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The Structure of Mercury(II) Isopropylxanthate*

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Abstract

Mercury(II) isopropylxanthate, $[\mathrm{Hg}\{\mathrm{S_2CO(iso\text{-}C_3H_7)}\}_2]$, $M_r = 471{\cdot}1$, is monoclinic, space group $P2_1/c$, with $a = 14{\cdot}226\,(8)$, $b = 9{\cdot}806\,(8)$, $c = 21{\cdot}410\,(10)$ Å, $\beta = 100{\cdot}13\,(10)°$, $Z = 8$, $D_m = 2{\cdot}00$ (flotation), $D_x = 2{\cdot}08$ Mg m^{-3}, μ(Mo $K\alpha$) = 10·95 mm^{-1}. The final R based on the anisotropic least-squares refinement was 0·063 for 1973 independent reflexions. Four Hg atoms and four bridging xanthate groups $[-\mathrm{S-C-S}-]_4$, link together alternately to form a centrosymmetric 16-membered ring. A xanthate group chelates the first Hg atom in the ring and another xanthate group bridges the second together with the corresponding one in the adjacent ring. The latter bridging groups are arranged around the twofold screw axis generating an infinite –Hg–S–C–S–Hg– helical chain along **b**. The two-dimensional sheets of the 16-membered rings interlinked by the helical chains are stacked along **a**.

Introduction

Many crystal structures of zinc-group (Group II*b* elements of the Periodic Table) salts of xanthogenic acid are characterized by the formation of a 16-membered ring consisting of four metal atoms and four bridging S–C–S groups. In zinc(II) isopropylxanthate (Ito, 1972), the molecule exists as an isolated tetramer with a centrosymmetric 16-membered ring. Each Zn atom is coordinated by an additional xanthate group (chelating group) (Fig. 3*a*). In zinc(II) ethylxanthate (Ikeda & Hagihara, 1966), cadmium(II) ethylxanthate (Iimura, Ito & Hagihara, 1972), cadmium(II) isopropylxanthate (Iimura, 1973) and mercury(II) ethylxanthate (Chieh & Moynihan, 1980; Watanabe, 1977), every xanthate group bridges two metal atoms to form a two-dimensional network of extended 16-membered rings (Fig. 3*b*). From an interest in these characteristic molecular aggregations the crystal structure analysis of mercury(II) isopropylxanthate, $[\mathrm{Hg}\{\mathrm{S_2CO(iso\text{-}C_3H_7)}\}_2]$, was undertaken.

Experimental

Mercury(II) isopropylxanthate, $[\mathrm{Hg}\{\mathrm{S_2CO(iso\text{-}C_3H_7)}\}_2]$, was precipitated from an aqueous solution of potassium isopropylxanthate and mercuric chloride. Yellow needle crystals were grown from acetone by rapid evaporation. The specimen used in this work was a needle elongated along the *b* axis with the dimensions 0·03 × 0·08 × 2·58 mm.

Intensities were collected on a READ-1 equi-inclination-type diffractometer (Sakurai, Ito & Iimura, 1970) with graphite-monochromated Mo $K\alpha$ radiation about the *b* axis (0 ~ 10 layers, 2046 reflexions).

Table 1. *Atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

The B_{eq} values are the equivalent isotropic temperature factors (Hamilton, 1959).

	x	y	z	B_{eq} (Å^2)
Hg(1)	6595 (1)	3076 (2)	597 (1)	3·8
Hg(2)	4175 (1)	14 (2)	1792 (1)	3·0
S(1)	7544 (8)	2833 (12)	1681 (5)	5·0
S(2)	8115 (7)	5048 (12)	875 (5)	4·4
S(3)	4992 (7)	4265 (10)	728 (5)	3·9
S(4)	5046 (6)	1344 (8)	1092 (4)	2·6
S(5)	2374 (8)	−565 (12)	1157 (5)	4·7
S(6)	3698 (7)	−2046 (11)	458 (4)	3·7
S(7)	4790 (6)	−2153 (10)	2332 (4)	3·1
S(8)	6524 (7)	−3811 (10)	2292 (5)	3·8
O(1)	8851 (20)	4449 (28)	2094 (14)	5·7
O(2)	3632 (17)	2942 (27)	1172 (11)	4·1
O(3)	1854 (16)	−1987 (25)	98 (11)	3·7
O(4)	5943 (16)	−1712 (23)	1574 (10)	3·3
C(1)	8211 (22)	4161 (34)	1558 (15)	2·7
C(2)	4528 (25)	2953 (36)	1083 (14)	3·1
C(3)	2589 (22)	−1475 (31)	518 (15)	2·5
C(4)	5713 (28)	−2513 (43)	2033 (17)	4·5
C(5)	9466 (24)	5744 (40)	2116 (19)	4·2
C(6)	9470 (36)	6187 (52)	2794 (23)	7·5
C(7)	10372 (35)	5231 (55)	1950 (31)	8·8
C(8)	3007 (31)	4228 (40)	1068 (21)	5·2
C(9)	2060 (37)	3627 (53)	842 (25)	7·3
C(10)	3108 (32)	4932 (48)	1694 (23)	6·5
C(11)	878 (26)	−1516 (35)	29 (18)	3·8
C(12)	409 (33)	−1515 (50)	−644 (22)	6·5
C(13)	463 (34)	−2588 (52)	397 (30)	8·2
C(14)	6780 (23)	−1953 (45)	1270 (17)	4·2
C(15)	6562 (44)	−1491 (73)	589 (24)	10·1
C(16)	7572 (29)	−1039 (52)	1521 (21)	6·1

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* IUPAC name: mercury bis(*O*-isopropyl dithiocarbonate).

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Table 2. *Intramolecular distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Notation: unprimed: *x,y,z*; single prime: 1 − *x*, −*y*, −*z*; double prime: 1 − *x*, *y* + ½, ½ − *z*.

$Hg(1)S_4$ group		$Hg(2)S_4$ group	
Hg(1)–S(1)	2·483 (10)	Hg(2)–S(4)	2·477 (9)
Hg(1)–S(2)	2·884 (10)	Hg(2)–S(5)	2·740 (10)
Hg(1)–S(3)	2·620 (10)	Hg(2)–S(7)	2·502 (9)
Hg(1)–S(6′)	2·442 (9)	Hg(2)–S(8″)	2·617 (10)
S(1)–Hg(1)–S(2)	66·8 (3)	S(4)–Hg(2)–S(5)	109·4 (3)
S(1)–Hg(1)–S(3)	106·4 (3)	S(4)–Hg(2)–S(7)	123·7 (3)
S(1)–Hg(1)–S(6′)	143·2 (3)	S(4)–Hg(2)–S(8″)	121·2 (3)
S(2)–Hg(1)–S(3)	108·3 (3)	S(5)–Hg(2)–S(7)	105·9 (3)
S(2)–Hg(1)–S(6′)	117·9 (3)	S(5)–Hg(2)–S(8″)	91·0 (3)
S(3)–Hg(1)–S(6′)	105·8 (3)	S(7)–Hg(2)–S(8″)	100·1 (3)
Fifth Hg(1)–S contact		Fifth Hg(2)–S contact	
Hg(1)–S(4)	3·112 (9)	Hg(2)–S(6)	3·466 (9)
S(1)–Hg(1)–S(4)	86·0 (3)	S(4)–Hg(2)–S(6)	81·6 (2)
S(2)–Hg(1)–S(4)	147·8 (2)	S(5)–Hg(2)–S(6)	55·9 (3)
S(3)–Hg(1)–S(4)	61·6 (3)	S(7)–Hg(2)–S(6)	83·6 (3)
S(6′)–Hg(1)–S(4)	94·2 (3)	S(8′)–Hg(2)–S(6)	146·0 (3)
Bridging group 1		Bridging group 2	
S(3)–C(2)	1·69 (3)	S(5)–C(3)	1·71 (3)
S(4)–C(2)	1·74 (3)	S(6)–C(3)	1·70 (3)
C(2)–O(2)	1·32 (4)	C(3)–O(3)	1·35 (3)
O(2)–C(8)	1·54 (4)	O(3)–C(11)	1·45 (4)
C(8)–C(9)	1·47 (6)	C(11)–C(12)	1·48 (5)
C(8)–C(10)	1·49 (6)	C(11)–C(13)	1·50 (6)
Hg(1)–S(3)–C(2)	97·2 (12)	Hg(2)–S(5)–C(3)	102·9 (11)
Hg(2)–S(4)–C(2)	103·2 (12)	Hg(1′)–S(6)–C(3)	101·3 (10)
S(3)–C(2)–S(4)	120 (2)	S(5)–C(3)–S(6)	122 (1)
S(3)–C(2)–O(2)	122 (2)	S(5)–C(3)–O(3)	120 (2)
S(4)–C(2)–O(2)	114 (2)	S(6)–C(3)–O(3)	117 (2)
C(2)–O(2)–C(8)	121 (3)	C(3)–O(3)–C(11)	125 (3)
O(2)–C(8)–C(9)	101 (3)	O(3)–C(11)–C(12)	111 (3)
O(2) -C(8)–C(10)	107 (3)	O(3)–C(11)–C(13)	101 (3)
C(9)–C(8)–C(10)	115 (4)	C(12)–C(11)–C(13)	111 (3)
Bridging group 3		Chelating group	
S(7)–C(4)	1·60 (4)	S(1)–C(1)	1·66 (3)
S(8)–C(4)	1·74 (4)	S(2)–C(1)	1·69 (3)
C(4)–O(4)	1·34 (4)	C(1)–O(1)	1·36 (4)
O(4)–C(14)	1·47 (4)	O(1)–C(5)	1·54 (5)
C(14)–C(15)	1·51 (6)	C(5)–C(6)	1·51 (6)
C(14)–C(16)	1·47 (5)	C(5)–C(7)	1·48 (7)
Hg(2)–S(7)–C(4)	104·3 (14)	Hg(1)–S(1)–C(1)	90·5 (10)
Hg(2)–S(8″)–C(4″)	104·0 (13)	Hg(1)–S(2)–C(1)	77·1 (11)
S(7)–C(4)–S(8)	125 (2)	S(1)–C(1)–S(2)	126 (2)
S(7)–C(4)–O(4)	119 (3)	S(1)–C(1)–O(1)	110 (2)
S(8)–C(4)–O(4)	115 (3)	S(2)–C(1)–O(1)	124 (2)
C(4)–O(4)–C(14)	123 (3)	C(1)–O(1)–C(5)	119 (3)
O(4)–C(14)–C(15)	110 (3)	O(1)–C(5)–C(6)	100 (3)
O(4)–C(14)–C(16)	112 (3)	O(1)–C(5)–C(7)	103 (3)
C(15)–C(14)–C(16)	101 (4)	C(6)–C(5)–C(7)	118 (4)
Van der Waals contact distances (Å) with e.s.d.'s			
C(7)–C(13,+*a*,+*b*)	3,98 (6)	C(11)–C(12′,−*a*)	3·84 (5)
C(11)–C(11′,−*a*)	3·87 (6)	C(6″,−*b*)–C(12′,−*a*)	3·39 (6)

Interlayer scale factors were determined from additional *c*-axis data. An ω-scan mode was used with a scanning speed of 1° min^{-1}. A total of 1973 independent reflexions with $I > 2{\cdot}5\sigma(I)$ were used for the structure analysis. An absorption correction was applied using the cylinder approximation ($\mu r = 0{\cdot}30$); this correction caused no significant changes in the atomic positional parameters.

The crystal structure was analysed by the usual heavy-atom Fourier method. Anisotropic block-diagonal least-squares refinement, in which the weight w was chosen as 1 for $0 < |F_o| < 250$ and $(250/F_o)^2$ for $|F_o| \geq 250$, converged to a final R of 0·064 with H atoms omitted.† The atomic scattering factors and anomalous-dispersion corrections for Hg and S atoms were taken from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are given in Table 1.† Bond distances and angles are listed in Table 2.

Discussion of the structure

Molecular aggregation

The atomic arrangement viewed along the *b* axis and the network of the 16-membered rings viewed along the a^* axis are shown in Figs. 1 and 2 respectively. Of the four crystallographically independent isopropylxanthate groups, the first [S(3), S(4), C(2), O(2), C(8), C(9) and C(10)] and the second [S(5), S(6), C(3), O(3), C(11), C(12) and C(13)] bridge Hg(1) and Hg(2), and Hg(1′) and Hg(2) respectively, forming a tetrameric unit with a 16-membered ring around the centre of symmetry (bridging groups 1 and 2). The third [S(7), S(8), C(4), O(4), C(14), C(15) and C(16)] interlinks the tetrameric units successively about the twofold screw axis, generating a helical –Hg–S–C–S–Hg– chain (bridging group 3). The fourth [S(1), S(2), C(1), O(1), C(5), C(6) and C(7)] is bonded to Hg(1) with the two sulphur ends S(1) and S(2) (chelating group). As a result, a two-dimensional sheet of 16-membered rings combined with the helical chains is built up parallel to the (100) plane.

Helical chains formed through bridging ligands play an important role in many mercury dithioacid structures. In mercury(II) ethylxanthate (Watanabe, 1977; Chieh & Moynihan, 1980) the chain constructed about the twofold screw axis contacts the neighbouring chain at the HgS_4 configuration generating a network of 16-membered rings. This molecular aggregation is similar to that of cadmium(II) isopropylxanthate (Iimura, 1973) (Fig. 3*b*). In the case of mercury(II) diisopropyldithiophosphate (Lawton, 1971) the helical chain produces a pseudo-polymeric compound.

Thus, the crystal structures of zinc-group isopropylxanthates are classified into three types according to the form of the 16-membered-ring assembly, as shown schematically in Fig. 3. The molecular aggregation of $[\mathrm{Hg}\{\mathrm{S_2CO}(\text{iso-}\mathrm{C_3H_7})\}_2]$ takes an intermediate struc-

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35749 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

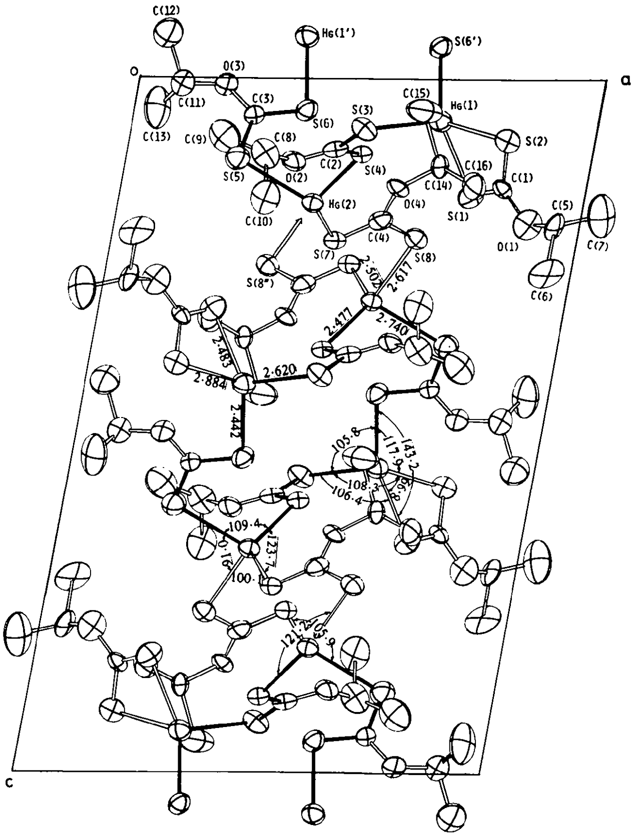

Fig. 1. The *b*-axis projection of the $[Hg\{S_2CO(iso\text{-}C_3H_7)\}_2]$ molecules with thermal ellipsoids (Johnson, 1965). The solid bonds show the 16-membered ring.

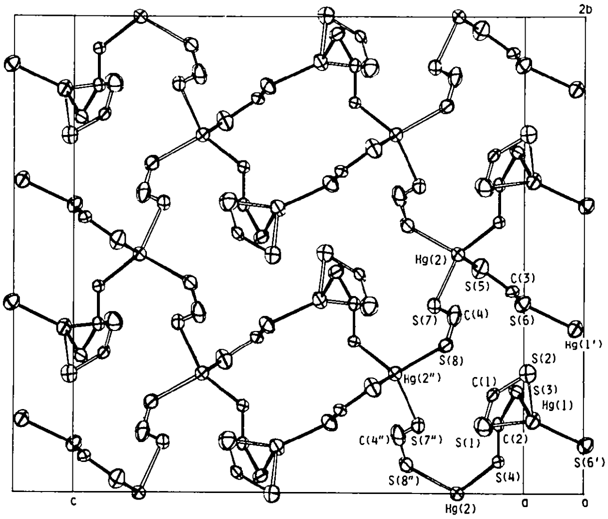

Fig. 2. Two-dimensional network of the molecules viewed along the *a** axis. The *O*-(iso-C_3H_7) groups are omitted.

ture between the tetrameric network of $[Cd\{S_2CO(iso\text{-}C_3H_7)\}_2]$ and the isolated tetramer of $[Zn\{S_2CO(iso\text{-}C_3H_7)\}_2]$.

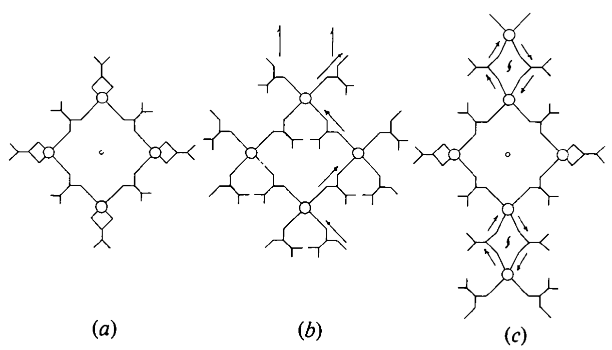

Fig. 3. Three types of molecular aggregation of zinc-group isopropylxanthates, showing (*a*) the isolated tetramer in $[Zn\{S_2CO(iso\text{-}C_3H_7)\}_2]$, (*b*) the two-dimensional network of the tetramer in $[Cd\{S_2CO(iso\text{-}C_3H_7)\}_2]$ and (*c*) the two-dimensional network of the tetramer linked with the helical chains represented by the arrows in $[Hg\{S_2CO(iso\text{-}C_3H_7)\}_2]$. The two-dimensional sheet is perpendicular to the plane of the paper.

Mercury–sulphur configuration

The environment of Hg(1) is quite different from that of Hg(2). While Hg(1) is coordinated by two S atoms of the ring member [S(3) and S(6′)] and two S ends of the chelating group [S(1) and S(2)], Hg(2) is bonded to two S atoms of the ring member [S(4) and S(5)] and two S ends of the two bridging groups 3 [S(7) and S(8″)]. The Hg–S distances range from 2·442 (9) to 2·884 (10) Å. The two short bond lengths, 2·442 (9) and 2·483 (10) Å in $Hg(1)S_4$ and 2·477 (9) and 2·502 (9) Å in $Hg(2)S_4$, are longer than the linear bicovalent distance of 2·36 Å in cinnabar (Aurivillius, 1950) and are comparable to the sum of the univalent radii of Hg and S atoms, 2·48 Å (Pauling, 1960).* The longest [2·884 (10) Å] is close to the ionic contact distance of Hg^{2+} and S^{2-}, 2·94 Å. Other Hg–S bond distances are distributed between the tetrahedral distances of metacinnabarite (2·5424 Å) (Aurivillius, 1964) and the ionic distance. The fifth Hg–S contact is found between Hg(1) and S(4), and Hg(2) and S(6) at distances of 3·112 (9) and 3·466 (9) Å respectively. The former is somewhat shorter and the latter is longer than the sum of the van der Waals radii of the S atom (1·85 Å) and one half of the Hg–Hg distance in crystalline mercury (1·50 Å) (Sutton, 1958).

The S–Hg–S angles between the two shortest bonds in $Hg(1)S_4$ and $Hg(2)S_4$ take the largest values, 143·2 (3) and 123·7 (3)° respectively, which deviate significantly from the ideal tetrahedral angle (109·5°). Similar wide angles are also found in other mercury compounds, as shown in Table 3. They are close to the mean value (144·7°) of the ideal tetrahedral angle and the linear bicovalent angle (180°). The coordination of S atoms to the Hg atom was classified into

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* Atomic radii are taken from Pauling (1960) unless otherwise stated.

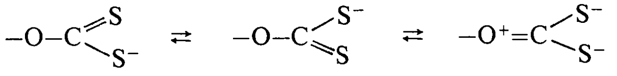
Table 3. *The widening effect of* S–Hg–S *bond angles between two short bonds in the* HgS_4 *configuration*

	S–Hg–S (°)	Two short bonds (Å)		Other two bonds (Å)	
$[Hg\{S_2P(iso\text{-}OC_3H_7)_2\}_2]$	149·7 (2)	2·391 (6)	2·388 (5)	2·748 (5)	2·888 (5)
$[Hg_2\{S_2CN(C_2H_5)_2\}_4]$	146·0 (2)	2·418 (7)	2·520 (6)	2·663 (6)	2·698 (6)
$[Hg(S_2COC_2H_5)_2](P2_1/c)$	147·7 (1)	2·417 (4)	2·421 (4)	2·789 (4)	2·854 (4)
$[Hg(S_2COC_2H_5)_2](P2_1)$	148·8 (3)	2·313 (8)	2·505 (9)	2·749 (8)	2·943 (10)
$[Hg\{S_2CO(iso\text{-}C_3H_7)\}_2]$	143·2 (3)	2·442 (9)	2·483 (10)	2·620 (10)	2·884 (10)
	123·7 (3)	2·477 (9)	2·502 (9)	2·617 (10)	2·740 (10)

two types by Lawton (1971). One is of HgS_2 type with two Hg–S bonds (2·36 ~ 2·49 Å) definitely shorter than the others. The bond angle between them tends to widen from the tetrahedral angle to approach the linear bicovalent bond. The other is of HgS_4 type with four intermediate bonds (2·49 ~ 2·66 Å) having tetrahedral or pseudo-tetrahedral symmetry. As can be seen from Table 3 the two phases of mercury(II) ethylxanthate are close to HgS_2 type; however, the four Hg–S bonds in mercury(II) isopropylxanthate consist of one long, one intermediate and two short bonds. Therefore, the S coordinations to the Hg atom in mercury(II) isopropylxanthate belong to a type intermediate between the HgS_2 and HgS_4. Another intermediate type, two relatively short and intermediate Hg–S bonds, was noted by Iwasaki (1973) in a study of mercury(II) diethyldithiocarbamate.

Xanthate ligands

The bridging and chelating xanthate ligands adopt structures similar to those in zinc(II) isopropylxanthate (Ito, 1972), whereas the coordinations of the four ligands about the Hg atoms are quite different, as shown in the two HgS_4 configurations. The S–C distances range from 1·60 (4) to 1·74 Å with a mean of 1·69 Å, and S_2C–O distances range from 1·32 (4) to 1·36 (4) Å with a mean of 1·34 Å. These lie between the single- and double-bond distances; S=C 1·607, S–C 1·812, C=O 1·207 and C–O 1·432 Å (Pauling, 1960). These intermediate distances are interpreted as being a result of the following resonance structures in the xanthate groups.



$$-O-C\begin{smallmatrix}\nearrow S\\ \searrow S^-\end{smallmatrix} \rightleftarrows -O-C\begin{smallmatrix}\nearrow S^-\\ \searrow S\end{smallmatrix} \rightleftarrows -O^+=C\begin{smallmatrix}\nearrow S^-\\ \searrow S^-\end{smallmatrix}$$

Van der Waals contacts

The two-dimensional network consists of 16-membered rings linked with the helical chains (Fig. 2). It is tightly packed with isopropyl–isopropyl, isopropyl–sulphur and sulphur–sulphur contacts. The network stacks along **a** through van der Waals contacts of the methyl ends of the bridging and chelating isopropyl groups with those of the adjacent networks. Inter-network van der Waals contacts shorter than 4·0 Å are shown in Table 2. The distance C(6″, −*b*)–C(12′, −*a*) (3·39 Å) is shorter than a normal methyl–methyl contact (4·9 Å).

Numerical calculations were carried out on a FACOM 230-75 computer of this Institute using the program system *UNICS* II (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). The author thanks Professor H. Hagihara and Dr H. Iwasaki for valuable discussions.

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