A STRUCTURAL INVESTIGATION OF THE
MERCURY - SULPHUR INTERACTION

A thesis submitted to the
UNIVERSITY OF CAPE TOWN
in fulfilment of the requirements for the degree of
MASTER OF SCIENCE

BY

ELLEMIEKE DIJKSTRA B.Sc.(Hons) (Cape Town)

Department of Physical Chemistry
University of Cape Town
Rondebosch
7700
Republic of South Africa

January 1982

ACKNOWLEDGEMENTS

My very sincere thanks and appreciation are due to

Professor L. Nassimbeni, for his enthusiasm, guidance and tolerance during my time in the Department of X-ray Crystallography,

Dr Klaus Koch, for his advice and assistance in the laboratory,

my colleagues Dianne Bond for her efficiency in the typing of this thesis, Dr Margaret Niven for her insight and Mike du Plessis for his interest,

my friends Gary Foulds and Janet Yates for their continued support and encouragement,

my parents who laid the foundations.

Financial assistance from the University of Cape Town and the South African Council for Scientific and Industrial Research is acknowledged with thanks.

ABSTRACT

The crystal and molecular structures of phenyl,2-mercaptopyrimidine mercury(II) and phenyl,mercaptobenzene mercury(II) have been determined by the methods of X-ray crystallography. The interaction between mercury and sulphur is investigated. This interaction is of interest both biochemically and toxicologically. More specifically, secondary Hg---S interactions are found to mimic that observed in NMR exchange processes, where they undergo a transition state as a four-membered bridging intermediate.

Structural correlations between compounds containing at least one mercury - sulphur covalent bond are examined. The coordination geometry about the mercury atom is generally found to be distorted tetrahedra or octahedra, with a very strong tendency to retain the linear character of the R - Hg - S angle. The electronegativity of sulphur is found to be the most influential parameter in determining the coordination geometry of the mercury atom. The transition from four- to six-coordinated structures is examined but did not reveal unambiguously whether this occurs by an S_N3 or $(S_N2)^2$ disubstitution process. The four-membered bridging structure formed by secondary Hg---S interactions is investigated to determine whether minimum energy pathways are evident. However, there is no evidence for pathways representing exchange as observed in solution.

CONTENTS

PART 1

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 THE STORY OF MERCURY

Mercury and sulphur form an association which has its roots deep in the days of the alchemists[1]. In the fundamental physical theory of the Four Elements (Fire, Water, Earth and Air) ascribed to Aristotle (*c.* 350 B.C.), Fire and Water were by far the most important, and they descended into the sulphur-mercury theory of metals.

According to an unknown medieval writer, "The natural principles in the mynes, are *Argent-vive* (Mercury) and *Sulphur*. All mettalls and minerals whereof there be sundrie and divers kinds, are begotten of these two: but I must tel you, that nature alwaies intendeth and striveth to the perfection of Gold: but many accidents coming between change the mettalls.... For according to the puritie and impuritie of the two aforesaid principles, *Argent-vive*, and *Sulphur*, pure and impure mettalls are ingendered."

The sulphur-mercury theory was supplemented by Paracelsus (1493 - 1541) the father of a new alchemical era known as the era of iatrochemistry, or chemistry in the service of medicine. He added the concept of salt (magnesium) forming the system of the *tria-prima* consisting of mercury, sulphur and salt which respectively represent man's soul, spirit and body.

Mercury in its elemental form was one of the first metals known to man. Archeologists have found a small vessel full of mercury in a grave at Kurna, dating back to the fifteenth or sixteenth century B.C.. Theophrastus (300 B.C.) spoke of liquid silver, or *quicksilver*, obtained from cinnabar (HgS). Pliny named the metal *hydrargyrum*, hence the symbol Hg. Aquinas studied solutions of metals in mercury and called them amalgams. The metallic nature of mercury was a matter of confusion and debate, ending with the discovery in 1759 by J.A. Brown, who froze it to a solid metal with a mixture of snow and nitric acid.

The most important source of mercury is the red crystalline sulphide, cinnabar, mined in Spain, Italy, the United States, Mexico, Canada and Russia[2].

The use of mercury goes back at least two or three millenia when, mined in China and Peru, it was used as a pigment. Its ability to kill bacteria was already noted in 400 B.C.. Medicines were produced by medieval physicians from cinnabar.

More recently, mercury has found wide industrial applications; electrolytic procedures, electrical apparatus, paints, industrial controls and catalysts, agricultural fungicides, pharmaceuticals, paper and pulp industries, to mention but a few[3].

It was only recently, however, that public concern for the properties of mercury began when fishermen of Minamata, Japan were stricken with a mysterious illness involving very severe damage to cells of the central nervous system[4]. Investigations of this illness led to the discovery that a vast amount of mercury had been discharged in the sea as industrial waste. Further incidents continued to emphasise the toxicity of this substance. Outbreaks of mercurial poisoning have occurred in Iraq, Pakistan and Guatemala as well as Sweden and Canada[3].

1.2 THE BIOCHEMISTRY OF MERCURY

Analysing the toxicological effects of mercury, in both organic and inorganic forms requires discussion on a biochemical level[5]. Interaction occurs predominantly with thiol, selenide, phosphate, amino and carboxyl groups of such cellular components as amino acids, proteins, enzymes, nucleic acids and lipids. As is common for most metals, mercury forms strong covalent bonds with atoms donating electron pairs, thus reacting readily with sulphur and other non-metals. Consequently it may be deduced that mercury would interact strongly with biological matter offering ligands such as phosphates, cysteinyl and histidyl side chains of proteins, purines, pteridines and porphyrins. Thus complexes of great stability are formed between mercury and sulphydryl groups of amino acids, proteins, nucleotides and nucleic acids.

The toxic effects of mercury depend *inter alia* on its chemical form. Whereas ingested metallic mercury passes through the gastro-intestinal tract with little effect, mercury vapour, upon inhalation, may cause acute or chronic poisoning. The organomercurials may be divided into three classes with respect to their toxicity: aryl, alkyl and alkoxyalkyl. Together these three groups range the toxicological spectrum from life-saving medicines to lethal poisons. Of the three the alkylmercurials are infinitely more poisonous[5,6]. Investigations carried out on phenylmercury, an arylmercurial, have shown it to be of relatively low toxicity. The elucidation of molecular structure by X-ray crystallographic methods in this work concerns itself only with phenylmercury compounds having sulphur-substituted organic ligands.

1.3 THE CHEMISTRY OF ORGANOMERCURY COMPOUNDS

The coordination chemistry of organomercury compounds is the predominant factor in determining their behaviour in biological systems.

Mercury has high *d*-electron levels in its electronic shell enabling dative $d\pi$ - $d\pi$ interaction to occur, stabilising bonds involving ligands with vacant *d*-orbitals of lower energy such as sulphur. It is thus classified as a B-group metal ion according to the Chatt-Ahrland and Davies theory[7]. A further characteristic property of this group is the formation of adducts with aromatic hydrocarbons.

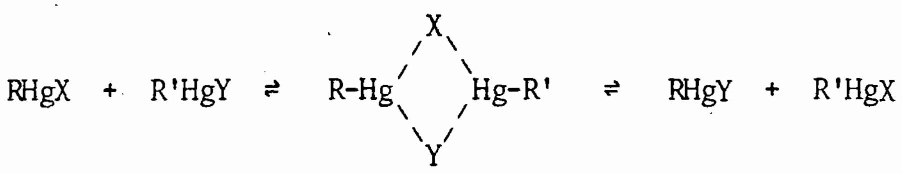
This theory is supported by the HSAB theory[8], according to which mercury lies in the category of soft acids, thus preferring to react with soft bases which are generally easily polarisable, less electronegative and readily oxidizable, having external occupied orbitals at higher energy levels relative to hard bases.

Methylmercury has been studied more extensively than the other organomercurials[9,10], and formation constant measurements favour sulphur-substituted ligands such as cysteine.

This exceptionally strong bond between mercury and sulphur has initiated the theory[11] that organomercury derivatives are transported through biological systems which have accessible sulphydryl groups as mercaptides according to

$$\mathrm{RHgSR'} + \mathrm{ORG\text{-}SH} \longrightarrow \mathrm{RHgS\text{-}ORG} + \mathrm{R'SH}.$$

This exchange process has been confirmed by NMR studies[12]. The rapid intermolecular exchange process proceeds along a second-order reaction pathway, with a transfer of the ligand on the mercury without cleavage of the mercury-carbon bond[13]. The proposed mechanism involves a four-centre bridged intermediate



$$\mathrm{RHgX} + \mathrm{R'HgY} \rightleftharpoons \mathrm{R\text{-}Hg}\overset{\mathrm{X}}{\underset{\mathrm{Y}}{\diamond}}\mathrm{Hg\text{-}R'} \rightleftharpoons \mathrm{RHgY} + \mathrm{R'HgX}$$

This observation supported theories questioning a proposed ionic pathway for the reaction discussed by Hughes, Ingold and co-workers[14].

1.4 THE STRUCTURES OF ORGANOMERCURY COMPOUNDS

The structural chemistry of mercury has been of interest, as the classification of coordination group seemed ambiguous. Grdenić[15,16] proposed two types of coordination, namely characteristic and effective coordination.

In the former, according to the stereochemistry of mercury, molecules have either two collinear, three co-planar or four tetrahedral bonds, with hybrid orbitals *sp*, sp^2 or sp^3 respectively. Trigonal bipyramidal and octahedral coordination are far less common. For each of these groups the covalent radius of mercury is in accordance with the additivity rule, *i.e.* the radius of mercury and the radius of the ligand atoms bonded to mercury are within agreement of the observed mercury-ligand bond length.

In practice the actual coordination of mercury is often found to be irregular and distorted, with bond lengths and angles covering a very wide range. This Grdenić classified as effective coordination, which may be defined as secondary bond formation arising from mercury interacting with ligands additional to characteristic coordination. This is found most commonly for mercury atoms which have two collinear bonds, giving rise to distorted octahedral effective coordination.

In the investigation of the structure of two phenylmercury compounds, the interaction of mercury and sulphur, possibly forming a four-centred bridge between two molecules, and the coordination of mercury were of specific interest.

The compounds studied were:

a) phenyl,2-mercaptopyrimidine mercury(II)

b) phenyl,mercaptobenzene mercury(II)

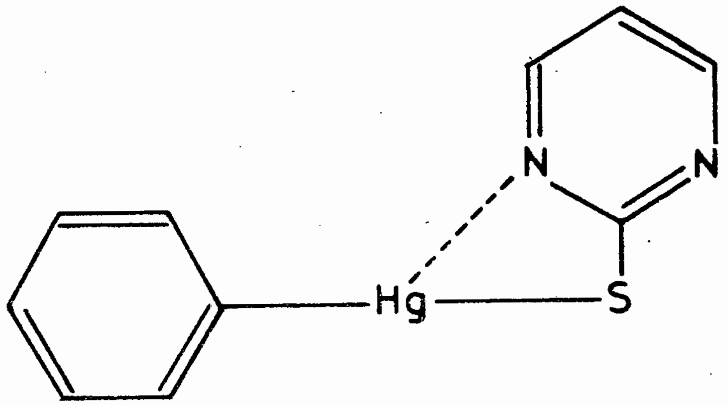
Henceforth these will be referred to as PMPM and PMBM respectively.
The structural formulae are given in Figure 1.

CHAPTER 2

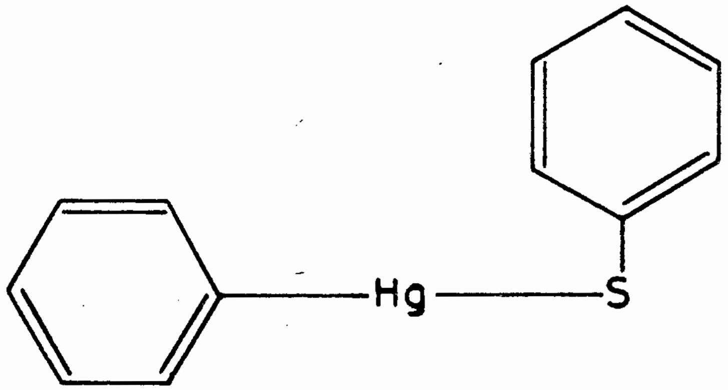
GENERAL EXPERIMENTAL

FIGURE 1 STRUCTURAL FORMULAE OF PHENYL,2-MERCAPTOPYRIMIDINE MERCURY(II) AND PHENYL,MERCAPTOBENZENE MERCURY(II)

(a) PMPM



(b) PMBM



CHAPTER 2

GENERAL EXPERIMENTAL

2.1 SYNTHESIS OF THE COMPOUNDS

Analytically pure reagents were used in the synthesis of the two mercury complexes. The phenyl,2-mercaptopyrimidinatomercury(II) complex was pre= pared by adding an aqueous solution of phenylmercury(II) acetate (0,337g : 1mmol) to an aqueous solution of 2-thiopyrimidine (0,112g : 1mmol). The resulting precipitate was isolated by filtration and recrystallised from a DMSO/aqueous ethanol mixture. The phenyl,mercaptobenzene mercury(II) complex was prepared in a similar manner, adding (0,086ml : 1mmol) thiophenol to an aqueous solution of phenylmercury(II) acetate.

The PMPM crystals were colourless needles, whereas those of PMBM formed small flat plates.

2.2 DENSITY DETERMINATION

The density of crystals of both PMPM and PMBM was determined by the flotation method, the former in CH_2I_2/CCl_4 and the latter in CH_2I_2/chlorobenzene mixtures. Their densities (D_m) were read off nomograms as 2,56gcm^{-3} and 2,22gcm^{-3} respectively.

2.3 PRELIMINARY X-RAY ANALYSIS[17,18,19,20]

Suitable single crystals were selected and mounted at the ends of glass fibres. In the case of PMPM oscillation and Weissenberg (zero layer and upper layer) photographs were obtained, taken about the needle axis which proved co-incident with the crystallographic *b* axis.

For PMBM oscillation and Weissenberg (zero layer and upper layer) photographs were taken about the crystallographic *a*, *b* and *c* axes.

The oscillation and Weissenberg photographs were taken on a camera with radius 28,65mm using a Stoe (Heidelberg) goniometer together with Philips PW 1008 and PW 1120 X-ray generators operating at 20mA and 40kV. Using a nickel filter and copper target Cu-K_α radiation (λ = 1,5418Å) was obtained, and the X-ray films (3M) were developed and fixed in the normal way. The unit cell parameters and space groups were obtained from appropriate analysis of the oscillation and Weissenberg photographs.

2.4 DIFFRACTOMETER DATA COLLECTION

Selected single crystals were mounted and sent to Dr G. Gafner (PMPM) and Mr J. Albain (PMBM) (National Physical Research Laboratory, C.S.I.R. Pretoria) for diffractometer data collection.

A computer controlled Philips PW 1100 four-circle diffractometer was used in conjunction with a Philips PW 1130 3kV X-ray generator operating at 50kV and 20mA. The radiation used was MoK_α, with a graphite monochrometer (λ = 0,7107Å).

Initially least squares analysis of the χ, ϕ and 2θ angles of a preset number (usually 25) of standard reflections centred on the diffractometer provided accurate cell parameters. This was followed by three-dimensional intensity data collection carried out by the ω - 2θ scan technique, in which the angular rate of the diffractometer detector rotation is double that of the crystal. In the ω - scan the reciprocal lattice (*i.e.* the crystal) is rotated by the ω circle carrying the lattice points across the sphere of reflection to the inside. This resembles a photometric trace made parallel to the centre line of the film on a zero-layer Weissenberg photograph, whereas the 2θ scan corresponds to a similar trace along the diagonal passing through reflections on a common central lattice row[18].

Throughout the duration of the data collection, instrumental and crystal stability were monitored by the periodic measurement of three standard reference reflections. Observed reflections were deemed "observed" if

$$I(\text{rel}) > 2\sigma I(\text{rel})$$

where $$\sigma I_{\text{rel}} = [N_{pk} + N_{bg} + N_{instr}]^{\frac{1}{2}}$$

σI_{rel} = standard error in relative integrated intensity
N_{pk} = gross peak count for a specific reflection
N_{bg} = background count
N_{instr} = $[0{,}02 \times (N_{pk} - N_{bg})]^2$

Lorentz and polarisation corrections were applied to the data. These are applicable in equating the structure factor modulus, $|F_{hkl}|$ to the intensity measured. Polarisation corrections are necessitated by the nature of the X-ray beam and the manner in which its reflection efficiency varies with the angle of reflection. The Lorentz factor arises because the time taken by a reciprocal lattice point to pass through the sphere of reflection is dependent on its position in reciprocal space and on direction of approach to the sphere[18].

2.5 METHODS OF COMPUTATION

Crystallographic data reduction, structure solution and subsequent refinement was carried out by means of the SHELX76[21] program system. Facilities of the program used include data reduction, automatic centro=symmetric methods for solving the phase problem, multi-solution refinement, full-matrix and accelerated full-matrix least squares refinement, geometric position and constrained refinement of hydrogen atoms, analysis of variance and automatic optimisation of weighting schemes, various Fourier syntheses with peak search, and structure factor lists.

Guidelines to the correctness of structure may be obtained from a number of criteria. Of relative importance is the residual index[19] which relates observed and calculated structure factors according to

$$R = \frac{\Sigma|\,|F_o| - |F_c|\,|}{\Sigma|F_o|} = \frac{\Sigma|\Delta|}{\Sigma|F_o|}$$

upon introduction of a weighting scheme this may also be expressed as R_ω, where

$$R_\omega = \frac{\Sigma\omega^{\frac{1}{2}}|\Delta|}{\Sigma\omega^{\frac{1}{2}}|F_o|}$$

$$\omega = \frac{1}{[\sigma^2(F) + gF^2]}$$

The analysis of variance computed upon completion of the final refinement cycle gives an indication of the effectiveness of the weighting scheme. Scattering factors used were from Cromer and Mann[22] for all non-hydrogen atoms, and from Stewart *et al*[23] for the hydrogen atoms. Atomic radii used were those of Pauling[24].

Bond distances, bond angles, torsion angles and least square planes were calculated using the program XANADU[25], and molecular illustrations and diagrams generated using PLUTO[26]. All computations were carried out on a Univac 1106 computer at the Computer Centre of the University of Cape Town.

CHAPTER 3

THE CRYSTAL AND MOLECULAR STRUCTURE OF PHENYL,2-MERCAPTOPYRIMIDINE MERCURY(II)

CHAPTER 3

THE CRYSTAL AND MOLECULAR STRUCTURE OF PHENYL,2-MERCAPTOPYRIMIDINE MERCURY(II) (PMPM)

3.1 CHEMICAL ANALYSIS

Elemental microanalysis was carried out on the crystals to determine their carbon, hydrogen and nitrogen content, confirming the composition of PMPM as $C_{10}H_8N_2SHg$.

TABLE 1 MICROANALYSIS RESULTS

	%C	%H	%N
Calculated:	30,89	2,07	7,20
Found:	31,02	2,04	7,07

3.2 PRELIMINARY X-RAY ANALYSIS

A suitable single crystal was selected and mounted along the needle axis. Initial alignment was achieved using a two circle optical goniometer, followed by fine adjustment based on the oscillation photographs. The oscillation photograph indicated that the unit cell was monoclinic[18]. This was confirmed by subsequent Weissenberg photographs. An initial estimate of the cell parameter based on these photographs yields a = 20,92Å, b = 6,75Å, c = 14,89Å, β = 111° and z = 8. The following conditions for non-extinction of reflections according to the zero and upper level Weissenberg photographs were evident:

hkl : No conditions
$h0l$: $l = 2n$
$0k0$: $k = 2n$

These conditions uniquely determine the space group to be $P2_1/c$[27]. For this space group there are four general positions, x,y,z, $\bar{x},\bar{y},\bar{z}$, $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$, $x,\frac{1}{2}-y,\frac{1}{2}+z$. As the number of molecules per unit cell was found to be 8 according to density determination and calculation, it was suspected that the molecules were held together by weak Hg---S interactions to form "dimers", the two molecules concerned being symmetrically unrelated.

3.3 INTENSITY DATA COLLECTION

Diffractometer data collection was carried out on a single mounted crystal of dimensions 0,04 x 0,12 x 0,41mm. The diffractometer scan width was 1,0°θ, scanning at a speed of 0,03°θs^{-1} and collecting reflections over a range of $3° < \theta < 23°$. A total of 3219 reflections were collected, of which 411 were systematically absent and 738 suppressed as they did not satisfy the criterion $I_{\mathrm{rel}} > 2\sigma I_{\mathrm{rel}}$. Every 51 relections three standard reflections were measured and were found to remain constant to within 0,74% of their mean value.

Accurate cell parameters, obtained from least squares analysis of the Χ, Φ and 2θ angles are given in Table 2. The expression

$$ZM = ND_m abc\sin\beta$$

where M : molecular weight
N : Avogadro constant
D_m : measured density
$abc\sin\beta$: volume of unit cell

was used to calculate the number of molecules per unit cell. Z was found to be 7,9 thus there are eight molecules per unit cell. This value in turn gave a calculated density, D_c, of 2,62Mgm^{-3}.

TABLE 2 CRYSTAL DATA

Molecular formula:	$C_{10}H_8N_2SHg$
Molecular weight:	388,8
Space group:	$P2_1/n$
a:	21,295(12)Å
b:	6,738(3)Å
c:	15,305(8)Å
β:	107,31(2)°
V:	2096,55Å^3
D_m:	2,56Mgm^{-3}
D_c:	2,60Mgm^{-3}
μ(Mo-K_α):	7,146mm^{-1}
$F(000)$:	704

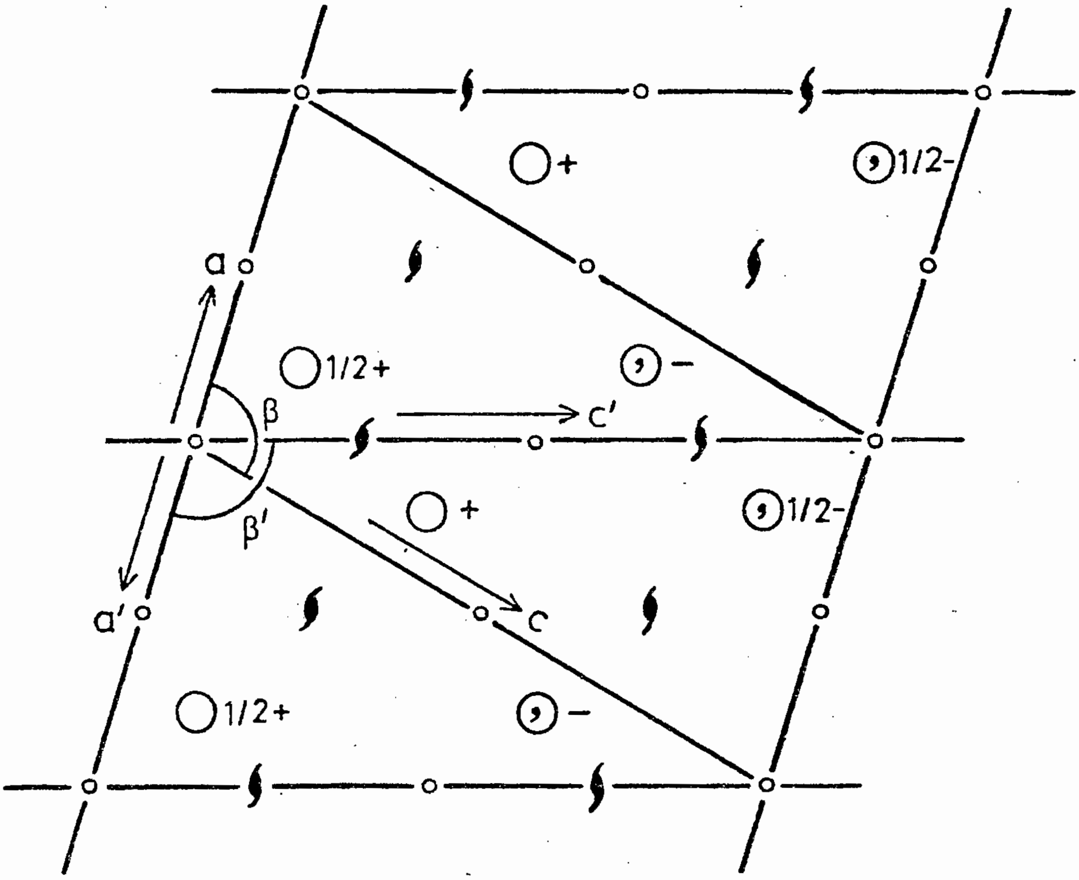
However, the diffractometer automatically selected a different unit cell, in the setting $P2_1/n$, and the intensity data collection was carried out for this latter setting. This was immediately understood by analysis of systematic absences namely

hkl : No conditions

$h0l$: $h + l = 2n$

$0k0$: $k = 2n$

FIGURE 2 THE RELATIONSHIP BETWEEN THE UNIT CELL (BOUNDED BY a, b AND c) CORRESPONDING TO THE SPACE GROUP $P2_1/n$ AND THE UNIT CELL (BOUNDED BY a', b' AND c') CORRESPONDING TO THE SPACE GROUP $P2_1/c$



Equivalent positions

$P2_1/n$: x, y, z $-x, -y, -z$ $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$

$P2_1/c$: x, y, z $-x, -y, -z$ $x, \frac{1}{2}-y, \frac{1}{2}+z$ $-x, \frac{1}{2}+y, \frac{1}{2}-z$

The two cells are projected onto (010).

Symmetry operation symbols are in accordance with those in ref. 27.

These uniquely define the space group $P2_1/n$, a non standard setting unlisted in International Tables for X-ray Crystallography[27]. $P2_1/n$ is related to $P2_1/c$ by a different choice of c-axis. This is shown in Figure 2. Thus PMPM was determined in the space group $P2_1/n$.

3.4 SOLUTION AND REFINEMENT OF THE STRUCTURE

Structure solution and refinement was achieved using the automatic centrosymmetric routine of the SHELX program system[20], in the space group $P2_1/n$. The asymmetric unit consists of two molecules held by weak secondary interactions.

Direct methods were used, resulting in three origin defining reflections and twelve additional reflections assigned positive or negative values with high E. These were expanded to 514 signs using 4948 relations with 4096 permutations. Two E-maps were generated, from which the positions of the two mercury atoms, Hg(1)A and Hg(1)B of the asymmetric unit were obtained. This was followed by three cycles of least squares refinement on the two mercury atoms, which were both treated anisotropically. This generated a weighted difference fourier map, which yielded the positions of the two sulphur atoms in addition to sixteen carbon atoms and two nitrogen atoms. The R value at this stage was 0,22. An additional three cycles of least squares refinement followed, still with only mercury treated anisotropically, resulting in the location of all non-hydrogen atoms and reduction of R to 0,13. At this stage convergence was hampered by a few reflections with very large deviations.

These were:

h	k	l	F_o	F_c	D/σ
0	2	0	431,61	649,40	14,25
0	2	1	351,05	537,51	12,20
6	0	2	366,57	458,92	6,04
3	1	2	298,18	414,53	7,61
7	0	3	405,50	498,68	6,10

These poor reflections may be ascribed to secondary extinction effects. This is generated by reflections of such intensity that an appreciable amount of the incident radiation is reflected at a given instant by the first planes encountered by the beam. Less incident intensity is reached by deeper planes which subsequently reflect less power. The effect is greater for reflections at low $(\sin\,\theta)/\lambda$ where intensities are generally the highest. The result is that $F_o << F_c$, as may be seen above.

A final three cycles of accelerated full-matrix refinement with these bad reflections selectively omitted followed. At this stage all hydrogen atoms were constrained to ride at 1,08Å from their parent carbon atoms with the geometry of the molecule dictating their positions.

The refinement converged to R = 0,0840, with R_ω = 0,0902 and the weighting scheme $\omega = (\sigma^2 F + gF^2)^{-1}$ where $g = 0{,}7 \times 10^{-3}$.

The thermal parameters for the anisotropic refinement were of the form

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]$$

TABLE 3 ANALYSIS OF VARIANCE*

a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	378	175	196	286	186	372	277	200	2070
V	734	753	740	686	766	697	715	784	729

b) As a function of sinθ

sinθ	0,00-0,18-0,22-0,25-0,28-0,30-0,33-0,34-0,36-0,38-0,40									
N		242	200	185	238	171	308	114	235	233	144
V		993	835	690	707	630	611	623	575	711	797

c) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$	0,00-0,21-0,24-0,26-0,29-0,32-0,36-0,40-0,45-0,54-1,00									
N		211	269	170	196	189	249	205	172	206	203
V		859	741	726	684	660	742	702	626	721	767

d) As a function of |Miller index|

$\lvert h \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	64	138	132	134	138	127	134	121	126	121	111	111	98	86	429
V	787	640	903	871	912	946	849	685	743	653	553	616	589	668	576

TABLE 3 CONT/....

TABLE 3 CONTINUED

$\lvert k \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	252	340	389	364	327	216	143	39	0	0	0	0	0	0	0
V	709	758	734	679	704	736	812	825	0	0	0	0	0	0	0
$\lvert l \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	91	194	193	184	190	184	167	158	146	129	102	97	85	60	90
V	617	749	882	902	851	759	631	619	653	598	562	686	706	502	679

*N = No. of reflections in the group

$V = 100[M\Sigma(\omega|F_o - F_c|^2)/N\Sigma\omega]$ where M = total no. of reflections.

TABLE 4 FRACTIONAL ATOMIC COORDINATES (x 10^3) AND ISOTROPIC THERMAL MOTION PARAMETERS (Å^2 x 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
Hg(1)A	459(1)	483(1)	102(1)	a
S(1)A	344(1)	484(1)	85(1)	a
N(1)A	412(1)	554(3)	256(1)	33(4)
N(3)A	293(1)	548(3)	220(1)	40(5)
C(2)A	351(1)	538(3)	199(2)	35(6)
C(4)A	306(2)	587(4)	310(2)	63(8)
C(5)A	363(1)	604(4)	377(2)	54(7)
C(6)A	418(1)	586(4)	348(2)	47(6)
C(7)A	562(1)	483(3)	121(1)	26(5)
C(8)A	595(1)	302(4)	131(2)	45(6)
C(9)A	663(1)	297(4)	152(2)	50(7)
C(10)A	696(2)	476(4)	166(2)	56(7)
C(11)A	662(1)	653(5)	153(2)	61(8)
C(12)A	596(1)	656(4)	134(2)	44(6)
H(4)A	264(2)	628(4)	332(2)	b
H(5)A	364(1)	606(4)	448(2)	b
H(6)A	465(1)	602(4)	398(2)	b
H(8)A	568(1)	164(4)	125(2)	b
H(9)A	688(1)	157(4)	154(2)	b
H(10)A	749(2)	474(4)	186(2)	b
H(11)A	689(1)	791(5)	161(2)	b
H(12)A	571(1)	797(4)	122(2)	b

TABLE 4 CONT/....

TABLE 4 CONTINUED

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
Hg(1)B	330(1)	-26(1)	437(1)	a
S(1)B	445(1)	-18(1)	120(1)	a
N(1)B	379(1)	374(3)	236(2)	52(6)
N(3)B	494(1)	604(4)	295(2)	55(6)
C(2)B	442(1)	33(3)	230(2)	42(6)
C(4)B	488(2)	103(4)	376(2)	58(8)
C(5)B	427(1)	112(4)	392(2)	58(7)
C(6)B	373(2)	94(4)	324(2)	62(8)
C(7)B	232(1)	-24(3)	-32(2)	29(5)
C(8)B	201(1)	146(4)	-71(2)	43(6)
C(9)B	136(1)	142(4)	-126(2)	52(7)
C(10)B	99(2)	-31(4)	-142(2)	66(8)
C(11)B	130(1)	-206(5)	-104(2)	66(8)
C(12)B	197(1)	-208(4)	-43(2)	53(7)
H(4)B	532(2)	136(4)	430(2)	b
H(5)B	425(1)	143(4)	459(2)	b
H(6)B	325(2)	105(4)	334(2)	b
H(8)B	226(1)	287(4)	-59(2)	b
H(9)B	111(1)	274(4)	-158(2)	b
H(10)B	49(2)	-42(4)	-186(2)	b
H(11)B	105(1)	-347(5)	-116(2)	b
H(12)B	217(1)	-347(4)	-13(2)	b

TABLE 4 CONT/....

TABLE 4 CONTINUED

[a]Anisotropic thermal parameters in the form

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*) \times 10^3]$$

with parameters

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg(1)A	35(1)	48(1)	44(1)	1(1)	24(1)	1(1)
S(1)A	37(4)	41(1)	42(4)	-1(3)	18(3)	-4(3)
Hg(1)B	31(1)	50(1)	52(1)	-1(1)	19(1)	3(1)
S(1)B	34(4)	43(4)	72(5)	-1(3)	27(4)	6(3)

[b]All H atoms have U_{iso} = 93(25)

TABLE 5 OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PMPM

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	0	0	124	-122	1	3	0	81	77	3	5	0	134	125	11	0	1	40	43	16	1	1	58	58
6	0	0	278	273	2	3	0	64	-65	4	5	0	115	112	13	0	1	77	73	18	1	1	212	196
8	0	0	310	-305	3	3	0	322	295	6	5	0	39	28	15	0	1	291	289	20	1	1	24	-25
10	0	0	260	-259	4	3	0	163	156	7	5	0	28	-26	17	0	1	29	19	-19	2	1	82	-84
14	0	0	215	-210	5	3	0	29	-24	10	5	0	112	111	19	0	1	41	-40	-17	2	1	147	-146
16	0	0	96	-100	6	3	0	26	16	11	5	0	112	-102	21	0	1	79	71	-16	2	1	57	-55
18	0	0	111	111	7	3	0	96	-90	12	5	0	28	-17	-22	1	1	62	-57	-15	2	1	139	128
22	0	0	53	49	9	3	0	46	41	13	5	0	68	-66	-20	1	1	209	-193	-14	2	1	25	-18
1	1	0	191	171	10	3	0	113	106	14	5	0	54	-54	-19	1	1	26	-29	-13	2	1	93	88
2	1	0	33	-31	11	3	0	221	-206	0	6	0	109	151	-16	1	1	64	58	-11	2	1	35	34
3	1	0	273	240	12	3	0	24	-15	1	6	0	89	82	-14	1	1	36	-33	-10	2	1	100	-93
4	1	0	86	81	13	3	0	127	-116	2	6	0	43	35	-13	1	1	38	-40	-9	2	1	464	430
5	1	0	65	-56	14	3	0	36	-30	6	6	0	54	49	-12	1	1	291	274	-8	2	1	54	49
7	1	0	158	-146	17	3	0	129	-116	7	6	0	115	110	-10	1	1	199	184	-7	2	1	177	160
9	1	0	75	70	18	3	0	40	-38	8	6	0	68	-68	-9	1	1	34	33	-6	2	1	75	69
10	1	0	49	52	20	3	0	32	-29	9	6	0	34	30	-6	1	1	319	283	-5	2	1	165	-137
11	1	0	295	-282	0	4	0	248	329	10	6	0	85	-86	-5	1	1	51	46	-3	2	1	356	297
13	1	0	179	-164	1	4	0	81	75	11	6	0	33	-33	-4	1	1	100	-87	-2	2	1	160	134
17	1	0	207	-192	2	4	0	71	64	1	7	0	32	32	-3	1	1	66	55	-1	2	1	167	-142
21	1	0	146	133	3	4	0	26	25	2	7	0	32	-24	-2	1	1	452	-371	0	2	1	77	-67
2	2	0	144	129	6	4	0	128	118	3	7	0	46	48	-1	1	1	21	-20	2	2	1	118	-149
4	2	0	21	21	7	4	0	147	141	4	7	0	67	71	0	1	1	42	35	3	2	1	57	-59
6	2	0	223	205	8	4	0	156	-151	6	7	0	34	19	1	1	1	47	65	4	2	1	43	49
7	2	0	117	111	9	4	0	33	34	-19	0	1	105	-102	2	1	1	239	-300	5	2	1	240	-247
8	2	0	262	-245	10	4	0	180	-169	-17	0	1	159	-158	3	1	1	32	39	6	2	1	20	-21
9	2	0	25	26	11	4	0	58	-59	-15	0	1	209	199	4	1	1	274	-291	7	2	1	222	-222
10	2	0	267	-253	13	4	0	60	57	-13	0	1	68	66	5	1	1	30	-33	8	2	1	117	-117
11	2	0	51	-48	14	4	0	137	-134	-9	0	1	583	561	6	1	1	41	46	9	2	1	241	238
13	2	0	56	54	15	4	0	51	-51	-7	0	1	208	192	7	1	1	29	31	11	2	1	73	66
14	2	0	204	-191	16	4	0	66	-63	-5	0	1	78	-65	8	1	1	129	-126	13	2	1	71	69
15	2	0	49	-48	17	4	0	85	-78	3	0	1	69	-78	9	1	1	20	-24	15	2	1	216	208
16	2	0	87	-84	18	4	0	74	74	5	0	1	278	-310	10	1	1	21	-27	17	2	1	43	36
17	2	0	75	-68	1	5	0	82	77	7	0	1	254	-273	11	1	1	36	-39	21	2	1	63	56
18	2	0	111	108	2	5	0	54	-49	9	0	1	298	311	12	1	1	255	252	-20	3	1	149	-138

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-19	3	1	77	-71	-15	4	1	75	70	-8	5	1	38	35	6	6	1	33	-26	-15	1	2	126	114
-16	3	1	33	27	-14	4	1	29	-21	-7	5	1	29	-24	7	6	1	63	-65	-14	1	2	26	24
-15	3	1	24	18	-13	4	1	46	46	-6	5	1	103	93	8	6	1	114	-120	-12	1	2	43	40
-14	3	1	29	-18	-11	4	1	29	24	-5	5	1	103	96	9	6	1	49	51	-11	1	2	378	-346
-13	3	1	98	-98	-10	4	1	115	-113	-3	5	1	97	91	11	6	1	33	27	-9	1	2	86	-73
-12	3	1	249	233	-9	4	1	279	267	-2	5	1	118	-109	-6	7	1	40	29	-8	1	2	40	33
-10	3	1	147	141	-8	4	1	70	72	-1	5	1	51	-55	-5	7	1	60	59	-7	1	2	141	-129
-9	3	1	57	56	-7	4	1	104	98	1	5	1	80	98	-3	7	1	57	54	-6	1	2	17	10
-8	3	1	33	28	-6	4	1	95	87	2	5	1	79	-94	-2	7	1	39	-40	-5	1	2	418	-355
-6	3	1	184	161	-5	4	1	59	-53	4	5	1	98	-105	1	7	1	51	56	-4	1	2	20	-18
-5	3	1	100	88	-3	4	1	141	124	5	5	1	98	-96	2	7	1	31	-40	-3	1	2	185	157
-4	3	1	52	-47	-2	4	1	158	139	6	5	1	26	10	4	7	1	33	-39	-1	1	2	31	26
-3	3	1	138	121	-1	4	1	186	-162	7	5	1	31	31	5	7	1	60	-58	1	1	2	60	-59
-2	3	1	178	-147	0	4	1	26	12	8	5	1	57	-53	-22	0	2	98	90	2	1	2	14	-19
-1	3	1	20	-25	1	4	1	231	-288	9	5	1	43	-49	-20	0	2	24	-19	4	1	2	22	25
0	3	1	24	10	2	4	1	87	-111	11	5	1	82	-83	-18	0	2	234	222	5	1	2	116	138
1	3	1	65	75	4	4	1	48	52	12	5	1	92	92	-16	0	2	158	155	6	1	2	37	39
2	3	1	181	-226	5	4	1	139	-146	13	5	1	27	27	-14	0	2	122	-116	7	1	2	38	44
3	3	1	36	36	6	4	1	29	-30	14	5	1	33	21	-12	0	2	134	126	8	1	2	24	-27
4	3	1	197	-208	7	4	1	134	-138	15	5	1	26	-9	-10	0	2	204	-188	9	1	2	301	319
5	3	1	73	-70	8	4	1	148	-149	16	5	1	38	39	-8	0	2	562	-525	10	1	2	25	31
6	3	1	34	33	9	4	1	131	133	-10	6	1	76	-80	-6	0	2	42	-40	11	1	2	41	-42
7	3	1	49	49	11	4	1	48	48	-9	6	1	125	129	-4	0	2	96	-84	12	1	2	27	22
8	3	1	99	-95	12	4	1	30	-27	-8	6	1	60	57	2	0	2	107	143	13	1	2	140	-141
9	3	1	33	-35	13	4	1	45	39	-7	6	1	51	50	4	0	2	33	40	15	1	2	57	58
11	3	1	99	-102	14	4	1	65	-59	-6	6	1	70	69	8	0	2	139	159	17	1	2	113	-115
12	3	1	213	205	15	4	1	148	136	-3	6	1	39	35	10	0	2	93	-99	19	1	2	143	-133
13	3	1	34	31	16	4	1	57	57	-2	6	1	98	87	12	0	2	78	81	21	1	2	41	32
16	3	1	35	35	17	4	1	37	40	-1	6	1	102	-92	14	0	2	161	-155	-22	2	2	89	79
18	3	1	168	158	-16	5	1	31	23	0	6	1	50	49	16	0	2	224	-216	-18	2	2	223	210
19	3	1	60	65	-13	5	1	91	-85	1	6	1	103	-116	20	0	2	85	-82	-16	2	2	144	135
-19	4	1	58	-59	-12	5	1	113	105	2	6	1	43	-46	-21	1	2	142	138	-15	2	2	50	46
-17	4	1	98	-96	-10	5	1	94	92	4	6	1	28	26	-19	1	2	175	164	-14	2	2	164	-147
-16	4	1	94	-83	-9	5	1	47	47	5	6	1	55	-65	-18	1	2	33	30	-12	2	2	126	115

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-11	2	2	36	35	-10	3	2	23	-25	-7	4	2	90	-79	-3	5	2	40	28	2	7	2	54	-70
-10	2	2	131	-121	-9	3	2	68	-59	-6	4	2	34	-29	-2	5	2	27	-24	3	7	2	36	45
-9	2	2	76	69	-8	3	2	71	59	-4	4	2	113	-101	0	5	2	30	-37	-23	0	3	103	-101
-8	2	2	473	-420	-7	3	2	117	-104	-3	4	2	29	-19	2	5	2	82	-98	-17	0	3	316	-296
-7	2	2	75	-66	-6	3	2	42	39	-2	4	2	253	-212	3	5	2	89	124	-15	0	3	90	-82
-6	2	2	34	-33	-5	3	2	292	-251	-1	4	2	266	-233	4	5	2	28	31	-11	0	3	336	-314
-4	2	2	176	-144	-4	3	2	139	-119	0	4	2	165	150	5	5	2	46	57	-9	0	3	240	223
-3	2	2	34	-29	-3	3	2	85	76	2	4	2	107	145	6	5	2	45	49	-7	0	3	344	310
-2	2	2	410	-339	1	3	2	24	-24	3	4	2	23	22	8	5	2	31	-41	-5	0	3	64	48
-1	2	2	299	-251	2	3	2	80	-109	4	4	2	42	47	9	5	2	98	105	-3	0	3	412	368
0	2	2	211	191	3	3	2	222	298	5	4	2	73	-81	10	5	2	75	76	-1	0	3	181	167
1	2	2	26	-28	4	3	2	26	32	6	4	2	206	228	12	5	2	49	43	1	0	3	120	-129
2	2	2	164	211	5	3	2	72	87	7	4	2	73	80	13	5	2	57	-52	3	0	3	29	33
4	2	2	52	55	6	3	2	67	70	8	4	2	93	97	14	5	2	27	-15	5	0	3	84	-101
5	2	2	55	-64	8	3	2	44	-47	9	4	2	71	71	-13	6	2	33	-10	9	0	3	96	-108
6	2	2	335	381	9	3	2	196	199	10	4	2	55	-57	-11	6	2	53	53	11	0	3	46	-46
7	2	2	53	60	10	3	2	75	78	12	4	2	39	45	-10	6	2	46	-41	13	0	3	141	-148
8	2	2	136	147	11	3	2	43	-39	13	4	2	57	62	-9	6	2	86	76	15	0	3	136	130
9	2	2	47	51	12	3	2	48	44	14	4	2	64	-60	-8	6	2	121	-118	17	0	3	97	90
10	2	2	131	-131	13	3	2	67	-62	15	4	2	29	26	-7	6	2	69	-64	19	0	3	25	21
12	2	2	88	90	15	3	2	34	31	16	4	2	121	-118	-6	6	2	30	-29	-21	1	3	34	28
13	2	2	46	41	16	3	2	59	54	17	4	2	44	-44	-4	6	2	50	-45	-20	1	3	184	-180
14	2	2	106	-96	17	3	2	111	-110	-16	5	2	29	-19	-2	6	2	98	-83	-18	1	3	90	-83
16	2	2	211	-203	19	3	2	109	-106	-15	5	2	47	42	-1	6	2	180	-169	-16	1	3	72	-69
20	2	2	63	-69	-19	4	2	50	-41	-14	5	2	37	40	0	6	2	81	76	-14	1	3	266	-250
-21	3	2	109	105	-18	4	2	126	123	-12	5	2	85	87	2	6	2	54	66	-13	1	3	33	-27
-19	3	2	134	129	-16	4	2	78	77	-11	5	2	114	-112	5	6	2	54	-62	-12	1	3	47	54
-18	3	2	69	67	-15	4	2	71	67	-10	5	2	34	-36	6	6	2	89	104	-10	1	3	207	186
-17	3	2	37	29	-14	4	2	85	-76	-9	5	2	46	-43	7	6	2	56	67	-9	1	3	18	16
-15	3	2	71	62	-12	4	2	67	63	-8	5	2	44	40	8	6	2	49	52	-8	1	3	35	29
-14	3	2	42	39	-11	4	2	63	60	-7	5	2	94	-84	9	6	2	57	61	-7	1	3	78	-67
-13	3	2	23	-16	-10	4	2	79	-76	-6	5	2	39	24	-7	7	2	39	-42	-6	1	3	406	354
-12	3	2	103	97	-9	4	2	97	94	-5	5	2	125	-115	-5	7	2	44	-42	-5	1	3	22	21
-11	3	2	233	-216	-8	4	2	277	-252	-4	5	2	109	-89	-4	7	2	82	-68	-4	1	3	401	332

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-3	1	3	75	60	0	2	3	143	133	3	3	3	71	87	14	4	3	70	-68	-1	6	3	93	83
-2	1	3	156	-129	1	2	3	218	-215	4	3	3	152	-191	15	4	3	91	86	0	6	3	142	130
-1	1	3	30	-24	3	2	3	51	56	5	3	3	30	-42	17	4	3	65	63	4	6	3	37	48
0	1	3	323	303	4	2	3	48	57	8	3	3	107	-121	-17	5	3	28	-29	5	6	3	32	-34
1	1	3	47	50	5	2	3	70	-82	10	3	3	194	-205	-16	5	3	51	-39	6	6	3	45	60
3	1	3	36	40	6	2	3	45	55	11	3	3	83	-89	-15	5	3	31	23	7	6	3	92	-113
4	1	3	221	-298	7	2	3	340	-397	12	3	3	32	28	-14	5	3	93	-87	8	6	3	56	-71
6	1	3	71	73	8	2	3	62	-69	17	3	3	76	-69	-13	5	3	86	-82	9	6	3	28	-31
8	1	3	171	-193	9	2	3	63	-63	18	3	3	111	113	-12	5	3	30	23	-7	7	3	55	-50
10	1	3	256	-279	11	2	3	78	-87	-19	4	3	29	-31	-11	5	3	44	-46	-6	7	3	53	43
11	1	3	32	-30	13	2	3	121	-124	-18	4	3	57	56	-10	5	3	57	53	-4	7	3	42	38
12	1	3	80	81	14	2	3	47	-53	-17	4	3	173	-162	-7	5	3	100	-88	-3	7	3	58	51
16	1	3	40	-38	15	2	3	134	131	-16	4	3	43	-47	-6	5	3	149	131	0	7	3	35	29
17	1	3	32	-28	17	2	3	88	87	-14	4	3	32	-31	-4	5	3	116	101	1	7	3	47	44
18	1	3	167	157	-21	3	3	70	69	-11	4	3	152	-140	-3	5	3	96	88	2	7	3	31	-9
20	1	3	63	54	-20	3	3	147	-141	-10	4	3	144	-127	-1	5	3	31	-22	3	7	3	41	49
-20	2	3	29	23	-18	3	3	87	-83	-9	4	3	125	115	0	5	3	104	98	-22	0	4	49	43
-19	2	3	35	-25	-16	3	3	34	-32	-8	4	3	60	-53	1	5	3	64	58	-20	0	4	113	-109
-18	2	3	36	37	-15	3	3	42	37	-7	4	3	201	174	3	5	3	64	77	-18	0	4	91	88
-17	2	3	263	-243	-14	3	3	182	-169	-6	4	3	65	56	4	5	3	89	-113	-16	0	4	271	258
-16	2	3	44	-47	-13	3	3	100	-93	-4	4	3	112	-99	6	5	3	24	-17	-12	0	4	194	185
-15	2	3	43	-44	-11	3	3	31	-31	-3	4	3	237	200	7	5	3	32	31	-10	0	4	342	314
-14	2	3	25	-23	-10	3	3	113	103	-2	4	3	67	58	8	5	3	68	-84	-8	0	4	263	-239
-13	2	3	21	-12	-9	3	3	25	21	-1	4	3	188	166	10	5	3	92	-97	-6	0	4	112	-93
-11	2	3	297	-266	-7	3	3	121	-103	0	4	3	192	177	11	5	3	68	-78	-4	0	4	133	114
-10	2	3	102	-91	-6	3	3	284	243	1	4	3	78	-77	-11	6	3	58	-52	-2	0	4	677	-698
-9	2	3	216	191	-5	3	3	43	31	4	4	3	53	70	-10	6	3	116	-108	0	0	4	285	-283
-8	2	3	58	-49	-4	3	3	268	221	5	4	3	50	-55	-9	6	3	64	55	2	0	4	32	37
-7	2	3	333	285	-3	3	3	91	74	6	4	3	59	72	-8	6	3	36	-40	4	0	4	176	-220
-6	2	3	69	57	-2	3	3	23	-21	7	4	3	205	-240	-7	6	3	83	77	6	0	4	189	236
-4	2	3	85	-74	-1	3	3	43	-34	8	4	3	78	-88	-6	6	3	28	25	8	0	4	221	269
-3	2	3	453	375	0	3	3	179	161	9	4	3	38	-44	-4	6	3	76	-69	10	0	4	29	28
-2	2	3	27	-18	1	3	3	89	88	11	4	3	53	-51	-3	6	3	106	94	12	0	4	189	199
-1	2	3	262	227	2	3	3	46	-51	13	4	3	71	-72	-2	6	3	83	78	14	0	4	95	96

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
16	0	4	90	-93	-17	2	4	50	-53	-15	3	4	133	132	-12	4	4	147	131	-1	5	4	86	-81
20	0	4	64	-53	-16	2	4	232	217	-13	3	4	228	205	-11	4	4	42	31	0	5	4	26	24
-23	1	4	111	-110	-15	2	4	41	43	-12	3	4	119	108	-10	4	4	168	152	1	5	4	125	-127
-19	1	4	163	155	-13	2	4	30	-30	-11	3	4	41	-36	-9	4	4	156	137	2	5	4	96	-101
-15	1	4	191	183	-12	2	4	217	195	-9	3	4	56	48	-8	4	4	121	-106	5	5	4	35	40
-13	1	4	305	280	-11	2	4	30	29	-8	3	4	21	-9	-6	4	4	44	-37	8	5	4	67	-80
-12	1	4	62	56	-10	2	4	283	253	-7	3	4	30	23	-5	4	4	28	27	9	5	4	88	107
-11	1	4	47	-47	-9	2	4	124	109	-6	3	4	118	102	-4	4	4	63	-49	11	5	4	61	60
-9	1	4	124	109	-8	2	4	202	-176	-5	3	4	359	-298	-3	4	4	139	125	12	5	4	37	48
-8	1	4	18	-16	-7	2	4	19	-16	-4	3	4	60	-52	-2	4	4	311	-272	-13	6	4	36	-37
-7	1	4	29	-18	-6	2	4	72	-59	-3	3	4	137	-113	-1	4	4	81	-70	-12	6	4	69	64
-6	1	4	36	30	-5	2	4	39	34	-1	3	4	71	-63	0	4	4	63	-61	-11	6	4	40	24
-5	1	4	448	-379	-4	2	4	110	-84	0	3	4	43	40	1	4	4	60	-63	-10	6	4	69	64
-3	1	4	74	-64	-3	2	4	95	82	1	3	4	266	-257	4	4	4	92	-112	-9	6	4	123	113
-2	1	4	19	-16	-2	2	4	533	-467	2	3	4	113	-122	5	4	4	99	-119	-8	6	4	44	-42
-1	1	4	223	-193	-1	2	4	84	-72	3	3	4	29	31	6	4	4	87	108	-6	6	4	31	-23
1	1	4	359	-368	0	2	4	101	-89	4	3	4	32	-35	8	4	4	137	161	-4	6	4	28	-16
2	1	4	40	-45	1	2	4	30	-29	5	3	4	76	87	9	4	4	45	59	-3	6	4	113	107
3	1	4	96	112	2	2	4	20	-20	7	3	4	40	-44	10	4	4	33	27	-2	6	4	141	-128
4	1	4	16	-18	4	2	4	165	-201	8	3	4	79	-92	12	4	4	104	103	-1	6	4	70	-64
5	1	4	138	169	5	2	4	69	-85	9	3	4	177	202	13	4	4	32	31	0	6	4	58	-59
7	1	4	75	-87	6	2	4	153	178	10	3	4	28	36	14	4	4	70	68	1	6	4	55	-56
8	1	4	43	-50	7	2	4	20	-21	11	3	4	108	113	15	4	4	60	60	4	6	4	35	-43
9	1	4	210	242	8	2	4	216	249	12	3	4	28	32	16	4	4	53	-53	5	6	4	78	-96
11	1	4	148	159	9	2	4	48	54	14	3	4	45	-43	-16	5	4	35	-28	6	6	4	46	50
12	1	4	23	21	10	2	4	22	30	15	3	4	82	72	-15	5	4	91	84	7	6	4	26	-22
13	1	4	37	-33	11	2	4	25	-19	16	3	4	35	38	-13	5	4	108	101	8	6	4	68	78
15	1	4	118	112	12	2	4	172	174	18	3	4	39	39	-12	5	4	107	99	9	6	4	33	28
19	1	4	128	-119	14	2	4	95	92	-19	4	4	63	-68	-9	5	4	32	19	-6	7	4	61	58
-22	2	4	45	43	15	2	4	50	51	-18	4	4	43	44	-8	5	4	33	28	-5	7	4	49	-50
-21	2	4	29	21	16	2	4	89	-92	-17	4	4	51	-53	-6	5	4	104	91	-4	7	4	41	-34
-20	2	4	101	-93	-20	3	4	51	-52	-16	4	4	151	144	-5	5	4	142	-124	-3	7	4	33	-20
-19	2	4	36	-45	-19	3	4	110	107	-15	4	4	64	60	-4	5	4	67	-62	-1	7	4	32	-37
-18	2	4	73	69	-16	3	4	32	-29	-13	4	4	44	-43	-3	5	4	60	-51	0	7	4	31	12

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	7	4	46	-43	-5	1	5	33	-33	-1	2	5	458	412	3	3	5	75	86	5	4	5	101	116
2	7	4	67	-67	-4	1	5	339	294	0	2	5	71	72	4	3	5	61	-69	6	4	5	106	123
-21	0	5	67	67	-3	1	5	58	50	1	2	5	43	37	5	3	5	38	-45	7	4	5	91	-100
-19	0	5	179	171	-2	1	5	45	39	3	2	5	167	190	6	3	5	36	43	9	4	5	49	-45
-17	0	5	155	-156	-1	1	5	49	-46	5	2	5	165	189	7	3	5	28	24	11	4	5	38	-43
-15	0	5	152	-139	0	1	5	287	270	6	2	5	85	98	8	3	5	36	36	12	4	5	40	35
-13	0	5	42	38	2	1	5	263	287	7	2	5	142	-162	9	3	5	77	85	13	4	5	114	-110
-11	0	5	410	-382	3	1	5	32	36	9	2	5	40	-51	10	3	5	174	-183	14	4	5	51	-48
-9	0	5	243	-220	4	1	5	91	-106	10	2	5	24	14	11	3	5	26	-25	15	4	5	32	-29
-7	0	5	89	84	5	1	5	27	-27	11	2	5	63	-65	12	3	5	41	-44	-15	5	5	76	74
-5	0	5	254	-227	6	1	5	56	65	12	2	5	29	26	15	3	5	29	25	-14	5	5	115	-108
-3	0	5	339	308	8	1	5	19	19	13	2	5	181	-176	16	3	5	122	-114	-12	5	5	85	-77
-1	0	5	511	509	9	1	5	36	38	14	2	5	29	-35	17	3	5	40	-47	-11	5	5	63	-59
3	0	5	157	187	10	1	5	220	-237	15	2	5	25	-31	-19	4	5	92	89	-10	5	5	39	-43
5	0	5	207	255	12	1	5	34	-34	-21	3	5	59	59	-18	4	5	83	85	-8	5	5	94	-86
7	0	5	171	-201	14	1	5	46	-46	-19	3	5	31	36	-17	4	5	71	-70	-7	5	5	92	-81
9	0	5	48	-59	16	1	5	162	-152	-18	3	5	33	-34	-15	4	5	68	-62	-6	5	5	27	19
11	0	5	31	-29	18	1	5	45	43	-16	3	5	32	27	-13	4	5	25	-2	-5	5	5	87	-82
13	0	5	219	-231	-21	2	5	62	57	-15	3	5	77	70	-12	4	5	104	101	-4	5	5	107	92
15	0	5	52	-54	-19	2	5	140	136	-14	3	5	239	-221	-11	4	5	225	-207	-3	5	5	58	59
17	0	5	33	36	-18	2	5	70	63	-12	3	5	154	-140	-10	4	5	69	-62	-1	5	5	76	-65
19	0	5	40	-43	-17	2	5	107	-106	-11	3	5	66	-57	-9	4	5	136	-123	0	5	5	115	112
-22	1	5	171	169	-15	2	5	118	-108	-10	3	5	58	-56	-8	4	5	103	-91	2	5	5	97	97
-20	1	5	34	-27	-12	2	5	91	84	-8	3	5	227	-193	-7	4	5	60	52	3	5	5	86	94
-19	1	5	27	18	-11	2	5	356	-323	-7	3	5	98	-85	-6	4	5	43	41	4	5	5	36	-31
-18	1	5	61	-50	-10	2	5	39	-39	-6	3	5	81	70	-5	4	5	96	-85	6	5	5	35	34
-16	1	5	24	25	-9	2	5	226	-197	-5	3	5	74	-63	-4	4	5	127	-110	7	5	5	37	45
-15	1	5	30	29	-8	2	5	78	-69	-4	3	5	210	172	-3	4	5	133	116	9	5	5	70	76
-14	1	5	296	-284	-7	2	5	137	118	-3	3	5	44	38	-2	4	5	97	-89	10	5	5	82	-87
-12	1	5	169	-159	-6	2	5	33	26	-2	3	5	23	-17	-1	4	5	281	256	11	5	5	35	-40
-11	1	5	34	-34	-5	2	5	165	-143	-1	3	5	76	-71	0	4	5	74	70	-12	6	5	70	70
-10	1	5	50	-42	-4	2	5	107	-89	0	3	5	220	205	1	4	5	34	38	-11	6	5	107	-104
-8	1	5	340	-296	-3	2	5	198	171	1	3	5	24	23	3	4	5	94	106	-10	6	5	50	-50
-7	1	5	61	-54	-2	2	5	86	-79	2	3	5	204	213	4	4	5	23	14	-9	6	5	63	-58

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-8	6	5	79	-66	-23	1	6	142	-144	-12	2	6	85	80	-6	3	6	163	138	-1	4	6	33	33
-5	6	5	44	-42	-21	1	6	169	-167	-11	2	6	75	-72	-5	3	6	85	-79	0	4	6	137	-126
-4	6	5	85	-72	-17	1	6	95	-91	-10	2	6	395	352	-4	3	6	28	26	2	4	6	35	-36
-3	6	5	63	60	-14	1	6	36	-34	-9	2	6	66	64	-3	3	6	27	-21	3	4	6	62	66
-2	6	5	72	-57	-13	1	6	301	285	-8	2	6	69	62	-1	3	6	21	23	4	4	6	157	-175
-1	6	5	120	117	-12	1	6	19	9	-6	2	6	104	88	0	3	6	109	100	5	4	6	54	-56
0	6	5	36	27	-11	1	6	87	81	-5	2	6	32	-30	1	3	6	261	-250	6	4	6	74	-77
3	6	5	38	44	-9	1	6	181	165	-4	2	6	304	263	2	3	6	36	-33	7	4	6	72	-81
5	6	5	47	54	-7	1	6	337	306	-3	2	6	117	103	3	3	6	112	-120	8	4	6	41	35
6	6	5	78	100	-6	1	6	46	43	-2	2	6	244	-215	4	3	6	44	-45	11	4	6	60	-59
7	6	5	39	-40	-5	1	6	133	-123	-1	2	6	34	29	6	3	6	32	38	12	4	6	46	44
-5	7	5	46	-50	-3	1	6	41	-37	0	2	6	211	-201	7	3	6	146	-151	14	4	6	92	86
-4	7	5	45	34	-1	1	6	36	33	2	2	6	37	-41	8	3	6	57	-68	-16	5	6	53	-50
-3	7	5	37	33	0	1	6	51	45	3	2	6	52	59	9	3	6	44	46	-14	5	6	84	-82
-1	7	5	49	-43	1	1	6	308	-310	4	2	6	247	-279	10	3	6	39	-33	-13	5	6	105	97
0	7	5	49	50	2	1	6	19	-20	5	2	6	40	-40	11	3	6	94	87	-11	5	6	48	40
-20	0	6	170	-179	3	1	6	145	-161	6	2	6	108	-117	12	3	6	25	25	-9	5	6	96	93
-18	0	6	140	-141	4	1	6	32	-34	7	2	6	52	-58	13	3	6	50	-47	-7	5	6	128	110
-16	0	6	118	121	5	1	6	19	19	8	2	6	81	81	14	3	6	29	-22	-6	5	6	134	119
-14	0	6	98	-90	6	1	6	18	22	10	2	6	32	-31	15	3	6	89	83	-5	5	6	44	-41
-12	0	6	111	99	7	1	6	194	-217	11	2	6	41	-42	-18	4	6	89	-87	-2	5	6	28	18
-10	0	6	481	444	8	1	6	21	-26	12	2	6	64	55	-17	4	6	83	-81	0	5	6	111	108
-8	0	6	99	94	9	1	6	29	27	14	2	6	143	135	-16	4	6	71	69	1	5	6	128	-119
-6	0	6	84	82	11	1	6	141	137	15	2	6	31	32	-15	4	6	28	29	2	5	6	39	-37
-4	0	6	326	299	13	1	6	46	-43	-21	3	6	118	-117	-13	4	6	56	-50	3	5	6	55	-64
-2	0	6	346	-332	14	1	6	23	-12	-20	3	6	35	-43	-12	4	6	61	52	4	5	6	27	-40
0	0	6	220	-215	15	1	6	105	103	-17	3	6	88	-81	-11	4	6	92	-92	6	5	6	29	38
4	0	6	288	-350	17	1	6	125	113	-16	3	6	46	-42	-10	4	6	245	224	7	5	6	71	-73
6	0	6	86	-96	-20	2	6	150	-154	-15	3	6	28	21	-9	4	6	67	65	8	5	6	62	-69
8	0	6	71	73	-18	2	6	154	-147	-14	3	6	83	-80	-8	4	6	49	45	10	5	6	43	-39
10	0	6	63	-68	-17	2	6	58	-58	-13	3	6	214	200	-6	4	6	58	54	11	5	6	51	50
12	0	6	103	99	-16	2	6	121	118	-11	3	6	62	57	-4	4	6	189	166	-12	6	6	44	29
14	0	6	165	163	-14	2	6	42	-44	-9	3	6	139	126	-3	4	6	142	117	-11	6	6	79	-75
18	0	6	70	56	-13	2	6	31	-29	-7	3	6	244	211	-2	4	6	139	-121	-10	6	6	110	105

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-9	6	6	60	52	-14	1	7	51	-50	-4	2	7	20	-20	2	3	7	200	197	11	4	7	56	56
-8	6	6	38	39	-12	1	7	156	-150	-3	2	7	294	-261	3	3	7	40	45	12	4	7	70	65
-6	6	6	32	27	-11	1	7	21	-20	-2	2	7	53	-47	6	3	7	85	87	13	4	7	70	-56
-4	6	6	67	62	-9	1	7	52	48	-1	2	7	167	145	8	3	7	148	143	-16	5	7	76	78
-3	6	6	108	94	-8	1	7	298	-278	1	2	7	26	33	9	3	7	72	73	-15	5	7	86	87
-2	6	6	50	-50	-6	1	7	269	-241	2	2	7	33	-38	10	3	7	32	-30	-13	5	7	48	48
-1	6	6	30	34	-5	1	7	74	-65	3	2	7	62	61	11	3	7	24	14	-12	5	7	66	-60
0	6	6	64	-60	-4	1	7	104	99	4	2	7	46	-51	14	3	7	44	38	-9	5	7	83	71
3	6	6	44	46	-2	1	7	183	-168	5	2	7	242	273	15	3	7	40	32	-8	5	7	118	-116
4	6	6	70	-80	-1	1	7	30	-31	6	2	7	46	47	-19	4	7	148	149	-6	5	7	113	-102
5	6	6	31	-46	0	1	7	23	19	7	2	7	40	36	-18	4	7	36	35	-5	5	7	88	-80
6	6	6	37	-42	1	1	7	43	-39	8	2	7	21	3	-17	4	7	36	42	-2	5	7	66	-62
7	6	6	57	-63	2	1	7	279	283	9	2	7	48	48	-16	4	7	37	39	-1	5	7	63	-61
-19	0	7	233	239	4	1	7	22	-17	11	2	7	91	85	-14	4	7	33	-30	1	5	7	77	-75
-17	0	7	74	71	6	1	7	106	112	12	2	7	56	55	-13	4	7	104	98	2	5	7	99	99
-13	0	7	202	197	8	1	7	219	221	13	2	7	102	-86	-12	4	7	102	91	3	5	7	53	59
-11	0	7	198	-187	9	1	7	23	28	15	2	7	76	-68	-11	4	7	92	-87	4	5	7	24	8
-9	0	7	283	-267	10	1	7	68	-63	-20	3	7	101	101	-10	4	7	67	62	6	5	7	56	64
-5	0	7	388	-363	14	1	7	55	60	-18	3	7	60	59	-9	4	7	163	-148	8	5	7	79	83
-3	0	7	251	-240	16	1	7	141	-125	-17	3	7	32	-32	-8	4	7	57	-57	9	5	7	67	73
-1	0	7	150	142	-20	2	7	45	-44	-16	3	7	131	133	-7	4	7	32	-20	-12	6	7	72	72
3	0	7	72	76	-19	2	7	222	222	-15	3	7	90	90	-6	4	7	51	51	-11	6	7	48	-43
5	0	7	277	323	-18	2	7	29	33	-14	3	7	54	-52	-5	4	7	179	-155	-10	6	7	44	47
7	0	7	74	77	-17	2	7	49	53	-13	3	7	49	45	-4	4	7	41	-39	-9	6	7	79	-73
9	0	7	43	46	-16	2	7	26	30	-12	3	7	103	-97	-3	4	7	150	-131	-8	6	7	32	-36
11	0	7	81	75	-15	2	7	34	-28	-9	3	7	94	87	-2	4	7	111	-101	-6	6	7	42	50
13	0	7	113	-99	-13	2	7	184	171	-8	3	7	232	-209	-1	4	7	73	63	-5	6	7	81	-70
15	0	7	77	-64	-12	2	7	69	66	-6	3	7	187	-165	2	4	7	55	-51	-4	6	7	48	-40
17	0	7	30	-20	-11	2	7	144	-135	-5	3	7	111	-96	3	4	7	38	38	-3	6	7	68	-50
-22	1	7	172	177	-10	2	7	46	47	-4	3	7	39	37	4	4	7	59	-59	-2	6	7	97	-94
-20	1	7	114	115	-9	2	7	274	-249	-2	3	7	156	-136	5	4	7	156	171	-1	6	7	29	18
-18	1	7	71	68	-8	2	7	29	-32	-1	3	7	68	-60	6	4	7	49	51	2	6	7	30	-33
-16	1	7	213	208	-6	2	7	20	18	0	3	7	42	43	7	4	7	38	37	4	6	7	43	-48
-15	1	7	34	34	-5	2	7	321	-281	1	3	7	95	-92	9	4	7	27	30	5	6	7	67	78

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
6	6	7	38	40	0	1	8	27	28	12	2	8	73	-65	-14	4	8	92	-92	7	5	8	79	-85
-22	0	8	75	79	1	1	8	80	-82	13	2	8	32	-27	-12	4	8	137	-127	9	5	8	66	-61
-20	0	8	65	-60	3	1	8	114	-119	14	2	8	81	70	-11	4	8	108	-101	-10	6	8	37	30
-18	0	8	233	-240	5	1	8	38	36	-19	3	8	39	-36	-10	4	8	97	86	-8	6	8	36	30
-14	0	8	149	-144	6	1	8	27	34	-18	3	8	42	39	-8	4	8	55	44	-6	6	8	31	18
-12	0	8	219	-216	7	1	8	189	-200	-17	3	8	119	-123	-5	4	8	71	-63	-5	6	8	64	-59
-10	0	8	162	163	9	1	8	123	-119	-15	3	8	169	-159	-4	4	8	227	199	-4	6	8	88	84
-8	0	8	117	108	10	1	8	30	-27	-14	3	8	91	-91	-3	4	8	90	82	-3	6	8	70	60
-6	0	8	42	-32	11	1	8	58	52	-12	3	8	25	-23	-2	4	8	97	84	-2	6	8	61	51
-4	0	8	325	311	13	1	8	85	-67	-10	3	8	38	-35	-1	4	8	48	44	-1	6	8	42	39
-2	0	8	244	238	15	1	8	30	-26	-8	3	8	98	-91	2	4	8	61	65	3	6	8	66	73
0	0	8	25	27	-22	2	8	59	62	-7	3	8	263	239	3	4	8	77	85	-21	0	9	136	-136
2	0	8	135	142	-20	2	8	55	-55	-6	3	8	36	30	4	4	8	67	-68	-19	0	9	107	109
4	0	8	137	-155	-19	2	8	38	37	-5	3	8	106	90	6	4	8	111	-116	-17	0	9	138	139
6	0	8	202	-226	-18	2	8	197	-200	-4	3	8	22	18	8	4	8	47	-43	-13	0	9	269	270
8	0	8	32	-34	-16	2	8	27	15	-3	3	8	57	52	9	4	8	26	21	-11	0	9	177	177
10	0	8	147	-140	-14	2	8	150	-140	-2	3	8	33	-29	10	4	8	80	-74	-9	0	9	103	-103
12	0	8	65	-59	-12	2	8	209	-195	-1	3	8	194	175	12	4	8	39	-44	-7	0	9	150	140
14	0	8	87	75	-11	2	8	95	-87	0	3	8	87	81	-15	5	8	92	-91	-5	0	9	88	-78
-21	1	8	112	-124	-10	2	8	156	144	1	3	8	54	-53	-14	5	8	79	-77	-3	0	9	320	-302
-20	1	8	26	-16	-8	2	8	61	54	2	3	8	37	36	-10	5	8	45	-46	-1	0	9	92	-90
-19	1	8	42	-44	-6	2	8	35	24	3	3	8	63	-64	-8	5	8	105	-102	1	0	9	114	-113
-18	1	8	25	16	-5	2	8	64	-58	4	3	8	27	-41	-7	5	8	137	125	3	0	9	133	-150
-17	1	8	161	-171	-4	2	8	352	315	5	3	8	44	49	-6	5	8	35	42	5	0	9	111	117
-15	1	8	228	-220	-3	2	8	91	85	6	3	8	64	69	-5	5	8	38	31	7	0	9	76	87
-14	1	8	37	-40	-2	2	8	148	136	7	3	8	154	-161	-4	5	8	26	22	9	0	9	49	47
-13	1	8	63	65	-1	2	8	39	36	9	3	8	102	-99	-3	5	8	52	45	11	0	9	175	156
-11	1	8	44	-40	2	2	8	123	123	10	3	8	50	-53	-2	5	8	28	-16	13	0	9	50	41
-10	1	8	30	-25	3	2	8	63	59	11	3	8	30	31	-1	5	8	111	103	-16	1	9	253	260
-8	1	8	24	-19	4	2	8	102	-108	13	3	8	62	-49	0	5	8	86	80	-14	1	9	156	150
-7	1	8	402	370	6	2	8	179	-194	14	3	8	32	-27	2	5	8	39	41	-10	1	9	187	176
-5	1	8	61	53	8	2	8	38	-41	-18	4	8	119	-122	3	5	8	40	-41	-9	1	9	31	33
-3	1	8	66	60	10	2	8	130	-120	-17	4	8	42	-48	4	5	8	31	-33	-8	1	9	38	-44
-1	1	8	317	296	11	2	8	31	-11	-15	4	8	28	18	6	5	8	46	44	-7	1	9	45	43

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-6	1	9	250	-234	7	2	9	47	55	-10	4	9	82	78	-3	6	9	96	-89	13	1	10	69	-54
-5	1	9	34	-30	9	2	9	61	59	-9	4	9	39	-36	-2	6	9	45	-43	-21	2	10	27	11
-3	1	9	22	17	10	2	9	28	-27	-8	4	9	31	-21	-1	6	9	39	-41	-20	2	10	110	114
-2	1	9	235	-226	11	2	9	169	144	-7	4	9	44	42	1	6	9	31	-36	-19	2	10	49	49
0	1	9	246	-241	12	2	9	27	21	-6	4	9	89	79	-22	0	10	109	116	-18	2	10	79	-85
1	1	9	35	-37	-20	3	9	26	23	-5	4	9	60	-57	-20	0	10	111	122	-14	2	10	27	-23
2	1	9	105	107	-17	3	9	54	-62	-4	4	9	74	73	-18	0	10	113	-115	-13	2	10	34	35
4	1	9	57	-65	-16	3	9	183	187	-3	4	9	179	-161	-16	0	10	37	31	-12	2	10	257	-247
5	1	9	24	1	-14	3	9	127	124	-2	4	9	71	-63	-12	0	10	300	-293	-11	2	10	35	-45
6	1	9	27	-26	-13	3	9	29	29	-1	4	9	70	-61	-10	0	10	115	-107	-10	2	10	89	-80
8	1	9	195	198	-12	3	9	34	34	1	4	9	86	-81	-8	0	10	34	-31	-8	2	10	31	-29
10	1	9	41	37	-11	3	9	26	-25	3	4	9	81	-85	-6	0	10	163	-155	-6	2	10	141	-128
14	1	9	119	95	-10	3	9	164	152	4	4	9	72	-75	-4	0	10	193	186	-5	2	10	82	-76
-21	2	9	98	-106	-9	3	9	86	80	5	4	9	59	66	-2	0	10	164	156	-4	2	10	138	129
-20	2	9	50	-53	-8	3	9	55	-51	7	4	9	42	39	2	0	10	224	229	-3	2	10	30	-33
-19	2	9	75	90	-7	3	9	57	55	9	4	9	36	37	4	0	10	78	85	-2	2	10	123	115
-17	2	9	98	100	-6	3	9	208	-186	-14	5	9	66	62	6	0	10	43	-31	0	2	10	38	42
-16	2	9	32	28	-5	3	9	38	-32	-13	5	9	44	42	8	0	10	38	41	1	2	10	39	-38
-14	2	9	27	-31	-3	3	9	49	50	-12	5	9	34	32	10	0	10	83	-70	2	2	10	197	190
-13	2	9	241	230	-2	3	9	159	-147	-10	5	9	84	82	12	0	10	145	-121	3	2	10	21	25
-11	2	9	166	162	0	3	9	179	-171	-9	5	9	72	65	-19	1	10	93	96	4	2	10	79	82
-10	2	9	49	46	1	3	9	96	-92	-7	5	9	73	68	-15	1	10	214	-227	5	2	10	29	30
-9	2	9	85	-82	2	3	9	67	65	-6	5	9	90	-84	-13	1	10	85	-87	10	2	10	74	-59
-7	2	9	77	77	6	3	9	26	-22	-5	5	9	35	-30	-11	1	10	177	-171	12	2	10	118	-90
-6	2	9	67	64	7	3	9	46	-42	-3	5	9	41	35	-9	1	10	264	-261	-19	3	10	87	85
-5	2	9	85	-77	8	3	9	135	131	-2	5	9	99	-97	-8	1	10	36	-37	-16	3	10	49	56
-4	2	9	61	55	10	3	9	54	50	0	5	9	87	-87	-7	1	10	95	92	-15	3	10	169	-172
-3	2	9	264	-236	-18	4	9	30	-15	1	5	9	78	-84	-5	1	10	66	64	-14	3	10	25	-26
-2	2	9	47	-47	-17	4	9	59	66	2	5	9	46	44	-2	1	10	36	-31	-13	3	10	60	-58
-1	2	9	76	-66	-16	4	9	33	29	7	5	9	56	-55	-1	1	10	250	242	-11	3	10	123	-122
1	2	9	130	-129	-14	4	9	45	-45	-7	6	9	31	23	1	1	10	116	117	-10	3	10	43	40
3	2	9	131	-134	-13	4	9	142	135	-6	6	9	74	64	3	1	10	57	-66	-9	3	10	192	-183
4	2	9	60	-63	-12	4	9	36	32	-5	6	9	34	-29	5	1	10	129	140	-8	3	10	93	-85
5	2	9	110	111	-11	4	9	104	101	-4	6	9	42	39	9	1	10	134	-128	-7	3	10	75	70

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	3	10	47	44	-1	5	10	107	105	8	1	11	36	27	-6	3	11	33	-36	-16	0	12	75	73
-2	3	10	71	-66	1	5	10	61	60	10	1	11	45	37	-4	3	11	86	82	-14	0	12	85	91
-1	3	10	201	189	2	5	10	40	34	12	1	11	35	-28	-3	3	11	41	36	-12	0	12	90	-102
0	3	10	31	24	5	5	10	48	40	-20	2	11	36	-23	-1	3	11	63	66	-10	0	12	65	-68
1	3	10	112	109	-21	0	11	149	-169	-19	2	11	72	-67	0	3	11	185	-176	-8	0	12	59	-53
2	3	10	38	38	-19	0	11	71	-64	-18	2	11	31	-26	4	3	11	30	-35	-6	0	12	213	-207
3	3	10	39	-43	-17	0	11	34	43	-17	2	11	41	41	6	3	11	97	-94	-4	0	12	90	-91
5	3	10	104	98	-15	0	11	88	-95	-15	2	11	59	-69	7	3	11	56	-52	0	0	12	91	-95
6	3	10	53	52	-13	0	11	81	83	-14	2	11	61	-64	8	3	11	31	25	2	0	12	80	84
8	3	10	29	23	-11	0	11	216	211	-13	2	11	63	64	-15	4	11	40	-46	4	0	12	115	112
9	3	10	113	-104	-7	0	11	200	197	-11	2	11	183	180	-14	4	11	78	-74	8	0	12	104	90
-15	4	10	36	31	-5	0	11	135	123	-9	2	11	28	23	-13	4	11	51	55	10	0	12	52	41
-14	4	10	27	-25	-3	0	11	127	-123	-8	2	11	35	-29	-12	4	11	43	-42	-19	1	12	106	127
-13	4	10	46	46	1	0	11	70	-63	-7	2	11	159	148	-11	4	11	107	108	-17	1	12	161	177
-12	4	10	161	-156	3	0	11	180	-186	-5	2	11	141	127	-10	4	11	53	44	-16	1	12	31	26
-11	4	10	57	-51	5	0	11	37	-35	-4	2	11	43	35	-8	4	11	36	-37	-15	1	12	35	-43
-10	4	10	70	-60	7	0	11	63	-66	-3	2	11	94	-84	-7	4	11	105	99	-12	1	12	25	27
-6	4	10	95	-91	9	0	11	74	-63	1	2	11	57	-59	-5	4	11	77	70	-11	1	12	49	48
-5	4	10	105	-92	11	0	11	81	67	2	2	11	36	32	-4	4	11	73	65	-9	1	12	255	-256
-4	4	10	74	69	-20	1	11	41	-51	3	2	11	166	-163	-3	4	11	42	-41	-7	1	12	96	-88
-3	4	10	36	-39	-19	1	11	26	3	4	2	11	29	-34	1	4	11	32	-34	-3	1	12	185	-181
-2	4	10	81	82	-18	1	11	170	-183	7	2	11	41	-42	2	4	11	39	37	-1	1	12	34	33
0	4	10	28	31	-17	1	11	27	-26	9	2	11	68	-57	3	4	11	109	-100	1	1	12	122	121
1	4	10	37	-42	-14	1	11	97	102	10	2	11	36	-33	4	4	11	47	-46	5	1	12	115	117
2	4	10	118	121	-10	1	11	246	248	11	2	11	72	49	-11	5	11	53	-40	7	1	12	106	94
3	4	10	40	33	-8	1	11	200	199	-18	3	11	123	-134	-10	5	11	94	91	9	1	12	42	-27
4	4	10	48	48	-7	1	11	44	39	-17	3	11	56	-60	-8	5	11	90	84	-19	2	12	27	23
5	4	10	56	56	-6	1	11	54	-51	-16	3	11	41	42	-7	5	11	69	60	-16	2	12	56	58
9	4	10	33	29	-4	1	11	89	85	-15	3	11	41	-44	-4	5	11	42	31	-14	2	12	94	94
-11	5	10	75	-74	-1	1	11	23	31	-14	3	11	85	88	-3	5	11	45	45	-13	2	12	70	64
-9	5	10	107	-103	0	1	11	238	-236	-11	3	11	34	-33	-1	5	11	71	67	-12	2	12	85	-89
-8	5	10	100	-95	4	1	11	29	-15	-10	3	11	179	175	0	5	11	93	-87	-10	2	12	56	-51
-7	5	10	43	34	6	1	11	136	-135	-8	3	11	145	140	1	5	11	36	-33	-9	2	12	24	-19
-2	5	10	78	-77	7	1	11	39	-29	-7	3	11	73	73	-20	0	12	150	174	-7	2	12	31	32

TABLE 5 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-6	2	12	214	-200	-8	4	12	33	-23	-8	1	13	170	171	-8	4	13	39	-32	-7	2	14	43	45
-5	2	12	33	-29	-7	4	12	41	37	-4	1	13	121	122	-7	4	13	53	50	-6	2	14	77	-75
-4	2	12	85	-84	-6	4	12	128	-116	-2	1	13	192	189	-5	4	13	107	93	-4	2	14	84	-77
-3	2	12	34	-20	-5	4	12	45	-42	-1	1	13	24	27	-4	4	13	37	39	-2	2	14	27	-30
0	2	12	68	-64	-4	4	12	56	-50	0	1	13	40	-40	-3	4	13	39	35	0	2	14	116	-114
1	2	12	44	-46	-3	4	12	27	-29	6	1	13	130	-123	-1	4	13	53	48	2	2	14	43	-38
2	2	12	61	65	0	4	12	47	-36	8	1	13	42	-44	1	4	13	52	51	4	2	14	30	26
4	2	12	91	91	1	4	12	62	-52	-15	2	13	139	-139	2	4	13	56	50	-13	3	14	55	60
8	2	12	91	78	2	4	12	55	52	-13	2	13	77	-82	-14	0	14	165	179	-12	3	14	32	-24
-17	3	12	109	123	4	4	12	61	55	-12	2	13	35	-35	-12	0	14	54	57	-11	3	14	125	131
-16	3	12	60	63	5	4	12	35	12	-11	2	13	52	49	-10	0	14	29	26	-10	3	14	57	58
-15	3	12	29	-22	-9	5	12	112	-109	-9	2	13	40	-39	-8	0	14	84	86	-9	3	14	27	-32
-13	3	12	28	19	-8	5	12	30	-25	-8	2	13	38	-31	-6	0	14	79	-83	-7	3	14	44	-45
-12	3	12	33	32	-7	5	12	34	-37	-7	2	13	60	61	-4	0	14	108	-104	-4	3	14	41	41
-10	3	12	58	59	-3	5	12	76	-72	-6	2	13	26	-16	-2	0	14	23	-31	-3	3	14	115	-110
-9	3	12	182	-180	-2	5	12	64	-58	-5	2	13	158	146	0	0	14	129	-128	-1	3	14	90	-84
-8	3	12	31	-29	-19	0	13	98	-111	-4	2	13	32	31	2	0	14	53	-45	0	3	14	46	-41
-7	3	12	84	-72	-15	0	13	156	-163	-3	2	13	49	43	4	0	14	36	42	-8	4	14	40	43
-6	3	12	28	-25	-13	0	13	83	-88	-1	2	13	68	69	-17	1	14	140	158	-7	4	14	56	57
-5	3	12	46	-37	-11	0	13	73	68	1	2	13	84	76	-15	1	14	54	61	-6	4	14	50	-44
-3	3	12	133	-126	-9	0	13	57	-55	2	2	13	37	39	-13	1	14	71	77	-4	4	14	56	-59
-2	3	12	54	-53	-7	0	13	43	45	3	2	13	72	-75	-11	1	14	168	175	-15	0	15	39	-54
-1	3	12	36	34	-5	0	13	168	164	5	2	13	35	-34	-10	1	14	32	29	-13	0	15	141	-149
0	3	12	34	-26	-3	0	13	71	75	-16	3	13	90	-94	-9	1	14	38	-38	-11	0	15	28	-28
1	3	12	89	86	-1	0	13	82	78	-15	3	13	31	-29	-7	1	14	63	-59	-9	0	15	96	-103
2	3	12	31	33	1	0	13	66	67	-12	3	13	106	-103	-3	1	14	159	-155	-7	0	15	66	-64
3	3	12	25	-19	3	0	13	78	-84	-11	3	13	65	-66	-1	1	14	96	-96	-5	0	15	84	84
4	3	12	48	-48	5	0	13	42	-46	-9	3	13	58	-50	3	1	14	76	-77	-1	0	15	49	42
5	3	12	81	80	7	0	13	35	-28	-8	3	13	141	136	-16	2	14	30	39	1	0	15	124	117
7	3	12	82	79	-18	1	13	155	-177	-4	3	13	89	83	-14	2	14	148	160	-15	1	15	26	-5
-14	4	12	68	69	-16	1	13	120	-124	-2	3	13	135	124	-12	2	14	46	49	-13	1	15	27	3
-13	4	12	81	81	-12	1	13	108	-118	-1	3	13	69	60	-11	2	14	30	18	-12	1	15	140	-150
-12	4	12	48	-51	-11	1	13	23	-20	5	3	13	34	26	-10	2	14	27	25	-10	1	15	130	-137
-10	4	12	50	-44	-9	1	13	34	-32	-12	4	13	61	-63	-8	2	14	67	65	-6	1	15	33	-32
-2	1	15	133	130	-9	2	15	75	-82	-10	3	15	102	-99	-8	0	16	125	128	-9	1	16	72	72
0	1	15	38	28	-7	2	15	61	-55	-9	3	15	39	-48	-6	0	16	34	38	-5	1	16	89	88
2	1	15	26	18	-6	2	15	30	-26	-3	3	15	36	-43	-4	0	16	26	-14	-1	1	16	80	-77
-13	2	15	116	-125	-5	2	15	53	53	-2	3	15	107	104	-2	0	16	41	46	-10	2	16	30	30
-12	2	15	30	-16	-1	2	15	41	47	-12	0	16	50	55	0	0	16	55	-54	-8	2	16	110	108
-11	2	15	30	-27	1	2	15	108	103	-10	0	16	36	40	-11	1	16	137	149	-6	2	16	50	43

U_{ij} represents the anisotropic temperature factors expressed in terms of mean square amplitudes of vibration in Å^2. Examination of the analysis of variance shown in Table 3 revealed that the weighting scheme was satisfactory with respect to all parameters.

The final atomic positional and thermal parameters are listed in Table 4 and the observed and calculated structure factors are reported in Table 5.

3.5 DESCRIPTION OF THE STRUCTURE

A perspective view of the two molecules making up the asymmetric unit, with atomic nomenclature, is shown in Figure 3. The intramolecular bond lengths and angles, together with their associated estimated standard deviations are listed in Tables 6 and 7 respectively.

Molecular structure

The phenylmercury moiety is covalently bonded to sulphur with a secondary intermolecular interaction to nitrogen in the pyrimidine ring. The mercury atom has digonal characteristic coordination[15,16], the two bonds involved being Hg - S and Hg - C(7) (2,39(1) and 2,12(2)Å respectively for A; 2,38(1) and 2,06(2)Å for B). These are in keeping with accepted values, as observed by Lawton[28] and Wong, Carty and Chieh[29] for Hg - S distances in digonally coordinated Hg compounds. Grdenić[15] proposes the range 2,39 to 2,43Å using observed values of Hg - L bond lengths. The S - Hg - C(7) angle is close to 180° (178,6(1)° for A and 175,2(1)° for B). This slight but significant deviation from linearity may be caused by additional inter- and intramolecular interactions with the mercury atom[29].

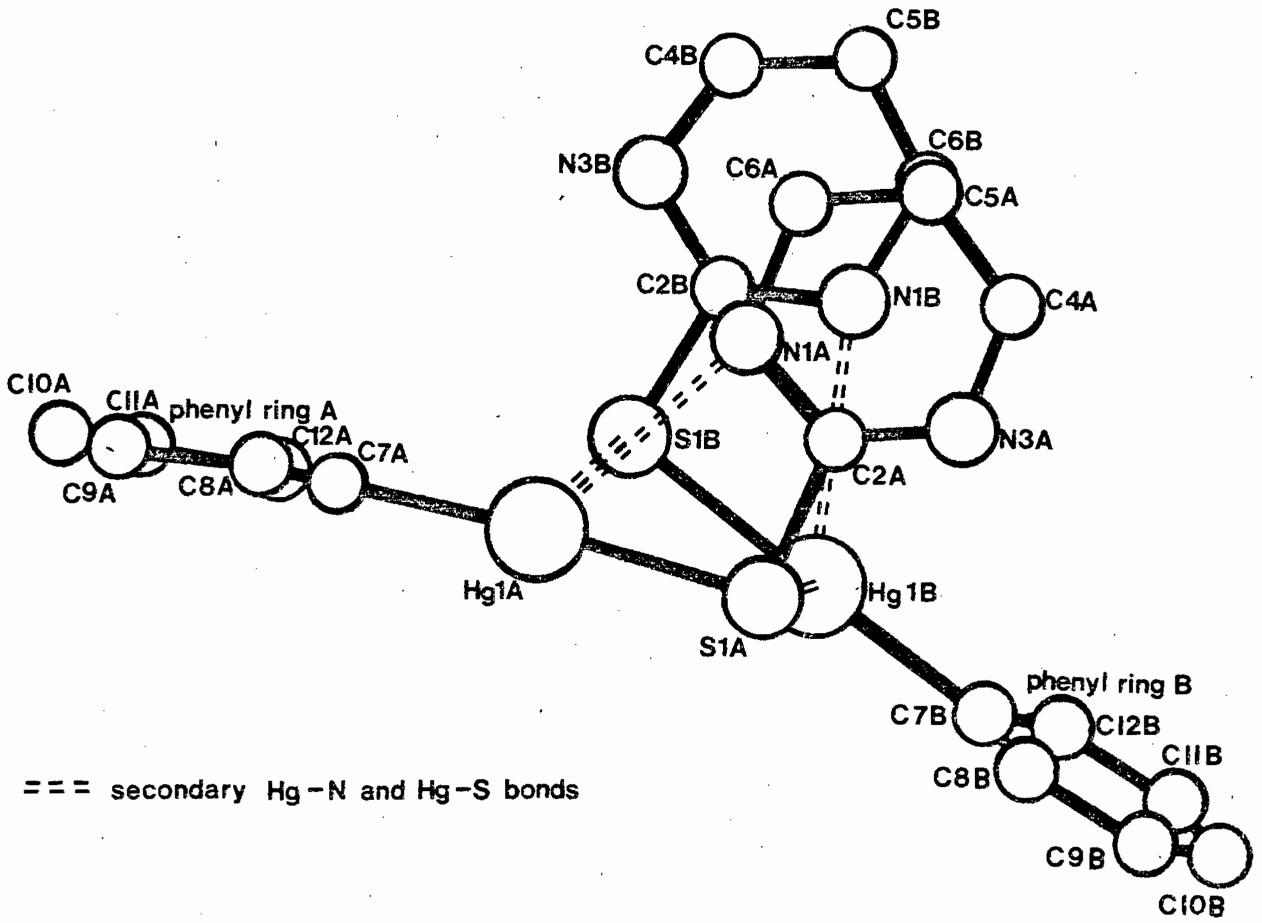


FIGURE 3   A PERSPECTIVE VIEW OF THE ASYMMETRIC UNIT OF PMPM

TABLE 6 BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	Molecule A	*Molecule B*
Hg - S	2,39(1)	2,38(1)
Hg - C(7)	2,12(2)	2,06(2)
S - C(2)	1,75(2)	1,75(2)
C(2) - N(1)	1,34(3)	1,36(3)
C(2) - N(3)	1,35(3)	1,27(3)
N(3) - C(4)	1,35(3)	1,32(3)
C(4) - C(5)	1,34(3)	1,39(4)
C(5) - C(6)	1,38(4)	1,30(4)
C(6) - N(1)	1,38(3)	1,44(3)
C(7) - C(8)	1,40(3)	1,37(3)
C(8) - C(9)	1,39(3)	1,40(3)
C(9) - C(10)	1,38(3)	1,38(4)
C(10) - C(11)	1,37(4)	1,39(4)
C(11) - C(12)	1,34(3)	1,44(3)
C(12) - C(7)	1,36(3)	1,43(3)
All C - H bond lengths[a]	1,08	1,08

[a] Bond lengths fixed.

TABLE 7 BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

	Molecule A	*Molecule B*
C(7) - Hg - S	179(1)	175(1)
Hg - S - C(2)	97(1)	98(1)
S - C(2) - N(1)	117(2)	113(2)
S - C(2) - N(3)	116(2)	120(2)
N(1) - C(2) - N(3)	128(2)	127(2)
C(2) - N(3) - C(4)	110(2)	117(3)
N(3) - C(4) - C(5)	130(3)	122(3)
C(4) - C(5) - C(6)	114(3)	120(3)
C(5) - C(6) - N(1)	121(2)	118(3)
C(6) - N(1) - C(2)	117(2)	115(2)
Hg - C(7) - C(8)	119(2)	122(2)
Hg - C(7) - C(12)	121(2)	118(2)
C(7) - C(8) - C(9)	120(2)	121(2)
C(8) - C(9) - C(10)	117(2)	122(2)
C(9) - C(10) - C(11)	121(3)	118(3)
C(10) - C(11) - C(12)	121(3)	122(3)
C(11) - C(12) - C(7)	120(2)	117(2)
C(12) - C(7) - C(8)	120(2)	120(2)

[a] All bond angles involving H bonded to C are fixed according to the hybridisation of the carbon atoms.

The phenyl ring lies slightly to one side of the Hg - S - pyrimidine ring moiety with a dihedral angle C(7) - Hg - S - C(2) of 7,2° for A and 148,8° for B. The mercury atom lies 0,03Å and 0,17Å (for A and B respectively) from the plane of the pyrimidine rings, and 0,22 and 0,05Å respectively from the plane of the phenyl rings.

The Hg---N distances of 2,87(2)Å (A) and 2,85(2)Å (B) are respectively 0,17 and 0,19Å within the sum (3,04Å) of the van der Waals radii according to Pauling (r(N) 1,50)[24] and Grdenić (r(Hg) 1,54Å)[15]. These thus form weak bonds. Similar interactions have been found in a number of other organomercury compounds[30,31].

The molecular conformation of the corresponding methylmercury adduct, namely methyl,2-mercaptopyrimidinatomercury(II) is very similar, with bond lengths of 2,39, 2,13 and 2,83Å for Hg - S, Hg - C and Hg - N respectively. The S - Hg - C angle is 174°, with the methyl group bending away from the pyrimidine ring[31]. It is the arrangement which, in both the methyl and phenyl derivatives gives rise to the chirality of the molecule.

The remainder of the effectively octahedral coordination sphere is completed by intermolecular interactions. With the exception of the phenyl ring, the molecule is essentially planar. The phenyl ring lies virtually perpendicular to the plane of the Hg - S - pyrimidine ring, at 101,6° for A and 90,6° for B. Equations of planes and atomic deviations therefrom are listed in Table 9. Upon inspection of the torsion angles it may be seen that S - Hg - C(7) - C(8) in molecule A, and S - Hg - C(7) - C(12) for molecule B are 92,1° and 121,0° respectively. (It must be pointed out that C(8) and C(12) occupy equivalent positions in the molecule and thus are comparable. The nomenclature is merely arbitrary.) The phenyl ring inclination in molecule A is thus about 30° less. It is this which renders the two molecules asymmetrical.

The pyrimidine ring

The plane defined by the pyrimidine ring may be expressed by the equations given for Plane 1 (A) and Plane 4 (B) in Table 9. All atoms lie within 0,3Å to these planes. Delocalisation of electrons is best expressed in terms of bond order, which is based on bond lengths. These may be related by the method of Burke-Laing and Laing[32], who plotted curves representing the dependence of bond lengths on bond order. With the use of these curves, bond order values for the pyrimidine ring atoms were found to be as follows:

	Molecule A	*Molecule B*
Bond	*Bond order*	*Bond order*
N(1) - C(2)	1,50	1,52
C(2) - N(3)	1,51	1,58
N(3) - C(4)	1,50	1,59
C(4) - C(5)	2,00	1,51
C(5) - C(6)	1,56	2,02
C(6) - N(1)	1,56	1,30

The bond order corresponds to 1 + P, where P is the double bond character as defined by Pauling[24]. There is obvious delocalisation of electrons in the pyrimidine ring system evident in the above data, as almost all bonds have orders of about 1,5, intermediate between single and double bond character. The pyrimidine ring lies at virtually 90° to the plane of the rest of the molecule, where the

Hg - S - C(2) angle is 97(1) and 98(1)° for A and B respectively.

Intermolecular interactions

In addition to the three intramolecular coordination interactions of S, C(7) and N(1) there are weak secondary interactions between the Hg atoms of the reference molecules and the S atoms of the molecules positioned at approximately half-cell intervals down the *y*-axis. Within the asymmetric unit the Hg(1)A - S(1)B and Hg(1)B - S(1)A distances are equal to 3,39 and 3,35Å respectively. The van der Waals radii for Hg and S being 1,54[15] and 1,85Å[24] respectively. These interactions may be considered to lie within the coordination sphere. The four atoms form a quadrilateral, with the two Hg atoms lying 0,22Å below the plane and the two S atoms 0,22Å above the plane of the four atoms. Together they form a four-centre bridge structure resembling that proposed by Bach and Weibel[12] for similar molecules in NMR monitored exchange processes.

Additional Hg---S interactions with the molecules above and below along the *y*-axis give rise to stacking (see Figure 4). The stacking is enhanced by the pyrimidine rings, which overlap as much as is stereo=chemically possible, enabling interaction between π-electrons between the two molecules. In the horizontal plane, phenyl ring π---Hg and phenyl-phenyl ring interactions are observed. (see Figure 5). Aromatic ring interactions have been observed, firstly demonstrated by NMR spectroscopy for 3-arylpropylmercurials and confirmed by structural analysis of one of these[33]. Phenyl rings of $[PhCH_2HgSCPh_3]$[34] and $[MeHg\overset{+}{N}H_2CH(CO_2^-)(p\text{-}OHPh)]$[35] are oriented consistently with the presence of weak π-interaction between Hg and a C = C bond of a phenyl ring. As may be seen from Figure 5, in the case of Hg(1)A for the molecule

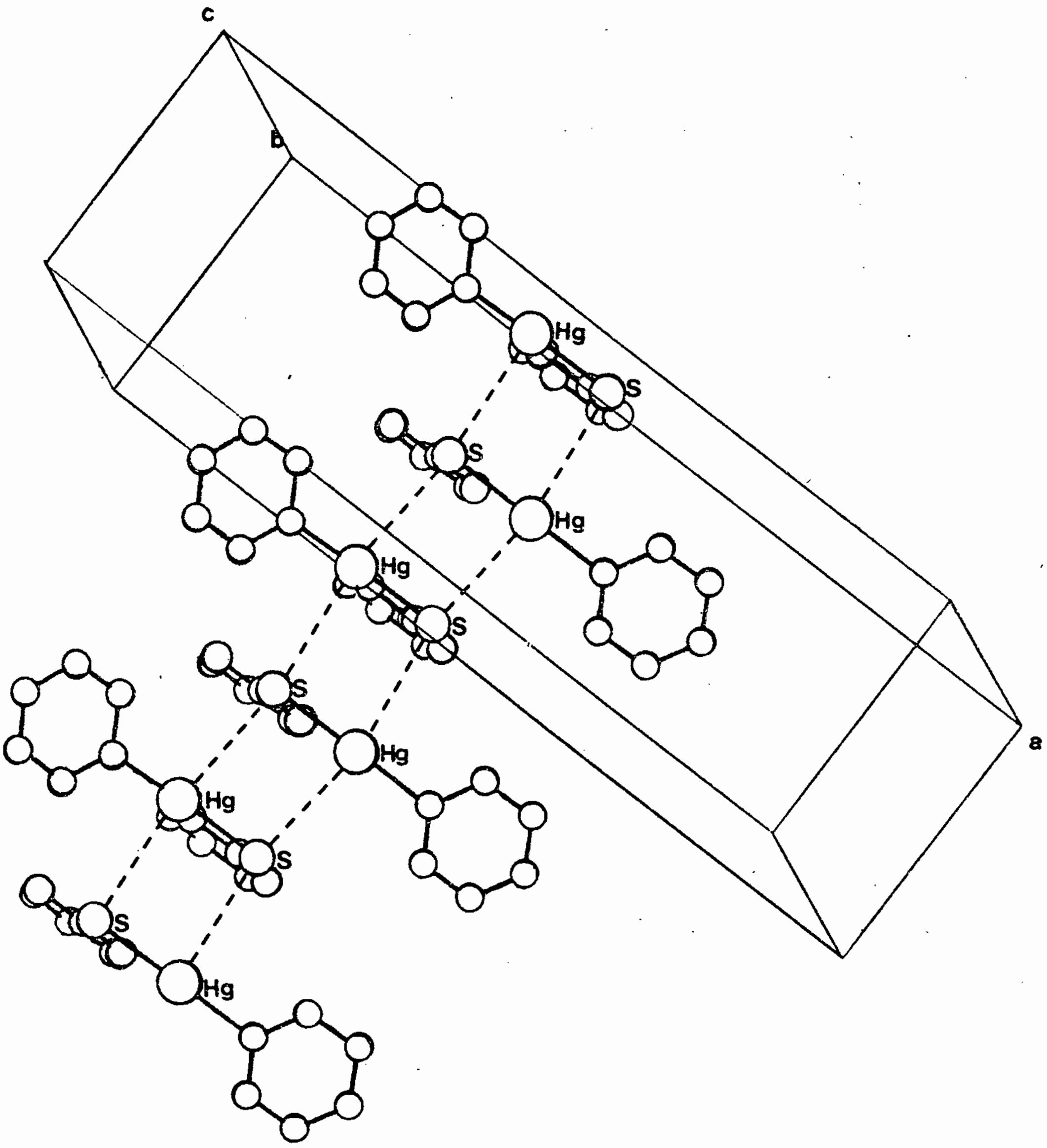


FIGURE 4 STACKING INTERACTIONS BETWEEN PMPM MOLECULES

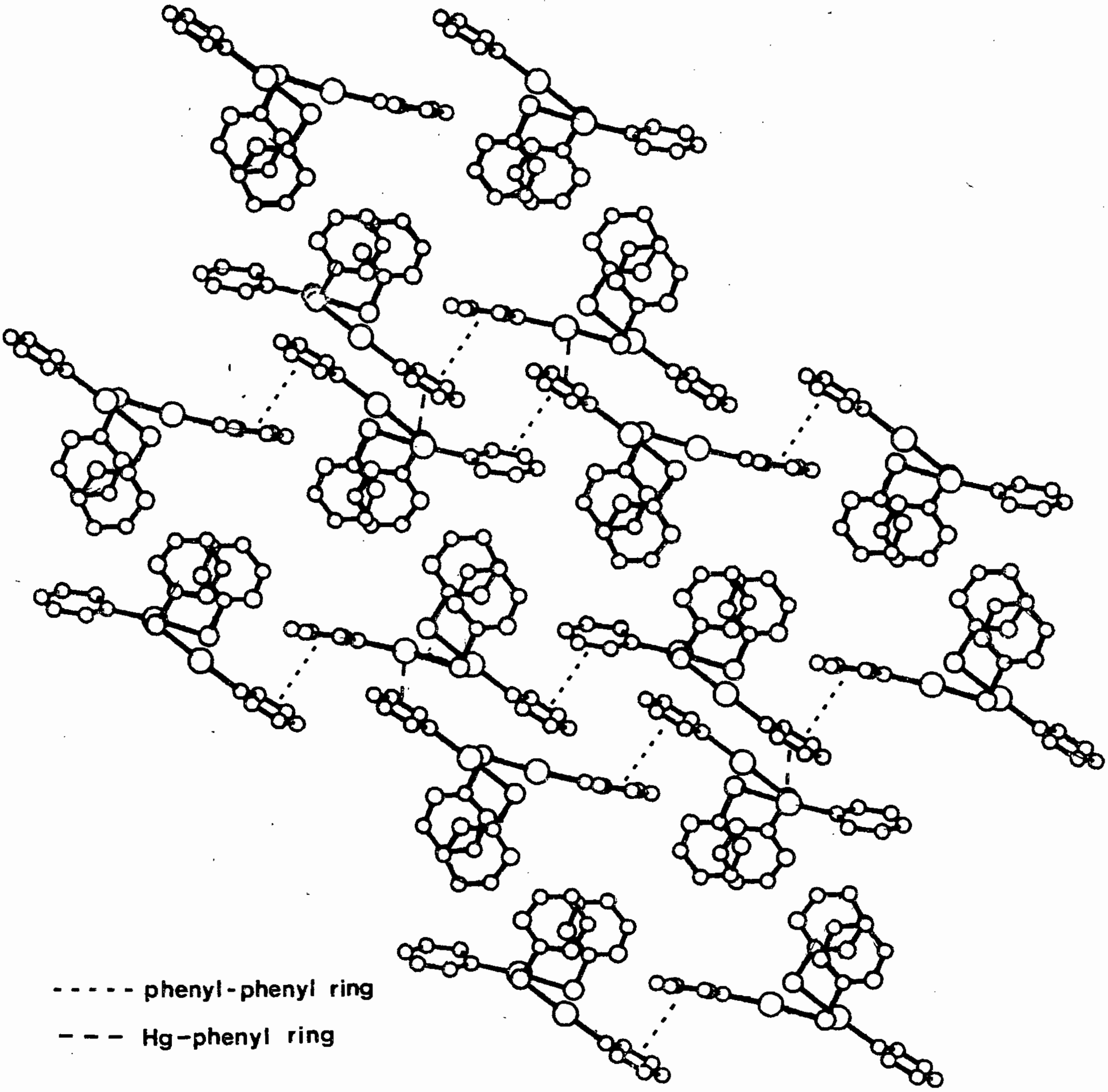


FIGURE 5 INTERMOLECULAR PHENYL RING INTERACTIONS IN PMPM

at x,y,z, interaction occurs with the phenyl ring at $1-x,y,-z$, with the Hg - C(7) distance of 3,32Å. This agrees with distances reported by Canty, Chaichit and Gatehouse[36] and Bach *et al*[34], and is somewhat larger than the intramolecular distance of 3,05Å reported by Kiefer *et al*[33].

TABLE 8 TORSION ANGLES (DEGREES)[a]

	Molecule A	*Molecule B*
C(7) - Hg - S - C(2)	7,2	148,8
Hg - S - C(2) - N(1)	-2,4	3,9
Hg - S - C(2) - N(3)	-178,4	-176,6
S - C(2) - N(3) - C(4)	178,9	178,4
S - C(2) - N(1) - C(6)	-176,5	-175,4
N(1) - C(2) - N(3) - C(4)	3,4	-2,1
C(2) - N(3) - C(4) - C(5)	-4,5	1,7
N(3) - C(4) - C(5) - C(6)	2,8	-5,1
C(4) - C(5) - C(6) - N(1)	0,0	7,9
C(5) - C(6) - N(1) - C(2)	-1,1	-7,8
C(6) - N(1) - C(2) - N(3)	-1,0	5,1
N(1) - C(2) - N(3) - C(4)	3,4	-2,1
S - Hg - C(7) - C(8)	92,1	-59,0
S - Hg - C(7) - C(12)	-79,8	121,0
Hg - C(7) - C(8) - C(9)	-173,4	176,9
Hg - C(7) - C(12) - C(11)	174,6	-173,9
C(7) - C(8) - C(9) - C(10)	1,71	0,0
C(8) - C(9) - C(10) - C(11)	-3,4	0,0
C(9) - C(10) - C(11) - C(12)	4,9	3,5
C(10) - C(11) - C(12) - C(7)	-4,4	-6,4
C(11) - C(12) - C(7) - C(8)	2,7	6,2
C(12) - C(7) - C(8) - C(9)	-1,4	-3,1

[a] The torsion angle $\omega(I\text{-}J\text{-}K\text{-}L)$ is defined as the angle between the vector $J\text{-}I$ and the vector $K\text{-}L$ when viewed down $J\text{-}K$. The sign of ω is positive if $J\text{-}I$ is to be rotated clockwise into $K\text{-}L$ and negative if anticlockwise[37].

TABLE 9 LEAST-SQUARES PLANES

(a) The equation of least-squares planes are expressed in orthogonalised space as $pX + qY + rZ = S$.

Plane 1 : Calculated from the pyrimidine ring atoms of molecule A (N(1)A, C(2)A, N(3)A, C(4)A, C(5)A, C(7)A)
$0{,}7006X + 6{,}6418Y - 2{,}5626Z = 3{,}3028$

Plane 2 : Calculated from phenyl ring A atoms (C(7)A, C(8)A, C(9)A, C(10)A, C(11)A, C(12)A)
$-4{,}9945X - 0{,}0865Y + 15{,}2710Z = 3{,}2506$

Plane 3 : Calculated from pyrimidine ring A with S(1)A and Hg(1)A
$0{,}7163X + 6{,}6288Y - 2{,}7272Z = -1{,}0004$

Plane 4 : Calculated from the pyrimidine ring atoms of molecule B (N(1)B, C(2)B, N(3)B, C(4)B, C(5)B, C(6)B)
$0{,}6978X + 6{,}5672Y - 3{,}3828Z = 6{,}3071$

Plane 5 : Calculated from phenyl ring B atoms (C(7)B, C(8)B, C(9)B, C(10)B, C(11)B, C(12)B)
$-12{,}1920X + 1{,}1789Y + 14{,}3116Z = -2{,}1150$

Plane 6 : Calculated from pyrimidine ring B with S(1)B and Hg(1)B
$0{,}9660X + 6{,}6019Y - 3{,}0524Z = 6{,}5677$

Plane 7 : Calculated from Hg(1)A, S(1)A, Hg(1)B and S(1)B
$0{,}0077X + 0{,}0269Y + 0{,}9969Z = -0{,}9658$

TABLE 9 CONT/....

TABLE 9 CONTINUED

(b) Deviations from planes (Å x 10^3)

Molecule A	*Plane 1*	*Plane 2*	*Plane 3*
Hg(1)A	-315	2212	48
S(1)A	-626	5364	-253
N(1)A	6	28128	152
N(3)A	-211	28467	-77
C(2)A	98	22402	277
C(4)A	179	41563	161
C(5)A	-12	48903	-132
C(6)A	-114	41713	-175
C(7)A	-85	-36	263
C(8)A	-12140	5	-11780
C(9)A	-12565	-73	-12229
C(10)A	-775	175	-480
C(11)A	11026	-208	11314
C(12)A	11310	138	11619

Molecule B	*Plane 4*	*Plane 5*	*Plane 6*
Hg(1)B	1719	-1360	480
S(1)B	502	-4405	-174
N(1)B	-289	20988	-739
N(3)B	50	15559	-111
C(2)B	82	12419	-222
C(4)B	45	28436	371
C(5)B	-282	38233	-63
C(6)B	394	34921	237
C(7)B	3698	-225	1948
C(8)B	15984	-7	14081
C(9)B	17131	121	14870
C(10)B	6079	13	3607
C(11)B	-6513	-245	-8837
C(12)B	-8205	343	10150

TABLE 9 CONT/....

TABLE 9 CONTINUED

	Plane 7
Hg(1)A	-2244
S(1)A	2270
Hg(1)B	-2282
S(1)B	2256
C(2)A	19405
C(2)B	19445
C(7)A	-5701
C(7)B	-7797

(c) Selected angles (degrees) between normals to planes

Planes 1 and 2	100,4
Planes 2 and 3	101,6
Planes 4 and 5	91,5
Planes 5 and 6	90,6
Planes 1 and 7	98,1
Planes 2 and 7	4,0
Planes 4 and 7	101,2
Planes 5 and 7	20,4

TABLE 10 INTRA- AND INTER-MOLECULAR DISTANCES (Å)

1) INTRAMOLECULAR DISTANCES	
Hg(1)A - N(1)A	2,87(2)
Hg(1)B - N(1)B	2,85(2)
2) INTERMOLECULAR DISTANCES	
Hg(1)A - S(1)B	3,39(2)
Hg(1)B - S(1)A	3,36(2)
Hg(1)A - C(7)[a]	3,32(2)

[a] Where C(7) has coordinates $1-x,y,-z$.

CHAPTER 4

THE CRYSTAL AND MOLECULAR STRUCTURE OF PHENYL,MERCAPTOBENZENE MERCURY(II)

CHAPTER 4

THE CRYSTAL AND MOLECULAR STRUCTURE OF PHENYL,MERCAPTOBENZENE MERCURY(II) (PMBM)

4.1 CHEMICAL ANALYSIS

Elemental analysis carried out on PMBM yielded the content of carbon and nitrogen, thus confirming the composition as $C_{12}H_{10}HgS$.

TABLE 11 MICROANALYSIS RESULTS

	%C	%H
Calculated:	37,26	2,60
Found:	37,85	2,57

4.2 PRELIMINARY X-RAY ANALYSIS

The unit cell parameters were obtained by oscillation photographs of three crystals mounted about their respective principal axes, followed by appropriate zero layer Weissenberg photographs. These parameters were initially estimated at a = 9,75Å, b = 5,46Å, c = 8,49Å, α = 75°, β = 103°, γ = 79°, with Z = 2. The symmetry displayed by the oscillation and Weissenberg photographs showed that the crystal was triclinic.

4.3 INTENSITY DATA COLLECTION

Small crystals were selected, mounted and sent to the C.S.I.R. for diffractometer data collection. Intensity data was collected from a crystal of dimensions 0,04 x 0,36 x 0,44mm. Accurate cell parameters were obtained from a least squares analysis of 25 standard reflections. These are listed in Table 12.

TABLE 12	CRYSTAL DATA
Molecular formula:	$C_{12}H_{10}HgS$
Molecular weight:	386,9
Space group:	$P\bar{1}$
a:	10,673(5)Å
b:	6,104(3)Å
c:	9,153(5)Å
α:	103,66(2)°
β:	105,23(2)°
γ:	83,54(2)°
D_m:	2,22Mgm^{-3}
D_c:	2,30Mgm^{-3}
μ(Mo-K_α):	13,412mm^{-1}
F(000):	352

2379 reflections were collected. The scan width was 1,2°θ, scanning at 0,04°θs^{-1} and reflections were collected over a range of $3° < \theta < 27°$. Every 56 reflections three reference reflections were collected to monitor crystal and instrumental stability.

Upon initial attempts at solution and refinement of this data, it became evident that absorption effects were present. In absorption processes[18], the intensity I of a beam passing through a crystal of thickness τ, may be represented by

$$I = I_o e^{-\mu\tau}$$

with I_o : intensity of the incident beam

μ : linear absorption coefficient

As a result of absorption, there is an optimum thickness for any crystal. This thickness is a function of the linear absorption coefficient. In the case of a crystal in the form of a flat plate, severe problems arise as the path of rays passing through the longest and shortest dimensions may differ by a factor of 10 or more, as is the case for PMBM, where the crystal dimensions are 0,004 x 0,036 x 0,044cm. The linear absorption coefficient μ is 134,12cm^{-1}, thus giving a minimum μR of 0,54 and a maximum μR of 5,94. According to the absorption correction factors A^* for the range scanned (3° - 27°θ) these cover 2,08 to 2,03 for μR_{min}, and 274 to 55,4 for μR_{max}. This results in A^* covering a total range of 2,03 to 274 for the crystal. This represents serious absorption effects, differing by hundred times in the two dimensions discussed. This could be rectified by applying absorption corrections, involving complicated mathematics. Alternatively, more suitable crystals could be used.

In order to rectify this disparity in crystal dimensions the crystals were ground to obtain small spheres. This was done according to the method of Bond[39], in which the crystal is set spinning about its centroid. It would then also be spinning about its axis of greatest moment of inertia. When tossed against an abrasive surface, the parts furthest from the centroid would be worn away first, ultimately resulting in a spherical crystal. The apparatus used was an air driven sphere grinder designed by Bond, in which the crystal is spun by air propulsion against emery paper.

However, upon resubmission of ground crystals to the C.S.I.R., it was found that upon grinding the crystals were damaged to such an extent due to their fragility, that an improved data collection was unobtainable.

The original data was then reassessed, and inspection of the three standard reflections *a*,*b* and *c*, monitoring crystal and instrumental stability, revealed deviations covering a range of 10% of their mean. Values for these three reflections, adjusted to a common scale, are plotted against time in Figure 6.

The graph may be divided into three distinct sections, referred to as Phases I, II and III. Phase I remains consistent to within 1,5% of the mean, and incorporates the first 1000 reflections. Phase II shows a rapid increase in *a*, *b* and *c* covering about 4% of the total range. This distinct trend is broken in Phase III, which, consisting of the last 826 reflections, resembles Phase I as the increase observed in Phase II ceases, and values stabilise to lie within 2% of their mean.

This change in stability may be ascribed to crystal instability as opposed to that of the instrument. It is known[40] that high-energy radiation reacts with crystals in different ways, usually causing some damage. This damage may take the form of localised static lattice defects such as interstitials and vacancies. X-ray diffraction effects expected when lattice atoms are displaced slightly from their sites have been calculated by Zachariasen[41], Ekstein[42] and Matsubara[43], and have been shown to produce diffuse maxima surrounding Bragg reflections of reciprocal lattice points. Further theories and

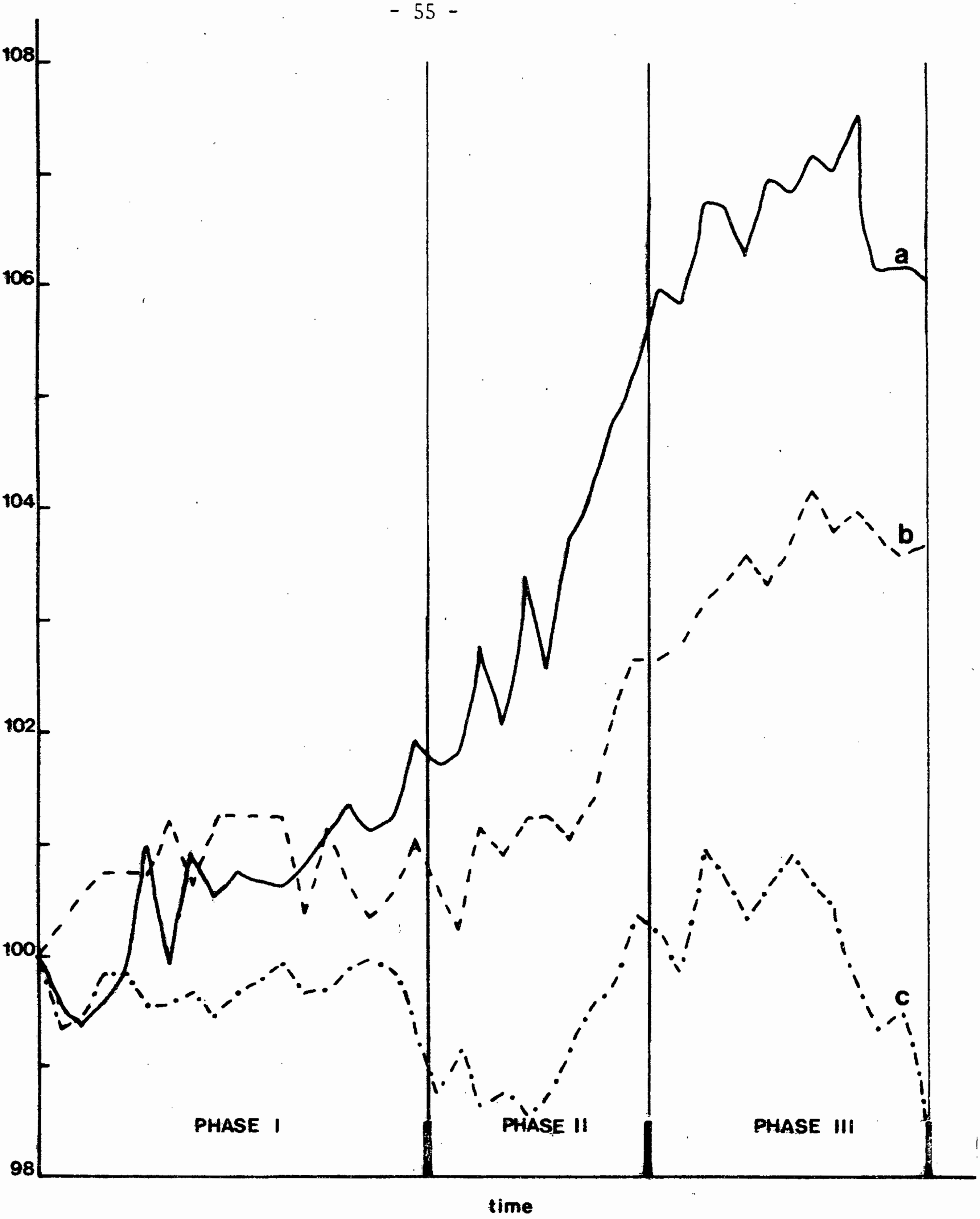


FIGURE 6 STABILITY OF THE THREE STANDARD REFLECTIONS, *a*, *b* AND *c* VERSUS TIME

Phase I : 1000 reflections

Phase II : 553 reflections

Phase III: 826 reflections

calculations have been given by Huang[44] and Konazaki[45]. Experimental work on irradiation of crystals supporting these predictions has been carried out by Prout and Brown[40].

Attempts to explain the cause of the changing stability of the PMBM crystal when subjected to X-radiation will not be made, as the subject is extremely complex and there is insufficient information as yet thereon. What may be said, however, is that the change is definitely caused by crystal instability as is indicated by the crystals turning black upon irradiation.

4.4 SOLUTION AND REFINEMENT OF THE STRUCTURE

4.4.1 Total Data

Solution was first attempted with the total intensity data in the space group $P\bar{1}$. A Patterson map was obtained to find the coordinates of the heavy atom - heavy atoms vectors. Without knowledge of the phases of the Fourier terms, the actual positions of atoms cannot be directly deduced. However, interatomic vectors can be measured, as Patterson showed by means of a Fourier synthesis computed using the squares of the structure factor amplitudes, $|F_{hkl}|^2$. The Patterson function is defined as

$$P_{UVW} = \frac{1}{V} \sum_{hkl}\sum\sum |F_{hkl}|^2 \cos 2\pi(hU + kV + lW)$$

for point U,V,W in a cell of volume V[19]. Interatomic vectors are represented by peaks. "Heavy" atoms, *i.e.* high atomic number, have greater powers of diffraction causing vectors between heavy atoms to be more prominant than those between heavy and light, and light - light atom vectors. The heavy atom can thus be located[18,20]. Deviation of the vector coordinates for the space group $P\bar{1}$ are shown in Figure 7. A heavy atom is placed at position x,y,z. According to the space group it will also be at $\bar{x},\bar{y},\bar{z}$. The vector UVW is then given by $2x,2y,2z$.

FIGURE 7 DERIVATION OF VECTOR COORDINATES FOR $P\bar{1}$

	x, y, z	$\bar{x}$, $\bar{y}$, $\bar{z}$
x, y, z	0 0 0	$-2x$ $-2y$ $-2z$
$\bar{x}$, $\bar{y}$, $\bar{z}$	$2x$ $2y$ $2z$	0 0 0

Ignoring origin peaks, the two vector types are evident at the peaks

0,037	0,376	0,678	$(2x,2y,2z)$
0,963	0,624	0,322	$(-2x,-2y,-2z)$

The Hg atom was thus established at coordinates 0,02, 0,19, 0,34. A subsequent electron density difference map revealed the position of all non-hydrogen atoms after four cycles of refinement, resulting in R = 0,25. The molecular structure seemed unusual at this stage, having a linear C - S - Hg bond and a S - Hg - C bond at 90°, as opposed to a characteristic linear S - Hg - C bond with the C - S - Hg bond at 90°. The following difference fouriers on all atoms, with Hg and S treated anisotropically and H atoms constrained to ride at

1,08Å from their parent atom, reduced *R* to 0,15. Upon inspection of reflections with deviations greater than 2σ, several bad reflections were evident. These were:

h	*k*	*l*	F_o	F_c	*D*/σ
2	0	0	63,67	110,74	6,49
-2	1	1	67,70	132,52	7,82
-1	1	1	29,16	61,95	7,92
1	1	1	69,53	161,60	11,11

As for PMPM, these poor reflections may be ascribed to secondary extinction effects, as is evident from $F_o << F_c$. These were selectively omitted in a further four cycles of refinement, with a final *R* of 0,14. No further refinement was possible, and the structure as such unacceptable. This was based on the following;

i) The *R* value of 0,14 shows there is still a large discrepency between F_o and F_c values. Upon examination it was found that there were still a large number of reflections with deviations > 2σ (82 altogether), with 16 reflections having deviations > 4σ. To omit these would mean considerable reductions of data, as is discussed later.

ii) Estimated standard deviations in bond lengths and angles are generally large, limiting accuracy of bond lengths to within 5×10^{-2}Å and bond angles to within 3° only.

iii) Isotropic and anisotropic thermal parameters have standard deviations that are extremely large. In most cases these are 50% of the thermal parameters and on occasion exceed it, for example U_{12} for C(21) was found to be 0,0019(0,1880) - a standard deviation 100 times greater than the parameter concerned.

All these factors represent a structure that is chemically and crystallographically unacceptable. The procedure was repeated in $P1$ which has the same conditions limiting reflections as $P\bar{1}$[27]. However, this space group is non-centrosymmetric. In $P\bar{1}$, Hg(1)A is placed at coordinates 0,0,0 and Hg(1)B at the vector position of the Patterson. Subsequent difference fourier calculations and refinement cycles yielded all non-hydrogen atoms, with Hg and S atoms treated anisotropically. R was reduced to 0,14, when correlation between corresponding atoms of the two molecules proved that the structure could not possibly be non-centrosymmetric. At this stage the intensity data was reassessed, and it was decided to reject reflections represented by Phase II, solving Phases I (first 1000 reflections) and III (last 826 reflections) separately, as these displayed greater self consistency in the data.

4.4.2 Reduced data: Phase I

The first 1000 reflections were used initially in an attempt to solve the structure in the space group $P1$. Upon finding high correlation between parameters relating corresponding atoms, solution and refinement were carried out in $P\bar{1}$. The Patterson map showed peaks at (0,034, 0,377, 0,686) and (0,882, 0,080, 0,192) corresponding to vector types $(2x,2y,2z)$ and $(-2x,-2y,-2z)$ respectively. From these, the mercury atom was placed at 0,02, 0,19 and 0,35. These coordinates correspond closely to those for the total data. This was followed by an electron density difference map yielding all other non-hydrogen atoms. Only the mercury atom was treated anisotropically and all hydrogen atoms were constrained at 1,08Å from their parent atoms in a subsequent difference fourier map with four cycles of least squares refinement. R was reduced to 0,15. No weighting scheme was employed. Final atomic coordinates are listed

TABLE 13 FRACTIONAL ATOMIC COORDINATES (x 10^3) AND ISOTROPIC THERMAL MOTION PARAMETERS (Å^2 x 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c	U_{iso}
Hg(1)	17(0)	188(0)	339(0)	a
S(1)	-104(2)	265(4)	531(3)	64(6)
C(11)	-257(7)	319(12)	422(11)	52(21)
C(12)	-364(9)	191(15)	414(13)	77(28)
C(13)	-495(9)	253(17)	334(14)	86(31)
C(14)	-528(12)	428(20)	256(16)	112(41)
C(15)	-415(9)	554(16)	267(13)	77(28)
C(16)	-288(8)	508(14)	349(12)	67(25)
C(21)	118(8)	113(14)	165(12)	63(23)
C(22)	188(8)	-83(14)	126(12)	65(24)
C(23)	261(9)	-127(17)	17(15)	84(30)
C(24)	252(10)	45(18)	-68(15)	91(33)
C(25)	185(11)	246(18)	-36(16)	96(35)
C(26)	122(8)	278(14)	67(13)	66(25)
H(12)	-348(9)	57(15)	462(13)	b
H(13)	-567(9)	164(17)	337(14)	b
H(14)	-618(12)	463(20)	196(16)	b
H(15)	-430(9)	684(16)	214(13)	b
H(16)	-218(8)	609(14)	356(12)	b
H(22)	184(8)	-207(14)	179(12)	b
H(23)	318(9)	-268(17)	0(14)	b
H(24)	294(10)	14(18)	-156(15)	b
H(25)	189(11)	369(18)	-90(16)	b
H(26)	68(8)	422(14)	83(13)	b

[a] Anisotropic thermal parameters of the same form as in Table 4.

where U_{11} = 75(2), U_{22} = 48(2), U_{33} = 32(5), U_{23} = 30(2), U_{13} = 26(2), U_{12} = 0(1)

[b] All H atoms have U_{iso} = 1543(1097)

TABLE 14 OBSERVED AND CALCULATED STRUCTURE FACTORS FOR REDUCED DATA (PHASE I) OF PMBM

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	58	111	-6	2	0	8	-11	8	3	0	6	-2	-3	6	0	31	27	-5	-4	1	55	-49
3	0	0	53	84	-5	2	0	7	-6	10	3	0	6	-3	-2	6	0	28	24	-4	-4	1	69	-60
4	0	0	66	88	-4	2	0	5	-8	-8	4	0	16	-16	-1	6	0	26	22	-3	-4	1	75	-63
5	0	0	45	53	-3	2	0	33	-34	-7	4	0	21	-19	0	6	0	22	18	-2	-4	1	90	-77
6	0	0	45	43	-2	2	0	68	-57	-6	4	0	23	-22	1	6	0	20	16	-1	-4	1	98	-84
7	0	0	45	41	-1	2	0	122	-100	-5	4	0	33	-31	2	6	0	17	12	0	-4	1	92	-78
8	0	0	46	38	0	2	0	135	-110	-4	4	0	29	-23	3	6	0	21	18	1	-4	1	68	-56
9	0	0	29	21	1	2	0	130	-110	-3	4	0	23	-21	4	6	0	11	10	2	-4	1	58	-49
10	0	0	25	16	2	2	0	128	-117	-2	4	0	14	-11	-5	-6	1	18	17	3	-4	1	42	-40
11	0	0	14	9	3	2	0	75	-76	-1	4	0	10	-5	-4	-6	1	17	17	4	-4	1	25	-26
-11	1	0	30	15	4	2	0	63	-73	0	4	0	15	14	-3	-6	1	28	22	5	-4	1	15	-12
-10	1	0	35	22	5	2	0	51	-58	1	4	0	20	17	-2	-6	1	28	23	6	-4	1	19	-17
-9	1	0	43	29	6	2	0	42	-52	2	4	0	24	21	-1	-6	1	15	13	7	-4	1	10	-9
-8	1	0	51	45	7	2	0	35	-36	3	4	0	20	18	0	-6	1	7	10	-10	-3	1	18	-16
-7	1	0	53	53	8	2	0	44	-41	4	4	0	18	16	1	-6	1	8	8	-9	-3	1	22	-22
-6	1	0	51	61	9	2	0	39	-32	5	4	0	24	20	3	-6	1	9	-4	-8	-3	1	27	-27
-5	1	0	48	66	10	2	0	33	-23	6	4	0	23	19	4	-6	1	9	-7	-7	-3	1	28	-30
-4	1	0	39	56	-9	3	0	23	-17	7	4	0	20	20	-6	-5	1	8	-7	-6	-3	1	27	-28
-3	1	0	54	68	-8	3	0	28	-29	8	4	0	18	19	-5	-5	1	17	-16	-5	-3	1	36	-32
-2	1	0	48	53	-7	3	0	40	-45	9	4	0	14	15	-4	-5	1	22	-19	-4	-3	1	30	-25
-1	1	0	75	68	-6	3	0	51	-57	-6	5	0	20	18	-3	-5	1	42	-36	-3	-3	1	5	1
0	1	0	65	52	-5	3	0	57	-57	-5	5	0	29	26	-2	-5	1	45	-43	-2	-3	1	13	10
1	1	0	85	78	-4	3	0	62	-61	-4	5	0	27	25	-1	-5	1	54	-47	-1	-3	1	33	27
2	1	0	4	3	-3	3	0	72	-68	-3	5	0	33	30	0	-5	1	57	-47	0	-3	1	13	8
3	1	0	6	6	-2	3	0	99	-84	-2	5	0	39	36	1	-5	1	48	-41	1	-3	1	11	7
4	1	0	8	10	-1	3	0	92	-74	-1	5	0	44	39	2	-5	1	40	-35	2	-3	1	31	25
6	1	0	17	-17	0	3	0	110	-90	0	5	0	44	38	3	-5	1	38	-37	3	-3	1	32	28
7	1	0	28	-32	1	3	0	100	-80	1	5	0	50	41	4	-5	1	41	-35	4	-3	1	37	31
8	1	0	26	-22	2	3	0	89	-74	2	5	0	66	56	5	-5	1	43	-39	5	-3	1	41	39
9	1	0	21	-15	3	3	0	91	-82	3	5	0	61	52	6	-5	1	33	-30	6	-3	1	43	40
10	1	0	27	-17	4	3	0	55	-53	4	5	0	45	42	-9	-4	1	25	-23	7	-3	1	35	32
11	1	0	18	-9	5	3	0	38	-40	5	5	0	37	34	-8	-4	1	33	-29	8	-3	1	30	26
-10	2	0	7	4	6	3	0	19	-19	6	5	0	29	27	-7	-4	1	33	-28	9	-3	1	25	22
-8	2	0	7	-6	7	3	0	10	-7	7	5	0	20	17	-6	-4	1	40	-36	-11	-2	1	6	3

TABLE 14 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-10	-2	1	6	7	2	-1	1	72	65	-4	1	1	57	-84	10	2	1	22	14	7	4	1	7	9
-9	-2	1	17	19	3	-1	1	51	48	-3	1	1	52	-89	-8	3	1	6	6	-6	5	1	10	4
-8	-2	1	23	25	4	-1	1	38	38	-2	1	1	61	-125	-7	3	1	13	13	-5	5	1	10	10
-7	-2	1	29	29	5	-1	1	9	-7	-1	1	1	26	-66	-6	3	1	17	24	-4	5	1	10	10
-6	-2	1	34	34	6	-1	1	8	-10	0	1	1	111	-114	-5	3	1	27	32	-3	5	1	8	6
-5	-2	1	56	50	7	-1	1	11	-14	1	1	1	63	-159	-4	3	1	31	35	0	5	1	7	-5
-4	-2	1	58	53	8	-1	1	11	-13	2	1	1	83	-168	-3	3	1	40	43	1	5	1	12	-13
-3	-2	1	102	86	9	-1	1	11	-7	3	1	1	68	-115	-2	3	1	40	37	2	5	1	23	-21
-2	-2	1	152	125	10	-1	1	14	-8	4	1	1	49	-74	-1	3	1	51	41	3	5	1	22	-18
-1	-2	1	161	131	-11	0	1	18	10	5	1	1	39	-46	0	3	1	98	73	4	5	1	23	-21
0	-2	1	178	144	-10	0	1	17	10	6	1	1	39	-39	1	3	1	99	78	5	5	1	22	-21
1	-2	1	151	124	-9	0	1	17	10	7	1	1	20	-12	2	3	1	93	88	6	5	1	18	-17
2	-2	1	134	113	-7	0	1	14	16	8	1	1	23	-17	3	3	1	75	77	7	5	1	12	-11
3	-2	1	119	110	-6	0	1	7	8	9	1	1	14	-9	4	3	1	51	61	-3	6	1	31	-25
4	-2	1	76	73	-5	0	1	6	8	10	1	1	12	-6	5	3	1	45	56	-2	6	1	31	-26
5	-2	1	57	54	-3	0	1	22	-30	-10	2	1	30	-19	6	3	1	32	41	-1	6	1	32	-27
6	-2	1	40	40	-2	0	1	35	-39	-9	2	1	31	-21	7	3	1	26	26	0	6	1	33	-27
7	-2	1	35	34	1	0	1	76	-71	-8	2	1	36	-30	8	3	1	23	18	1	6	1	28	-22
8	-2	1	33	34	2	0	1	123	-146	-7	2	1	40	-39	9	3	1	21	14	2	6	1	22	-19
9	-2	1	26	21	3	0	1	83	-113	-6	2	1	38	-44	-8	4	1	18	18	3	6	1	30	-23
10	-2	1	23	16	4	0	1	49	-67	-5	2	1	44	-63	-7	4	1	24	22	-6	-6	2	26	-24
-11	-1	1	27	15	5	0	1	37	-48	-4	2	1	36	-50	-6	4	1	37	37	-5	-6	2	29	-28
-10	-1	1	37	23	6	0	1	48	-48	-3	2	1	40	-52	-5	4	1	51	52	-4	-6	2	29	-29
-9	-1	1	37	29	7	0	1	48	-45	-2	2	1	47	-50	-4	4	1	58	55	-3	-6	2	38	-40
-8	-1	1	61	63	8	0	1	44	-35	-1	2	1	54	-44	-3	4	1	62	55	-2	-6	2	43	-45
-7	-1	1	56	70	9	0	1	43	-30	0	2	1	5	-1	-2	4	1	69	59	-1	-6	2	50	-49
-6	-1	1	61	76	10	0	1	37	-23	1	2	1	5	6	-1	4	1	66	52	0	-6	2	49	-46
-5	-1	1	64	77	-11	1	1	11	-4	2	2	1	6	7	0	4	1	57	42	1	-6	2	42	-41
-4	-1	1	90	100	-10	1	1	21	-12	4	2	1	18	25	1	4	1	55	41	2	-6	2	32	-32
-3	-1	1	68	65	-9	1	1	34	-25	5	2	1	12	17	2	4	1	40	32	3	-6	2	24	-25
-2	-1	1	67	57	-8	1	1	47	-40	6	2	1	12	10	3	4	1	34	30	-8	-5	2	27	-25
-1	-1	1	83	65	-7	1	1	56	-56	7	2	1	11	10	4	4	1	27	24	-7	-5	2	27	-25
0	-1	1	160	131	-6	1	1	73	-81	8	2	1	29	24	5	4	1	20	21	-6	-5	2	26	-26
1	-1	1	95	81	-5	1	1	65	-84	9	2	1	20	15	6	4	1	14	19	-5	-5	2	31	-28

TABLE 14 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-4	-5	2	24	-26	-4	-3	2	79	71	-9	-1	2	16	-17	3	0	2	8	-12	-5	2	2	66	83
-3	-5	2	8	-8	-3	-3	2	91	82	-8	-1	2	33	-39	4	0	2	8	-10	-4	2	2	62	92
-2	-5	2	17	-18	-2	-3	2	104	90	-7	-1	2	44	-48	6	0	2	5	4	-3	2	2	58	103
-1	-5	2	16	-16	-1	-3	2	86	75	-6	-1	2	71	-76	7	0	2	12	11	-2	2	2	43	96
0	-5	2	6	-8	0	-3	2	100	86	-5	-1	2	95	-92	8	0	2	16	15	-1	2	2	45	87
1	-5	2	8	5	1	-3	2	78	68	-4	-1	2	110	-103	9	0	2	17	13	0	2	2	73	70
2	-5	2	8	6	2	-3	2	74	65	-3	-1	2	98	-89	10	0	2	16	11	1	2	2	37	70
4	-5	2	14	11	3	-3	2	57	47	-2	-1	2	125	-104	-11	1	2	16	-7	2	2	2	36	64
5	-5	2	16	17	4	-3	2	42	40	-1	-1	2	143	-120	-10	1	2	16	-11	3	2	2	43	61
6	-5	2	18	15	5	-3	2	15	13	0	-1	2	151	-127	-9	1	2	20	-15	4	2	2	45	59
-9	-4	2	7	10	6	-3	2	5	6	1	-1	2	163	-141	-8	1	2	6	-4	5	2	2	34	43
-8	-4	2	12	12	-11	-2	2	18	13	2	-1	2	138	-125	-7	1	2	9	10	6	2	2	26	33
-7	-4	2	17	14	-10	-2	2	17	12	3	-1	2	130	-123	-6	1	2	18	22	7	2	2	13	11
-6	-4	2	24	20	-9	-2	2	15	13	4	-1	2	94	-93	-5	1	2	11	17	8	2	2	10	6
-5	-4	2	31	25	-8	-2	2	25	24	5	-1	2	65	-65	-4	1	2	25	39	9	2	2	11	5
-4	-4	2	30	30	-7	-2	2	30	26	6	-1	2	46	-49	-3	1	2	32	45	-9	3	2	27	21
-3	-4	2	50	45	-6	-2	2	28	26	7	-1	2	24	-21	-2	1	2	56	55	-8	3	2	25	20
-2	-4	2	77	71	-5	-2	2	16	15	8	-1	2	17	-16	-1	1	2	13	15	-7	3	2	25	23
-1	-4	2	88	78	-4	-2	2	38	35	9	-1	2	17	-11	0	1	2	141	110	-6	3	2	20	22
0	-4	2	90	81	-3	-2	2	9	7	10	-1	2	15	-8	1	1	2	74	70	-5	3	2	17	25
1	-4	2	98	88	-2	-2	2	5	0	-11	0	2	26	-15	2	1	2	64	73	-4	3	2	23	28
2	-4	2	90	78	-1	-2	2	45	-36	-10	0	2	41	-27	3	1	2	69	88	-3	3	2	19	22
3	-4	2	68	62	0	-2	2	106	-84	-9	0	2	37	-30	4	1	2	75	106	-2	3	2	21	24
4	-4	2	42	37	1	-2	2	78	-64	-8	0	2	39	-37	5	1	2	54	80	-1	3	2	21	16
5	-4	2	42	39	2	-2	2	75	-64	-7	0	2	48	-59	6	1	2	40	43	0	3	2	21	12
6	-4	2	38	36	3	-2	2	55	-49	-6	0	2	66	-82	7	1	2	32	26	1	3	2	10	8
7	-4	2	29	26	4	-2	2	50	-44	-5	0	2	77	-92	8	1	2	36	26	2	3	2	20	-24
8	-4	2	26	21	5	-2	2	46	-42	-4	0	2	87	-95	9	1	2	26	16	3	3	2	16	-24
-10	-3	2	24	22	6	-2	2	40	-37	-3	0	2	87	-90	10	1	2	25	12	4	3	2	15	-28
-9	-3	2	32	32	7	-2	2	35	-36	-2	0	2	132	-118	-10	2	2	21	13	5	3	2	18	-24
-8	-3	2	50	48	8	-2	2	30	-28	-1	0	2	16	-3	-9	2	2	23	13	6	3	2	22	-23
-7	-3	2	66	61	9	-2	2	26	-21	0	0	2	37	-27	-8	2	2	34	28	7	3	2	15	-12
-6	-3	2	74	66	-11	-1	2	8	-5	1	0	2	44	-31	-7	2	2	45	42	8	3	2	15	-11
-5	-3	2	84	74	-10	-1	2	13	-9	2	0	2	55	-47	-6	2	2	54	62	9	3	2	15	-9

TABLE 14 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-7	4	2	6	-8	-2	-6	3	26	28	4	-4	3	24	-22	1	-2	3	65	-61	-5	0	3	87	84
-6	4	2	13	-18	-1	-6	3	29	34	5	-4	3	28	-26	2	-2	3	31	-29	-4	0	3	141	128
-5	4	2	21	-24	0	-6	3	38	39	6	-4	3	19	-18	3	-2	3	28	-22	-3	0	3	164	147
-4	4	2	32	-34	1	-6	3	41	43	7	-4	3	18	-17	4	-2	3	26	-26	-2	0	3	161	137
-3	4	2	42	-43	2	-6	3	35	37	-9	-3	3	12	-9	5	-2	3	21	-19	-1	0	3	107	95
-2	4	2	60	-54	3	-6	3	31	33	-8	-3	3	28	-27	6	-2	3	7	-9	0	0	3	145	125
-1	4	2	54	-42	-8	-5	3	33	32	-7	-3	3	40	-38	9	-2	3	7	7	1	0	3	106	90
0	4	2	53	-41	-7	-5	3	42	40	-6	-3	3	54	-51	-11	-1	3	19	-17	2	0	3	87	73
1	4	2	52	-39	-6	-5	3	49	48	-5	-3	3	72	-64	-10	-1	3	23	-25	3	0	3	75	69
2	4	2	46	-39	-5	-5	3	60	57	-4	-3	3	81	-72	-9	-1	3	17	-15	4	0	3	85	82
3	4	2	46	-46	-4	-5	3	49	53	-3	-3	3	71	-68	-8	-1	3	10	-8	5	0	3	53	58
4	4	2	33	-37	-3	-5	3	50	53	-2	-3	3	65	-67	-7	-1	3	8	-7	6	0	3	38	43
5	4	2	24	-33	-2	-5	3	54	59	-1	-3	3	89	-87	-6	-1	3	18	-13	7	0	3	26	28
6	4	2	22	-28	0	-5	3	50	56	0	-3	3	118	-111	-5	-1	3	8	9	8	0	3	17	15
7	4	2	20	-21	1	-5	3	58	60	1	-3	3	107	-100	-4	-1	3	13	12	9	0	3	12	8
-6	5	2	17	-16	2	-5	3	56	53	2	-3	3	106	-95	-3	-1	3	22	19	-11	1	3	36	22
-5	5	2	24	-23	3	-5	3	40	39	3	-3	3	103	-94	-2	-1	3	27	21	-10	1	3	34	26
-4	5	2	33	-27	4	-5	3	23	23	4	-3	3	84	-78	-1	-1	3	26	27	-9	1	3	38	31
-3	5	2	40	-33	5	-5	3	19	17	5	-3	3	50	-45	0	-1	3	58	50	-8	1	3	35	34
-2	5	2	41	-34	6	-5	3	11	11	6	-3	3	39	-35	1	-1	3	85	72	-7	1	3	37	44
-1	5	2	44	-35	-10	-4	3	22	19	7	-3	3	28	-25	2	-1	3	94	81	-6	1	3	39	47
0	5	2	38	-30	-9	-4	3	22	20	8	-3	3	20	-17	3	-1	3	103	94	-5	1	3	47	53
1	5	2	30	-22	-8	-4	3	27	25	-11	-2	3	23	-21	4	-1	3	69	68	-4	1	3	62	63
2	5	2	20	-14	-7	-4	3	31	29	-10	-2	3	30	-27	5	-1	3	58	55	-3	1	3	57	55
3	5	2	14	-10	-6	-4	3	34	33	-9	-2	3	34	-33	6	-1	3	44	42	-2	1	3	84	74
4	5	2	8	-6	-5	-4	3	29	28	-8	-2	3	47	-45	7	-1	3	33	29	-1	1	3	81	58
5	5	2	7	-2	-4	-4	3	37	37	-7	-2	3	68	-65	8	-1	3	27	27	0	1	3	24	22
-1	6	2	10	8	-3	-4	3	21	22	-6	-2	3	85	-79	9	-1	3	20	16	1	1	3	21	14
0	6	2	13	9	-2	-4	3	10	10	-5	-2	3	114	-102	-11	0	3	17	12	2	1	3	4	-9
1	6	2	10	6	-1	-4	3	8	-6	-4	-2	3	129	-113	-10	0	3	21	18	3	1	3	7	-14
-6	-6	3	6	7	0	-4	3	13	-11	-3	-2	3	107	-91	-9	0	3	12	12	4	1	3	6	-9
-5	-6	3	8	9	1	-4	3	22	-19	-2	-2	3	110	-99	-8	0	3	29	34	5	1	3	13	-15
-4	-6	3	13	14	2	-4	3	29	-24	-1	-2	3	85	-77	-7	0	3	44	49	6	1	3	14	-14
-3	-6	3	23	25	3	-4	3	32	-33	0	-2	3	83	-75	-6	0	3	65	68	7	1	3	17	-17

TABLE 14 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
8	1	3	13	-11	4	3	3	16	-18	-8	-5	4	8	-8	-7	-3	4	27	-29	8	-2	4	19	18
9	1	3	12	-7	5	3	3	13	-11	-7	-5	4	15	-16	-6	-3	4	17	-20	-11	-1	4	28	26
-9	2	3	6	2	6	3	3	11	-11	-6	-5	4	25	-23	-5	-3	4	8	-12	-10	-1	4	41	38
-8	2	3	6	3	7	3	3	13	-12	-5	-5	4	35	-36	-4	-3	4	14	-12	-9	-1	4	45	42
-7	2	3	5	6	-8	4	3	22	-17	-4	-5	4	29	-33	-3	-3	4	11	-10	-8	-1	4	54	54
-6	2	3	13	-15	-7	4	3	17	-18	-3	-5	4	36	-43	-1	-3	4	14	12	-7	-1	4	60	59
-5	2	3	24	-33	-6	4	3	13	-13	-2	-5	4	40	-47	0	-3	4	13	15	-6	-1	4	64	64
-4	2	3	35	-48	-5	4	3	8	-10	-1	-5	4	43	-53	1	-3	4	30	33	-5	-1	4	64	61
-3	2	3	40	-52	-4	4	3	7	-9	0	-5	4	43	-52	2	-3	4	45	41	-4	-1	4	110	97
-2	2	3	82	-81	0	4	3	11	9	1	-5	4	49	-57	3	-3	4	58	56	-3	-1	4	113	97
-1	2	3	75	-62	1	4	3	7	4	2	-5	4	53	-57	4	-3	4	44	40	-2	-1	4	108	94
0	2	3	67	-56	2	4	3	5	7	3	-5	4	52	-55	5	-3	4	41	39	-1	-1	4	98	81
1	2	3	58	-53	3	4	3	8	10	4	-5	4	46	-46	6	-3	4	36	35	0	-1	4	59	50
2	2	3	57	-62	4	4	3	10	14	5	-5	4	34	-35	7	-3	4	23	23	1	-1	4	57	51
3	2	3	40	-50	5	4	3	16	19	-10	-4	4	19	-18	8	-3	4	15	14	2	-1	4	30	27
4	2	3	36	-47	6	4	3	16	19	-9	-4	4	25	-27	-11	-2	4	8	5	4	-1	4	7	-5
5	2	3	37	-48	7	4	3	15	14	-8	-4	4	43	-43	-10	-2	4	10	9	5	-1	4	10	-13
6	2	3	47	-54	-5	5	3	14	16	-7	-4	4	57	-56	-9	-2	4	14	14	8	-1	4	7	-5
7	2	3	30	-30	-4	5	3	19	20	-6	-4	4	62	-65	-8	-2	4	27	25	-11	0	4	13	8
8	2	3	26	-21	-3	5	3	22	21	-5	-4	4	78	-77	-7	-2	4	45	42	-10	0	4	13	12
9	2	3	18	-12	-2	5	3	35	29	-4	-4	4	94	-97	-6	-2	4	61	58	-9	0	4	18	20
-9	3	3	30	-21	-1	5	3	47	35	-3	-4	4	78	-80	-5	-2	4	95	91	-8	0	4	14	13
-8	3	3	32	-25	0	5	3	46	34	-2	-4	4	72	-78	-4	-2	4	113	104	-7	0	4	9	8
-7	3	3	32	-28	1	5	3	38	29	-1	-4	4	65	-73	-3	-2	4	128	120	-6	0	4	5	-6
-6	3	3	31	-33	2	5	3	27	24	0	-4	4	52	-62	-2	-2	4	137	129	-5	0	4	17	-19
-5	3	3	41	-49	3	5	3	21	20	1	-4	4	38	-46	-1	-2	4	93	92	-4	0	4	32	-33
-4	3	3	39	-55	4	5	3	16	16	2	-4	4	34	-38	0	-2	4	96	97	-3	0	4	57	-52
-3	3	3	35	-63	-6	-6	4	28	30	3	-4	4	44	-43	1	-2	4	93	90	-2	0	4	75	-56
-2	3	3	32	-71	-5	-6	4	29	32	4	-4	4	32	-34	2	-2	4	95	92	-1	0	4	85	-68
-1	3	3	42	-70	-4	-6	4	23	28	5	-4	4	16	-15	3	-2	4	80	76	0	0	4	71	-62
0	3	3	57	-59	-3	-6	4	18	24	6	-4	4	10	-9	4	-2	4	76	72	1	0	4	68	-61
1	3	3	25	-44	-2	-6	4	13	17	-10	-3	4	25	-24	5	-2	4	60	55	2	0	4	55	-51
2	3	3	20	-33	-1	-6	4	7	12	-9	-3	4	27	-25	6	-2	4	43	41	3	0	4	67	-61
3	3	3	25	-32	2	-6	4	7	-4	-8	-3	4	30	-27	7	-2	4	30	27	4	0	4	65	-60

TABLE 14 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
5	0	4	52	-51	6	1	4	25	-26	-6	3	4	5	10	1	4	4	17	31	-3	-5	5	17	-21
6	0	4	44	-48	7	1	4	15	-17	-5	3	4	11	15	2	4	4	11	19	-2	-5	5	12	-16
7	0	4	32	-31	8	1	4	11	-11	-4	3	4	21	22	3	4	4	10	15	-1	-5	5	11	-9
8	0	4	23	-23	-10	2	4	30	-22	-3	3	4	36	39	4	4	4	11	11	1	-5	5	13	12
9	0	4	20	-16	-9	2	4	34	-29	-2	3	4	54	51	5	4	4	9	7	2	-5	5	15	16
-11	1	4	20	-13	-8	2	4	29	-31	-1	3	4	73	57	-1	5	4	9	-8	3	-5	5	16	19
-10	1	4	32	-27	-7	2	4	28	-31	0	3	4	73	58	0	5	4	13	-10	4	-5	5	20	19
-9	1	4	31	-34	-6	2	4	29	-30	1	3	4	53	49	1	5	4	12	-12	-7	-4	5	15	22
-8	1	4	29	-34	-5	2	4	38	-39	2	3	4	36	42	2	5	4	8	-11	-6	-4	5	29	34
-7	1	4	31	-37	-4	2	4	32	-33	3	3	4	27	32	-5	-6	5	41	-52	-5	-4	5	58	60
-6	1	4	52	-53	-3	2	4	24	-20	4	3	4	22	27	-4	-6	5	45	-57	-4	-4	5	65	69
-5	1	4	70	-68	-2	2	4	6	-6	5	3	4	18	19	-3	-6	5	43	-58	-3	-4	5	66	74
-4	1	4	91	-79	-1	2	4	39	-27	6	3	4	20	21	-2	-6	5	40	-55	-2	-4	5	72	82
-3	1	4	95	-81	0	2	4	8	-7	7	3	4	21	17	-1	-6	5	33	-51	-1	-4	5	67	81
-2	1	4	170	-134	3	2	4	5	6	-7	4	4	29	25	0	-6	5	28	-43	0	-4	5	58	72
-1	1	4	132	-105	4	2	4	13	15	-6	4	4	27	27	1	-6	5	26	-40	1	-4	5	52	68
0	1	4	116	-99	5	2	4	14	21	-5	4	4	23	29	-8	-5	5	25	-29	2	-4	5	47	60
1	1	4	90	-81	6	2	4	12	15	-4	4	4	22	30	-7	-5	5	24	-29	3	-4	5	51	58
2	1	4	78	-69	7	2	4	10	11	-3	4	4	17	27	-6	-5	5	19	-25	4	-4	5	43	47
3	1	4	42	-37	8	2	4	17	15	-2	4	4	16	32	-5	-5	5	20	-27	5	-4	5	44	44
4	1	4	31	-25	-8	3	4	9	9	-1	4	4	24	32	-4	-5	5	26	-32	6	-4	5	35	35
5	1	4	28	-24	-7	3	4	9	10	0	4	4	30	30										

TABLE 15 ANALYSIS OF VARIANCE*

a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	86	88	89	95	79	77	85	85	684
V	168	156	168	173	133	160	227	226	179

b) As a function of $\sin\theta$

$\sin\theta$ 0,00-0,37-0,39-0,40-0,41-0,42-0,43-0,44-0,45-0,46-0,47

N	99	49	74	85	89	86	81	90	31	0
V	139	151	188	194	210	182	190	173	158	0

c) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$ 0,00-0,35-0,39-0,43-0,46-0,50-0,54-0,57-0,62-0,70-1,00

N	76	71	59	68	74	71	61	76	66	62
V	233	172	209	212	179	181	151	141	153	126

d) As a function of |Miller index|

$\|h\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	35	74	72	72	63	63	55	49	48	47	41	40	25	0	0
V	151	153	163	204	194	198	177	183	198	149	179	187	168	0	0

TABLE 15 CONT/....

TABLE 15 CONTINUED

$\|k\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	54	124	111	101	97	87	68	42	0	0	0	0	0	0	0
V	127	163	158	177	167	280	152	135	0	0	0	0	0	0	0
$\|l\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	0	0	23	52	61	63	64	91	139	120	71	0	0	0	0
V	0	0	230	189	174	301	219	162	131	133	142	0	0	0	0

*N = No. of reflections in the group

$V = 100\,[M\Sigma(\omega|F_o - F_c|^2)/N\Sigma\omega]$ where M = total no. of reflections.

TABLE 16 FRACTIONAL ATOMIC COORDINATES (x 10^3) AND ISOTROPIC THERMAL MOTION PARAMETERS (Å^2 x 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
Hg(1)	17(0)	188(0)	339(0)	a
S(1)	-106(1)	262(2)	529(1)	58(2)
C(11)	-269(5)	333(8)	427(3)	59(6)
C(12)	-36(6)	211(9)	428(4)	71(8)
C(13)	-490(11)	261(19)	350(8)	96(15)
C(14)	-514(12)	452(19)	269(8)	99(17)
C(15)	-406(8)	539(14)	265(6)	83(11)
C(16)	-285(6)	506(10)	348(4)	70(8)
C(21)	115(4)	116(7)	166(3)	56(6)
C(22)	199(8)	-66(12)	144(6)	78(10)
C(23)	244(7)	-107(12)	23(5)	74(10)
C(24)	251(5)	54(8)	-65(4)	63(7)
C(25)	172(5)	272(7)	-28(3)	59(6)
C(26)	105(6)	287(10)	82(4)	68(8)
H(12)	-341(6)	84(9)	483(4)	b
H(13)	-563(11)	171(19)	349(8)	b
H(14)	-604(12)	509(19)	222(8)	b
H(15)	-417(8)	642(14)	191(6)	b
H(16)	-212(6)	599(10)	352(4)	b
H(22)	224(8)	-165(12)	221(6)	b
H(23)	279(7)	-265(12)	-11(5)	b
H(24)	303(5)	24(8)	-146(4)	b
H(25)	170(5)	399(7)	-81(3)	b
H(26)	46(6)	424(9)	105(4)	b

TABLE 16 CONT/....

TABLE 16 CONTINUED

[a] Anisotropic thermal parameters defined as in Table 4.

U_{11} = 68(1), U_{22} = 59(1), U_{33} = 50(1), U_{23} = 17(0), U_{13} = 24(0), U_{12} = 0(0)

[b] All H atoms have U_{iso} = 502(228)

TABLE 17 OBSERVED AND CALCULATED STRUCTURE FACTORS FOR REDUCED DATA (PHASE III) OF PMBM

H	K	L	FO	FC
-11	3	2	19	15
-10	3	2	22	20
10	3	2	12	-9
11	3	2	9	-8
-10	4	2	6	-1
8	4	2	12	-15
9	4	2	11	-9
10	4	2	6	-5
-9	5	2	11	-11
-8	5	2	13	-14
-7	5	2	14	-16
-6	6	2	5	-6
-3	6	2	5	2
2	6	2	10	9
3	6	2	12	12
4	6	2	10	10
5	6	2	8	9
6	6	2	8	11
-2	7	2	16	13
-1	7	2	15	14
0	7	2	16	14
1	7	2	16	13
2	7	2	11	8
-7	-7	3	14	-13
-6	-7	3	13	-12
-5	-7	3	12	-11
-4	-7	3	10	-10
-3	-7	3	10	-9
-2	-7	3	7	-8
-1	-7	3	7	-6
4	-6	3	21	18
5	-6	3	17	15
6	-6	3	16	13
-11	-5	3	7	6
-10	-5	3	14	12
-9	-5	3	20	20
-12	-4	3	11	10
-11	-4	3	12	14
8	-4	3	15	-15
9	-4	3	13	-14
9	-3	3	12	-11
10	-3	3	9	-9
-12	-2	3	18	-17
10	-2	3	8	8
11	-2	3	7	6
-12	-1	3	16	-14
10	-1	3	15	13
11	-1	3	14	11
-12	0	3	10	10
-12	1	3	24	20
10	1	3	10	-9
11	1	3	11	-10
-11	2	3	6	4
10	2	3	13	-8
11	2	3	9	-5
-11	3	3	16	-12
-10	3	3	20	-19
-10	4	3	13	-11
-9	4	3	15	-16
8	4	3	11	11
9	4	3	10	8
-6	5	3	6	9
5	5	3	9	13
6	5	3	9	12
7	5	3	7	10
8	5	3	7	8
-6	6	3	11	11
-5	6	3	11	11
-4	6	3	12	11
-3	6	3	13	12
-2	6	3	13	12
-1	6	3	14	13
0	6	3	13	12
1	6	3	12	12
2	6	3	7	8
-7	-7	4	15	14
-6	-7	4	17	17
-5	-7	4	19	18
-4	-7	4	19	17
-3	-7	4	18	15
-2	-7	4	19	17
-1	-7	4	19	17
0	-7	4	20	18
1	-7	4	19	19
2	-7	4	17	16
3	-7	4	15	13
-9	-6	4	12	11
-8	-6	4	14	13
-7	-6	4	18	16
3	-6	4	7	-5
5	-6	4	5	-4
6	-6	4	5	-4
6	-5	4	19	-17
7	-5	4	14	-12
8	-5	4	10	-8
-12	-4	4	13	-12
-11	-4	4	14	-13
9	-4	4	5	2
-12	-3	4	15	-15
-11	-3	4	15	-17
9	-3	4	11	10
10	-3	4	9	9
9	-2	4	7	7
-12	-1	4	20	19
10	-1	4	7	-6
11	-1	4	8	-7
-12	0	4	12	10
10	0	4	12	-10
11	0	4	11	-6
-12	1	4	13	-11
9	1	4	7	-8
10	1	4	6	-4
-12	2	4	17	-12
-11	2	4	20	-17
9	2	4	11	11
10	2	4	8	6
8	3	4	13	16
9	3	4	10	13
-10	4	4	14	12
-9	4	4	17	16
-8	4	4	20	21
-7	5	4	8	9
-6	5	4	7	9
3	5	4	6	-8
4	5	4	6	-6
5	5	4	7	-6
6	5	4	7	-8
-5	6	4	6	-9
-4	6	4	10	-10
-3	6	4	11	-11
-2	6	4	11	-10
-1	6	4	15	-13
0	6	4	17	-15
1	6	4	18	-17
2	6	4	13	-14
3	6	4	9	-11
-5	-7	5	6	-6
-4	-7	5	8	-6
-3	-7	5	11	-9
-2	-7	5	11	-9
-1	-7	5	9	-9
0	-7	5	14	-11
1	-7	5	17	-14
2	-7	5	18	-15
-9	-6	5	13	-11
-8	-6	5	16	-14
-7	-6	5	20	-18
-6	-6	5	24	-24
2	-6	5	17	-17
3	-6	5	17	-15
4	-6	5	14	-13
5	-6	5	11	-9
-11	-5	5	13	-13
-10	-5	5	15	-14
-9	-5	5	16	-16
5	-5	5	13	12
6	-5	5	12	10
7	-5	5	9	7
7	-4	5	19	19
8	-4	5	11	10
-12	-3	5	16	15
-11	-3	5	22	23
-12	-2	5	12	10
8	-2	5	18	-20
9	-2	5	12	-11
10	-2	5	8	-5
-12	-1	5	7	-9
9	-1	5	8	-9
-12	0	5	16	-17
9	0	5	6	6

TABLE 17 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-12	1	5	6	-6	-1	-7	6	7	-7	9	1	6	9	-8	-4	-6	7	8	8	1	1	7	29	-27
-11	1	5	6	-7	-6	-6	6	9	9	-11	2	6	5	5	-10	-5	7	6	-4	2	1	7	33	-33
8	1	5	12	18	-5	-6	6	14	13	6	2	6	13	-15	-9	-5	7	7	-6	3	1	7	25	-27
9	1	5	13	15	1	-6	6	18	17	7	2	6	8	-10	-8	-5	7	7	-8	4	1	7	18	-20
10	1	5	10	9	2	-6	6	18	16	8	2	6	6	-7	2	-5	7	25	-23	5	1	7	11	-14
-12	2	5	8	8	3	-6	6	19	18	-10	3	6	10	-11	3	-5	7	19	-17	6	1	7	6	-7
-11	2	5	12	12	4	-6	6	19	16	-9	3	6	12	-15	4	-5	7	17	-15	7	1	7	6	-5
-10	2	5	14	17	-11	-5	6	15	14	-8	3	6	15	-20	5	-5	7	13	-12	-10	2	7	14	-15
-11	3	5	11	11	-10	-5	6	19	18	5	3	6	6	-8	-11	-4	7	17	-15	-9	2	7	15	-16
-10	3	5	11	12	-9	-5	6	25	21	-8	4	6	6	-7	-10	-4	7	23	-22	-8	2	7	17	-16
-9	3	5	11	13	-8	-5	6	24	23	-6	4	6	6	-6	-9	-4	7	31	-29	-7	2	7	17	-18
7	3	5	6	-9	4	-5	6	10	9	-5	4	6	6	-6	4	-4	7	8	-8	-6	2	7	18	-18
8	3	5	6	-7	5	-5	6	8	6	2	4	6	9	11	-12	-3	7	12	-12	-5	2	7	18	-17
-9	4	5	7	-6	-12	-4	6	13	10	3	4	6	8	10	-11	-3	7	12	-12	-4	2	7	18	-17
-8	4	5	8	-10	-11	-4	6	15	14	4	4	6	7	11	-10	-3	7	14	-13	-3	2	7	18	-16
-7	4	5	10	-13	-10	-4	6	21	20	5	4	6	5	7	6	-3	7	13	14	-2	2	7	9	-8
5	4	5	10	-12	6	-4	6	16	-15	-5	5	6	7	12	7	-3	7	12	13	-1	2	7	8	-6
6	4	5	8	-6	7	-4	6	14	-12	-4	5	6	10	14	-11	-2	7	6	5	1	2	7	5	6
7	4	5	6	-7	-11	-3	6	7	-8	-3	5	6	12	15	6	-2	7	13	11	2	2	7	9	11
-7	5	5	10	-13	7	-3	6	19	-17	-2	5	6	14	14	7	-2	7	10	7	3	2	7	7	8
-6	5	5	11	-17	8	-3	6	13	-14	-1	5	6	17	12	8	-2	7	7	6	4	2	7	9	10
-5	5	5	11	-19	-12	-2	6	16	-17	0	5	6	14	11	-12	-1	7	16	16	5	2	7	8	9
-4	5	5	10	-19	-11	-2	6	22	-22	1	5	6	14	12	-11	-1	7	17	20	6	2	7	6	6
-3	5	5	7	-17	-12	-1	6	11	-12	2	5	6	10	12	6	-1	7	5	-3	7	2	7	5	4
-2	5	5	7	-12	-11	-1	6	10	-11	3	5	6	7	11	8	-1	7	5	-6	-7	3	7	10	10
-1	5	5	10	-12	8	-1	6	15	17	-5	-7	7	15	16	-12	0	7	9	9	-6	3	7	14	14
0	5	5	8	-9	9	-1	6	11	13	-4	-7	7	19	18	-11	0	7	10	10	-5	3	7	18	18
1	5	5	5	-9	-11	0	6	10	10	-3	-7	7	19	17	-10	0	7	8	9	-4	3	7	30	28
2	5	5	5	-9	8	0	6	7	4	-2	-7	7	20	18	6	0	7	15	-14	-3	3	7	30	26
-6	-7	6	11	-9	9	0	6	5	4	-1	-7	7	20	18	7	0	7	11	-10	-2	3	7	22	19
-5	-7	6	10	-9	-12	1	6	13	15	-8	-6	7	17	16	8	0	7	9	-8	-1	3	7	21	18
-4	-7	6	12	-11	-11	1	6	14	17	-7	-6	7	17	16	-11	1	7	8	-9	0	3	7	23	18
-3	-7	6	9	-10	7	1	6	8	-10	-6	-6	7	14	15	-10	1	7	12	-13	1	3	7	23	20
-2	-7	6	7	-9	8	1	6	7	-10	-5	-6	7	8	10	0	1	7	35	-32	2	3	7	20	19

TABLE 17 CONTINUED

H	K	L	FO	FC
3	3	7	17	18
4	3	7	15	18
5	3	7	11	14
-7	4	7	12	13
-6	4	7	15	16
-5	4	7	16	17
-4	4	7	18	18
-3	4	7	23	20
-2	4	7	18	17
-1	4	7	14	12
0	4	7	13	11
1	4	7	13	10
2	4	7	7	6
3	4	7	6	2
-7	-6	8	21	-20
-6	-6	8	21	-21
-5	-6	8	22	-20
-4	-6	8	21	-22
-3	-6	8	20	-20
-2	-6	8	18	-20
-1	-6	8	19	-19
0	-6	8	18	-18
1	-6	8	17	-16
2	-6	8	12	-12
-9	-5	8	12	-12
-8	-5	8	14	-13
-7	-5	8	17	-15
-6	-5	8	19	-17
-5	-5	8	16	-15
-4	-5	8	10	-10
-1	-5	8	8	5
0	-5	8	7	5
1	-5	8	8	8
2	-5	8	6	7
3	-5	8	8	7
4	-5	8	7	6
-9	-4	8	12	10
-8	-4	8	19	16
-7	-4	8	24	24
-6	-4	8	26	24
-5	-4	8	27	27
-4	-4	8	29	29
-3	-4	8	28	29
-2	-4	8	28	29
-1	-4	8	32	33
0	-4	8	34	34
1	-4	8	34	33
2	-4	8	32	32
3	-4	8	27	25
4	-4	8	19	18
5	-4	8	14	11
-11	-3	8	16	16
-10	-3	8	22	22
-9	-3	8	28	27
-8	-3	8	31	31
-7	-3	8	40	38
-6	-3	8	54	51
-5	-3	8	47	43
-4	-3	8	37	39
-3	-3	8	34	35
-2	-3	8	31	33
-1	-3	8	24	25
0	-3	8	17	18
1	-3	8	17	16
2	-3	8	14	16
3	-3	8	10	9
4	-3	8	6	6
-12	-2	8	15	13
-11	-2	8	14	14
-10	-2	8	13	12
-9	-2	8	12	11
-8	-2	8	8	8
-4	-2	8	9	-9
-3	-2	8	8	-9
-1	-2	8	10	-11
0	-2	8	22	-22
1	-2	8	33	-34
2	-2	8	29	-28
3	-2	8	23	-22
4	-2	8	21	-23
5	-2	8	16	-16
6	-2	8	12	-10
-11	-1	8	9	-9
-10	-1	8	12	-11
-9	-1	8	18	-18
-8	-1	8	27	-28
-7	-1	8	38	-37
-6	-1	8	47	-44
-5	-1	8	53	-51
-4	-1	8	57	-55
-3	-1	8	48	-47
-2	-1	8	42	-43
-1	-1	8	40	-39
0	-1	8	41	-40
1	-1	8	35	-34
2	-1	8	34	-34
3	-1	8	26	-26
4	-1	8	20	-21
5	-1	8	15	-17
6	-1	8	11	-11
7	-1	8	6	-5
-11	0	8	20	-20
-10	0	8	21	-20
-9	0	8	25	-24
-8	0	8	29	-28
-7	0	8	26	-27
-6	0	8	28	-27
-5	0	8	27	-25
-4	0	8	31	-29
-3	0	8	34	-33
-2	0	8	24	-22
-1	0	8	19	-17
0	0	8	10	-10
3	0	8	6	6
-6	1	8	18	17
-5	1	8	24	21
-4	1	8	26	24
-3	1	8	25	23
-2	1	8	25	24
-1	1	8	28	27
0	1	8	25	23
1	1	8	24	22
2	1	8	24	23
3	1	8	20	21
4	1	8	21	21
5	1	8	16	17
6	1	8	11	12
-9	2	8	14	15
-8	2	8	19	18
-7	2	8	23	21
-6	2	8	27	24
-5	2	8	28	27
-4	2	8	36	33
-3	2	8	36	34
-2	2	8	32	31
-1	2	8	28	27
0	2	8	26	23
1	2	8	17	14
2	2	8	12	9
3	2	8	9	8
4	2	8	7	7
-8	3	8	10	10
-7	3	8	12	9
-6	3	8	8	8
-5	3	8	6	6
-3	3	8	6	4
3	3	8	7	-7
4	3	8	7	-7
-4	4	8	12	-12
-3	4	8	17	-16
-2	4	8	18	-16
-1	4	8	18	-15
0	4	8	14	-12
-5	-6	9	7	10
-4	-6	9	10	11
-3	-6	9	9	11
-2	-6	9	13	12
-1	-6	9	14	15
-8	-5	9	22	21
-7	-5	9	24	23
-6	-5	9	26	26
-5	-5	9	27	26
-4	-5	9	28	28
-3	-5	9	26	26
-2	-5	9	20	21
-1	-5	9	16	17
0	-5	9	12	14
1	-5	9	11	11
2	-5	9	10	11
-10	-4	9	14	13

TABLE 17 CONTINUED

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-9	-4	9	13	13	-5	-2	9	36	-34	-1	0	9	36	34	1	3	9	11	-10	-2	-2	10	37	36
-8	-4	9	9	10	-4	-2	9	37	-35	0	0	9	28	27	-6	-5	10	18	-16	-1	-2	10	32	32
-7	-4	9	8	8	-3	-2	9	31	-31	1	0	9	22	20	-5	-5	10	18	-17	0	-2	10	21	23
-6	-4	9	7	8	-2	-2	9	23	-24	2	0	9	18	16	-4	-5	10	19	-18	1	-2	10	17	17
-5	-4	9	5	6	-1	-2	9	19	-19	3	0	9	16	15	-3	-5	10	17	-18	2	-2	10	16	16
-3	-4	9	7	4	0	-2	9	16	-15	4	0	9	11	10	-2	-5	10	15	-17	3	-2	10	12	12
-1	-4	9	7	-7	1	-2	9	8	-7	5	0	9	8	7	-1	-5	10	15	-16	-9	-1	10	24	21
0	-4	9	9	-10	2	-2	9	7	-6	-9	1	9	19	17	-8	-4	10	18	-19	-8	-1	10	27	24
1	-4	9	12	-12	-11	-1	9	12	-10	-8	1	9	21	19	-7	-4	10	20	-22	-7	-1	10	24	23
2	-4	9	13	-12	-10	-1	9	12	-9	-7	1	9	20	18	-6	-4	10	23	-25	-6	-1	10	21	21
3	-4	9	13	-11	-9	-1	9	9	-8	-6	1	9	18	17	-5	-4	10	23	-25	-5	-1	10	20	20
4	-4	9	10	-11	-8	-1	9	7	-6	-5	1	9	16	14	-4	-4	10	23	-23	-4	-1	10	17	18
-10	-3	9	7	-7	-7	-1	9	5	-3	-4	1	9	7	8	-3	-4	10	25	-25	-3	-1	10	15	16
-9	-3	9	9	-11	-6	-1	9	9	8	-3	1	9	8	7	-2	-4	10	23	-22	-2	-1	10	12	14
-8	-3	9	14	-14	-5	-1	9	16	14	-2	1	9	6	7	-1	-4	10	18	-18	-1	-1	10	11	11
-7	-3	9	25	-24	-4	-1	9	17	17	-1	1	9	5	7	0	-4	10	13	-14	0	-1	10	8	9
-6	-3	9	32	-31	-3	-1	9	18	18	0	1	9	7	6	1	-4	10	8	-8	1	-1	10	5	3
-5	-3	9	35	-34	-2	-1	9	23	22	3	1	9	5	-5	2	-4	10	6	-5	-7	0	10	7	-2
-4	-3	9	40	-39	-1	-1	9	18	19	4	1	9	5	-7	-9	-3	10	11	-11	-5	0	10	7	-7
-3	-3	9	39	-39	0	-1	9	13	13	-5	2	9	12	-11	-8	-3	10	13	-11	-4	0	10	17	-15
-2	-3	9	32	-33	1	-1	9	13	13	-4	2	9	20	-17	-7	-3	10	7	-6	-3	0	10	19	-18
-1	-3	9	26	-28	2	-1	9	22	22	-3	2	9	21	-19	-3	-3	10	9	8	-2	0	10	20	-20
0	-3	9	26	-26	3	-1	9	21	20	-2	2	9	22	-19	-1	-3	10	8	8	-1	0	10	20	-20
1	-3	9	25	-26	4	-1	9	18	18	-1	2	9	22	-20	0	-3	10	10	9	0	0	10	21	-20
2	-3	9	23	-22	5	-1	9	14	15	0	2	9	19	-19	1	-3	10	10	10	1	0	10	15	-13
3	-3	9	22	-20	-10	0	9	16	15	1	2	9	17	-14	2	-3	10	10	11	2	0	10	12	-11
4	-3	9	18	-18	-9	0	9	20	19	2	2	9	15	-13	3	-3	10	11	11	3	0	10	11	-9
5	-3	9	15	-14	-8	0	9	21	20	3	2	9	13	-10	-9	-2	10	15	15	-7	1	10	21	-19
-11	-2	9	22	-19	-7	0	9	22	23	-5	3	9	15	-13	-8	-2	10	14	16	-6	1	10	21	-19
-10	-2	9	22	-22	-6	0	9	33	30	-4	3	9	16	-13	-7	-2	10	13	17	-5	1	10	21	-19
-9	-2	9	25	-25	-5	0	9	36	35	-3	3	9	17	-14	-6	-2	10	24	25	-4	1	10	21	-20
-8	-2	9	28	-29	-4	0	9	40	39	-2	3	9	16	-14	-5	-2	10	29	28	-3	1	10	25	-22
-7	-2	9	26	-26	-3	0	9	40	38	-1	3	9	15	-13	-4	-2	10	31	31	-2	1	10	22	-19
-6	-2	9	31	-31	-2	0	9	37	36	0	3	9	12	-12	-3	-2	10	35	33	-1	1	10	18	-18
0	1	10	17	-17	1	1	10	15	-15	2	1	10	11	-10	-5	2	10	9	-8					

together with thermal parameters in Table 13, while observed and calculated structure factors are presented in Table 14. Inspection of the estimated standard deviations in Table 13 reveals that these are very large, as is the discrepancy between F_o and F_c values in Table 14, indicating that there are already traces of crystal instability.

4.4.3 Reduced data: Phase III

The intensity data collected for the last 826 reflections gave rise to the same coordinates for the mercury atom in the space group $P\bar{1}$, as in Phase I. This was followed by difference fourier map, yielding positions of all non-hydrogen atoms, with the residual index reduced to 0,086 after four cycles of least squares refinement. A further four cycles of refinement which included all phenyl hydrogen atoms constrained at 1,00Å from their parent carbon atoms, and with the mercury treated anisotropically, left *R* unchanged. Although no weighting scheme had been introduced, the analysis of variance (Table 15) computed after the final cycle of refinement, was satisfactory. In view of the conditions of data collection and limited data, the structure elucidated for Phase III was taken as being the most representative of the crystal structure of PMBM. Table 16 lists the final atomic coordinates and thermal parameters, while Table 17 presents the observed and calculated structure factors.

4.5 DESCRIPTION OF THE STRUCTURE

Description of the structure will be based on results obtained for Phase III, the last 826 reflections. These results are virtually the same as those for Phase I, the first 1000 reflections, except they display a greater degree of accuracy. The molecule, with its symmetry

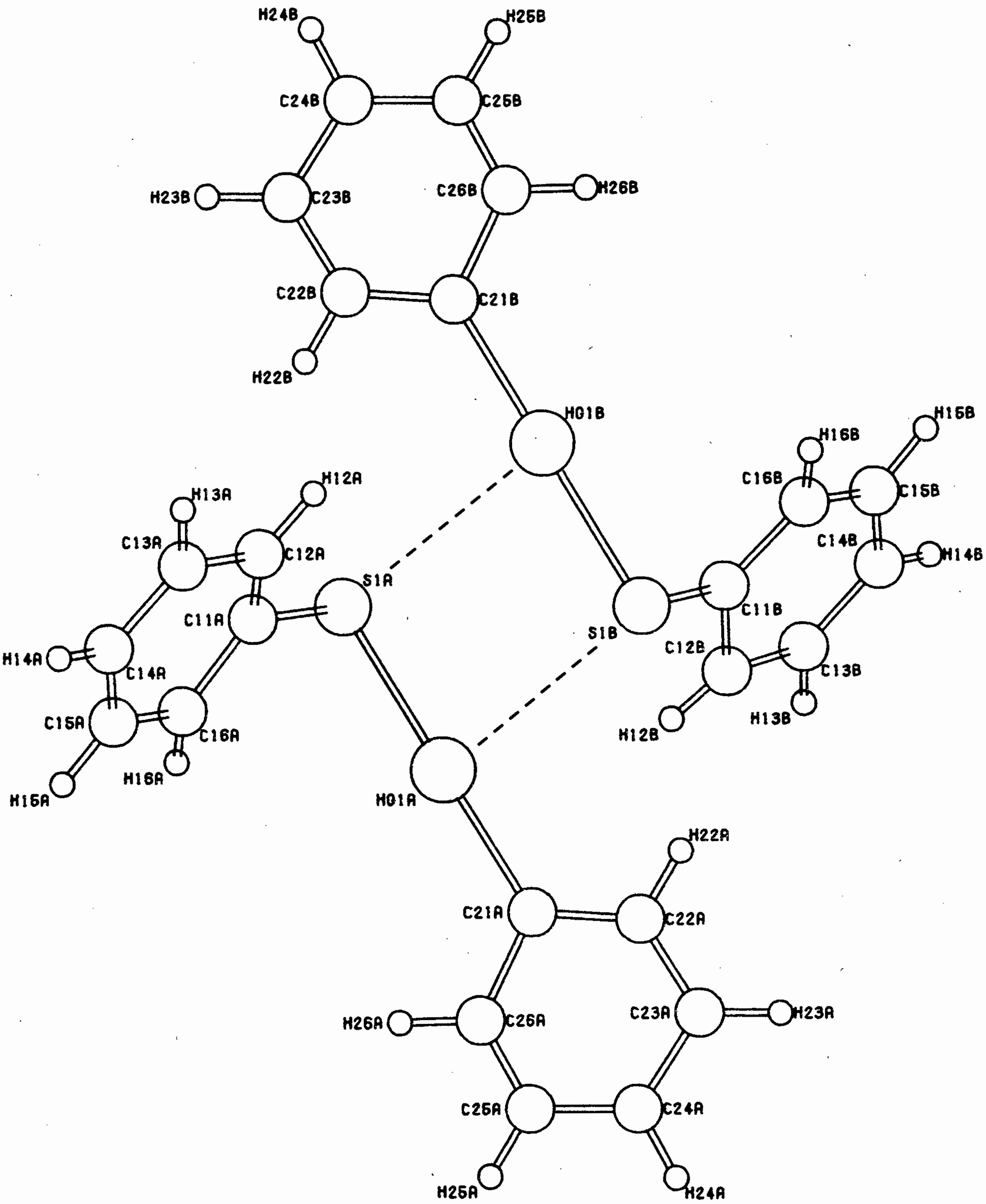


FIGURE 8   PERSPECTIVE VIEW OF PMBM WITH SYMMETRY RELATED COUNTERPART

related counterpart is shown in a perspective view with atomic nomenclature in Figure 8. Intramolecular bond lengths and angles, together with their estimated standard deviations are listed in Tables 18 and 19 respectively.

Molecular structure

The phenylmercury moiety is bonded to the sulphur atom of the thiophenol group. The molecule is planar with the exception of the phenyl ring attached to the sulphur atom. The characteristic coordination of the mercury atom is digonal with a virtually linear C(21) - Hg - S bond. The C(21) - Hg and Hg - S bonds are 2,06(3) and 2,37(1)Å respectively, with an angle of 177(1)° between them. These bond lengths compare favourably with those calculated from theoretical covalent radii, where $r(\mathrm{Hg}) = 1{,}30$ (Grdenić)[15] and $r(\mathrm{S}) = 1{,}04$, $r(\mathrm{C}) = 0{,}77$Å (Pauling)[24]. Calculated covalent bond distances for Hg - C and Hg - S are respectively 2,07 and 2,34Å. These co-incide with bond lengths in similar structures[28,29]. The slight (3°) deviation from linearity may be caused by geometric constraints[29] on the molecule within the crystal lattice. The Hg - S - phenyl moiety is remarkably planar, with maximum deviation displayed by C(22), at 0,10Å above the plane which is defined by

$$7{,}3093X + 2{,}2195Y + 3{,}5755Z = 1{,}7221.$$

Phenyl ring I, attached to the sulphur atom, is defined by the plane

$$-3{,}1350X + 2{,}8249Y + 6{,}7875Z = 4{,}6602.$$

This plane is oriented at 60,77° to that of the remainder of the molecule. The torsion angle of C(21) - Hg - S - C(11) is -35,92°, which shows that the phenyl ring I lies to one side of the

S - Hg - phenyl ring II group. The Hg - S - C(11) angle is 105(1)°, in keeping with the hybridisation of sulphur, and supported by numerous similar structures[30,31,37,46] including PMPM reported in Chapter 3.

Intermolecular interactions

As before, Hg---S secondary interactions take place, this time across the centre of symmetry. The approach is closer than in the case of PMPM, with a Hg---S distance of 3,20Å. This is well within the limits set by van der Waals radii (3,39Å based on r_{vdw} for Hg and S given by Grdenić[15] and Pauling[24] respectively). By virtue of the centre of symmetry a four membered bridging interaction in the shape of rhomboid is formed. The mercury atoms are separated by 4,24Å, and the sulphur atoms by 4,09Å along the diagonals. Hg - phenyl ring interactions, if they do occur, are extremely weak. The Hg atom of the molecule placed at x,y,z lies 3,87Å from the nearest carbon atom, C(24), of the phenyl ring attached to the Hg atom of the molecule at $\bar{x},\bar{y},\bar{z}$. This distance is greater than those currently observed, which range from 3,05 to 3,52Å[33,34,36,47]. Although the orientation of the phenyl ring is favourable, the interaction, if any, is almost negligable. Similarly, phenyl - phenyl ring interactions between the thiophenol moieties of the molecules placed at x,y,z and $1\text{-}x,1\text{-}y,1\text{-}z$ are not possible as there is a distance of about 8Å separating them.

The mercury atom has digonal characteristic coordination, with one additional secondary intermolecular interaction to sulphur. Mercury thus displays irregular three-coordination with T-shaped geometry at the Hg atom. This is unusual, as the largest category of organomercury compounds display digonal coordination which is commonly supplemented by two additional secondary interactions yielding distorted tetrahedra.

Nevertheless, a few examples of three-coordinate mercury (II) complexes have been reported[48,49,50].

TABLE 18 BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Hg - S	2,37(1)
Hg - C(21)	2,06(3)
S - C(11)	1,80(5)
C(21) - C(22)	1,36(8)
C(22) - C(23)	1,29(8)
C(23) - C(24)	1,43(6)
C(24) - C(25)	1,51(6)
C(25) - C(26)	1,37(5)
C(26) - C(21)	1,41(5)
C(11) - C(12)	1,30(7)
C(12) - C(13)	1,41(12)
C(13) - C(14)	1,49(13)
C(14) - C(15)	1,34(14)
C(15) - C(16)	1,33(9)
C(16) - C(11)	1,39(6)
All C - H	1,00

TABLE 19 BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

C(21) - Hg - S	177(1)
Hg - S - C(11)	105(1)
S - C(11) - C(12)	117(4)
S - C(11) - C(16)	118(4)
C(11) - C(12) - C(13)	120(6)
C(12) - C(13) - C(14)	118(9)
C(13) - C(14) - C(15)	114(9)
C(14) - C(15) - C(16)	127(7)
C(15) - C(16) - C(11)	115(6)
C(16) - C(11) - C(12)	125(5)
Hg - C(21) - C(22)	124(3)
Hg - C(21) - C(26)	115(3)
C(21) - C(22) - C(23)	118(6)
C(22) - C(23) - C(24)	126(6)
C(23) - C(24) - C(25)	114(4)
C(24) - C(25) - C(26)	116(4)
C(25) - C(26) - C(21)	122(5)
C(26) - C(21) - C(22)	120(4)

[a] All H - C bond angles are fixed according to the hybridisation of the C atom

TABLE 20 TORSION ANGLES (DEGREES)[a]

C(21) - Hg - S - C(11)	-35,9
Hg - S - C(11) - C(12)	122,5
Hg - S - C(11) - C(16)	-54,5
S - C(11) - C(12) - C(13)	180,0
S - C(11) - C(16) - C(15)	174,9
C(11) - C(12) - C(13) - C(14)	0,0
C(12) - C(13) - C(14) - C(15)	7,3
C(13) - C(14) - C(15) - C(16)	-13,8
C(14) - C(15) - C(16) - C(11)	11,4
C(15) - C(16) - C(11) - C(12)	-1,9
C(16) - C(11) - C(12) - C(13)	-3,2
S - Hg - C(21) - C(22)	-99,7
S - Hg - C(21) - C(26)	89,9
Hg - C(21) - C(22) - C(23)	173,0
Hg - C(21) - C(26) - C(25)	174,8
C(21) - C(22) - C(23) - C(24)	22,1
C(22) - C(23) - C(24) - C(25)	-13,1
C(23) - C(24) - C(25) - C(26)	0,0
C(24) - C(25) - C(26) - C(21)	4,4
C(25) - C(26) - C(21) - C(22)	3,9
C(26) - C(21) - C(22) - C(23)	-16,9

[a] The torsion angle is defined as in Table 8.

TABLE 21 LEAST-SQUARES PLANES

(a) The equations of least-squares planes are expressed in orthogonalised space as $pX + qY + rZ = S$.

Plane 1 : Calculated from phenyl ring 1 atoms

$-3,1350X + 2,8249Y + 6,7875Z = 4,6602$

Plane 2 : Calculated from phenyl ring 2 atoms

$7,3599X + 2,2190Y + 3,5254Z = 1,7273$

Plane 3 : Calculated from phenyl ring 2, Hg and S

$7,3093X + 2,2195Y + 3,5755Z = 1,7221$

(b) Deviation from planes (Å x 10^3)

	Plane 1	*Plane 2*	*Plane 3*
H	-1878	12	34
S	1	-63	-26
C(11)	22	-1459	-1419
C(12)	-26	-2408	-2363
C(13)	-10	-3524	-3477
C(14)	54	-3562	-3517
C(15)	-65	-2585	-2545
C(16)	25	-1479	-1442
C(21)	-3567	-41	-34
C(22)	-4489	102	104
C(23)	-5573	-84	-89
C(24)	-5740	9	-21
C(25)	-4621	44	39
C(26)	-3616	-29	-25

TABLE 21 CONT/....

TABLE 21 CONTINUED

(c) Selected angles (degrees) between normals to planes

Planes 1 and 2	61,1
Planes 1 and 3	60,8
Planes 2 and 3	0,4

CHAPTER 5

DISCUSSION

CHAPTER 5

DISCUSSION

Interest in the structural chemistry of mercury, combined with detailed studies of the toxicology of mercury on a biochemical level, emphasises the relationship of mercury and sulphur in both primary and secondary coordination.

Upon examination of stability constants of 1 : 1 mercuric complexes in Table 22, the cysteine ligand has a logk_1 value three times greater than any other, by virtue of the Hg - S affinity.

TABLE 22 STABILITY CONSTANTS OF 1 : 1 MERCURIC COMPLEXES

Ligand	*Log*k_1	*ref*
Cl^-	6,74	51
Br^-	9,05	51
I^-	12,87	51
OH^-	10,30	52
NH_3	8,80	53
Imidazole	3,57	53
Ethylenediamine (N - N)	14,30	53
Cysteine (N - S)	45,40	53
Glycine (N - O)	10,30	53
Histidine	7,90	53

Although the thermodynamic stability of organomercury complexes (predominantly $MeHg^+$) with sulphydryl groups of sulphur containing peptides and proteins is high, the Hg - S bond is labile as it exchanges among a vast number of available sulphydryl groups to ultimately combine with target molecules in the brain. This lability is made use of with sulphydryl containing chemotherapeutic agents such as *N*-acetyl-*D*,*L*-penicillamine which extract organomercurials from red blood cells and tissues

This lability has also been observed by a totally different technique, an *in vitro* system which may be likened to the *in vivo* system discussed above, namely nuclear magnetic resonance, by Bach and Weibel[12].

The Hg - S bridging in both PMPM and PMBM indicates that the molecules may be "frozen" shortly before exchange would occur were they in solution. The secondary Hg - S distance is somewhat shorter in PMBM than in PMPM (3,20 and 3,37Å respectively). The primary Hg - S bonds, however, are the same (2,37(1) and 2,38(1)Å respectively). This is also the case with $[Hg(CH_3)(C_5H_6N_3S)]$, where Hg - S is 2,39Å and Hg---S is 3,67Å.

It is interesting to note that the methyl derivative corresponding to PMPM displays no such Hg---S interactions, and has an entirely different packing arrangement. The molecular structure, however, is virtually identical to that of PMPM, with an intramolecular Hg---N interaction of 2,83Å (that of PMPM is 2,86Å). This arrangement is also shared by the two substituted thiopyrimidine derivatives of methylmercury, $[Hg(CH_3)(C_5H_6N_3S)]$ and $[Hg(CH_3)(C_4H_4N_3OS)]$, which have Hg---N distances of 2,80 and 2,95Å[30]. In all examples of thiopyrimidine organomercurials, the pyrimidine ring and the S and H atoms are co-planar, with the characteristic Hg---N interaction.

When the pyrimidine ring is replaced by a benzene ring, as was the case for PMBM, this pattern changes. The phenyl - Hg - S moiety is planar, with the phenyl ring at 61° to this plane, away from the centre of symmetry about which the Hg---S interaction occurs. The Hg---N interaction must therefore be the restraint upon the pyrimidine deviations keeping them in a planar conformation for closest approach to the mercury atom. The structures of PMPM and PMBM clearly illustrate Grdenić's classification of coordination types. Both molecules, by virtue of their Hg - S and Hg - C bonds, are classified as having digonal characteristic coordination. In PMPM this is supplemented by four additional weak interactions (2 x Hg---S, Hg---N, Hg---phenyl) resulting ultimately in octahedral effective coordination. In the case of PMBM, the digonal characteristic coordination is supplemented only by one Hg---S secondary interaction (discounting the very weak Hg---phenyl interaction), creating an effectively 3-coordinated species. This has also been found for phenyl- and methylmercury(II) dithizonate[54]. Grdenić has remarked on the larger Hg - C bonds in aryl- compared with alkylmercury(II) derivatives. This is found for the two dithizonate derivatives (2,12 and 2,06Å for phenyl- and methyl- substituted molecules respectively)[54], and is again evident for PMPM and its corresponding methylmercury derivative[31], these being 2,12 and 2,09Å respectively.

PART 2

CHAPTER 6

INTRODUCTION

CHAPTER 6

INTRODUCTION

6.1 THE PRINCIPLE OF STRUCTURAL CORRELATION

Until recently, it seemed as if the field of chemical crystallography and that of reacting systems could share little common ground.

In 1974 Dunitz and Bürgi entered into this grey area, and generated a relationship between the two with a whole new concept, namely that of structural correlation. They describe this as follows[55]:

> "The basic idea behind the structural approach is to search for correlations between certain selected parameters describing the geometry of some sub-system (say, a tetrahedral centre), frozen in a variety of crystal or molecular environments. Each kind of environment can be regarded as a perturbation that acts on the sub-system, which will slightly modify its structure so as to minimize the potential energy of the crystal as a whole.... These structural modifications should occur along local energy valleys in the parameter space defining the sub-system. Accordingly, if some correlation can be found among the experimentally observed parameters, then the correlation function can be taken as describing a minimum energy path in the Born-Oppenheimer surface of the sub-system in question. If the pattern of parameter changes can be identified in a general sense, with that expected to occur in the course of a chemical reaction, then the path found from such experimental data should be a fair approximation to the corresponding reaction path."

A forerunner in this field, Bent[56] proposed that "certain kinds of attractive intermolecular interactions may be viewed as incipient valence shell expansions and often as the first stage of bimolecular nucleophilic replacement reactions." He stressed the correlation between the two I---I distances in the linear triatomic I_3^- anion, represented by a hyperboloid curve. Similar curves for the systems S—S---S and O—H---O showing correlation have also been published (See Fig. 9)[57]. The relationship between these curves and the minimum energy path on the calculated potential energy surface was exposed by Liu[58], in studies of the linear H_3 system, as equilibrium H---H distances may be superimposed directly on the minimum energy path (See Fig. 10). This brings us to the question, also posed at a meeting of the Chemical Society's Crystallography Group, "How much of a bond is a bond?"[59]. Grdenić[16], in his review on the structural chemistry of mercury is confronted by this same issue:

> "... nearest neighbours of mercury in a crystal structure are those in 'contact' with it. In a free molecule these contacts are chemical bonds.... With a crystal structure the position is less clear, and it is necessary to restrict the consideration of nearest neighbours of mercury to those within a defined distance. This is difficult for mercury, as frequently the distances between the surrounding atoms and mercury do not follow the additivity rule of the atomic radii currently accepted, yet are less than the sum of the van der Waals radii".

He acknowledges the necessity of adopting a suitable set of atomic radii, and proposes values based on those of Aurivillius[60], Pauling and Huggins[61], Grdenić[16], and those observed experimentally, for mercury in its different coordination states.

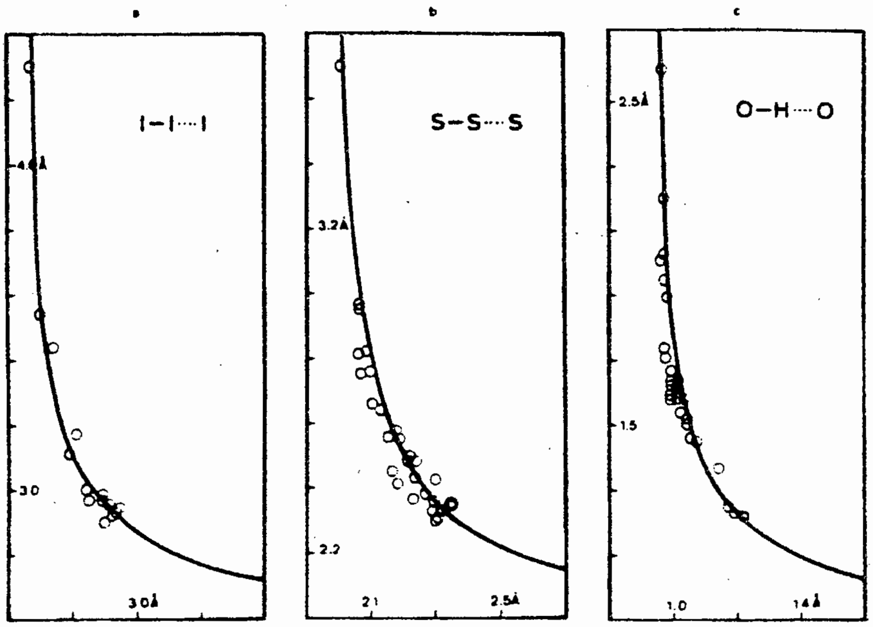


FIGURE 9 CORRELATION PLOTS OF INTERATOMIC DISTANCES IN LINEAR TRIATOMIC SYSTEMS. (a) TRIIODIDE ANIONS, (b) THIATHIOPHTHENES, AND (c) O - H---O HYDROGEN BONDS. FROM Bürgi, *Angew. Chem., Intern. Ed.* *14* (1975) 460.

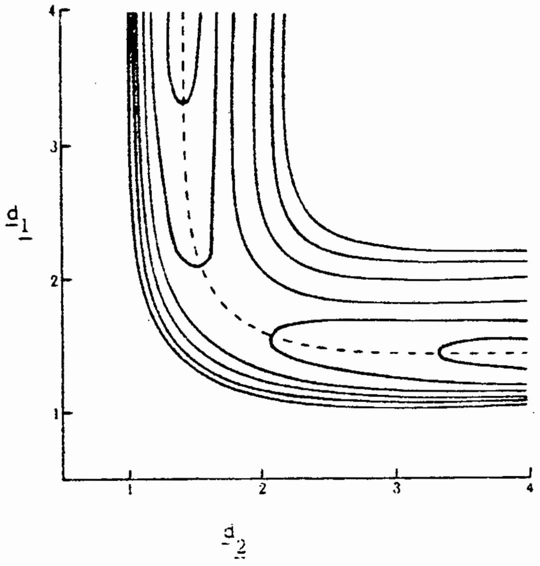


FIGURE 10 POTENTIAL ENERGY SURFACE FOR LINEAR H_3 SYSTEM DRAWN FROM DATA CALCULATED BY Liu, *J. Chem. Phys.* *58* (1973) 1925. Distances are in bohr units (1 bohr = 0,529Å), and contour lines are drawn at energy intervals of 0,01 hartrees. (1 hartree = 27,21 eV)

It is this flexibility of bond length and other parameters such as distortion of molecular geometry which forms the basis of the concept of structural correlation.

This technique has in recent years found successful application in the investigation of reaction pathways. Examples include the ligand-exchange reaction

$$XCdL_3 + Y \rightarrow X{-}{-}{-}CdL_3{-}{-}{-}Y \rightarrow X + L_3CdY$$

involving a S_N2 mechanism[62], pathways for S_N2 and S_N3 substitution at Sn(IV)[63], nucleophilic addition to a carbonyl group[64], and interactions of nucleophiles with quaternary phosphonium centres[65]. Comprehensive reviews have already been compiled by Bürgi[57] and Murray-Rust[59].

6.2 THE STRUCTURAL CHEMISTRY OF MERCURY

The structural chemistry of mercury has been reviewed by both Wells[66] and Grdenič[15,16]. In his discussion of mercuric (Hg(II)) compounds, Wells acknowledges the tendency of mercury to form either two collinear or four tetrahedral bonds. In cases of formation of two collinear bonds, further coordination occurs to complete a distorted octahedron. He compares this (2 + 4)-coordination to the (4 + 2)- or less likely (2 + 4)-coordination often found for Cu(II) complexes. The formation of tetrahedral species is described as the addition of two more ligands causing deviation from linearity in the two existing bonds. The discussion of bond lengths in this review is neglected.

Grdenič completes this picture, adding much detail. The initial problem faced was that of classification of coordination, as difficulty arises from inconsistencies between observed bond lengths and the additivity rule of atomic radii currently accepted. This is overcome by using the connection principle for classification.

The connection principle is based on the fact that certain links of a given atom with other atoms may be selected in order to identify a repeating unit and thus to elucidate the building pattern of the structure, these units possibly being isolated groups, chains, columns, layers or lattices. More specifically, he proposes two types of coordination contributing to this connection principle, namely characteristic and effective coordination.

The mercury coordination sphere comprises all atoms surrounding mercury at a distance less than the sum of the van der Waals radii, *i.e.* $[d(\text{Hg} - \text{L}) < r(\text{Hg}) + r(\text{L})]$. The characteristic coordination number, m, applies to the system HgL_m when all m Hg - L bond distances are equivalent. Characteristic coordination numbers of two, three and four, yielding two collinear, three co-planar and four tetrahedral bonds formed by means of sp, sp^2 or sp^3 hybridisation of the mercury atom, are commonly observed. Octahedral and trigonal bipyramidal (sp^3d^2 and sp^3d) are less common.

In each case a different covalent radius of mercury is applicable. These are listed in Table 23.

The relationship between m and $r_m(\text{Hg})$ may be expressed by $r_m(\text{Hg}) = 0{,}095m + 1{,}110$.

TABLE 23 COVALENT RADII OF MERCURY (Å)

m[a]	r_m(Hg)
2	1,30 (or 1,34)[b]
3	1,39
4	1,49
5	1,60
6	1,68

[a] m : characteristic coordination number

[b] In his second review Grdenić states that the most reliable values for r_2(Hg) are 1,34Å proposed by Aurivillius (1965)[60], and 1,30Å proposed by himself (1965)[15] based on observed bond lengths in compounds having Hg - L, where L has low electronegativity.

The characteristic coordination is supplemented by a secondary bond formation, the effective coordination. This is the actual coordination of mercury observed, often irregular and causing distortion. Thus we arrive at HgL_mL_{n-m}, where n is the effective coordination number, and the L_{n-m} ligands have bond distances within the sum of the relevant van der Waals radii. A van der Waals radius of 1,54Å is currently proposed for mercury.

The most frequently observed effective coordination occurs for $m = 2$, yielding HgL_2L', HgL_2L_2', HgL_2L_4'. The linearity of the HgL_2 moiety is usually disturbed, and the Hg - L bond distance often lengthened. The most common arrangement is distorted tetrahedral effective coordination, with parameters between $n = 4$, $m = 2$ and $m = 4$, *i.e.* HgL_2L_2' and HgL_4.

In their revision of covalent radii and the additivity rule for the lengths of partially ionic single covalent bonds, Schomaker and Stevenson propose corrections to covalent bonds taking the electro=negativities of participating atoms into account.

This has been applied in the calculation of covalent bonds in mercury compounds, with an electronegativity $x(\mathrm{Hg}) = 1{,}9$ assigned to mercury. Classification of crystal structures of mercury compounds may be made on the basis of the electronegtivity difference of mercury and the ligand, *i.e.* $[x(\mathrm{Hg}) - x(\mathrm{L})]$. $x(\mathrm{L}) = 2{,}5$ has been shown to be a critical value, as when $x(\mathrm{L}) > 2{,}5$, digonal characteristic coordination is generally observed, whereas for $x(\mathrm{L}) < 2{,}5$ a tetrahedral effective coordination is more common. In the case of sulphur and iodine ($x(\mathrm{L}) = 2{,}5$ in both cases), the former is usually digonal whereas the latter is tetrahedral. The majority of mercury compounds have $x(\mathrm{L}) > 2{,}5$, accounting for the predominance of $m = 2$ and $n = 6$ in this category.

6.3 THE CALCULATION OF COVALENT AND VAN DER WAALS RADII

Covalent radii have been calculated in cases of two collinear or four tetrahedral bonds, using radii for Hg as recommended by Grdenić[16], and those of other atoms from Pauling[24]. Electronegativity effects influencing bond length have been accounted for by using the Schomaker-Stevenson[67] equation:

$$r_{AB} = r_A + r_B - \beta(x_A - x_B)$$

where r_N : single covalent radius of the atom N

x_N : electronegativity of atom N

β : constant = 0,09

Covalent radii, electronegativities and proposed covalent bond lengths are listed in Table 24, while the corresponding van der Waals radii are reported in Table 25. The latter are calculated by the simple convention of additivity.

TABLE 24 COVALENT ATOMIC RADII (Å)[a], ELECTRONEGATIVITIES[b] AND BOND LENGTHS (Å)[a]

Atom	r	x	*Bond*	$r_{AB}(dig)$	$r_{AB}(tet)$
Hg(tet)	1,49	1,9	Hg - S	2,39(2,34)	2,58
Hg(dig)	1,30(1,34)	1,9	Hg - C	2,12(2,16)	2,31
S	1,04	2,5	Hg - O	2,10(2,14)	2,29
C	0,77	2,5	Hg - N	2,10(2,14)	2,29
O	0,66	3,5	Hg - Cl	2,39(2,43)	2,58
N	0,70	3,0	Hg - Br	2,52(2,56)	2,71
Cl	0,99	3,0	Hg - I	2,68(2,72)	2,87
Br	1,14	2,8	Hg - Hg	2,64(2,68)	2,97
I	1,33	2,5			

[a] According to Grdenič[16] for Hg, otherwise according to Pauling[24].
[b] According to Pauling[24].

TABLE 25 VAN DER WAALS Hg - L DISTANCES (Å)[a]

Atom	r_{vdw}	*Bond*	r_{AB}
Hg	1,54	Hg - S	3,39
S	1,85	Hg - C	3,24
C	1,70	Hg - O	2,94
O	1,40	Hg - N	3,04
N	1,50	Hg - Cl	3,34
Cl	1,80	Hg - Br	3,49
Br	1,95	Hg - I	3,69
I	2,15	Hg - Hg	3,08

[a] According to Pauling[24].

CHAPTER 7

STRUCTURAL CORRELATIONS
OF
MERCURY - SULPHUR COMPOUNDS

CHAPTER 7

7.1 MERCURY AND SULPHUR

The interaction of mercury and sulphur is of great biochemical interest and of toxicological importance, as has been discussed in detail in Part I of this work.

Attention is now given to their relationship in crystalline form. Structures containing at least one Hg - S covalent bond are considered with respect to their molecular geometry. Parameters defining this molecular geometry are investigated by methods involving structural correlation.

As mentioned previously, sulphur has an electronegativity of 2.5[24], which means that both tetrahedral and digonal characteristic coordination is observed according to the criteria set by Grdenić[15].

Upon inspection of structural data, virtually all of the compounds display geometries based on digonal characteristic coordination. The 4 - coordinated structures generally form very distorted tetrahedra, favouring a linear bond despite the fact that mercury has equal capability of sp, sp^2 or sp^3 hybridisation. We observe mercury displaying the ability to expand its coordination number of two, to form stereochemically non-rigid four- and six-coordinated complexes.

In the application of structural correlations, structures having one mercury - sulphur primary interaction were selected. It was found that the vast majority were distorted tetrahedra, and almost all had an additional mercury - sulphur primary interaction. Pathways from two-to four- and four- to six-coordinate Hg(II) are investigated. These pathways are assumed to follow the theoretical potential energy valleys for such reactions. Changes from two- to four- and four- to six-coordination would involve a three-body collision in a chemical reaction, which although highly improbable, has been observed in the gaseous phase.

Nevertheless, nominally tetrahedral moldecules, R_2MX_2 in crystal environments are often found coordinated to two additional ligands Y, and this is commonly referred to as an S_N3 type displacement.

i.e. $$R_2Hg + X_2 \rightleftharpoons [R_2HgX_2] + Y_2 \rightleftharpoons R_2HgX_2Y_2$$

This has been investigated in the examination of reaction pathways for substitution at Sn(IV)[63].

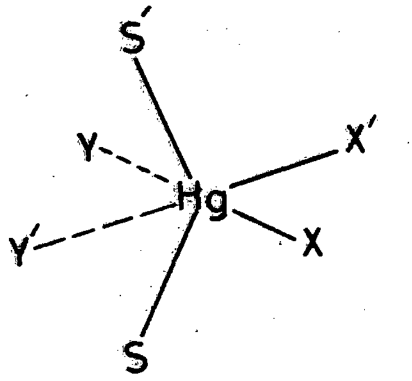
Geometrically there are three possible ways in which the Y atoms can approach a tetrahedral centre. These are shown in Figure 11. These can be seen to yield octahedral structures with (a) trans R, cis X, cis Y groups, (b) trans X, cis R, cis Y groups and (c) cis R, cis X, cis Y groups. The structures examined all relate to 11(a), where R represents sulphur atoms, X represents atoms coordinating to form a tetrahedron and Y represents atoms coordinating weakly to form octahedra.

7.2 CLASSIFICATION OF THE DATA

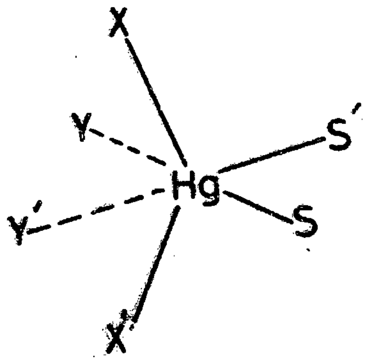
An investigation covering all compounds containing mercury was carried out using the Cambridge Crystallographic Data File. The search yielded 360 compounds, of which only 125 contained both mercury and sulphur.

FIGURE 11 POSSIBLE DIRECTIONS OF APPROACH OF TWO NUCLEOPHILIC GROUPS Y AND Y' TO HgS_2XX'.

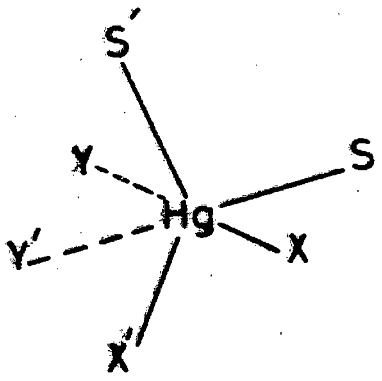
(a) S trans, X cis, Y cis:



(b) X trans, S cis, Y cis:



(c) S cis, X cis, Y cis:



Of those eliminated, the majority had extremely weak or no interaction between sulphur and mercury at all, and a few were rejected on grounds of disorder, or had no positional coordinates given. The 47 compounds selected are classified and correlations are examined.

In the classification of the data, each type of mercury environment $HgS_pX_qY_r$ is considered. There are three main groups based on the effective coordination *i.e.* octahedral, tetrahedral and digonal. The characteristic coordination, which is predominantly digonal, is not used as a criterion in the classification. All ligands within their respective van der Waals distance (see Table 25) were considered as interacting with mercury and contributing to the coordination sphere.

(a) Octahedral coordination: This group has seven examples only, displaying distorted octahedra.
There is one example only of HgS_6, as there is for HgS_4X_2 where X = Br. In the group HgS_3X_3 we see two examples, where X = Br and X = Cl. For HgS_2X_4 there are three examples, namely X = Cl, Br and N.

(b) Tetrahedral coordination: There are thirty-six examples of mercury in a tetrahedral environment; once again these are very distorted.
Twelve examples have HgS_4, one has HgS_3X where X = C. For HgS_2X_2 there are twenty-one examples, *i.e.* four HgS_2Br_2, nine HgS_2Cl_2, four HgS_2I_2, three HgS_2N_2 and one HgS_2P_2. In the case of $HgSX_3$, both examples have X = Cl.

(c) In the other coordination types there are few examples. Digonal coordination, which is proposed by Grdenič as very feasible for

Hg - S, in usually supplemented by further interactions forming geometries classified in (a) and (b) above. There is one example of digonal coordination, HgSC. In addition, three examples of five-coordinated species were found: HgS_4N, HgS_2O_2N, HgS_2O_3.

The picture that emerges is one of predominantly tetrahedral geometry, although very distorted and based on digonal coordination. The majority of structures have an HgS_2 moiety, in which the sulphur molecules generally lie trans to each other.

Upon initial consideration the concept of structural correlation seems an easy, straightforward analysis of data - a mere examination of a series of conformations frozen into various stages of a reaction pathway, in a crystalline state. However, the correlations involve relatively complex systems from which only the mercury atom and surrounding atoms are isolated. The properties of these surrounding atoms (*i.e.* those within the sphere of coordination) such as their electronegativity, atomic radius, the atoms with which they in turn interact and the stereochemistry imposed by crystal packing, are extremely influential in the geometry. It is very difficult to include all of these factors in a single scheme or correlation. This sometimes leads to large scatter along a correlation curve, as will be seen in the following correlation involving bond angles, electronegativities, van der Waals radii and bond lengths.

7.3 TRENDS IN COORDINATION GEOMETRY

Upon critical examination of the data in Table 26, it may be seen that not only do the vast majority of compounds display tetrahedral coordination to the mercury atom, but in the case of the octahedral

TABLE 23: DATA FROM CAMBRIDGE CRYSTALLOGRAPHIC DATA FILE.

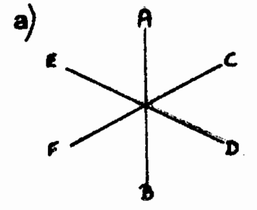
a) Six-coordinated Mercury

ref:	descr	A:	Hg-A: Å	Δd_A Å	B:	Hg-B: Å	Δd_B Å	C:	Hg-C: Å	Δd_C: Å	D:	Hg-D: Å	Δd_D Å	E:	Hg-E: Å	Δd_E Å	F:	Hg-F: Å	Δd_F: Å	A-Hg-B: (deg)	C-Hg-D: (deg)	E-Hg-F: (deg)
MEDSBT	HgS_6	S	2·48	0·09	S	2·45	0·06	S	3·54	1·15	S	3·54	1·15	S	3·54	1·15	S	3·54	1·15	178·6	90·0	90
BHGETC	HgS_4Br_2	S	2·38	-0·01	S	2·36	-0·03	S	3·11	0·72	S	3·09	0·70	Br	3·15	0·76	Br	3·06	0·67	164·4	115·4	85·8
ETACHG	HgS_3Br_3	S	2·45	0·06	S	2·43	0·04	Br	2·81	0·39	Br	2·99	0·47	S	2·80	1·11	Br	3·21	0·69	162·9	95·9	95·7
CMCPHG	HgS_2Cl_4	S	2·46	0·07	S	2·46	0·07	Cl	2·62	0·23	Cl	2·62	0·23	Cl	3·74	1·35	Cl	3·74	1·35	139·8	116·8	93·8
METHGD	HgS_3Cl_3	S	2·43	0·04	S	2·43	0·04	Cl	2·71	0·32	Cl	2·92	0·53	Cl	3·06	0·67	S	3·46	1·07	163·1	99·3	94·5
TSCHGB	HgS_2Br_4	S	2·45	0·06	S	2·45	0·06	Br	2·86	0·34	Br	2·86	0·34	Br	3·44	0·92	Br	3·44	0·92	155·0	97·1	91·4
TCPOLM	HgS_2N_4	S	2·62	0·23	N	2·43	0·33	S	2·58	0·19	N	2·52	0·42	N	2·52	0·42	N	2·42	6·32	160·3	93·1	91·4

b) Four-coordinated Mercury

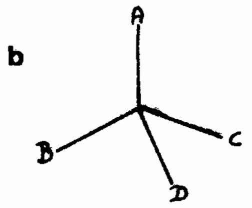
ref:	descr	A:	Hg-A: Å	Δd_A Å	B:	Hg-B: Å	Δd_B Å	C:	Hg-C: Å	Δd_C: Å	D:	Hg-D: Å	Δd_D Å	A-Hg-B:	C-Hg-D:
BMTUHG	HgS_2Br_2	S	2·41	0·02	S	2·41	0·02	Br	2·71	0·19	Br	2·93	0·41	148·5	94·6
BTETHG	HgS_2Br_2	S	2·66	0·27	S	2·66	0·27	Br	2·80	-0·02	Br	2·50	-0·02	98·5	134·8
CETCHG	HgS_2Cl_2	S	2·42	0·03	S	2·41	0·02	Cl	2·72	0·33	Cl	2·77	0·38	154·3	99·7
CLTCHG	HgS_2Cl_2	S	2·45	0·06	S	2·42	0·03	Cl	2·62	0·23	Cl	2·58	0·19	129·9	96·1
ENHGTC	HgS_2N_2	S	2·43	0·04	S	2·53	0·14	N	2·31	0·21	N	2·33	0·23	111·3	79·4
HGCSCD	HgS_2Cl_2	S	2·53	0·14	S	2·59	0·20	Cl	2·49	0·10	Cl	2·51	0·12	109·2	98·9
HGCTOX	HgS_2Cl_2	S	2·54	0·15	S	2·53	0·14	Cl	2·43	0·04	Cl	2·52	0·13	114·6	114·0
HGITUR	HgS_2I_2	S	2·46	0·07	S	2·46	0·07	I	2·84	0·16	I	2·84	0·16	123·7	101·4
HGTHZO	HgS_2N_2	S	2·42	0·03	S	2·42	0·03	N	2·56	0·46	N	2·56	0·46	155·5	101·7
IETHGH	HgS_2I_2	S	2·74	0·35	S	2·67	0·28	I	2·67	-0·01	I	2·67	-0·01	96·3	134·0
IHGTUR	HgS_2I_2	S	2·83	0·44	S	2·66	0·27	I	2·67	-0·01	I	2·65	-0·03	85·8	135·3
IMTSHG	HgS_2I_2	S	2·65	0·26	S	2·88	0·49	I	2·66	-0·02	I	2·85	-0·03	93·1	142·1
MTBRHG	HgS_2Br_2	S	2·45	0·06	S	2·42	0·03	Br	2·81	0·29	Br	2·99	0·47	162·9	95·9
SBHGAP	HgS_2Br_2	S	2·61	0·06	S	2·50	0·11	Br	2·71	0·19	Br	2·84	0·32	135·1	93·0
SURHGC	HgS_2Cl_2	S	2·54	0·22	S	2·37	-0·02	Cl	2·24	-0·14	Cl	2·36	-0·02	109·0	177·0
TAMHGC	HgS_2Cl_2	S	2·42	0·03	S	2·46	0·07	Cl	2·36	-0·03	Cl	2·52	0·13	180·0	89·1
TCTPHG	HgS_2P_2	S	2·51	0·12	S	2·49	0·10	P	2·60	0·11	P	2·57	0·08	96·6	118·3
TEHHGI	HgS_2N_2	S	2·43	0·04	S	2·46	0·07	N	2·38	0·18	N	2·32	0·19	122·1	78·0
TTPHGC	HgS_2Cl_2	S	2·58	0·19	S	2·69	0·30	Cl	2·41	0·03	Cl	2·42	0·04	83·2	117·5
CTSCHG	HgS_2Cl_2	S	2·42	0·03	S	2·42	0·03	Cl	2·82	0·30	Cl	2·82	0·30	160·7	96·6
MTCTHG	HgS_2Cl_2	S	2·58	0·19	S	2·69	0·30	Cl	2·41	0·03	Cl	2·42	0·04	83·1	119·3

a)



where C,D = X,X'
E,F = Y,Y'

b



....CTD

TABLE 23: ctd

Ib) ctd

ref:	descr:	A:	Hg-A:	Δd_A:	B:	Hg-B:	Δd_B	C:	Hg-C:	Δd_C:	D:	Hg-D:	Δd_D:	A-Hg-B:°	C-Hg-D:°
CONGPY	HgS_4	S	2.53	0.14	S	2.53	0.14	S	2.55	0.16	S	2.55	0.16	114.5	104.3
HGETCB	HgS_4	S	2.42	0.03	S	2.52	0.13	S	2.66	0.27	S	2.70	0.31	146.1	96.7
HGEXAN	HgS_4	S	2.42	0.03	S	2.42	0.03	S	2.79	0.40	S	2.85	0.46	147.7	84.3
HGEXAN	HgS_4	S	2.31	-0.08	S	2.50	0.11	S	2.75	0.36	S	2.94	0.55	148.8	81.8
NRPRPT	HgS_4	S	2.39	0.0	S	2.39	0.0	S	2.75	0.36	S	2.89	0.50	149.7	81.6
IPTCHG	HgS_4	S	2.45	0.06	S	2.45	0.06	S	2.64	0.25	S	2.64	0.25	149.7	117.5
MTCLUE	HgS_4	S	2.47	0.08	S	2.53	0.14	S	2.59	0.20	S	2.61	0.22	120.2	106.1
TPTCHG	HgS_4	S	2.50	0.11	S	2.55	0.16	S	2.49	0.10	S	2.57	0.18	109.7	109.5
TUHGCL	HgS_4	S	2.51	0.12	S	2.53	0.14	S	2.54	0.15	S	2.62	0.23	116.6	112.2
TUHGCL	HgS_4	S	2.49	0.10	S	2.50	0.11	S	2.55	0.16	S	2.60	0.21	124.2	106.1
TUHGCS	HgS_4	S	2.52	0.13	S	2.52	0.13	S	2.58	0.19	S	2.60	0.21	117.2	111.9
HGDMCP	HgS_4	S	2.39	0.0	S	2.40	0.01	S	2.42	0.03	S	2.41	0.02	140.0	83.2
MEDTHG	HgS_3C	S	2.42	0.03	C	2.04	0.07	S	2.96	0.57	S	3.15	0.76	171.2	94.3
CMPRTM	$HgSCl_3$	S	2.42	0.03	Cl	2.38	-0.01	Cl	2.57	0.18	Cl	2.77	0.38	131.9	87.2
HGCLTU	$HgSCl_3$	S	2.40	0.01	Cl	2.39	0.00	Cl	2.84	0.45	Cl	2.94	0.55	155.0	89.3

c) Five-coordinated Mercury

ref:	descr:	A:	Hg-A:	Δd_A:	B:	Hg-B:	Δd_B	C:	Hg-C:	Δd_C:	D:	Hg-D:	Δd_D:	E:	Hg-E:°	Δd_E:
NPHHGI	HgS_4N	S	2.46	0.07	S	2.46	0.07	S	2.59	0.20	N	2.41	0.31	S	2.59	0.20
PMTAHG	HgS_2O_2N	S	2.43	0.04	S	2.47	0.08	O	2.43	0.33	N	2.46	0.36	O	2.68	0.58
BTCHGP	HgS_2O_3	S	2.39	0.00	S	2.40	0.01	O	2.42	0.32	O	2.70	0.60	O	2.82	0.72

A-HgB:°	C-Hg-D:°
130.8	120.7
143.0	80.9
159.0	98.1

d Two-coordinated Mercury

ref:	descr:	A:	Hg-A:	Δd_A:	B:	Hg-B:	Δd_B	A-Hg-B:
MPYMHG	HgSC	S	2.39	0.00	C	2.13	0.01	174.0°

where -

ref: 6 letter acronym corresponding to CCDF.
descr: Hg coordination sphere

coordination spheres the characteristic coordination is generally tetrahedral, with the two additional ligands held by weak interactions at a distance considerably larger than the covalent radii.

For these tetrahedra with C_{2v} symmetry, there are three types of angle, S - Hg - S, S - Hg - X and X - Hg - X, of which the first and third are independent. According to a hybridisation model[68], the two angles α_1 and α_2, defined as α_1 = X - Hg - X and α_2 = S - Hg - S are related by the following function:

$$\cos\alpha_1 - 3\cos\alpha_1\cos\alpha_2 + \cos\alpha_2 = -1$$

The correlation between these two angles are shown in Figure 12. All 47 structures having tetrahedral or higher coordination are represented. Generally the structures display a geometry intermediate between octahedral and tetrahedral, irrespective of the number of coordinating atoms. In the case of six-coordinated mercury, the two Y ligands are clearly discernable by virtue of their longer bonds to mercury, relative to the X ligands. The structures display a tendency towards retaining their tetrahedral configuration with the Y ligands imposing some octahedral character. Both octahedral and tetrahedral coordination spheres are represented on the graph, as it is the character of the X and S substituents that is of interest. The Y substituents are not represented as the conversion of tetrahedral to octahedral is adequately demonstrated by the S - Hg - S and X - Hg - X angles. In addition it may be seen that a number of 4-coordinated species already display bond angles that may be associated with octahedral geometries, despite the absence of Y substituents.

There is only one example of a regular octahedron, namely HgS_6, where the ligands all exercise the same influence in the coordination sphere.

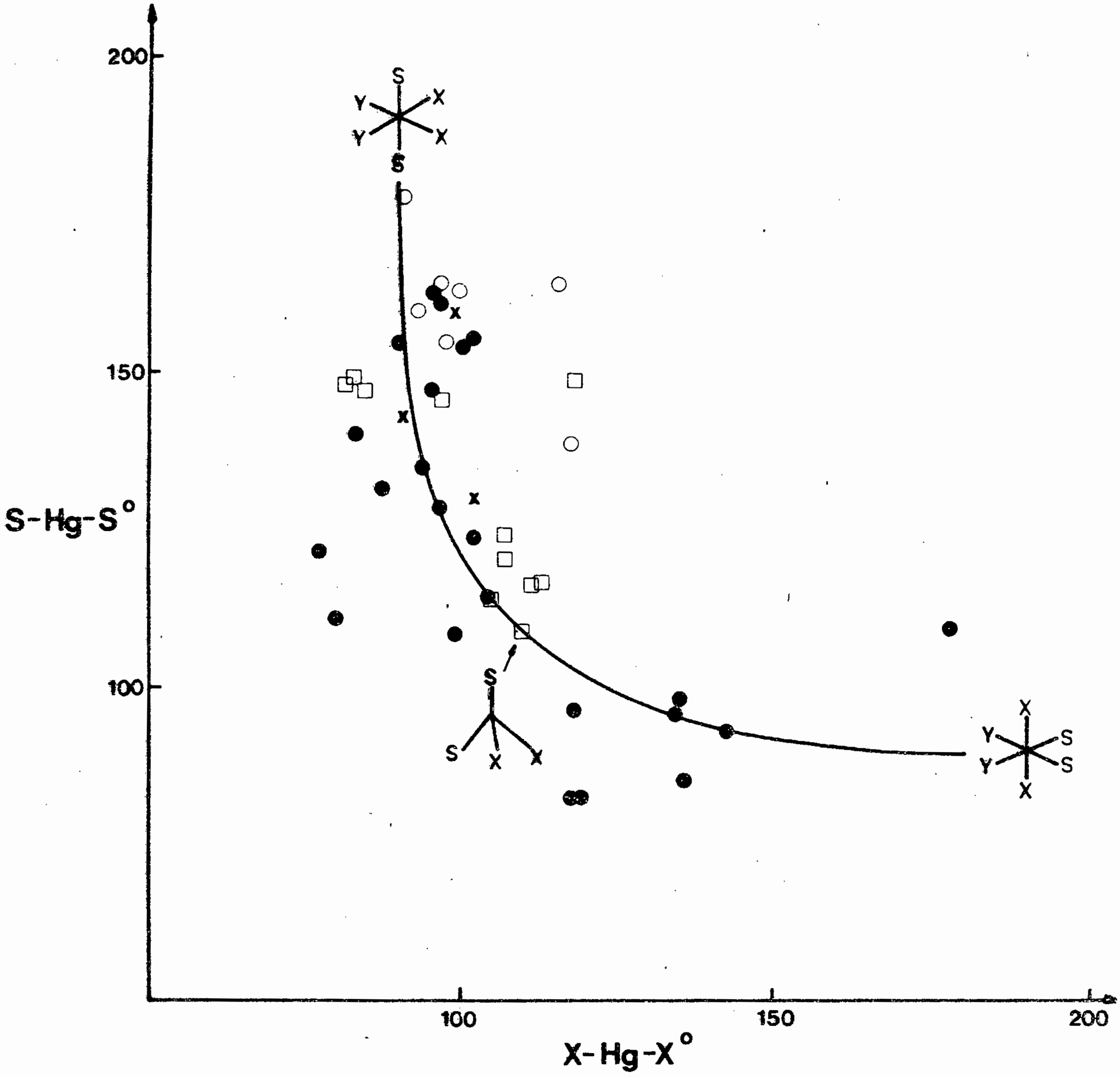


FIGURE 12 X - Hg - X (α_1) VERSUS S - Hg - S (α_2) FOR $HgS_2X_2Y_2$ AND HgS_2X_2 MOLECULES

○ : six-coordinated $HgS_2X_2Y_2$

● : tetrahedral HgS_2X_2

□ : tetrahedral HgS_4

x : tetrahedral $HgSCX_2$

The other examples all have halogens as additional ligands. These are seen to lie near the top of the curve in Figure 12, approaching an S - Hg - S angle of 180° with the X and Y ligands between 90° and 100°.

However, these are flanked by structures having tetrahedral mercury coordination by definition, yet having no further ligands to justify an octahedral coordination geometry. The four-coordinated species may be divided into two groups, those having the S - Hg - S angle distinctly greater than the regular tetrahedral 109°, and those that have the X - Hg - X angle greater. In the former case the angle lies on average at 138° for S_2HgX_2 and at 144° for HgS_4 species. This indicates that the S - Hg - S bond angle stabilises at about midway (145°) between a linear 180° angle and a tetrahedral 109° angle. In examples where S - Hg - S $<$ 109° the angle is found on average at about 92°. The corresponding X - Hg - X angle is commonly found at about 95° for HgS_2X_2 where X are ligands other than sulphur, and at 101° when the X ligands are sulphur groups. The HgS_4 moieties are, as would be expected, most representative of true tetrahedra. With the exception of these, the area of the graph surrounding the characteristic α_1 and α_2 tetrahedral angles of 109° is remarkably unpopulated. Although the majority of examples investigated have the S - Hg - S angle $>$ X - Hg - X angle, there are several structures displaying the opposite. This may be explained in terms of a number of different factors. Of these, one of the most relevant is electronegativity. When X - Hg - X $>$ S - Hg - S, the X substituent is most frequently iodine. In the case of sulphur and iodine, Grdenić[15] has pointed out that these occupy a transitional position in classification of crystal structures based on electronegativity, as they are both equivalent to the $\chi(L)$ value of 2,5. He points out that digonal coordination is more stable for sulphur whereas tetrahedral is for iodine. But in this case factors other than electronegativity are influential. There is a reasonable difference in their atomic radius, with the van der Waals radius of sulphur at 1,85Å, and that of iodine at 2,15Å[24]. Sterically, the iodine atoms would be forced further apart than the sulphur atoms, yielding angles of I - Hg - I > S - Hg - S as observed. This is depicted in Figure 13, where ideal tetrahedral angles and van der Waals interaction distances are shown. In theory, the two iodine ligands are separated by 4,67Å, of which 4,50Å is within their van der Waals radii leaving 0,37Å between them. In the case of the two sulphur ligands, this gap is 0,50Å, and in the case of one sulphur and one iodine atom, it lies at the intermediate distance of 0,44Å. The average I - Hg - I and S - Hg - S angles found in the structures examined were 128,2° and 99,7° respectively, and the Hg - I and Hg - S distances both 2,67Å. The separation in space of the iodine atoms is thus 4,80Å, widening the distance between their van der Waals radii from 0,37Å in regular tetrahedra to 0,5Å. The sulphur atoms are separated by 4,08Å, with 0,38Å separating the van der Waals radii. (See Figure 13). The S - Hg - I angles have an average value of 105,3°, and the S and I substituents are separated by 4,24Å, their van der Waals radii being separated by 0,24Å. Thus the iodine atoms are exerting a strong influence separating them, and minimising the S - Hg - S and more specifically the S - Hg - I angles.

7.4 DISTORTIONS INDUCED BY ELECTRONEGATIVITY

Electronegativity is often referred to as an elusive parameter[69], ill-defined and described by Pauling as "the power of an atom to draw electrons to itself"[24].

Of primary importance is the ligand sulphur which, by virtue of its electronegativity dictates the geometry of the coordination sphere,

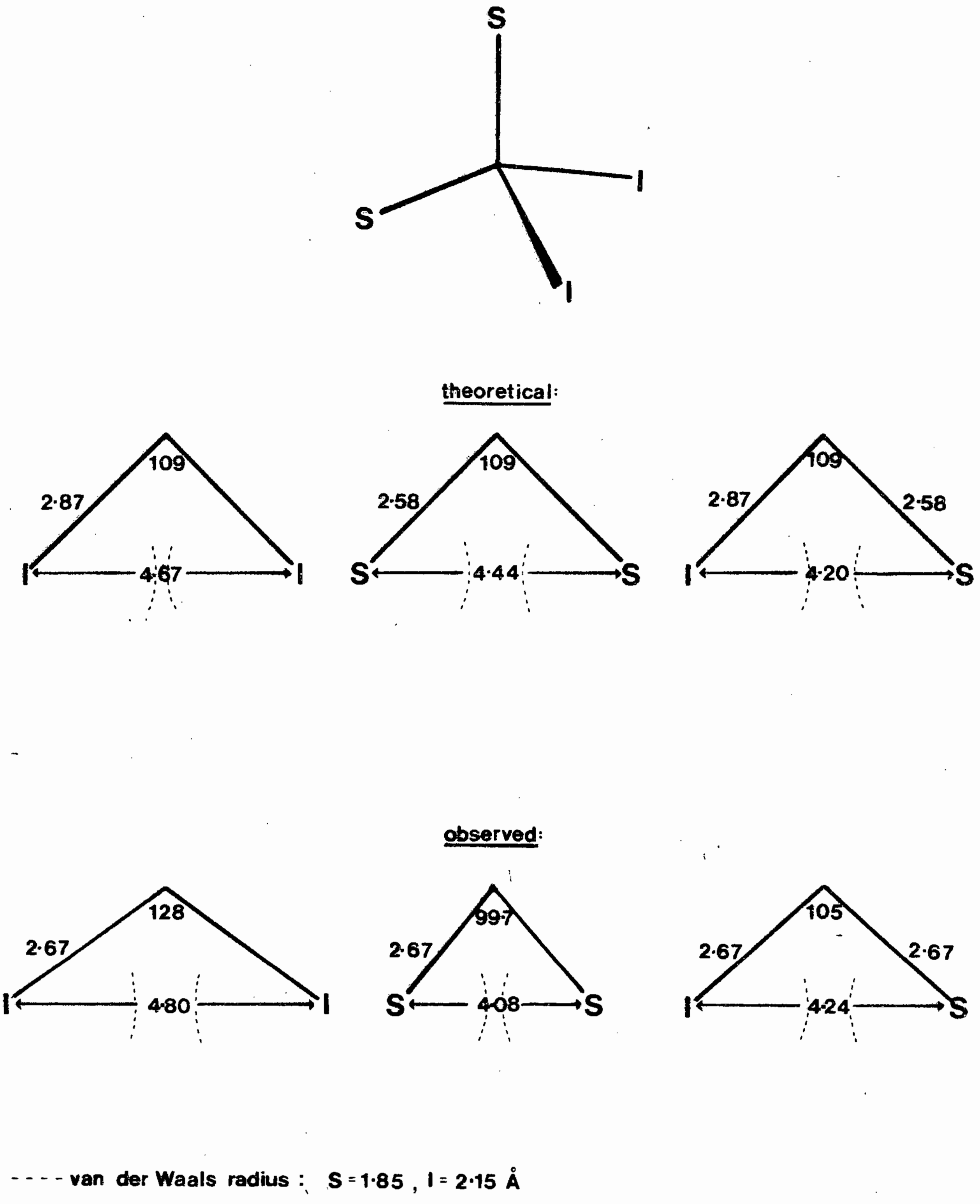


FIGURE 13 STERIC HINDRANCE IN THE CASE OF A MERCURY COORDINATION SPHERE CONSISTING OF TETRAHEDRAL HgS_2I_2

as has been discussed the previous chapter. This limits all structures to digonal or tetrahedral characteristic coordination, as they all have been selected on the basis of having at least one Hg - S bond. The effect of electronegativity is investigated in the largest class of structures found, namely HgS_2X_2, a grouping to which C_{2v} symmetry would be allocated. The electronegativity of the X substituents would be expected to affect the bond angles of the tetrahedron by removing electron density towards the substituents, polarising the bonds to some extent. Figure 14 represents the angular dependence of both S - Hg - S and X - Hg - X on the electronegativity of the X substituents. The S - Hg - S angle tends to increase with increasing electronegativity of the X substituent. This is in keeping with the valence-shell electron-pair repulsion model[70] and from Bent's[56] rule. It has also been observed by Ho and Zuckerman[71] for organotin compounds. It will be seen that the spread of the angles is large, as they obviously depend on other factors besides electronegativity. This is illustrated in Figure 15, a plot revealing the dependence of the S - Hg - S and X - Hg - X angles on the van der Waals radius (considered as most representative of atomic size with respect to steric factors) of the substituent atoms *i.e.* X. The graph shows increasing X - Hg - X with increasing R_{vdw}, which is sterically logical, and simultaneously a tendency for S - Hg - S to decrease. The result corresponds to that found for electronegativity, but of interest here is the difference between N and Cl as the X substituents, as they share the same electronegativity and differ in their R_{vdw} by 0,3Å. A trend consistent with this is shown in Figure 15, where N - Hg - N is sterically favoured to be less than Cl - Hg - Cl. Once again, the scatter of points is large, the deviation incorporating a number of other influential parameters.

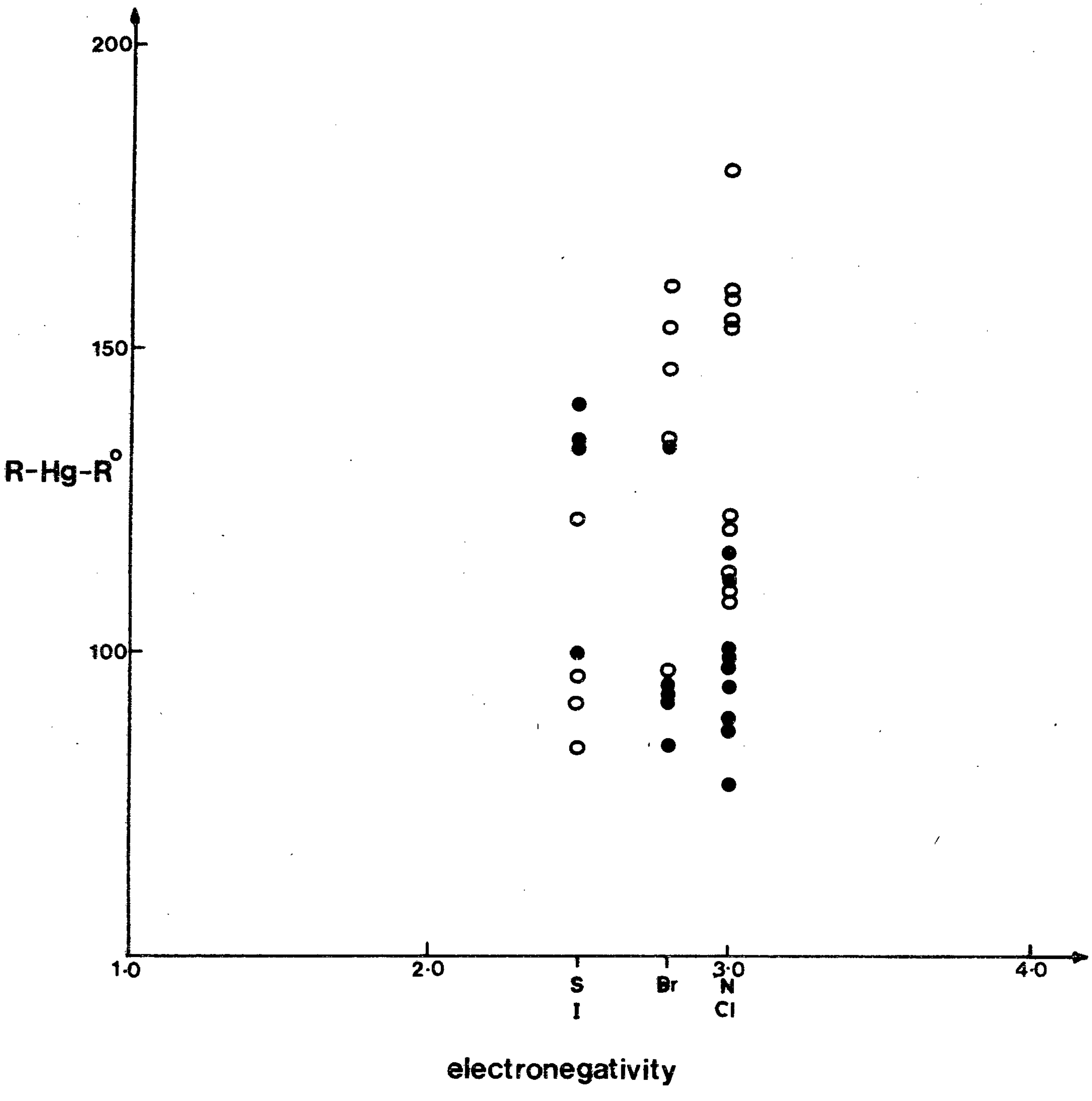


FIGURE 14 R - Hg - R ANGULAR DEPENDENCE UPON ELECTRONEGATIVITY OF X SUBSTITUENTS

○: S - Hg - S angles versus electronegativity of X

●: X - Hg - X angles versus electronegativity of X

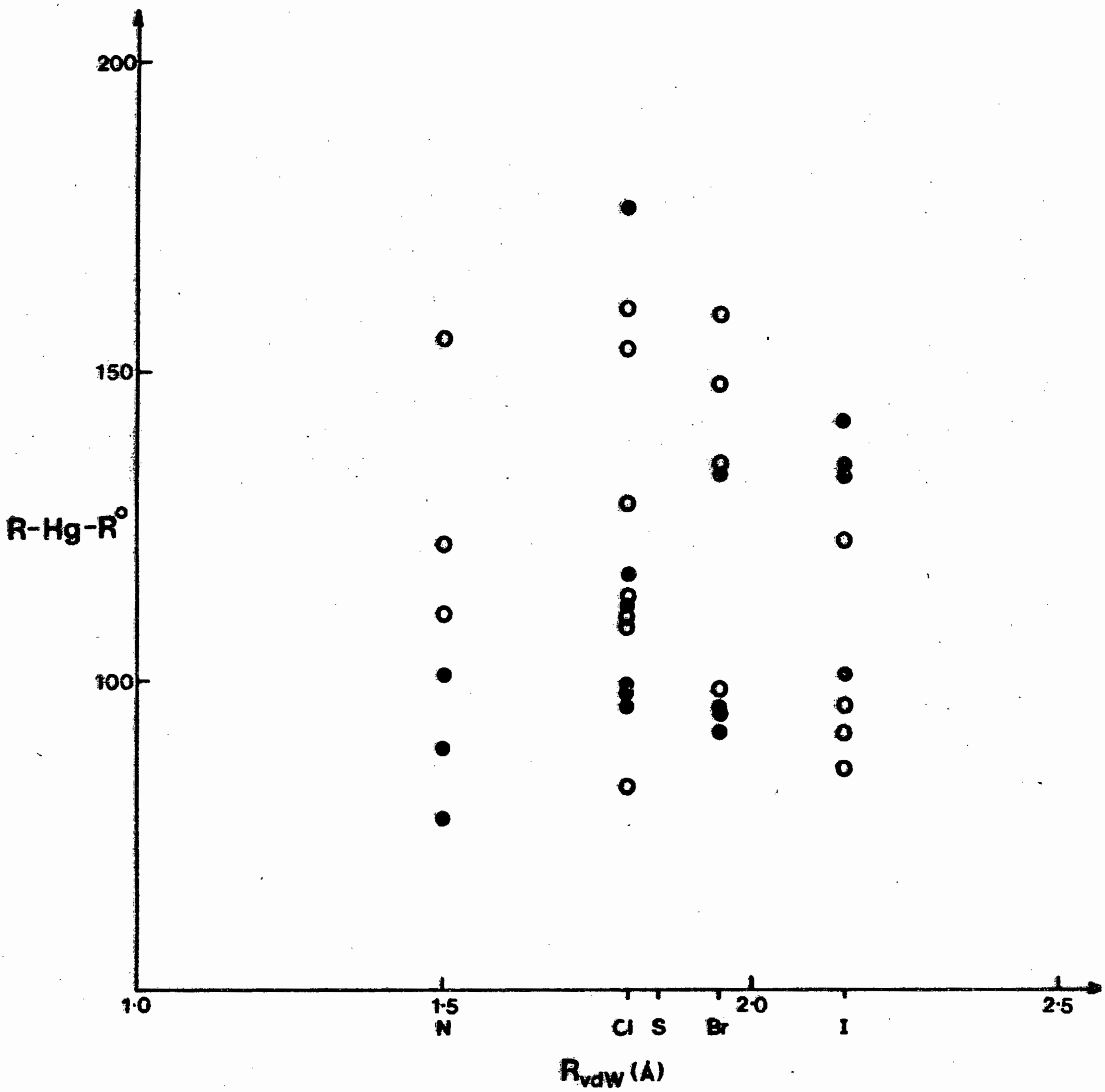


FIGURE 15 R - Hg - R ANGULAR DEPENDENCE UPON VAN DER WAALS RADIUS OF X SUBSTITUENTS

○: S - Hg - S angles versus van der Waals radius of X

●: X - Hg - X angles versus van der Waals radius of X

7.5 EXAMINATION OF PROPOSED RADII

Grdenić[15] proposes different covalent bond radii for mercury in digonal and tetrahedral coordination, these resulting in 2,39 and 2,58Å for Hg - S respectively. A shortening of bond length would thus be expected to accompany a transition from a two- to four-coordinated species. This is exactly what is observed in Figure 16. The majority of structures have bond lengths lying widely distributed within the limits of the two coordination types. The examples exceeding the Hg - S bond distance for tetrahedral coordination generally have the X ligands tending towards linearity. In most cases these are iodine ligands. Here Hg - S bond distances may be regarded as displaying weak or secondary interactions with mercury, supplementing a characteristic coordination of 2 and resulting in tetrahedral effective coordination.

From the histogram (See Figure 17) for the Hg - S distances observed in all the structures, there are two distinct maxima. These occur at 2,42 - 2,43 and at 2,52 - 2,53Å.

TABLE 27 PROPOSED Hg - S BOND LENGTHS (Å) FOR THE CHARACTERISTIC COORDINATION OF Hg

Coordination number	*Hg - S*
2	2,34 (or 2,38)
3	2,43
4	2,53
5	2,64
6	2,72

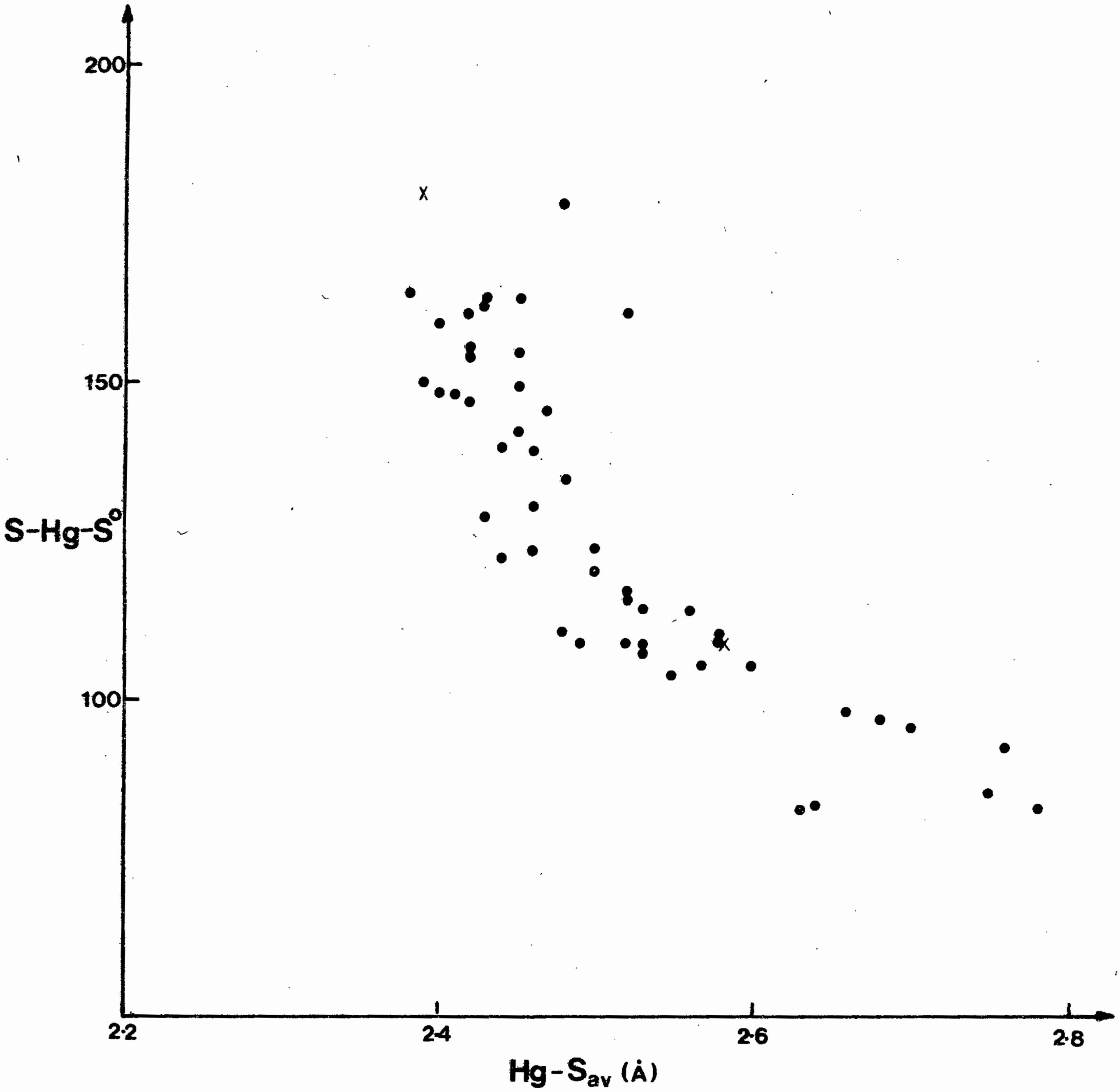


FIGURE 16 S - Hg - S BOND ANGLE (DEGREES) VERSUS THE AVERAGE Hg - S DISTANCE (Å) OF THE TWO BONDS

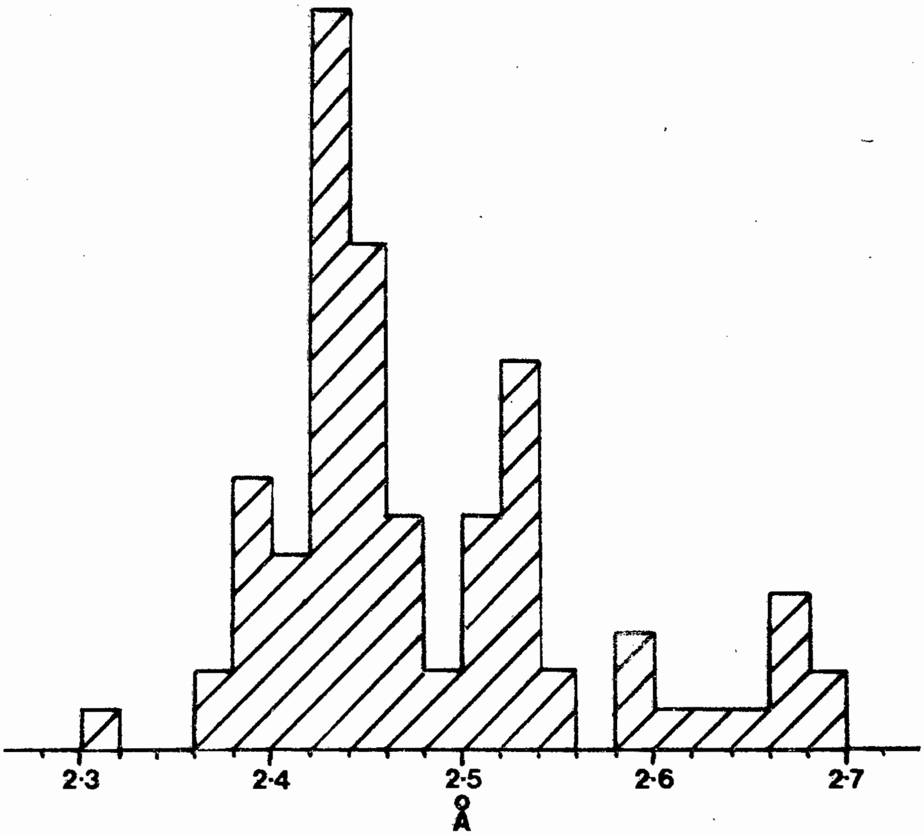


FIGURE 17 HISTOGRAM OF THE Hg - S DISTANCES (Å) OBSERVED IN ALL THE STRUCTURES EXAMINED

Considering the bond lengths given in Table 27, based on proposed covalent radii of mercury for the different coordination numbers, it can be seen that the second observed maximum of 2,52 — 2,53Å corresponds to the theoretical tetrahedral bond length of 2,53Å. It is of interest to note that the HgS_4 group were chief contributors in this category. The first very prominent maximum in Figure 17 at 2,42 - 2,43Å corresponds to a bond length equivalent to that of three-coordinate mercury. This may be more accurately interpreted as an average between two- and four-coordinate, again giving evidence of the very strong tendency of the Hg - S bonds in tetrahedrally coordinated mercury to adopt digonal characteristics, as has also been shown by the S - Hg - S angle.

7.6 DISUBSTITUTION AT TETRAHEDRAL MERCURY

The examples of six-coordinated mercury may be described as having a local composition of $HgS_2X_2Y_2$, with transoid S atoms in all cases but one, and distorted octahedral symmetry. There are two mechanisms by which the transition of tetrahedral to octahedral coordination may occur, namely S_N3 or $(S_N2)^2$. These two pathways are best represented as in Figures 18 and 19. Initially, correlations between Δd_x and Δd_y were examined where

$$\Delta d = d(\text{observed bond length}) - d(\text{theoretical covalent bond length})$$

As the Hg - Y distance d_y becomes shorter, the Hg - X distance d_x lengthens. Figure 20 shows the interdependence of these two bond lengths. The solid curve represents the bond-order conservation function

$$10^{-\Delta d_x/c} + 10^{-\Delta d_y/c} = 1$$

with c = 2,23Å

FIGURE 18 THE S_N3 PATHWAY: SYMMETRIC APPROACH OF 2Y TO AN HgS_2X_2 MOLECULE

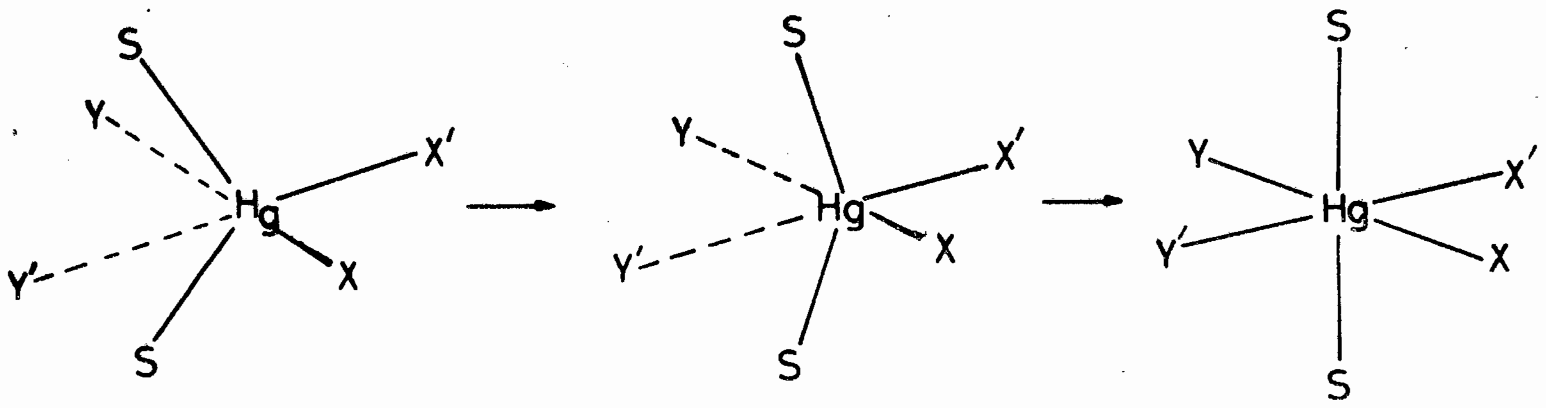
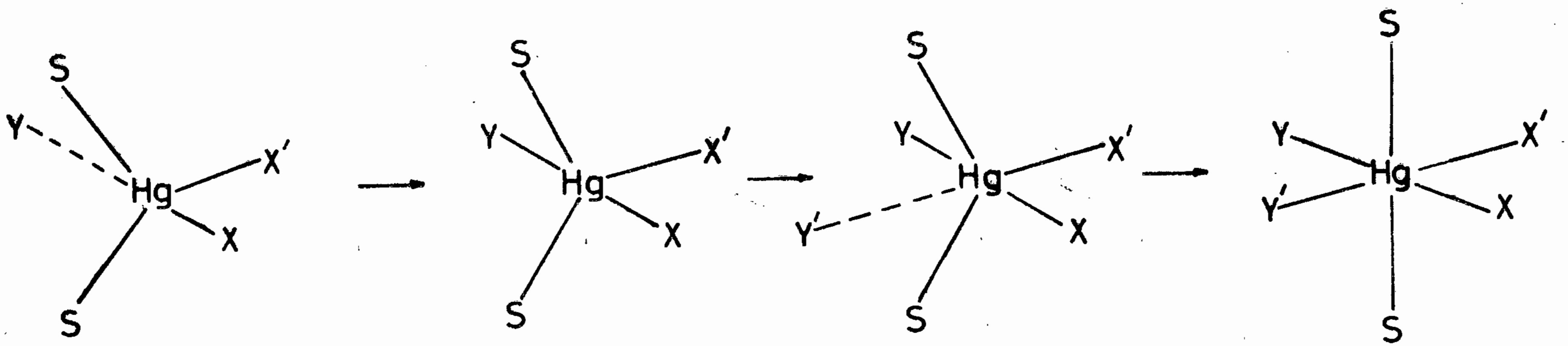


FIGURE 19 THE $(S_N2)^2$ PATHWAY: SEQUENTIAL APPROACH OF 2Y TO HgS_2X_2



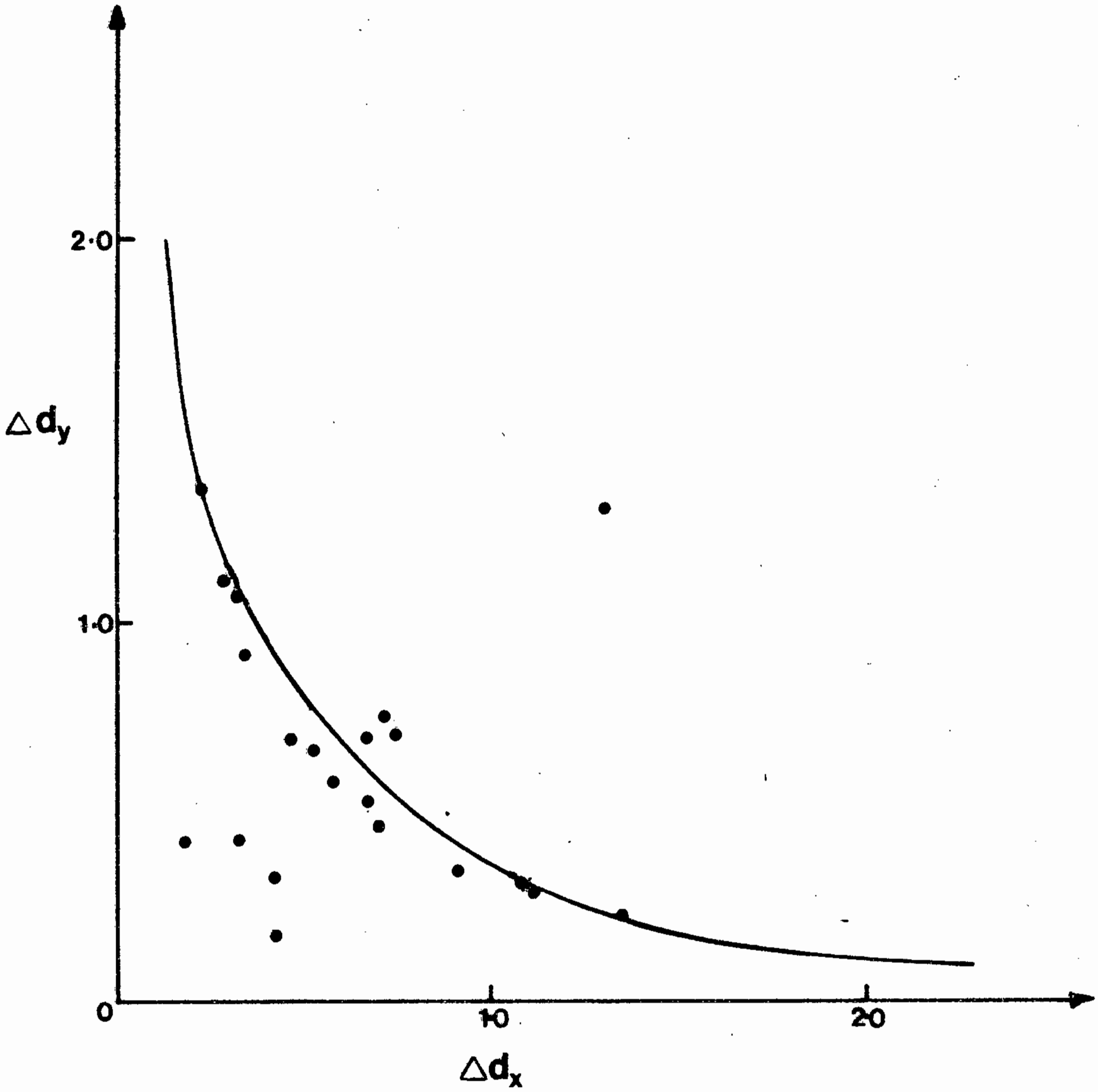


FIGURE 20 Δd_y VERSUS Δd_x FOR OCTAHEDRALLY COORDINATED MERCURY

This is associated with the relationship between bond length and bond order as proposed by Pauling[24].

$$d(n) = d(n) - d(1) = -c\log n$$

where $d(n)$: observed bond length

$d(1)$: single bond length

c : constant dependent on type of bond.

As such this has no great theoretical significance, but has proved useful in the reproduction of experimental[57] and theoretical[74] reaction paths. Upon addition of two Y ligands to an essentially tetrahedral molecule, the X - Hg - X would be expected to decrease from 109° to 90°, and S - Hg - S to increase from 109° to 180°. In the former case, $\Delta d_y = \infty$ would thus correspond to X - Hg - X = 109°, and $\Delta d_y = 0$ to X - Hg - X = 90°. Figure 21 shows the curve representing this conversion, passing through $\Delta d_y = 0$ at 90°, and approaching 109° asymptotically as $\Delta d_y \rightarrow \infty$. The few data points show reasonable agreement with this curve.

However, in the case of the S - Hg - S, which would be expected to have $\Delta d_y = 0$ at S - Hg - S = 180°, and $\Delta d_y \rightarrow \infty$ at S - Hg - S = 90°, the data points deviate considerably from this curve. Generally the S - Hg - S angles are observed to be greater than the expected values, lying above the curve. This may once again be ascribed to the very strong tendency of this angle to retain its digonal character.

Finally of interest is the mechanism by which this conversion occurs *i.e.* by S_N3 or $(S_N2)^2$ substitution. Using the few data points available, an ambiguous picture emerges (See Figure 22). The points follow the path of the $(S_N2)^2$ mechanism, but only as far as an S - Hg - X angle of 106°. Thus they never exceed 109°, as is required for an S_N3 mechanism. However, the S - Hg - X' is generally too small

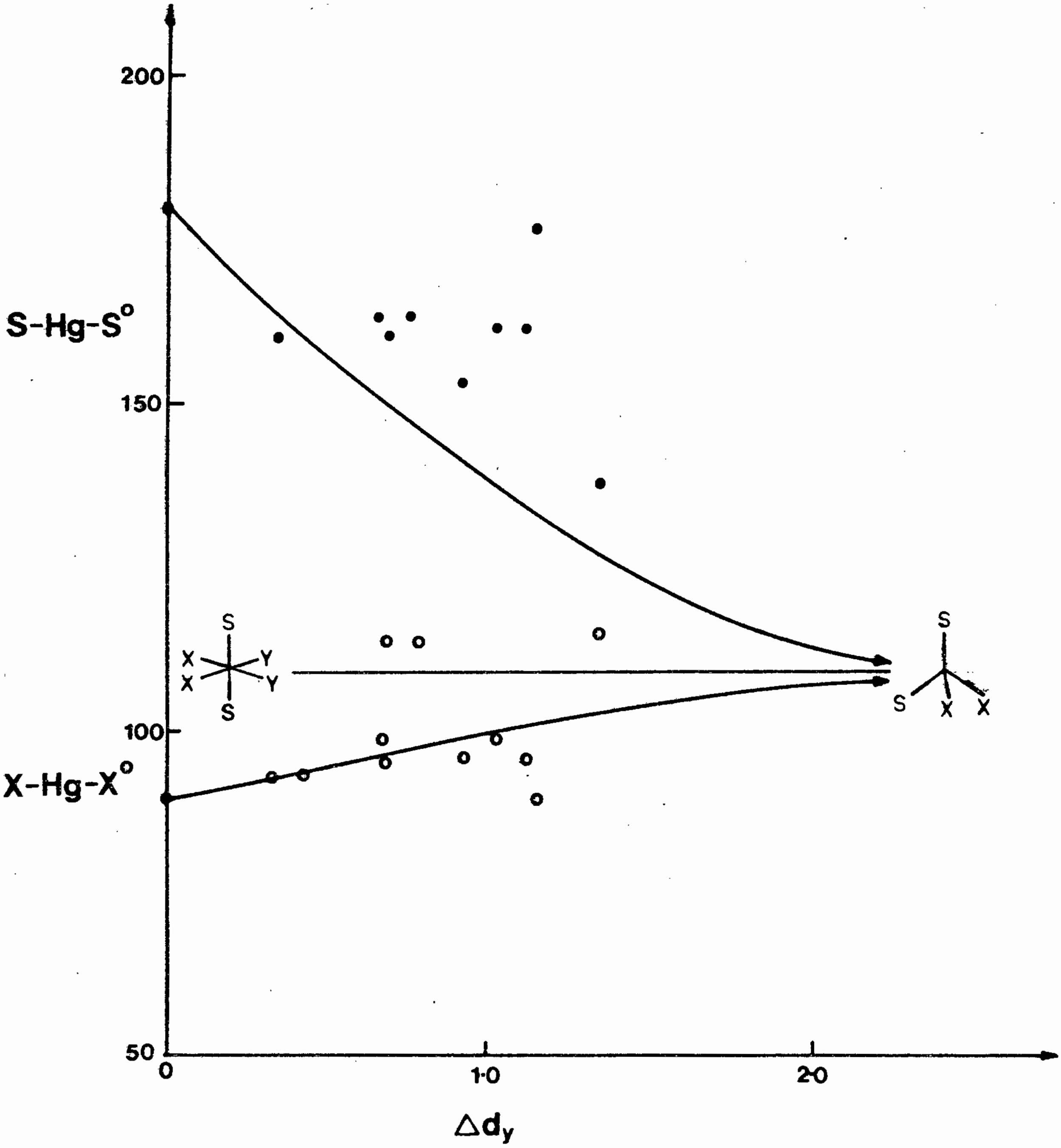


FIGURE 21 INFLUENCE OF APPROACHING Y LIGANDS ON THE S - Hg - S AND X - Hg - X ANGLES

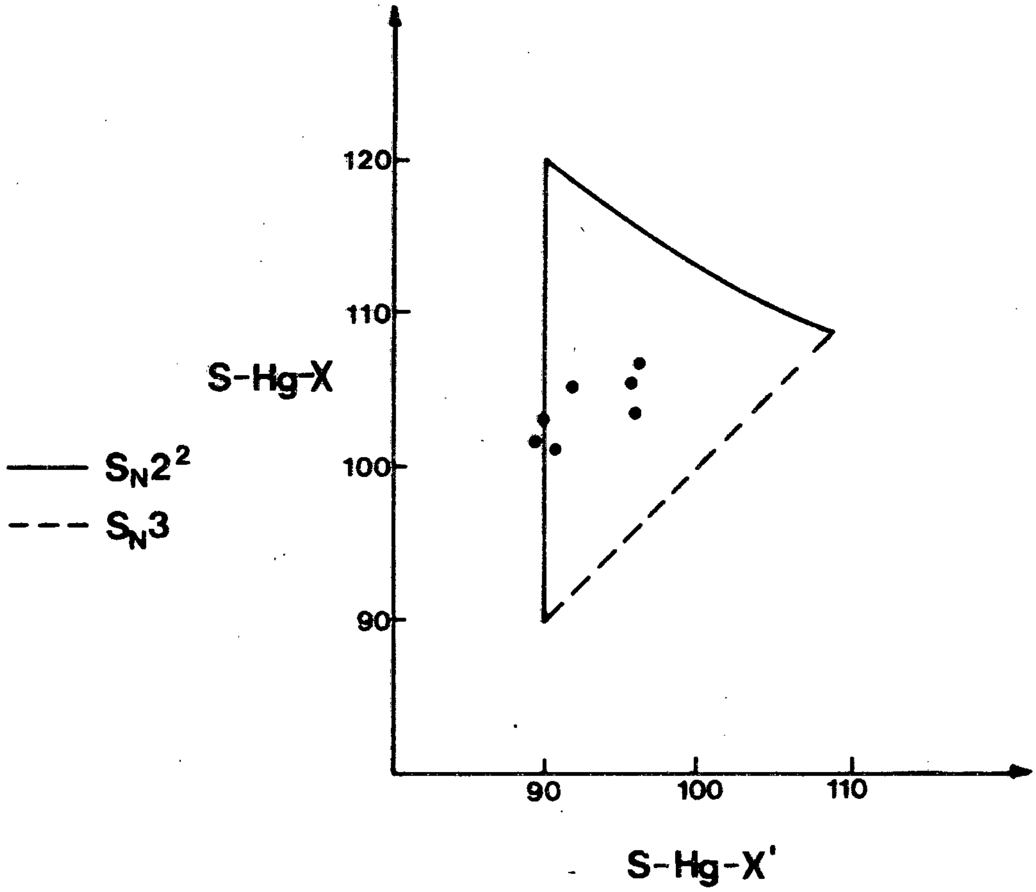


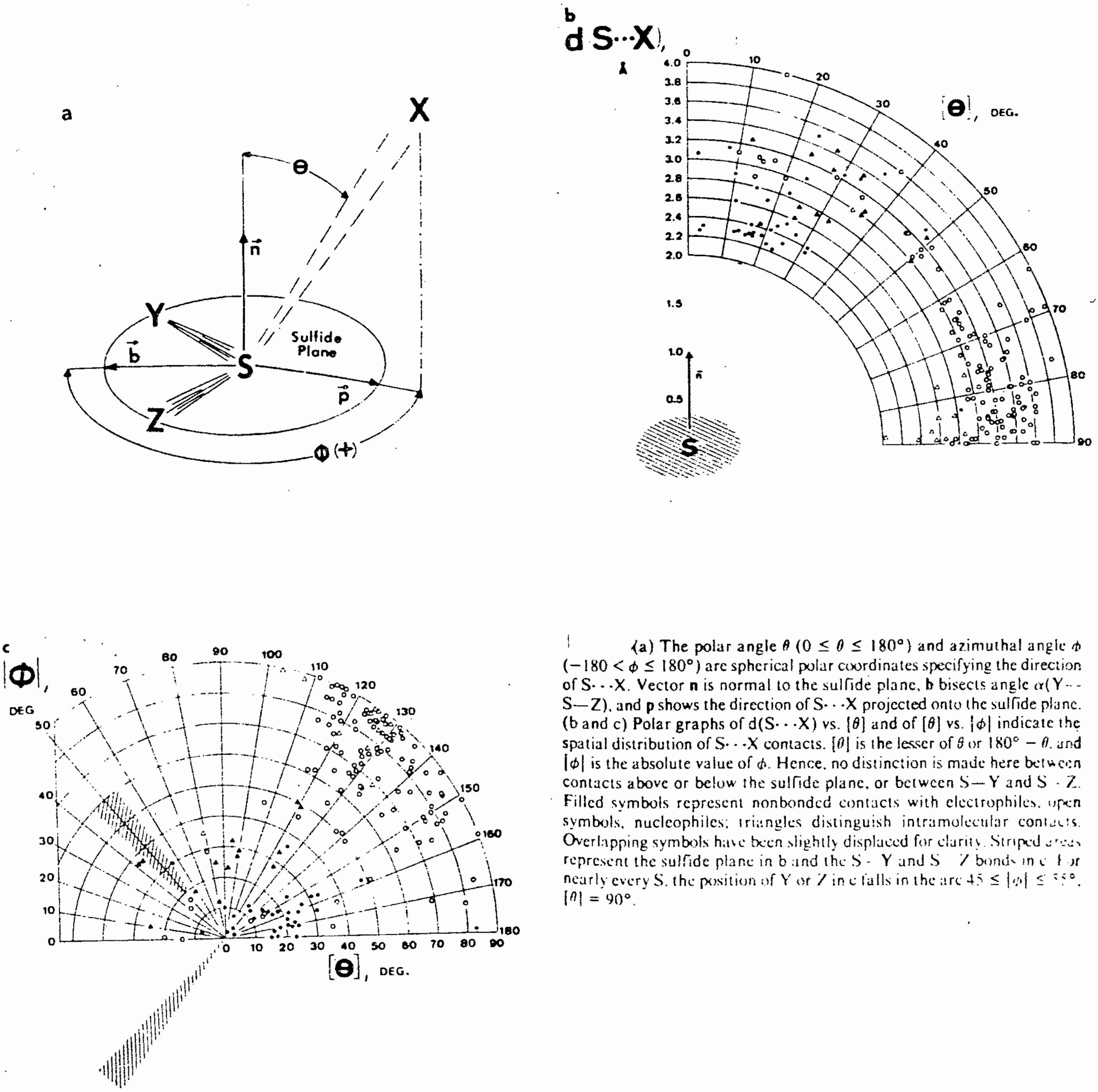
FIGURE 22 S - Hg - X VERSUS S - Hg - X', SHOWING PATHWAYS OF THE TWO SUBSTITUTION MECHANISMS

and in better agreement with the $(S_N2)^2$ mechanism. The evidence as such is inconclusive. In the case of similar transformations in Sn(IV)[63], the system clearly follows an S_N3 mechanism, with some slight deviations. The majority of correlations observed thus far for mercury(II) have generally been analogous to the Sn(IV) case. The similar distances between the two Hg - Y and Hg - Y' bonds suggest an S_N3 mechanism. In the case of Figure 22, distortions as observed previously, are induced by parameters such as the electro=negativity of sulphur. These, as well as the shortage of data points, result in an unclear picture from which no unambiguous conclusion may be drawn.

7.7 MERCURY - SULPHUR SECONDARY INTERACTIONS

One of the primary points of investigation in Part I of this work has been the four-membered mercury-sulphur bridging intermediate as observed in NMR exchange processes[12]. Part II would not be complete without paying attention to this particular Hg - S interaction.

A very large part of the groundwork for this has already been carried out by Rosenfield, Parthasarathy and Dunitz[72], in their investigations of the directional preferences of nonbonded atomic contacts with divalent sulphur. Figure 23(a), (b) and (c) are a visual representation of their investigations, which pertain to electrophilic and nucleophilic contacts. Contacts with metals such as Cu(I), Cu(II), Ni(II), Pd(II) and, of greatest relevance, Hg(II), were regarded as "nonbonded". These were also grouped with electrophilic atoms, which were generally found to form S---X contacts with directions $< 40°$ from the perpendicular to the Y - S - Z plane, $(0 \leqslant \theta \leqslant 40°)$ as opposed to nucleophilic species having directions $< 30°$ from that plane $(60 \leqslant \theta \leqslant 90°)$ (See Figure 23).



(a) The polar angle θ ($0 \le \theta \le 180°$) and azimuthal angle ϕ ($-180 < \phi \le 180°$) are spherical polar coordinates specifying the direction of S···X. Vector **n** is normal to the sulfide plane, **b** bisects angle α(Y—S—Z), and **p** shows the direction of S···X projected onto the sulfide plane. (b and c) Polar graphs of d(S···X) vs. $[\theta]$ and of $[\theta]$ vs. $|\phi|$ indicate the spatial distribution of S···X contacts. $[\theta]$ is the lesser of θ or $180° - \theta$, and $|\phi|$ is the absolute value of ϕ. Hence, no distinction is made here between contacts above or below the sulfide plane, or between S—Y and S—Z. Filled symbols represent nonbonded contacts with electrophiles, open symbols, nucleophiles; triangles distinguish intramolecular contacts. Overlapping symbols have been slightly displaced for clarity. Striped areas represent the sulfide plane in b and the S—Y and S—Z bonds in c. For nearly every S, the position of Y or Z in c falls in the arc $45 \le |\phi| \le 55°$, $[\theta] = 90°$.

<ins>FIGURE 23</ins> DIRECTIONAL PREFERENCES OF DIVALENT SULPHUR (REFERENCE 72)

It was noted that the second category, namely the nucleophilic species, formed contacts which tended to lie along the extension of one of the sulphur bonds. These results proved in keeping with the "frontier orbital" model[73], with electrophiles interacting preferentially with the highest occupied (HOMO) and nucleophiles with the lowest unoccupied (LUMO) molecular orbitals. The HOMO orbital is proposed to be a sulphur lone-pair orbital extending almost at 90° to the Y - S - X plane, whereas the LUMO orbital is characterised at a $\sigma^*(S - Y)$ or $\sigma^*(S - Z)$ orbital. Although there is an additional lone-pair electron orbital at $|\phi| \sim 180°$, this seems unfavourable for interaction with nucleophiles. Thus in conclusion, the preferred directions of electrophilic and nucleophilic attack on divalent sulphur occur respectively perpendicular to the Y - S - Z plane and along the extension of the S - Y or S - Z bonds.

Five examples of four-membered Hg - S bridging interactions were found amongst the structure listed in the Cambridge Crystallographic Data File. An additional two structures displaying the same were elucidated in Part I of this work. In all cases the directional preference of the sulphur atom dictated the orientation of the interaction with the Hg atom, in keeping with the orientation of the HOMO lone-pair orbital. This may clearly be seen in Figure 4 of PMPM, where these interactions give rise to stacking rather than forming sheets in the plane of the generally flat molecule. Of vital interest in the bridging structure is whether lengthening of the Hg - S intramolecular bond is accompanied by a concomitant shortening of the Hg---S interaction, as would occur in an exchange process (See Figure 24). The relevant bond lengths are listed in Table 28, and Figure 25 represents a plot examining the relationship between the Hg - S primary and secondary interactions. Unfortunately no distinct pattern of lengthening primary and shortening

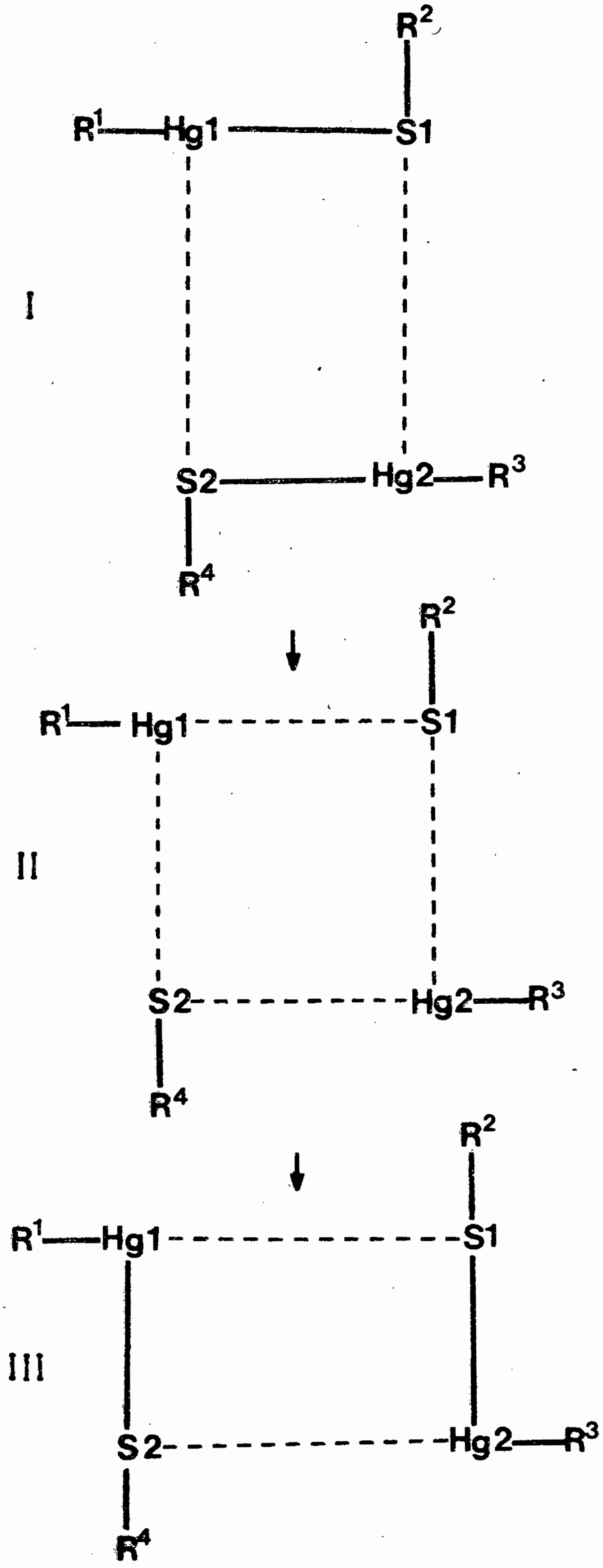


FIGURE 24 Hg - S EXCHANGE BETWEEN TWO MOLECULES

secondary bonds can be seen.

TABLE 28 Hg - S INTERACTIONS (Å)

ref	*Hg(A) - S(A)*	*Hg(B) - S(B)*	*Hg(A)---S(B)*	*Hg(B)---S(A)*
PEHGME	2,38	2,36	3,46	3,36
MERSET	2,45	2,45	3,54	3,54
PHHGDT	2,37	2,37	3,69	3,69
PHHGDT	2,39	2,39	3,58	3,58
MEDTHG	2,96	2,96	3,15	3,15
PMPM	2,39	2,37	3,39	3,35
PMBM	2,37	2,37	3,20	3,20

The bond lengths fall within a very narrow range, with Hg - S primary interactions lying between 2,37 and 2,45Å, and Hg---S secondary interactions between 3,20 and 3,69Å. As no crystal structures corresponding to Figure 24(III) have yet been found, it is suspected that the molecular geometry is very unfavourable, generating stereo=chemical strain on the molecule. In Figure 24(III) the R - Hg - S bond is required to form a 90° angle, which in the light of all correlations carried out is totally out of keeping with the strong trend of retention of linearity of this bond angle.

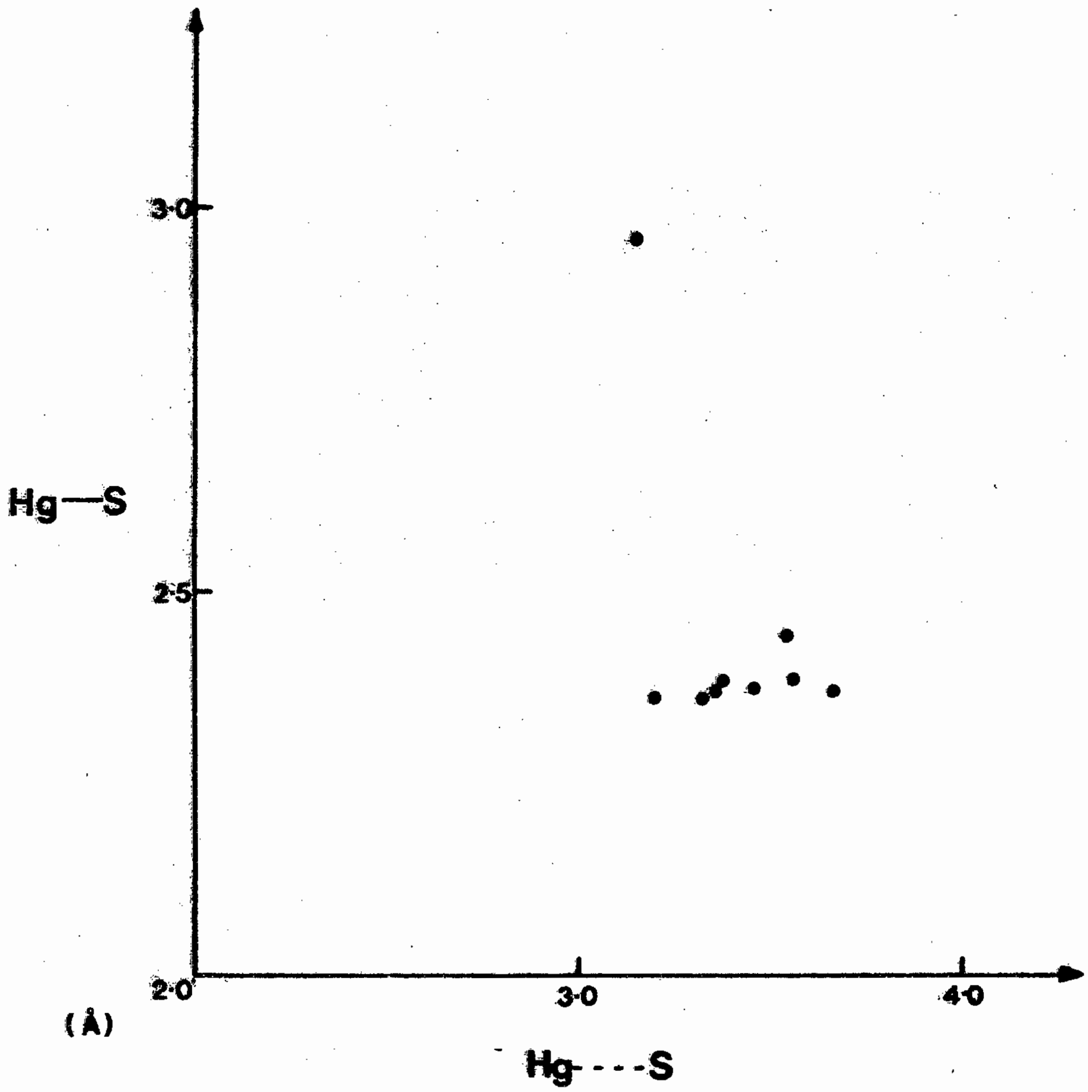


FIGURE 25 RELATIONSHIP BETWEEN PRIMARY AND SECONDARY Hg - S INTERACTIONS

CHAPTER 8

DISCUSSION

CHAPTER 8

DISCUSSION

Structural correlations have been defined as representing minimum energy pathways for chemical reactions, compiled from a large number of comparable molecular "segments" which have crystallised out at some stage along the path. The correlations examined have revealed and confirmed interesting information about the mercury - sulphur interaction, and provided a basis for critical examination of some of the material presented by Grdenić 1965[15] in his review of the structural chemistry of mercury. However, as is experienced here, there is not necessarily a gradual change of parameters as a moiety changes from one conformation to the next.

We have seen that in the case of sulphur, its electronegativity largely dictates the coordination geometry of mercury. This is in support of Grdenić's statement that the electronegativity difference between mercury and its ligands presents the most suitable criterion for a rational classification of the crystal structures of mercury compounds, with $x(L) = 2{,}5$ as the border between digonal characteristic coordination ($x(L) > 2{,}5$) and tetrahedral characteristic and effective coordination ($x(L) < 2{,}5$). Sulphur lies at the transition, and Grdenić observes that digonal coordination is favoured.

The picture that emerges in this respect from the various structural correlations, yields an overall compromise between digonal and tetrahedral coordination, for although the molecule is four coordinated, there is an extremely strong tendency for retention of linearity of the S - Hg - R bond. This gives rise to very distorted tetrahedra.

The electronegativity effect is supplemented by other factors, such as the size of the substituent ligands. This is illustrated in Figure 13, where the electronegativity of both sulphur and iodine is 2,5.

The covalent radii proposed by Grdenić correspond very closely to those found, with the average radius for structures intermediate between digonal and tetrahedral within 0,02Å of the average proposed radius (found : 2,42 - 2,43Å, proposed :(2,34 + 2,53)/2 = 2,44Å). This corresponds with the average S - Hg - S angle in the HgS_4 groups, which lies at 144°, exactly intermediate between tetrahedral 109° and digonal 180°.

The examination of the tetrahedral to octahedral conversion by disubstitution yields inconclusive results. Upon consideration of all the limited data, an S_N3 process seems possible, as has been observed for Sn(IV)[63]. This pathway is entropically disfavoured in solution, and has been found only rarely in gaseous phase, as the three-body collision required is statistically improbable. However, an S_N3 process should correspond to a reasonably well defined valley in the potential energy hypersurface.

Initially it was suggested that the method of structural correlation could form the missing link between kinetics in solution and static crystallography. The S_N3 case shows that the method has an additional advantage, namely, highlighting mechanisms not necessarily feasible in solution.

In the case of the Hg - S four-centred bridge intermediate as seen in NMR exchange processes, it was hoped that there might be evidence of this exposed by structural correlations. Unfortunately, this seems unlikely based on the retention of linearity at mercury. In Figure 24 (III) the R' - Hg(1) - S(2) bond is at 90°, which is stereochemically totally disfavoured. It is thus highly unlikely that this may be found. Transitions such as 24 (I) to 24 (II) are, however, feasible. Investigations were also limited by lack of sufficient data. In conclusion it may be said that all investigations carried out based on the structural parameters of the mercury coordination sphere are in total agreement with those proposed by Grdenić. Mechanistic investigations of disubstitution processes have been disappointing, largely due to the lack of availability of data. However, structural correlations have in the past proved representative of chemical reactions, and in addition to this may reveal totally new pathways of minimum energy, unfeasibl~~y~~e in solution but manifested structurally.

REFERENCES

REFERENCES

1. Read, J., *The Alchemist in Life*, (1947), Thos. Nelson and Sons LTD.
2. Sneed, M.C. and Brasted, R.C., *Comp. Inorg. Chem. IV*, (1955) van Nostrand and Co.
3. Pryde, L.T., *Environmental Chemistry*, (1973), Cummings.
4. Chang, L.W., *Environmental Research, 14* (1977) 329.
5. Falchuk, K.H., Goldwater, L.J. and Vallee, B.L. *The Chemistry of Mercury,* p 272.
6. Thayer, J.S., *J. Organometallic Chem. 76* (1974) 265 - 295.
7. Ahrland, S., Chatt, J., and Davies, N.K., *Quart. Rev., Chem. Soc. 12* (1958) 265.
8. Pearson, R.G., *Science, 151* (1966) 172.
9. Rabenstein, D.L., *J. Chem. Ed., 55:5* (1978) 292.
10. Rabenstein, D.L. and Evans, C.A., *Bioinorg. Chem. 8* (1978) 107.
11. Webb, J.L.A. *et al., J. Amer. Chem. Soc. 72* (1950) 91.
12. Bach, R.D. and Weibel, A.T., *J. Amer. Chem. Soc. 86* (1976) 6241.
13. Simpson, R.B., *J. Amer. Chem. Soc. 83* (1961) 4711.
14. Hughes, E.D. *et al., J. Chem. Soc.* (1961) 1133.
15. Grdenić, D., *Quart. Rev., Chem. Soc. 19* (1965) 303.
16. Grdenić, D., *Structural studies* (1981) Clarendon Press, Oxford.207.
17. Gluster, J.P. and Trueblood, K.M., *Crystal Structure Analysis,* Oxford Univ. Press, London (1972).
18. Stout, G.H. and Jensen, L.H., *X-ray Structure Determination,* Macmillan (1968).
19. Buerger, M.J., *Crystal-structure Analysis,* J. Wiley and Sons, Inc., New York (1967).
20. Bunn, C.W., *Chemical Crystallography,* Oxford Univ. Press, London (1961).
21. Sheldrick, G.M., *The ShelX program system,* Univ. Chem. Lab., Cambridge (1976).

REFERENCES CONTINUED

22. Cromer, D.T. and Mann, J.B., *Acta Cryst. A24* (1968) 321.

23. Stewart, R.F., Davidson, E.R. and Simpson, W.T., *J. Phys. Chem. 42* (1965) 3175.

24. Pauling, L., *The Nature of the Chemical Bond,* Cornell Univ. Press, Ithaca (1960).

25. Roberts, P. and Sheldrick, G.M., Cambridge, unpublished.

26. Motherwell, W.D.S., Cambridge, unpublished.

27. Kasper, J.S. and Lonsdale, K. ed. *International Tables for X-ray Crystallography vol II,* Kyndoch Press, Birmingham (1967).

28. Lawton, S.L., *Inorg. Chem. 10:2* (1971) 328.

29. Wong, Y.S., Carty, A.J., Chieh, C., *J.C.S. Dalton* (1977) 1801.

30. Stuart, D.A., Nassimbeni, L.R., Hutton, A.L., Koch, K.R., *Acta Cryst. 336* (1980) 2227.

31. Chich, C., *Can. J. Chem. 56* (1978) 560.

32. Burke-Laing, M., Laing, M., *Acta Cryst. B32* (1976) 3216.

33. Kiefer, E.F., Waters, W.L., Carlson, D.A., *J Amer. Chem. Soc. 90:19* (1968) 5127.

34. Bach, R.D., Weibel, A.T., Schmonsees, W., Glick, M.D., *J.C.S. Chem.* Comm. (1974) 961.

35. Alcock, N.W., Lampe, P.A., Moore, P., *J. Chem. Soc., Dalton* (1978) 1324.

36. Canty, A.J., Chaichit, N., Gatehouse, B.M., *Acta Cryst. B36* (1980) 786.

37. Klyne, W., Prelog, V., *Experientia 16* (1960) 521.

38. Kasper, J.S., Lonsdale, K., *Int. Tables for X-ray Cryst. II* (1967) Kynoch Press, U.K.

39. Bond, W.L., *Rev. Sci. Instr. 22* (1951) 344.

40. Prout, E.G., Brown, M.E., *Nature 203:4943* (1964) 398.

REFERENCES CONTINUED

41. Zachariasen, W.H., *Theory of X-ray Diffraction in Crystals* (Wiley and Sons, New York, 1945).
42. Ekstein, M., *Phys. Rev. 68* (1945) 120.
43. Matsubara, T.J., *Proc. Phys. Soc. (Japan), 7* (1952) 270.
44. Huang, K., *Proc. Roy. Soc., A190* (1947) 102.
45. Konazaki, H., *J. Phys. Chem. Solids, 2* (1957) 107.
46. Chieh, C., *Can. J. Chem. 55* (1977) 1115.
47. McEwen, R.S., Sim, G.A., *J. Chem. Soc. (A)* (1967) 1552.
48. Barba Behrens, N., Cartwright, B.A., Goodgame, D.M.L., Skapski, A.C., *Inorg. Chim. Acta. 31* (1978) L 471.
49. Canty, A.J., Gatehouse, B.M., *J. Chem. Soc. Dalton Trans.* (1976) 2018.
50. Fatuzzo, E., Nitsche, R., Roetschi, H., Zingg, S., *Phys. Rev. 125* (1962) 514.
51. Sillén, K.G., *Acta Chem. Scand. 3* (1949) 539.
52. Hietarien, S., Sillén, K.G., *Acta Chem. Scand. 6* (1952) 747.
53. Sillén, K.G., Martell, A.E., *Stability Constants of Metal-Ion Complexes* (Chem. Soc. London) (1964).
54. Hutton, A.T., Irving, H.M.N.H., Nassimbeni, L.R., *Acta Cryst. B36* (1980) 2064.
55. Bürgi *et al., Tetrahedron 30* (1974) 1563.
56. Bent, H.A., *Chem. Rev. 68* (1968) 587.
57. Bürgi, H.B., *Angew. Chem., internat. Edit. 14* (1975) 460.
58. Liu, B., *J. Chem. Phys. 58* (1973) 1925.
59. Murray-Rust, P. *Molecular Structure by Diffraction Methods, The Chemical Society, 6* (1978).
60. Aurivillius, K., *Ark. Kemi. 23* (1965) 205.
61. Pauling, L., Huggins, M.L., *Z. Kristallogr. Kristallgeom. 37* (1934) 205.

REFERENCES CONTINUED

62. Bürgi, H.B., *Inorg. Chem. 12* (1973) 2321.

63. Britton, D., Dunitz, J.D., *J. Am. Chem. Soc. 103* (1981) 2971.

64. Bürgi, H.B., Dunitz, J.D., Shefter, E., *Acta Cryst. B30* (1974) 1517.

65. Archer, S.J., Modro, T.A., Nassimbeni, L.R., *Phosphorus and Sulphur 11* (1981) 101.

66. Wells, *Structural Inorganic Chemistry, 4th edn* (1962) 916.

67. Schomaker, V., Stevenson, D.P., *J. Am. Chem. Soc. 63* (1941) 47.

68. Mislow, K., *Introduction to Stereochemistry. W.A. Benjamin, New York* (1965) 16.

69. Cotton, F.A., Wilkinson, G., *Advanced Inorganic Chemistry 3rd Edn* (1972) J. Wiley and Sons, Inc.

70. Gillespie, R.J., *Molecular Geometry, Van Nostrand-Reinhold:* London (1972).

71. Ho, Y.K., Zuckerman, J.J., *J. Organomet. Chem. 49* (1973) 1

72. Rosenfiled, R.E., Parthasarathy, R., Dunitz, J.D., *J. Am. Chem. Soc. 99:14* (1977) 4860.

73. Fukui, K., Yonezawa, T., Shingu, H., *J. Chem. Phys. 20* (1952) 722.

74. Agmon, N., *Chem. Phys. Lett. 45* (1977) 343.

REFERENCES FOR STRUCTURAL CORRELATION WITH 6 - FIGURE ACRONYMS CORRESPONDING TO CAMBRIDGE CRYSTALLOGRAPHIC DATA FILE.

ATCTHG Alcock, N.W., Herron, N., Moore, P., *J. Chem. Soc., Dalton,* (1978) 394.

BHGETC Chieh, C., *Can. J. Chem. 56* (1978) 564.

BMTUHG Battaglia, L.P., Corradi, A.B., Marcotrigiano, G., Pellacani, G.C., *J. Chem. Soc., Dalton,* (1979) 1089.

BTCHGP Canty, A.J., Raston, C.L., White, A.H., *Aust. J. Chem. 31* (1978) 677.

REFERENCES CONTINUED

BTETHG	Chieh, C., *Can. J. Chem. 56* (1978) 974.
CETCHG	Book, L., Chieh, C., *Acat Cryst. B36* (1980) 300.
CLTCHG	Bandoli, G., Clemente, D.A., Sindellare, L., Tondello, E., *J. Chem. Soc., Dalton,* (1975) 449.
CMCPHG	Lavertue, P., Hubert, J., Beauchamp, A.L., *Inorg. Chem. 15* (1976) 322.
CMPRTM	Brotherton, P.D., Epstein, J.M., White, A.H., Willis, A.C., *J. Chem. Soc., Dalton,* (1974) 2341.
COHGPY	Beauchamp, A.L., Pazdernik, L., Rivest, R., *Acta Cryst. B32* (1976) 650.
CTSCHG	Chieh, C., *Can. J. Chem. 55* (1977) 1583.
ENHGTC	Duplancic, T., *et al., J. Chem. Soc., Dalton,* (1976) 887.
ETACHG	Canty, A.J., Raston, C.L., White, A.H., *Aust. J. Chem. 32* (1979) 311.
HGCLTU	Brotherton, P.D., and White, A.H., *J. Chem. Soc., Dalton,* (1973) 2698.
HGCSCD	Cheung, K.K., Sim, G.A., *J. Chem. Soc.* (1965) 5988.
HGCTOX	McEwen, R.S., Sim, G.A., *J. Chem. Soc. A* (1967) 271.
HGDMOP	McEwen, R.S., Sim, G.A., *J. Chem. Soc. A* (1967) 1552.
HGETCB	Iwasaki, H., *Acta Cryst. B29* (1973) 2115.
HGEXAN	Chieh, C., Moynihan, K.J., *Acta Cryst. B36* (1980) 1367.
HGEXAN	Watanabe, Y., *Acta Cryst. B33* (1977) 3566.
HGITUR	Korczynski, A., *Rocz. Chem. 42* (1968) 393.
HGTHZO	Harding, M.M., *J. Chem. Soc.* (1958) 4136.
HRPRPT	Lawton, S.L., *Inorg. Chem. 10* (1971) 328.
IETHSH	Chieh, C., *Can. J. Chem. 55* (1977) 1115.
IHGTUR	Skelton, B.W., White, A.H., *Aust. J. Chem. 30* (1977) 1693.
IMTSHG	Beurskens, P.T., *et al., J. Cryst. Mol. Struct. 1* (1971) 93.

REFERENCES CONTINUED

IPTCHG Ito, M., Iwasaki, H., *Acta Cryst. B35*

MEDTHG Chieh, C., Leung, L.P.C., *Can. J. Chem. 54*

MERSET Bradley, D.C., Kunchur, N.R., *Can. J. Chem. 43*

METHGD Canty, A.J., Rashton, C.L., White, A.H., *Aust. J. Chem 32* (1979) 1165.

MPYMHG Chieh, C., *Can. J. Chem. 56* (1978) 560.

MTBRHG Canty, A.J., Rashton, C.L., White, A.H., *Aust. J. Chem. 32* (1979) 311.

MTCCUE Scouloudt, H., *Acta Cryst. 6* (1953) 651.

NPHHGI Pakhomov, V.I., *Kristallografiya 8* (1963) 789.

PMTAHG Canty, A.J., Rashton, C.L., White A.H., *Aust. J. Chem. 31* (1978) 677.

SBHGAF Terzis, A., Faught, J.B., Pouskoulelis, G., *Inorg. Chem. 19* (1980) 1060.

SURHGC Korczynski, A., *Rocz. Chem. 42* (1968) 1207.

TAMHGC Rolies, M., De Ranter, C.J., *Cryst. Struct. Commun. 6* (1977) 157.

TCPOLM Beauchamp, A.L., Saperas, B., Rivest, R., *Can. J. Chem. 52* (1974) 2923.

TCTPHG Makhija, R.C., Beauchamp, A.L., Rivest, R., *J. Chem. Soc., Dalton,* (1973) 2447.

TENHGT Cannas, M., Cristini, A., Marongiv, G.M., *Cryst. Struct. Commun. 7* (1978) 37.

TPTCHG Sakhri, A., Beauchamp, A.L., *Acta Cryst. B31* (1975) 409.

TSCHGB Chieh, C., Lee, L.P.C., Chiu, C., *Can. J. Chem. 56* (1978) 2526.

TTPHGC Alcock, N.W., Herron, N., Moore, P., *J. Chem. Soc., Dalton* (1978) 394.

TUHGCL Brotherton, P.D., White, A.H., *J. Chem. Soc., Dalton* (1973) 2696.

TUHGCL Korczynski, A., *Proc. Sem. Cryst. Coord. CPDS.* (1973) 48.

REFERENCES CONTINUED

TUHGCS Criado, A., Conde, A., Moreno, E., *Z. Kristallogr.* *141* (1975) 193.