The Crystal and Molecular Structures of some Molecules showing S...O Interaction. III. 3,5-Bis(pivaloylmethylene)-1,2,4-trithiolane

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Crystals of 3,5-bis(pivaloylmethylene)-1,2,4-trithiolane, $C_{14}H_{20}O_2S_3$, belong to the monoclinic system, $a = 5.936$ (7), $b = 13.023$ (10), $c = 22.732$ (15), $\beta = 108.02$ (2)°, space group $P2_1/c$, $Z = 4$ molecules per cell. The structure was solved by Patterson methods. The molecule is approximately symmetric about the mid line and shows S···O distances of 2.509 (5) and 2.517 (5) Å.

The third compound of the series to be studied in connexion with the S···O interactions was 3,5-bis-(pivaloylmethylene)-1,2,4-trithiolane, BPMT, (I).

(I)
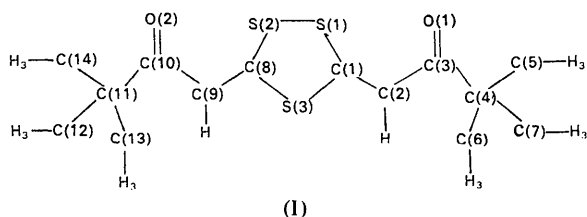
Crystals of BPMT prepared by Gompper & Töpfl's (1962) method, kindly supplied by Professor P. Yates, had been crystallized from a chloroform–hexane mixture as yellow needles elongated along the *x* monoclinic axis (*y* unique).

Preliminary photographic examination showed the crystals to be monoclinic, space group $P2_1/c$. The cell dimensions obtained were subsequently refined by 2θ measurements on a Picker four-circle diffractometer yielding: $a = 5.936$ (7), $b = 13.023$ (10), $c = 22.732$ (15) Å, $\beta = 108.02$ (2)°. The calculated unit-cell volume, 1757·3 Å³, and M.W. of 316·5 give, for $Z = 4$ molecules per cell, a calculated density 1·206 g.cm⁻³ compared with a measured 1·22 g.cm⁻³.

For X-ray intensity measurements a portion of crystal was cut from a needle and it then measured approximately $0.15 \times 0.15 \times 0.2$ mm. The linear absorption coefficient for Cu $K\alpha$ is calculated as 37·5 cm⁻¹ and no absorption corrections were applied to the intensity data.

Three-dimensional intensity data were collected by diffractometer in θ–2θ scan mode using Ni-filtered Cu $K\alpha$ radiation. The procedure adopted in collecting the data was as set out in part II (Mellor & Nyburg, 1971). Intensity measurements were made on 2778 independent reflexions within the range $0 < 2\theta \le 130°$. After data reduction, 530 of these reflexions were classified as unobserved.

Normalized structure amplitudes, E, were generated as in part II, giving 129 reflexions with $|E| > 2.0$, but with only a third of these in the parity group for which $k + l$ is odd. When the range of $|E|$ was extended down

to 1·5 this distribution was less marked but still apparent, implying that some or all of the sulphur atoms lie near the (020) planes.

The structure was solved from the sharpened, origin-removed Patterson function using $(E^2 - 1)$ as coefficients. Sufficient is known of the geometry of this type of molecule to allow one to assume with some confidence that the S(1)S(2)S(3) triangle will have S(1)–S(2) approximately 2·1 Å and S(1)···S(3) approximately 3·0 Å. A set of three atomic positions having this geometry could be postulated which accounted for the highest 22 peaks on the Patterson function. These (sulphur) positions, when used for phasing, yielded all the non-hydrogen atomic positions on an electron density map which was free from false symmetry.

The refinement procedure followed was the same as in part II of this series. After several cycles of refinement with isotropic temperature factors it was noted that the three reflexions with large intensity values 011, 023 and 024 had been insufficiently attenuated owing to an unnoticed malfunction of the diffractometer programmer. These intensity values were excluded from subsequent refinement cycles.

The final cycle of least-squares anisotropic refinement had a conventional R of 0·11 and gave the parameters listed in Table 1. Derived bond lengths and angles together with their standard deviations are given in Fig. 1. The thermal motion of the three t-butyl methyl carbon atoms is very pronounced and highly anisotropic (Fig. 1). The hydrogen atoms attached to atoms C(2) and C(9) were clearly revealed on a Fourier synthesis but those associated with t-butyl methyl groups were poorly defined and of low electron density.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). A list of observed and calculated structure factors is given in Table 2. No hydrogen atoms were included in the F_c values.

Discussion

The structure analysis confirms the 1,2,4-trithiacyclopentane structure assigned by Gompper & Töpfl (1962) and later confirmed by Lynch (1966). In addition it reveals that the molecule has one of the two possible
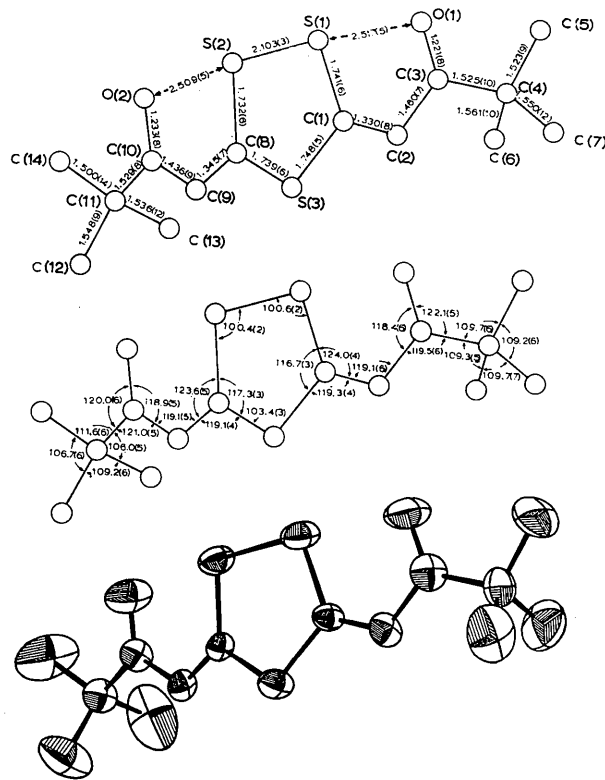
cis conformations with the α,β unsaturated carbonyl *s–cis* (Fig. 1). Least-squares planes for various groups of atoms in BPMT are given in Table 3. Note that four atoms of the central ring, C(1)–S(1)–S(2)–C(8), (plane *A*) are closely coplanar but S(3) is significantly displaced from this plane by 0·215 Å.

Hordvik (1966) has surveyed the available structural data for molecules containing an X–S^{II}–S^{II}–Y bond and has shown that the S–S bond length is correlated with the dihedral angle between planes X–S–S and S–S–Y. Lone-pair repulsion would be most pronounced at a dihedral angle of 0° and π bonding most favourable at 90°. Hence the shortening of S^{II}–S^{II} observed with increasing dihedral angle. In BPMT close planarity of C(1)–S(1)–S(2)–C(8) makes the dihedral angle in question very small (2°). The S^{II}–S^{II} bond length found, 2·103 Å, fits in very well with Hordvik's curve and implies that the bond is not affected by any possible interaction between the sulphur atoms and the closely adjacent keto oxygen atoms.

The molecule in the crystal is not required crystallographically to have any symmetry although of course the (isolated) molecule would be expected to have a mirror plane. That this is closely so can be seen not only by comparing the bond lengths and angles in Fig. 1 but also by *Best Molecular Fit* (Nyburg, 1969). This best least-squares molecular fit is illustrated in Fig. 2. The four independent C(sp^2)–S bond lengths do not differ significantly from their mean, 1·740 Å, which in turn matches closely that in PDM (paper II) and the C(3)–C(4) and C(10)–C(11) bond lengths 1·525 and 1·529 Å are consistent with those normally accepted for the C(sp^3)–CO bond (Sutton, 1958, 1965). Mean bond lengths for C–CH$_3$ at 1·532 Å and tetrahedral CH$_3$–C–CH$_3$ angles are normal.

As to the S···O interaction, each of the sets of five atoms S(1)–C(1)–C(2)–C(3)–O(1) (plane *C*) and S(2)–

C(8)–C(9)–C(10)–O(2) (plane *D*) is quite closely coplanar having maximum deviations from the least-squares planes of 0·035 and of 0·046 Å for C(3) and C(10) respectively (see Table 3).

Fig. 1. Atomic numbering scheme, bond lengths, angles and e.s.d.'s of BPMT, and perspective view of the molecule seen from about 80 Å showing 50 % probability thermal ellipsoids (Johnson, 1965).

Table 1. *Fractional atomic coordinates of non-hydrogen atoms, anisotropic thermal parameters* (Å^2) *and their standard deviations*

The temperature factor T is of form $\exp\left[-\frac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2lkb^*c^*B_{23})\right]$.

	10^4x	10^4y	10^4z	10^2B_{11}	10^2B_{22}	10^2B_{33}	10^2B_{12}	10^2B_{13}	10^2B_{23}
S(1)	2936 (3)	−142 (13)	1446 (8)	263 (6)	516 (8)	544 (9)	−77 (6)	151 (6)	−234 (7)
S(2)	1956 (3)	−1087 (13)	657 (7)	277 (7)	460 (8)	480 (8)	−20 (6)	150 (6)	−168 (7)
S(3)	−2295 (3)	−192 (12)	882 (7)	282 (6)	371 (7)	416 (8)	57 (6)	70 (5)	−144 (6)
O(1)	3849 (7)	944 (37)	2407 (21)	311 (21)	777 (31)	742 (29)	−57 (20)	191 (21)	−359 (25)
O(2)	562 (8)	−2329 (35)	−225 (22)	399 (23)	589 (27)	799 (31)	−52 (20)	221 (21)	−356 (24)
C(1)	160 (8)	203 (40)	1491 (24)	234 (23)	247 (24)	326 (25)	−30 (20)	56 (20)	−60 (21)
C(2)	−177 (10)	752 (41)	1950 (25)	377 (28)	261 (26)	333 (28)	−42 (22)	61 (23)	−113 (23)
C(3)	1879 (11)	1109 (45)	2448 (28)	415 (31)	292 (29)	451 (33)	−43 (25)	119 (26)	−66 (26)
C(4)	1512 (11)	1664 (50)	3002 (27)	477 (33)	463 (35)	334 (30)	−23 (28)	118 (26)	−129 (27)
C(5)	3902 (13)	1975 (69)	3450 (36)	490 (39)	1194 (64)	665 (46)	−161 (42)	30 (35)	−578 (47)
C(6)	−125 (15)	2614 (60)	2770 (35)	1032 (58)	600 (46)	718 (49)	373 (43)	241 (44)	−125 (39)
C(7)	291 (15)	898 (69)	3328 (36)	839 (53)	1037 (60)	673 (47)	−332 (46)	405 (42)	−8 (46)
C(8)	−1099 (9)	−1064 (39)	481 (23)	298 (24)	205 (23)	280 (24)	57 (20)	118 (20)	−19 (20)
C(9)	−2566 (9)	−1663 (40)	47 (24)	352 (27)	228 (25)	300 (26)	33 (21)	119 (22)	−66 (21)
C(10)	−1583 (10)	−2360 (43)	−298 (26)	371 (28)	263 (27)	360 (29)	−8 (23)	89 (24)	−59 (23)
C(11)	−3129 (11)	−3167 (45)	−725 (27)	417 (31)	306 (29)	417 (33)	−1 (29)	107 (26)	−129 (25)
C(12)	−5363 (14)	−2656 (63)	−1171 (37)	590 (42)	750 (50)	812 (52)	55 (40)	−121 (38)	−216 (44)
C(13)	−3882 (19)	−3921 (65)	−301 (40)	1530 (83)	643 (51)	802 (55)	−568 (55)	135 (54)	122 (45)
C(14)	−1847 (16)	−3674 (80)	−1121 (48)	788 (55)	1538 (83)	1493 (79)	−256 (53)	512 (55)	−1288 (70)

Planes C and D intersect at 10·1°, S(3) being significantly displaced from each plane as it is from the plane of the central ring. The S···O distances at 2·509 and

2·517 Å are the smallest of those found in this series of three structure analyses.

Intermolecular interatomic distances of less than

Table 2. *Calculated and observed structure factors*

F_o marked 'E' were insufficiently attenuated before counting. They were not included in the refinement.

(Large multi-column table of H, L, $10F_c$, $10F_o$ values — numeric data not legibly reproducible.)

Table 2 (cont.)

H	L	10F_o	10F_c	... (structure factor listing, illegible)

Table 3. Some least-squares planes

Distances with asterisks refer to atoms excluded from the least-squares plane analysis. All planes of form $Px + Qy + Rz = S$ with x, y, z in fractional coordinates.

	Plane A Δ(Å)	Plane B Δ(Å)	Plane C Δ(Å)	Plane D Δ(Å)
S(1)	−0·0145	0·3170*	−0·0218	−0·2672*
S(2)	0·0145	0·3611*	−0·1474*	−0·0268
S(3)	0·2145*	0·0	0·1180*	0·1395*
O(1)	−0·1438*		0·0329	
O(2)	−0·1729*			0·0417
C(1)	0·0111	0·0	0·0206	
C(2)	−0·0938*		0·0031	
C(3)	−0·2204*		−0·0349	
C(8)	−0·0112	0·0		0·0238
C(9)	−0·1661*			0·0070
C(10)	−0·3098*			−0·0457
P	−0·9624	−2·1053	−0·9892	−0·7946
Q	−10·299	−9·6764	−10·834	−9·5099
R	13·898	14·763	12·613	15·424
S	1·8589	1·9710	1·6655	1·8649

4·0 Å are listed in Table 4, and the packing illustrated in Fig. 3. None deserve special comment except that the van der Waals radius of sulphur appears to be about 1·72 Å.

There are now sufficient crystal structure analyses known of molecules showing S···X (X=S,O,Se,N) interactions for some generalizations to be possible.

The interaction always occurs across the open ends of a five-membered ring of atoms S···C···C···C···X in which the carbon atoms are sp^2 hybridized. Clearly for efficient π orbital overlap in this ring it needs to be planar. It can only be assumed then that, for some

Table 4. Interatomic distances less than 4·0 Å

Atom B is generated from the coordinates of Table 1 using the unit-cell translation shown together with the following symmetry operations:

1	x, y, z	3	$x, \frac{1}{2}+y, \frac{1}{2}+z$
2	$-x, -y, -z$	4	$-x, \frac{1}{2}+y, \frac{1}{2}-z$.

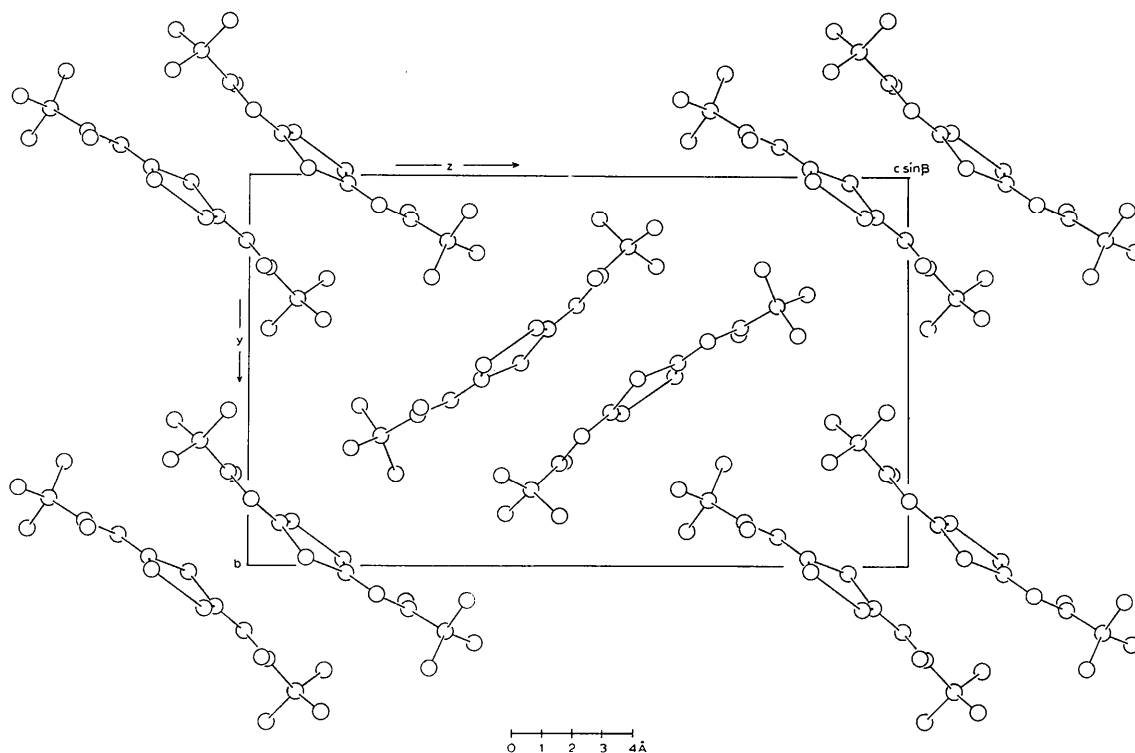| Atom A	Atom B	Unit cell translation of atom B	Distance
S(1)	S(3)₁	(1, 0, 0)	3·45 Å
S(2)	S(3)₁	(1, 0, 0)	3·49
S(2)	S(3)₂	(1, 0, 0)	3·93
S(3)	O(2)₂	(1, 0, 0)	3·88
S(2)	C(5)₄	(1,−1, 0)	3·67
S(2)	C(8)₂	(0, 0, 0)	3·74
S(2)	C(9)₁	(1, 0, 0)	3·98
S(2)	C(9)₂	(0, 0, 0)	3·98
S(3)	C(9)₂	(−1, 0, 0)	3·95
O(1)	C(2)₁	(1, 0, 0)	3·99
O(1)	C(7)₁	(1, 0, 0)	3·75
O(1)	C(12)₂	(1, 0, 0)	3·90
O(2)	C(1)₂	(0, 0, 0)	3·93
O(2)	C(12)₁	(1, 0, 0)	3·72
O(2)	C(13)₁	(1, 0, 0)	3·94
C(1)	C(6)₄	(0,−1, 0)	3·77
C(6)	C(12)₂	(−1, 0, 0)	3·79
C(7)	C(14)₃	(0,−1, 0)	3·54
C(8)	C(8)₂	(0, 0, 0)	3·99

Fig. 2. Best least-squares molecular fit.

Fig. 3. Molecular packing viewed along [100].

reason, there is insufficient repulsion between S and X to prevent the molecule being planar and hence achieving maximum π-orbital overlap. This has led to the view that S and X are actually chemically bonded albeit weakly.

In the thiathiophthens there are two fused systems S⚊⚊C⚊⚊ C⚊⚊ C⚊⚊ S having one S···C in common. There is spectroscopic support for the view that all the three sulphur atoms are bonded (involving d-orbital participation of the central S atom), the rings together constituting a 10 π-electron system akin to that in naphthalene (Johnstone & Ward, 1969). There are however no calculations available for cases where an atom X replaces one of the outer sulphur atoms. When, as will be usually the case, the length of C–X is different from that of C–S, this might cause the S–S–X angle to be different from 180° and presumably militate against d-orbital involvement.

It is in any case clear that the bonds S···S are weak or, more precisely, have a flat potential energy curve. The observed S···X distances show quite a wide variation from molecule to molecule (see Table 1, part I). Inspection of the molecular geometries shows immediately however that this is due to variations in the bond angles in the rings and not in the other bond lengths, which are remarkably similar from molecule to molecule. This of course is due to the well-known fact that interbond angles are readily changed by 5° or more because of inter- or intramolecular forces whereas the lengths of comparable bonds vary by as little as 0·01 Å.

Some calculations of intermolecular crystal forces on the sulphur atoms of certain symmetric thiathiophthens showing different S···S lengths have been carried out (Nyburg, 1970) but the calculations do not correctly predict the observed differences in S···S lengths in every case.

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