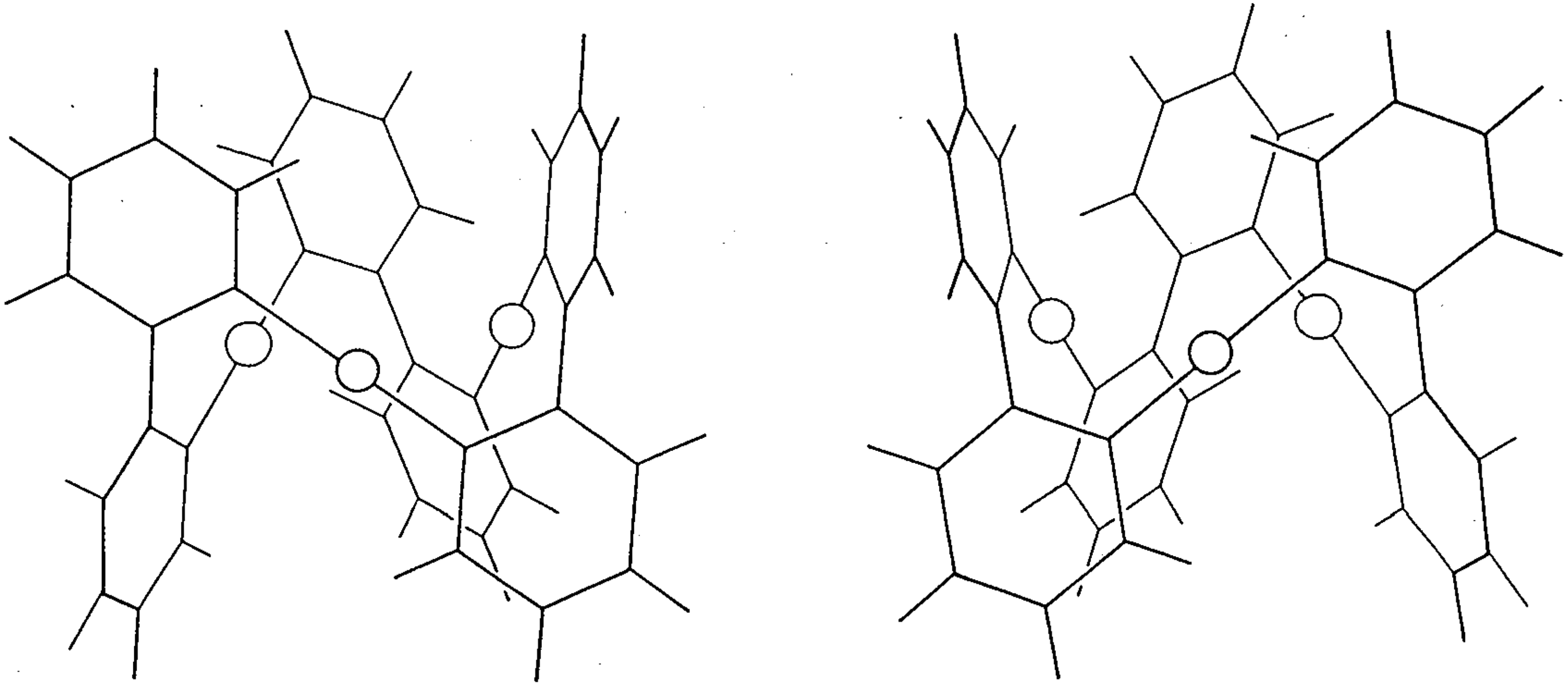


Figure 3.5b: Side views of the two biphenylenemercury enantiomers.

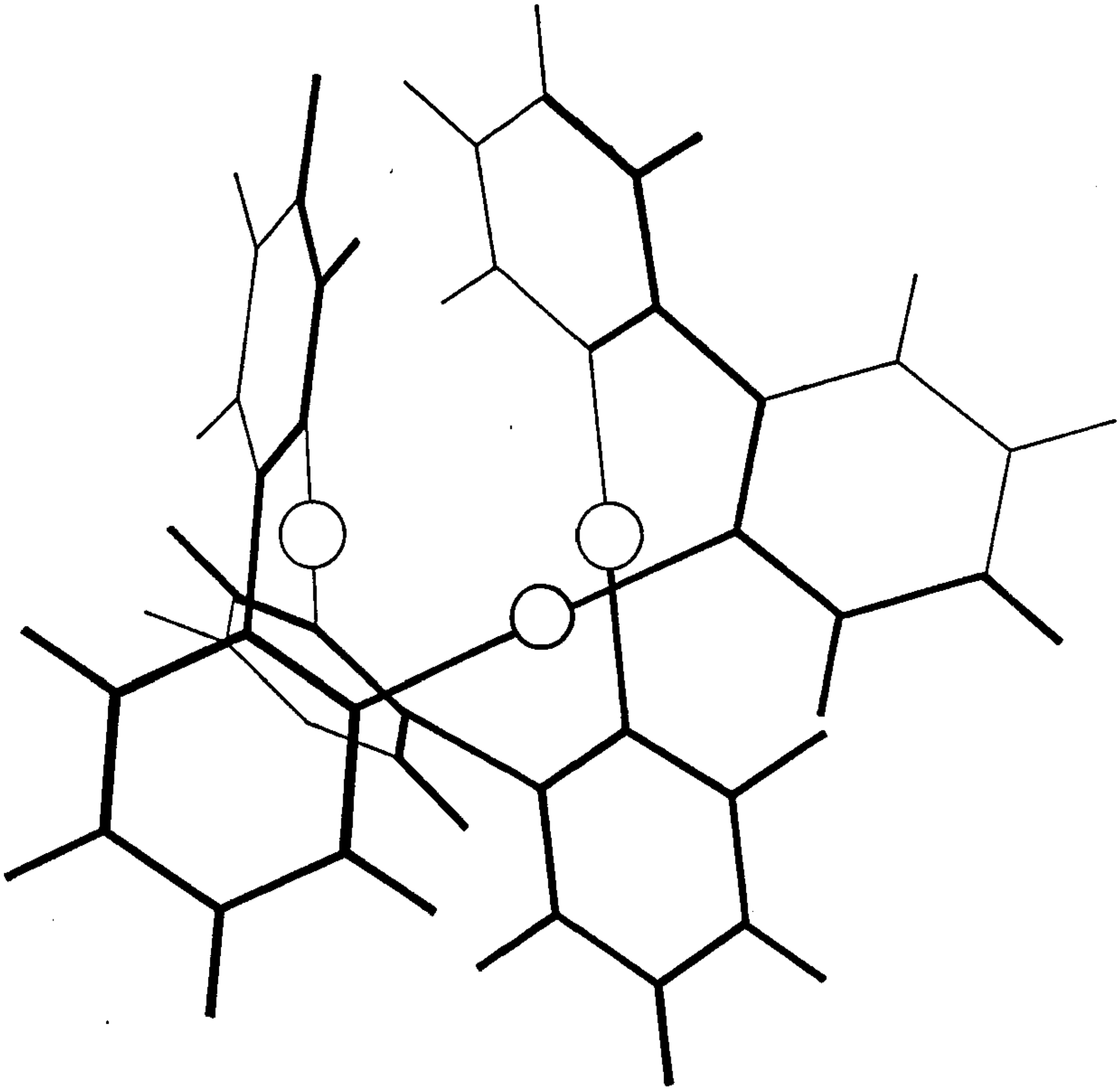


Figure 3.6: The third isomer of biphenylenemercury.

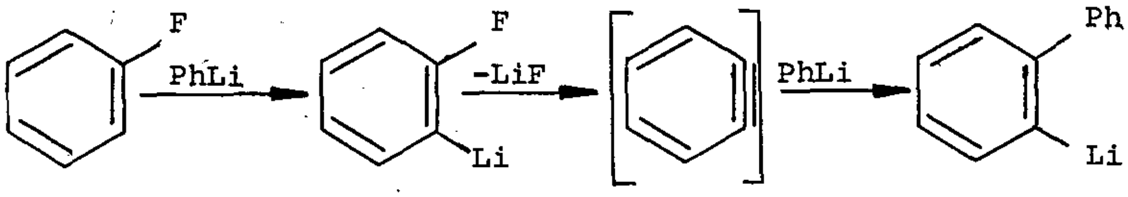
Chapter 4

2-Chlorophenyl Derivatives of Group V

The preparation of organolithium compounds by metal halogen exchange reactions was discovered independently by Gilman(1) and Wittig(2)

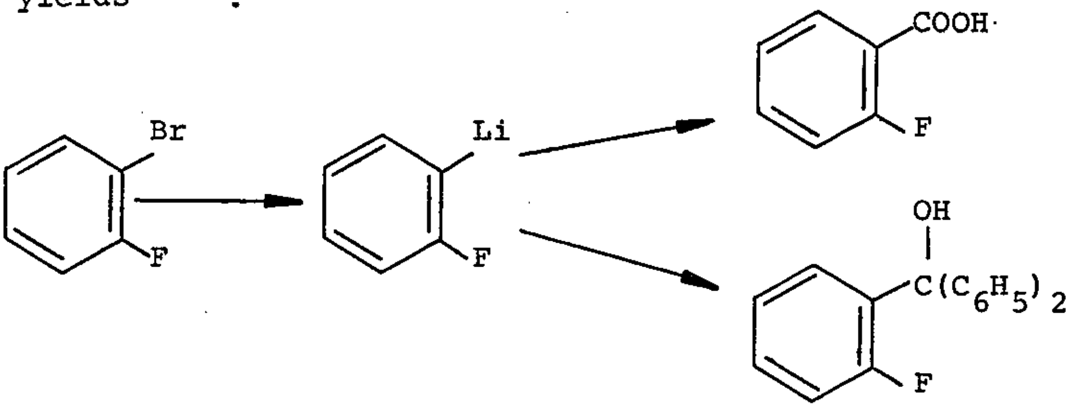
$$RLi + R'X \rightleftharpoons R'Li + RX.$$

In this reaction, lithium becomes preferentially attached to the more electronegative organic radical. The exchange is faster in electron-donating solvents than in hydrocarbon solvents and it takes place most readily with iodides and bromides; for chlorides and fluorides the lithium-halogen exchange is sufficiently slow to allow other reactions to occur, such as ortho-metalation, leading in most cases to aryne formation:(3)



When no hydrogen atoms are present in the ring as in perchlorobenzene chlorine-lithium exchange occurs reasonably readily(4) whilst hexafluorobenzene undergoes alkylation exclusively(5). In mixed perhalobenzenes as expected, lithium-bromine exchange is preferred to lithium-chlorine exchange and both take precedence over nucleophilic displacement of fluorine(3).

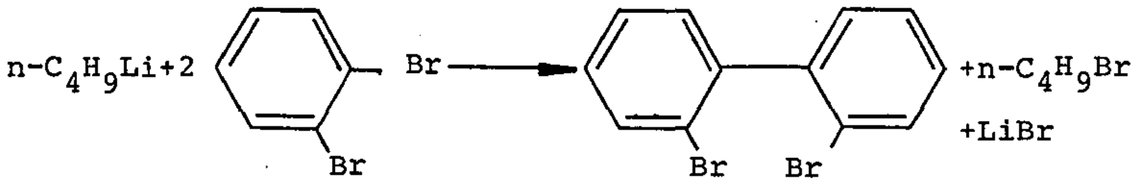
n-Butyllithium in ether has been shown to react with a number of dihalobenzenes replacing a single halogen atom by lithium; for example, p-dibromobenzene gives p-bromophenyllithium in 50 - 70% yield, whilst m- and p-chlorophenyllithium similarly can be prepared from the corresponding bromochlorobenzenes(6). The metal-halogen exchange reaction also provides a route to 2-halophenyllithium compounds, and for example, 2-fluorophenyllithium can be prepared in high yields at -70°C by the reaction of 2-fluorobromobenzene with n-butyllithium in ether and it may be intercepted below -60°C with benzophenone or carbon dioxide in excellent yields(7,8):



Similarly, 2-chlorophenyllithium may be prepared in almost quantitative yield at -90°C by adding butyllithium to 2-chlorobromobenzene as determined by carbonation, but the synthesis fails completely at -30°C. Carbonation has to be carried out at -100°C; when attempted by the usual method of pouring the lithium reagent onto a slurry of powdered carbon dioxide in ether, only a 6% yield of 2-cholorobenzonic acid is obtained due to extensive thermal decomposition via benzyne formation. Immediate carbonation, after preparation of 2-bromophenyllithium even at -100°C gave only a 23% yield of 2-bromobenzoic acid(8); this lithium reagent can be trapped in reasonable yield at -130°C with chlorodiethylphosphine,(9) but in almost every other case the 2-halophenyllithium reagents are too unstable to form organometallic derivatives on treatment with metal or metalloidal halides.

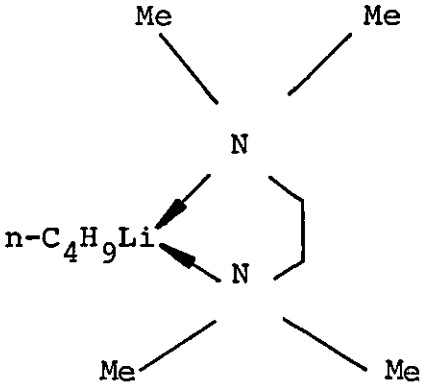
The polyhalophenyllithium compounds are much more stable than the compounds with only one halogen atom, for example, o-chlorophenyllithium in diethyl ether eliminates lithium chloride below -60°C(8) whereas pentachlorophenyllithium decomposes only slowly at 20°C(4).

The solvent has a considerable effect on the lithium-halogen exchange reaction, a striking example being the influence of tetrahydrofuran on the high yield synthesis of 2,2'-dibromobiphenyl from the reaction of n-butyllithium with two moles of o-dibromobenzene at -78°C(10):

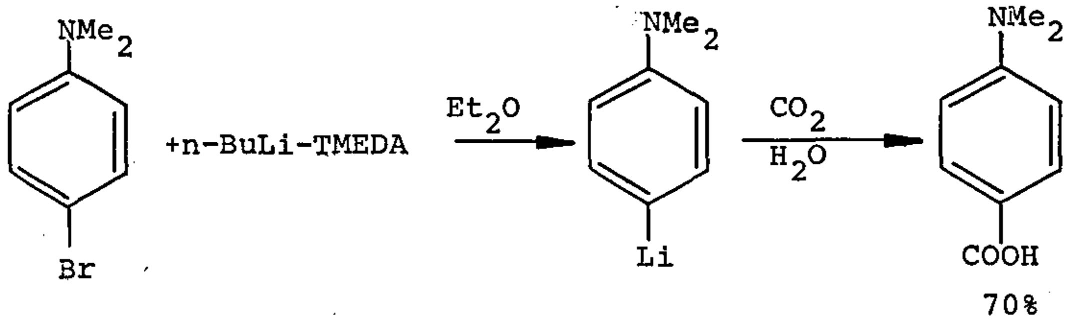


When o-dibromobenzene is treated with n-butyllithium in diethyl ether under identical conditions, and using the same quantities of reactants, it has been found that the only products are an unidentified ether-insoluble material and a highly viscous oil(10).

n-Butyllithium in ether or light petroleum ether, and phenyllithium in ether, are the preferred compounds for use in lithium-halogen exchanged reactions. However, phenyllithium is in general less reactive than n-butyllithium and is more prone to side reactions. Alkyllithium reagents cleave ether slowly, so a low temperature and short reaction times are advised(11); the workable temperatures for methyl- , n-butyl- and phenyllithium in tetrahydrofuran are 0°C, below 35°C and 0°C to -30°C, respectively(12). A number of dihalobenzenes have been shown to react with magnesium and much wider use has been made of halophenyl-Grignard reagents; for example, p-bromophenylmagnesium bromide with a variety of co-reactants gives the expected product, generally in yields of 40-50%; all the chlorophenylmagnesium and p-fluorophenylmagnesium bromides and iodides have also been used(11). Although the halophenylmagnesium reagents can be used to introduce up to two halophenyl groups into an organometallic compound, the attempted introduction of three such groups invariably gives yields quoted as "always low"(13) or "very low"(14) and in this thesis the yields of tris(2-chlorophenyl) derivatives of phosphorus and antimony were always about 1%. As mentioned before, the lithium-halogen exchange reaction is particularly rapid in electron-donating solvents, also the reactivities of organolithium compounds are enhanced by chelating ditertiary aliphatic amines such as N,N,N',N'-tetramethylethylene diamine (TMEDA)$^{(15)}$; such a discovery has greatly stimulated studies involving the synthetic application of these reagents, such as LiBu.TMEDA shown below.



Most of the studies using TMEDA have so far been concerned with metalation reactions, since the chelated organolithiums are extremely powerful metalating agents. Some studies have also demonstrated the enhanced reactivity of the butyllithium-TMEDA complex in halogen-lithium exchange reactions; Hallas and Waring$^{(16)}$ have reported that a good yield of p-dimethylaminophenyllithium can be obtained by reaction between p-bromo-N,N-dimethylaniline and butyllithium-TMEDA:



Whereas other workers have found that the phenyllithium-TMEDA complex selectively enhances metalation over halogen-lithium exchange(17). Thus the reaction between phenyllithium and 2-iodothiophene in ether exclusively gives halogen-lithium exchange to yield 2-thienyllithium and iodobenzene but the presence of one equivalent of TMEDA induces exclusive metalation leading to 5-iodo-2-thienyllithium and benzene.

Experimental.

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware. Tetramethylethylene diamine was dried by refluxing over calcium hydride. Diethyl ether and tetrahydrofuran were dried by refluxing over sodium wire and distilled under nitrogen immediately prior to use.

Preparation of 2-chloroiodobenzene.(13)

2-Chloroaniline (200 gm) was dissolved in a mixture of water (1200 mℓ) and concentrated hydrochloric acid (270 mℓ) at 70°C. A further 270 mℓ of acid were added before the stirred solution was chilled to -5°C to precipitate fine crystals of the hydrochloride. A solution of sodium nitrite (110 gm) in 250 mℓ water was then added in small quantities with stirring, whilst the temperature was kept below 10°C during the addition. When the diazotisation was completed, a solution of

potassium iodide (400 gm) in water (400 mℓ) was added slowly with stirring to the cold diazo solution when a vigorous reaction ensued; the mixture was then allowed to stand overnight at room temperature. The dark heavy oil which formed was separated, added to 33% sodium hydroxide solution (200 mℓ) and steam-distilled, the resulting 2-chloroiodobenzene was separated from the aqueous layer and dried over calcium chloride;
b.p. 226-228°C.

Attempted preparation of tris(2-chlorophenyl)antimony from 2-chlorophenyllithium.

A solution of 2-chlorobromobenzene (7.68 gm; 40 mmole) in dry ether (40 mℓ) was added, with stirring, over a period of two minutes to a hexane solution of n-butyllithium (32 mℓ; 40 mmole) held at -95°C; stirring was continued for a further 30 minutes. At this point a solution of antimony trichloride (3.0 gm; 13.3 mmole) in 50 mℓ dry ether was added and stirring continued for one hour. The cooling bath was then removed and the reaction mixture allowed to warm up slowly up to room temperature when the resulting white solid was filtered off and washed with acetone. The ether filtrate and acetone washings were combined and the solvents removed under vacuum to leave a sticky, white solid, which on recrystallization from acetone, gave a 5% yield of what was apparently tris(2'-chlorobiphenyl)antimony, m.p. 220-221°C (Found: C, 62.95; H, 3.5; Cℓ; 15.4%. $C_{36}H_{24}C\ell_3Sb$. calcd: C, 63.15; H, 3.5; Cℓ, 15.5%).

Preparation of tris(2-chlorophenyl)phosphorus using 2-chlorophenylmagnesium iodide.

A solution of 2-chloroiodobenzene (9.54 gm; 40 mmole) in dry ether (2o mℓ) was added dropwise to 0.96 gm (40 mmole) of magnesium turnings in 20 mℓ of dry ether. The mixture was stirred at room temperature for one hour until the whole of the magnesium had reacted and the flask was then cooled to 0°C as a solution of phosphorus trichloride (1.16 mℓ; 13.28 mmole) in 20 mℓ ether was added; stirring was continued at room temperature for a further one hour. After hydrolysing the reaction mixture, the ether layer was separated and dried over $MgSO_4$; filtration, followed by evaporation of the ether, gave an oil which after extraction and crystallization from ethanol yielded 50 mg (1.0%) of tris(2-chlorophenyl)-phosphorus m.p. 184-185°C (Lit.$^{(13)}$ 185°C).

Preparation of tris(2-chlorophenyl)antimony from 2-chlorophenyllithium in the presence of TMEDA.

A hexane solution of n-butylithium (18 mℓ; 21 mmole) was placed in a 250 mℓ three-necked flask fittied with a mechanical stirrer, addition funnel and a nitrogen inlet. Addition of dry tetramethylethylene diamine (3 mℓ; 21 mmole) gave a yellow-orange mixture from which some crystals, presumably of LiBu. TMEDA, were deposited. The flask was cooled to -95°C in a toluene slush bath before a solution of 2-chloroiodobenzene (5.0 gm; 21 mmole) in dry ether was added, with stirring, over a period of 5 minutes; stirring was continued for a further 20 minutes and during the addition of antimony trichloride (1.6 gm; 7 mmole in 20 mℓ dry ether); after one hour the cold bath was removed and the mixture allowed to warm up slowly to room temperature. The ether layer was separated and the solvent removed under reduced pressure to yield white, feathery crystals (3.0 gm; 94%) of tris(2-chlorophenyl)antimony. Recrystallization from ethanol gave the analytical sample; m.p. 135-136°C (Lit(14) 136-137°C), (Found: C, 47.0; H, 2.6; Cℓ, 23.7%. $C_{18}H_{12}C\ell_3Sb$ calcd: C, 47.3; H, 2.6; Cℓ, 23.3%).

Preparation of tris(2-chlorophenyl)phosphorus in the presence of TMEDA.

The 2-chlorophenyllithium was prepared at -95°C as described previously from 2-chloroiodobenzene (5.0 gm; 21 mmole), n-butyllithium (20 mℓ, 21 mmole) and TMEDA (3 mℓ; 21 mmole). Phosphorus trichloride (0.6 mℓ; 7 mmole) was added and the mixture was stirred for one hour. The cold bath was removed, the mexture allowed to warm slowly to room temperature and the resulting yellow solid filtered before being washed with hot acetone. The ether filtrate and acetone washings were combined and the solvents removed under vacuum to give 2.5 gm (78%) of tris(2-chlorophenyl)phosphorus. Recrystallization from ethanol gave white crystals m.p. 184-185°C (Lit[(13)]. 185°C), (Found: C, 58.9; H, 3.3; $C\ell_3$, 29.4%. $C_{18}H_{12}PC\ell_3$ calcd: C, 59.1; H, 3.3; Cℓ, 29.1%).

Preparation of tris(2-chlorophenyl)arsenic in the presence of TMEDA.

In a similar reaction to that described above, arsenic trichloride (0.6 mℓ; 7 mmole) was added to a stirred solution of 2-chlorophenyllithium at -95°C and after working up the mixture in the usual way, there was obtained 2.5 gm (87%) of tris(2-chlorophenyl)arsenic, which on recrystallization from ethanol gave white crystals m.p. 156-157°C (Found; C, 52.7; H, 2.8; Cℓ, 25.6%. $C_{18}H_{12}C\ell_3As$ calcd: C, 52.8; H, 2.9; Cℓ, 26.0%).

Preparation of tris(2-chlorophenyl)bismuth in the presence of TMEDA.

Similarly a solution of bismuth trichloride (2.2 gm; 7 mmole) in 20 mℓ dry ether was stirred with 2-chlorophenyllithium at -95°C for one hour. After warming the reaction mixture to room temperature and working up, the yield of white feathery crystals was 2.5 gm (63%). Recrystallization from ethanol gave the analytical sample, m.p. 140-141°C (Found: C, 39.8;

H, 2.1; Cℓ, 17.7%. $C_{18}H_{12}Cl_3Bi$ calcd: C, 39.8; H, 2.2; Cℓ, 19.6%).

Preparation of bis(2-chlorophenyl)mercury in the presence of TMEDA.

A solution of mercuric chloride (2.85 gm; 10.5 mmole) in dry ether (200 mℓ) was treated with a stirred solution of 2-chlorophenyllithium-TMEDA at -95°C. After one hour the mixture was left to warm up to room temperature and then the ether layer separated; the solvents were removed under reduced pressure giving white feathery crystals (2.3 gm; 71%) of bis(2-chlorophenyl)mercury. Recrystallization from ethanol gave the analytical sample, m.p. 149-150°C.(Found: C, 33.7; H, 1.9; Cℓ, 16.6%. $C_{12}H_8Cl_2Hg$ calcd: C, 34.0; H, 1.9; Cℓ, 16.8%).

Reaction of bis(2-chlorophenyl)mercury with mercuric chloride.

Bis(2-chlorophenyl)mercury (0.7 gm; 1.65 mmole) and mercuric chloride (0.45 gm; 1.65 mmole) were refluxed together in mesitylene for 20 minutes. The mesitylene solution was filtered and on cooling gave colourless, needle crystals of 2-chlorophenylmercuric chloride (0.6 gm; 52%), recrystallization from chloroform gave the analytical sample m.p. 149-150°C (Lit(18). 147-148°C) (Found: C, 20.8; H, 1.0; Cℓ, 19.7%. $C_6H_4ClHgCl$ calcd: C, 20.75; H, 1.15; Cℓ, 20.5%).

Attempted preparation of 1,6-diphosphatriptycene.

A mixture of n-butylithium (32 mℓ; 42 mmole) and TMEDA (6 mℓ; 42 mmole) was cooled to -95°C before a solution of 2-chloroiodobenzene (5.0 gm; 21 mmole) in dry ether (20 mℓ) was added dropwise. Stirring was continued for 20 minutes and then phosphorus trichloride (1.2 mℓ; 14 mmole) was added. After one hour the mixture was warmed up to room temperature and stirred with distilled water, after which the ether layer was removed and evaporated to give 1.6 gm of biphenyl (identified by the melting point and its infrared spectrum) and a mixture of unidentified oils.

Reaction of tris(2-chlorophenyl)phosphine with n-butylithium.

To a stirred solution of tris(2-chlorophenyl)phosphine (2.89 gm; 7.93 mmole) in 50 mℓ tetrahydrofuran was added 10 mℓ (23.8 mmole) of n-butyllithium at -40°C; after one hour the solution had turned to a dark red colour. Then a solution of phosphorus trichloride (0.23 mℓ; 2.64 mmole) was added, and the mixture was stirred for another hour. After warming up, the mixture was filtered and the solvent removed but resulted only in a mixture of brown,unidentified oils.

Reaction of tris(2-chlorophenyl)antimony with n-butylithium.

Tris(2-chlorophenyl)antimony (2.8 gm; 6 mmole) was dissolved in dry ether (150 mℓ) and cooled to -78°C (CO_2 - EtOH bath). n-Butylithium as a hexane solution (7.6 mℓ; 18 mmole) was added by a syringe to the above solution, and the stirring continued for one hour during which time the solution assumed a yellow colouration; then a solution of antimony trichloride (1.368 gm; 6 mmole) in 20 mℓ ether was added and after one hour of stirring the mixture was allowed to warm up to room temperature. Filtration and removal of the solvent under vacuum gave a mixture of oils which solidified on long standing at room temperature to a solid melting over a range of 50-60°C. All attempts to separate this oily mixture using thin layer chromotography were unsuccessful.

Attempted preparation of 2-bromophenyllithium in the presence of TMEDA.

A mixture of hexane solution of n-butylithium (12.5 mℓ; 20 mmole) and tetramethylethylene diamine (3 mℓ; 20 mmole) was cooled to -95°C when a solution of 2-bromoiodobenzene (5.658 gm; 20 mmole) in dry ether (40 mℓ) was added dropwise with stirring; a yellow mixture was formed. After 5 minutes, a solution of arsenic trichloride (0.55 mℓ; 6.66 mmole) in ether (20 mℓ) was added and the reaction mixture stirred for about one hour before it was warmed slowly to room temperature. The ether solution was filtered and the solvent removed under reduced pressure to give a mixture of unidentified oils.

The above reaction was repeatedly carried out applying different reaction times (15 minutes, 30 minutes) for the lithiation of 2-bromoiodobenzene, and in all cases a similar oily mixture was obtained. When 1,2-dibromobenzene was reacted with n-butyllithium complexed with TMEDA following the same procedure as described before, the product was again only a mixture of oils.

Infrared absorptions are quoted in cm^{-1} for mulls in Nujol using CsI disks.

$P(C_6H_4C\ell)_3$: 1570w, 1551w, 1426s, 1417sh, 1268w, 1249m, 1158w, 1105m, 1034sh, 1030s, 944w, 759m, 749s, 746s, 728m, 721s, 657w, 647vw, 527w, 515m, 470m, 438m, 414m, 373w, 356w, 332w.

$As(C_6H_4C\ell)_3$: 1556m, 1425s, 1416sh, 1269w, 1254m, 1157m, 1117m, 1096m, 1033m, 1025s, 1021s, 942m, 857w, 751sh, 746s, 742s, 712s, 639w, 502vw, 497w, 440s, 433m, 428sh, 371m, 286m, 273w.

$Sb(C_6H_4C\ell)_3$: 1567w, 1555m, 1423s, 1419sh, 1269m, 1256m, 1159w, 1155vw, 1114m, 1090s, 1030m, 1020s, 1016s, 1007wsh, 945w, 753s, 748s, 709s, 437m, 434sh, 425sh, 357w.

$Bi(C_6H_4C\ell)_3$: 1551m, 1417s, 1265m, 1250m, 1157w, 1106m, 1078s, 1023s, 1009s, 1006s, 940m, 749sh, 744s, 700s, 693sh, 481w, 428s, 414sh, 343w.

$Sb(C_6H_4C_6H_4C\ell)_3$: 1527w, 1245w, 1233w, 1153w, 1123w, 1073m, 1046m, 1030m, 999s, 938w, 763s, 757s, 748s, 727s, 716sh, 680m, 742w, 614w, 550w, 455m, 448w, 430vw.

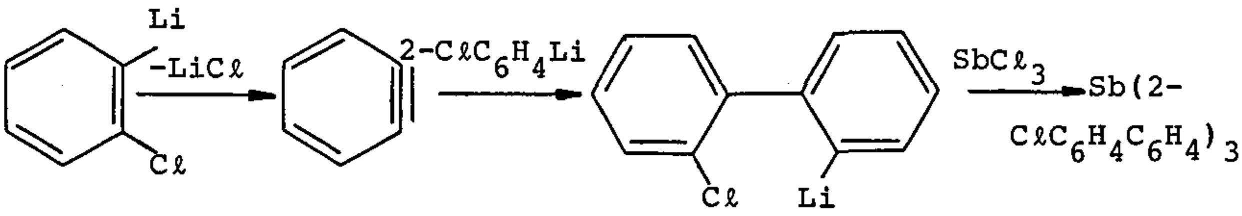
$Hg(C_6H_4C\ell)_2$: 1565w, 1550w, 1444s, 1420m, 1269m, 1153m, 1108s, 1094s, 1029m, 1023s, 1018m, 928w, 863w, 756s, 720m, 708sh, 705s, 642w, 497w, 430s, 358m.

$C_6H_4C\ell HgC\ell$: 1556w, 1443s, 1420s, 1268w, 1251m, 1100m, 1028m, 1018s, 1015s, 940w, 856w, 758w, 743s, 718m, 711s, 640m, 423s, 362m, 313s.

Figure 4.1: Shows the infrared spectrum of tris(2-Chlorophenyl)antimony.

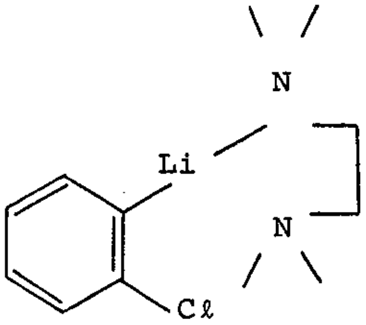
Discussion.

2-Halophenyllithium reagents are thermally unstable and have to be synthesised at very low temperatures(8). Benzyne-derived products were obtained when antimony trichloride was added to 2-chlorophenyllithium at -90°C and the mixture allowed to warm up slowly to room temperature. The only isolable product from the reaction was apparently tris(2'-chlorobiphenyl)antimony, which presumably arose from the reaction sequence:

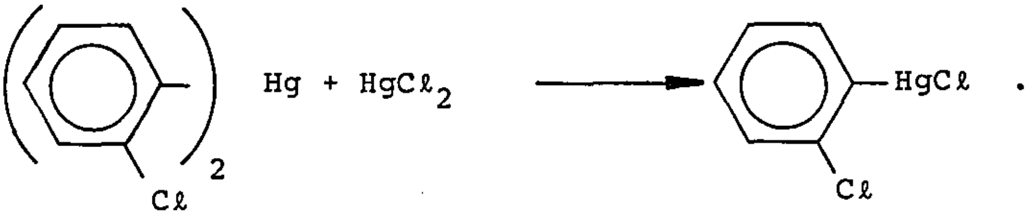


occurring at temperatures well below that required for attack of antimony trichloride by 2-chlorophenyllithium. Obviously the thermal fragility of 2-chlorophenyllithium precludes its use in many potentially-useful synthetic reactions.

The corresponding Grignard reagents, 2-chlorophenylmagnesium bromide and iodide, are somewhat more stable but still slowly decomposes via benzyne intermediate, the yields of tris(2-chlorophenyl)phosphorus(13) and tris(2-chlorophenyl)antimony(14) derived from them being described as always "low" and "very low", respectively. These Grignard preparations were repeated here and the results confirmed the consistently very low yields (ca. 1%). The addition of tetramethylethylene diamine (TMEDA) to 2-chlorophenyllithium could possibly hinder the benzyne formation reaction by complexing with lithium atom and making it sterically larger and less able to attack the ortho chlorine atom.



To check this, 2-chlorophenyllithium was prepared at -90°C from a mixture of n-butylithium, 2-chloroiodobenzene and TMEDA; after addition of antimony trichloride, the temperature was allowed to rise slowly to ambient when a yield of over 90% of tris(2-chlorophenyl)antimony resulted. Obviously the 2-chlorophenyllithium has been stabilized sufficiently for it to survive intact at the temperature required for reaction with antimony trichloride; the other Group V trichlorides reacted in similar fashion. Another demonstration of the increased thermal stability of 2-chlorophenyllithium in the presence of tetramethylethylene diamine is shown in this work by its reaction with mercuric chloride to give bis(2-chlorophenyl)mercury in 71% yield. Typically when bis(2-chlorophenyl)mercury was refluxed with mercuric chloride in mesitylene for 20 minutes, colourless crystals of 2-chlorophenylmercuric chloride were obtained:



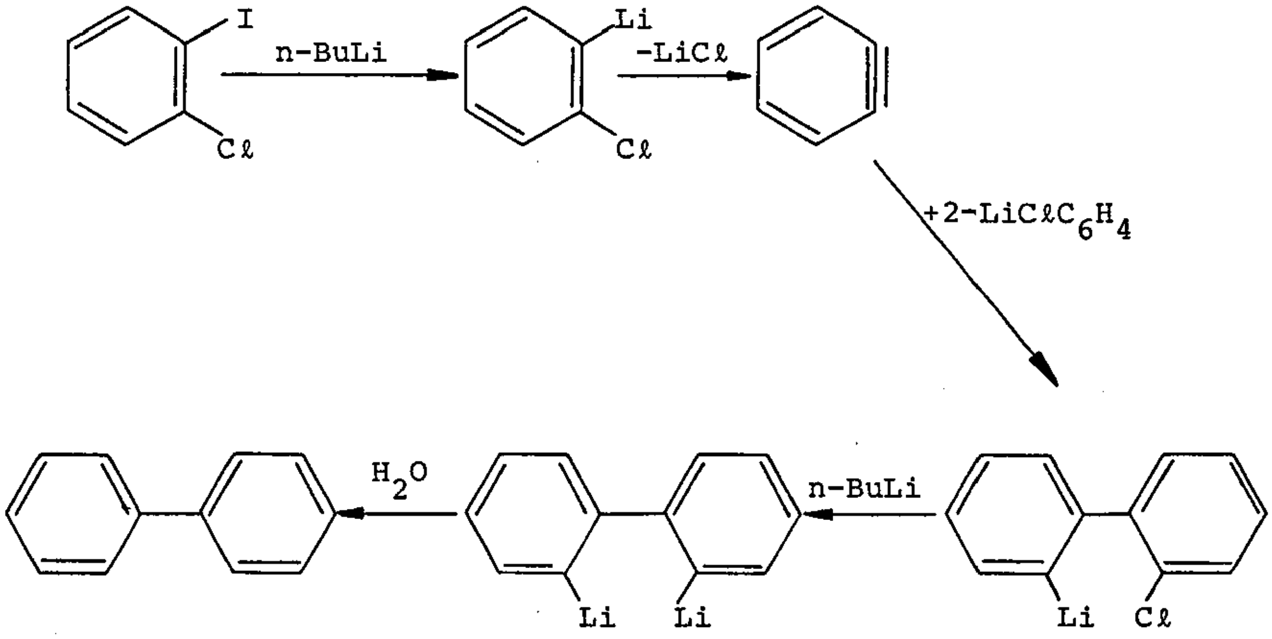
The mass spectrum of tris(2-chlorophenyl)phosphine has a strong parent ion peak $P(C_6H_4C\ell)_3^+$, which is the base peak in the spectrum, while the parent ions in the other 2-chlorophenyl derivatives have increasing lower intensity in going from As to Bi; the parent ion of $Bi(2\text{-}C\ell C_6H_4)_3$ is barely visible against the background. The mass spectra of all the $M(C_6H_4C\ell)_3$ compounds (M = P,As,Sb,Bi) show a strong ion for $M(C_6H_3)(C_6H_4C\ell)^+$ which arises from the loss of HCℓ from $M(C_6H_4C\ell)_2^+$. The actual mass spectra of tris(2-chlorophenyl)phosphine and bismuth as extreme examples of the series are shown in Figure 4.2 & Figure 4.3, respectively, while Tables 4.1 to 4.5 list the important ions in all the mass spectra of the tris(2-chlorophenyl) derivatives and bis(2-chlorophenyl)mercury.

The considerable efforts expended on devising a high yield synthesis of the Group V tris(2-chlorophenyl) derivatives was done in the hope that the three chlorine atoms would be readily lithiated and, by simply adding $MC\ell_3$ to the solution, 1,6-triptycene derivatives could be formed (in a similar manner to the synthesis described for the perfluorotriptycenes described in Chapter 6). However, this hope turned out to be unfounded because all attempts to lithiate the chlorines failed. The work, however, was not entirely wasted since the organometallic chemist now has an excellent way of producing 2-chlorophenyl derivatives of the elements which could prove useful in other ways.

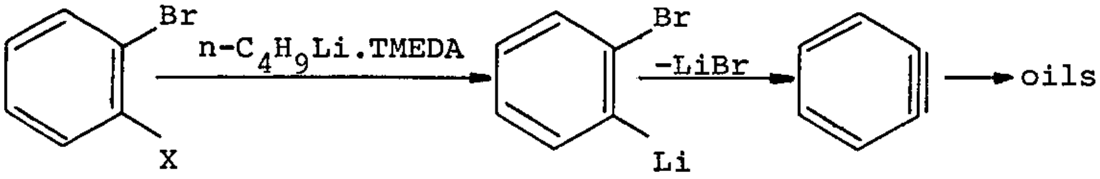
In attempts to prepare 1,6-disubstituted triptycenes, reactions of the tris(2-chlorophenyl) derivatives of Group V elements with either n-butyllithium or lithium metal followed by addition of the corresponding trihalides were carried out under a variety of different conditions. When tris(2-chlorophenyl)phosphorus in ether reacted with n-butyllithium at -78°C for three hours and allowing the reaction mixture to react with phosphorus trichloride, the unreacted starting material was recovered in high yield; carrying out the same reaction at room temperature gave a mixture of unidentified oils together with some unreacted starting material. When tris(2-chlorophenyl)-phosphorus in tetrahydrofuran was treated with n-butyllithium at -40°C, a dark red-brown solution was formed but again on addition of phosphorus trichloride, only a mixture of unidentified oils was obtained. On reacting tris(2-chlorophenyl)arsenic in ether with either n-butyllithium or lithium metal and then adding arsenic trichloride at different temperatures(-78°, -40°, room temperature)and refluxing with lithium, no reaction was observed and tris(2-chlorophenyl)arsenic was recovered intact; in tetrahydrofuran below -40°, the similar oils were obtained as for the reactions involving tris(2-chlorophenyl)phosphorus. Tris(2-chlorophenyl)antimony in ether was reacted with n-butyllithium at -78° for one hour when the resulting solution was yellow; on treatment with antimony trichloride, a mixture of oils was again obtained, which solidified on long standing at room temperature and melted over a range of 50-60°C. From the results of lithiation of tris(2-chlorophenyl) derivatives of phosphorus, arsenic in tetrahydrofuran and antimony in diethyl ether, it is obvious that these compounds were cleaved (or metalated) instead of the chlorine atoms being replaced; cleavage of certain organometallics by lithium in tetrahydrofuran has previously been reported(19). For example, triphenylphosphorus, triphenylarsine and triphenylstibine are cleaved by lithium in tetrahydrofuran and in all cases the reactions were exothermic giving rise to dark red colours typical of R_2MLi derivatives:

$$(C_6H_5)M \xrightarrow{2Li} (C_6H_5)MLi + C_6H_5Li \qquad M = P, As, Sb.$$

In an attempted "single-step" preparation of 1,6-diphosphatriptycene from 2-chloriodobenzene, the latter was reacted with two equivalents of n-butyllithium, complexed with tetramethylethylene diamine, and then phosphorus trichloride added at -95°. After warming up the mixture to room temperature and hydrolysing it with distilled water, the product was biphenyl (and unidentified oils). The formation of biphenyl may have occurred by benzyne formation:



The reaction of 1,2-dibromobenzene and 2-bromoiodobenzene with n-butyllithium in the presence of TMEDA carried out in attempts to obtain stabilized 2-bromophenyllithium failed completely, probably because the bromine atom in o-bromophenyllithium is so highly reactive, and is readily lost as lithium bromide to give a benzyne-derived mixture of oils.



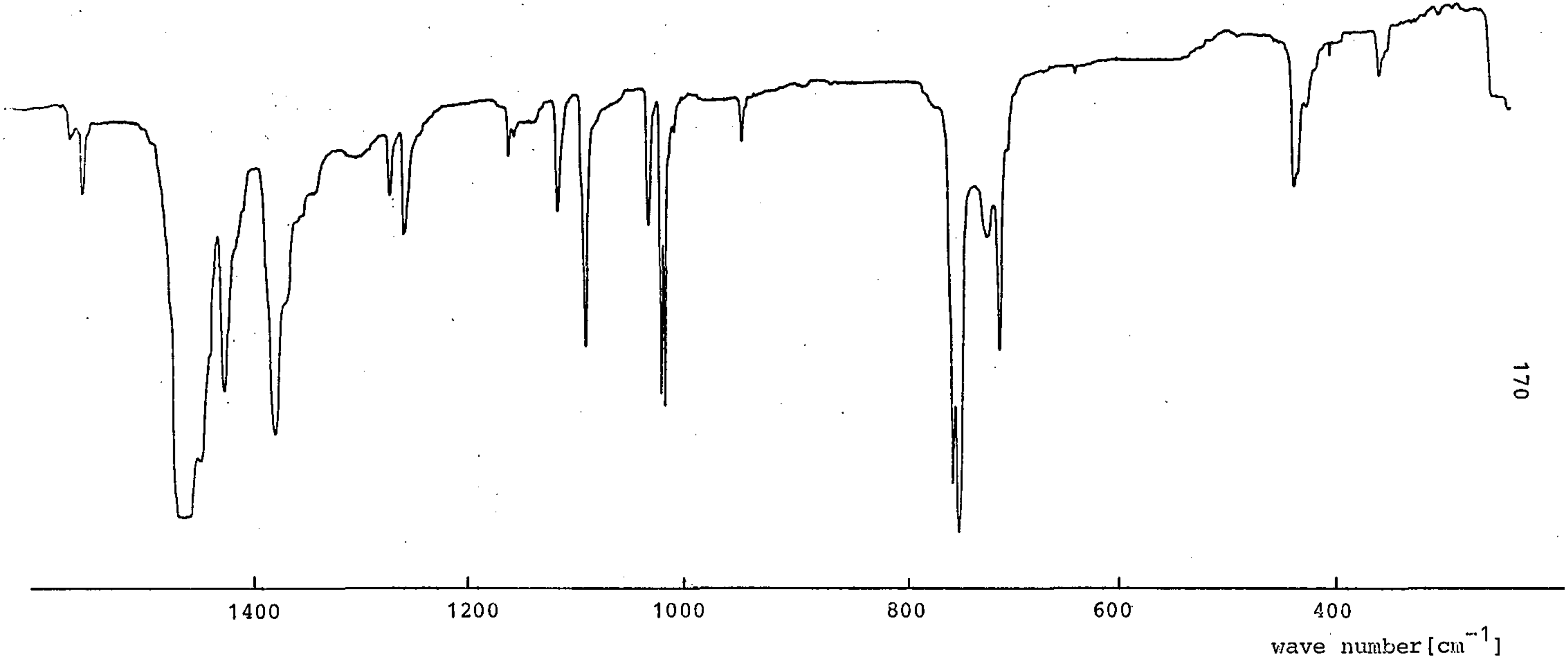


Figure 4.1: Infrared spectrum of tris(2-chlorophenyl)antimony.

TABLE 4.1: Partial Mass Spectrum of Tris(2-Chlorophenyl)phosphine

m/e	Ion	Relative Abundance
364	$C_{18}H_{12}C\ell_3P^+$	100
329	$C_{18}H_{12}C\ell_2P^+$	14.27
293	$C_{18}H_{11}C\ell P^+$	4.40
257	$C_{18}H_{10}P^+$	8.86
217	$C_{12}H_7C\ell P^+$	36.21
181	$C_{12}H_6P^+$	13.40
152	$C_{12}H_8^+$	4.96
107	$C_6H_4P^+$	9.34
75	$C_6H_3^+$	9.36
50	$C_4H_2^+$	3.69

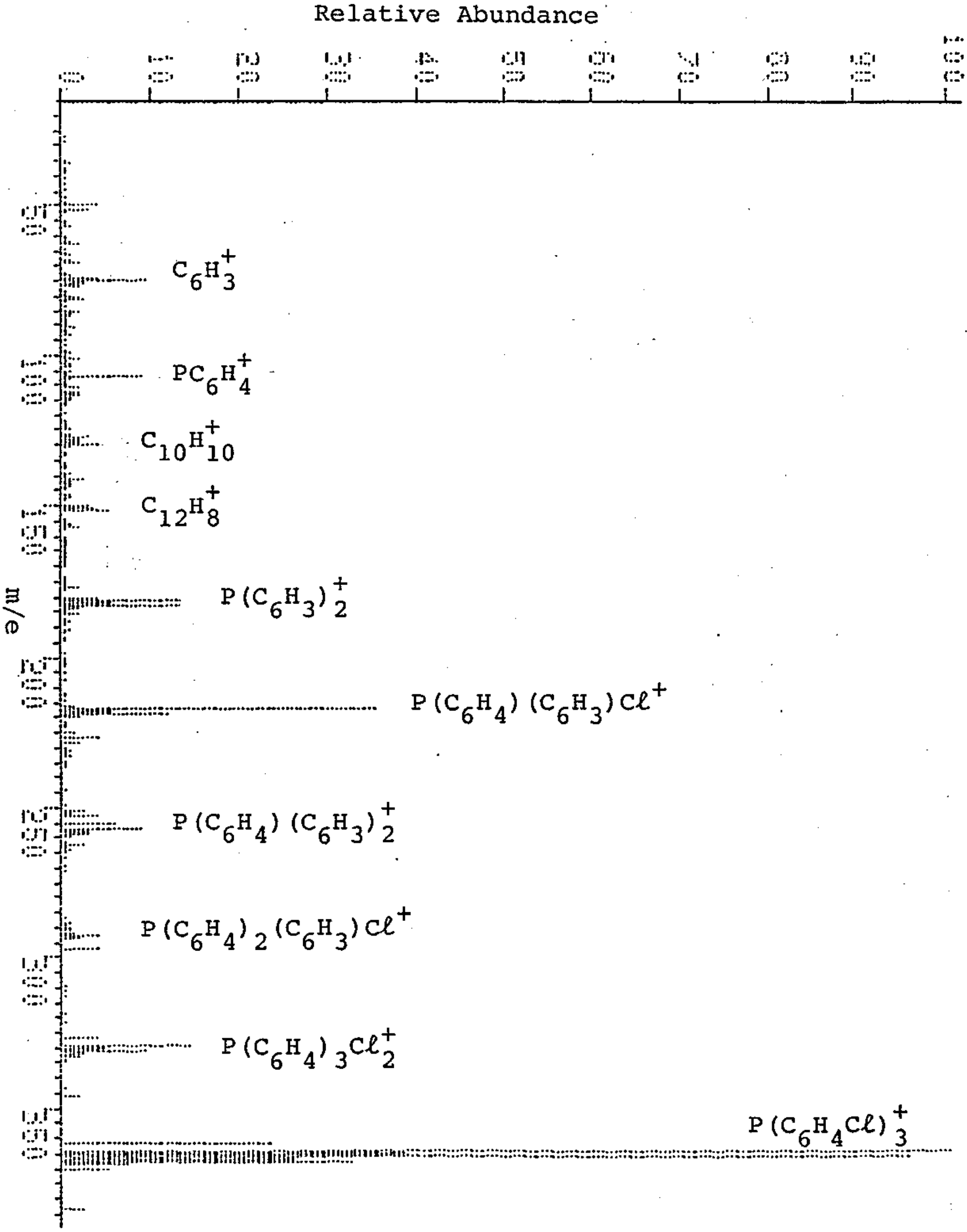


Figure 4.2: Partial Mass Spectrum of tris(2-Chlorophenyl)phosphine

TABLE 4.2: Partial Mass Spectrum of Tris(2-Chlorophenyl)arsine

m/e	Ion	Relative Abundance
408	$C_{18}H_{12}C\ell_3As$	31.87
297	$C_{12}H_8C\ell_2As$	11.24
261	$C_{12}H_7C\ell As$	100.00
227	$C_{12}H_8As$	16.42
186	$C_{12}H_7C\ell$	98.37
151	$C_{12}H_7$	72.00
111	$C_6H_4C\ell$	13.03
75	C_6H_3	67.38
50	$C_4H_2^+$	44.25

TABLE 4.3: Partial Mass Spectrum of Tris(2-Chlorophenyl)antimony

m/e	Ion	Relative Abundance
456	$C_{18}H_{12}C\ell_3Sb^+$	10.28
345	$C_{12}H_8C\ell_2Sb^+$	4.74
309	$C_{12}H_7C\ell Sb^+$	26.37
269	$C_6H_4C\ell_2Sb^+$	5.76
234	$C_6H_4C\ell Sb^+$	14.47
193	$SbC\ell_2^+$	12.20
186	$C_{12}H_7C\ell^+$	23.49
152	$C_{12}H_8^+$	48.23
123	$C_{10}H_3^+$	17.64
108	$C_8H_{12}^+$	39.22
95	$C_7H_{11}^+$	11.14
75	$C_6H_3^+$	47.3
69	$C_5H_9^+$	92.93

continued......

TABLE 4.3: Continued.

m/e	Ion	Relative Abundance
55	$C_4H_7^+$	40.07
51	$C_4H_3^+$	72.39
44	$C_3H_8^+$	100
43	$C_3H_7^+$	94.92
41	$C_3H_5^+$	50.30
40	$C_3H_4^+$	60.01

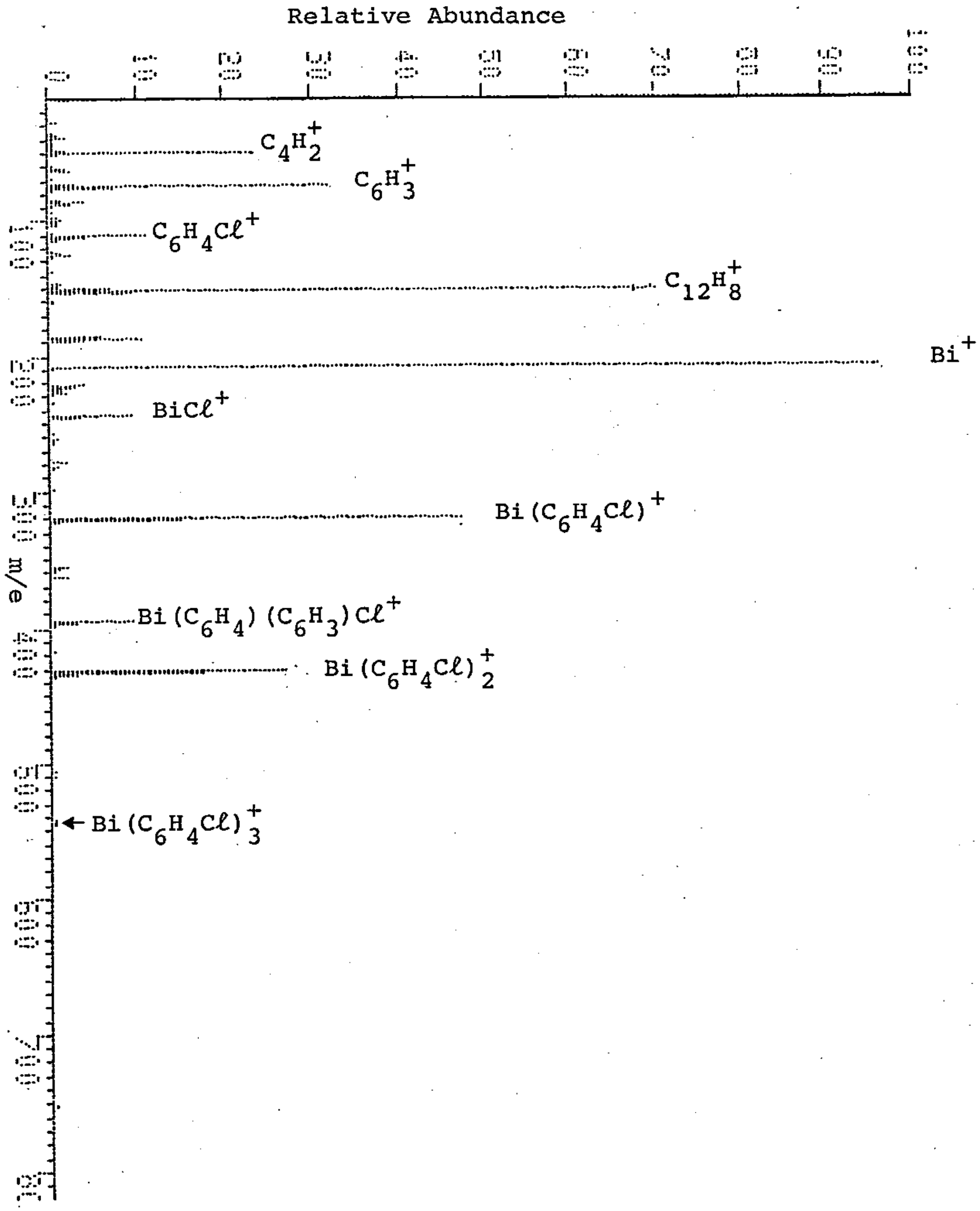


Figure 4.3: Partial Mass Spectrum of tris(2-Chlorophenyl)Bismuth.

TABLE 4.4: Partial Mass Spectrum of Tris(2-Chlorophenyl)bismuth

m/e	Ion	Relative Abundance
542	$C_{18}H_{12}Cl_3Bi^+$	Very low
431	$C_{12}H_8Cl_2Bi^+$	26.50
395	$C_{12}H_7ClBi^+$	8.91
320	$C_6H_4ClBi^+$	47.02
244	$BiCl^+$	9.11
209	Bi^+	100
187	$C_{12}H_8Cl^+$	10.37
152	$C_{12}H_8^+$	67.52
111	C_6H_4Cl	10.91
75	$C_6H_3^+$	31.97
50	$C_4H_2^+$	23.45

TABLE 4.5: Partial Mass Spectrum of Bis(2-Chlorophenyl)mercury

m/e	Ion	Relative Abundance
24	$C_{12}H_8C\ell_2Hg^+$	9.20
313	$C_6H_4C\ell Hg^+$	10.64
152	$C_{12}H_8^+$	5.30
111	$C_6H_4C\ell^+$	100.00
75	$C_6H_3^+$	59.23

Chapter 5

An Introduction to Perfluoro-Organometallic Compounds

The preparation of perfluoroalkyl-lithium and -magnesium compounds has presented special problems since they are very unstable, due to the ease with which they eliminate metal fluoride; for example$^{(1)}$:

$$\begin{tikzcd} n\text{-}C_3F_7I + n\text{-}C_4H_9Li \arrow[r, "\text{ether}", "-78^{\circ}"'] & n\text{-}C_3H_7Li + n\text{-}C_4H_9I \arrow[d, "-LiF"] \\ & CF_3CF = CF_2 \end{tikzcd}$$

Nevertheless, the carbon-iodine bond in perfluoroalkyl iodides is usually susceptable to homolytic fission and this was exploited in early work in the direct synthesis of many perfluoroorganometallic compounds. Diethylzinc was the first metal alkyl, reported by Frankland in 1849$^{(2)}$ who prepared it by the action of metallic zinc on ethyliodide, followed by thermal disproportionation of the resulting ethylzinc iodide:

$$Zn + C_2H_5I \xrightarrow{72^{\circ}C} C_2H_5ZnI$$

$$2C_2H_5ZnI \xrightarrow{120^{\circ}C} (C_2H_5)_2Zn + ZnI_2$$

Ever since then, most chemists have preferred to carry out the preparation of organometallic compounds directly from the corresponding metal whenever that is possible; some of the typical reactions are listed below

$$C_2F_5I \xrightarrow[300\,°C]{Cd/Hg} (C_2F_5)_2Hg$$ Ref. 3.

$$S + n\text{-}C_3F_7I \longrightarrow (n\text{-}C_3F_7)_2S + (n\text{-}C_3F_7)_2S_2 + (n\text{-}C_3F_7)_2S_3$$

Ref. 4.

$$P + CF_3I \longrightarrow CF_3PI_2 + (CF_3)_2PI + (CF_3)_3P$$

Ref. 5.

In cases where the metal is insufficiently reactive, a catalyst, usually another metal such as copper or silver, is employed as in the reactions of Si(6), Ge(7), Sn(8) with methyl chloride:

$$2CH_3C\ell + Si \xrightarrow[350°]{Cu} (CH_3)_2SiC\ell_2$$ Ref. 6.

$$2CH_3C\ell + Ge \xrightarrow[320°]{Cu} (CH_3)_2GeC\ell_2$$ Ref. 7.

$$2CH_3C\ell + Sn \xrightarrow[315°]{Cu} (CH_3)_2SnC\ell_2$$ Ref. 8.

while in the identical synthesis of tetraethyllead, sodium-lead alloy is reacted with ethyl chloride:

$$4C_2H_5C\ell + 4NaPb \xrightarrow[60\,°C]{Pyridine} (C_2H_5)_4Pb + 3Pb + 4NaC\ell$$

Metalloids, such as selenium and tellurium also react with alkyl halides giving organometallic derivatives, though in a specialised and rather peculiar way(9):

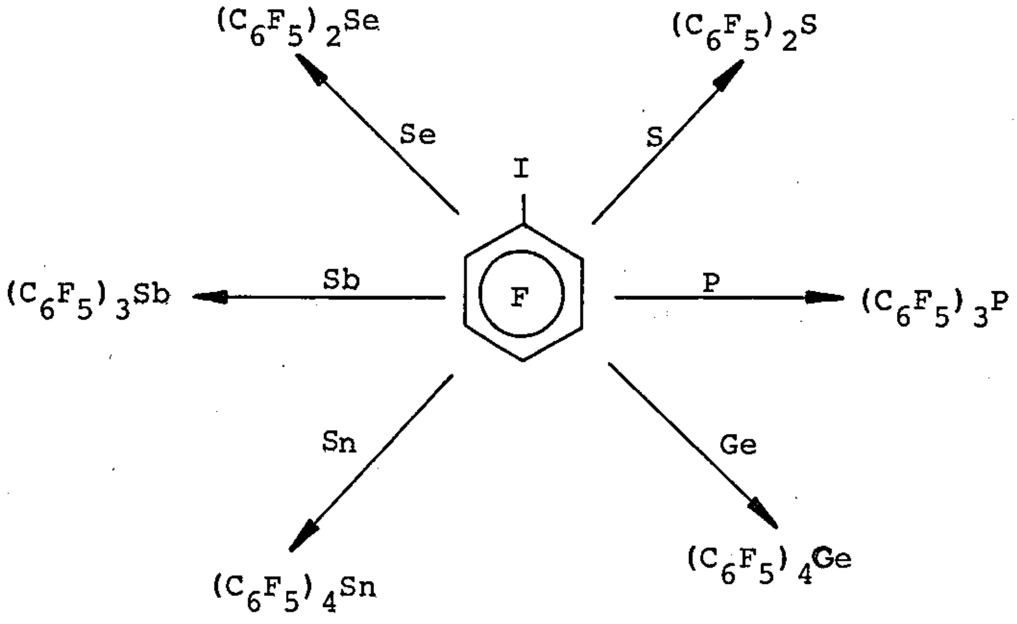
$$Se + RI \xrightarrow[H_2O]{NaOH} R_2Se$$

$$Te + RX \xrightarrow[H_2O]{NaOH} R_2Te$$

The first success of the application of direct synthesis in the preparation of perfluoro-aromatic metal derivatives was reported by Haszeldine(10), who obtained bis(pentafluorophenyl)mercury by heating iodopentafluorobenzene with mercury at 300°C in an evacuated sealed tube for 30 hours.

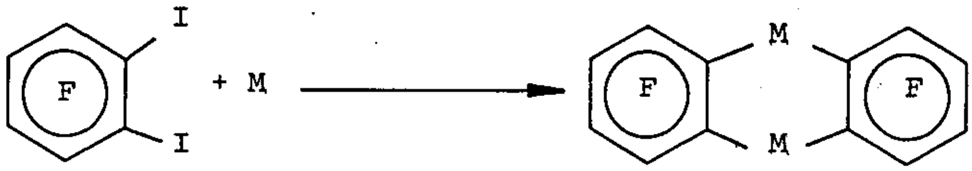
$$2C_6F_5I + 2Hg \longrightarrow (C_6F_5)_2Hg + HgI_2$$

Subsequently, several of the pentafluorophenyl derivatives of sulphur, selenium, tellurium, germanium, tin, phosphorus and antimony have been synthesized in high yield by "direct methods":



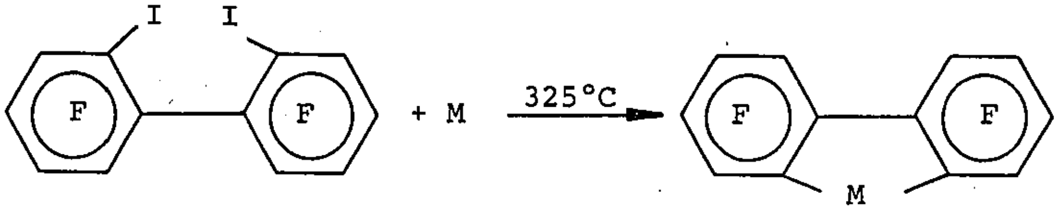
Typical Ullmann reactions occur when 1,2-diiodotetrafluorobenzene and copper are heated under vacuum at 230°C, giving a mixture of polyphenylenes(12) having the general formula $(C_6F_4)_X$ (X = 2,3,4), from which the particularly interesting compound, perfluorotriphenylene is isolated, previously thought to be incapable of existence(13) due to adverse F---F steric factors.

The high thermal stability of many polyfluoroaromatic derivatives of metals and metalloids greatly aids their small-scale preparation by the direct method because often high temperature must be used, thus several heterocyclic compounds have been prepared by heating 1,2-diiodotetrafluorobenzene or 2,2'-diiodooctafluorobiphenyl with a metal or metalloid(11,14):



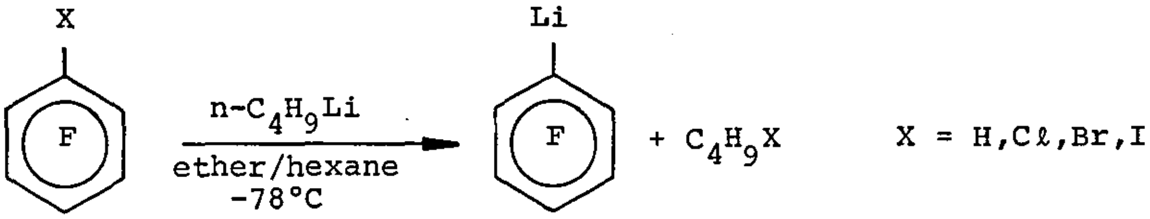
M = S , 230°C

M = Se, 320°C

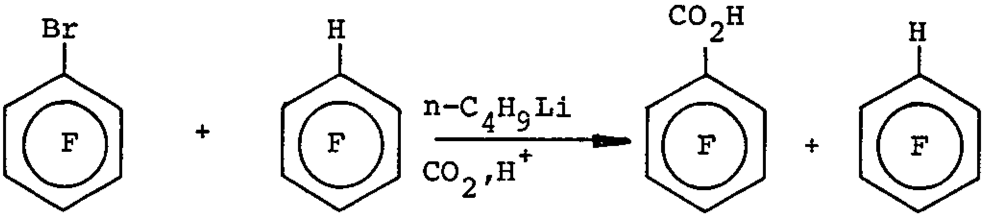


M = Se,Te

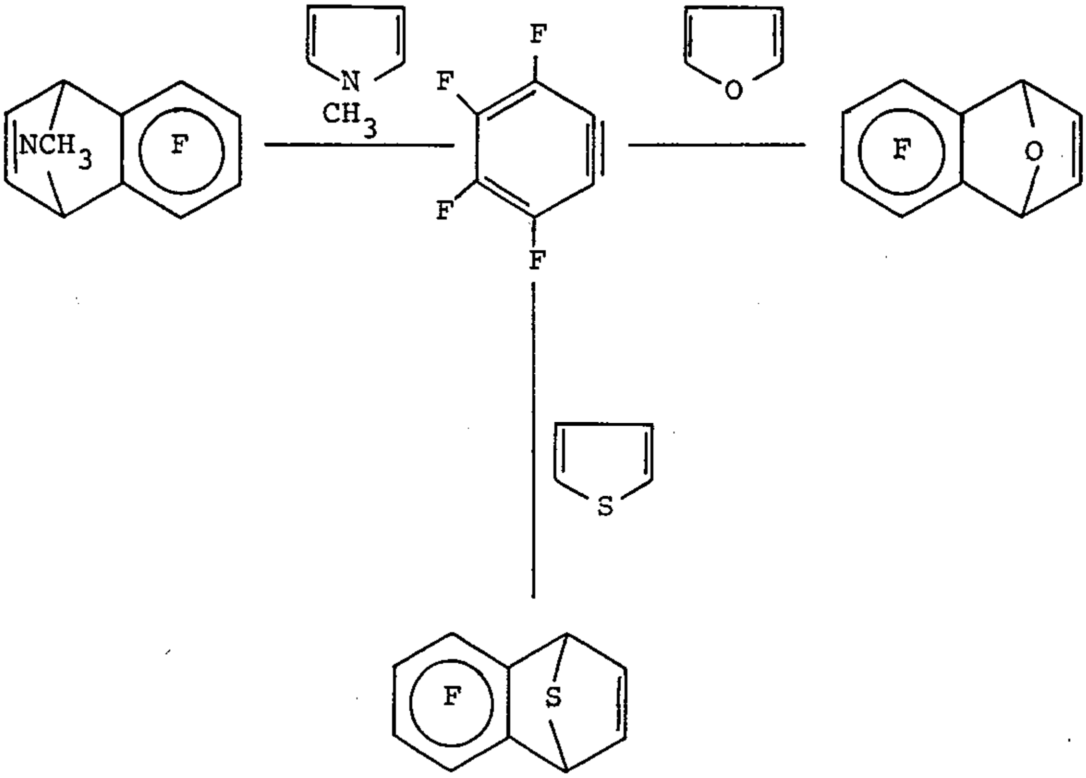
The relative ease with which hydrogen or another halogen bonded to a fluoroaromatic nucleus will undergo lithium/X exchange with n-butyllithium when compared to fluorine(15), has enabled a large number of polyfluoroaromatic lithium derivatives to be synthesized. For example, pentafluorophenyllithium can be obtained from the reaction of lithium amalgam with bromopentafluorobenzene in ether or furan at 0°C(16), or more conveniently by either lithium/hydrogen exchange with pentafluorobenzene(17) or by lithium/halogen exchange with halopentafluorobenzenes(16,18,19,20) using n-butyllithium:



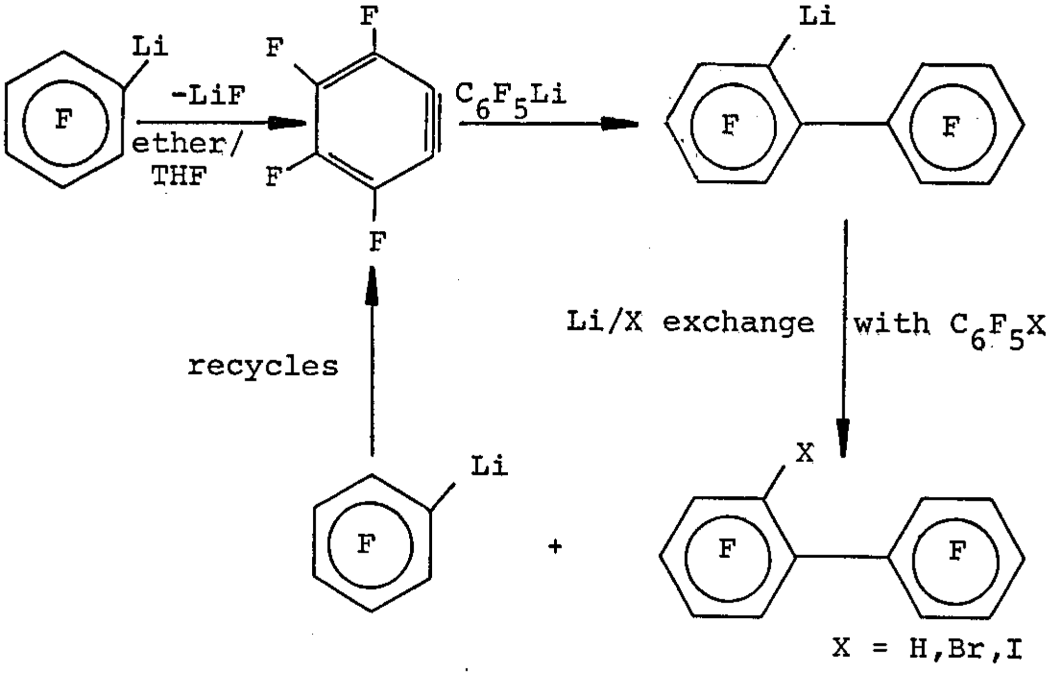
The exchange reactions all take place with considerable ease and proceed virtually quantitatively within the range of solvent used, varying from ether(16,17), ether/tetrahydrofuran(17,18) to a mixture of pure hydrocarbons(20). It was noticed that lithium/bromine exchange takes place in preference to lithium/hydrogen exchange in ether/hexane(21) as shown by the reaction sequence:



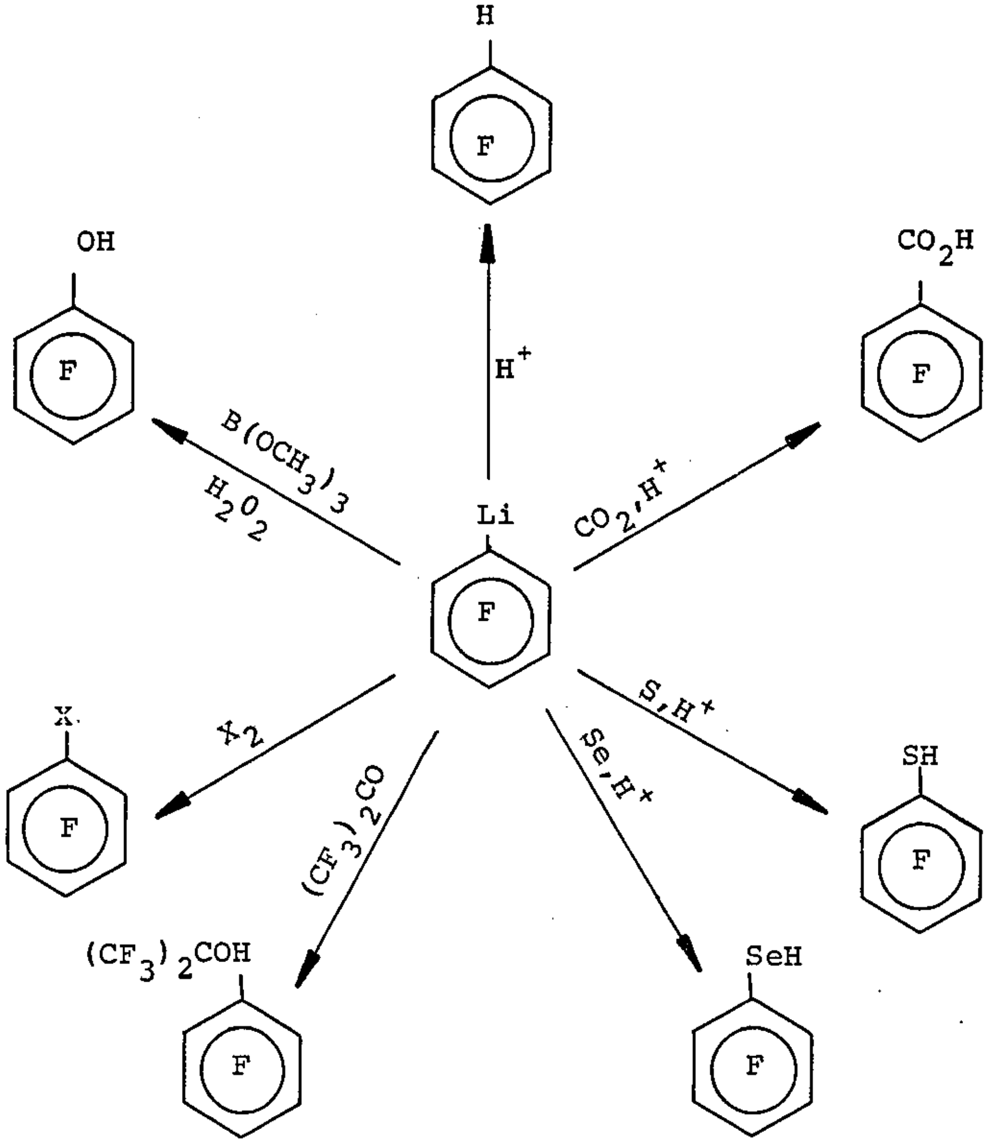
Pentafluorophenyllithium is thermally very unstable and decomposes by intramolecular loss of lithium fluoride apparently forming tetrafluorobenzyne in the solution; thus if the decomposition is allowed to occur in the presence of furan$^{(16)}$, thiophene or 1-methylpyrrole$^{(22)}$, 3,4-addition occurs to give derivatives of 1,2,3,4-tetrafluoro-5,8-dihydronaphthalene:



If, while in the presence of pentafluorobenzene$^{(23)}$, bromo- or iodo-pentafluorobenzene$^{(18)}$, pentafluorophenyllithium is allowed to decompose at about 0°C, a molecule of undecomposed pentafluorophenyllithium is found to add across the tetrafluorobenzyne to give 2-lithiononafluorobiphenyl which then undergoes lithium/hydrogen or halogen exchange with C_6F_5X giving 2-hydro- or 2-halononafluorobiphenyl in high yield

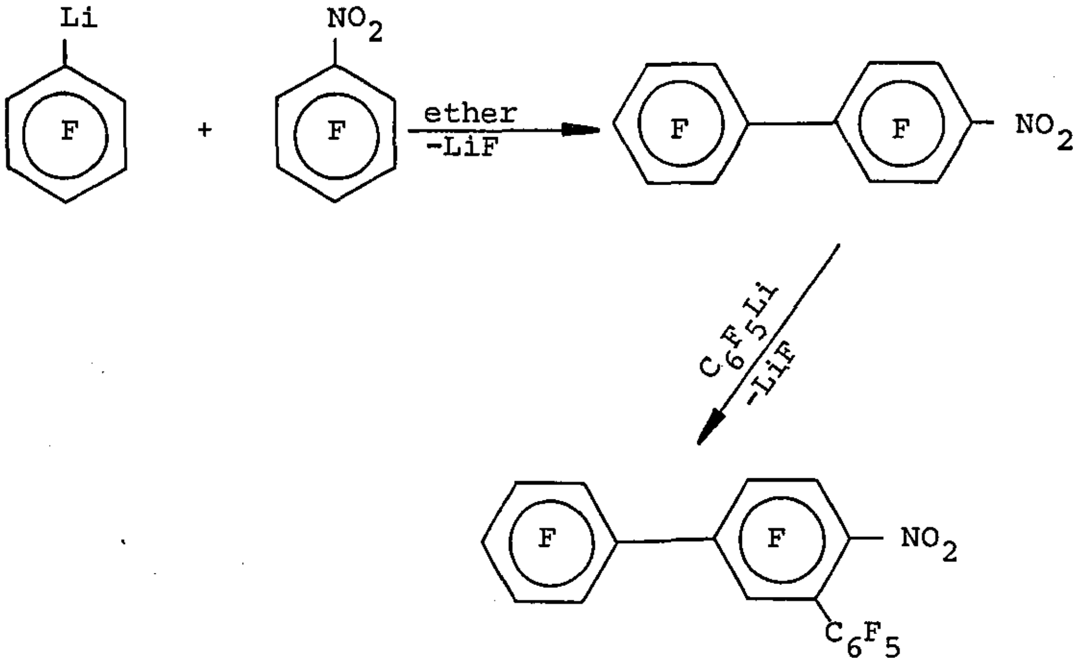


Pentafluorophenyllithium reacts readily with water, halogens, carbon dioxide$^{(16)}$, trimethylborate/hydrogen peroxide$^{(24)}$, hexafluoroacetone$^{(25)}$, sulphur$^{(26)}$ and selenium$^{(19)}$:

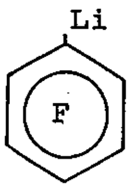


By allowing a metal or metalloid halide to react with pentafluorophenyllithium below -10 °C, good yields of pentafluorophenyl derivates have been obtained, for example, with boron(20), silicon(27), sulphur(28), iron(29), nickel(30), copper(31), tin(27) and mercury(32).

Pentafluorophenyllithium can be utilized as a source of the nucleophile $C_6F_5^-$ if low temperatures are used to prevent loss of lithium fluoride and consequent formation of tetrafluorobenzyne. Thus at -40 °C, pentafluorophenyllithium reacts with bromopentafluorobenzene in ether to give mainly a mixture of para-linked bromopolyfluoropolyphenyls, $C_6F_5(C_6F_4)_nC_6F_4Br$ (n = 1-5)(33), whereas the reaction with pentafluoronitrobenzene gives 4-nitrononafluorobiphenyl and 4-nitroperfluoro-m-terphenyl:(33)

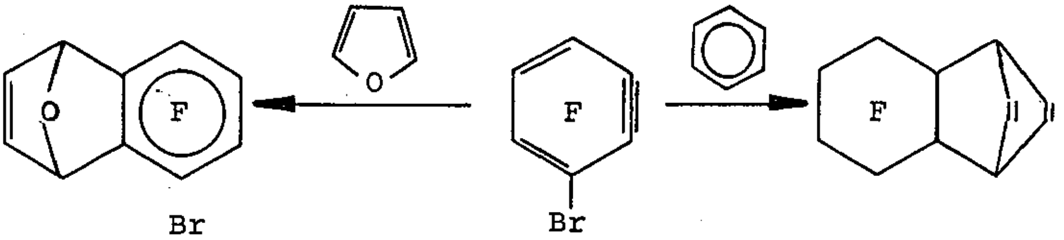


The pentafluorophenyl "anion" also replaces fluorine atoms in fluoro-olefins at -78°C, as with chlorotrifluoroethylene(33):

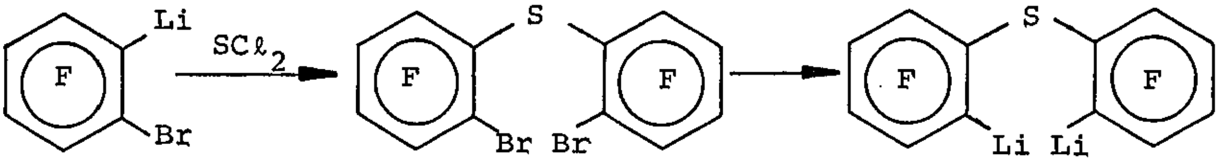


$$+ CF_2 = CFC\ell \longrightarrow (C_6F_5)CF = CC\ell(C_6F_5)$$

1,2-Dibromotetrafluorobenzene quantitatively forms a monolithio derivative in ether/hexane(18,34) at -78°C, furan(35) at -70°C and benzene(36) at 0°C. In furan(35) and benzene(36), lithium fluoride is eliminated intramolecularly to form 1-bromo-2,3-4-trifluorobenzyne and adducts similar to those obtained with tetrafluorobenzyne result:

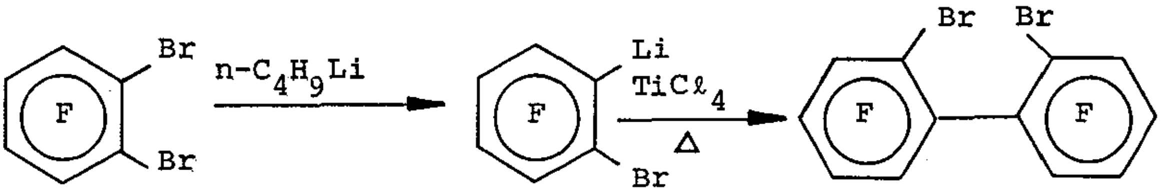


1-Lithio-2-bromotetrafluorobenzene forms various derivatives of sulphur(37), selenium(19), mercury(35), silicon(35), germanium(38) and tin(19). In some of these derivatives, the substitution of the bromine atoms in the aromatic ring enables further lithio derivatives to be readily synthesized and studied, for example(38):



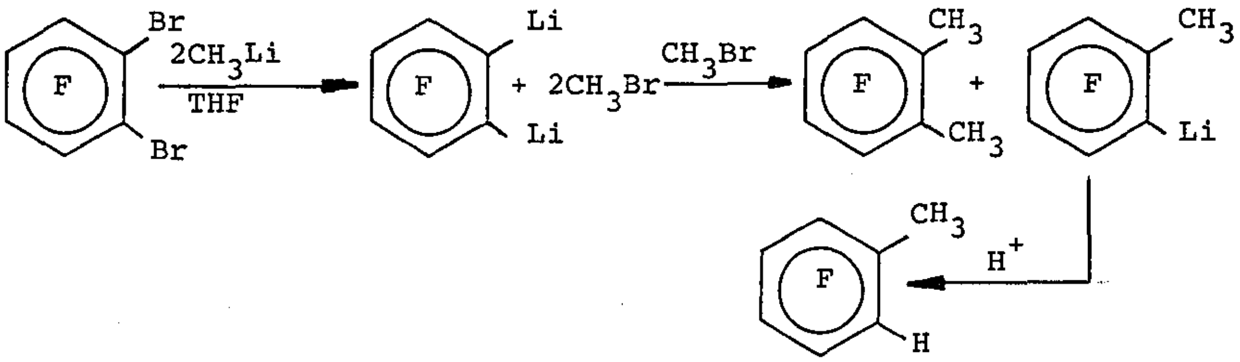
In this thesis several fluoroaromatic derivatives of silicon and Group V elements were prepared from the reaction of 1-lithio-2-bromotetrafluorobenzene with the corresponding metal chlorides. Further lithiation of these fluoroorganometallics, followed by treatment with the corresponding metal chlorides gave perfluoro-1,6-ditriptycenes.

1-Lithio-2-bromotetrafluorobenzene undergoes a coupling reaction in the presence of an excess of titanium tetrachloride, to give an almost quantitative yield of the synthetically useful 2,2'-dibromooctafluorobiphenyl(32):

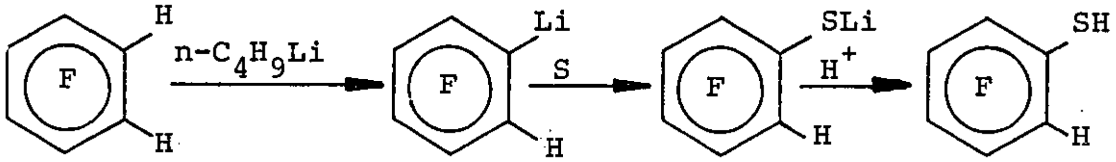


The attempts to prepare 1,2-dilithotetrafluorobenzene in tetrahydrofuran or diethylether from 1,2-dibromotetrafluorobenzene using two equivalents of n-butyllithium yielded a mixture of 1,2-dilithiotetrafluorobenzene and 1-lithio-2-bromotetrafluorobenzene as indicated by its hydrolysis(39). While the use of excess of n-butyllithium(2.4 equivalents)gave the 1,2-dilithio derivative (but, of course, the resulting reaction mixture still contained the excess n-butyllithium) which on hydrolysis gave 1,2,3,4-tetrafluorobenzene in 95% yield(39). However, in other reactions the excess n-butyllithium present introduces complications and, for example, on treatment with dimethylchlorosilane gave a complex mixture of at least seven products indicating that the excess n-butyllithium had reacted further with the initially formed silylated products(39).

Cullen(40) has reported that when 1,2-diiodotetrafluorobenzene is treated with methyllithium at -78°C in ether dilithiotetrafluorobenzene is formed which on addition of the appropriate metal chloride gives perfluoro-1,6-triptycenes of arsenic, antimony and bismuth. However, his data for the physical properties of $Sb_2(C_6F_4)_3$ disagree markedly with those obtained for our samples. Another report has demonstrated that the reaction of methyllithium with 1,2-dibromotetrafluorobenzene in ether gave incomplete conversion to the dilithio compound, and in tetrahydrofuran the alkylated product perfluoro-o-xylene and 2,3,4,5-tetrafluorotoluene were obtained(39):

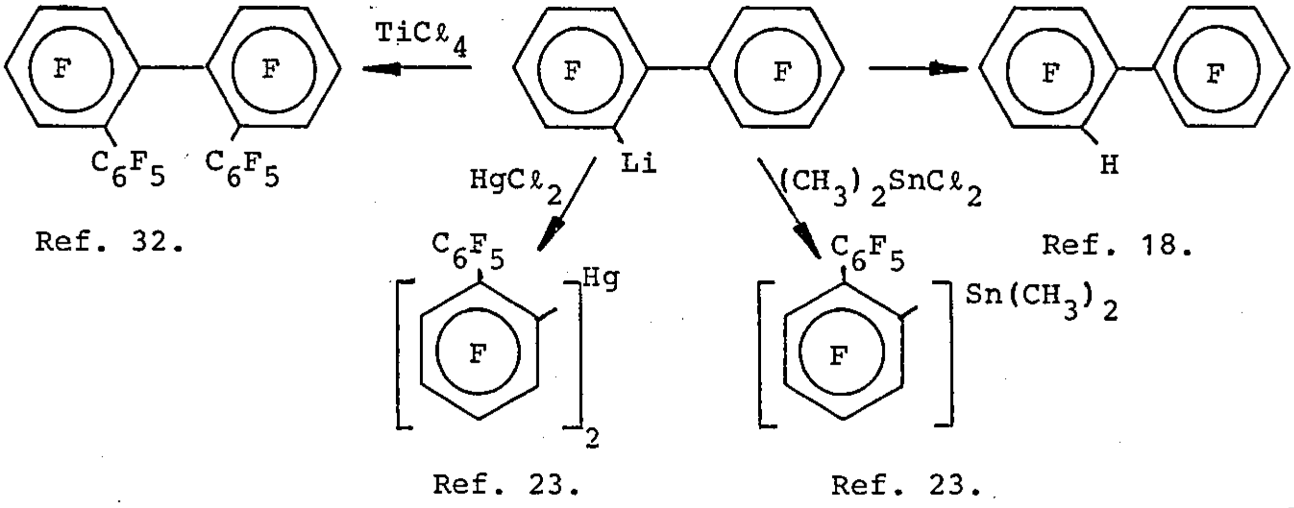


However, 1,4-dibromo-and 1,4-dihydrotetrafluorobenzenes react with n-butyllithium to give a mixture of the mono- and dilithio derivatives(17,21) depending on the solvent used. Generally, monolithiation is favoured in ether/hexane, while dilithiation occurs in tetrahydrofuran/hexane. Both the mono and dilithio species undergo the conventional reactions of aryllithium reagents(17,21). 1,2-Dihydrotetrafluorobenzene monolithiated readily in tetrahydrofuran/hexane solvents which has been demonstrated by its reaction with sulphur(26):

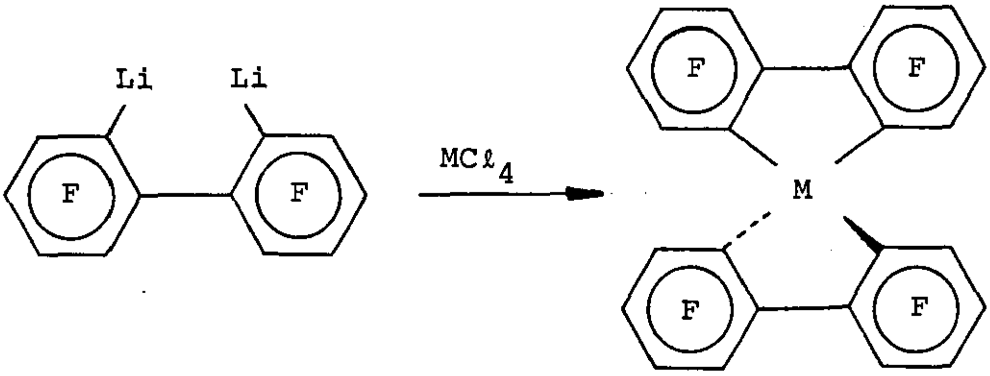


In this work the intermediate 1-lithio-2-hydrotetrafluorobenzene was reacted with arsenic trichloride when the corresponding arsenic derivative was obtained.

Lithium derivatives of polyfluorobiphenyls have been studied by several workers since 1964, and this has opened up an interesting new branch of fluoroaromatic chemistry in the synthesis of both organic and organometallic derivatives. Thus, 2-lithiononafluorobiphenyl has been prepared(18,23) by the action of n-butyllithium on 2-halononafluorobiphenyl and some of its chemistry is illustrated below:



2,2'-Dilithio-octafluorobiphenyl has been extensively studied(12,32,42,43) and is readily prepared by the reaction of n-butyllithium with 2,2'-dihydro-(43), 2,2'-dibromo- and 2,2'-diiodo-octafluorobiphenyls in ether/hexane or THF/hexane(12,32). It reacts with chlorine, bromine and iodine giving the corresponding 2,2'-dihalooctafluorobiphenyl and with water, 2,2'-dihydrooctafluorobiphenyl is obtained(12). 2,2'-Dilithio-octafluorobiphenyl also reacts with metal and metalloidal chlorides forming novel heterocyclic compounds for example:

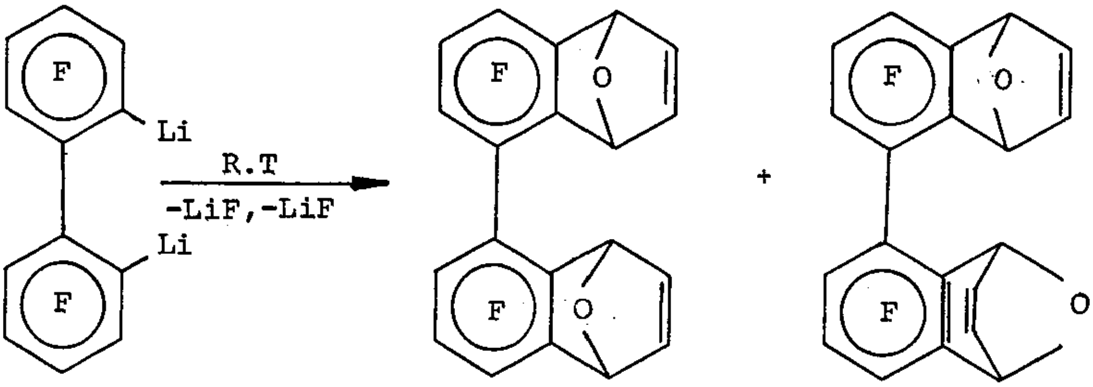


Ref. 12

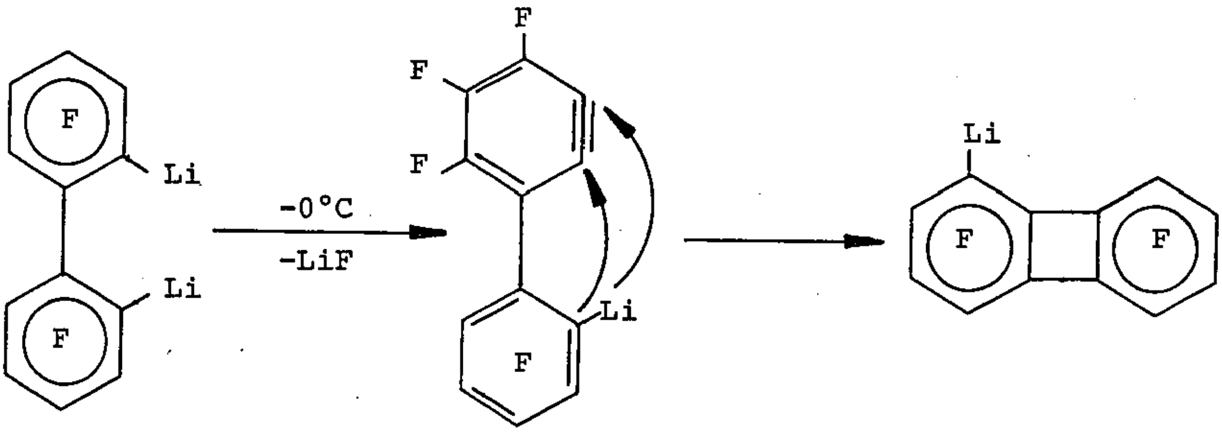
M = Si,Ge,Sn

These compounds are somewhat unusual because it was originally thought they would be sterically unstable due to the F---F interaction in the 6-6' positions. X-ray studies have shown that these fluorine atoms do indeed approach each other closer than twice the van der Waals radius of fluorine and some molecular distortion does occur. However, the heterocycles are still exceedingly stable thermally and, for example, the germanium derivative can be synthesized directly at 390°C(19).

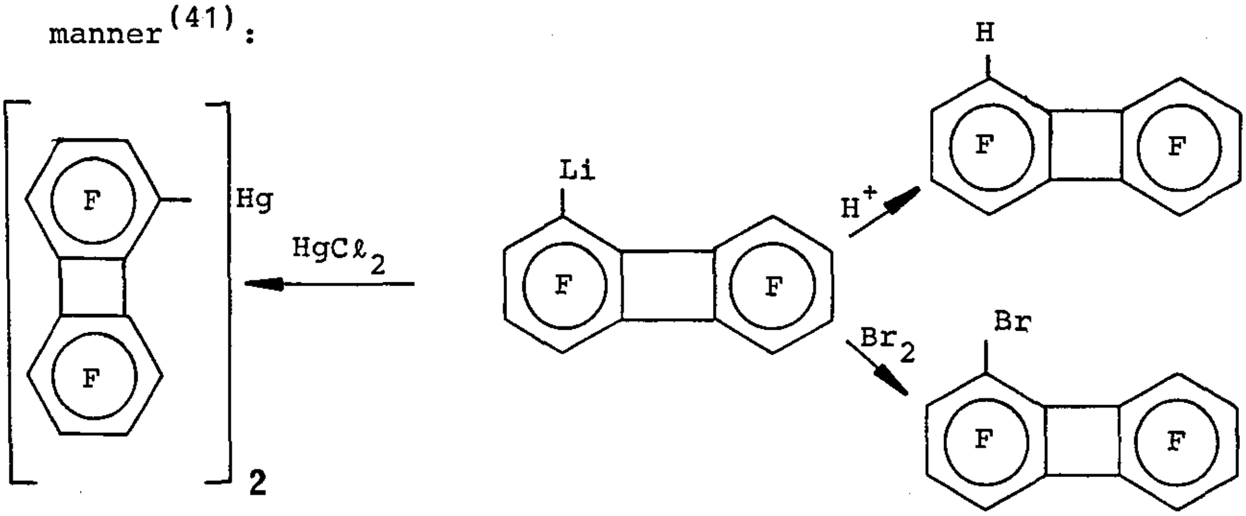
In the presence of furan at room temperature, 2,2'dilithiooctafluorobiphenyl eliminates lithium fluoride from each tetrafluorophenyl ring and two isomeric furan adducts are formed(41):



If the decomposition occurs at 0°C in the absence of a benzyne-trapping reagent, only one mole of lithium fluoride is eliminated and this is then followed by an unusual intramolecular addition of the intact half of the molecule to the benzyne(41):



1-Lithioheptafluorobiphenylene reacts with water, bromine and mercuric chloride, in the conventional manner(41):



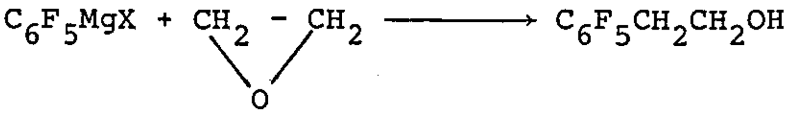
The greater stability of polyfluoroaromatic Grignard reagents compared with the corresponding lithium derivatives might suggest that the Grignards would be more suitable in polyfluoroaromatic syntheses since there is no need for strict temperature control during the reaction to prevent loss of fluoride ion. However, the formation of the Grignard reagent is considerably more solvent-dependent, and they are often more difficult to prepare than the corresponding lithium reagents; this has resulted in the preparation of relatively fewer polyfluoroaromatic Grignard reagents(19).

Pentafluorophenylmagnesium halides have been prepared by the action of magnesium on chloro-(44), bromo- and iodopentafluorobenzene(45) in ether or tetrahydrofuran and by exchange reaction using alkylmagnesium halides on pentafluorobenzene(17) and bromopentafluorobenzene(46).

For the use of chloropentafluorobenzene, activation of the magnesium by ethylene dibromide is sometimes required(44).

Solvent effects on the reactivity of pentafluorophenylmagnesium halides have been studied by its reaction with carbon dioxide(44,45,47) and ethylene oxide(48,49) in various solvents to give pentafluorobenzoic acid and 2-pentafluorophenylethanol after hydrolysis. It was found from these reactions that the highest yield of the products was obtained when the solvent was tetrahydrofuran.

$$C_6F_5MgX \xrightarrow[2.\ H^+]{1.\ CO_2} C_6F_5CO_2H \qquad X = C\ell,Br,I$$

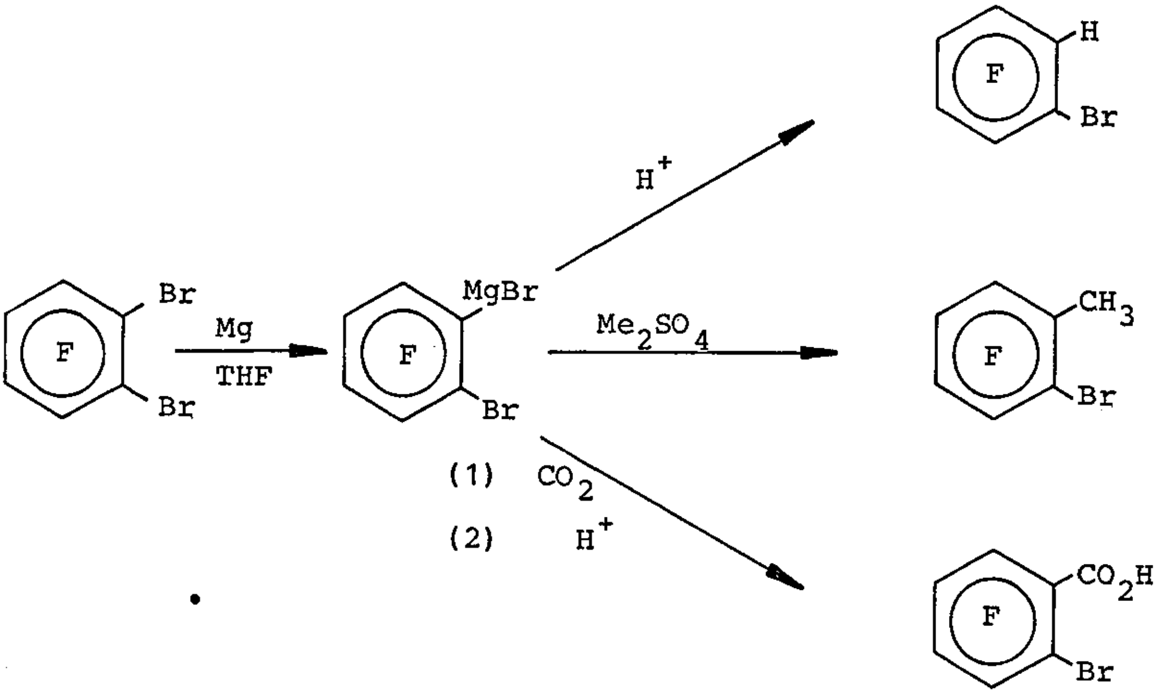


X = Cℓ,Br

However, the use of tetrahydrofuran has one drawback in that when the Grignard reagent is formed in it, nucleophilic reactions are favoured and troublesome polymeric by-products are obtained(44).

Numerous pentafluorophenyl derivatives of metals and metalloids have been obtained by reacting pentafluorophenylmagnesium halide with the appropriate metal or metalloidal halide, normally the chloride, in ether or tetrahydrofuran; for example, derivatives have been synthesized of boron(50), silicon(51), phosphorus(51), arsenic(51), antimony(51), mercury(52) and tin(53).

1,2-Dibromotetrafluorobenzene reacts with magnesium in ether(34), ether/tetrahydrofuran(18) and tetrahydrofuran(55) at 0°C, the mono-Grignard reagent being formed, which hydrolysed(18), and reacted with dimethylsulphate and carbon dioxide in the usual manner(54):



1,4-Dihydrotetrafluorobenzene forms both the mono- and di-Grignard derivatives when treated with ethylmagnesium bromide as shown by carbonation experiments; a mixture of both mono- and dicarboxylic acids were obtained(17). In contrast, 1,2-dihydrotetrafluorobenzene does not form even the mono-Grignard reagent under the same conditions(17).

Chapter 6

Disubstituted 1,6-Triptycenes of Silicon and the Group V Elements

Experimental.

The direct syntheses, and reactions with mercurials, were carried out in sealed, evacuated pyrex tubes which had been thoroughly baked out under vacuum using a free flame. A dry, nitrogen atmosphere was provided for those reactions involving the use of butyllithium. Diethyl ether and tetrahydrofuran were dried by refluxing over sodium wire and distilled under nitrogen immediately prior to use.

Ortho-phenylenemercury trimer was prepared, in about a 2% yield, as previously described in Chapter 2. 1,2-Dibromotetrafluorobenzene and 1,2,3,4-tetrafluorobenzene were purchased from Bristol Organics Limited.

Quoted analyses were carried out by Dornis and Kolbe, 4330 Mülheim/Ruhr and by the Micro-analytical Laboratory, Manchester University.

Reaction of 1,2-diiodobenzene with antimony.

1,2-Diiodobenzene (0.5 gm) and antimony (0.2 gm) were heated in a sealed tube at 300°C for 48 hours. The tube was then cooled, cut open and the contents extracted with ether. The ether extract was shaken with aqueous sodium thiosulphate and the separated organic phase dried with anhydrous magnesium sulphate; removal of the solvent gave a tiny amount of pale yellow solid which was shown to be mainly triphenylene from its mass spectrum.

Reaction of 1,2-dibromobenzene with antimony.

Similarly, when 1,2-dibromobenzene (0.5 gm) and antimony (0.2 gm) were heated at 300°C for 96 hours in a sealed tube, no 1,6-distibatriptycene resulted; much unchanged starting material was present in the tube.

Reaction of o-phenylenemercury trimer with antimony.

Powdered antimony was ground as fine as possible in an agate mortar before o-phenylenemercury was added to the mortar and the two ground carefully to an intimate mixture prior to being loaded into a reaction tube. The sealed, evacuated tube was heated to 260°C (below the m.pt. of the mercurial) for two hours when mercury droplets were visible on the inside. After cooling, the tube was cut open, the contents extracted with boiling hexane and the filtered solution evaporated to small volume. A tiny amount of colourless crystals of 1,6-distibatriptycene separated out overnight; the mother liquor was decanted off and crystals quickly washed with cold 40-60% petroleum ether before being dried in the open air, m.p. 254-255°C, yield 5%. (Found: C,48.9, 49.35; H,3.5, 3.6%; $C_{18}H_{12}Sb_2.0.5$ hexane, calcd.: C,48.9; H,3.7%).

The direct synthesis of perchloro-1,6-distibatriptycene.

Antimony (1 gm) and 1,2-diiodotetrachlorobenzene (1 gm) were heated in a sealed tube to 250°C for four hours. By arranging a slight temperature gradient in the oven it was possible to make most of SbI_3 co-product distil to the colder end of the tube leaving the essentially involatile mixture of perchloro-1,6-distibatriptycene and antimony at the other. After opening the tube the product was extracted with 5 or 6 aliquots (ca. 25 cm^3) of boiling dimethylformamide; the first aliquot contains virtually all of the remaining antimony triiodide and, if very deeply coloured, may be discarded. On concentrating the extracts by boiling, the perchloro-1,6-distibatriptycene separated as tiny crystals of the hemi-solvate (yield 5%); the analytical sample was washed twice with acetone and dried on a vacuum line at room temperature for one hour. (Found: C,25.7, 25.65; H,0.4, 0.4; N,0.7, 0.7; Cℓ,44.3%. $C_{18}C\ell_{12}Sb_2.0.5$ DMF, calcd.: C,25.4; H,0.4; N,0.7;

Cℓ,46.2%). The identity of the occluded dimethylformamide was confirmed by driving off the solvent in a mass spectrometer and measuring the mass of the peak at m/e = 73 (observed mass, 73.0538: calculated for $^{12}C_3H_7{}^{14}N^{16}O$: 73.0528).

The solvate does not melt below 320°C but loses the dimethylformamide above about 100°C; on rapid heating in a tiny bunsen flame a sample held in a melting point tube first melted and then exploded with an audible "crack". $Sb_2(C_6C\ell_4)_3$ is insoluble in boiling hexane, chloroform, alcohol, ethyl acetate and acetone. It dissolves in, and may be recrystallized from, hot pyridine and hot nitrobenzene.

The product $Sb_2(C_6C\ell_4)_3$ may also be extracted from the reaction residue by using 3 × 50 cm^3 aliquots of boiling nitrobenzene (after SbI_3 has been removed by boiling with 25 cm^3 of dimethylformamide). The tiny, glistening crystals obtained on boiling down the extracts contain half a mole of nitrobenzene (Found: C,26.9; H,0.3; N,0.75; Cℓ,45.1. $C_{18}C\ell_{12}Sb_2.0.5(C_6H_5NO_2)$, calcd.: C,26.6; H,0.3; N,0.7; Cℓ,45.0%).

On heating 52.8 mg of solvate in a vacuum at 150°C for 45 minutes a weight loss of 3.6 mg (6.8%) was recorded; calculated for loss of half a mole of nitrobenzene, 6.5%. The remaining solid was subjected to a full microanalysis (Found: C,24.1; H,0.0; N,0.0; Cℓ,46.8, 47.1. $C_{18}C\ell_{12}Sb_2$ calcd.: C,24.4; H,0.0; N,0.0; Cℓ,48.1%).

Similarly when recrystallized from pyridine or diethylformamide $Sb_2(C_6Cl_4)_3$ separates out as hemisolvates (Found: C,25.65; H,0.4; N,0.9; Cℓ,45.2%. $C_{18}Cl_{12}Sb_2 \cdot 0.5\ C_5H_5N$, calcd.: C,26.6; H,0.3; N,0.8; Cℓ,46.0%. Found: C,26.55; H,0.7; N,0.8; Cℓ,43.4%. $C_{18}Cl_{12}Sb_2 \cdot 0.5$ DEF, calcd.: C,26.3; H,0.6; N,0.75; Cℓ,45.5%). As can be seen from the analytical figures some problems were encountered with the accurate determination of chlorine in these polychloro-aromatic derivatives; almost always the figures obtained were 1-2% low.

The direct synthesis of perfluoro-1,6-distibatriptycene.

Approximately 1 gm samples of powdered antimony and 1,2-diiodotetrafluorobenzene were heated together in a sealed tube at 250°C overnight. On cooling, the tube was cut open and the solid product crushed to a powder before being extracted with 4 × 25 cm^3 aliquots of 60-80°C petroleum ether in which the co-product antimony triiodide is practically insoluble. The slight yellow or pink colours sometimes observed in the extracts can be removed by boiling with charcoal; the yield of recrystallized product is about 60%. An analytical sample was obtained by heating the crystals from petroleum ether to 140°C in a vacuum to drive off the trapped solvent, m.p. 258-259°C (Lit.(1) 155°C) (Found: C,31.1, 31.4; H,0.0, 0.0; F,33.8,33.0%.

$C_{18}F_{12}Sb_2$ calcd.: C,31.4; H,0.0; F,33.2%). A small quantity of product was lost by sublimation during the drying procedure which lasted for 10-20 minutes.

Reaction of antimony with mercuric tetrafluorophthalate.

A mixture of antimony (1 gm) and mercuric tetrafluorophthalate (1 gm) was heated on a vacuum line. Extraction of the residues with 60-80°C petroleum ether gave a small quantity (ca. 5%) of perfluoro-1,6-distibatriptycene solvate identified by comparison of its infrared spectrum with that of an authentic sample.

Some reactions of perfluoro-1,6-distibatriptycene.

(i) Iodine.

A chloroform solution of perfluoro-1,6-distibatriptycene was refluxed with an excess of iodine for two hours. Removal of the solvent gave only the starting material as a white solid melting at 258°C.

(ii) Methyl iodide.

A mixture of perfluoro-1,6-distibatriptycene (0.5 gm) and methyl iodide (50 mℓ) was refluxed for two and a half hours, after which time the solvent methyl iodide was removed and the remaining solid dried under vacuum, m.p. 258-259°C. A portion of the solid was shaken with distilled water which was then tested with silver nitrate; no silver iodide was precipitated. Hence under these conditions there appeared to be no reaction with methyl iodide.

(iii) Chlorine.

When chlorine was passed into a carbon tetrachloride solution of perfluoro-1,6-distibatriptycene the solution suddenly became turbid after a few seconds at room temperature and began to precipitate a white solid. After 5 minutes the chlorine cylinder was closed and the solid collected, after washing with copious amounts of carbon tetrachloride. The analytical sample of $Sb_2(C_6F_4)_3(OH_2)_2C\ell_4$ was recrystallized from an un-dried $CC\ell_4/CHC\ell_3$ mixture by cooling in a refrigerator for two weeks (Found: C,24.9, 25.0, 25.0; H,0.1, 0.4, 0.3; Cℓ,16.5; F,25.2, 25.9, 25.8%. $Sb_2C_{18}F_{12}H_4O_2C\ell_4$ calcd.: C,25.0; H,0.5; Cℓ,16.4; F,26.3%). The unhydrated compound, $Sb_2(C_6F_4)_3C\ell_4$ has a very sharp melting-decomposition point of 184°C and is very soluble in ether, alcohol, chloroform and toluene; it is sparingly soluble in 60-80°C petroleum ether and carbon tetrachloride. When the chloride is in contact with damp solvents a peak begins to develop at 3515 cm^{-1} in the infrared spectrum and the compound then analyses as the dihydrate as shown above.

(iv) Nitric acid.

Perfluoro-1,6-distibatriptycene did not dissolve in concentrated nitric acid until the boiling point had almost been reached when it dissolved quite readily. The solution was diluted with about twice its volume of distilled water, filtered and set aside for two days at room temperature (or overnight in a refrigerator).

The mass of tiny, needle-like crystals of the dinitrate, $Sb_2(C_6F_4)_3(OH)_2(NO_3)_2$ was removed from the mother liquor and washed quickly with a small amount of cold water before being dried at room temperature on a vacuum line (Found: C,25.3, 25.3; H,0.6, 0.6; N,2.25,2.15; F,26.0%. $Sb_2C_{18}F_{12}(NO)_2(OH)_2$ calcd.: C,25.6; H,0.2; N,3.3; F,26.6%).

The compound is soluble in warm water and when such solutions are left at room temperature for an hour or so, small bubbles of gas (possibly oxygen) can be seen in the liquid. As the samples were repeatedly recrystallized, the nitrogen content decreased from 2.25 to 0.8 to 0.6% and, finally, to about 0.3% (this final value is only approximate and represents, essentially, a nitrogen-positive test only since the determination was at the limit of sensitivity of the method). At this point the analyses corresponded to the tetrahydroxo compound $Sb_2(C_6F_4)_3(OH)_4$ (Found: C,28.4; H,0.3; (N,0.3); F,29.9; Sb + O by difference, 41.1%; $Sb_2C_{18}F_{12}H_4O_4$ calcd.: C,28.6; H,0.5; N,0.0; F,30.2; Sb + O, 40.7%). The melting-decomposition point was not sharp and occurred at about 310°C.

Reaction of perfluoro-1,6-distibatriptycene tetrachloride with water.

A sample of $Sb_2(C_6F_4)_3C\ell_4$ was hydrolysed by boiling with three aliquots of distilled water, each aliquot of excess water being decanted from the insoluble solid before more water was added. The isolated solid $Sb_2(C_6F_4)_3O_2$, after drying overnight at 70°C, had a rather poorly defined melting-decomposition point of about 336°C; a sublimate of needle crystals ($Sb_2(C_6F_4)_3$?) was evident in the melting point tube some 20°C below the melting point (Found: C,29.3, 29.3; H,0.1, 0.1; F,31.7%. $Sb_2C_{18}F_{12}O_2$ calcd.: C,30.0; H,0.0; F,31.7%). When heated in a vacuum the oxide gave a white sublimate which the infrared and mass spectra showed was pure perfluoro-1,6-distibatriptycene. On being heated on a mass spectral probe the oxide gave no spectrum up to 250°C at which point the spectrum of $Sb_2(C_6F_4)_3$ began to appear.

Attempts to make $Sb_2(C_6F_4)_2O$

(i) 1,2-Diiodotetrafluorobenzene was heated in a sealed tube at 250°C with approximately equal amounts of antimony powder and Sb_2O_3. After cooling and opening the tube, the contents were extracted with boiling 60-80°C petroleum ether and the solution clarified with charcoal. The resulting crystals, which melted at 257-258°C, were of $Sb_2(C_6F_4)_3$; a minor second crop of crystals melted, before recrystallization, at 255°C. Thus no $Sb_2(C_6F_4)_2O$ had been formed under similar conditions to those which produced $As_2(C_6F_4)_2O^{(2)}$.

Furthermore, it is obvious that perfluoro-1,6-distibatriptycene does not react with Sb_2O_3.

(ii) Approximately 0.5 gm of perfluoro-1,6-distibatriptycene were heated with two drops of distilled water in a sealed, evacuated tube; there was no apparent reaction after five hours at 250°C. After 18 hours at 300°C the tube was opened and the solid remaining crystallized from petroleum ether, m.p. 257-258°C; before purification the melting point was 254-257°C. Hence there is no reaction with water under these conditions.

(iii) Oxidation of approximately 1 gm of perfluoro-1,6-distibatriptycene with 5 gm potassium dichromate, 12 cm^3 water, 5 cm^3 concentrated sulphuric acid and 12 cm^3 of glacial acetic acid gave only one or two crystals of impure starting material on neutralizing the mixture with sodium bicarbonate and extracting with diethyl ether. Using these reagents tris(pentafluorophenyl)phosphine gave the oxide, $(C_6F_5)_3PO$(3).

The Step-wise-Syntheses of Perfluoro-1,6-Disubstituted Triptycenes containing Silicon and Group V elements.

Preparation of tris(2-bromotetrafluorophenyl)methylsilane.

n-Butyllithium (8.52 mℓ; 20 mmole) was added to a stirred solution of 1,2-dibromotetrafluorobenzene

(6.16 gm; 20 mmole) in ether (100 mℓ) at -78°C; after half an hour methyltrichlorosilane (0.77 mℓ; 6.66 mmole) was added, stirring being continued for 10 minutes before the bath was removed and the mixture allowed to warm up to room temperature; filtration and removal of the solvent gave colourless crystals of tris(2-bromotetrafluorophenyl)methylsilane, m.p. 130-131°C; yield 32%. (Found: C,31.1; H,0.4; F,31.5%. $C_{18}F_{12}Br_3(SiMe)$ calcd.: C.31.4; H,0.4; F,31.4%).

Preparation of 1,6-dimethyl-dodecafluoro-1,6-disilatriptycene.

A solution of tris(2-bromotetrafluorophenyl)-methylsilane (4,6 gm; 6.32 mmole) in ether (200 mℓ) was reacted with n-butyllithium (8.1 mℓ; 18.96 mmole) at -78°C for one hour with stirring. Methyltrichlorosilane (0.74 mℓ; 6.32 mmole) was added and after working up the reaction mixture as described above, a yellow solid was obtained which recrystallized from alcohol to give 1,6-dimethyl-dodecafluoro-1,6-disilatriptycene, m.p. 252-253°C; yield 15%. (Found: C,45.3; H,1.0; F,43.1%. $C_{18}F_{12}(SiMe)_2$ calcd.: C,45.3; H,1.1; F,43.0%).

Preparation of tris(2-bromotetrafluorophenyl)phosphine.

n-Butyllithium (8.52 mℓ of a hexane solution; 20 mmole) was added to a solution of 1,2-dibromotetrafluorobenzene (6.16 gm; 20 mmole) in dry ether (100 mℓ) at -78°C and the mixture stirred for half an hour; phosphorus trichloride (0.5 mℓ; 6.66 mmole) was then added and after 5 minutes the cold bath removed to allow the stirred mixture to attain room temperature. After two hours the lithium chloride was filtered off and the ether removed under reduced pressure to give colourless crystals (yield 27%) of tris(2-bromotetrafluorophenyl)-phosphine. Recrystallization from ethanol gave an analytical sample melting at 164-165°C (Found: C,30.6; F,31.5; Br,33.35%. $C_{18}F_{12}Br_3P$ calcd.: C,30.2; F,31.0; Br,33.5%).

Preparation of perfluoro-1,6-diphosphatriptycene.

Tris(2-bromotetrafluorophenyl)phosphine (3 gm; 4.2 mmole) was dissolved in 100 mℓ of dry ether and cooled to -78°C before butyllithium (5.38 mℓ; 12.6 mmole) was added as a hexane solution; after one hour phosphorus trichloride (0.36 mℓ; 4.2 mmole) was added and the cold bath removed to allow the clear,stirred solution to warm up to room temperature. After one hour the mixture was filtered and the ether removed under reduced pressure to leave an oily residue which, after boiling with 5 mℓ of 40-60°C petroleum ether, filtering and cooling in a refrigerator gave colourless crystals of perfluoro-1,6-diphosphatriptycene (yield 5%), m.p. 208-209°C (Lit.(4) 160°C) (Found; C,42.65; P,12.3%. $C_{18}F_{12}P_2$ calcd.: C,42.7; P,12.2%).

Preparation of tris(2-bromotetrafluorophenyl)arsenic.

A solution of 1,2-dibromotetrafluorobenzene (6.16 gm; 20 mmole) in dry ether (100 mℓ) was stirred with n-butyllithium (8.52 mℓ of a hexane solution; 20 mmole) at -78°C for half an hour. Arsenic trichloride (0.74 mℓ; 6.66 mmole) was then added; after 5 minutes the cold bath was removed and the mixture allowed to warm up to room temperature when filtration and removal of the solvent gave colourless crystals of tris(2-bromotetrafluorophenyl)arsenic (yield 30%), m.p. 161-162°C (Found: C,28.8; Br,31.2%. $C_{18}F_{12}Br_3As$ calcd.: C,28.5; Br,31.6%).

Preparation of perfluoro-1,6-diarsatriptycene.

Tris(2-bromotetrafluorophenyl)arsenic (2.88 gm; 3.8 mmole) was dissolved in 100 mℓ of dry ether and cooled to -78°C before n-butyllithium 4.87 mℓ; 11.4 mmole) was added and the mixture stirred for one hour. Arsenic trichloride (0.30 mℓ; 3.8 mmole) was added and the clear, stirred solution allowed to warm up slowly to room temperature; filtration and removal of solvent gave an oily residue from which perfluoro-1,6-diarsatriptycene (yield 5%) was extracted, with boiling 40-60°C petroleum ether, as colourless crystals; m.p. 206-207°C (Lit.(1) 200°C) (Found: C,36.0; F,38.5%. $C_{18}F_{12}As_2$ calcd.: C,36.4; F,38.4%).

Preparation of perfluoro-1,6-arsaphosphatriptycene.

A mixture of tris(2-bromotetrafluorophenyl)arsenic (3.8 gm; 5 mmole) in ether (150ℓm) and n-butyllithium (6.4 mℓ; 15 mmole) was stirred for one hour at -78°C, then phosphorus trichloride (0.44 mℓ; 5 mmole) added before the pale yellow solution was allowed to warm up to room temperature; filtration and removing the solvent under vacuum, gave an oily residue. On boiling this residue with 40-60°C petroleum ether, filtration and cooling gave colourless crystals of perfluoro-1,6-arsaphosphatriptycene (yield 7%) m.p. 214-215°C (Found: C,39.8, 39.6; F,39.4, 39.7; P,6.05% $C_{18}F_{12}PAs$ calcd.: C,39.5; F,41.4; P,5.6%).

Preparation of tris(2-bromotetrafluorophenyl)antimony,

A solution of 1,2-dibromotetrafluorobenzene (6.16 gm; 20 mmole) in 100 mℓ of dry ether was reacted with n-butyllithium (10 mℓ; 20 mmole) at -78°C;after half an hour a solution of antimony trichloride (1.5 gm; 6.66 mmole) in ether (20 mℓ) was added and the mixture, after working up in the usual manner, gave tris(2-bromotetrafluorophenyl)antimony (yield 27%). The analytical sample was recrystallized from ethanol, m.p. 134-135°C (Found: C,26.9; Br,29.8%. $C_{18}F_{12}Br_3Sb$ calcd.: C,26.8; Br,29.75%).

Preparation of perfluoro-1,6-distibatriptycene.

Reaction of a solution of tris(2-bromotetrafluorophenyl)antimony (3.9 gm; 4.84 mmole) in ether (150 mℓ) with n-butyllithium (6.20 mℓ as a hexane solution; 14.52 mmole) at -78°C for one hour, followed by the addition of a solution of antimony trichloride (1.11 gm; 4.84 mmole) in 20 mℓ of ether, and working up the reaction mixture as described before, gave an oily residue from which, perfluoro-1,6-distibtriptycene (yield 2%) was extracted with 40-60°C petroleum ether as colourless crystals, m.p. 258-259°C (Lit.(1) 155°C) (Found: C,31.4; F,33.0%. $C_{18}F_{12}Sb_2$ calcd.: C,31.4; F.33.2%).

Preparation of perfluoro-1,6-arsastibatriptycene.

A solution of tris(2-bromotetrafluorophenyl)arsenic (4 gm; 5.27 mmole) in 150 mℓ of ether was stirred with n-butyllithium (6.8 mℓ; 15.81 mmole) at -78°C; after one hour, a solution of antimony trichloride (1.2 gm; 5.27 mmole) in ether (20 mℓ) was added. The mixture was allowed to warm up to room temperature and then filtered; removal of the solvent gave a brown-yellowish oil from which perfluoro-1,6-arsastibatriptycene was extracted with 40-60°C petroleum ether (yield 7%) as pale yellow crystals, m.p. 222-223°C (Found: C,34.4; H,0.1%. $C_{18}F_{12}AsSb$ calcd.: C,33.7; H,0.0%).

Preparation of perfluoro-1,6-phosphastibatriptycene.

Similarly, a solution of tris(2-bromotetrafluorophenyl)phosphine (5.47 gm; 7.48 mmole) in ether (150 mℓ) was reacted with n-butyllithium (9.81 mℓ, 22.45 mmole) at -78°C for one hour and then a solution of antimony trichloride (1.7 gm; 7.48 mmole) in ether (20 mℓ) was added; after working up the reaction mixture as usual, a brown solid was obtained. Perfluoro-1,6-phosphastibatriptycene was extracted from the latter with 40-60°C petroleum ether (yield 6%), m.p. 198-199°C (Found; C,37.6; H,0.1; F,38.1, 38.3; P,5.0%. $C_{18}F_{12}PSb$ calcd.: C,36,2; H,0.0; F,38.2; P,5.2%).

Preparation of tris(2-bromotetrafluorophenyl)bismuth.

A mixture of 1,2-dibromotetrafluorobenzene (6.16 gm; 20 mmole) in 100 mℓ of ether and n-butyllithium (10 mℓ; 20 mmole) was stirred at -78°C for half an hour. A solution of bismuth trichloride (2.08 gm; 6.66 mmole) in ether (20 mℓ) was then added and stirring continued for 15 minutes; warming up the mixture to room temperature, filtration and removal of the solvent gave colourless crystals of tris(2-bromotetrafluorophenyl)bismuth (yield 50%), m.p. 134-136°C, which was not stable enough to carry out carbon and fluorine analyses since it readily lost all its C_6F_4Br groups on standing in the air for a few hours. It was analysed using mass spectroscopy.

Preparation of perfluoro-1,6-dibismuthtriptycene.

Tris(2-bromotetrafluorophenyl)bismuth (3 gm; 3.36 mmole) was prepared as described above and lithiated directly in its preparation vessel without prior isolation, by the addition of n-butyllithium (4.30 mℓ; 10.2 mmole); after one hour, bismuth trichloride (1.05 gm; 3.6 mmole) was added and the orange-yellow mixture allowed to reach room temperature when removal of the solvent gave an orange solid which recrystallized from diethylether to give colourless crystals of perfluoro-1,6-dibismuthtriptycene, m.p. 314°C (Lit.(1) > 300°C decomposition); yield 10%. (Found: C,25.1; H,0.1; F,25.6%. $C_{18}F_{12}Bi_2$ calcd.: C,25.1; H,0.0; F,26.4%). The analytical data were obtained on a sample which had been heated to 100°C under vacuum (10^{-4} mm Hg) for approximately two hours to drive off adhering solvent.

Lithiation of tris(2-bromotetrafluorophenyl)arsenic.

A solution of tris(2-bromotetrafluorophenyl)arsenic (2.27 gm; 3 mmole) in dry ether (100 mℓ) was treated with n-butyllithium (4.26 mℓ; 9 mmole) at -78°C. The mixture was stirred for 40 minutes before being hydrolysed with distilled water. On warming to room temperature, the ether layer was removed and evaporated to give 1.0 gm of tris(2-hydrotetrafluorophenyl)arsenic. The analytical sample was recrystallized from ethanol, m.p. 139-140°C; yield 64%. (Found: C,41.5; H,0.6; Br,0.0%. $C_{18}F_{12}H_3As$ calcd.; 41.4; H,0.6; Br,0.0%).

Preparation of tris(2-hydrotetrafluorophenyl)arsenic from 1,2,3,4-tetrafluorobenzene.

A solution of 1,2,3,4-tetrafluorobenzene (5 gm; 33.3 mmole) in dry tetrahydrofuran (150 mℓ) was treated with n-butyllithium (14.24 mℓ; 33.3 mmole) at -95°C giving a clear, yellow-orange solution. After 25 minutes of stirring, arsenic trichloride (0.93 mℓ; 11.1 mmole) was added and the cold bath removed allowing the mixture to warm up slowly to room temperature. Filtration and removal of solvent gave a white solid, m.p. 139-140°C (yield 17%) which had an infrared spectrum identical to that of the sample described above.

Attempted preparation of perfluoro-1,6-diarsatriptycene from tris(2-hydrotetrafluorophenyl)arsenic.

Treatment of tris(2-hydrotetrafluorophenyl)arsenic (2.5 gm; 4.79 mmole) with n-butyllithium (6.14 mℓ; 14.37 mmole) in tetrahydrofuran (100 mℓ) at -95°C for one hour, followed by addition of arsenic trichloride, gave only unidentified oils and unreacted starting material on work-up of the reaction mixture.

Retention of solvent by perfluoro-1,6-disubstituted triptycenes.

Prior to analysis all the compounds after recrystallization were heated in an oven to about 80°C for at least two hours to drive off adhering solvent; the following compounds seemed to retain solvent the most strongly:

Perfluoro-1,6-disbismuthtriptycene.

$Bi_2(C_6F_4)_3$ when recrystallized from diethyl ether and dried in the oven for two hours the crystals still contained half a mole of ether (Found: C,27.0; H,0.6%. $C_{18}F_{12}Bi_2.0.5(C_2H_5)_2O$ calcd.: C,26.7; H,0.6%). C-H stretching frequencies occurred at 2955, 2920 and 2865 cm^{-1} in the infrared spectrum.

Perfluoro-1,6-phosphastibatriptycene.

When $PSb(C_6F_4)_3$ was recrystallized from ethanol the melting point dropped from 198-199°C to 165°C. Again half a mole of ethanol seemed to be strongly retained on crystallization (Found: C,37.9; H,0.4; F,37.3%. $C_{18}F_{12}PSb.0.5C_2H_5OH$ calcd.: C,36.8; H,0.5; F,36.8%).

Perfluoro-1,6-distibatriptycene.

(i) If the sample of $Sb_2(C_6F_4)_3$ was recrystallized from hexane and air-dried at room temperature the following typical analytical figures were obtained: Found: C,33.9, 34.1; H,0.9, 0.9; F,25.3,25.4%. $C_{18}F_{12}Sb_2$. 0.5 hexane calcd.: C,34.5; H,1.0; F,31.2%. These samples still melted at 258-259°C presumably because the hexane was driven off at some lower temperature and the recorded m.p. was that of unsolvated $Sb_2(C_6F_4)_3$. The low fluorine figures quoted above typify the extreme problems several different microanalysts had in obtaining meaningful data for this compound unless great care was taken; apparently, this stems from the simultaneous presence of both fluorine and antimony. Sharp melting points and identical mass spectra for the various samples showed that it was unlikely the decrepancies in analysis arose from impure samples.

The perfluoro-1,6-distibatriptycene-hexane solvate (110.988 mg) was heated in an open tube to 70°C and the weight loss measured after varying times: 5.121 mg loss in half an hour (4.61%), 6.482 mg loss in one hour (5.84%), 6.520 mg loss in two and a half hours (5.87%) and 6.519 mg loss in 24 hours (5.87%). The calculated loss for removal of all hexane from $Sb_2(C_6F_4)_3.0.5(C_6H_{14})$ is 5.90%. The temperature of 70°C was chosen for heating because samples of $Sb_2(C_6F_4)_3$ showed long-term weight stability whereas at 100°C slow sublimation out of the weighing bottles occurred to the extent of about 200 μg per day.

Hexane is slowly lost from the solvent on standing at room temperature. A 95.691 mg sample left in an open tube at 17-20°C lost 0.387 mg of hexane after two days (6.8% dissociation), 3.77 mg after eight days (66.9%), 5.413 mg after two weeks (95.9%) and 5.533 mg after six weeks (98.0%). The loss in weight as a function of days is shown in Figure (6.32).

(ii) Crystallization of a hot solution of perfluoro-

1,6-distibatriptycene in cyclohexane produced a crop of tiny crystals which lost their lustre and collapsed to a powdery solid on heating to 70°C in an oven. On monitoring the weight loss which occurred it was apparent that the cyclohexane solvate lost solvent more slowly than the n-hexane solvate described above. A sample of 49.178 mg lost 0.232 mg after half an hour at 70°C (0.47% loss), 0.664 mg after one and a half hours (1.35%) and 2.859 mg after seventeen hours (5.81%). Calculated loss for removal of all the cyclohexane from $Sb_2(C_6F_4)_3 \cdot$ 0.5 cyclohexane is 5.76%. Analysis confirmed the presence of half a mole of cyclohexane in the solvate (Found: C,34.5; H,0.8; F,31.2. $C_{21}H_6F_{12}Sb_2$ calcd.: C,34.6; H,0.8; F,31.2%).

(iii) Perfluoro-1,6-distibatriptycene is very soluble in chloroform and the solvent had to be allowed to evaporate off completely at room temperature in order to isolate the solvate. A sample of solvate which had been allowed to stand overnight in the air to dry completely, showed evidence of efflorescence in that the solid had become somewhat opaque instead of remaining as transparent crystals. On heating to 70°C a weighed sample collapsed to a white powder as the remaining chloroform was driven off. Although the solid behaved as a solvate in initially forming crystalline material which became white and amorphous on heating, the weight loss (4.82%) was considerably less than the loss calculated for half a mole of chloroform (7.99%). If a solvate had been formed the discrepancy between the above figures must represent the extent of efflorescence which occurred during the overnight period whilst the solid was drying at room temperature. The solid which separated from acetone behaved in a similar manner to this chloroform solvate in not retaining stoichiometric quantities of solvent after drying overnight.

(iv) Very large crystals of solvate were formed when hot, concentrated solutions of $Sb_2(C_6F_4)_3$ in toluene were allowed to cool. After allowing the crystals to dry on a filter paper for half an hour in the open air, analysis showed the retention of half a mole of solvent (Found: C,35.7; H,0.7; F,31.0%. $C_{21.5}H_4F_{12}Sb_2$ calcd.: C,35.2; H,0.5; F,31.1%).

(v) The crystals which separated from concentrated benzene solutions of perfluoro-1,6-distibatriptycene held solvent relatively tenaciously on heating at 70°C. A 176.259 mg sample lost 5.098 mg after nineteen hours (2.89%), 8.305 mg after three days (4.71%), 8.540 mg after six days (4.85%). The calculated loss for 0.5 mole of benzene is 5.37%. Elemental analysis of the solvate confirmed the presence of the hemi-solvate (Found: C,34.0; H,0.3; F,29.6%. $C_{21}H_3F_{12}Sb_2$ calcd.: C,34.7; H,0.4; F,31.4%). The C-H stretching frequencies occurred at 3091, 3075 and 3035 cm^{-1} in the infrared spectrum, being essentially identical to those of benzene dissolved in hexachlorobutadiene.

Infrared absorptions are quoted in cm^{-1} for mulls in nujol, using CsI optics (s - strong, m - medium, w - weak, sh - shoulder, vs - very strong, vm - very weak, sb - strong broad, msh - medium shoulder, mb - medium broad.

$P(C_6F_4Br)_3$: 1610m, 1498s, 1310m, 1269vw, 1245vw, 1112s, 1040vs, 841vs, 805m, 793s, 725sh, 718m, 640w, 611w, 533vw, 484w, 421m, 382vw, 350vw, 338vw,.

$As(C_6F_4Br)_3$: 1612m, 1600m, 1494s, 1330w, 1301m, 1263w, 1246vw, 1105s, 1023vs, 827vs, 778m, 718m, 663vw, 603vw, 470vw, 394w, 367vw, 268m,.

$Sb(C_6F_4Br)_3$: 1613s, 1600sh, 1497s, 1322m, 1312sh, 1299s, 1255m, 1118m, 1103vs, 1037w, 1020vs, 833vs, 770s, 420w, 638w, 593w, 470w, 418vw, 410vw, 363w, 345w,.

$Bi(C_6F_4Br)_3$: 1622m, 1510s, 1493s, 1347w, 1334w, 1266m, 1230vw, 1196vs, 1177w, 1102vs, 1093vs, 1018m, 1009vs, 994sh, 847s, 882vs, 710vs, 556vw, 540m, 343vw,.

$(MeSi)(C_6F_4Br)_3$: 1615m, 1498vs, 1308m, 1260m, 1238w, 1104vs, 1040sh, 1033s, 853s, 838w, 818vw, 803w, 786s, 728m, 720sh, 690w, 613vw, 543w, 478m, 421s, 414sh, 372w, 345vw, 331vw,.

$As(C_6F_4H)_3$: 1620m, 1600sh, 1560m, 1316s, 1196w, 1688sh, 1098s, 1087s, 1002s, 990sh, 867sh, 863s, 811m, 720s, 706s, 632vw, 553m, 403w, 315vw,.

$P_2(C_4F_4)_3$: 1608m, 1593m, 1397w, 1346m, 1310sh, 1304m, 1268m, 1165w, 1146w, 1109s, 1074w, 1038s, 856m, 800m, 754m, 651m, 529w, 479m, 438s, 406m, 309w.

$As_2(C_6F_4)_3$: 1609w, 1593m, 1350m, 1332w, 1324m, 1294s, 1261s, 1101vs, 1059w, 1024vs, 827m, 768m, 727m, 643m, 516w, 465w, 387s, 352w, 301m, 288w,.

$Sb_2(C_6F_4)_3$: 1610w, 1584m, 1431vs, 1325w, 1306w, 1281m, 1256m, 1091s, 1047w, 1013s, 808m, 754m, 708w, 640w, 467w, 361m, 348sh.

$Bi_2(C_6F_4)_3$: 1611m, 1583w, 1416s, 1357m, 1352sh, 1308m, 1292w, 1272m sh, 1262s, 1236w, 1077s, 1040w, 1029w, 1002s, 790m, 738m, 696w, 636w, 464w, 344w, 290w,.

$(MeSi)_2(C_6F_4)_2$: 1609w, 1593m, 1331m, 1306m, 1271w, 1258m, 1228m, 1100s, 1070w, 1030s, 844m, 774m, 763s, 645m, 516vw, 490s, 437s, 369w, 340m, 309w,.

$PAs(C_6F_4)_3$: 1607w sh, 1598m, 1353w, 1335m, 1302m, 1261sh, 1255m, 1105s, 1054w, 1028s, 842m, 780m, 741m, 647m, 522w, 469w, 424m, 403m, 317w, 284w, 275w,.

$PSb(C_6F_4)_3$: 1611sh, 1605sh, 1597m, 1354m, 1345w, 1328m, 1299s, 1260sh, 1253s, 1105s, 1098s, 1046w, 1029s, 1019sh, 836m, 773m, 736m, 650m, 560w, 525w, 471w, 429m, 408m, 394m, 322w, 290w,.

$AsSb(C_6F_4)_2$: 1612w, 1594m, 1341m, 1336sh, 1319m, 1294s, 1261s, 1101s, 1094s, 1058w, 1040w, 1021s, 822m, 764m, 721m, 644m, 517w, 468w, 412m, 373m, 291m, 254m, 247sh,.

$Sb_2(C_6C\ell_4)_3$: 1311s, 1296m, 1280s, 1265sh, 1175w, 1143s, 1126m, 839s, 814s, 639m, 580w, 339m,.

$Sb_2(C_6H_4)_3$: 3055w, 3020w, 1426m, 1420sh, 1253m, 1163w, 1077m, 1023w, 942w, 873w, 741vs, 684w, 421m, 364m, 296m, 255m,.

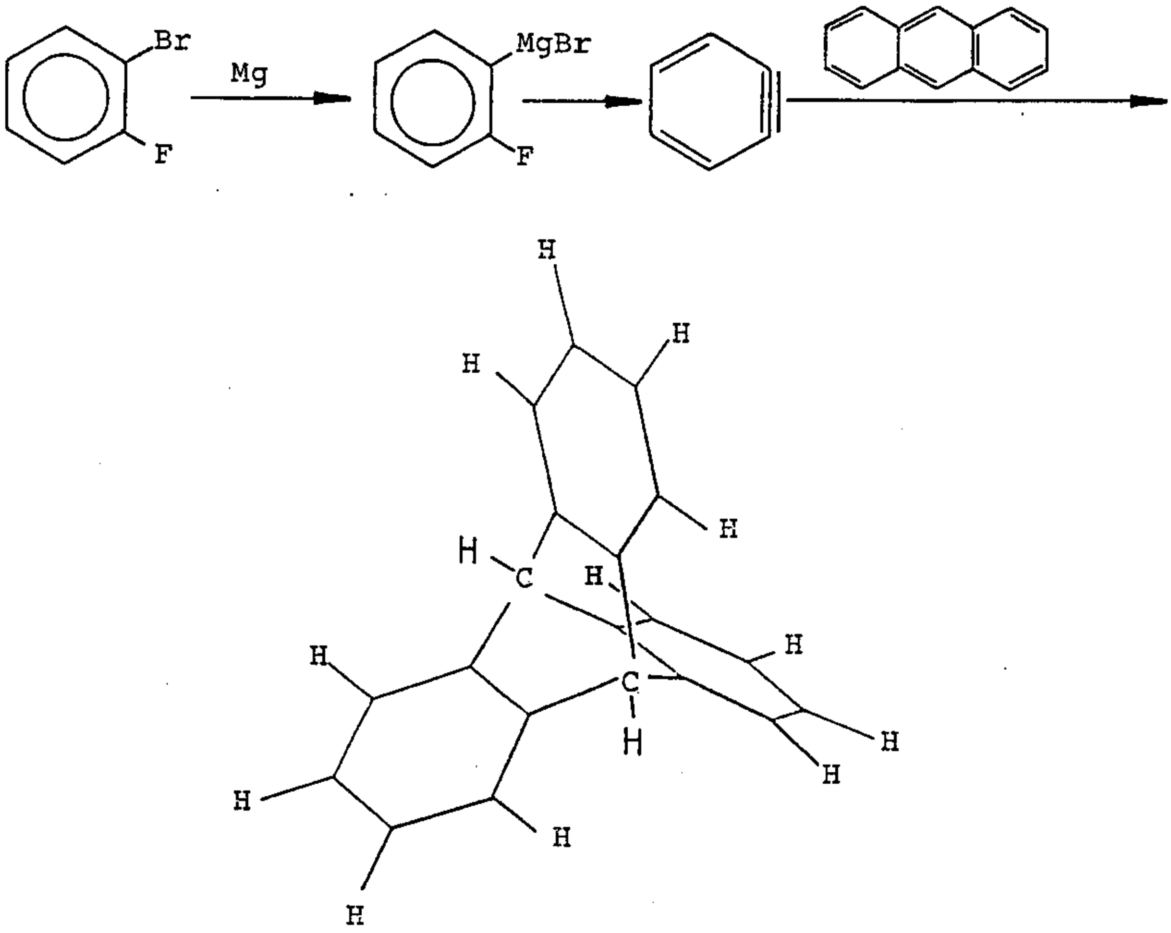
$Sb_2(C_6F_3)C\ell_4$: 1610w, 1587w, 1484s, 1320w, 1305w, 1294w, 1240m, 1231sh, 1109s, 1024s, 816m, 770m, 758m, 706m sharp, 639m, 467w, 423w, 370m, 324m, 296m,.

$Sb_2(C_6F_4)O_2$: 1596m, 1327w, 1308w, 1296w sh, 1290w, 1261w, 1245m, 1235m, 1130w, 1113,1107 doublet s, 1047w, 1032s sh, 1026s, 832vw, 812w, 799w, 765w, 640s, 595w, 576w, 544m, 513w, 469w, 372m, 365m sh, 305w, 277m, 270m sh,.

$Sb_2(C_6F_4)_3(OH)_4$: 1595mb, 1477sb, 1429sb, 1329w, 1310w, 1295sh, 1290w, 1262w, 1245w, 1235w, 1130w, 1107s, 1046w, 1023s, 833w, 812m, 799m, 768w, 646m, 624sh, 594m, 578m sh, 546mb, 514w, 471w, 373m, 366m sh, 303w, 276w.

Discussion

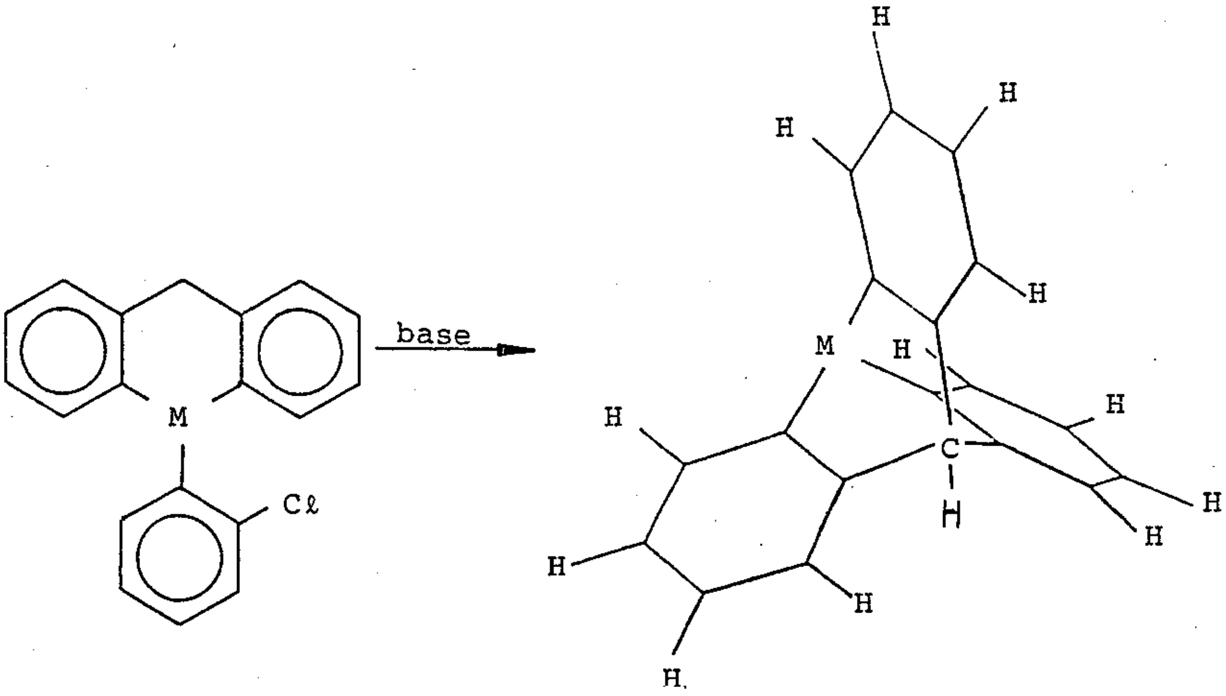
Triptycene was first prepared by Bartlett(5) via a six-step degradation of the anthracene-p-benzoquinone adduct but it can now be obtained in a more convenient manner by generating benzyne from the Grignard derivative of o-fluorobromobenzene in a tetrahydrofuran solution of anthracene, when addition occurs across the reactive 9,10-positions(6):



Quite surprisingly the compound is entirely lacking in reactivity of its aliphatic hydrogen atoms towards potassium exchange, chlorination or oxidation which are so characteristic of the CH group in triphenylmethane(5).

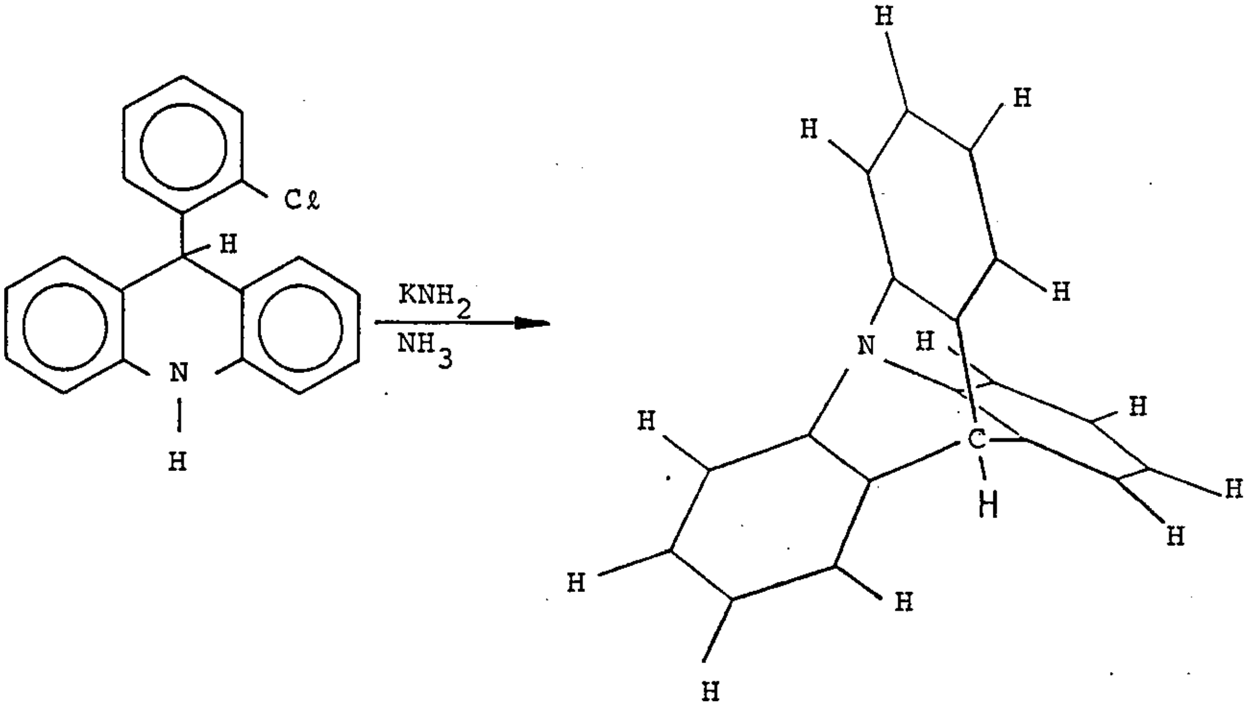
There has been considerable interest over the years in the synthesis of triptycenes with either one or two hetero atoms in the bridgehead positions.

The synthesis of triptycenes with both a hetero atom and a carbon atom in the bridgehead position have been achieved for phosphorus(7), arsenic(8) and antimony(8) by cyclization of the corresponding 9-(o-chlorophenyl)-9,10-dihydro-9-subsituted anthracene with an excess of either lithium di-isopropylamide or lithium piperidide as a base:



M = P, As, Sb

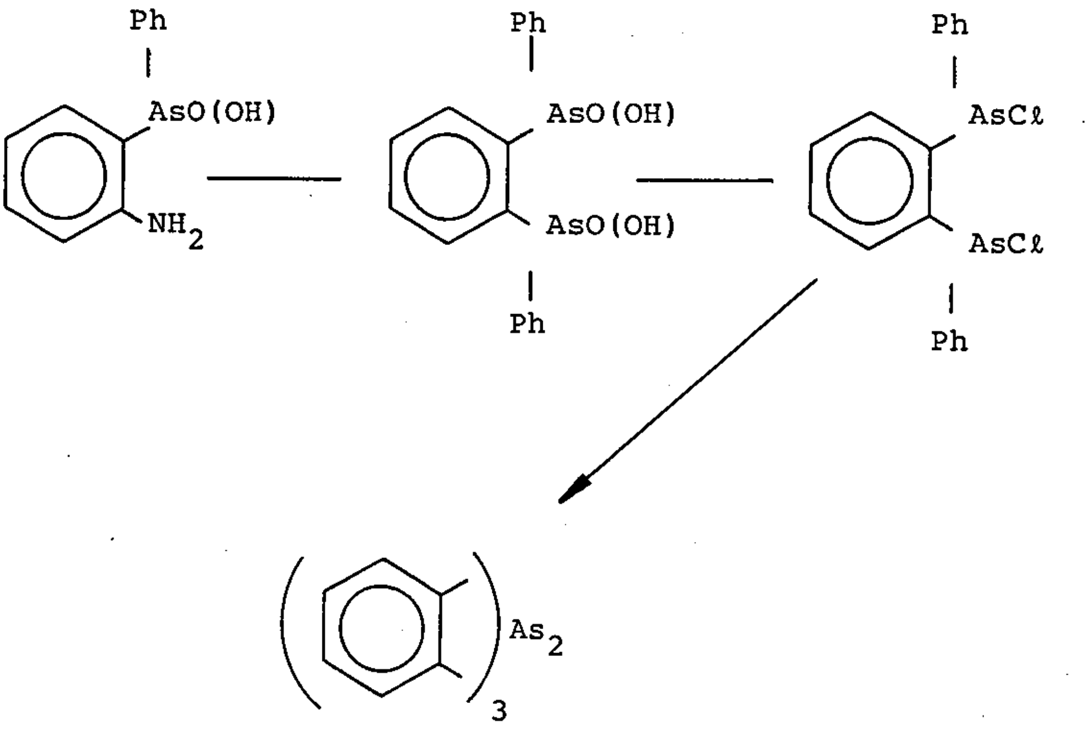
while azatriptycene was prepared by treating 9-(o-chlorophenyl)-9,10-dihydroacridine with KNH_2 in liquid ammonia(9):



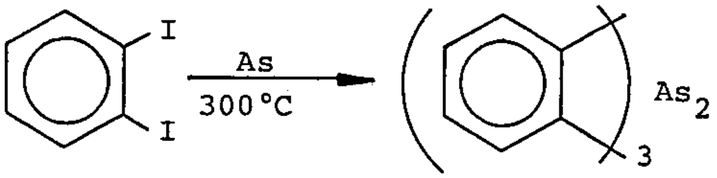
Rather few heterocyclic compounds have been described which possess structures similar to triptycene but with two hetero atoms in the 1,6-positions. The dinitrogen analogue was the first to be synthesised over 100 years ago by von Dechend and Wichelhaus(10) from the reaction of nitrobenzene with aniline:

$$2C_6H_5NH_2 + C_6H_5NO_2 \longrightarrow C_{18}H_{12}N_2 + NH_3 + 2H_2O$$

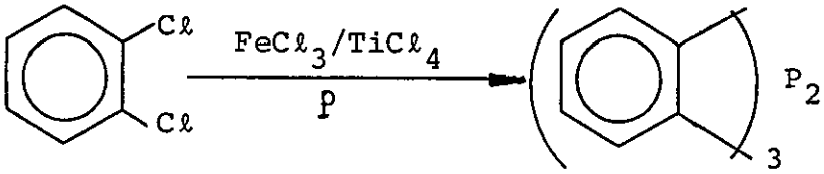
followed many years later by the diarsa(11) derivative which was prepared by diazotization of o-aminodiphenylarsinic acid and then coupling the product with oxophenylarsine, $C_6H_5As = O$, to give o-phenylenebis-(phenylarsinic acid). This was treated with phosphorus trichloride, being converted thereby into o-phenylenebis-(chlorophenylarsine) which, without isolation, was heated under reduced pressure to give hydrogen chloride and the 1,6-diarsatriptycene:



1,6-Diarsatriptycene is also obtained when 1,2-diiodobenzene and arsenic powder are heated together at 300°C in an evacuated, sealed tube(4).



Likewise, 1,6-diphosphatriptycene can be prepared in a one-step synthesis by treating o-dichlorobenzene and white phosphorus in the presence of catalytic amounts of ferric chloride/titanium tetrachloride in a sealed tube at 280°C(12,13):



While 1,6-distibatriptycene has not yet been described in the literature, it was found that when antimony was heated with a mixture of 1,2-diiodotetrafluorobenzene and 1,2-diiodobenzene three products were formed: $Sb_2(C_6F_4)_{3-n}(C_6H_4)_n$ where n = 0,1 and 2(14). This showed that the distibatriptycene structure must be stable when at least partial substitution of halogen for hydrogen occurs. Consequently we have expended considerable effort in trying to make the fully hydrogen-substituted species

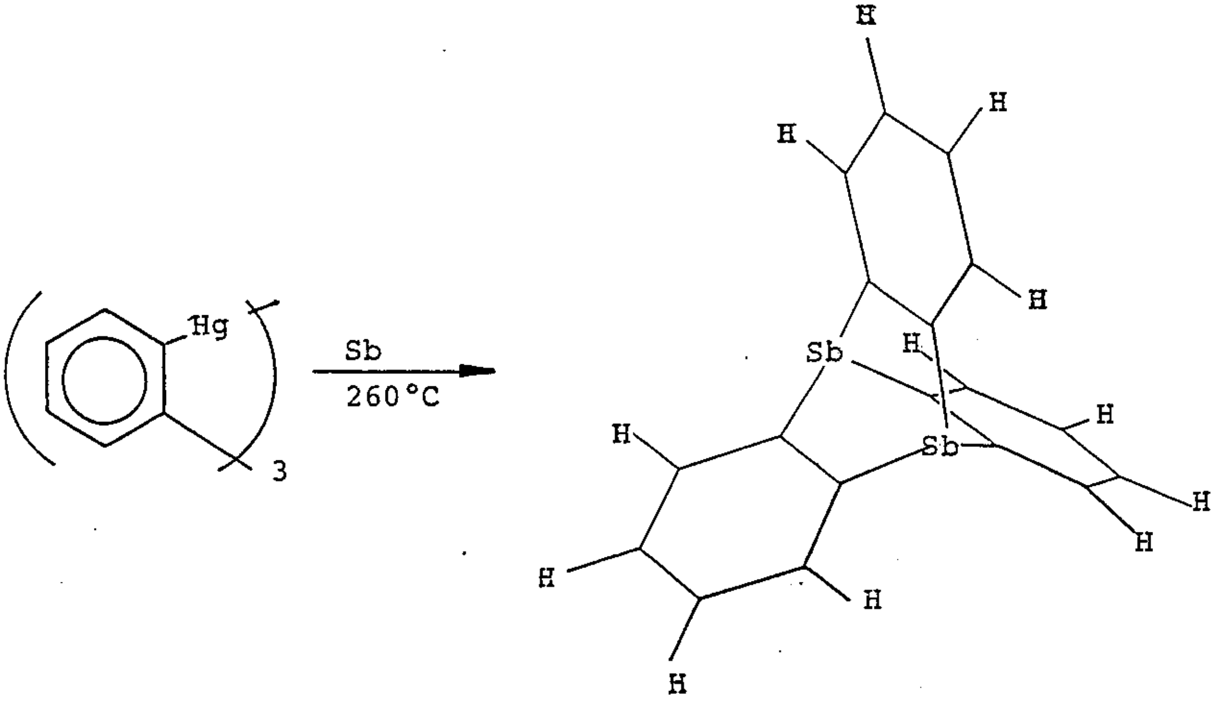
$Sb_2(C_6H_4)_3$. In this work our first attempts involved heating 1,2-dibromobenzene and 1,2-diiodobenzene with antimony powder in sealed, evacuated tubes at a variety of temperatures; however, the only product sometimes isolated was triphenylene. It is noteworthy that in the "mixed" synthesis mentioned above, $Sb_2(C_6H_4)_3$ was entirely missing from amongst the products(14) not being detectable even at high gain in a mass spectrometer.

By adding LiBu.TMEDA to 2-chloroiodobenzene it was found possible to make tris(2-chlorophenyl)antimony in high yield but all attempts to lithiate the 2-chlorine atoms and then treat the tri-lithio species so formed with antimony trichloride in order to prepare $Sb_2(C_6H_4)_3$ were entirely unsuccessful (see Chapter 4).

It is known that if antimony is heated in sealed tubes with perfluoro-ortho-phenylenemercury trimer, $Sb_2(C_6F_4)_3$ is formed(14). When this synthesis was repeated at 260°C with finely ground antimony powder intimately mixed with ortho-phenylenemercury trimer, about a 5% yield of 1,6-distibatriptycene could be isolated on extraction of the residues with 60-80°C petrol ether or hexane.

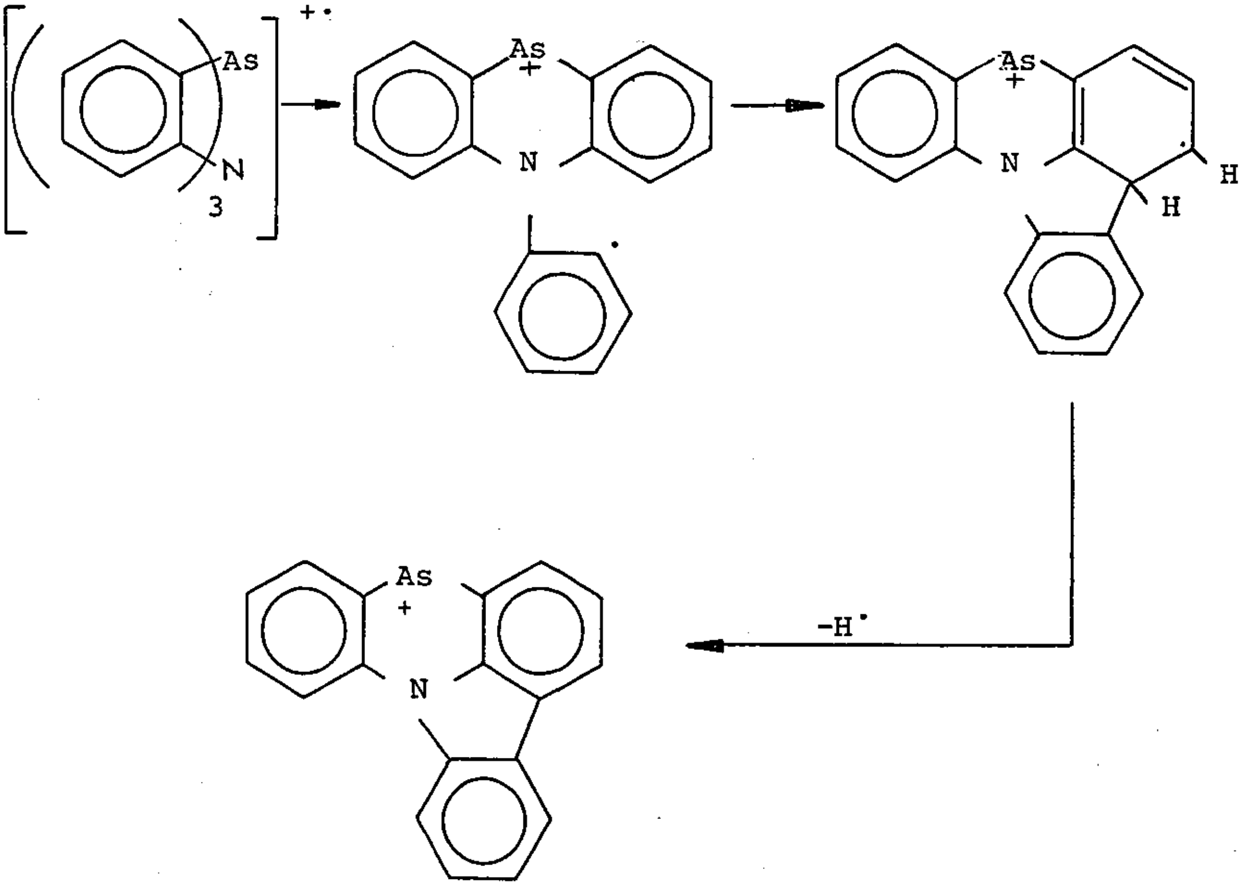
A series of repeated mass spectra verified the homogeneity of the sample, the identity of which was confirmed by accurate mass measurement of the isotopomeric ions present in the parent ion and $(P-H)^+$:

Isotopomeric Parent ion	Mass Measurements Observed (calcd.)
$C_{18}H_{12}{}^{121}Sb_2$	469.900(469.901 m.u.)
${}^{13}CC_{17}H_{12}{}^{121}Sb_2$	470.899(470.905 m.u.)
$C_{18}H_{12}{}^{121}Sb{}^{123}Sb$	471.899(471.902 m.u.)
${}^{13}CC_{17}H_{12}{}^{121}Sb{}^{123}Sb$	472.905(472.905 m.u.)
$C_{18}H_{12}{}^{123}Sb_2$	473.906(473.902 m.u.)
${}^{13}CC_{17}H_{12}{}^{123}Sb_2$	474.917(474.906 m.u.)
$C_{18}H_{11}{}^{121}Sb_2$	468.898(468.894 m.u.)

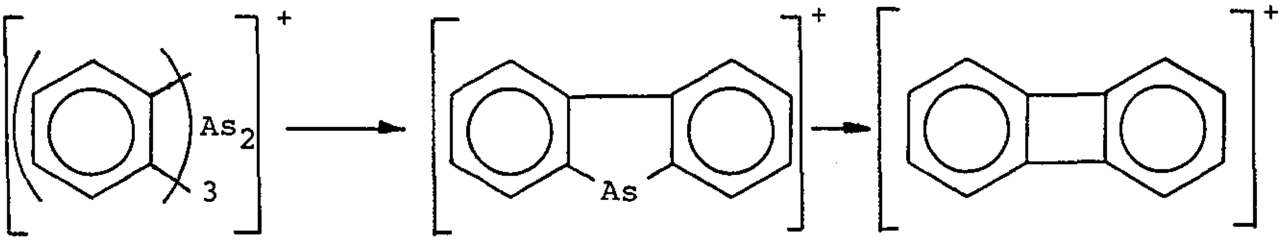


The parent ion cluster in the mass spectrum of 1,6-distibatriptycene is shown in Figure 6.1 and is entirely consistent with that expected for an ion containing two antimony atoms. The main antimony-containing ions in the mass spectrum were $Sb_2(C_6H_4)_3^+$ (34% measured for the major peak in the ion cluster), $Sb(C_6H_4)_2^+$ (43%), $SbC_6H_4^+$ (52%) and Sb^+ (13%); Figure 6.2 and Table 6.1. The base peak was due to the ion $C_{18}H_{12}^+$, presumably ionized triphenylene; tlc of the mass spectral sample showed the compound to consist of a single component with a different R_F value to triphenylene. A mixture of $Sb_2(C_6H_4)_3$ and triphenylene showed two spots on the silica tlc plate; hence the ion $C_{18}H_{12}^+$ in the mass spectrum must arise, via a fragmentation process, from the $Sb_2(C_6H_4)_3$ sample and not from any triphenylene impurity. Again, in the mass spectrum of pure $Sb_2(C_6F_4)_3$ there is a fairly intense peak due to $C_{18}F_{12}^+$ supporting the latter conclusion.

The mass spectra of triptycene and 9,10-dideuterotriptycene have been the subject of careful study$^{(15,16)}$. They are both characterized by a very strong $[M-1]^+$ peak (100%) and a strong $[M-2]^+$ peak (50%); the intense $[M-1]^+$ fragment has been shown to arise by loss of a hydrogen from one of the aromatic rings and not from the bridgehead position as initially supposed$^{(15)}$. The base peak of the spectrum of azarsatriptycene$^{(17)}$ is also at $[M-1]^+$ as is the case for triptycene; however, since this obviously cannot arise by loss of a bridgehead proton, re-arrangement must have occurred which involved breaking of an arsenic-carbon bond followed by cyclization of the resulting phenyl group and loss of an aromatic hydrogen atom to give the species $C_{18}H_{11}AsN^{+}$:



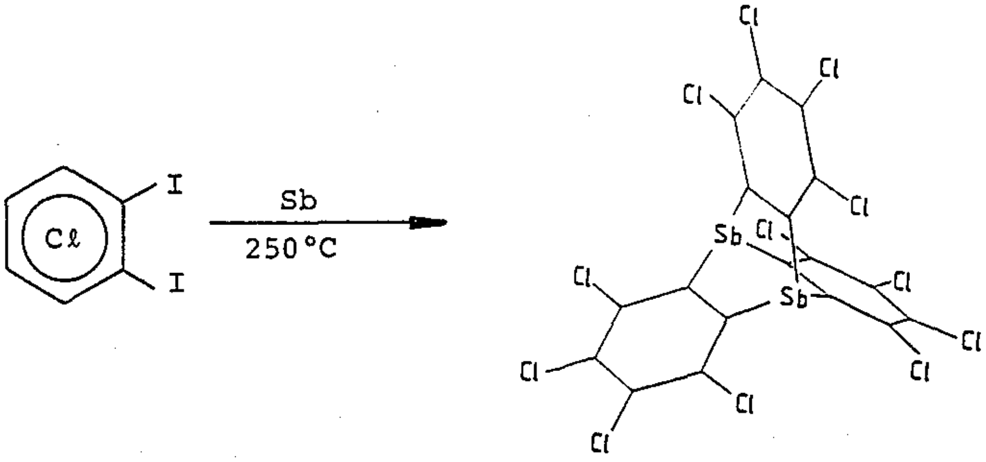
The fragmentation of 1,6-diarsatriptycene is quite different; the stable molecular ion $(C_6H_4)_3As_2$ (94%) loses both a bridging o-phenylene unit and one arsenic atom with ring closure to give the 9-arsafluorenyl ion, $(C_6H_4)_2As^{+}$ (69%), which in turn fragments to the ion $(C_6H_4)_2^{+}$ (100%)(18):



Unexpectedly, no $C_{18}H_{12}^{+}$ ions were quoted as being present in the mass spectra of the mono-substituted triptycenes and the phosphorus and arsenic disubstituted-triptycenes which suggests that the atoms in the bridgehead position in these compounds are bonded more strongly to the three phenyl rings compared with weaker Sb-C bonds which occur in $(C_6H_4)_3Sb_2$; in apparent agreement with this it appears that $Bi_2(C_6H_4)_3$ partially decomposes thermally to triphenylene during its synthesis.

The infrared spectrum of 1,6-distibatriptycene is very similar to that quoted for the diphosphorus analogue(13). The C-H out of plane bending vibrations occur as a strong doublet at 742 and 736 cm^{-1} whereas in $P_2(C_6H_4)_3$(13) these occur at 740 and 725 cm^{-1}. The C-H stretching vibrations in the aromatic ring occur at 3055, 3020 and 3005 cm^{-1} (weak absorptions) as shown in Figure 6.3.

Perchloro-1,6-distibatriptycene was prepared via "direct synthesis" by simply heating 1,2-diiodotetrachlorobenzene with an excess of antimony powder; it proved to be very insoluble in most organic solvents and had to be extracted from the reaction mixture using several aliquots of boiling dimethylformamide or boiling nitrobenzene; virtually all the SbI_3 co-product was soluble in the first aliquot which could then be discarded:



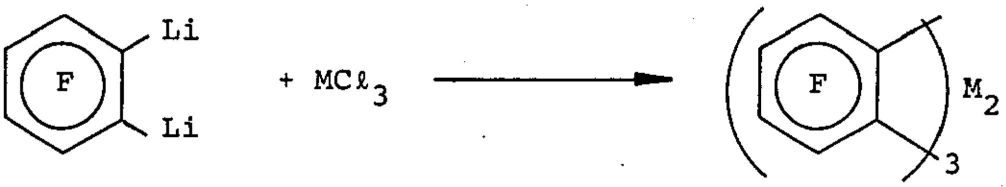
Hemi-solvates were formed when $Sb_2(C_6C\ell_4)_3$ crystallized out on cooling from dimethylformamide, diethylformamide, pyridine and nitrobenzene these being some of the few solvents it would dissolve in; the adhering solvent can be removed by heating the solvates above 120°C in vacuum.

Close examination of a typical cold preparative tube revealed the presence of a few large, colourless crystals mixed with the antimony triiodide at what had been the cooler end of the tube when it had been in the oven. These crystals proved to be hygroscopic, they attacked caesium iodide infrared plates producing a red-orange deposit of antimony triiodide and gave a positive test for chloride on being dissolved in water, all of which are typical reactions of antimony trichloride.

Obviously attack of the chloroaromatic groups is occurring during the heating process helping to explain both the relatively low yields of $Sb_2(C_6Cl_4)_3$ (ca. 5%) and the carbon-like appearance of the insoluble residues mixed with the excess of elemental antimony.

Perchloro-1,6-distibatriptycene has a very rich mass spectrum with $SbC_6Cl_4^+$ ion being responsible for the base peak; the parent ion has a high relative intensity (44.7%) and the other important antimony-containing species were $Sb_2C_{18}Cl_{10}^+$, $SbC_{18}Cl_{11}^+$, $SbC_{18}Cl_{10}^+$, $SbC_{18}Cl_9^+$, $SbC_{12}Cl_{10}^+$, $SbC_{12}Cl_8^+$, $SbC_{12}Cl_6^+$, $SbC_6Cl_2^+$, $SbCl_2^+$ and $SbCl^+$. The occurrence of several chlorine-migration reactions is evident by the observation of "chlorine-rich" ions such as $C_{12}Cl_{10}^+$, $C_6Cl_6^+$, $C_6Cl_5^+$, $SbC_6Cl_6^+$, $SbCl_2^+$ and $SbCl^+$; Figure 6.4 and Table 6.2 show the partial mass spectrum of $Sb_2(C_6Cl_4)_3$.

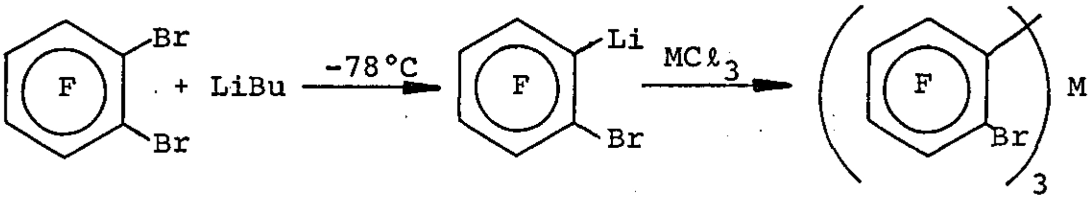
Perfluoro-1,6-disubstituted-triptycenes of arsenic, antimony and bismuth were described in 1976 by Cullen and Wu$^{(1)}$ who made them by treating the corresponding trichlorides with 1,2-dilithiotetrafluorobenzene:



M = As,Sb,Bi.

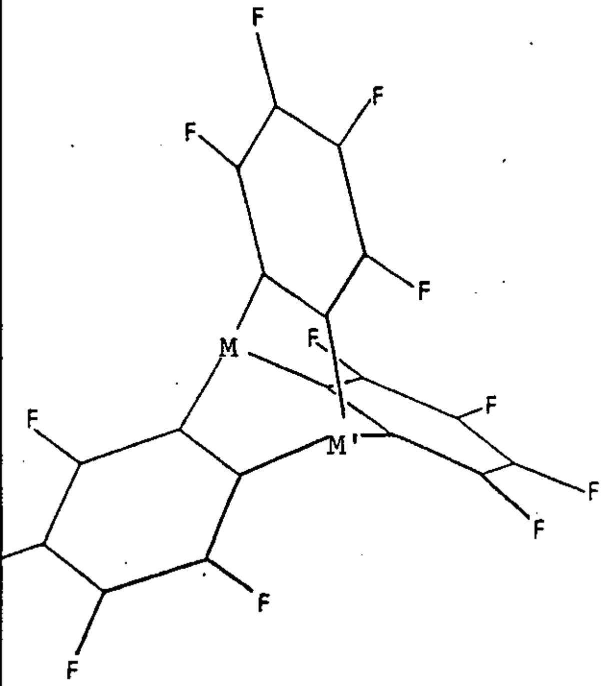
However, their physical data describing $Sb_2(C_6F_4)_3$ differed from that of the sample made by simply heating together antimony powder with 1,2-diiodotetrafluorobenzene in a sealed tube(4,14). In this thesis a step-wise, but low yield, synthesis of eight perfluoro-1,6-disubstituted-triptycenes of silicon and Group V elements (I-V) is described and the $Sb_2(C_6F_4)_3$ obtained is identical to that formed by direct synthesis; thus it would appear that Cullen and Wu's work is in error and they did not make $Sb_2(C_6F_4)_3$.

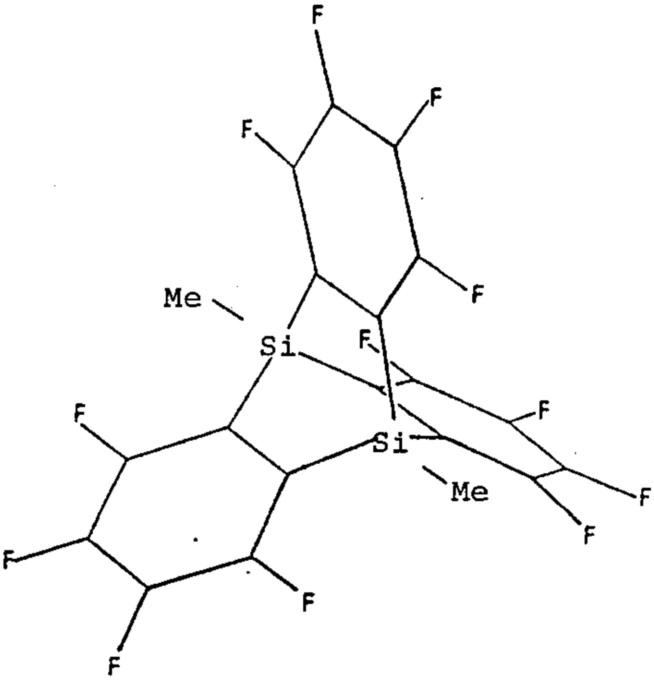
1,2-Dibromotetrafluorobenzene was first monolithiated by butyllithium at -78°C in ether solution and then treated with either methyltrichlorosilane or Group V trichloride to produce the corresponding tris(2-bromotetrafluorophenyl) derivatives in high yield:



M = CH_3Si,P,As,P,Sb

The bromine atoms in the $(C_6F_4Br)_3M$ compounds were readily exchanged with butyllithium as demonstrated by the reaction of tris(2-bromotetrafluorophenyl)arsenic





V

I ; M = M' = P

II ; M = M' = As

III ; M = M' = Sb

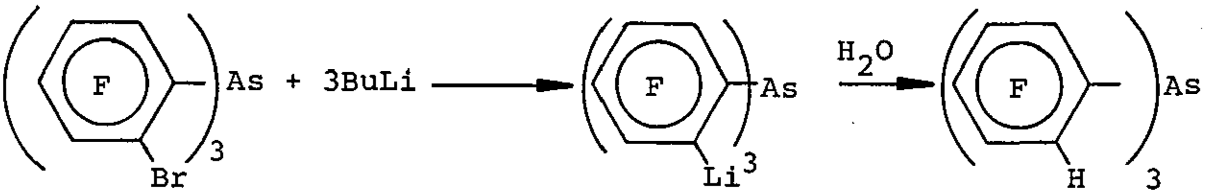
IV ; M = M' = Bi

VI ; M = P ; M' = As

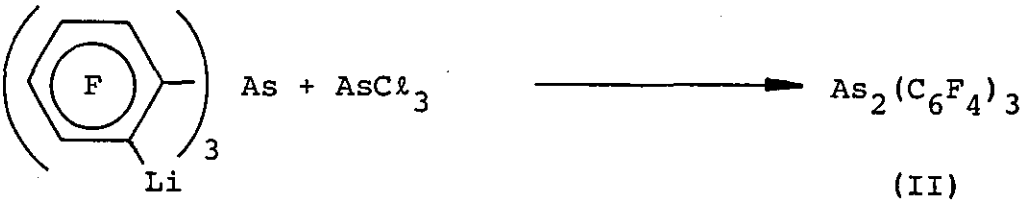
VII ; M = P ; M' = Sb

VIII ; M = As ; M' = Sb

with butyllithium at -78°C in diethyl ether solvent when, on hydrolysis, tris(2,3,4,6-tetrafluorophenyl)-arsenic was obtained:



When tris(2-lithiotetrafluorophenyl)arsenic was treated with arsenic trichloride instead of water, perfluoro-1,6-diarsatriptycene (II) was formed in low yield (ca. 4%):



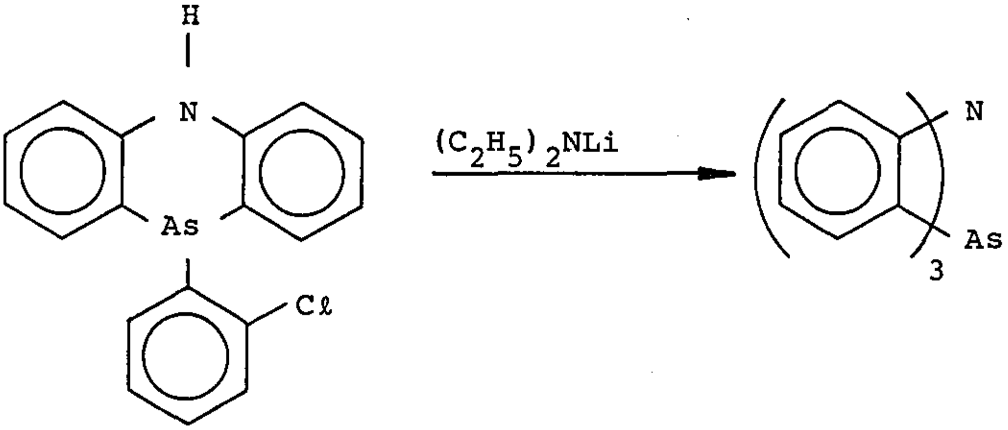
(II)

Similarly, the bromine atoms in the other $(C_6F_4Br)_3M$ compounds could lithiated and on subsequent treatment with $MCℓ_3$ gave the corresponding perfluoro-triptycenes. The low yield of these triptycenes apparently arises from the production of polymeric material when $(Li\text{-}C_6F_4)_3M$ attacks two, or three, separate molecules of $MCℓ_3$ instead of the single molecule required if triple-ring closure is to occur. The intermediate tris(2-bromotetrafluorophenyl)bismuth is quite water-sensitive, readily losing all its C_6F_4Br groups on standing in the air for a few hours; this was shown by taking the infrared spectrum of a pure sample immediately after preparation which showed all the usual absorption bands which occur for the fluoro-aromatic groups when the infrared spectrum was taken for a sample which had stood in the air for a few hours, there was no infrared absorption at all. It has been reported that tris(pentafluorophenyl)bismuth similarly hydrolysed rapidly on exposure to atmospheric moisture, and on treatment with larger quantities of water at room temperature gave pentafluorobenzene and bismuth hydroxide(19):

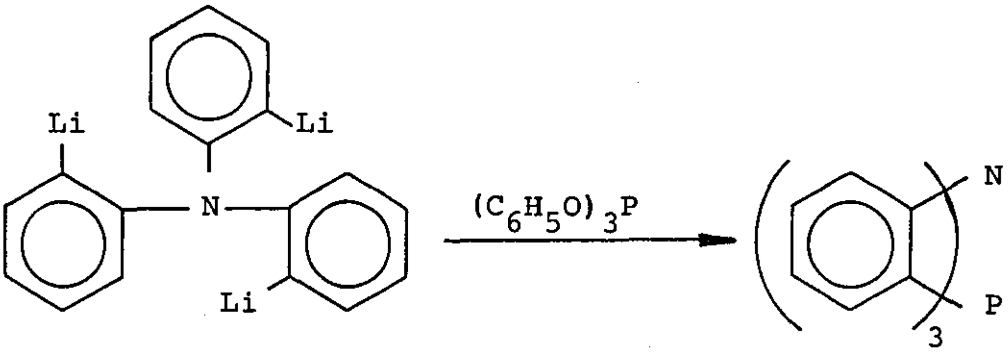
$$(C_6F_5)_3Bi + 3H_2O \longrightarrow Bi(OH)_3 + 3C_6F_5H$$

For this reason we found it was more convenient to make $Bi_2(C_6F_4)_3$ via a "one-pot" synthesis: the $Bi(C_6F_4Br)_3$ was lithiated directly in its preparation flask without prior isolation when further addition of $BiC\ell_3$ completed the formation of perfluoro-1,6-dibismuthtriptycene.

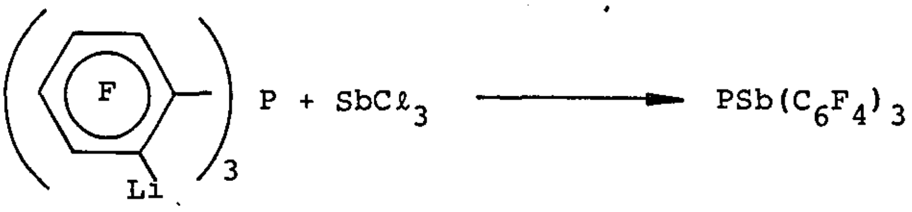
Mixed species of 1,6-disubstituted-triptycene are also known containing one nitrogen with either a phosphorus(20) or an arsenic(21) atom. Azarsatriptycene had been isolated from the reaction of 10-(2-chlorophenyl)-5,10-dihydrophenarsazine with excess lithium diethylamide in ether(21):



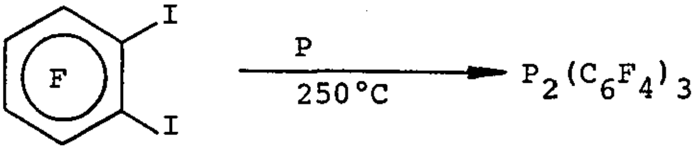
while azaphosphatriptycene was formed from the reaction between tris(2-lithiophenyl)amine and triphenyl phosphite$^{(20)}$:



The only "perfluoro-mixed" triptycene reported in the literature is $AsSb(C_6F_4)_3$ which had been detected mass spectroscopically among the products formed by heating 1,2-diiodotetrafluorobenzene with a mixture of arsenic and antimony$^{(14)}$. It was found in this work that when tris(2-lithiotetrafluorophenyl)arsenic was treated with either phosphorus or antimony trichlorides the mixed species $AsP(C_6F_4)_3$ and $AsSb(C_6F_4)_3$ were formed, respectively. Similarly, the action of antimony trichloride on tris(2-lithiotetrafluorophenyl)phosphine gave perfluoro-1,6-phosphastibatriptycene:



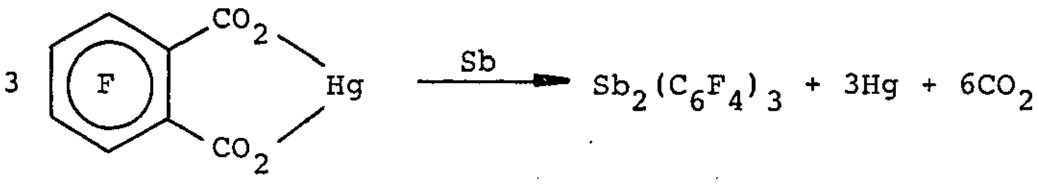
The formation of perfluoro-1,6-diphosphatriptycene by direct synthesis gave a product of reported(4) melting point 160°C:



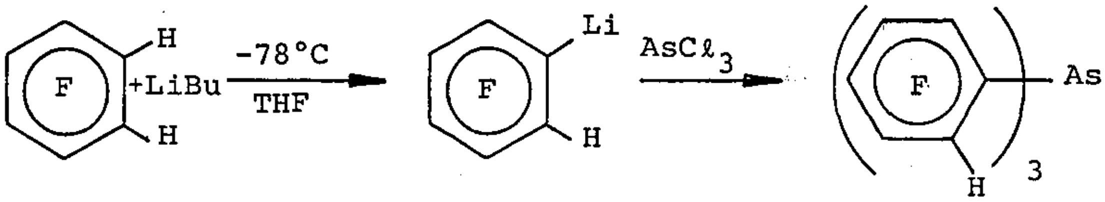
Although this compound has an identical infrared spectrum to our sample and shows a peak at m/e 506 in its mass spectrum corresponding to the molecular ion, the original melting point is low (m.p. of our sample is 208-209°C) and must have been measured on a grossly impure sample.

It was shown previously(14) that perfluoro-1,6-distibatriptycene can be made by heating together antimony powder and perfluoro-o-phenylenemercury trimer. As the latter mercurial is prepared by thermal decarboxylation of mercuric tetrafluorophthalate(22) it appeared reasonable to attempt the synthesis of

$Sb_2(C_6F_4)_3$ directly from a mixture of Sb and $Hg(OOC)_2C_6F_4$ heated on a vacuum line. The reaction resulted in a small quantity (ca. 5%) of $Sb_2(C_6F_4)_3$:



1,2-Dihydrotetrafluorobenzene reacted readily with n-butyllithium at -78°C in tetrahydrofuran solvent, and on reaction with arsenic trichloride gave tris(3,4,5,6-tetrafluorophenyl)arsenic in high yield:



The attempted preparation of perfluoro-1,6-diarsatriptycene from the reaction of $As(C_6F_4H)_3$ with butyllithium in tetrahydrofuran at -95°C, followed by addition of arsenic trichloride gave unidentified oils and much unreacted starting material. It would appear that the hydrogen atoms in the arsenical are very difficult to lithiate quantitatively; it is possible that a much longer reaction time is required for the lithiation.

The identity of compounds I-VIII was confirmed both by elemental analysis and by accurate mass measurements on the molecular ions in their mass spectra;

Table 6.3. The base peak in the mass spectrum of $(CH_3Si)_2(C_6F_4)_3$ is due to the molecular ion at 530 m.u. which, on losing one methyl group, gives rise to a peak at 515 m.u. due to the ion $MeSi_2(C_6F_4)_3^+$ (46%). The other silicon-containing fragment ions are $Si_2(C_6F_4)_3^+$, $MeSiC_{18}F_{12}^+$, $MeSiC_{18}F_8^+$, $SiC_{18}F_8^+$, SiF_3^+ and SiF^+ as shown in Figure 6.5 and Table 6.4. The mass spectrum of perfluoro-1,6-dibismuthtriptycene shows the base peak at 209 m.u. due to the ion Bi^+; the other bismuth-containing ions of reasonable intensities were $Bi_2(C_6F_4)_3^+$, Bi_2^+, $C_6F_4Bi^+$ and $(C_6F_4)_2Bi^+$; see Figure 6.6 and Table 6.5 (the base peaks of the other Group V triptycenes were due to the ions $MC_6F_4^+$). Typically, the mass spectrum of $P_2(C_6F_4)_3$ has three main phosphorus-containing ions, $P_2(C_6F_4)_3^+$, $P(C_6F_4)_2^+$ and $PC_6F_4^+$ of which the latter is the base peak in the spectrum; Figure 6.7, Table 6.6. Fragmentation with fluorine migration to phosphorus is relatively favourable as shown by the metastable transition:

$$P_2(C_6F_4)_3 \longrightarrow PF_2 + PC_{18}F_{10}^+ \quad \text{(Obs. m/e 386.1; calcd. 386.2)}$$

and the occurrence of the PF_2^+ ion at m/e = 69(obs. 68.970, $^{31}P^{19}F_2$ calcd.: 68.971; for $^{12}C^{19}F_3$ calcd.: 68.995). In the spectrum of $As_2(C_6F_4)_3$ a number of other metastable peaks were visible for the transitions:

$As_2(C_6F_4)_3^+ \longrightarrow As(C_6F_4)_2 + As(C_6F_4)^+$ (Obs. 83.7; calcd. 83.7)

$As(C_6F_4)_2^+ \longrightarrow AsF_2 + (C_6F_3)_2^+$ (Obs.179.5; calcd.179.4)

$As(C_6F_4)_2^+ \longrightarrow As + C_{12}F_8^+$ (Obs.236.2; calcd.236.2)

$AsC_6F_4^+ \longrightarrow C_6F_2 + AsF_2^+$ (Obs. 57.3; calcd. 57.3)

The parent ion in the mass spectrum of perfluoro-1,6-distibatriptycene shows a relatively intense (40%) group of peaks around 688 m.u. The number and relative intensities of the peaks comprising this ion are in good agreement with the calculated isotopomeric pattern, Figure 6.8. The mass spectra of perfluoro-1,6-diarsatriptycene and -distibatriptycene are shown in Figure 6.9; Table 6.7 and Figure 6.10; Table 6.8 respectively.

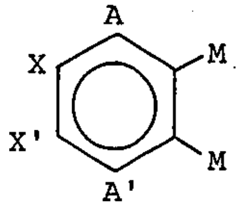
A "mixed" derivative such as $PSb(C_6F_4)_3$ shows a strong molecular ion (87%) with two major peaks for $SbC_6F_4^+$ (100%) and $PC_6F_4^+$ (52%). The only other ions containing either phosphorus or antimony were $P(C_{12}F_4)_3^+$, $P(C_6F_4)_2^+$, SbF_2^+, SbF^+ and Sb^+. The mass spectra of the "mixed" triptycenes VI, VII and VIII are shown in Figures 6.11, 6.12, 6.13 and listed in Tables 6.9, 6.10, 6.11, respectively.

The mass spectra of the $M(C_6F_4Br)_3$ derivatives are much richer than those of the triptycenes. When M = P the base peak is due to the ion $P(C_6F_4)_2^+$, and PF_2^+ has over 90% relative abundance; the peak at m/e 444, presumably representing ionized perfluorotriphenylene, $(C_6F_4)_3^+$, has an intensity of 63% and gives rise to a fairly high background of $C_xF_y^+$ ions. Apart from the molecular ion, the only bromine-containing ion having an intensity greater than 3% is $P(C_6F_4Br)_2C_6F_4^+$ (12%); Figure 6.14; Table 6.12. The molecular ion in the spectrum shows a cluster of peaks centred at 714 m.u. of relative intensity 47%; Figure 6.15 shows the comparison of the observed and calculated intensities of the peaks making up this ion cluster. The mass spectra of $M(C_6F_4Br)_3$ derivatives of As, Sb and Bi have more bromine-containing ions and the $(C_6F_4)_3^+$ ion is of low intensity as shown in Figures 6.16 - 6.18. The base peak in $Bi(C_6F_4Br)_3$ is due to Bi^+ ion, while the parent ion has the lowest intensity compared with the other compounds presumably because of the relative instability of Bi-C bonds as mentioned before.

All the compounds I-VIII have similar infrared spectra, showing a common structure; typically, perfluoro-1,6-distibatriptycene (III) exhibits strong bands at 1091 and 1013 cm^{-1}, characteristic of the carbon-fluorine stretching frequencies in disubstituted tetrafluorophenyl derivatives. As the X-sensitive stretching vibration in perfluoro-aromatic compounds usually occurs between 760-900 cm^{-1}, the band at 808 cm^{-1} of medium intensity can probably be assigned to the

C-Sb stretching vibration in the molecule. The infrared spectra of the compounds I-VIII and the $M(C_6F_4Br)_3$ intermediates are shown in Figures 6.19-6.25.

The ^{19}F NMR spectrum of a typical "symmetrical" derivative such as $Bi_2(C_6F_4)_3$ shows just the two expected resonances for AA'XX' systems; the chemical shifts of a 5%



solution in deutero-acetone (ortho F 108.5; meta F 154.6 ppm relative $CFCl_3$) are essentially identical to those quoted by Cullen and Wu(1) for an unspecified solvent system (109.4; 154.0 ppm), Figure 6.26. In the case of the $MM'(C_6F_4)_3$ systems four ^{19}F resonances can be distinguished, as in the spectrum of $AsSb(C_6F_4)_3$ which shows four groups of lines centred at 123.0, 124.8, 151.2 and 152.2 ppm (relative to $CFCl_3$) for the two ortho and two meta fluorines, respectively. In the unique molecule of the series, $(CH_3Si)_2(C_6F_4)_3$, the two groups of peaks in the ^{19}F NMR spectrum at 121.7 and 147.2 ppm ($CDCl_3$ solution) are not mirror images of each other because of spin interaction between the ortho fluorines and the protons in the methyl groups; the proton NMR resonance of the methyl groups shows splitting which appears to confirm this deduction; Figure 6.27 shows the ^{19}F NMR of $(CH_3Si)_2(C_6F_4)_3$. Four groups of peaks occur in the ^{13}C NMR spectrum corresponding to the three types of aromatic carbon and to the carbon atoms in the two identical methyl groups; the resonance of the latter, which is 4.8 ppm to high field of the TMS signal, shows evidence of fluorine splitting. ^{13}C NMR data for compounds III, IV, V and 1,2-diiodotetrafluorobenzene (for comparison) are listed in Table 6.13 and shown in Figures 6.28, 6.29 and 6.30, respectively. Glistening crystals of perfluoro-1,6-distibatriptycene grown from hexane slowly lost their bright transparent appearance and changed to white, opaque lumps on standing in the air at room temperature. This behaviour suggested that a metastable crystalline phase might have been formed; however, on placing the crystals in a mass spectrometer and slowly warming up the insertion probe it was found that hexane (m/e = 86) was evolved. After pumping away the hexane and heating the probe further, the normal mass spectrum of $Sb_2(C_6F_4)_3$ was observed. Obviously, though unexpectedly, a solvate had been formed with the hexane. Elemental analysis of crystals grown from hexane and air-dried at room temperature demonstrated the presence of half a mole of solvent per mole of $Sb_2(C_6F_4)_3$. Thermogravimetric analysis showed that the hexane was held only weakly and began to come off quite rapidly only a few degrees above room temperature. Crystals of the solvate which had been pumped dry under vacuum at room temperature for 5 minutes and stored in a stoppered bottle for a week showed a 4.0% weight loss on heating due to evolution of hexane (the calculated weight loss for a solvate of composition $Sb_2(C_6F_4)_3$. 0.5 hexane is 5.90%). A more accurate determination of the weight loss at a constant 70°C for crystals taken straight from the mother liquor and air dried to constant weight at room temperature, showed that all the hexane was lost within two and a half hours (5.87% weight loss). Even at room temperature the hexane solvate effloresced, losing 2.5% of the hexane in 24 hours, 67% in eight days and 96% after two weeks; Figure 6.31. The C-H stretching frequencies in the solvate occurred at 2955, 2921, 2865 and 2850sh cm^{-1} which are virtually identical in position to those recorded for a dilute solution of hexane in hexachlorobutadiene; very minor variation in the relative peak heights were apparent, in particular, the shoulder at 2850 cm^{-1} in the solvate becomes slightly more intense and forms a doublet with the peak at 2865 cm^{-1} in the hexane spectrum. The instability of this solvate and the infrared data, suggest that the hexane is simply trapped in the crystal lattice and, as expected, has essentially no chemical interaction with the $Sb_2(C_6F_4)_3$ molecules.

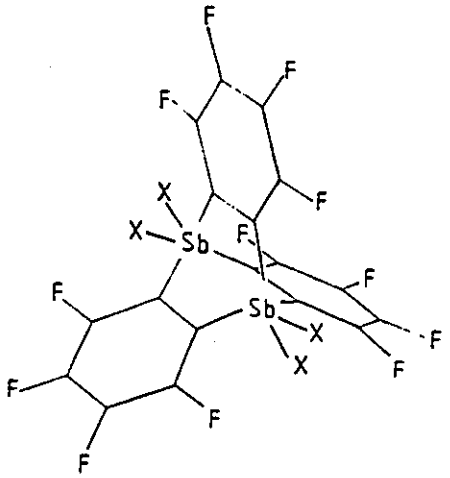
Cyclohexane, toluene and benzene similarly form hemi-solvates with $Sb_2(C_6F_4)_3$ but which appear to be slightly more stable than that formed by hexane; the benzene solvate lost solvent least readily and even after 5 days at 70°C suffered only 90% dissociation. Chloroform and acetone do not form solvates that are stable at room temperature.

Perfluoro-1,6-dibismuthtriptycene, recrystallized from diethylether and dried in the oven at 80°C for two hours, still retained half a mole of ether; the C-H stretching frequencies of the solvating ether occurred at 2955, 2920 and 2865 cm^{-1} in the infrared spectrum. Thus, to drive off adhering solvent, the sample of $Bi_2(C_6F_4)_3$ was heated to 100°C under vacuum 10^{-4} mm Hg for approximately 2 hours; slight loss of sample by sublimation occurred during this process. Normally the solvates effloresced readily on heating so that the melting points obtained for them were, in fact, the melting points of the unsolvated species; unexpectedly, when $PSb(C_6F_4)_3$ was recrystallized from ethanol the melting point dropped from 198-199°C to 165°C. Again half a mole of alcohol seemed to be strongly held on recrystallization as judged from the elemental C,H analysis.

Perfluoro-1,6-distibatriptycene is a very stable molecule resisting attack by water even at 300°C; in contrast, addition of water to a solution of tris(pentafluorophenyl)antimony caused cleavage of one of the C-Sb bonds, and on subsequent condensation gave a binuclear oxo-bridged derivative(23):

$$2(C_6F_5)_3Sb + H_2O \longrightarrow 2C_6F_5H + (C_6F_5)_2SbOSb(C_6F_5)_2$$

Although $Sb_2(C_6F_4)_3$ does not react with iodine in refluxing chloroform, chlorine causes rapid oxidation and produces a precipitate of $Sb_2(C_6F_4)_3C\ell_4$ (IX) within a few seconds at room temperature in carbon tetrachloride. The chloride does not appear to hydrolyse to any appreciably extent in air at room temperature but it does absorb two molecules of water quite readily to form a dihydrate . Although no parent ion, $Sb_2(C_6F_4)_3C\ell_4^+$, could be detected in the mass spectrum other chloro-ions $Sb_2(C_6F_4)_3C\ell_3^+$, $Sb_2(C_6F_4)_3C\ell_2^+$ and $Sb_2(C_6F_4)_3C\ell^+$ gave readily identifiable peaks with about 22, 25 and 95% intensities realtive to the base peak at m/e

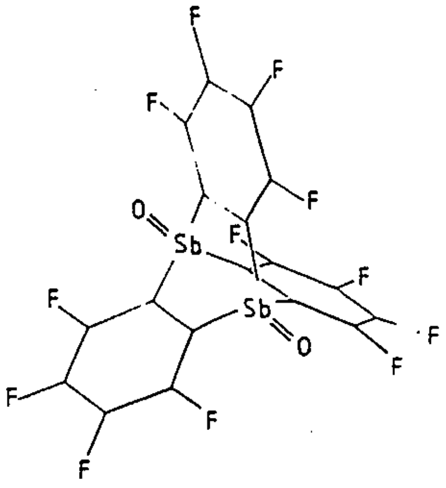


IX : X = Cℓ

X : X = OH

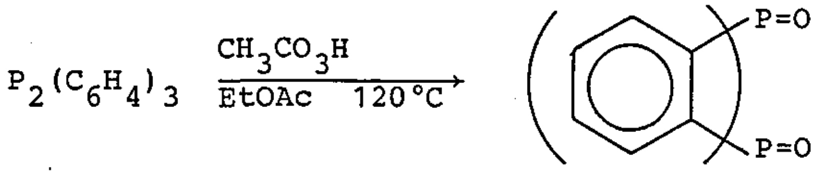
269 due to $SbC_6F_4^+$. Thermal decomposition in a vacuum gave a complex mixture of products which included $Sb_2(C_6F_4)_3$ together with unidentified carbon-chlorine and biphenyl species.

On boiling with a large excess of distilled water $Sb_2(C_6F_4)_3C\ell_4$ was hydrolysed to give a water-insoluble solid which analysed as the dioxide $Sb_2(C_6F_4)_3O_2$. In view of Chremos and Zingaro's work(24) it seems unlikely that this is the simple compound shown in (XI) and it may be, at least partially, polymeric. The large number of infrared bands in the spectrum of $Sb_2(C_6F_4)_3O_2$ also suggests a molecule with a more complex structure than that with the relatively high symmetry of (XI). Attempts to obtain a molecular weight mass spectrometrically were foiled because of a ready thermal decomposition which occurs before the oxide begins to volatilize; the major

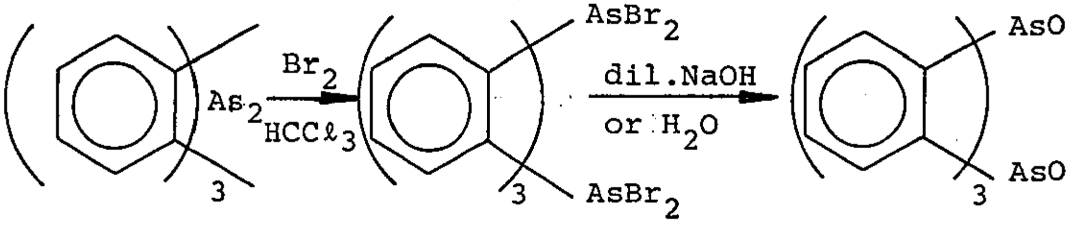


XI

product of this decomposition was shown by infrared and mass spectroscopy to be perfluoro-1,6-distipatriptycene. The dioxides of the other perfluoro-triptycenes are not yet known; on the other hand the oxidation of diphosphatriptycene with peracetic acid in ethyl acetate gave the dioxide(12):

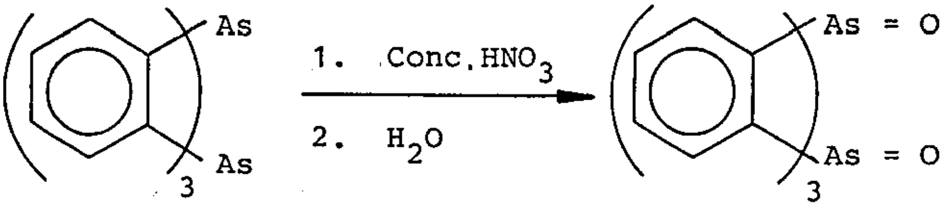


and addition of bromine to diarsatriptycene gave the tetrabromide which on addition of water produced the dioxide(11):

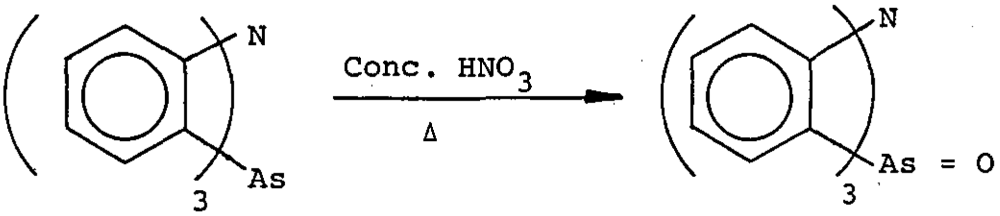


Hot, concentrated nitric acid readily dissolves perfluoro-1,6-distibatriptycene. On cooling and dilution with distilled water it was found that nothing could be extracted from the solution by diethyl ether. However, on standing for two days the solution deposited colourless, needle-like crystals of what is probably the dinitrate, $Sb_2(C_6F_4)_3(OH)_2(NO_3)_2$. During attempts to recrystallize the nitrate from water it was noticed that tiny bubbles of gas (probably oxygen) formed in the solution on standing and that the amount of "nitrogen" in the recrystallized samples fell with each successive crystallization being virtually zero after four recrystallizations; the compound then analysed as the tetrahydroxo compound (X). Obviously the nitrate is hydrolytically unstable even at room temperature. The infrared spectrum of (X) is virtually identical to that of the oxide, $Sb_2(C_6F_4)_3O_2$, except for a slight change in the position of the broad Sb-O band at 624 cm^{-1} (which is at about 640 cm^{-1} in the oxide). The analysis would, of course, fit the formula for the dihydrate of the oxide, $Sb_2(C_6F_4)_3O_2(H_2O)_2$; however, as the oxide is not soluble in water, even on boiling, whereas X is freely soluble in tepid water, it is highly unlikely that X is simply a hydrate of the oxide. Certainly no bands for coordinated water could be seen in the infrared spectrum of X and no water was lost on heating to 200°C in air.

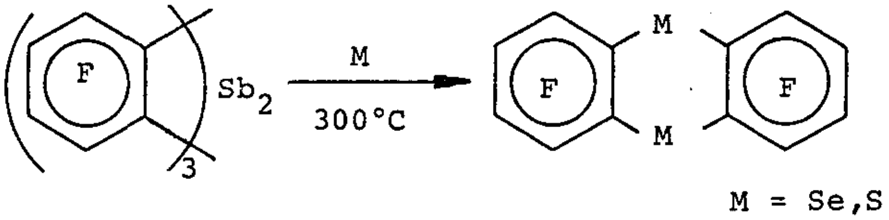
The action of nitric acid on a few other disubstituted triptycenes has been reported; for example, diarsatriptycene when boiled with nitric acid gave the dioxide derivative$^{(11)}$:



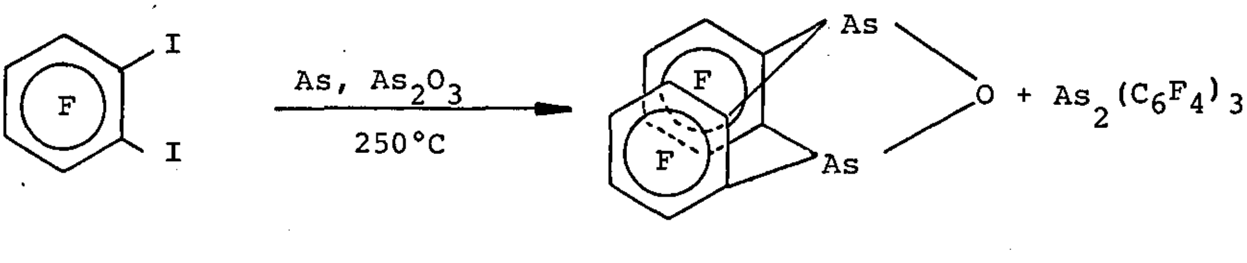
Similarly, the oxide of azarsatriptycene was formed with concentrated nitric acid$^{(21)}$:



Perfluoro-1,6-distibatriptycene is very stable thermally and showed no change on being heated overnight at 350°C in a sealed, evacuated tube; a slow decomposition was observed only at 400°C and sublimation takes place rapidly in the open air above about 160°C; no reaction occurred when it was refluxed with methyl iodide. When heated with selenium or sulphur, $Sb_2(C_6F_4)_3$ gave octafluoroselanthrene and octafluorothianthrene respectively$^{(14)}$:



The reaction of 1,2-diiodotetrafluorobenzene with partially oxidized arsenic powder at 250°C for 18 hours in a sealed, evacuated tube gave some octafluoro-5,10-epoxpy-5,10-dihydroarsanthrene$^{(2)}$:



In a similar reaction, 1,2-diiodotetrafluorobenzene heated with antimony powder and Sb_2O_3 at 250°C gave $Sb_2(C_6F_4)_3$ only. Thus no $Sb_2(C_6F_4)_2O$ has been formed under similar conditions to those which produced $As(C_6F_4)_2O$(2); furthermore, it is obvious that $Sb_2(C_6F_4)_3$ does not react with Sb_2O_3.

No reaction was observed when oxidation of perfluoro-1,6-distibatriptycene with potassium dichromate/sulphuric acid/acetic acid mixture was attempted, while a similar oxidation of tris(pentafluorophenyl)phosphine gave tris(pentafluorophenyl)phosphorus oxide(3):

$$(C_6F_5)_3P \xrightarrow{CrO_3} (C_6F_5)_3PO$$

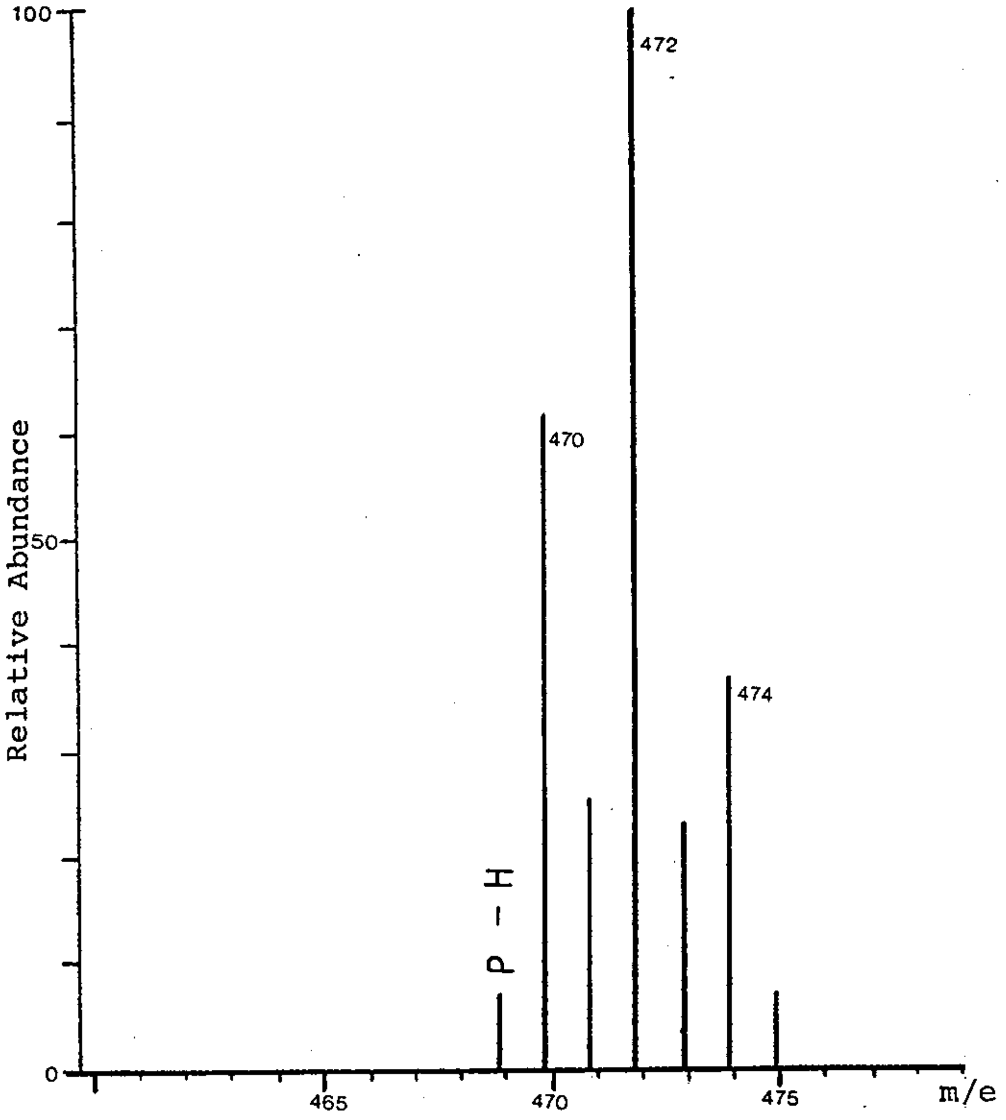


Figure 6.1 : Parent ion cluster in the mass spectrum of $Sb_2(C_6H_4)_3$ showing typical pattern for a $C_{18}H_{12}Sb_2$ species.

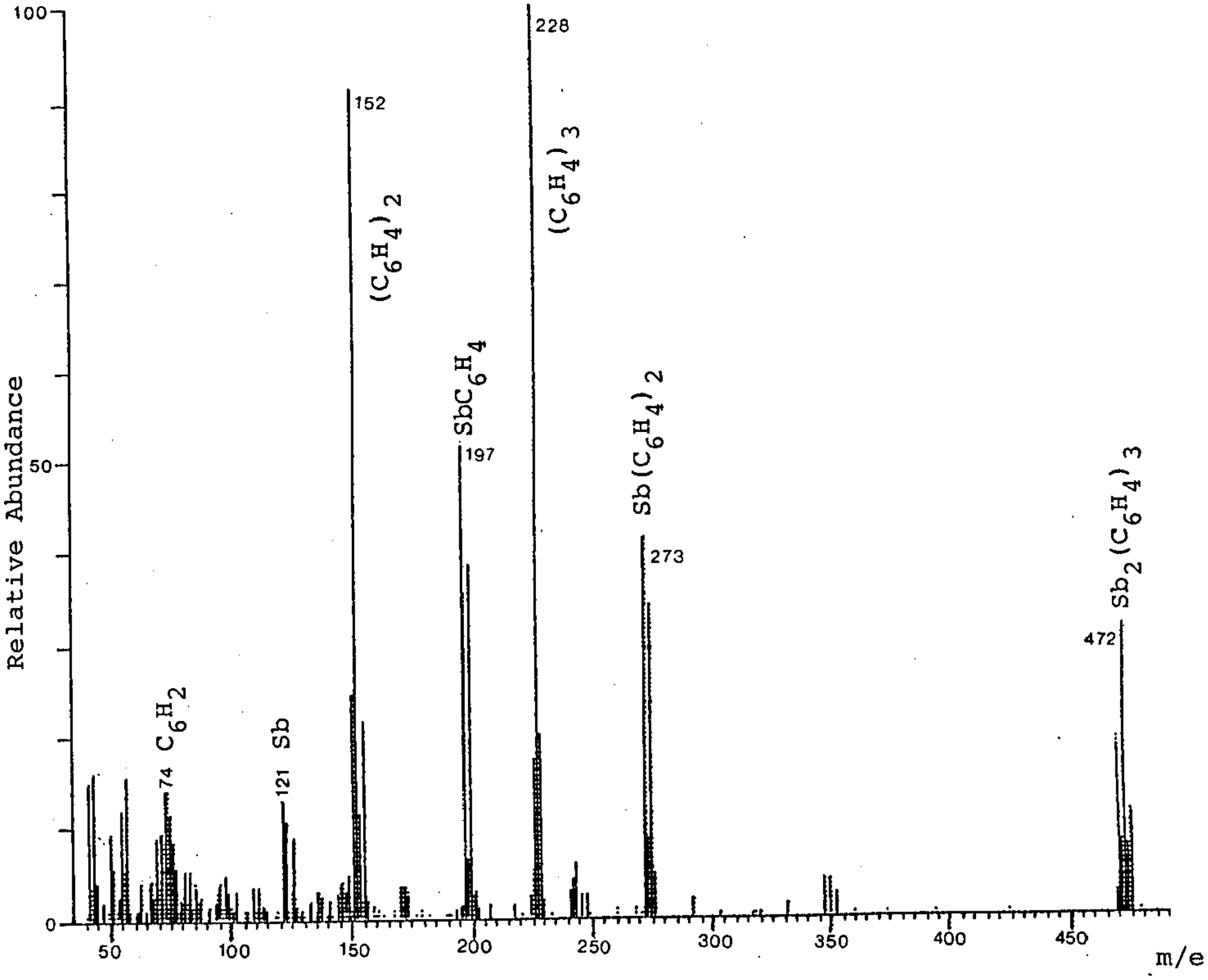


Figure 6.2 : Partial Mas Spectrum of 1,6-Distibatriptycene

Table 6.1

Partial Mass Spectrum of 1,6-distibatriptycene (only the relative abundance of ions containing ^{121}Sb isotope is recorded except for the parent ions).

m/e	Ion	Relative Abundance
474	$C_{18}H_{12}{}^{123}Sb_2$	11.14
472	$C_{18}H_{12}{}^{121}Sb^{123}Sb$	30.66
470	$C_{18}H_{12}{}^{121}Sb_2$	18.99
469	$C_{18}H_{11}{}^{121}Sb_2^+$	2.16
349	$C_{18}H_{12}Sb^+$	3.40
273	$C_{12}H_8Sb^+$	41.64
244	$C_{10}H_3Sb^+$	6.05
228	$C_{18}H_{12}^+$	100.0
227	$C_{18}H_{11}^+$	12.22
226	$C_{18}H_{10}^+$	16.77
197	$C_6H_4Sb^+$	51.79
152	$C_{12}H_8^+$	91.76
151	$C_{12}H_7^+$	24.3
121	Sb^+	12.57
74	$C_6H_2^+$	13.87
50	$C_4H_2^+$	9.16

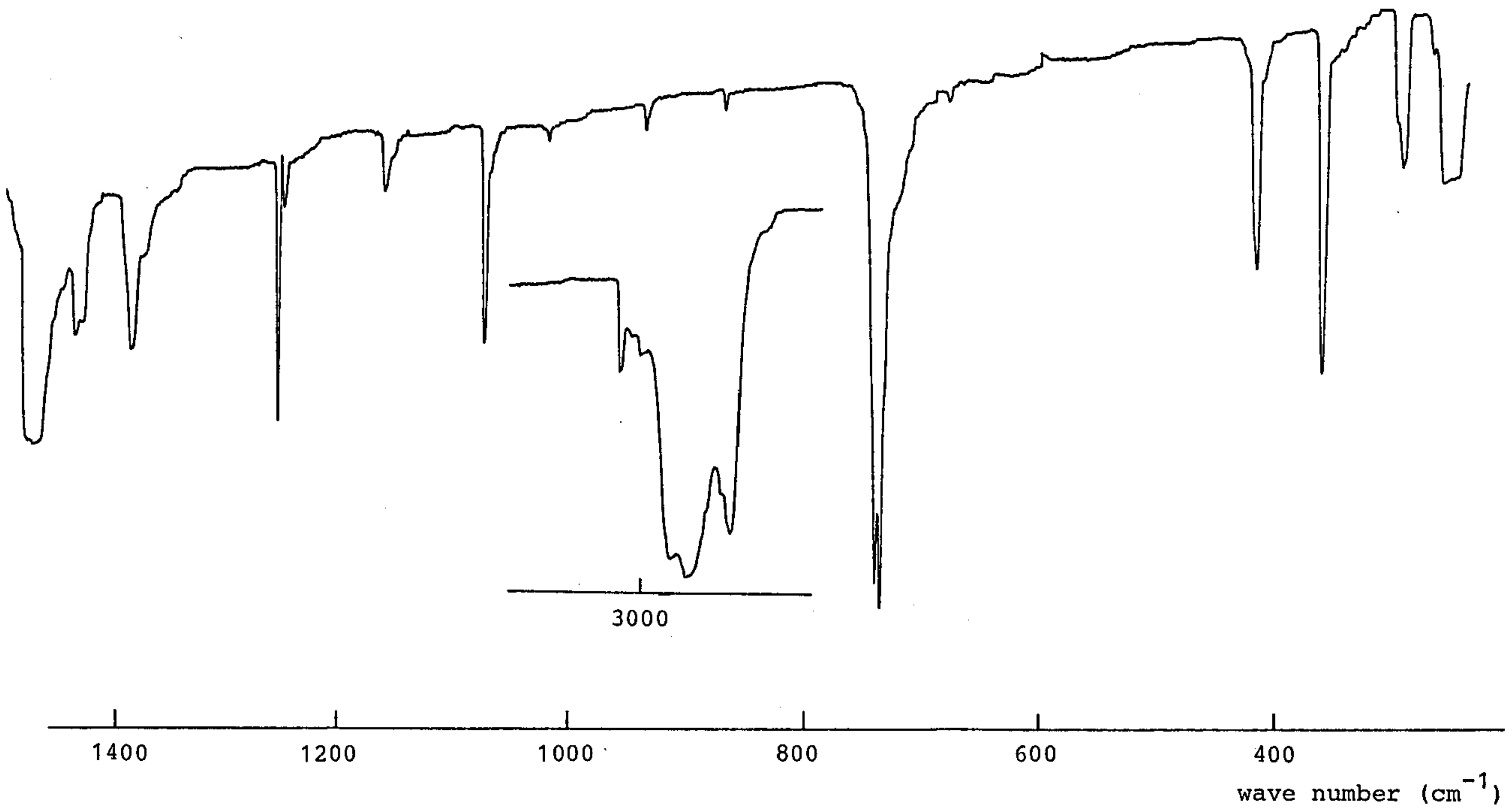


Figure 6.3 : Infrared Spectrum of 1,6-Distibatriptycene in Nujol.

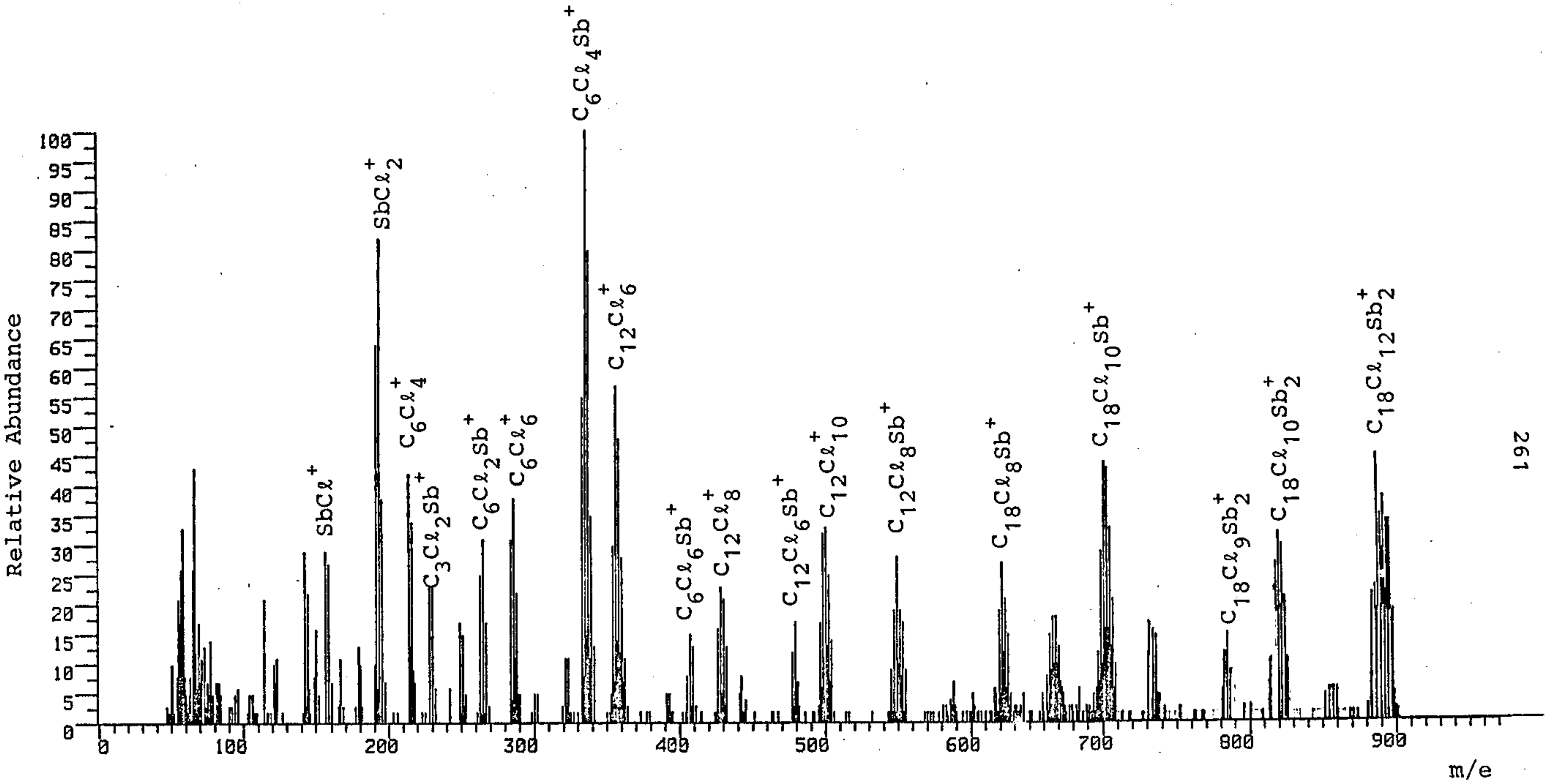


Figure 6.4 : Partial Mass Spectrum of Perchloro-1,6-distibatriptycene.

Table 6.2

Partial Mass Spectrum of Perchloro-1,6-distibatriptycene (only the most intense peak is recorded for isotopomeric clusters of peaks).

m/e	Ion	Relative Abundance
882	$C_{18}C\ell_{12}Sb_2^+$	44.7
848	$C_{18}C\ell_{11}Sb_2^+$	5.4
812	$C_{18}C\ell_{10}Sb_2^+$	27.0
779	$C_{18}C\ell_9Sb_2^+$	14.2
746	$C_{18}C\ell_8Sb_2^+$	2.5
726	$C_{18}C\ell_{11}Sb^+$	16.0
693	$C_{18}C\ell_{10}Sb^+$	42.1
656	$C_{18}C\ell_9Sb^+$	17.0
621	$C_{18}C\ell_8Sb^+$	26.1
588	$C_{18}C\ell_7Sb^+$	6.5
549	$C_{12}C\ell_8Sb^+$	27.2
504	$C_{12}C\ell_7Sb^+$	13.8
500	$C_{12}C\ell_{10}$	32.7
479	$C_{12}C\ell_6Sb^+$	16.3
428	$C_{12}C\ell_8^+$	22.5
407	$C_6C\ell_6Sb^+$	14.5
356	$C_{12}C\ell_6^+$	56.3

Table 6.2 continued..

m/e	Ion	Relative Abundance
335	$C_6Cl_4Sb^+$	100
286	$C_6Cl_6^+$	37.4
265	$C_6Cl_2Sb^+$	30.1
249	$C_6Cl_5^+$	16.3
230	$C_3Cl_2Sb^+$	30.0
214	$C_6Cl_4^+$	41.0
193	$SbCl_2^+$	81.8
156	$SbCl^+$	28.0

Table 6.3

Accurate Mass Measurements on $MM'(C_6F_4)_3$ Species.

Compound	Molecular ion	Observed mass	Calculated mass
I	$^{12}C_{18}{}^{19}F_{12}{}^{31}P_2^+$	505.930	505.928
	$^{12}C_{17}{}^{13}C^{19}F_{12}{}^{31}P_2^+$	506.930	506.932
II	$^{12}C_{18}{}^{19}F_{12}{}^{75}As_2^+$	593.824	593.824
III	$^{12}C_{18}{}^{19}F_{12}{}^{121}Sb_2^+$	685.789	685.789
IV	$^{12}C_{18}{}^{19}F_{12}{}^{209}Bi_2$	861.9425	861.942
V	$^{12}C_{20}{}^{1}H_6{}^{19}F_{12}{}^{28}Si_2^+$	529.982	529.965
	$^{12}C_{20}{}^{1}H_6{}^{19}F_{12}{}^{28}Si^{30}Si^+$	531.972	531.978
VI	$^{12}C_{18}{}^{19}F_{12}{}^{31}P^{75}As^+$	549.876	549.876
VIII	$^{12}C_{18}{}^{19}F_{12}{}^{75}As^{121}Sb^+$	639.804	639.806

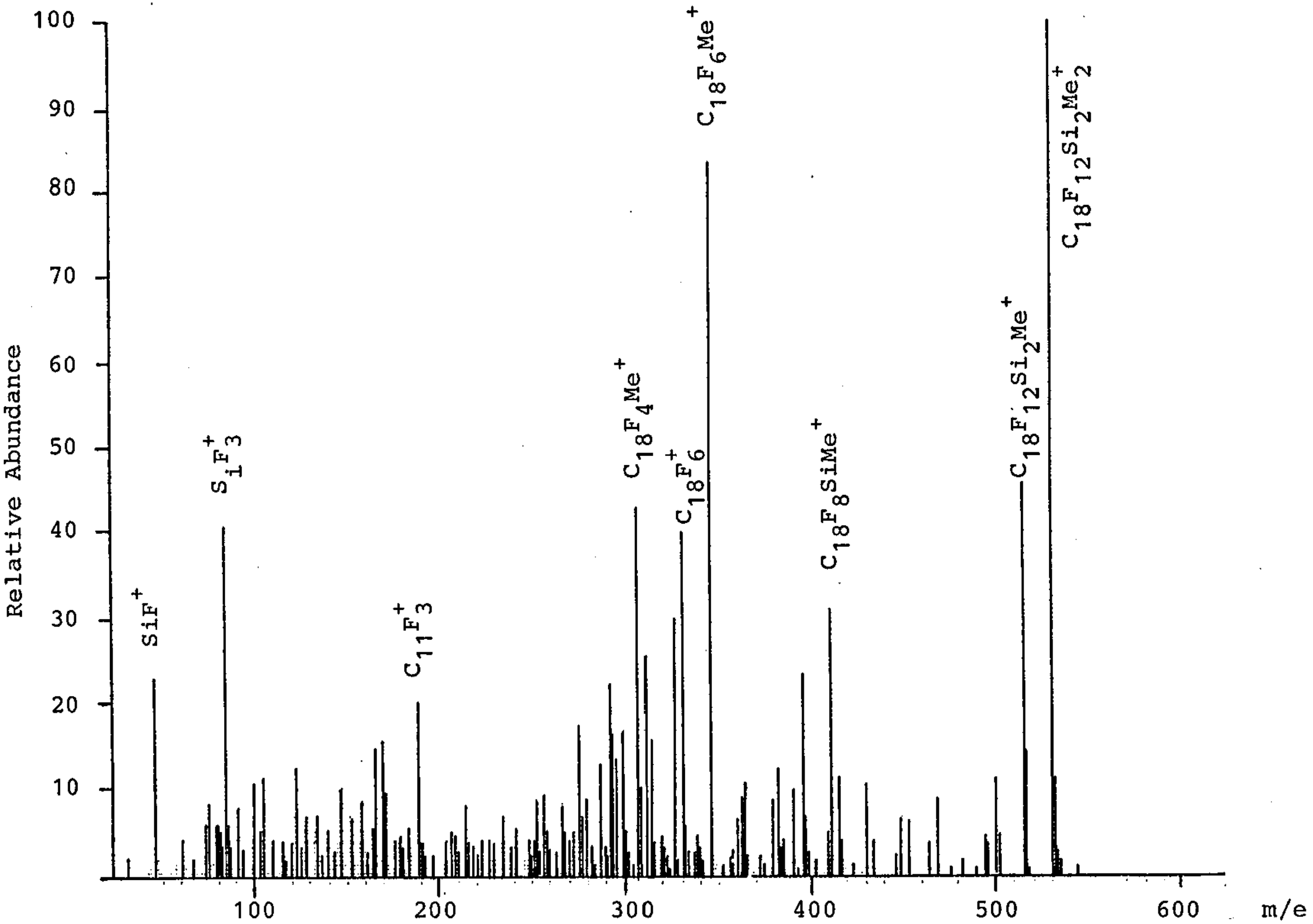


Figure 6.5 : Partial Mass Spectrum of 1,6-Dimethyl-dodecafluoro-1,6-disilatriptycene.

Table 6.4

Partial Mass Spectrum of 1,6-Dimethyldodecafluoro-1,6-disilatriptycene (the relative abundance of ^{28}Si for isotopomeric clusters of peaks is recorded).

m/e	Ion	Relative Abundance
530	$C_{18}F_{12}Si_2Me_2^+$	100.0
515	$C_{18}F_{12}Si_2Me^+$	46.0
500	$C_{18}F_{12}Si_2^+$	2.5
468	$C_{18}F_{11}SiMe$	8.83
430	$C_{18}F_9SiMe^+$	10.8
411	$C_{18}F_8SiMe^+$	31.3
396	$C_{18}F_8Si^+$	30.0
345	$C_{18}F_6Me^+$	85.11
330	$C_{18}F_6^+$	40.0
311	$C_{18}F_5^+$	25.3
307	$C_{18}F_4^+Me$	43.8
292	$C_{18}F_4^+$	22.1
189	$C_{11}F_3^+$	20.4
176	$C_6F_4Si^+$	4.0
157	$C_6F_3Si^+$	7.7
85	SiF_3^+	40.8
47	SiF^+	22.5

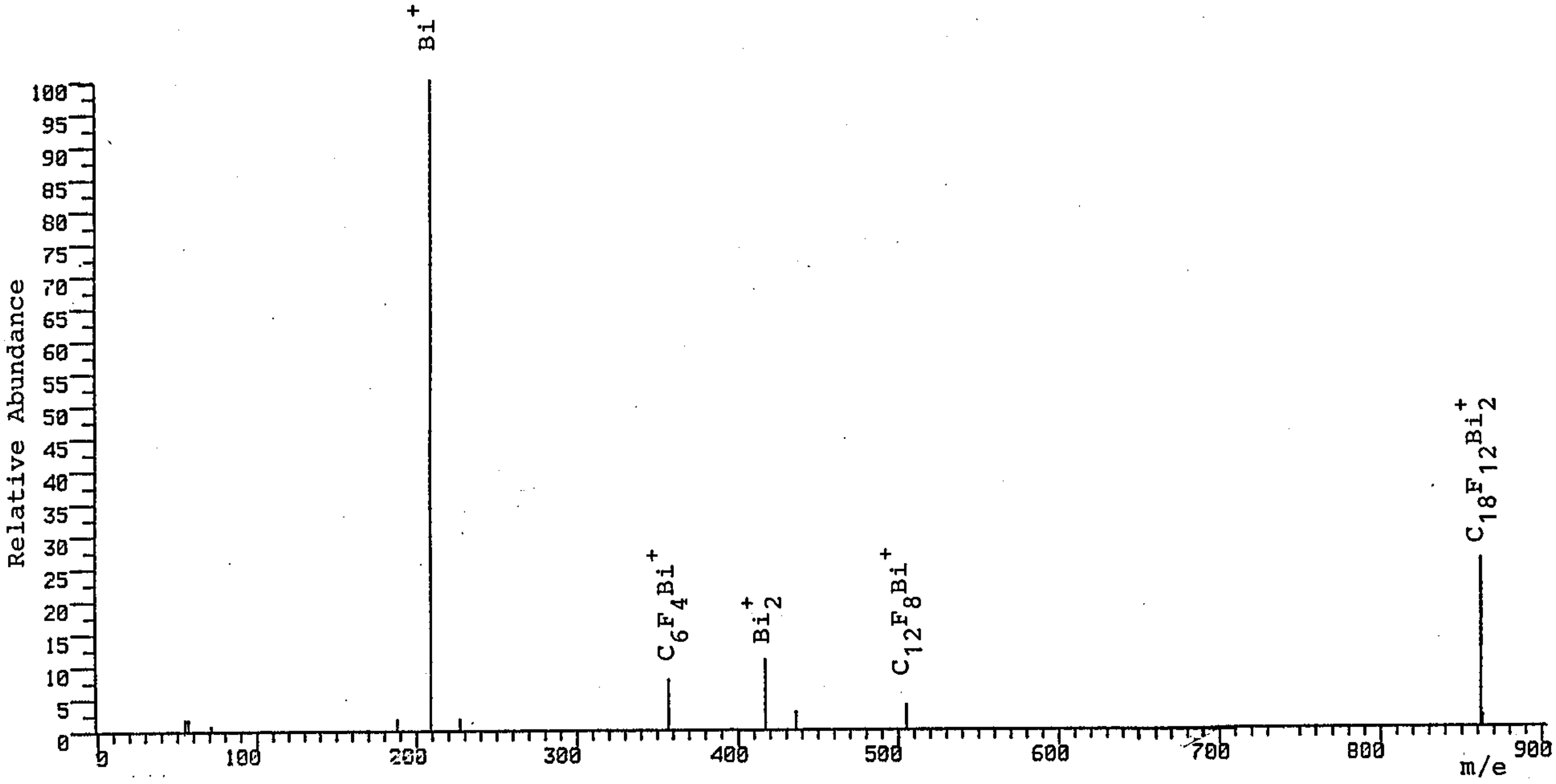


Figure 6.6 : Partial Mass Spectrum of Perfluoro-1,6-dibismuthtriptycene.

Table 6.5

Partial Mass Spectrum of Perfluoro 1,6-dibismuthtriptycene.

m/e	Ion	Relative Abundance
862	$C_{18}F_{12}Bi_2^+$	25.4
505	$C_{12}F_8Bi^{+\cdot}$	3.9
437	Bi_2F^+	2.2
418	Bi_2^+	10.9
357	$C_6F_4Bi^+$	7.2
228	BiF^+	1.6
209	Bi^+	100.0
189	$C_{11}F_3^+$	1.4
57	F_3^+	1.6
55	C_3F^+	1.1

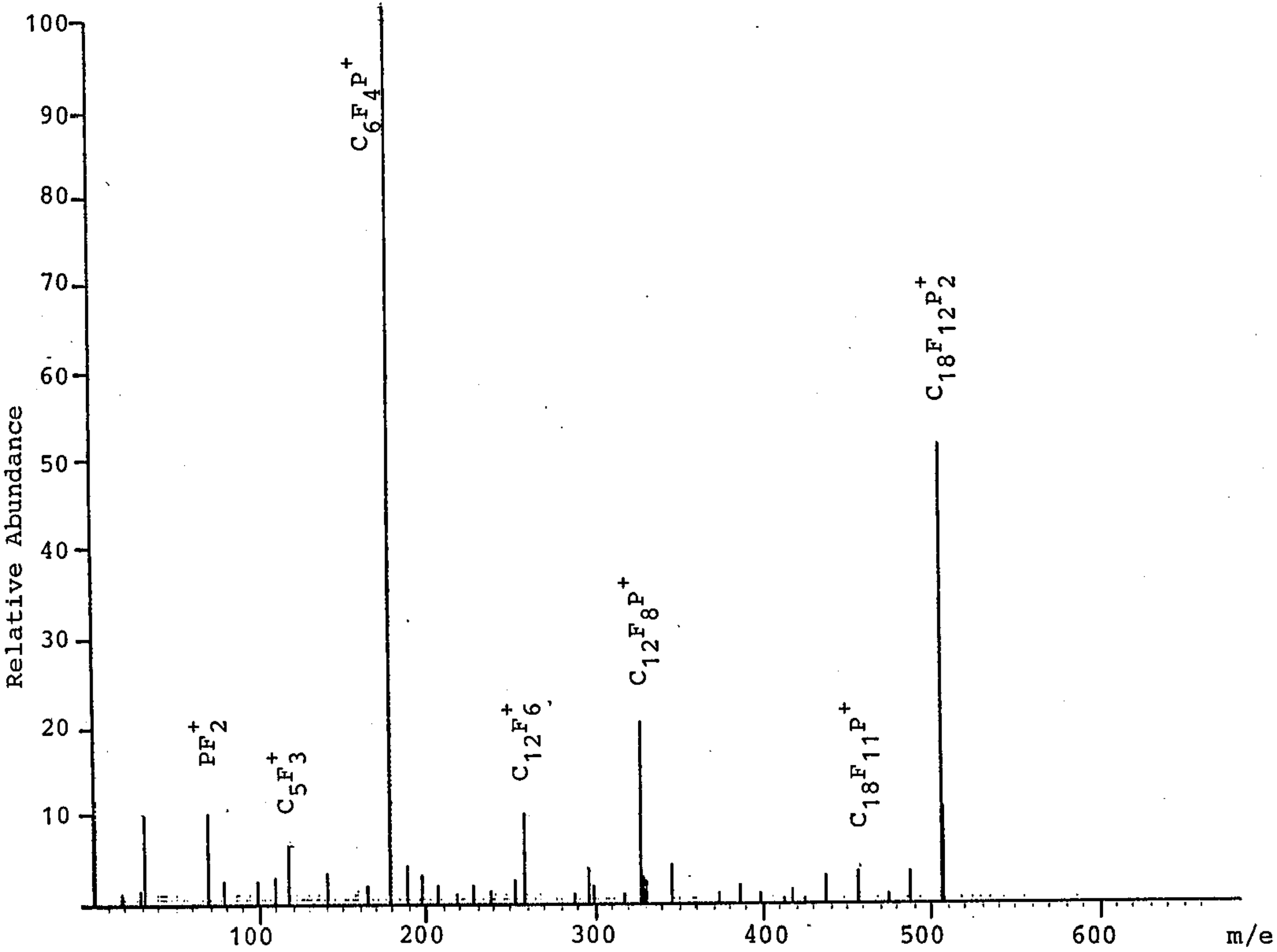


Figure 6.7 : Partial Mass Spectrum of Perfluoro-1,6-diphosphatriptycene.

Table 6.6

Partial Mass Spectrum of Perfluoro-1,6-diphosphatriptycene.

m/e	Ion	Relative Abundance
506	$C_{18}F_{12}P_2^+$	51.6
487	$C_{18}F_{11}P_2^+$	3.3
456	$C_{18}F_{11}P^+$	3.3
437	$C_{18}F_{10}P^+$	2.8
327	$C_{12}F_8P^+$	20.5
296	$C_{12}F_8^+$	3.7
258	$C_{12}F_6^+$	9.5
179	$C_6F_4P^+$	100.0
117	$C_5F_3^+$	6.3
110	$C_6F_2^+$	0.3
69	PF_2^+	1.0

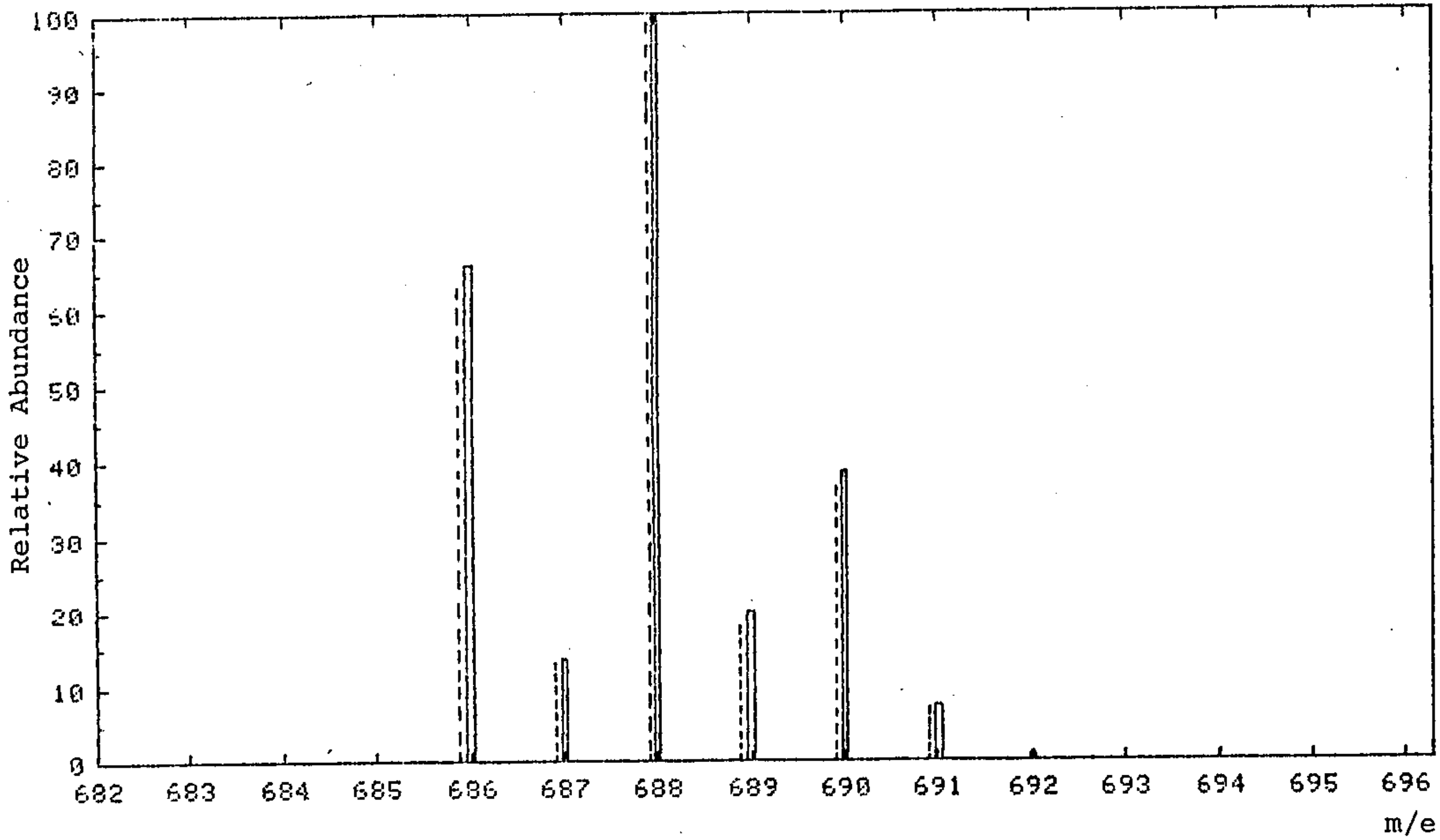


Figure 6.8 : Comparison of the Observed (broken line) and Theoretical (solid line) Mass Spectral Intensities for the Parent ion $Sb_2(C_6F_4)_3^+$.

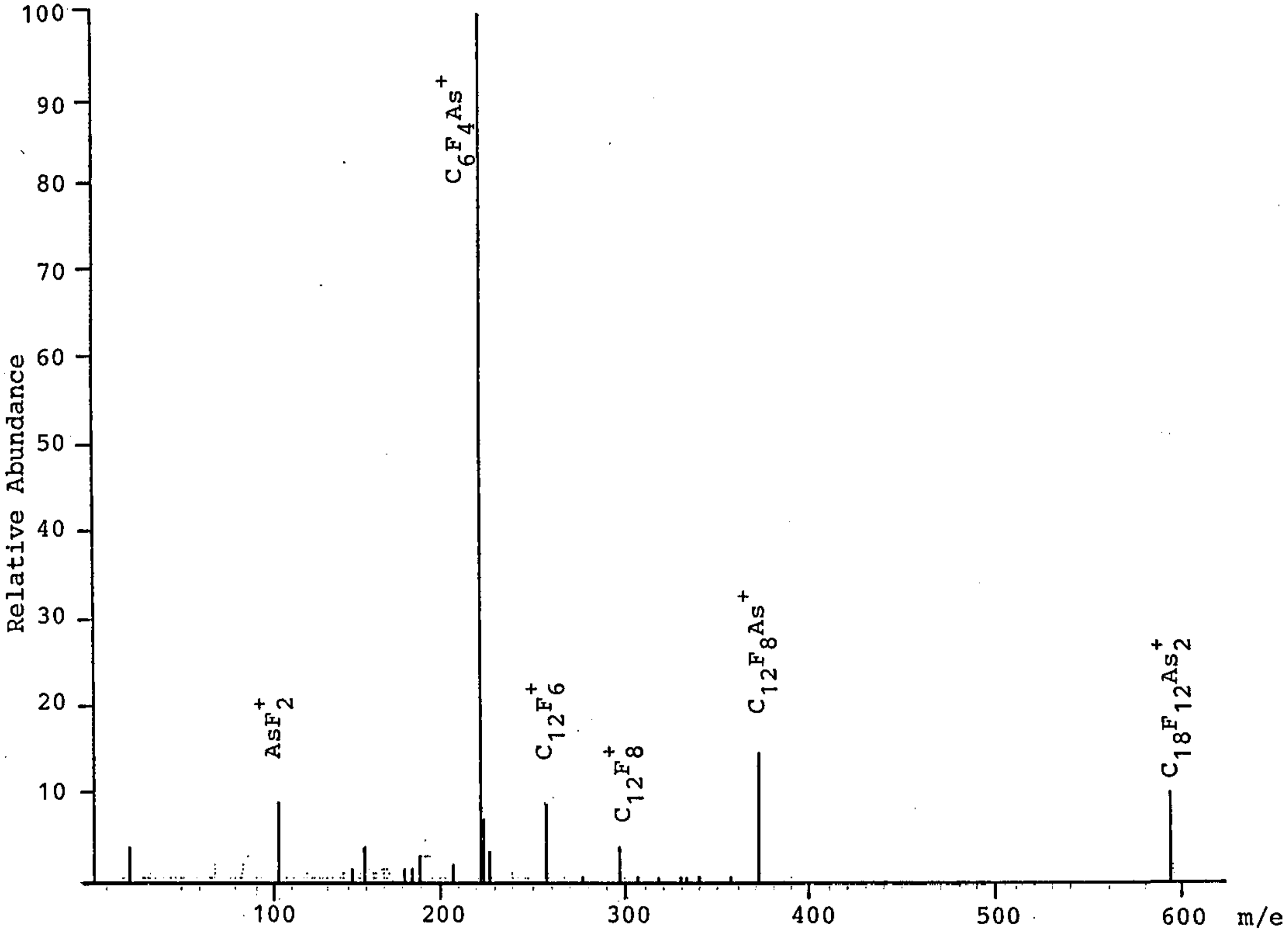


Figure 6.9 : Partial Mass Spectrum of Perfluoro-1,6-diarsatriptycene.

Table 6.7

Partial Mass Spectrum of Perfluoro-1,6-diarsatriptycene.

m/e	Ion	Relative Abundance
594	$C_{18}F_{12}As_2^+$	9.48
575	$C_{18}F_{11}As_2^+$	0.8
500	$C_{18}F_{11}As^+$	0.4
481	$C_{18}F_{10}As^+$	1.6
462	$C_{18}F_9As^+$	0.2
371	$C_{12}F_8As^+$	14.34
296	$C_{12}F_8^+$	3.49
258	$C_{12}F_6^+$	9.35
246	$C_{11}F_6^+$	0.3
227	$C_{11}F_5^+$	3.0
223	$C_6F_4As^+$	100.0
189	$C_{11}F_3^+$	2.90
113	AsF_2^+	8.7

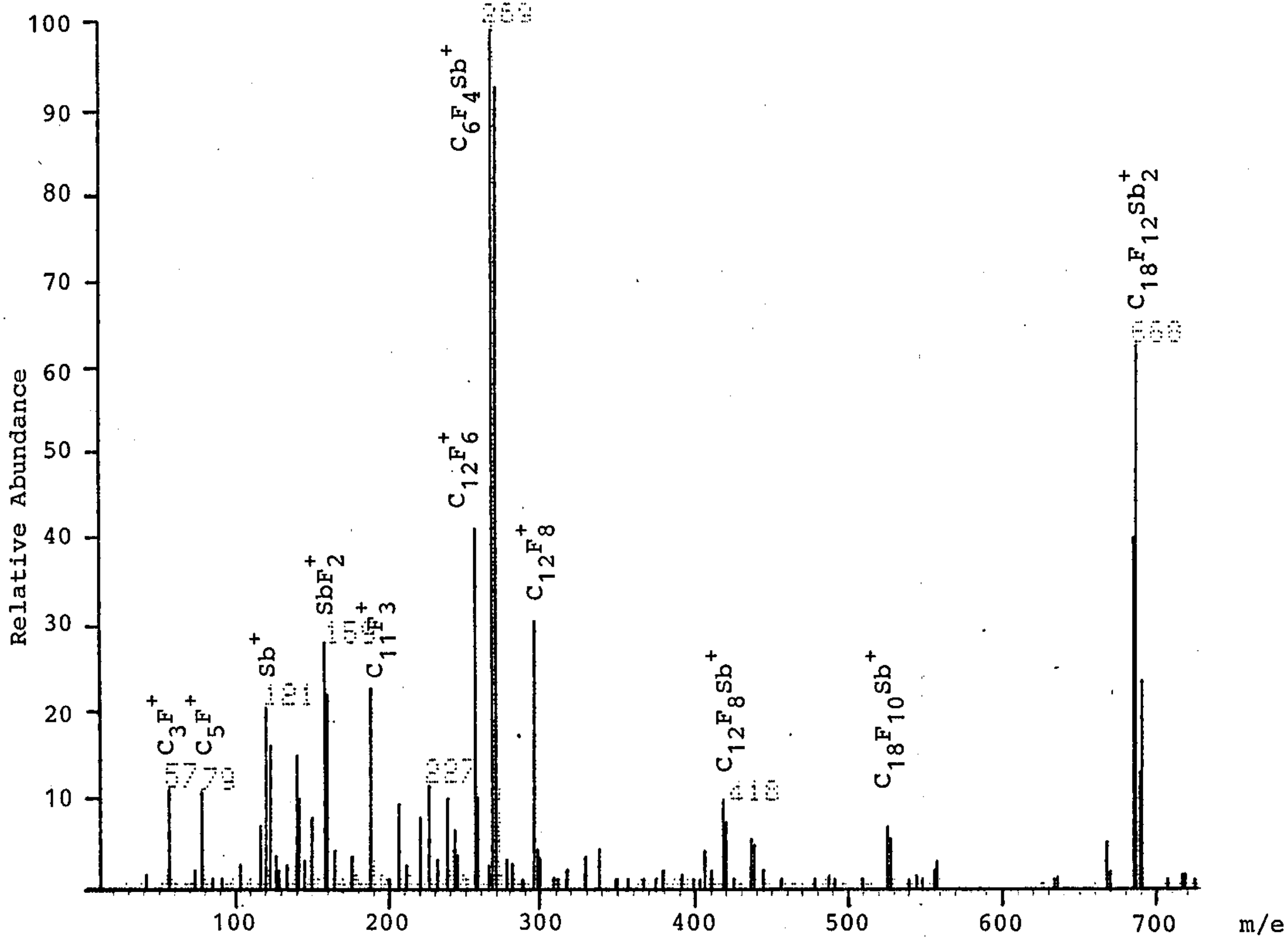


Figure 6.10 : Partial Mass Spectrum of Perfluoro-1,6-distibatriptycene.

Table 6.8

Partial Mass Spectrum of Perfluoro-1,6-distibatriptycene (the relative abundance of ions containing the ^{121}Sb isotope is recorded).

m/e	Ion	Relative Abundance
688	$C_{18}F_{12}Sb_2^+$	62.7
669	$C_{18}F_{11}Sb_2$	4.9
527	$C_{18}F_{10}Sb^+$	6.9
444	$C_{18}F_{12}^+$	0.2
418	$C_{12}F_8Sb^+$	9.8
406	$C_{18}F_{10}^+$	3.8
337	$C_{18}F_7^+$	4.1
330	$C_{18}F_6^+$	3.2
296	$C_{12}F_8^+$	30.6
269	$C_6F_4Sb^+$	100.0
258	$C_{12}F_6^+$	41.1
233	$C_6F_2Sb^+$	2.5
227	$C_{11}F_5^+$	11.8
208	$C_{11}F_4^+$	9.3
189	$C_{11}F_3^+$	22.7
159	SbF_2^+	28.3
140	SbF^+	14.8

Table 6.8 continued...

m/e	Ion	Relative Abundance
121	Sb^+	20.7
117	$C_5F_3^+$	6.5
79	C_5F^+	11.0
57	C_3F^+	11.4

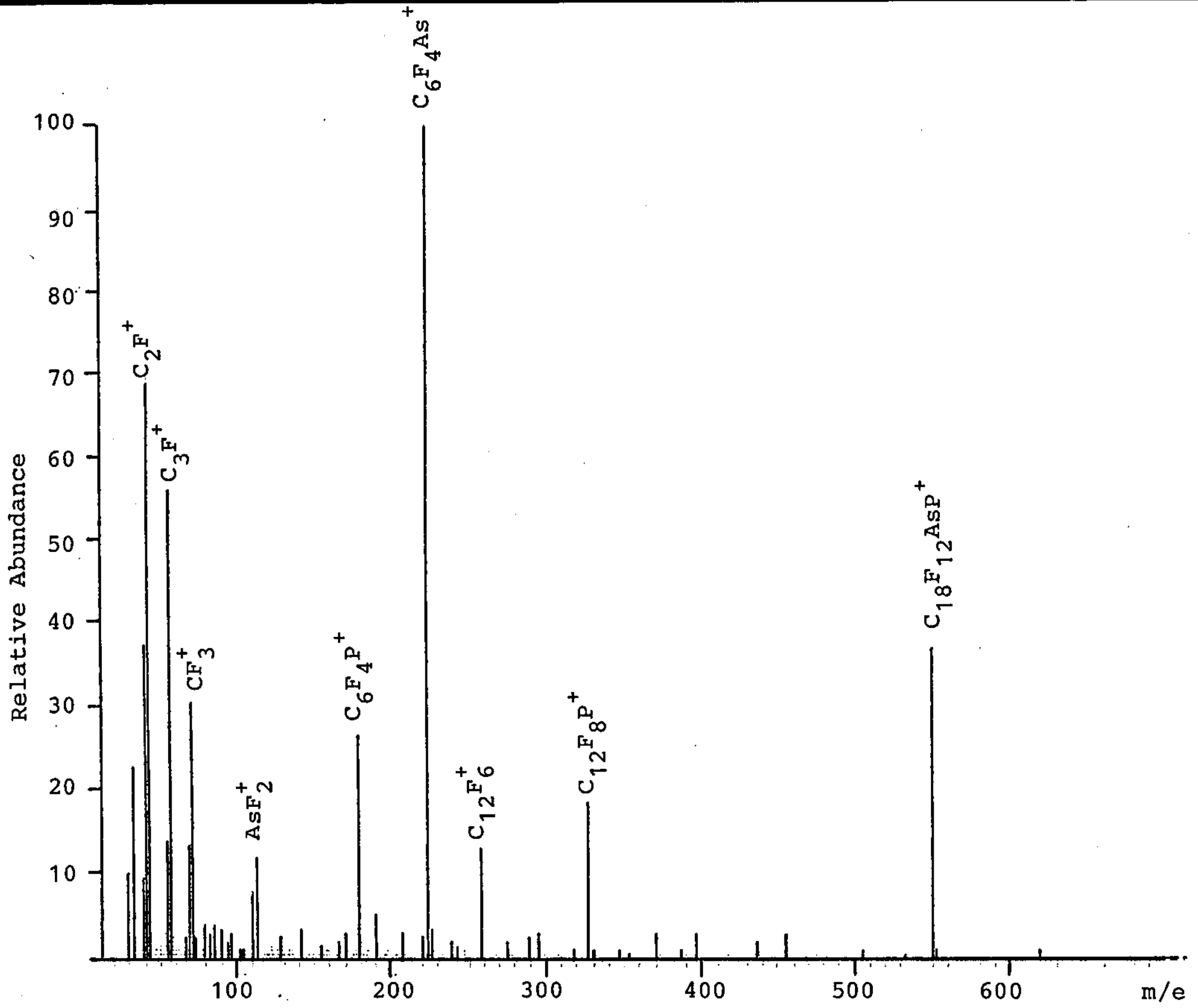


Figure 6.11 : Partial Mass Spectrum of Perfluoro-1,6-arsaphosphatriptycene.

Table 6.9

Partial Mass Spectrum of Perfluoro-1,6-arsaphosphatriptycene

m/e	Ion	Relative Abundance
550	$C_{18}F_{12}AsP^+$	37.0
456	$C_{18}F_{11}P^+$	2.3
371	$C_{12}F_8As^+$	2.8
327	$C_{12}F_8P^+$	18.4
296	$C_{12}F_8^+$	2.6
258	$C_{12}F_6^+$	12.6
227	$C_{11}F_5^+$	3.25
223	$C_6F_4As^+$	100.0
208	$C_{11}F_4^+$	2.8
189	$C_{11}F_3^+$	4.5
179	$C_6F_4P^+$	26.6
113	AsF_2^+	11.7
79	C_5F^+	3.8
71	CF_3^+	30.5
57	C_3F^+	56.0
43	C_2F^+	69.6

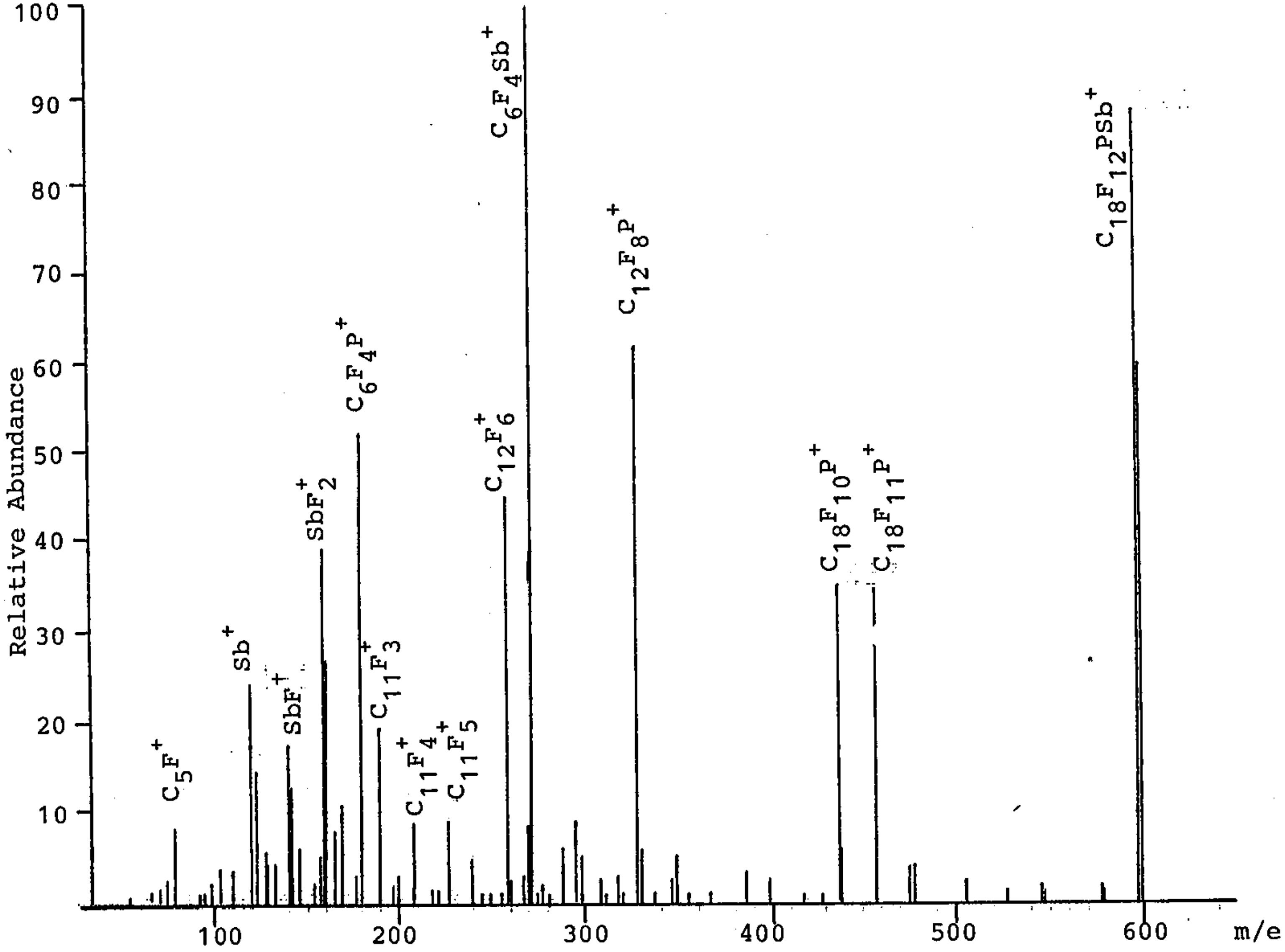


Figure 6.12 : Partial Mass Spectrum of Perfluoro-1,6-phosphastibatriptycene.

Table 6.10

Partial Mass Spectrum of Perfluoro-phosphastibatriptycene (the relative abundance of ions containing the ^{121}Sb isotope is recorded).

m/c	Ion	Relative Abundance
596	$C_{18}F_{12}PSb^+$	87.44
475	$C_{18}F_{12}P^+$	4.0
456	$C_{18}F_{11}P^+$	35.2
437	$C_{18}F_{10}P^+$	35.2
330	$C_{18}F_6^+$	5.8
327	$C_{12}F_8P^+$	62.4
296	$C_{12}F_8^+$	8.8
271	$C_6F_4Sb^+$	100.0
258	$C_{12}F_6^+$	44.7
227	$C_{11}F_5^+$	9.0
208	$C_{11}F_4^+$	8.6
189	$C_{11}F_3^+$	19.5
179	$C_6F_4P^+$	52.0
159	SbF_2^+	38.8
140	SbF^+	16.6
121	Sb^+	24.0
79	C_5F^+	7.6

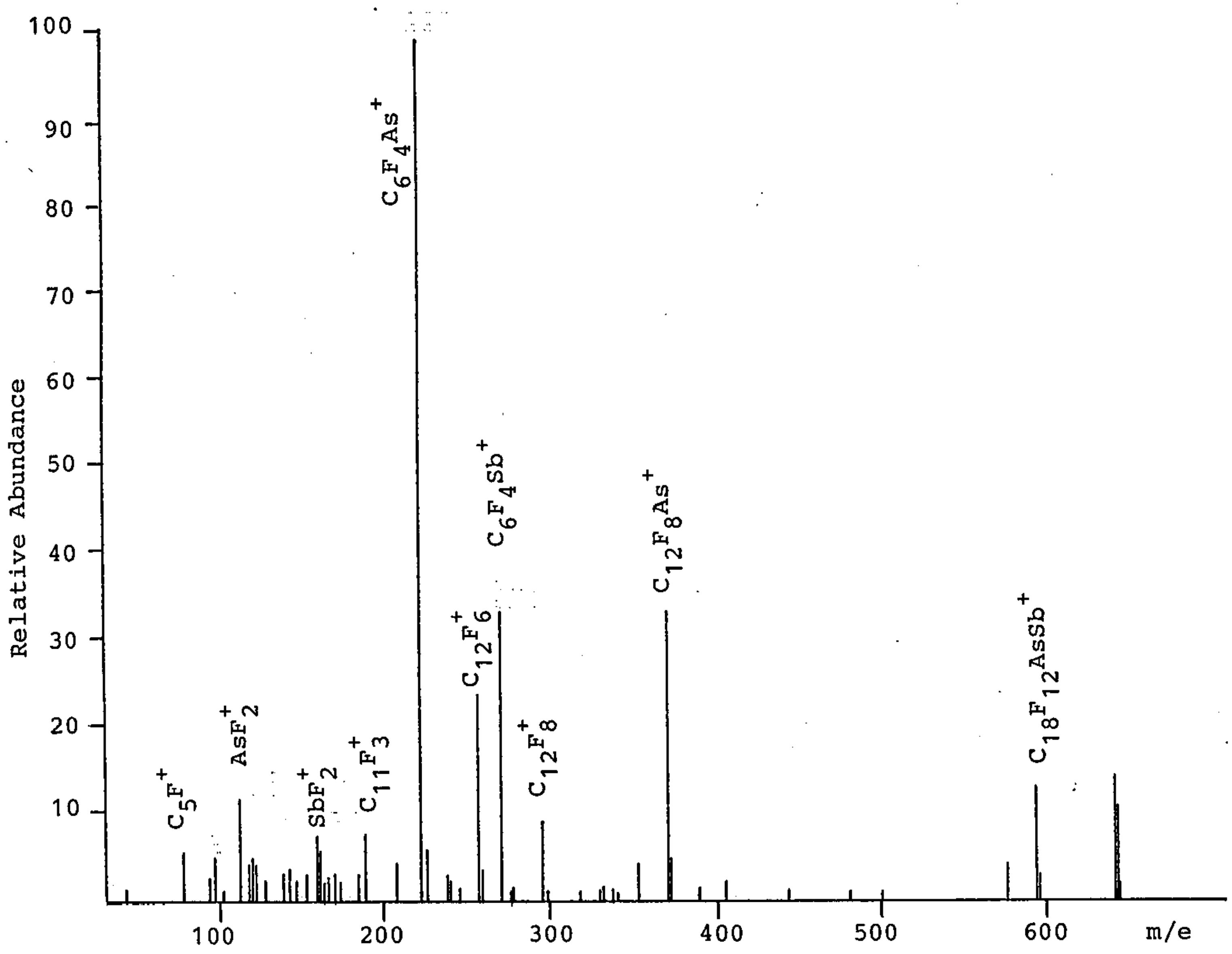


Figure 6.13 : Partial Mass Spectrum of Perfluoro-1,6-arsastibatriptycene.

Table 6.11

Partial Mass Spectrum of Perfluoro-arsastibatriplycene (the relative abundance of ions containing the ^{121}Sb isotope is recorded).

m/e	Ion	Relative Abundance
640	$C_{18}F_{12}AsSb^+$	14.0
371	$C_{12}F_8As^+$	32.8
353	$C_{12}F_7As^+$	4.1
296	$C_{12}F_8^+$	8.69
269	$C_6F_4Sb^+$	46.0
258	$C_{12}F_6^+$	23.0
227	$C_{11}F_5^+$	5.7
223	$C_6F_4As^+$	100
208	$C_{11}F_4^+$	3.5
189	$C_{11}F_3^+$	7.5
159	SbF_2^+	7.2
140	SbF^+	2.7
121	Sb^+	4.7
117	$C_5F_3^+$	3.8
113	AsF_2^+	11.9
98	$C_5F_2^+$	4.3
79	C_5F^+	5.5

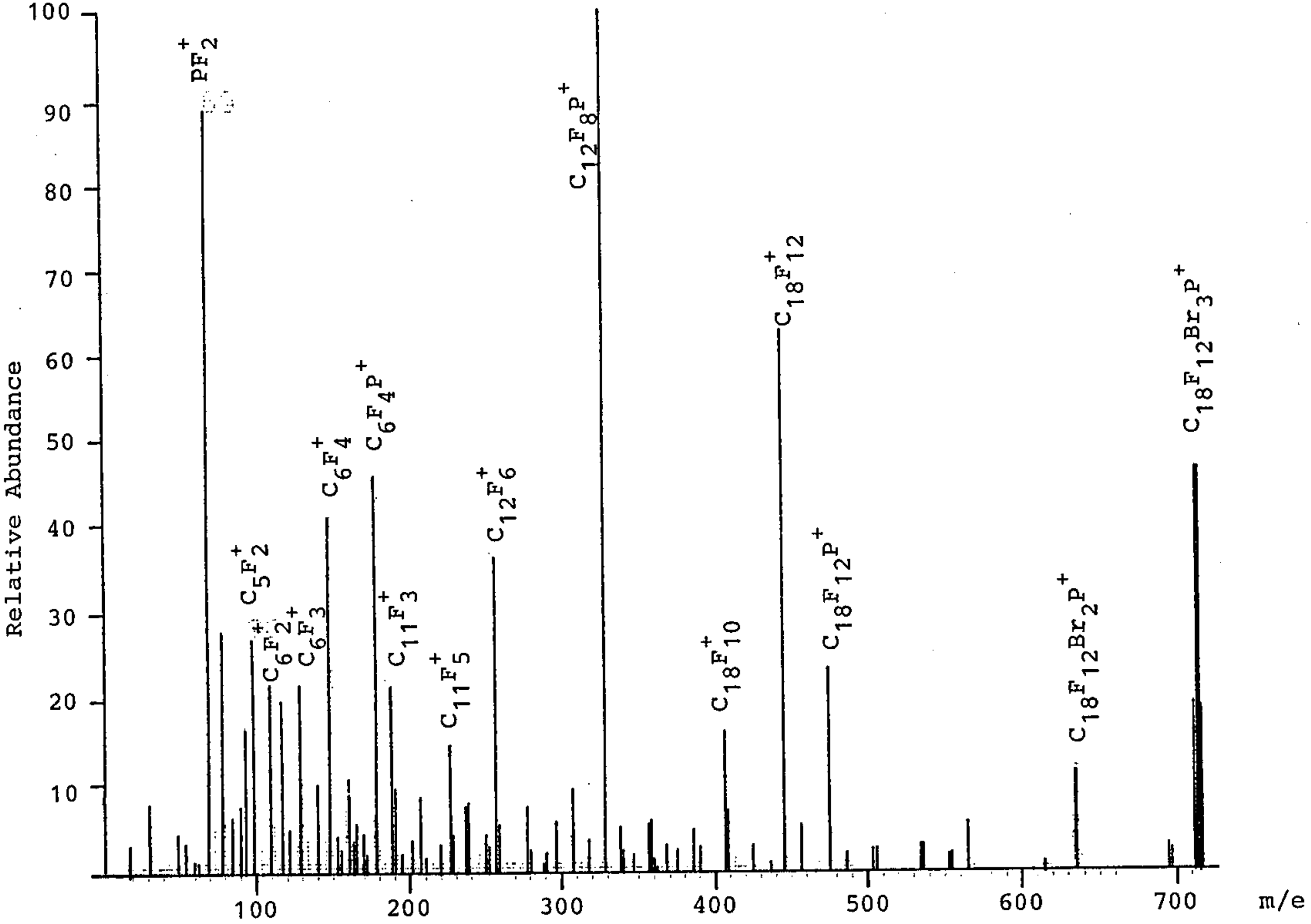


Figure 6.14 : Partial Mass Spectrum of Tris(2-bromotetrafluorophenyl)phosphine.

Table 6.12

Partial Mass Spectrum of Tris(2-bromotetrafluorophenyl)phosphine (only the most intense peak is recorded for isotopomeric clusters of peaks).

m/e	Ion	Relative Abundance
714	$C_{18}F_{12}Br_3P^+$	46.8
697	$C_{18}F_{11}BrP^+$	2.3
635	$C_{18}F_{12}Br_2P^+$	11.87
535	$C_{18}F_{11}BrP^+$	2.4
504	$C_{18}F_{11}Br^+$	2.17
475	$C_{18}F_{12}P^+$	23.38
444	$C_{18}F_{12}^+$	63.0
327	$C_{12}F_8P^+$	100.0
258	$C_{12}F_6^+$	36.7
227	$C_{11}F_5^+$	14.0
298	$C_{11}F_4^+$	8.2
189	$C_{11}F_3^+$	21.2
179	$C_6F_4P^+$	43.7
179	$C_{11}F_2^+$	4.0
148	$C_6F_4^+$	40.7
129	$C_6F_3^+$	9.7
117	$C_5F_3^+$	20.1

Table 6.12 continued...

m/e	Ion	Relative Abundance
110	$C_6F_2^+$	21.2
98	$C_5F_2^+$	27.1
93	CF_2P^+	16.6
91	C_6F^+	7.1
79	C_5F^+	21.7
69	PF_2^+	89.0

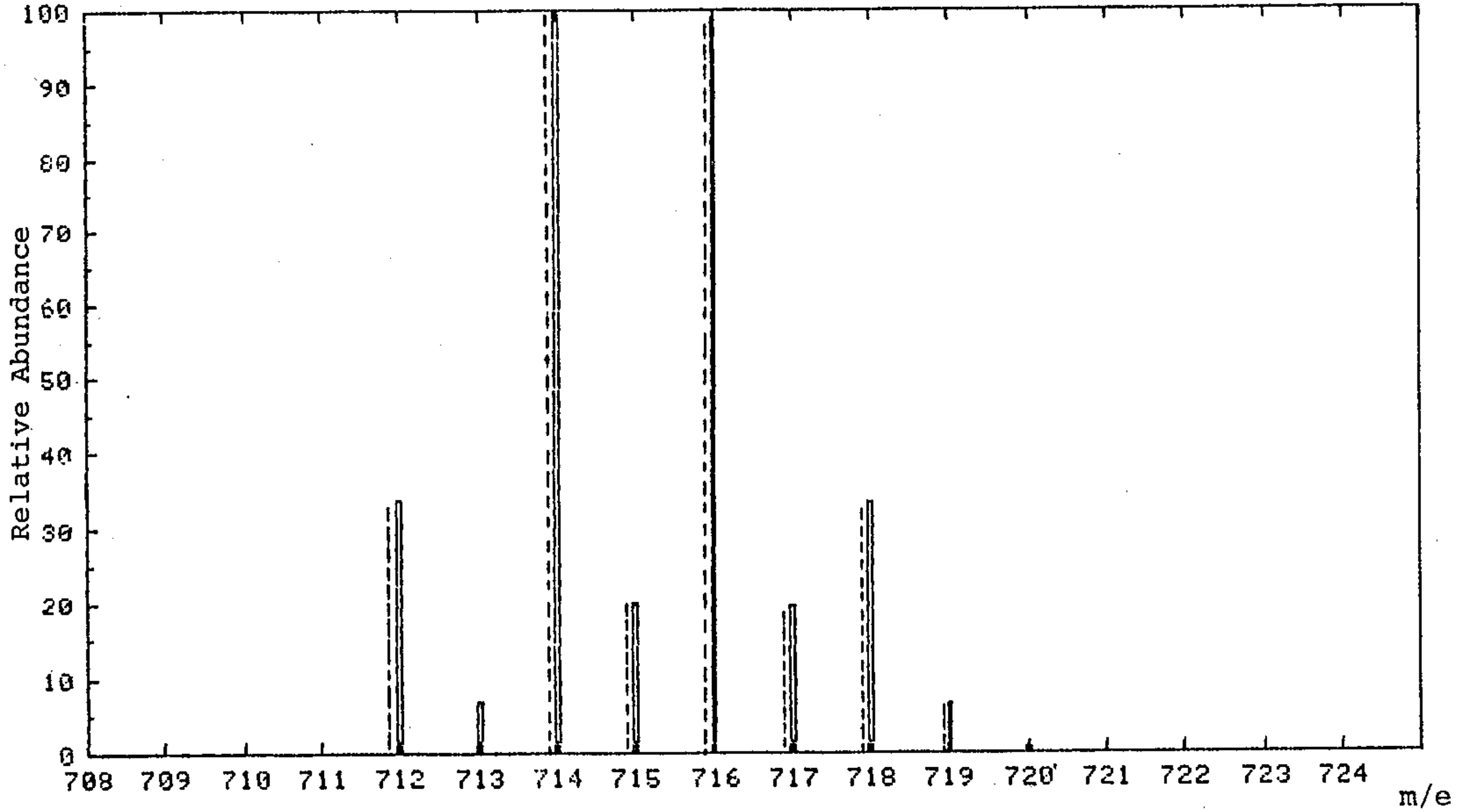


Figure 6.15 : Comparison of the Observed (broken line) and Theoretical (solid line) Mass Spectral Intensities for the Parent Ion $P(C_6F_4Br)_3^{+}$.

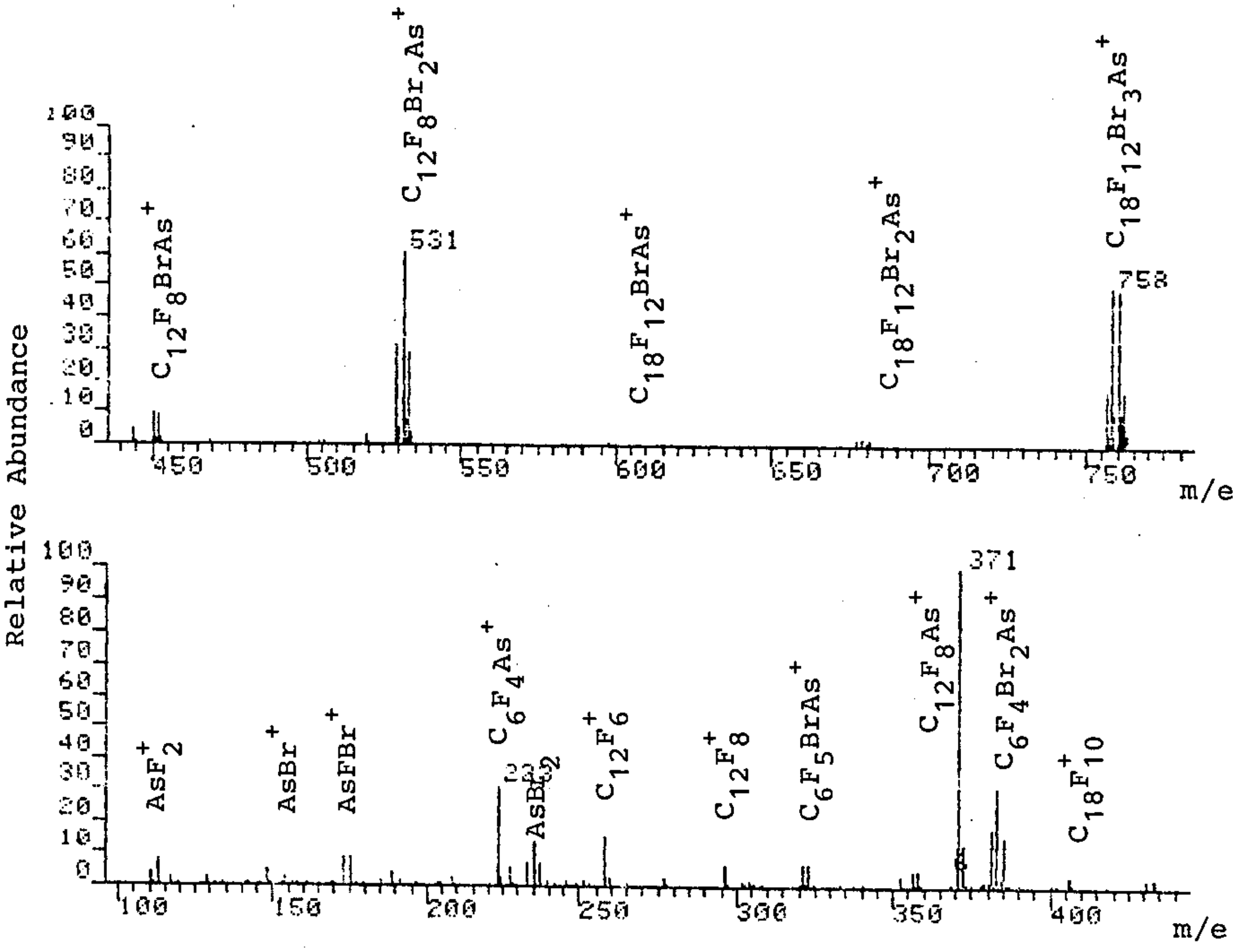


Figure 6.16 : Partial Mass Spectrum of Tris(2-bromotetrafluorophenyl)arsenic.

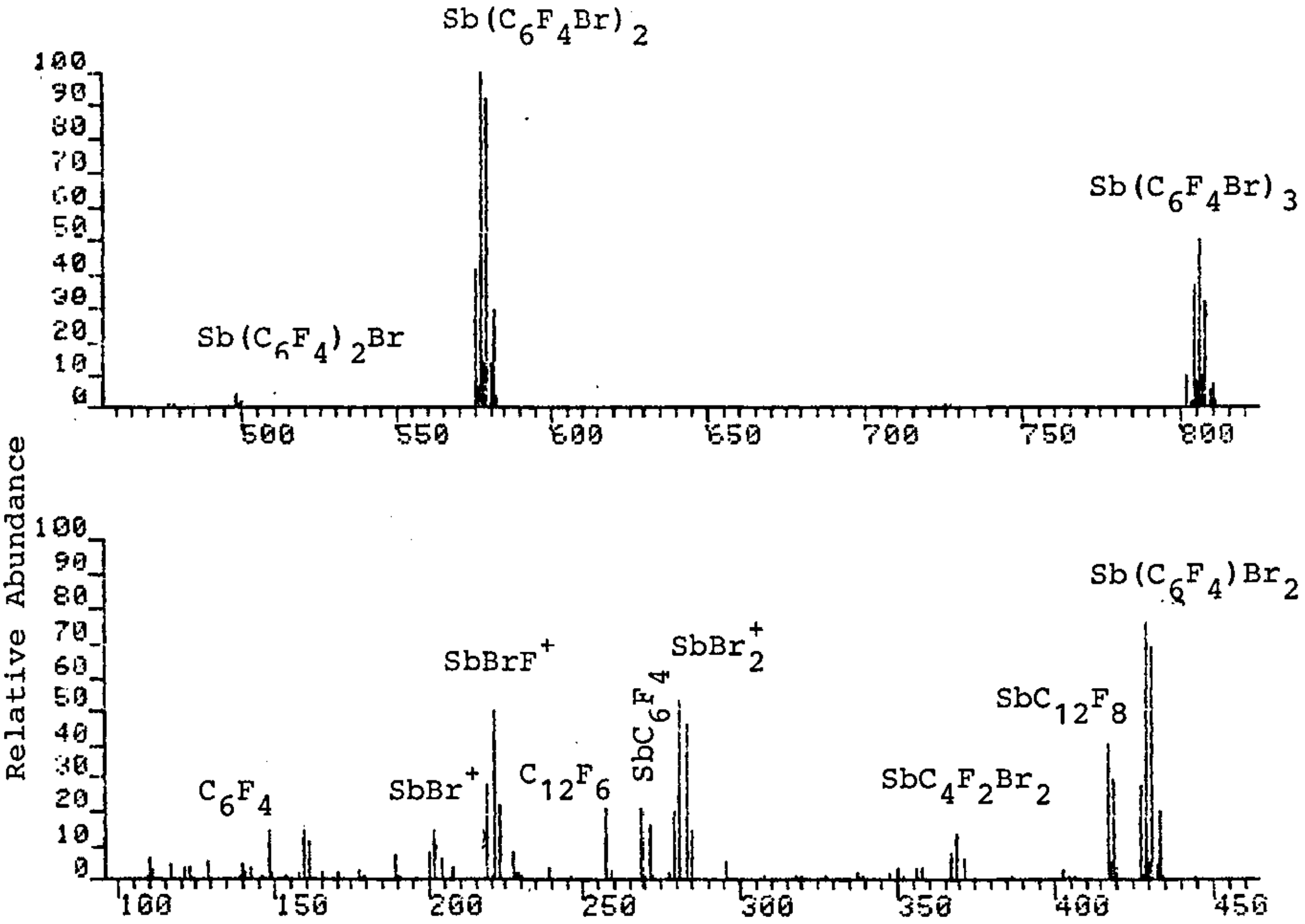


Figure 6.17 : Partial Mass Spectrum of Tris(2-bromotetrafluorophenyl)antimony.

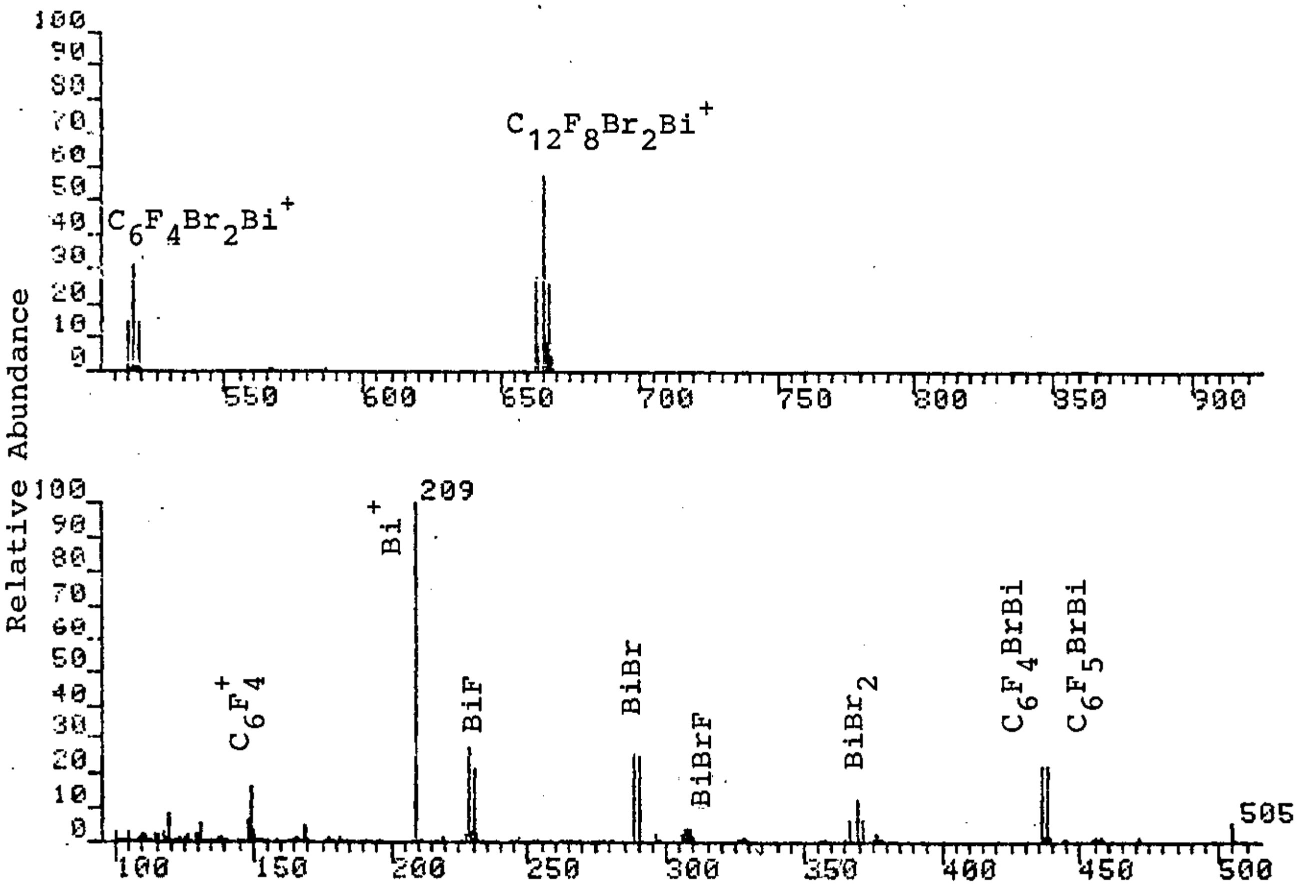


Figure 6.18 : Partial Mass Spectrum of Tris(2-bromotetrafluorophenyl)bismuth.

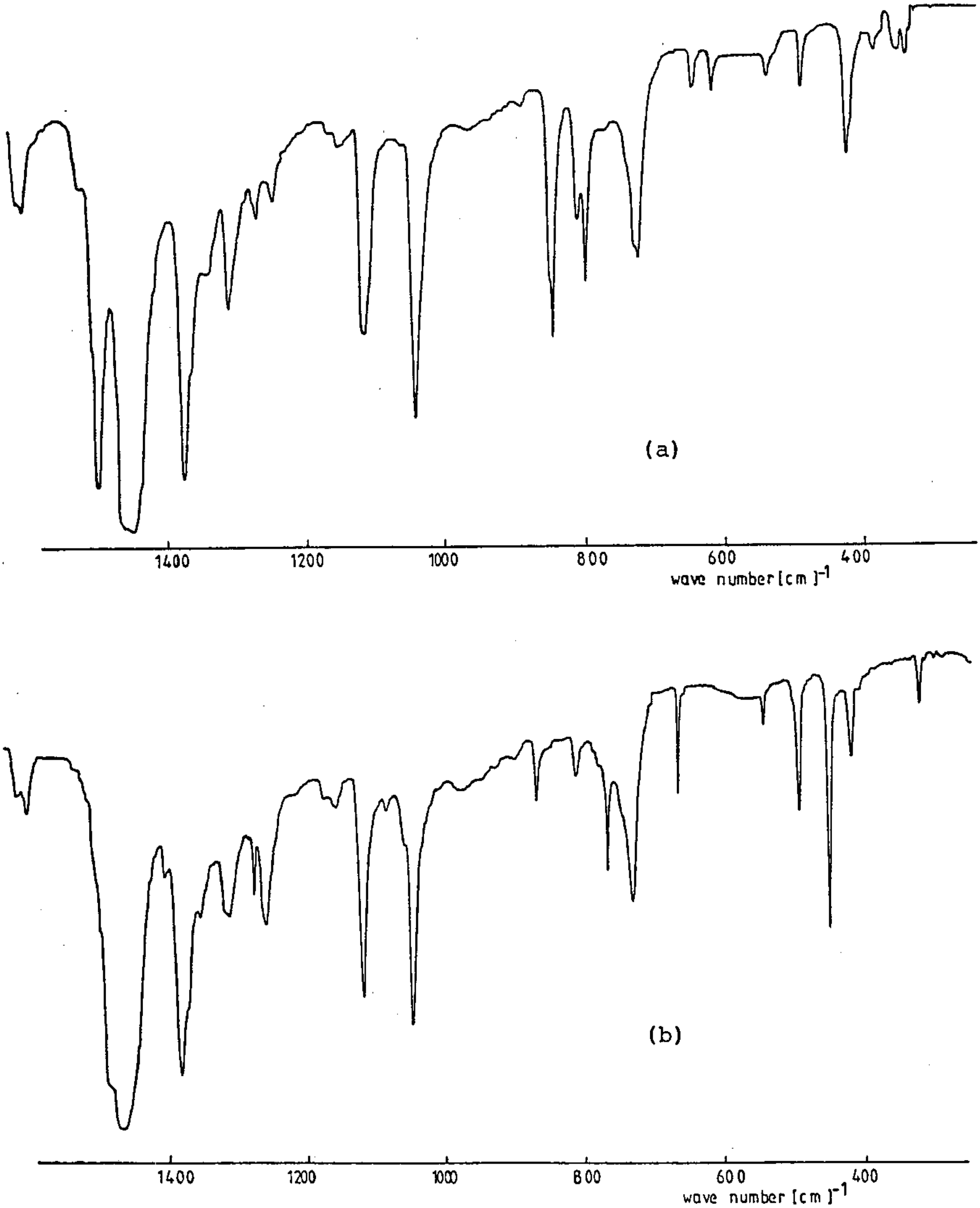


Figure 6.19 : Infrared Spectrum of

a) Tris(2-bromotetrafluorophenyl)phosphine

b) Perfluoro-1,6-diphosphatriptycene.

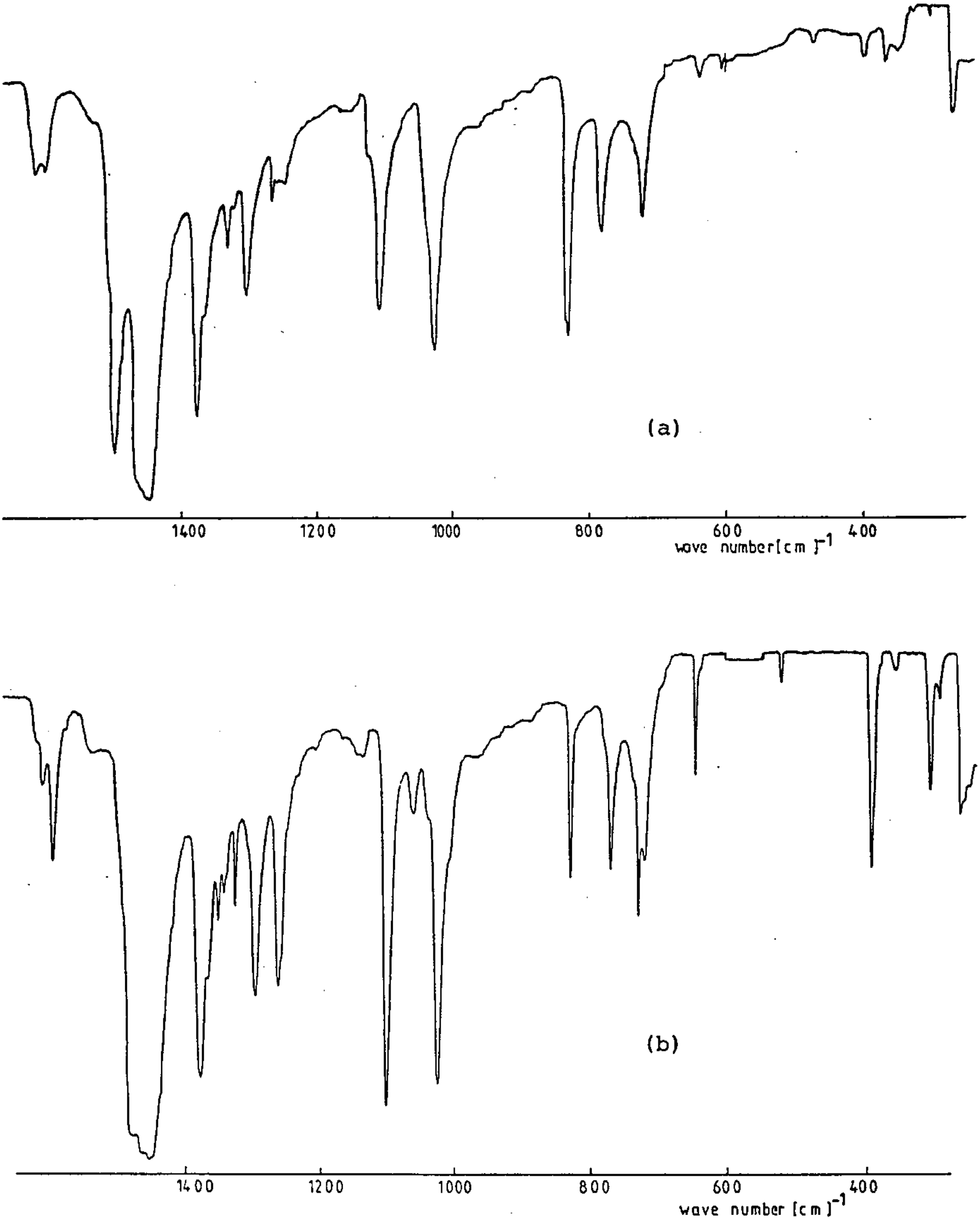


Figure 6.20 : Infrared Spectrum of

a) Tris(2-bromotetrafluorophenyl)arsenic

b) Perfluoro-1,6-diarsatriptycene.

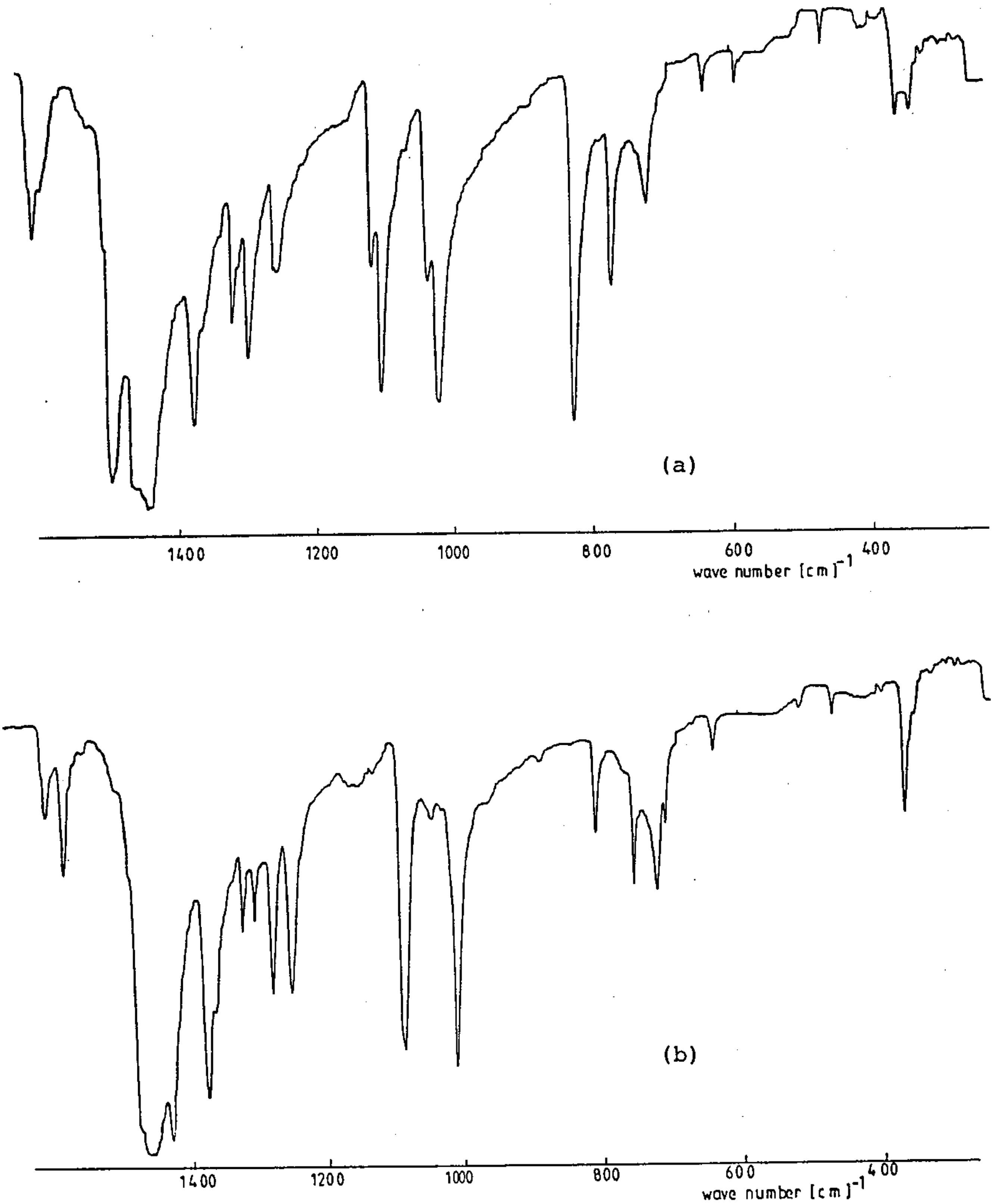


Figure 6.21 : Infrared Spectrum of

a) Tris(2-bromotetrafluorophenyl)antimony

b) Perfluoro-1,6-distibatriptycene.

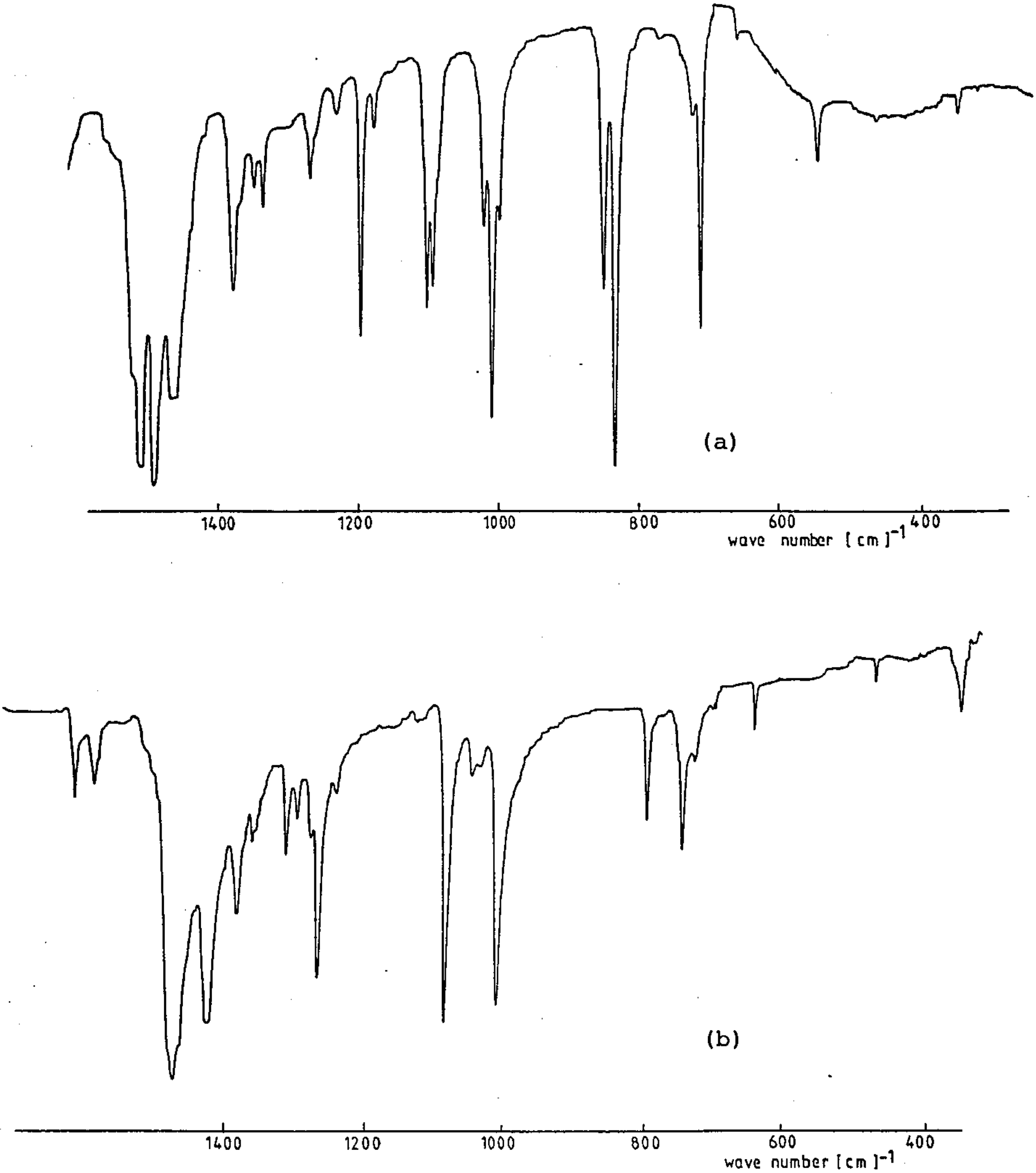


Figure 6.22 : Infrared Spectrum of

a) Tris(2-bromotetrafluorophenyl)bismuth

b) Perfluoro-1,6-dibismuthtriptycene.

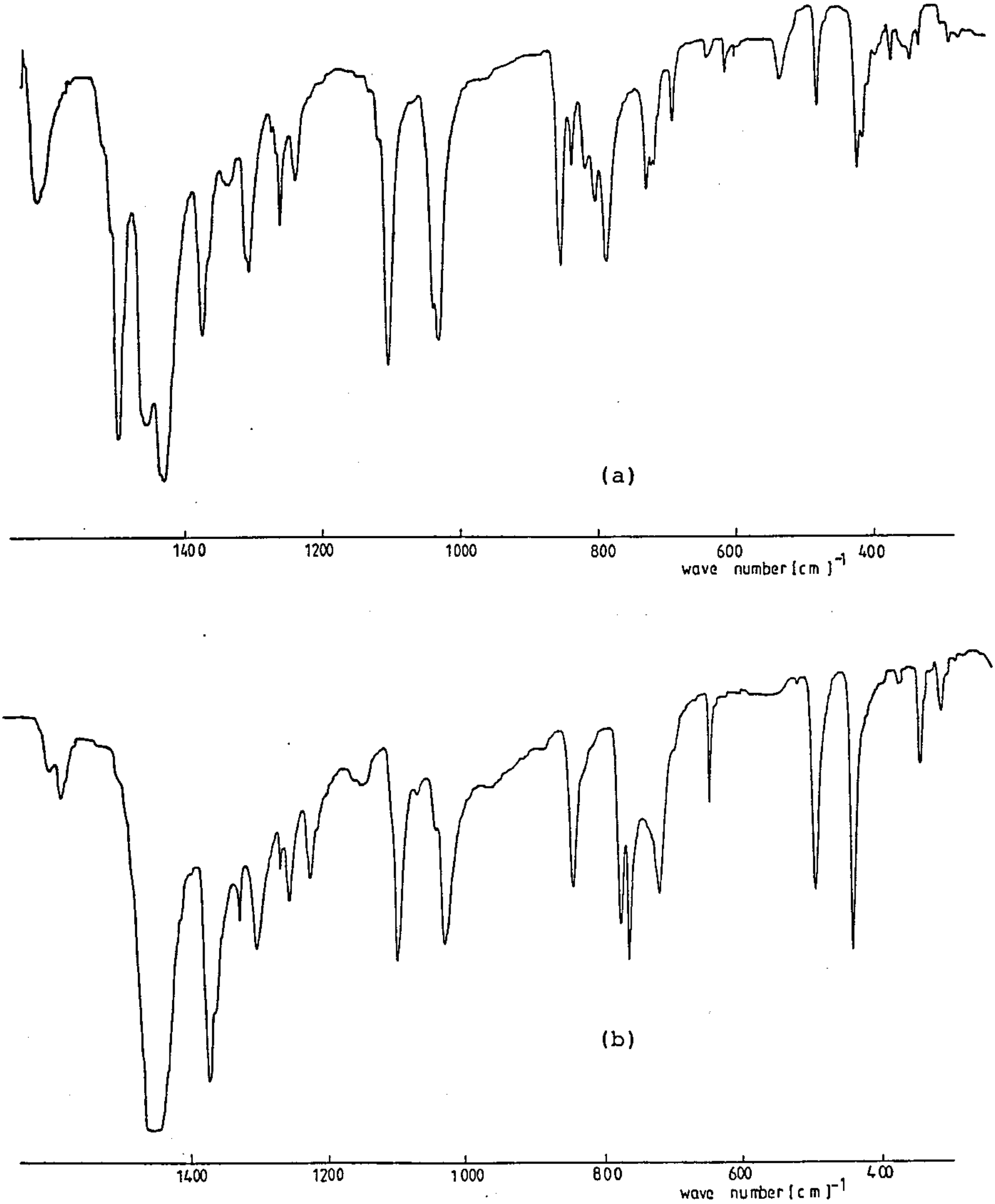


Figure 6.23 : Infrared Spectrum of

a) Tris(2-bromotetrafluorophenyl)methylsilane

b) 1,6-Dimethyl-dodecafluoro-1,6-disilatriptycene.

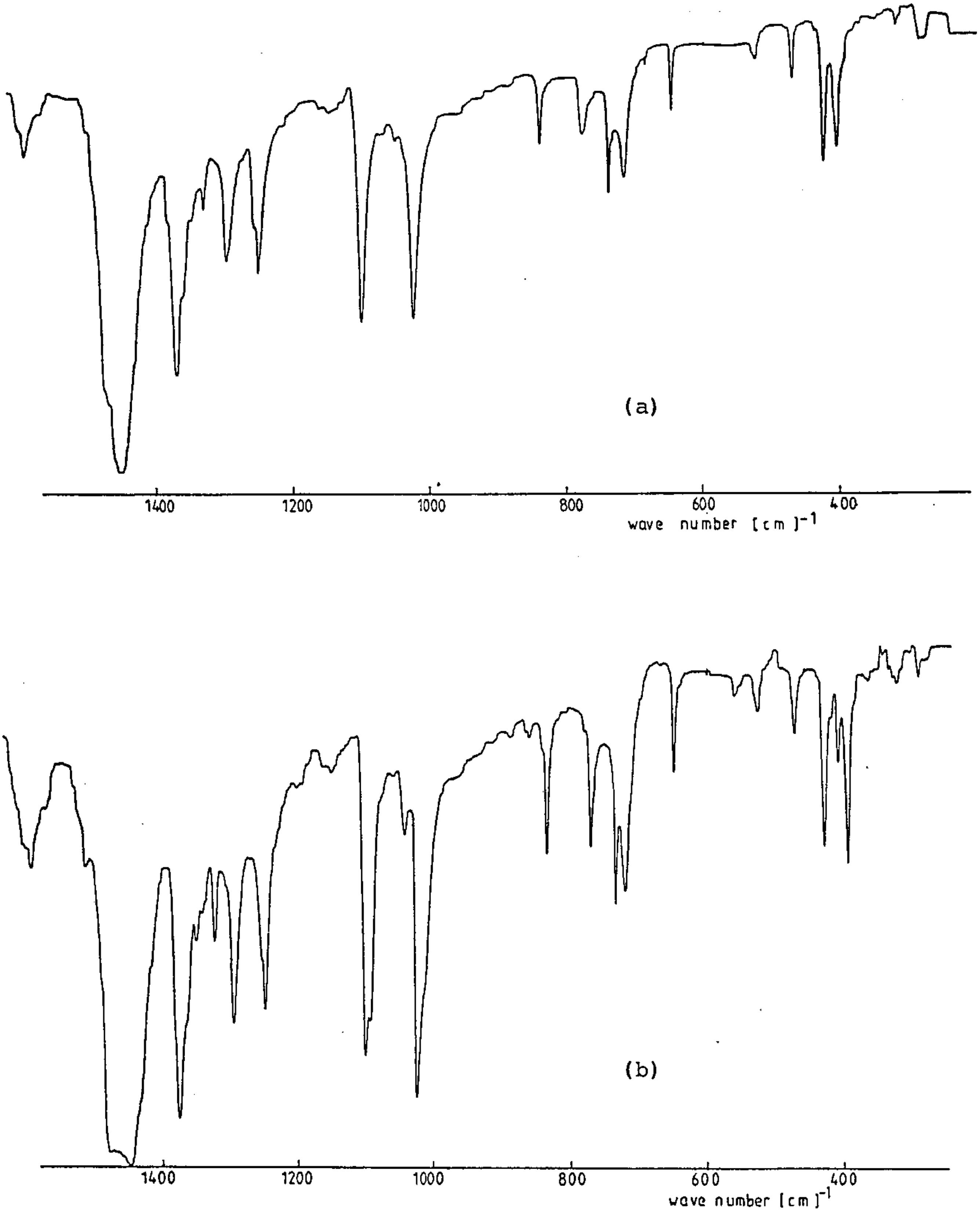
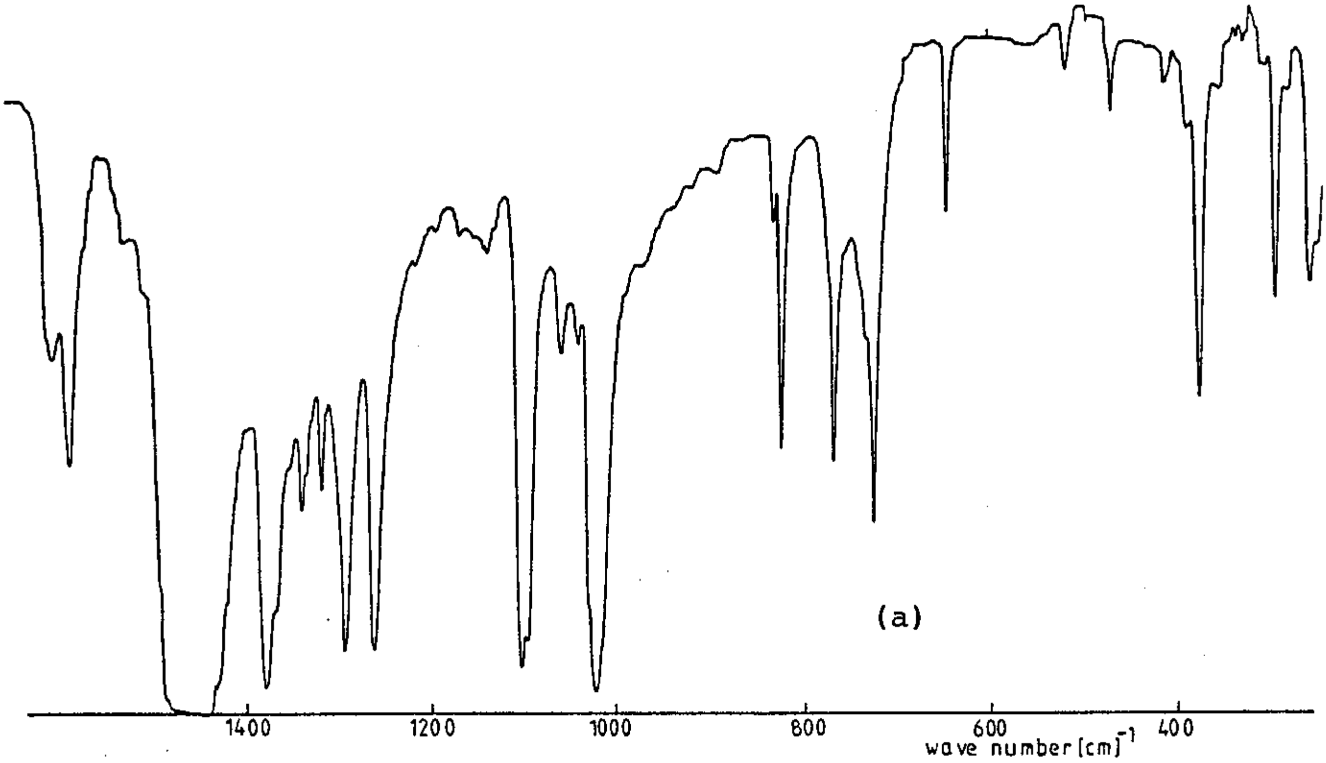


Figure 6.24 : Infrared Spectrum of

a) Perfluoro-1,6-arsaphosphatriptycene

b) Perfluoro-1,6-phosphastibatriptycene.



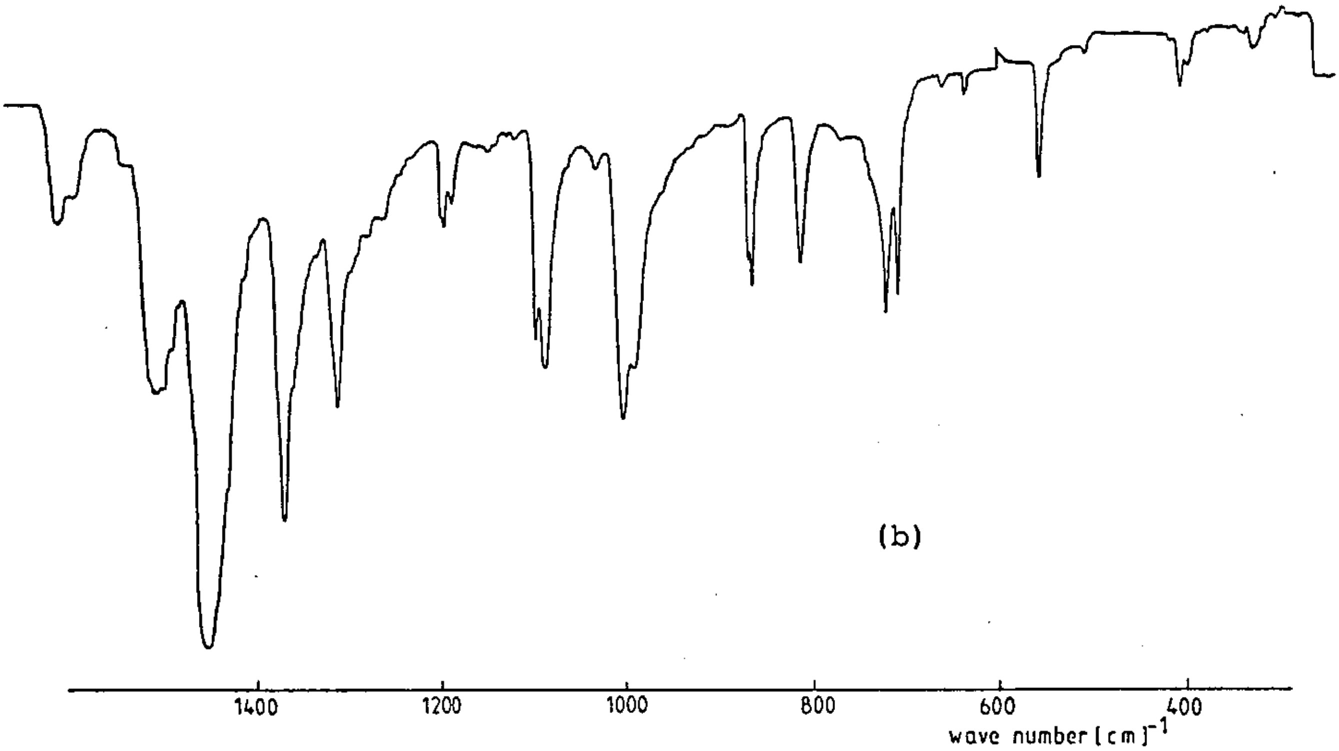


Figure 6.25 : Infrared Spectrum of

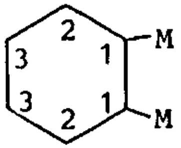
a) Perfluoro-1,6-arsastibatriptycene

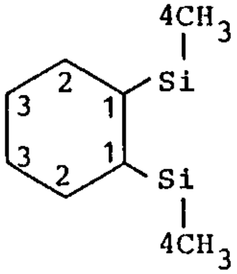
b) Tris(3,4,5,6-tetrafluorophenyl)arsenic.

Table 6.13

^{13}C NMR Data for Compounds III, IV, V and 1,2-$I_2C_6F_4$

		$Sb_2(C_6F_4)_3$	$Bi_2(C_6F_4)_3$	$(MeSi)_2(C_6F_4)_3$	1,2-$I_2C_6F_4$
Chemical shift[a],	C(1)	129.7	157.2	121.9	91.9
	C(2)	151.1	150.8	151.6	148.5
	C(3)	14.10	140.2	140.9	140.5
	C(4)	-	-	4.8	-
Solvent		$(CD_3)_2C{=}O$	$(CD_3)_2C{=}O$	$CDC\ell_3$	$(CD_3)_2C{=}O$
Concentration		20%	5%	5%	20%
Double splitting		C(2)235	C(2)234	C(2)244	C(2)242
on peaks[b] (Hz)		C(3)244	C(3)246	C(3)250	C(3)252





a) ppm relative to tetramethylsilane. b) Spectra not fluorine-decoupled.

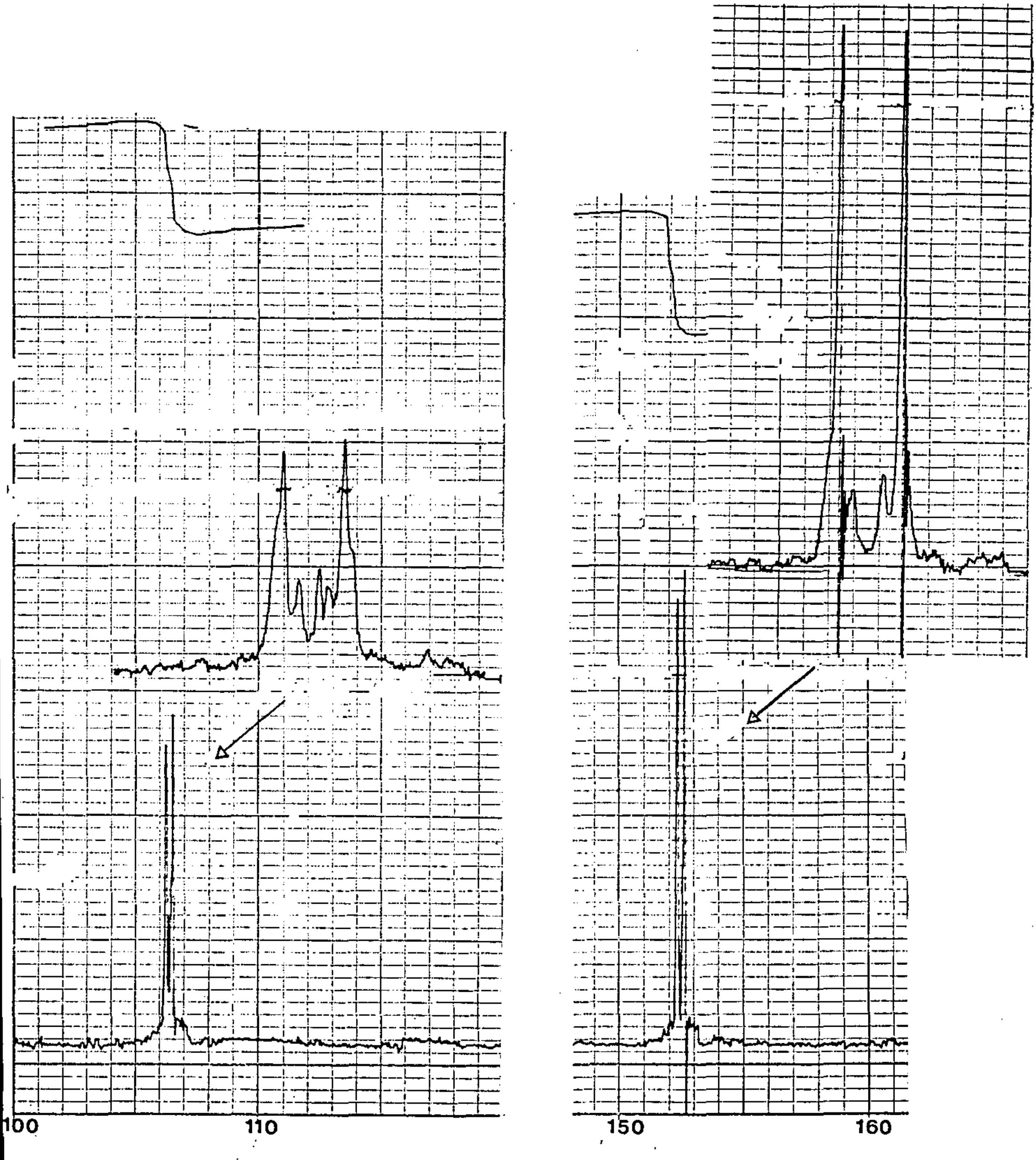


Figure 6.26 : ^{19}F NMR Spectrum of

Perfluoro-1,6-dibismuthtriptycene in $(CD_3)_2CO$

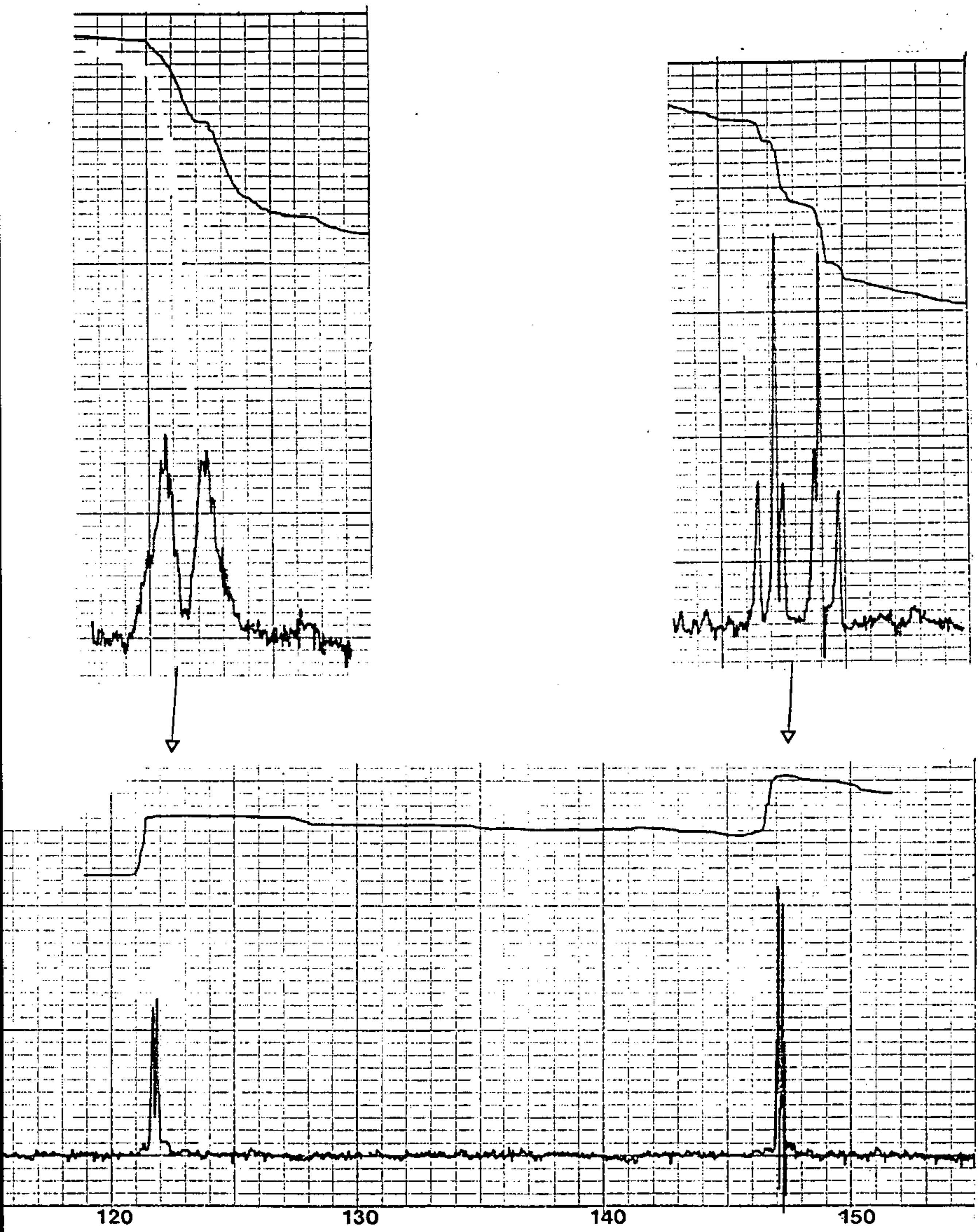


Figure 6.27 : ^{19}F NMR Spectrum of 1,6-Dimethyl-dodecafluoro-1,6-disilatriptycene in $CDCl_3$

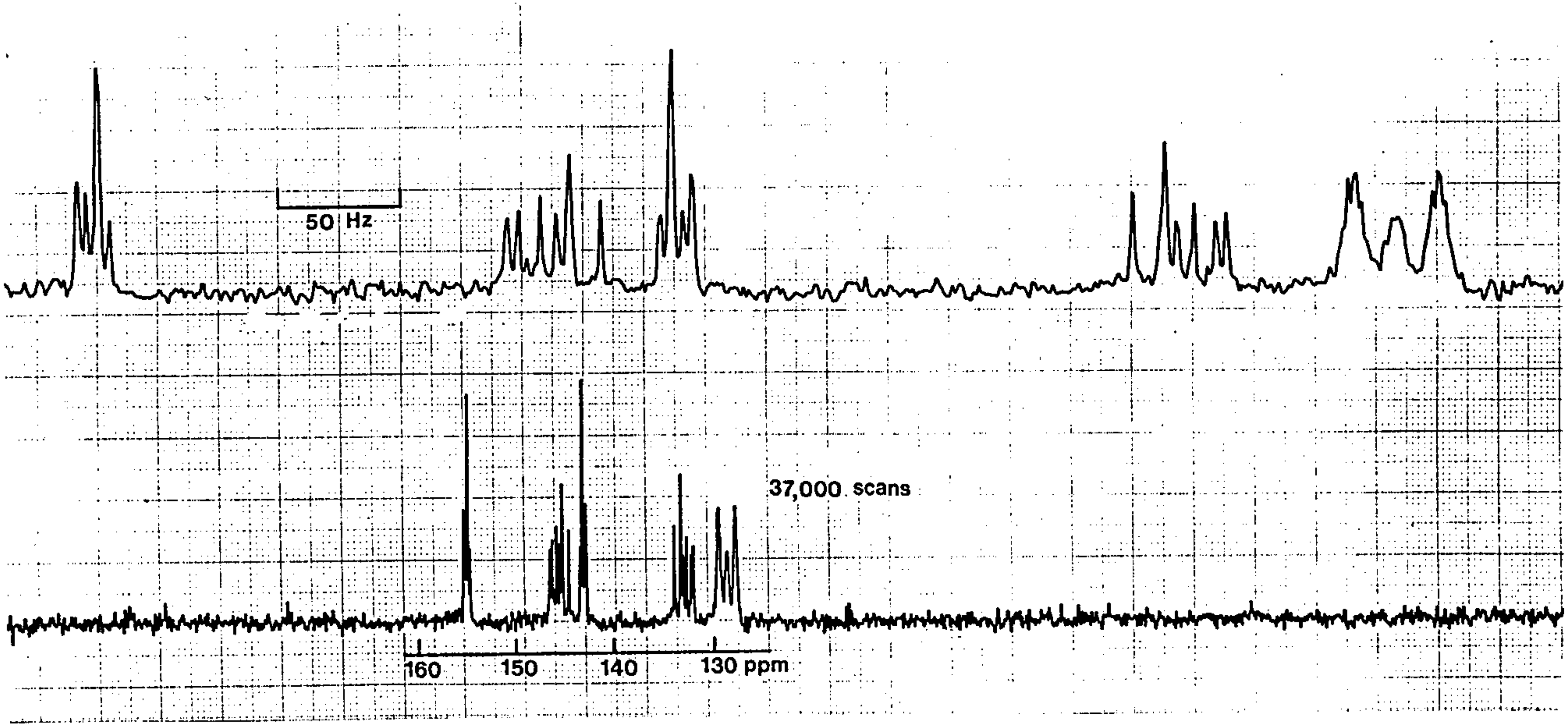
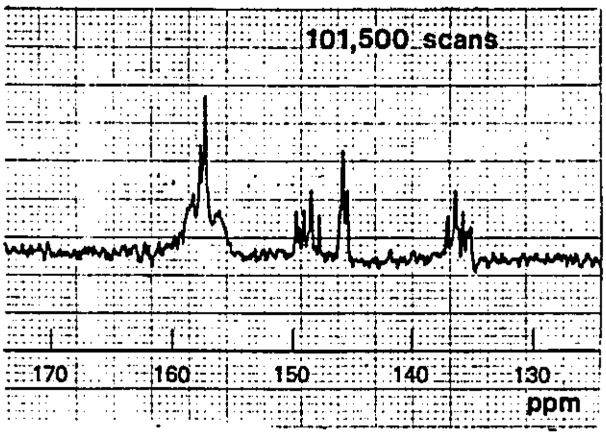


Figure 6.28 : ^{13}C NMR Spectrum of Perfluoro-1,6-distibatriptycene in $(CD_3)_2CO$



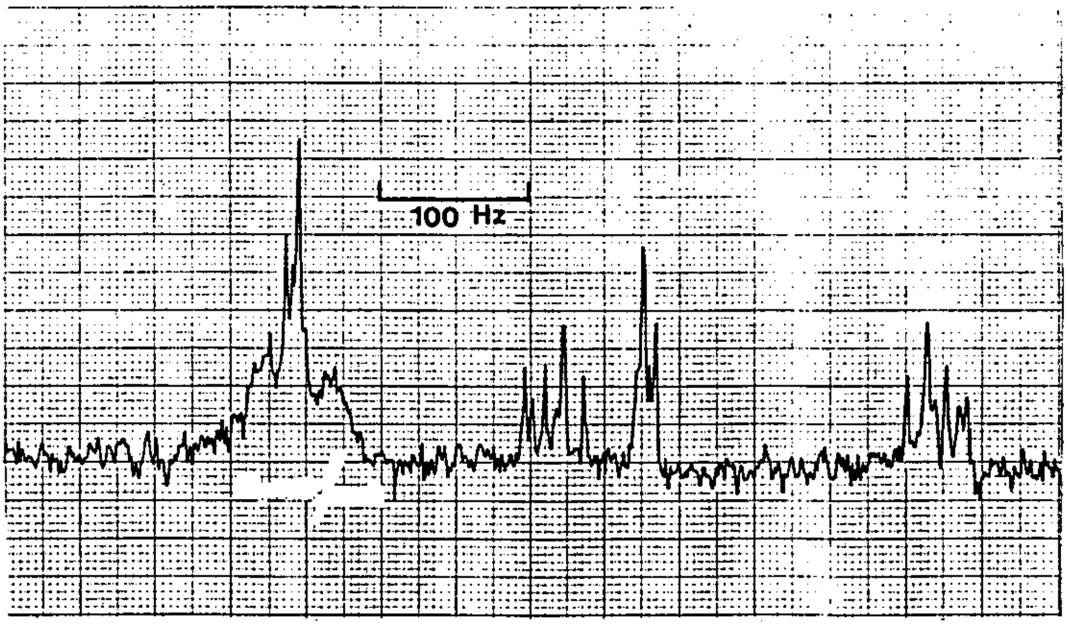


Figure 6.29 : ^{13}C NMR Spectrum of Perfluoro-1,6-dibismuthtriptycene in $(CD_3)_2CO$

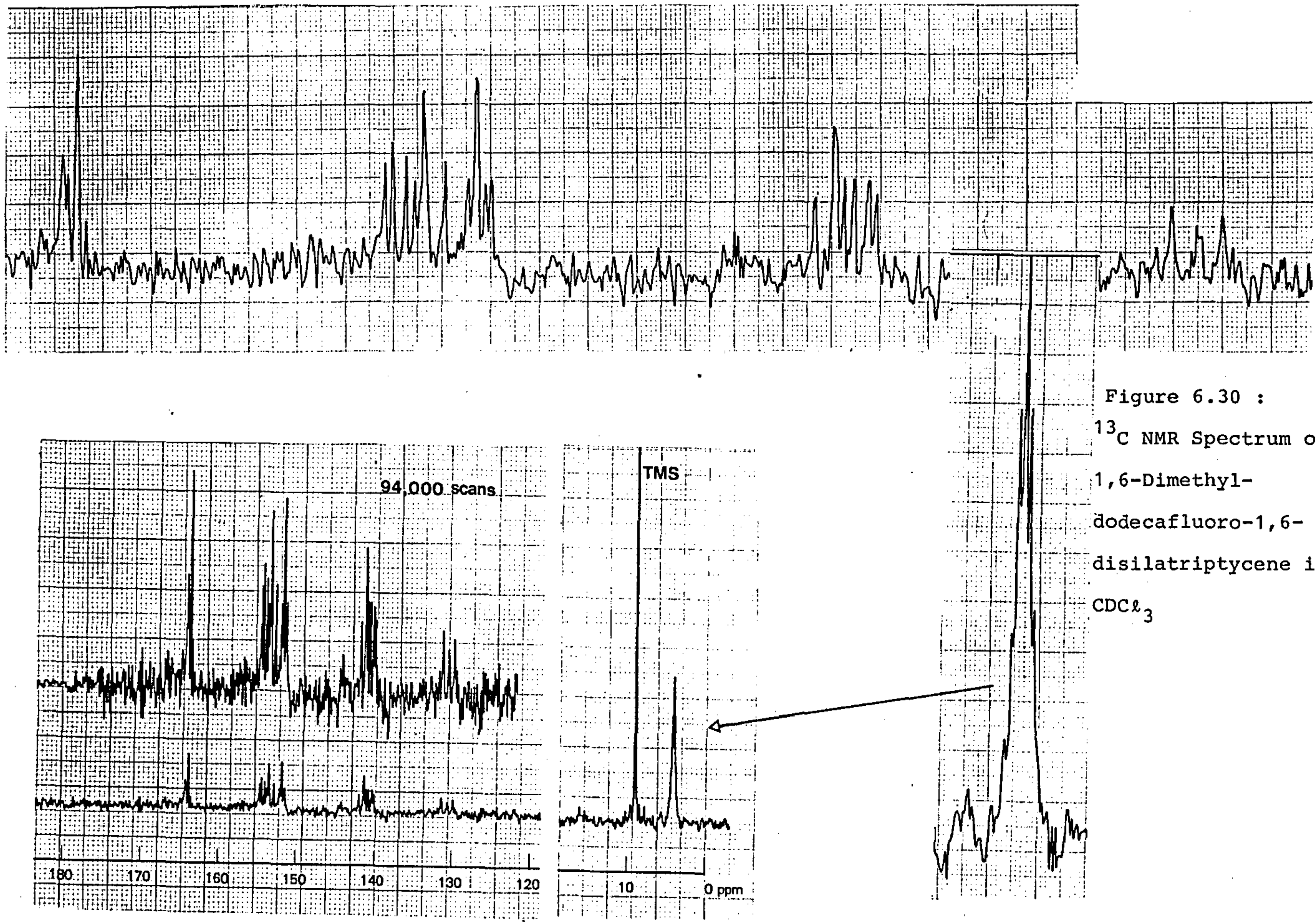


Figure 6.30 :
^{13}C NMR Spectrum of
1,6-Dimethyl-
dodecafluoro-1,6-
disilatriptycene in
CD$C\ell_3$

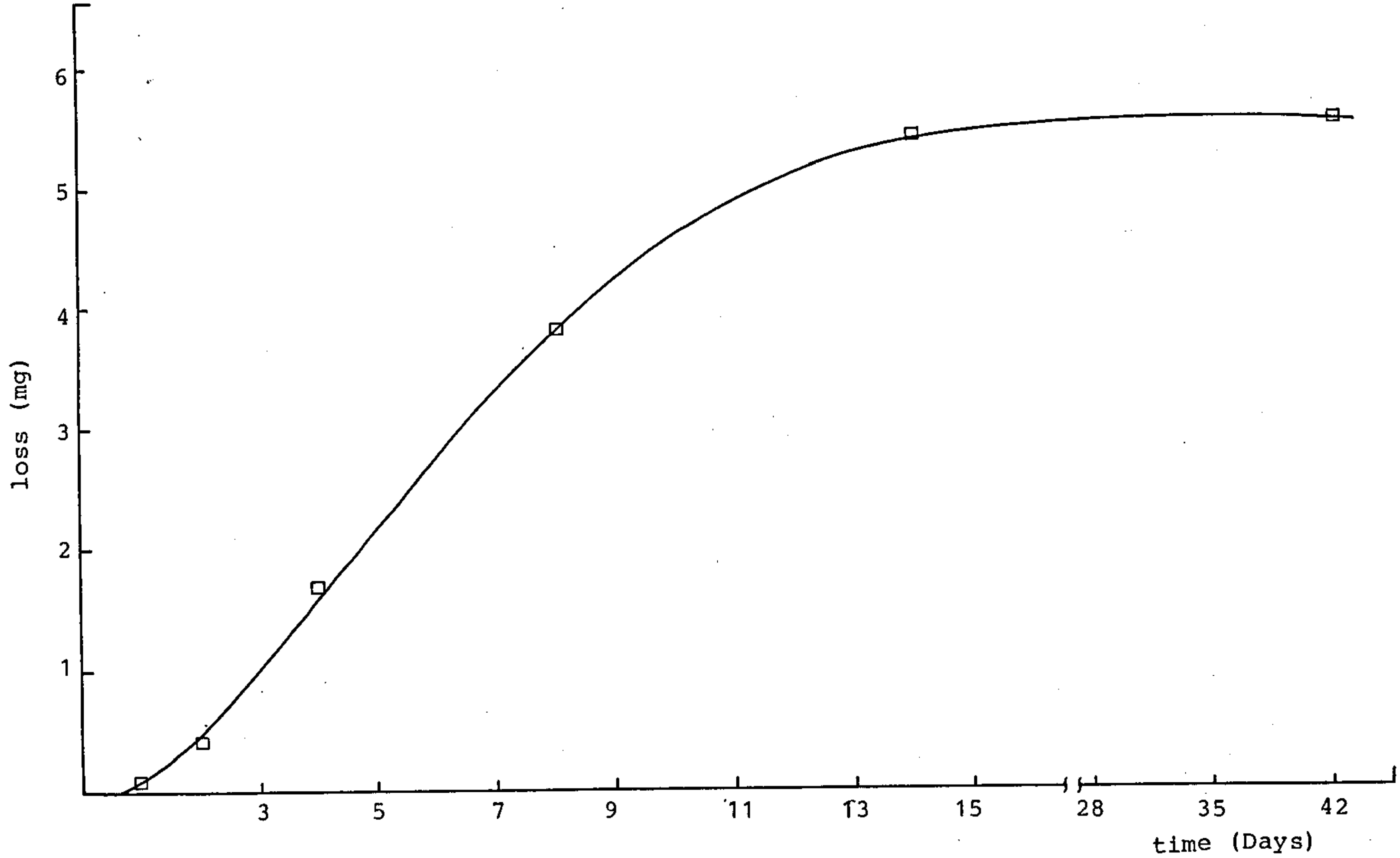
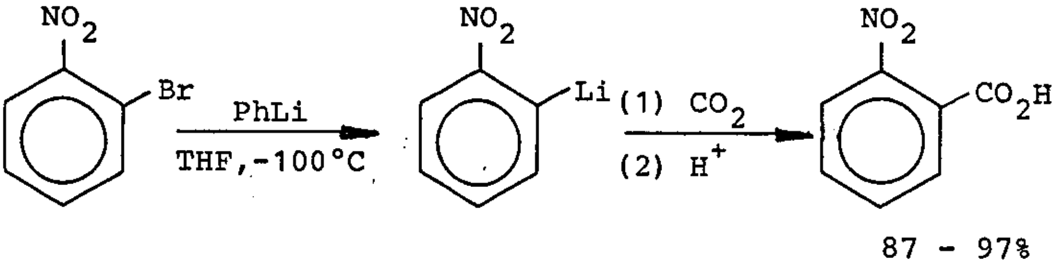


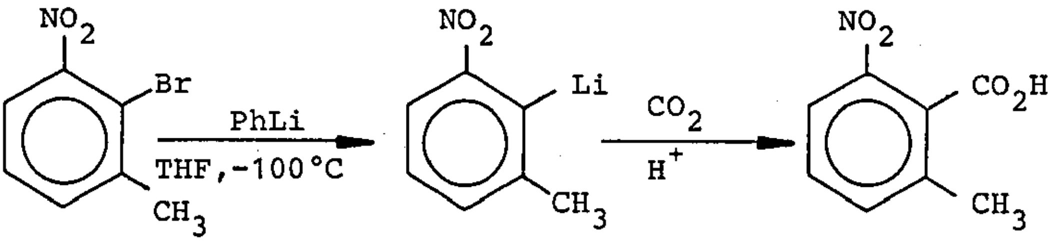
Figure 6.31 : The Loss of Hexane from $Sb_2(C_6F_4)_3$. 0.5 hexane as a function of time at room temperature.

Chapter 7

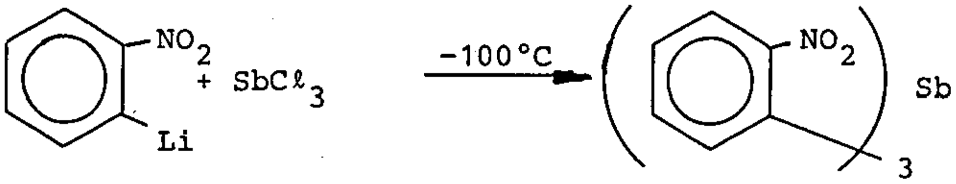
Suggestions for Further Work

Köbrich and Buck(1) have shown that 2-bromonitrobenzene and 2-bromo-3-methylnitrobenzene react with phenyllithium in tetrahydrofuran at -100°C according to the following equations:

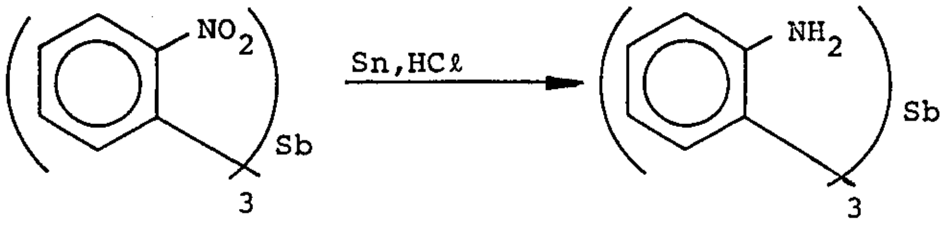




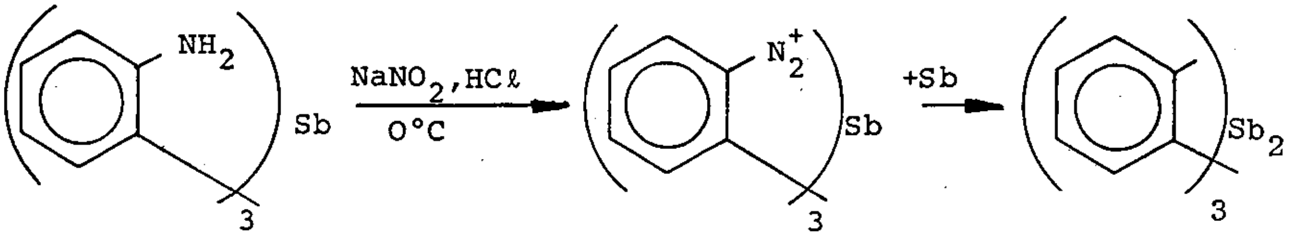
It seems reasonable to expect that o-nitrophenyl derivatives of other metals or metalloids may be prepared following the same reaction route mentioned above, for example, the preparation of tris(2-nitrophenyl)antimony:



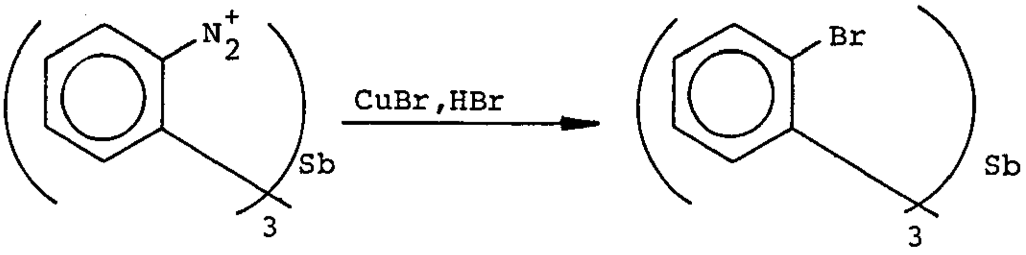
The nitro group in tris(2-nitrophenyl)antimony may be reduced to give the amino derivative as shown below:



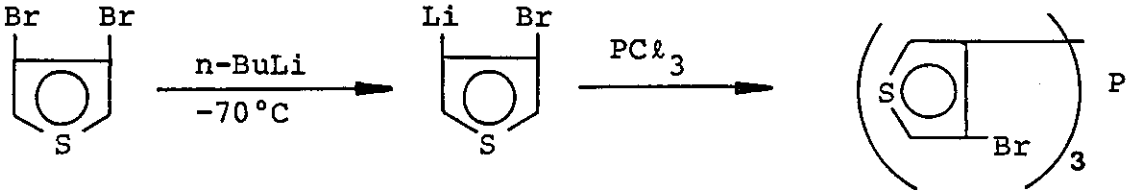
Diazotization of tris(2-aminophenyl)antimony and then decomposition of the diazonium salt in the presence of antimony powder may give the 1,6-distibatriptycene we failed to prepare by a "step-wise" synthesis:



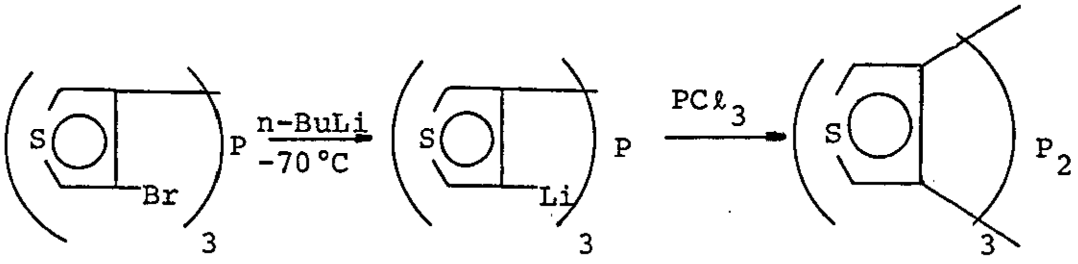
The diazonium salt of tris(2-aminophenyl)antimony may also be used to prepare tris(2-bromophenyl)antimony by reaction with cuprous bromide:



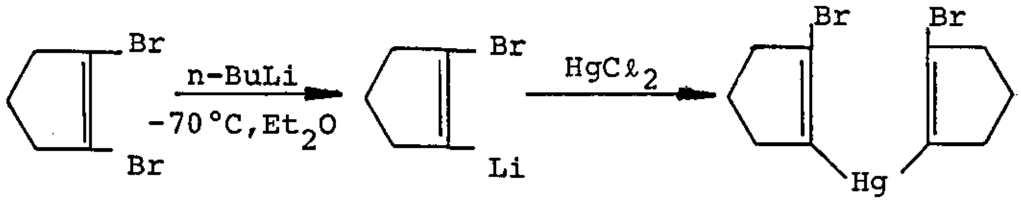
Various organolithium intermediates may be used in the synthesis of other organo-metals or metalloids, for example, 3-bromo-4-thienyllithium(2) (which is prepared at -70°C from n-butyllithium and 3,4-dibromothiophen) when reacted with phosphorus trichloride, may give tris(3-bromothienyl)phosphine:



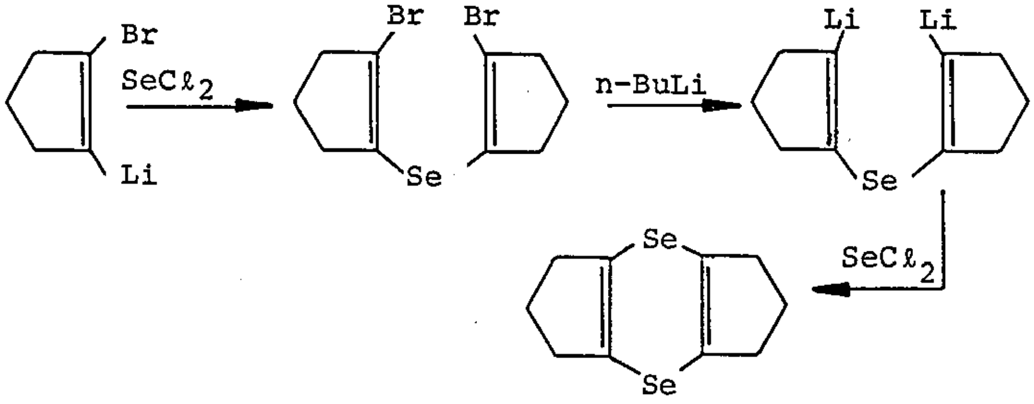
Tris(3-bromothienyl)phosphine may undergo further lithiation and on treatment with phosphorus trichloride give the diaphosphorus derivative:



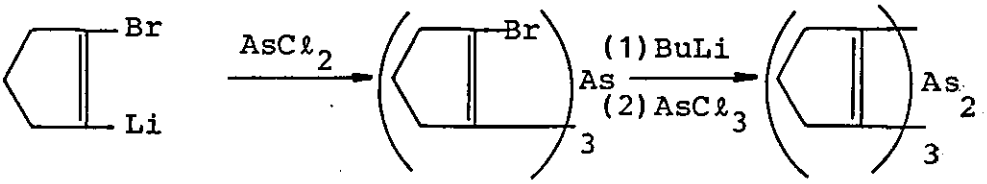
1,2-Dibromocyclopentene has been reacted with n-butyllithium and mercuric chloride giving bis(2-bromocyclopentenyl)mercury(3):



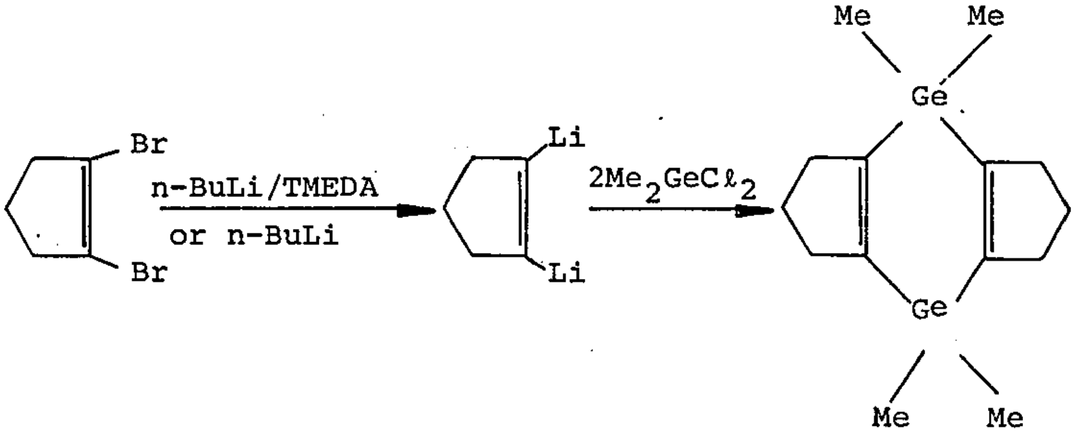
The above lithiation reaction may be used in preparation of other heterocyclics such as:



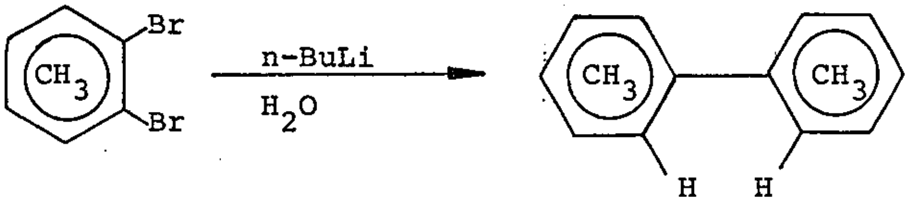
or



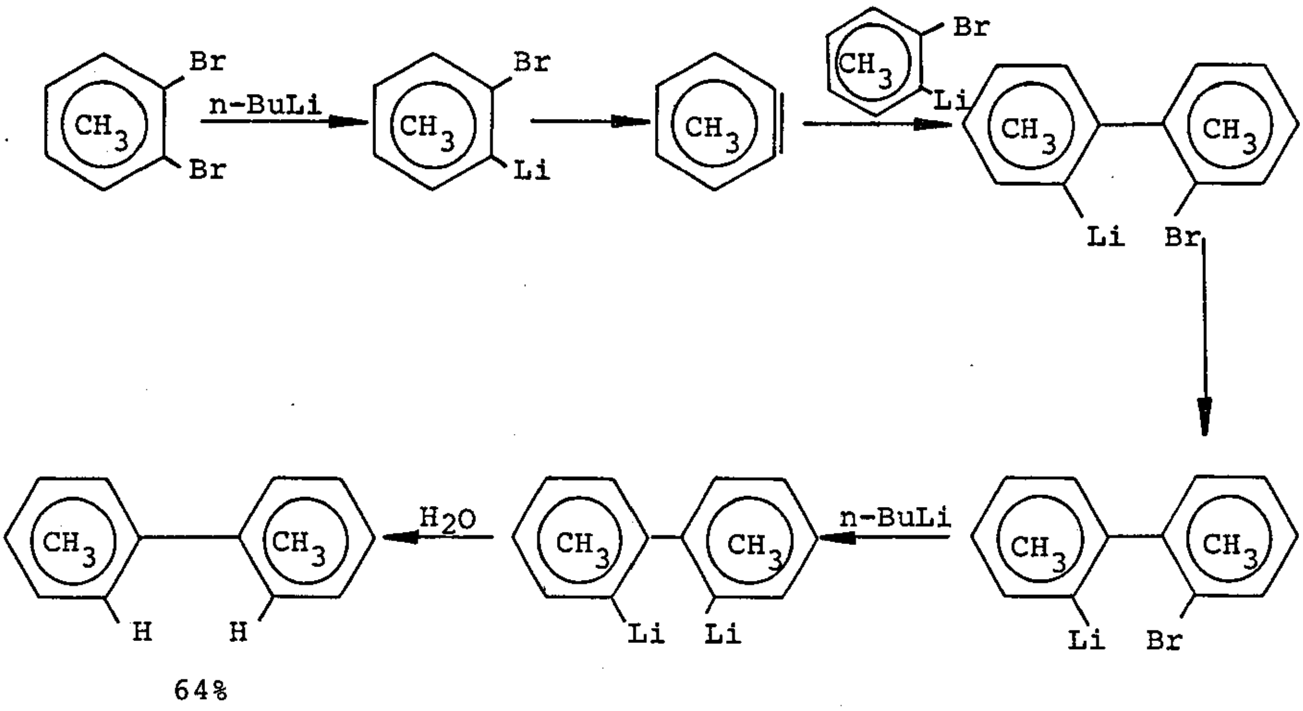
Dilithiation of 3,4-dibromothiophen and 1,2-dibromocyclopentene in one step could possibly be achieved using n-butyllithium or the butyllithium/TMEDA complex and then the dilithio species will react with $Me_2GeC\ell_2$ or $Me_2SnC\ell_2$:



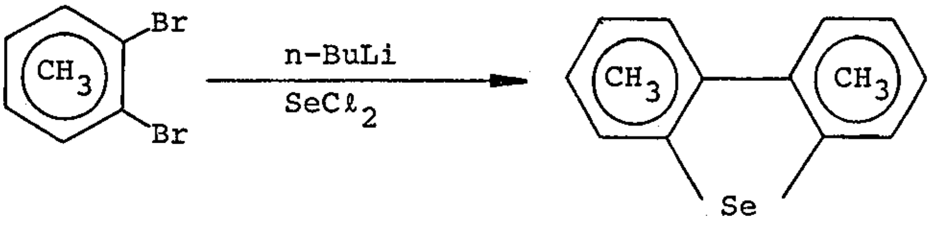
Addition of 1,2-dibromotetramethylbenzene to a solution of n-butyllithium in (1:6.4 ratio) in ether at -78°C and hydrolysis of the resulting mixture gives octamethylbiphenyl$^{(4)}$:



Formation of octamethylbiphenyl could be attributed to the formation of benzyne as illustrated in the following scheme:

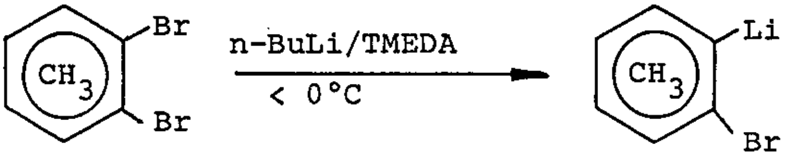


The above mixture of 1,2-dibromotetramethylbenzene and n-butyllithium can be treated with $SeC\ell_2$ or $GeC\ell_4$ as follows:



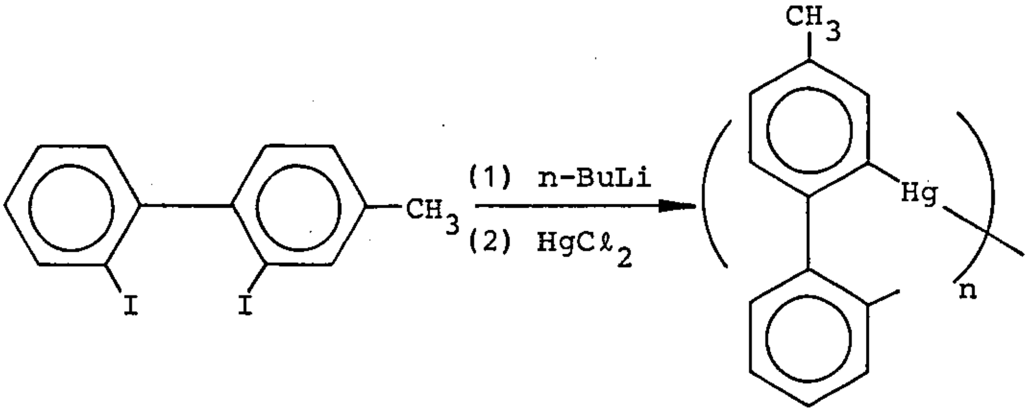
in which case the 6,6' steric interaction of the methyl groups in such heterocycles would be worthy of an X-ray structure study.

1,2-Dibromotetramethylbenzene can be reacted with the n-Buli/TMEDA complex in an attempt to prevent benzyne formation and hence give 1-bromo-2-lithiotetramethylbenzene:

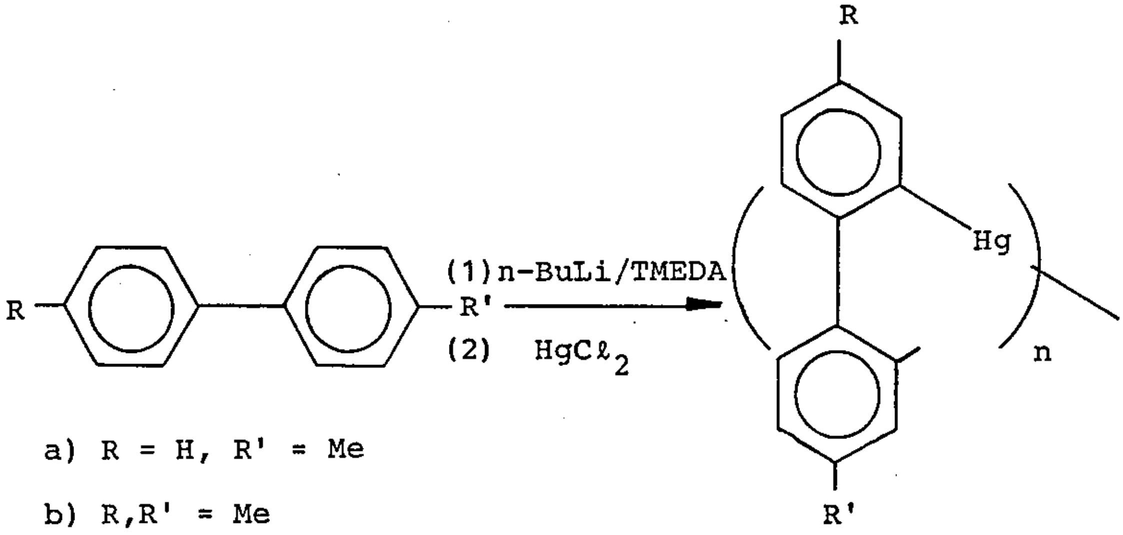


which again would open the way to the syntheses of a whole variety of heterocycles, but in this case the insolubility of any products may make their study difficult.

In this thesis many organomercurials were prepared; including biphenylene - and 4,4'-dimethylbiphenylenemercury; the 4-methylbiphenylenemercury can no doubt be prepared from 2,2'-diiodo-4-methylbiphenyl:



The crystal structures of 4,4'-dimethyl- and 4-methylbiphenylenemercury ought to be studied and their degree of polymerization investigated other than just by mass spectrometry in case the tetramers were too involatile to be detected in the vapour state. These substituted biphenylenemercurials can probably also be prepared directly by metallation of 4,4'-dimethyl- and 4-methylbiphenyl with a mixture of n-BuLi/TMEDA complex in refluxing hexane (as in the metallation of biphenyl$^{(5)}$) assuming that the methyl groups are not also attacked by n-butyllithium:

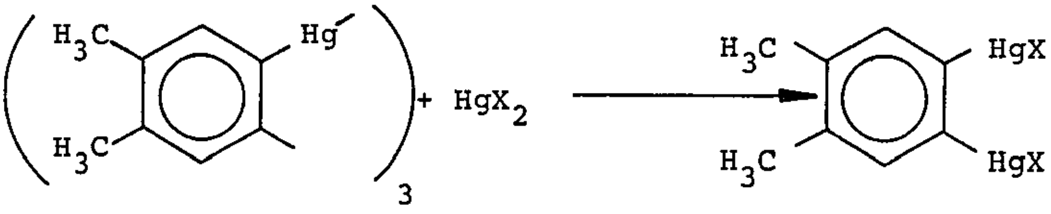


a) R = H, R' = Me

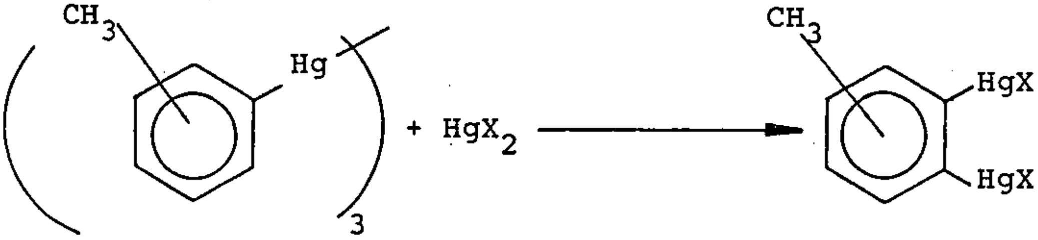
b) R,R' = Me

Such a reaction would make their study much easier as the 2,2'-diiodides are difficult to prepare in large amounts.

Desymmetrization reactions of the above substituted biphenylenemercurials as well as the other substituted phenylenemercurials which have been prepared in this work may be studied; for example, the reactions of methyl- and 4,5-dimethyl-phenylenemercury with mercuric halides:

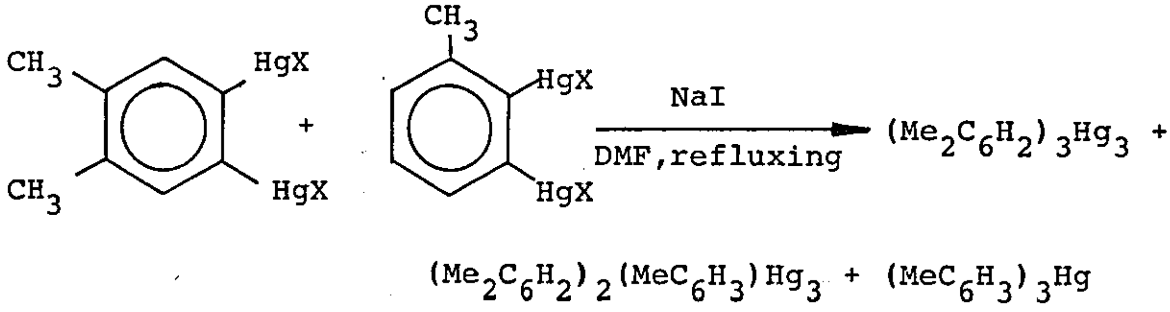


X = Cℓ,Br,I



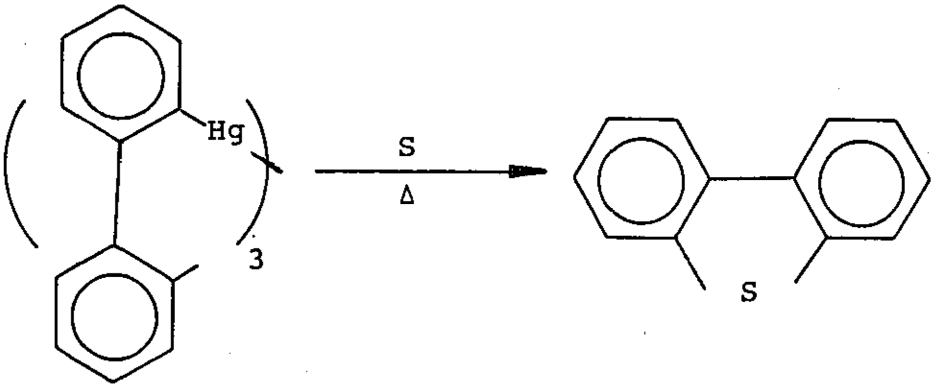
o- or m-CH_3

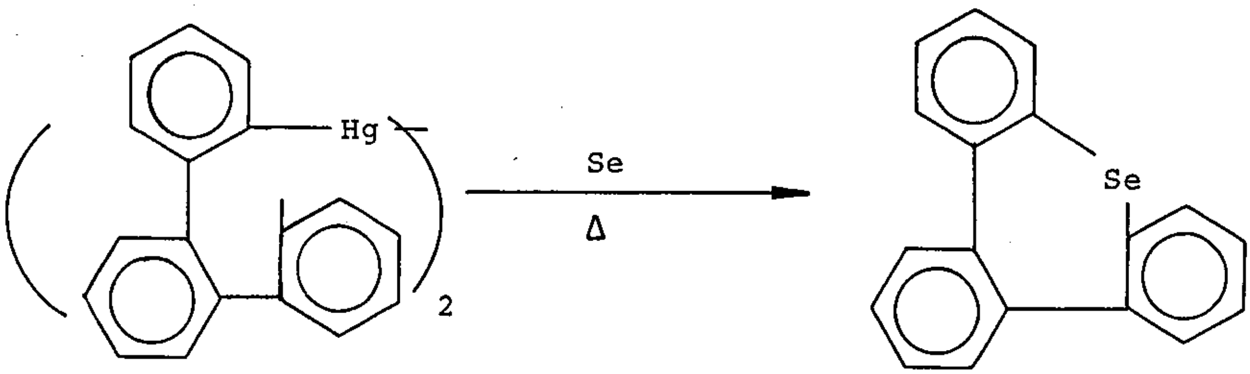
Symmetrization of the above organomercury salts using sodium iodide or by heating can be carried out in further attempts to make the tetramers or hexamers suggested by Wittig. The "mixed" substituted phenylene- or biphenylenemercurials are also made possible by the symmetrization method and could be separated by thin layer chromatography:



$$\xrightarrow[\text{DMF, refluxing}]{\text{NaI}} (Me_2C_6H_2)_3Hg_3 + (Me_2C_6H_2)_2(MeC_6H_3)Hg_3 + (MeC_6H_3)_3Hg$$

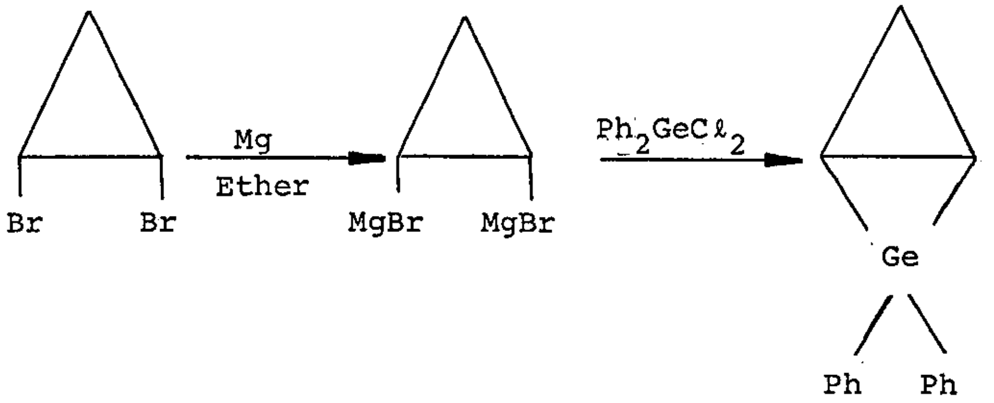
Many organomercurials have undergone transmetallation reactions when heated in sealed tubes with other metals, as in the preparation of 1,6-distibatriptycene from o-phenylenemercury trimer (see Chapter 6). As an extension, it seems possible to prepare many other heterocyclic compounds by reacting o-biphenylenemercury trimer or o-terphenylenemercury dimer with sulphur or selenium:



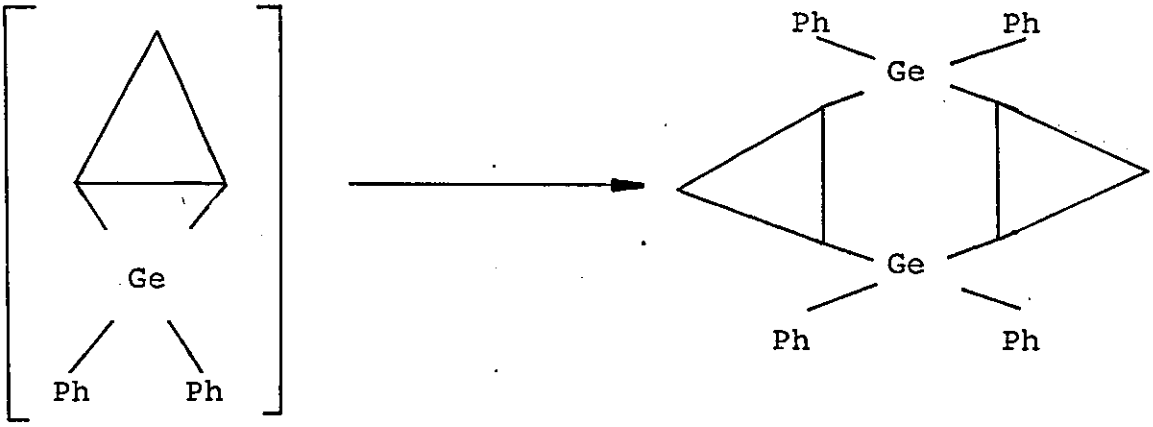


Models show that the latter sulphur (and selenium or tellurium) heterocycle should be capable of existence without steric strain.

Finally, the Grignard reagent derived from dibromocyclopropane(6) might be used in preparation of other heterocyclic derivatives; for example, when reacted with diphenylgermanium dichloride:



but again the three-membered ring may be unstable and the compound may revert to other systems, e.g.



As is obvious from this short discussion there are many possibilities for extending the study of heterocycles of the type prepared in this thesis.

Appendix 1

Least squares planes in the biphenylenemercury molecule

Plane number	Atoms of the plane	Equation of the Plane	e.s.d of the atoms from the plane, Å×10^3
1	C(1) -C(2) -C(3) -C(4) -C(5) -C(6)	$-10.362X+10.495Y-2.182Z=0.920$	25
2	C(7) -C(8) -C(9) -C(10)-C(11)-C(12)	$26.341X-1.036Y+3.301Z=4.721$	31
3	C(13)-C(14)-C(15) -C(16)-C(17)-C(18)	$26.678X+0.127Y-2.186Z=0.164$	29
4	C(19)-C(20)-C(21) -C(22)-C(23)-C(24)	$12.463X+10.136Y-0.878Z=9.195$	12
5	C(25)-C(26)-C(27) -C(28)-C(29)-c(30)	$17.448X+8.551Y+2.761Z=12.609$	9
6	C(31)-C(32)-C(33) -C(34)-C(35)-C(36)	$14.959X-9.356Y-2.888Z=-4.310$	34

Appendix 2

Observed and Calculated Structure factors for Biphenylenemercury

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	0	0	483	-491	2	4	0	1441	-1430	16	9	0	247	257
6	0	0	521	-499	4	4	0	488	452	0	10	0	215	-236
8	0	0	3396	-3415	6	4	0	1661	1687	2	10	0	192	175
10	0	0	428	422	8	4	0	332	-341	6	10	0	283	-282
12	0	0	1166	1150	10	4	0	309	313	8	10	0	247	261
14	0	0	408	-415	14	4	0	1286	-1316	14	10	0	207	213
16	0	0	1682	1743	16	4	0	409	397	16	10	0	185	-136
18	0	0	499	-523	22	4	0	662	660	22	10	0	206	-152
20	0	0	1041	-1055	24	4	0	317	-332	2	11	0	217	212
22	0	0	589	596	26	4	0	177	-157	4	11	0	327	338
24	0	0	606	-612	30	4	0	267	-267	8	11	0	290	-283
26	0	0	246	265	2	5	0	626	-646	10	11	0	219	-240
28	0	0	527	541	4	5	0	370	-370	16	11	0	306	272
30	0	0	323	-329	10	5	0	612	640	0	12	0	725	-767
6	1	0	410	412	12	5	0	166	183	8	12	0	587	593
8	1	0	473	-440	14	5	0	148	-97	12	12	0	251	-286
10	1	0	1170	-1131	18	5	0	304	-356	16	12	0	319	-281
12	1	0	158	160	22	5	0	276	262	20	12	0	262	236
14	1	0	139	-129	30	5	0	231	-193	18	13	0	226	-116
16	1	0	450	470	0	6	0	429	-432	3	1	1	480	473
18	1	0	673	690	2	6	0	303	314	4	1	1	174	171
20	1	0	330	-313	6	6	0	280	-295	6	1	1	131	115
24	1	0	194	-227	8	6	0	422	427	7	1	1	581	568
26	1	0	327	-318	10	6	0	248	-259	8	1	1	129	-99
28	1	0	247	240	14	6	0	187	213	9	1	1	970	971
0	2	0	151	-145	16	6	0	239	-249	10	1	1	176	187
4	2	0	95	-90	2	7	0	1088	-1119	11	1	1	752	-746
10	2	0	163	-166	4	7	0	178	192	12	1	1	186	-174
12	2	0	300	307	6	7	0	629	-668	13	1	1	147	-158
18	2	0	263	290	10	7	0	1165	1201	17	1	1	581	-600
20	2	0	251	-269	12	7	0	308	-349	18	1	1	179	-179
24	2	0	200	156	18	7	0	673	-696	19	1	1	610	627
26	2	0	255	-250	20	7	0	267	241	21	1	1	206	228
2	3	0	835	-802	22	7	0	203	172	23	1	1	170	-140
4	3	0	2768	2840	26	7	0	332	367	25	1	1	209	222
6	3	0	692	-712	28	7	0	210	-149	27	1	1	241	-285
8	3	0	382	-402	0	8	0	779	836	31	1	1	244	199
10	3	0	386	387	2	8	0	510	529	1	2	1	347	359
12	3	0	1385	-1419	4	8	0	244	-234	3	2	1	352	-344
14	3	0	441	453	6	8	0	780	-798	4	2	1	152	157
16	3	0	635	643	8	8	0	477	-498	5	2	1	1024	-1050
18	3	0	540	-561	12	8	0	408	419	6	2	1	294	-314
20	3	0	696	709	14	8	0	506	515	7	2	1	738	734
22	3	0	209	-226	16	8	0	185	169	9	2	1	149	110
24	3	0	465	-464	20	8	0	310	-313	11	2	1	590	596
26	3	0	362	363	4	9	0	602	616	13	2	1	450	462
28	3	0	289	-250	8	9	0	232	-263	14	2	1	240	241
32	3	0	208	232	12	9	0	313	-350	15	2	1	782	-801

H	K	L	FO	FC	H	K	L	FO	FC
19	2	1	196	-229	23	5	1	223	-194
21	2	1	201	-206	27	5	1	253	266
23	2	1	498	505	0	6	1	483	-488
31	2	1	232	-244	1	6	1	1618	1623
1	3	1	211	203	3	6	1	408	424
2	3	1	220	185	7	6	1	1226	1281
3	3	1	1591	1562	8	6	1	392	431
4	3	1	543	546	9	6	1	1400	-1445
5	3	1	1479	-1516	11	6	1	458	-488
6	3	1	208	-184	12	6	1	151	-122
7	3	1	482	-500	13	6	1	342	363
8	3	1	123	-110	15	6	1	575	-582
9	3	1	179	156	17	6	1	825	854
11	3	1	688	-717	19	6	1	293	310
12	3	1	261	-248	21	6	1	477	-468
13	3	1	911	945	23	6	1	286	252
15	3	1	382	384	25	6	1	364	-377
16	3	1	156	139	27	6	1	221	-160
17	3	1	454	-455	1	7	1	669	-691
19	3	1	330	354	2	7	1	162	-150
21	3	1	527	-519	3	7	1	230	255
23	3	1	172	-187	7	7	1	669	684
24	3	1	171	-95	9	7	1	404	403
25	3	1	382	393	11	7	1	433	-428
29	3	1	193	132	15	7	1	380	-386
1	4	1	116	87	19	7	1	339	359
2	4	1	336	315	23	7	1	219	153
5	4	1	205	-206	27	7	1	219	-214
7	4	1	230	226	9	8	1	163	118
8	4	1	149	-151	11	8	1	174	-173
9	4	1	133	-97	19	8	1	222	186
11	4	1	203	-223	3	9	1	765	-754
13	4	1	317	314	5	9	1	814	852
15	4	1	195	-195	7	9	1	180	164
19	4	1	290	287	11	9	1	551	567
21	4	1	182	-199	13	9	1	624	-640
1	5	1	638	644	15	9	1	205	-179
2	5	1	217	232	17	9	1	233	220
3	5	1	232	-228	19	9	1	269	-249
4	5	1	161	167	21	9	1	387	347
5	5	1	192	-193	1	10	1	263	286
7	5	1	499	-528	3	10	1	488	-555
8	5	1	144	-129	5	10	1	529	-576
9	5	1	381	-356	7	10	1	492	522
10	5	1	193	-166	11	10	1	319	369
11	5	1	438	466	13	10	1	325	352
15	5	1	546	575	15	10	1	489	-492
19	5	1	380	-412	1	11	1	310	315

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
5	11	1	272	-258	19	1	2	247	241	3	4	2	478	-481
7	11	1	245	-258	20	1	2	338	-360	4	4	2	179	124
9	11	1	220	-207	23	1	2	158	125	5	4	2	554	-564
13	11	1	293	290	24	1	2	193	-134	6	4	2	1569	1606
1	12	1	211	-198	26	1	2	196	-207	7	4	2	535	546
7	12	1	209	-183	27	1	2	194	-141	8	4	2	241	-241
1	13	1	342	371	28	1	2	219	216	9	4	2	148	-155
3	13	1	240	-262	1	2	2	145	-162	10	4	2	445	446
9	13	1	309	-308	3	2	2	148	133	11	4	2	246	258
4	0	2	525	-497	4	2	2	100	96	12	4	2	210	-227
6	0	2	478	454	5	2	2	560	-527	13	4	2	376	372
7	0	2	692	675	6	2	2	220	-227	14	4	2	1175	-1193
8	0	2	2620	-2664	7	2	2	203	197	15	4	2	435	-427
9	0	2	1168	-1138	8	2	2	232	218	16	4	2	361	363
10	0	2	605	604	10	2	2	310	-315	21	4	2	167	-158
11	0	2	265	-254	12	2	2	264	262	22	4	2	578	579
12	0	2	1124	1103	13	2	2	140	128	23	4	2	287	286
13	0	2	433	441	16	2	2	159	-174	24	4	2	269	-275
14	0	2	499	-496	18	2	2	242	278	30	4	2	213	-237
15	0	2	321	-319	20	2	2	195	-195	1	5	2	159	157
16	0	2	1343	1375	26	2	2	171	-194	2	5	2	660	-674
17	0	2	636	650	1	3	2	283	267	4	5	2	509	-496
18	0	2	494	-500	2	3	2	535	-512	5	5	2	123	77
19	0	2	249	217	3	3	2	828	-848	6	5	2	149	-163
20	0	2	897	-909	4	3	2	2076	2116	8	5	2	131	129
21	0	2	470	-497	5	3	2	627	679	9	5	2	307	-324
22	0	2	534	513	6	3	2	552	-560	10	5	2	575	572
24	0	2	532	-508	8	3	2	515	-533	11	5	2	282	298
25	0	2	234	-236	9	3	2	141	-125	12	5	2	243	259
26	0	2	207	212	10	3	2	444	456	18	5	2	309	-335
28	0	2	442	482	11	3	2	363	378	19	5	2	179	-133
29	0	2	195	256	12	3	2	1245	-1260	22	5	2	247	236
30	0	2	298	-322	13	3	2	451	-475	0	6	2	333	-359
3	1	2	67	34	14	3	2	432	408	1	6	2	212	-244
4	1	2	117	-93	16	3	2	626	632	2	6	2	226	200
5	1	2	141	-137	17	3	2	326	327	3	6	2	186	171
6	1	2	594	566	18	3	2	464	-463	5	6	2	183	189
7	1	2	699	665	19	3	2	266	-264	6	6	2	235	-241
8	1	2	301	-286	20	3	2	587	596	8	6	2	326	341
9	1	2	338	332	21	3	2	233	242	10	6	2	213	-196
10	1	2	913	-887	22	3	2	256	-225	14	6	2	222	252
11	1	2	327	-327	24	3	2	406	-404	16	6	2	175	-195
12	1	2	300	284	25	3	2	184	-193	22	6	2	174	-170
13	1	2	118	-132	26	3	2	317	337	1	7	2	424	438
14	1	2	228	-251	28	3	2	228	-222	2	7	2	996	-991
15	1	2	206	-222	0	4	2	212	171	3	7	2	267	-316
16	1	2	320	325	1	4	2	316	304	4	7	2	232	254
18	1	2	523	510	2	4	2	1297	-1279	5	7	2	194	216

H	K	L	FO	FC
6	7	2	498	-510
7	7	2	243	-249
9	7	2	423	-432
10	7	2	1044	1033
11	7	2	345	349
12	7	2	294	-327
17	7	2	214	214
18	7	2	571	-599
19	7	2	254	-267
26	7	2	315	306
0	8	2	655	666
2	8	2	451	446
3	8	2	304	339
5	8	2	195	213
6	8	2	672	-649
8	8	2	432	-440
11	8	2	208	-245
12	8	2	372	369
14	8	2	429	408
15	8	2	250	210
20	8	2	250	-245
22	8	2	220	-180
1	9	2	178	-190
3	9	2	177	-195
4	9	2	494	522
7	9	2	181	196
8	9	2	190	-218
12	9	2	282	-285
15	9	2	189	-152
16	9	2	199	245
0	10	2	189	-266
6	10	2	203	-232
8	10	2	205	234
1	11	2	190	-142
4	11	2	326	290
6	11	2	183	143
8	11	2	228	-217
16	11	2	247	224
0	12	2	630	-657
8	12	2	498	527
12	12	2	238	-264
2	13	2	211	-203
4	13	2	219	-157
3	1	3	467	441
4	1	3	405	383
6	1	3	392	-355
7	1	3	832	791
8	1	3	167	-135
9	1	3	704	701
10	1	3	826	804
11	1	3	647	-646
12	1	3	281	-277
13	1	3	291	-293
15	1	3	249	-241
17	1	3	363	-378
18	1	3	527	-533
19	1	3	461	460
21	1	3	218	267
22	1	3	176	191
26	1	3	243	259
27	1	3	228	-259
0	2	3	193	159
1	2	3	106	130
2	2	3	911	897
3	2	3	1309	-1297
4	2	3	114	-111
5	2	3	907	-928
6	2	3	982	-992
7	2	3	585	575
10	2	3	406	-406
11	2	3	638	646
13	2	3	493	491
14	2	3	712	716
15	2	3	548	-542
19	2	3	223	-238
22	2	3	324	-328
23	2	3	416	406
3	3	3	972	963
4	3	3	1061	1083
5	3	3	1078	-1095
6	3	3	195	-214
7	3	3	264	-285
8	3	3	325	-345
9	3	3	185	162
10	3	3	212	225
11	3	3	409	-433
12	3	3	763	-759
13	3	3	751	766
14	3	3	182	181
15	3	3	325	310
16	3	3	431	425
17	3	3	362	-336
18	3	3	184	-117
19	3	3	207	244
20	3	3	245	240
21	3	3	434	-419

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
23	3	3	231	-191	15	6	3	418	-414	15	10	3	395	-386
24	3	3	278	-314	16	6	3	487	-489	5	11	3	229	-253
25	3	3	245	267	17	6	3	665	672	7	11	3	193	-210
0	4	3	261	-293	18	6	3	224	193	10	11	3	204	-202
1	4	3	146	77	19	6	3	268	265	13	11	3	282	239
2	4	3	287	272	20	6	3	357	381	2	13	3	250	283
3	4	3	120	94	21	6	3	387	-363	4	0	4	329	-322
4	4	3	181	157	22	6	3	219	-205	5	0	4	489	-488
6	4	3	306	-316	23	6	3	237	183	6	0	4	333	339
7	4	3	224	230	24	6	3	207	200	7	0	4	1232	1254
12	4	3	176	-159	25	6	3	307	-303	8	0	4	1503	-1508
13	4	3	145	161	28	6	3	240	-237	9	0	4	1691	-1693
14	4	3	213	224	1	7	3	559	-557	10	0	4	581	579
17	4	3	150	-130	2	7	3	390	-395	11	0	4	372	-355
20	4	3	200	196	3	7	3	232	220	12	0	4	793	783
25	4	3	182	112	6	7	3	202	-204	13	0	4	832	826
26	4	3	173	131	7	7	3	497	508	14	0	4	331	-334
1	5	3	586	587	9	7	3	320	318	15	0	4	660	-645
2	5	3	563	553	10	7	3	396	397	16	0	4	793	804
3	5	3	170	-193	11	7	3	368	-322	17	0	4	870	905
4	5	3	354	360	14	7	3	161	122	18	0	4	344	-360
5	5	3	124	100	15	7	3	256	-252	19	0	4	373	356
6	5	3	328	338	16	7	3	227	-206	20	0	4	525	-527
7	5	3	601	-622	18	7	3	180	-173	21	0	4	712	-702
8	5	3	240	-257	19	7	3	304	301	22	0	4	251	268
9	5	3	332	-312	9	8	3	175	152	23	0	4	300	276
10	5	3	468	-454	3	9	3	565	-611	24	0	4	343	-336
11	5	3	341	354	4	9	3	567	-584	25	0	4	354	-386
14	5	3	200	-178	5	9	3	680	698	28	0	4	299	311
15	5	3	376	369	6	9	3	246	217	29	0	4	474	459
16	5	3	237	266	8	9	3	183	181	30	0	4	202	-193
18	5	3	222	227	11	9	3	299	318	3	1	4	376	356
19	5	3	290	-293	12	9	3	320	358	4	1	4	93	-100
27	5	3	193	217	13	9	3	504	-523	5	1	4	109	-118
0	6	3	1294	-1324	16	9	3	235	-192	6	1	4	562	558
1	6	3	1289	1294	17	9	3	200	199	7	1	4	699	690
2	6	3	318	329	19	9	3	187	-175	9	1	4	445	431
3	6	3	296	293	20	9	3	258	-217	10	1	4	704	-686
4	6	3	143	159	21	9	3	322	313	11	1	4	560	-538
6	6	3	194	-198	2	10	3	391	412	12	1	4	313	301
7	6	3	761	764	3	10	3	527	-538	13	1	4	122	110
8	6	3	917	948	5	10	3	509	-482	14	1	4	300	-309
9	6	3	1011	-1044	6	10	3	474	-511	15	1	4	394	-394
10	6	3	263	-266	7	10	3	360	407	16	1	4	190	165
11	6	3	304	-332	10	10	3	192	-186	18	1	4	361	382
12	6	3	440	-458	11	10	3	342	315	19	1	4	363	356
13	6	3	252	276	13	10	3	293	297	20	1	4	225	-252
14	6	3	226	236	14	10	3	355	364	23	1	4	174	162

H	K	L	FO	FC
27	1	4	229	-222
28	1	4	215	189
0	2	4	388	-362
1	2	4	112	99
2	2	4	253	250
3	2	4	108	88
5	2	4	166	-188
6	2	4	143	-136
7	2	4	150	161
8	2	4	308	301
10	2	4	276	-264
11	2	4	176	-168
12	2	4	117	77
13	2	4	195	180
16	2	4	238	-255
17	2	4	164	-159
18	2	4	165	170
19	2	4	223	239
21	2	4	209	-187
25	2	4	200	157
2	3	4	191	-168
3	3	4	1040	-1058
4	3	4	1268	1265
5	3	4	1210	1239
6	3	4	336	-314
7	3	4	149	155
8	3	4	429	-455
9	3	4	427	-442
10	3	4	279	284
11	3	4	634	666
12	3	4	863	-861
13	3	4	838	-848
14	3	4	323	310
15	3	4	289	-267
16	3	4	425	417
17	3	4	530	506
18	3	4	232	-198
19	3	4	358	-360
20	3	4	350	352
21	3	4	475	460
22	3	4	191	-172
23	3	4	189	169
24	3	4	298	-286
25	3	4	372	-364
26	3	4	195	222
29	3	4	242	-162
1	4	4	473	464
2	4	4	1002	-958
3	4	4	1039	-975
5	4	4	1200	-1188
6	4	4	1243	1234
7	4	4	891	900
9	4	4	175	-169
10	4	4	310	326
11	4	4	601	618
12	4	4	249	-245
13	4	4	574	581
14	4	4	838	-847
15	4	4	738	-726
16	4	4	237	234
21	4	4	245	-272
22	4	4	441	411
23	4	4	474	465
24	4	4	192	-182
1	5	4	497	513
2	5	4	382	-343
3	5	4	234	-245
4	5	4	575	-574
6	5	4	145	-103
7	5	4	330	-341
8	5	4	170	135
9	5	4	336	-359
10	5	4	399	373
11	5	4	329	341
12	5	4	283	310
13	5	4	184	169
17	5	4	238	235
18	5	4	228	-224
19	5	4	228	-245
0	6	4	226	-211
1	6	4	292	-283
2	6	4	163	160
3	6	4	134	97
6	6	4	224	-216
7	6	4	172	-190
8	6	4	184	214
9	6	4	171	164
14	6	4	169	162
15	6	4	206	179
17	6	4	161	-161
23	6	4	191	-116
25	6	4	180	90
1	7	4	564	647
2	7	4	710	-708
3	7	4	654	-649
5	7	4	251	317

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
6	7	4	302	-296	7	1	5	307	309	18	3	5	237	-213
7	7	4	330	-334	8	1	5	120	-114	20	3	5	386	377
9	7	4	546	-563	9	1	5	328	299	21	3	5	222	-202
10	7	4	650	639	10	1	5	1222	1183	24	3	5	365	-345
11	7	4	639	635	11	1	5	185	-196	0	4	5	325	-331
17	7	4	317	337	12	1	5	322	-307	1	4	5	129	-129
18	7	4	400	-407	13	1	5	231	-246	2	4	5	157	162
19	7	4	467	-460	15	1	5	160	-159	6	4	5	282	-296
26	7	4	210	181	18	1	5	649	-647	8	4	5	206	213
27	7	4	251	227	19	1	5	209	184	9	4	5	126	113
0	8	4	477	479	22	1	5	247	213	14	4	5	273	277
2	8	4	303	296	24	1	5	161	-179	20	4	5	211	227
3	8	4	553	544	26	1	5	310	304	1	5	5	357	347
5	8	4	385	375	30	1	5	187	-193	2	5	5	558	566
6	8	4	382	-374	0	2	5	96	87	3	5	5	160	-169
8	8	4	352	-360	2	2	5	941	951	4	5	5	231	244
9	8	4	206	-244	3	2	5	550	-545	5	5	5	150	150
11	8	4	315	-337	5	2	5	475	-456	6	5	5	500	494
12	8	4	204	232	6	2	5	1169	-1199	7	5	5	311	-355
14	8	4	284	287	7	2	5	218	200	8	5	5	256	-263
15	8	4	250	217	8	2	5	139	127	9	5	5	260	-247
16	8	4	172	94	10	2	5	468	-452	10	5	5	494	-473
20	8	4	207	-175	11	2	5	384	360	11	5	5	211	215
3	9	4	326	-265	12	2	5	162	161	14	5	5	158	-157
4	9	4	298	337	13	2	5	266	251	15	5	5	201	176
5	9	4	360	374	14	2	5	932	915	16	5	5	284	276
7	9	4	251	212	15	2	5	323	-316	17	5	5	152	115
12	9	4	249	-233	16	2	5	181	-156	18	5	5	209	243
13	9	4	272	-232	20	2	5	163	-152	19	5	5	230	-236
15	9	4	202	-195	22	2	5	434	-430	22	5	5	182	97
1	10	4	211	-220	23	2	5	225	254	24	5	5	223	-202
5	10	4	183	138	24	2	5	180	185	26	5	5	186	-90
7	10	4	185	-235	30	2	5	189	188	0	6	5	1677	-1697
13	10	4	222	-173	1	3	5	180	155	1	6	5	601	582
15	10	4	211	173	2	3	5	261	-251	2	6	5	468	445
21	10	4	188	131	3	3	5	433	415	4	6	5	287	274
1	11	4	215	-218	4	3	5	1463	1475	6	6	5	330	-340
2	11	4	248	201	5	3	5	544	-554	7	6	5	373	371
7	11	4	234	251	6	3	5	311	-311	8	6	5	1235	1273
15	11	4	212	-194	7	3	5	165	-151	9	6	5	596	-571
0	12	4	357	-443	8	3	5	479	-474	10	6	5	394	-381
1	12	4	425	-362	10	3	5	199	190	11	6	5	166	-173
8	12	4	309	361	11	3	5	207	-211	12	6	5	545	-563
9	12	4	417	347	12	3	5	981	-890	13	6	5	160	80
6	13	4	200	-98	13	3	5	432	413	14	6	5	265	269
4	1	5	193	188	14	3	5	247	252	15	6	5	175	-146
5	1	5	163	148	16	3	5	555	549	16	6	5	694	-696
6	1	5	577	-563	17	3	5	162	-116	17	6	5	406	372

H	K	L	FO	FC	H	K	L	FO	FC
18	6	5	267	284	5	0	6	137	-120
20	6	5	499	501	7	0	6	1593	1546
22	6	5	248	-263	8	0	6	595	-582
24	6	5	267	269	9	0	6	1914	-1873
28	6	5	276	-283	10	0	6	142	166
1	7	5	324	-324	11	0	6	586	-577
2	7	5	610	-586	12	0	6	122	128
6	7	5	340	-370	13	0	6	646	644
7	7	5	281	281	15	0	6	773	-779
8	7	5	195	186	16	0	6	297	301
9	7	5	210	187	17	0	6	1033	1040
10	7	5	478	494	19	0	6	405	394
11	7	5	211	-225	21	0	6	685	-676
15	7	5	168	-138	23	0	6	386	399
16	7	5	216	-194	25	0	6	416	-437
17	7	5	188	-95	27	0	6	203	-219
18	7	5	304	-292	29	0	6	484	477
19	7	5	248	224	3	1	6	428	416
24	7	5	226	111	4	1	6	135	-126
1	8	5	191	-167	5	1	6	145	-133
14	8	5	179	106	6	1	6	297	285
18	8	5	188	-147	7	1	6	736	717
24	8	5	193	-76	8	1	6	174	-144
2	9	5	183	204	9	1	6	569	553
4	9	5	895	-901	10	1	6	405	-398
5	9	5	423	370	11	1	6	644	-627
8	9	5	230	224	12	1	6	218	184
12	9	5	590	586	15	1	6	495	-505
13	9	5	320	-303	18	1	6	294	283
14	9	5	258	-230	19	1	6	505	494
16	9	5	297	-278	20	1	6	152	-143
18	9	5	178	168	27	1	6	305	-323
20	9	5	316	-302	0	2	6	426	-414
2	10	5	557	568	2	2	6	245	234
3	10	5	274	-309	5	2	6	107	-95
6	10	5	662	-693	6	2	6	323	-303
10	10	5	235	-211	8	2	6	386	358
11	10	5	193	189	9	2	6	147	116
14	10	5	548	556	10	2	6	160	-143
15	10	5	206	-230	11	2	6	212	-210
2	11	5	218	223	14	2	6	239	230
4	11	5	250	234	16	2	6	237	-232
10	11	5	199	-249	17	2	6	187	-187
18	11	5	227	143	19	2	6	268	270
8	12	5	210	-151	25	2	6	179	176
2	13	5	363	343	27	2	6	201	-196
6	13	5	272	206	3	3	6	1404	-1354
4	0	6	155	-153	4	3	6	497	491

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
5	3	6	1502	1524	2	6	6	182	153	7	13	6	244	-199
6	3	6	178	-184	3	6	6	156	133	3	1	7	395	-397
7	3	6	281	287	7	6	6	290	-288	5	1	7	315	301
8	3	6	153	-157	9	6	6	247	237	6	1	7	450	-435
9	3	6	319	-326	15	6	6	185	198	7	1	7	112	74
11	3	6	771	764	17	6	6	183	-175	10	1	7	957	968
12	3	6	215	-216	1	7	6	763	740	11	1	7	255	254
13	3	6	1025	-1026	2	7	6	225	-208	12	1	7	151	-147
14	3	6	197	143	3	7	6	634	-634	13	1	7	215	-193
15	3	6	316	-330	5	7	6	261	275	17	1	7	163	130
16	3	6	157	147	7	7	6	469	-473	18	1	7	613	-615
17	3	6	477	490	9	7	6	593	-596	20	1	7	181	144
19	3	6	379	-374	11	7	6	652	664	22	1	7	188	207
21	3	6	525	548	17	7	6	430	429	26	1	7	317	273
23	3	6	196	202	19	7	6	560	-525	30	1	7	210	-194
25	3	6	431	-440	25	7	6	206	-206	0	2	7	284	276
27	3	6	187	186	27	7	6	295	251	1	2	7	155	-142
29	3	6	229	-187	0	8	6	292	304	2	2	7	1067	1032
0	4	6	178	-167	1	8	6	178	193	3	2	7	134	-137
1	4	6	512	492	3	8	6	602	597	4	2	7	241	-249
2	4	6	426	-401	5	8	6	455	458	6	2	7	1199	-1218
3	4	6	1245	-1193	6	8	6	189	-142	7	2	7	102	-41
4	4	6	122	93	9	8	6	309	-328	9	2	7	179	182
5	4	6	1204	-1179	11	8	6	396	-394	10	2	7	252	-237
6	4	6	453	445	13	8	6	227	-163	12	2	7	247	239
7	4	6	914	907	15	8	6	261	219	14	2	7	878	866
11	4	6	692	695	17	8	6	260	241	20	2	7	204	-185
13	4	6	654	662	23	8	6	219	-191	22	2	7	460	-455
14	4	6	292	-297	1	9	6	172	-222	24	2	7	182	193
15	4	6	889	-889	3	9	6	277	-284	1	3	7	138	153
19	4	6	187	-167	5	9	6	380	394	2	3	7	187	-190
21	4	6	302	-301	7	9	6	312	309	4	3	7	1382	1398
23	4	6	545	561	13	9	6	349	-336	5	3	7	125	97
1	5	6	578	572	15	9	6	180	-200	6	3	7	289	-298
4	5	6	416	-415	21	9	6	185	153	7	3	7	143	-134
5	5	6	155	-140	1	10	6	220	-230	8	3	7	437	-445
7	5	6	400	-396	7	10	6	202	-216	10	3	7	201	200
8	5	6	204	189	13	10	6	197	-192	12	3	7	875	-870
9	5	6	429	-433	15	10	6	212	169	14	3	7	221	244
11	5	6	285	278	1	11	6	263	-241	16	3	7	478	483
12	5	6	216	208	5	11	6	216	215	18	3	7	193	-163
13	5	6	336	311	7	11	6	272	274	20	3	7	374	375
17	5	6	225	212	15	11	6	204	-220	24	3	7	335	-329
19	5	6	288	-265	1	12	6	457	-391	26	3	7	173	157
21	5	6	250	-238	3	12	6	256	-254	0	4	7	127	-96
27	5	6	181	143	7	12	6	255	-216	1	4	7	364	-366
0	6	6	228	-243	9	12	6	445	423	3	4	7	224	202
1	6	6	338	-329	11	12	6	208	206	4	4	7	146	138

H	K	L	FO	FC
6	4	7	213	-212
7	4	7	273	-282
8	4	7	130	123
9	4	7	129	138
12	4	7	184	-191
14	4	7	165	185
15	4	7	208	204
20	4	7	213	204
23	4	7	177	-116
1	5	7	217	177
2	5	7	644	621
4	5	7	191	207
6	5	7	395	393
7	5	7	136	-110
8	5	7	277	-269
9	5	7	230	-194
10	5	7	524	-521
16	5	7	317	306
18	5	7	290	291
24	5	7	203	-195
0	6	7	1884	-1854
2	6	7	315	316
4	6	7	291	273
6	6	7	175	-168
8	6	7	1318	1323
10	6	7	359	-355
12	6	7	562	-554
14	6	7	263	239
16	6	7	719	-717
18	6	7	293	276
20	6	7	473	463
22	6	7	236	-221
24	6	7	279	270
28	6	7	244	-267
2	7	7	641	-623
5	7	7	168	-108
6	7	7	383	-376
8	7	7	208	191
10	7	7	481	495
14	7	7	165	129
16	7	7	201	-178
18	7	7	332	-333
1	8	7	198	-206
7	8	7	161	-186
1	9	7	184	-82
4	9	7	929	-926
6	9	7	210	218
8	9	7	247	246
12	9	7	590	600
14	9	7	245	-258
16	9	7	270	-282
20	9	7	295	-283
2	10	7	599	574
6	10	7	725	-715
14	10	7	567	553
2	11	7	220	202
4	11	7	250	270
10	11	7	199	-198
1	12	7	199	-29
2	13	7	345	350
4	0	8	181	191
5	0	8	237	-247
6	0	8	282	-299
7	0	8	1342	1425
8	0	8	414	422
9	0	8	1471	-1520
10	0	8	170	-159
11	0	8	425	-428
12	0	8	222	-215
13	0	8	469	507
14	0	8	233	229
15	0	8	561	-684
16	0	8	257	-241
17	0	8	912	943
19	0	8	287	296
20	0	8	225	203
21	0	8	534	-551
22	0	8	208	-172
23	0	8	289	316
25	0	8	385	-404
27	0	8	249	-166
28	0	8	183	-112
29	0	8	374	397
3	1	8	415	442
4	1	8	225	-238
5	1	8	206	-203
7	1	8	776	774
8	1	8	115	104
9	1	8	503	505
11	1	8	564	-573
12	1	8	164	130
15	1	8	392	-420
17	1	8	193	-200
19	1	8	468	495
23	1	8	188	165
27	1	8	318	-289

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	2	8	402	-394	23	4	8	532	513	3	12	8	251	-256
1	2	8	135	-126	1	5	8	538	512	9	12	8	389	374
2	2	8	186	198	2	5	8	278	276	3	1	9	567	-551
3	2	8	105	90	4	5	8	227	-245	4	1	9	209	-192
4	2	8	106	102	5	5	8	253	-267	5	1	9	443	442
6	2	8	379	-371	7	5	8	425	-420	6	1	9	324	-315
7	2	8	148	-148	9	5	8	293	-309	8	1	9	151	146
8	2	8	305	313	10	5	8	306	-328	9	1	9	354	-338
9	2	8	205	232	11	5	8	151	184	10	1	9	704	701
11	2	8	168	-191	12	5	8	202	225	11	1	9	486	470
12	2	8	168	-169	13	5	8	355	361	13	1	9	129	-118
14	2	8	282	318	18	5	8	205	230	17	1	9	242	257
16	2	8	185	-174	19	5	8	187	-190	18	1	9	439	-440
17	2	8	197	-214	20	5	8	165	-94	19	1	9	292	-307
22	2	8	205	-187	21	5	8	206	-232	25	1	9	184	-192
25	2	8	195	186	1	6	8	325	-345	0	2	9	557	550
2	3	8	113	132	7	6	8	233	-263	1	2	9	322	-314
3	3	8	1139	-1142	9	6	8	263	246	2	2	9	939	919
4	3	8	299	-315	17	6	8	186	-160	3	2	9	376	377
5	3	8	1223	1250	1	7	8	662	625	4	2	9	296	-288
7	3	8	246	267	2	7	8	179	249	5	2	9	259	262
9	3	8	276	-282	3	7	8	489	-479	6	2	9	1035	-1048
10	3	8	162	-166	4	7	8	222	-225	7	2	9	258	-249
11	3	8	686	690	5	7	8	230	212	8	2	9	226	-229
12	3	8	242	214	7	7	8	405	-410	10	2	9	263	-281
13	3	8	895	-908	9	7	8	534	-516	11	2	9	123	-144
15	3	8	262	-244	10	7	8	214	-234	12	2	9	291	304
16	3	8	179	-100	11	7	8	526	512	13	2	9	246	-190
17	3	8	418	430	17	7	8	333	333	14	2	9	776	774
19	3	8	322	-324	19	7	8	452	-430	15	2	9	277	256
20	3	8	178	-117	1	8	8	199	201	20	2	9	184	-206
21	3	8	487	486	3	8	8	496	496	21	2	9	171	115
25	3	8	371	-379	5	8	8	422	398	22	2	9	365	-372
27	3	8	190	158	9	8	8	282	-298	23	2	9	193	-169
0	4	8	187	-197	11	8	8	421	-405	3	3	9	402	-406
1	4	8	568	544	15	8	8	178	178	4	3	9	1010	1024
2	4	8	146	148	17	8	8	249	248	5	3	9	336	338
3	4	8	942	-916	1	9	8	282	-272	6	3	9	145	-184
5	4	8	889	-908	4	9	8	189	-180	8	3	9	323	-322
6	4	8	162	-198	5	9	8	325	329	9	3	9	134	-160
7	4	8	702	731	7	9	8	309	327	11	3	9	314	308
8	4	8	136	168	13	9	8	307	-305	12	3	9	652	-639
11	4	8	604	614	1	10	8	193	-160	13	3	9	314	-279
13	4	8	553	544	13	10	8	195	-135	14	3	9	216	213
14	4	8	176	142	1	11	8	212	-234	16	3	9	366	398
15	4	8	771	-791	7	11	8	220	269	17	3	9	242	195
19	4	8	168	-162	15	11	8	235	-270	20	3	9	272	274
21	4	8	262	-232	1	12	8	368	-313	22	3	9	203	-152

H	K	L	FO	FC	H	K	L	FO	FC
24	3	9	243	-257	6	10	9	633	-626
1	4	9	363	-363	10	10	9	210	-191
5	4	9	178	171	14	10	9	476	467
7	4	9	394	-388	4	11	9	229	293
9	4	9	209	220	12	11	9	209	-181
13	4	9	188	-213	0	12	9	222	173
15	4	9	226	220	2	12	9	212	-118
18	4	9	171	-137	2	13	9	267	295
20	4	9	166	103	4	0	10	251	259
23	4	9	171	-133	5	0	10	94	-70
2	5	9	589	573	6	0	10	486	-482
6	5	9	422	409	7	0	10	762	781
7	5	9	168	183	8	0	10	959	954
8	5	9	277	-263	9	0	10	999	-1010
10	5	9	536	-521	10	0	10	317	-319
16	5	9	251	222	11	0	10	222	-189
18	5	9	324	317	12	0	10	397	-398
0	6	9	1490	-1435	13	0	10	346	350
1	6	9	551	-507	14	0	10	373	376
4	6	9	260	235	15	0	10	451	-449
7	6	9	369	-353	16	0	10	532	-531
8	6	9	1042	1033	17	0	10	622	624
9	6	9	400	379	19	0	10	162	141
10	6	9	263	-255	20	0	10	363	344
11	6	9	159	146	21	0	10	328	-318
12	6	9	432	-425	22	0	10	291	-260
13	6	9	239	-203	23	0	10	183	151
15	6	9	269	231	24	0	10	206	210
16	6	9	554	-537	25	0	10	304	-294
17	6	9	244	-227	28	0	10	263	-238
18	6	9	255	251	29	0	10	301	251
20	6	9	407	372	3	1	10	387	391
21	6	9	221	178	4	1	10	160	-165
2	7	9	578	-567	5	1	10	218	-213
6	7	9	381	-373	6	1	10	167	-156
10	7	9	478	466	7	1	10	540	536
18	7	9	292	-298	8	1	10	123	126
1	8	9	172	-154	9	1	10	470	453
7	8	9	176	-179	10	1	10	180	181
4	9	9	778	-756	11	1	10	506	-512
8	9	9	250	231	14	1	10	145	131
12	9	9	464	473	15	1	10	332	-329
13	9	9	197	154	17	1	10	268	-231
14	9	9	218	-213	18	1	10	170	-103
16	9	9	201	-250	19	1	10	410	401
20	9	9	240	-232	27	1	10	218	-243
22	9	9	190	149	0	2	10	347	-347
2	10	9	549	534	1	2	10	341	-350

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	2	10	137	139	23	4	10	375	377	0	10	10	275	233
3	2	10	147	155	1	5	10	311	303	1	11	10	213	-196
6	2	10	258	-260	2	5	10	473	465	7	11	10	268	214
7	2	10	266	-248	3	5	10	163	178	15	11	10	201	-163
8	2	10	263	267	4	5	10	152	-144	0	12	10	231	258
9	2	10	283	275	5	5	10	306	-343	3	12	10	208	-202
12	2	10	199	-186	6	5	10	204	178	8	12	10	212	-214
13	2	10	153	-118	7	5	10	312	-319	9	12	10	245	252
14	2	10	256	240	9	5	10	158	-122	11	12	10	214	160
15	2	10	235	213	10	5	10	409	-397	3	1	11	389	-401
17	2	10	246	-214	13	5	10	345	361	4	1	11	292	-298
1	3	10	182	-150	18	5	10	330	307	5	1	11	202	223
2	3	10	180	177	21	5	10	256	-235	7	1	11	283	-274
3	3	10	757	-739	0	6	10	157	137	9	1	11	503	-474
4	3	10	781	-768	1	6	10	238	-255	10	1	11	284	285
5	3	10	841	852	5	6	10	146	160	11	1	11	534	529
6	3	10	242	239	7	6	10	187	-242	12	1	11	158	145
7	3	10	246	242	8	6	10	164	-156	16	1	11	159	-156
8	3	10	280	290	9	6	10	190	188	17	1	11	321	313
10	3	10	295	-265	17	6	10	166	-143	18	1	11	156	-161
11	3	10	463	470	18	6	10	163	-44	19	1	11	345	-337
12	3	10	541	538	1	7	10	468	458	25	1	11	197	-185
13	3	10	670	-671	2	7	10	501	489	27	1	11	239	191
14	3	10	163	-181	3	7	10	268	-241	0	2	11	320	320
15	3	10	212	-167	4	7	10	293	-302	1	2	11	208	-191
16	3	10	281	-270	6	7	10	261	249	2	2	11	451	449
17	3	10	225	233	7	7	10	308	-281	3	2	11	514	511
18	3	10	162	158	9	7	10	369	-348	4	2	11	112	-135
19	3	10	196	-182	10	7	10	460	-435	5	2	11	435	440
20	3	10	250	-240	11	7	10	306	290	6	2	11	586	-597
21	3	10	385	363	12	7	10	220	216	7	2	11	370	-363
24	3	10	179	212	17	7	10	200	180	8	2	11	189	-200
25	3	10	224	-232	18	7	10	344	328	10	2	11	149	-127
0	4	10	184	-167	19	7	10	280	-269	11	2	11	293	-280
1	4	10	242	231	20	7	10	195	-138	12	2	11	269	284
2	4	10	506	509	1	8	10	195	160	13	2	11	286	-276
3	4	10	797	-777	2	8	10	238	-210	14	2	11	507	493
5	4	10	763	-754	3	8	10	415	380	15	2	11	380	373
6	4	10	631	-620	5	8	10	226	207	20	2	11	173	-177
7	4	10	510	514	6	8	10	252	222	21	2	11	163	120
10	4	10	217	-212	9	8	10	300	-282	22	2	11	196	-210
11	4	10	492	489	11	8	10	309	-282	23	2	11	284	-285
13	4	10	411	407	14	8	10	176	-163	2	3	11	169	140
14	4	10	447	420	17	8	10	206	208	3	3	11	596	-580
15	4	10	514	-521	1	9	10	246	-264	4	3	11	625	615
16	4	10	182	-171	4	9	10	298	-270	5	3	11	529	534
19	4	10	186	-197	5	9	10	259	205	7	3	11	177	178
22	4	10	263	-224	7	9	10	213	239	8	3	11	148	-159

H	K	L	FO	FC	H	K	L	FO	FC
9	3	11	162	-177	18	7	11	231	-225
11	3	11	336	336	0	8	11	218	220
12	3	11	424	-411	6	8	11	192	172
13	3	11	384	-368	13	8	11	185	-124
16	3	11	202	174	24	8	11	206	-86
17	3	11	216	227	3	9	11	293	330
19	3	11	201	-209	4	9	11	499	-481
21	3	11	182	165	5	9	11	427	-377
0	4	11	188	203	12	9	11	286	295
1	4	11	254	-237	13	9	11	351	302
2	4	11	151	-125	2	10	11	370	355
5	4	11	139	118	3	10	11	409	339
7	4	11	287	-271	6	10	11	446	-425
8	4	11	192	-220	7	10	11	241	-227
9	4	11	181	173	11	10	11	185	-182
13	4	11	242	-234	14	10	11	329	311
14	4	11	155	-118	15	10	11	252	230
21	4	11	182	166	4	11	11	263	263
1	5	11	220	-166	4	0	12	208	223
2	5	11	464	459	5	0	12	150	162
6	5	11	273	254	6	0	12	403	-415
7	5	11	257	248	7	0	12	248	260
8	5	11	181	-147	8	0	12	1148	1162
10	5	11	434	-434	9	0	12	472	-465
18	5	11	265	277	10	0	12	295	-292
28	5	11	189	93	11	0	12	184	-199
0	6	11	831	-793	12	0	12	355	-371
1	6	11	740	-690	14	0	12	321	322
3	6	11	150	-166	15	0	12	150	-95
7	6	11	517	-501	16	0	12	634	-635
8	6	11	629	612	17	0	12	371	367
9	6	11	602	595	18	0	12	209	217
11	6	11	167	193	20	0	12	389	364
12	6	11	250	-252	22	0	12	266	-284
13	6	11	202	-210	24	0	12	239	241
15	6	11	271	273	25	0	12	229	-201
16	6	11	297	-273	3	1	12	320	328
17	6	11	415	-379	5	1	12	197	-210
18	6	11	215	202	6	1	12	197	-186
20	6	11	193	188	7	1	12	419	419
21	6	11	268	243	8	1	12	136	161
26	6	11	208	-123	9	1	12	316	314
1	7	11	237	215	10	1	12	358	355
2	7	11	406	-418	11	1	12	385	-386
6	7	11	284	-269	15	1	12	151	-164
7	7	11	261	-243	16	1	12	227	-230
9	7	11	161	-86	17	1	12	190	-206
10	7	11	368	395	18	1	12	267	-256

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
19	1	12	311	322	10	5	12	436	-423	13	2	13	171	-216
1	2	12	452	-450	13	5	12	214	262	15	2	13	376	378
3	2	12	185	200	18	5	12	323	305	17	2	13	150	122
5	2	12	150	151	22	5	12	179	-147	23	2	13	290	-271
7	2	12	334	-337	0	6	12	156	168	2	3	13	210	244
9	2	12	288	285	1	6	12	171	-222	3	3	13	501	-527
12	2	12	172	-190	2	6	12	148	-95	4	3	13	194	211
13	2	12	139	-205	8	6	12	209	-185	5	3	13	479	520
15	2	12	276	267	10	6	12	156	104	7	3	13	160	188
17	2	12	145	-185	16	6	12	168	118	10	3	13	171	-200
20	2	12	173	190	1	7	12	168	182	11	3	13	312	326
23	2	12	182	-164	2	7	12	564	524	12	3	13	165	-142
1	3	12	117	-113	6	7	12	338	318	13	3	13	378	-385
2	3	12	214	182	10	7	12	552	-530	17	3	13	202	162
3	3	12	369	-349	18	7	12	369	352	18	3	13	166	146
4	3	12	1042	-1042	20	7	12	176	-132	21	3	13	209	196
5	3	12	372	391	1	8	12	195	175	25	3	13	199	-185
6	3	12	217	210	2	8	12	234	-232	0	4	13	266	265
7	3	12	134	154	3	8	12	261	220	2	4	13	198	-203
8	3	12	272	267	6	8	12	301	275	5	4	13	149	121
10	3	12	155	-169	8	8	12	165	168	6	4	13	189	226
12	3	12	703	683	9	8	12	200	-198	7	4	13	141	-87
13	3	12	310	-297	11	8	12	197	-179	8	4	13	236	-237
14	3	12	184	-224	12	8	12	138	-140	13	4	13	167	-175
15	3	12	188	-137	14	8	12	240	-211	16	4	13	159	145
16	3	12	312	-319	17	8	12	189	160	22	4	13	182	120
17	3	12	154	96	1	9	12	221	-194	1	5	13	237	-248
18	3	12	210	159	4	9	12	371	-325	2	5	13	410	430
20	3	12	298	-291	12	9	12	217	178	6	5	13	186	207
21	3	12	232	212	3	1	13	226	-259	7	5	13	249	232
24	3	12	245	236	4	1	13	285	-310	10	5	13	317	-321
2	4	12	621	602	7	1	13	289	-313	15	5	13	199	-222
3	4	12	473	-457	8	1	13	125	130	18	5	13	191	200
5	4	12	399	-398	9	1	13	346	-384	19	5	13	214	168
6	4	12	767	-748	11	1	13	316	325	0	6	13	267	-273
7	4	12	214	220	16	1	13	155	-202	1	6	13	698	-692
10	4	12	227	-218	17	1	13	293	234	3	6	13	269	-266
11	4	12	294	311	19	1	13	260	-293	6	6	13	213	228
13	4	12	267	254	0	2	13	233	245	7	6	13	487	-499
14	4	12	602	593	2	2	13	183	186	8	6	13	188	209
15	4	12	219	-213	3	2	13	515	566	9	6	13	641	646
22	4	12	299	-315	5	2	13	454	510	11	6	13	249	238
23	4	12	225	202	6	2	13	228	-283	15	6	13	236	234
2	5	12	489	482	7	2	13	300	-304	17	6	13	431	-396
3	5	12	258	267	8	2	13	138	-146	19	6	13	221	-130
4	5	12	137	140	9	2	13	169	-188	21	6	13	209	204
5	5	12	320	-334	11	2	13	339	-355	1	7	13	217	212
6	5	12	212	197	12	2	13	139	206	2	7	13	288	-289

H	K	L	FO	FC
6	7	13	244	-180
7	7	13	228	-224
9	7	13	191	-119
10	7	13	264	269
11	7	13	162	186
15	7	13	180	152
18	7	13	206	-152
0	8	13	242	256
8	8	13	194	-232
3	9	13	274	312
4	9	13	200	-179
5	9	13	434	-410
11	9	13	255	-220
13	9	13	349	324
21	9	13	198	-176
3	10	13	333	321
5	10	13	300	285
7	10	13	260	-236
11	10	13	202	-204
15	10	13	299	249
4	0	14	178	221
5	0	14	166	180
6	0	14	150	-149
7	0	14	114	-138
8	0	14	890	940
10	0	14	174	-209
12	0	14	332	-389
13	0	14	157	-156
14	0	14	181	170
16	0	14	575	-603
18	0	14	224	229
20	0	14	397	389
22	0	14	186	-201
24	0	14	243	227
3	1	14	189	202
5	1	14	158	-161
6	1	14	314	-307
7	1	14	110	118
8	1	14	187	207
9	1	14	242	242
10	1	14	407	413
11	1	14	195	-191
16	1	14	149	-190
17	1	14	165	-113
18	1	14	273	-285
0	2	14	140	157
1	2	14	404	-417
2	2	14	106	-91

H	K	L	FO	FC
3	2	14	125	130
5	2	14	176	202
7	2	14	286	-298
9	2	14	221	248
13	2	14	192	-232
15	2	14	245	244
21	2	14	185	166
2	3	14	153	169
4	3	14	823	-843
6	3	14	137	155
8	3	14	218	228
12	3	14	536	531
14	3	14	195	-192
16	3	14	302	-276
18	3	14	193	181
20	3	14	285	-272
22	3	14	202	120
2	4	14	497	512
6	4	14	576	-567
10	4	14	165	-160
14	4	14	488	481
22	4	14	237	-267
24	4	14	173	150
2	5	14	327	320
3	5	14	298	271
4	5	14	308	342
5	5	14	246	-221
9	5	14	165	152
10	5	14	315	-311
11	5	14	260	-249
2	7	14	445	425
6	7	14	293	286
10	7	14	462	-458
18	7	14	315	283
0	8	14	330	-347
2	8	14	234	-210
6	8	14	305	294
8	8	14	244	231
14	8	14	234	-204
4	9	14	325	-295
3	1	15	110	-96
4	1	15	335	-352
6	1	15	131	140
7	1	15	283	-301
8	1	15	129	120
9	1	15	234	-233
10	1	15	157	-151
11	1	15	178	156

H	K	L	FO	FC
12	1	15	138	180
13	1	15	142	162
16	1	15	154	-168
18	1	15	199	190
19	1	15	191	-180
0	2	15	203	212
3	2	15	484	510
5	2	15	456	475
7	2	15	177	-164
9	2	15	157	-151
11	2	15	375	-399

H	K	L	FO	FC
13	2	15	189	-182
15	2	15	263	267
23	2	15	216	-206
2	3	15	165	155
3	3	15	326	-343
5	3	15	422	446
7	3	15	174	167
10	3	15	196	-218
11	3	15	144	142
12	3	15	149	106
13	3	15	347	-353

H	K	L	FO	FC
21	3	15	215	207
0	4	15	389	363
6	4	15	192	202
8	4	15	241	-224
14	4	15	161	-154
16	4	15	170	153
20	4	15	169	-122
1	5	15	355	-356
3	5	15	135	109
7	5	15	319	323
9	5	15	170	167

H	K	L	FO	FC
11	5	15	154	-181
15	5	15	221	-229
19	5	15	180	195
1	6	15	545	-523
3	6	15	317	-293
6	6	15	176	197
7	6	15	347	-347
8	6	15	166	-122
9	6	15	606	575
11	6	15	279	257
17	6	15	390	-382

H	K	L	FO	FC
1	7	15	260	253
7	7	15	256	-238
9	7	15	185	-155
11	7	15	181	192
19	7	15	225	-169
6	8	15	168	158
3	9	15	235	253
5	9	15	352	-320
13	9	15	297	262
3	10	15	293	254
5	10	15	243	236

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