observed C—H distances are in the ranges (I) 0·95–1·10 Å and (II) 0·87–1·12 Å.*

The connectivity of the compounds revealed by crystallographic analysis agrees with the predictions based upon chemical and spectroscopic evidence (Delecki, 1970). In the hydrogenation product (II), the H atoms were added to C(1) and C(7) on the same side of the cyclopropyl ring as the O(1) substituent (Fig. 2). The bond lengths and angles in the *A* rings of the two structures are in excellent agreement, and the overall conformations of the rings are nearly identical despite differences in crystal packing. A least-squares fit of atoms C(8) to C(16), O(1) and O(2) in the two structures yields a mean-square difference in the relative position of these atoms of 0·03 Å. The *A* rings have a chair conformation in which atoms C(9) and C(15) are 'above' and C(12) is 'below' the plane of atoms C(10), C(11), C(13) and C(14). The ring has mirror symmetry across a plane bisecting the C(9)—C(15) bond and intersecting C(12). The *C* ring of (II) has a similar chair conformation with atoms C(1) and C(7) 'above' and atom C(4) 'below' the plane of atoms C(2), C(3), C(5) and C(6). This ring is more symmetric and more puckered than the *A* rings as indicated by the magnitudes of its torsion angles. The *C* ring of (I) also has a chair conformation with a mirror plane intersecting C(4) and bisecting the C(1)—C(7) bond. This ring however is much flatter due to the double bond in the cyclopropyl ring. The positions of C(1), C(7) and C(4) relative to the other four atoms of the *C* ring in (I) are reversed as indicated by the change of signs of the torsion angles from those of the *C* ring of (II). There are no intermolecular contacts less than 3·35 Å between nonhydrogen atoms.

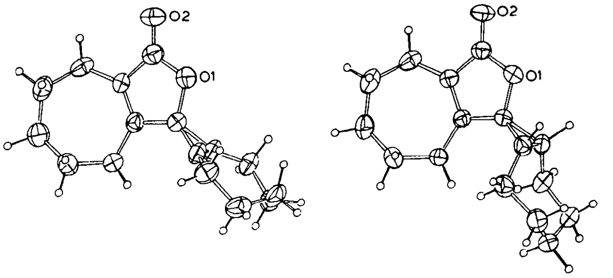

Fig. 2. *ORTEP* drawings of (I) (left) and (II) (right) with thermal ellipsoids for nonhydrogen atoms scaled to 50% probability.

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* Tables of structure factors, positional and thermal parameters for H, anisotropic thermal parameters for the non-H atoms and packing diagrams have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39379 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Low-Temperature X-ray Study of Thianthrene 5,5,10,10-Tetraoxide, $C_{12}H_8O_4S_2$

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Abstract. $M_r = 280·33$, orthorhombic, $Pbcn$, $a = 19·613\ (9)$, $b = 12·161\ (2)$, $c = 14·433\ (8)$ Å, $V = 3442\ (3)$ Å^3, $Z = 12$, $D_m = 1·59\ (2)$ (294 K), $D_x = 1·623$ g cm^{-3} (163 K), $\lambda(\text{Mo } K\alpha_{1,2}) = 0·71069$ Å, $\mu = 4·57$ cm^{-1}, $F(000) = 1728$. Final $R = 0·050$ for 3077 observed reflections. There are 1·5 molecules in the asymmetric unit. In one unit cell, there are eight molecules located on general position *d*, while four molecules lie around twofold axes in such a way that the S···S intramolecular axes are perpendicular to the

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twofold axes. The dihedral angle, which is defined as the angle between planes composed of each phenyl ring with the two S atoms, is different for the two crystallographically distinct sets of molecules. For the molecule in general positions this angle is 138·01 (5)° whereas the molecule around the twofold axis has a dihedral angle of 144·01 (5)°.

Introduction. The wide range of dihedral angles determined for thianthrene by various methods has been attributed to thermally induced flapping motion and to intermolecular interactions, the latter of which includes aromatic-ring interactions and interactions at the S atoms (Larson, Simonsen, Martin & Puig-Torres, 1984; Fujiwara, Kawamura, Takagi & Sasaki, 1983). This report is the first part of a systematic investigation of the geometry of the oxides of thianthrene to study the effects that bonding interactions at the S atoms have on the dihedral angle of these compounds. Hosoya (1958) reported preliminary data on the title compound and estimated the dihedral angle to be 127° from the shape of the phenyl rings using a two-dimensional Fourier projection.

Table 1. *Summary of data collection and structure refinement for thianthrene* 5,5,10,10-*tetraoxide*

A. Data collection (163 K)[a,b]	
Systematic absences	$0kl\ k = 2n + 1$ $h0l\ l = 2n + 1$ $hk0\ h + k = 2n + 1$
Range of *h,k,l*	0–20, 0–25, 0–16
Mode	ω scan
Scan range	Symmetrically over 1·0° about $K\alpha_{1,2}$ maximum
Background	Offset 1·0 and −1·0° in ω from $K\alpha_{1,2}$ maximum
Scan rate (° min^{-1})	2·0–5·0
Exposure time (h)	90·6
Stability analysis[b]	
Computed *s, t*	−0·0036, 0·00004
Max. correction (on *I*) (%)	1·095
2θ range (°)	4·0–60·0
Total reflections measured	4972
Data-crystal volume (mm^3)	0·041
Data-crystal faces	$(11\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{1})$, $(1\bar{1}1)$, $(\bar{2}10)$, $(2\bar{1}0)$, $(\bar{1}11)$, $(1\bar{1}\bar{1})$, (001), $(00\bar{1})$, $(0\bar{1}0)$, (010), (111), $(\bar{1}\bar{1}\bar{1})$, (210), $(\bar{2}\bar{1}0)$
Transmission-factor range	0·845–0·882
B. Structure refinement[c]	
Ignorance factor *p*	0·04
Reflections used, $F > 4\sigma_F$	3077
No. of variables	292
Goodness-of-fit, *S*	1·52
R, *wR*, *R* for all data	0·050, 0·054, 0·093
Max. Δ/σ (H)	−0·036
Max., min. peak in $\Delta\rho$ map (e Å^{-3})	0·49, −0·40

(*a*) Unit-cell parameters were obtained by least-squares refinement of the setting angles of 30 reflections with $20{\cdot}0 < 2\theta < 39{\cdot}0°$. Crystal density was measured by flotation in CCl_4 with a small amount of hexane.

(*b*) Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described in Riley & Davis (1976). Crystal and instrument stability were monitored by re-measurement of four check reflections after every 96 reflections. These data were analysed as detailed in Henslee & Davis (1975).

(*c*) Function minimized was $\sum w(F_o - F_c)^2$, where $w = \sigma_F^{-2}$.

Experimental. All chemicals used in this study were purchased from commercial sources and used without further purification. The thianthrene tetraoxide was prepared by oxidation of thianthrene with excess H_2O_2 in refluxing acetic acid as described by Kaiser & Eargle (1965). Single crystals were obtained by sublimation and were ellipsoidally shaped with 16 well defined faces. Details of data collection and structure refinement are listed in Table 1.

The structure was solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) which afforded positions of three S atoms and one phenyl ring. Subsequent Fourier maps revealed the positions of all non-H atoms. After several cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms, positions for the H atoms were located from a difference Fourier map. After refinement with isotropic thermal parameters for the H atoms was begun, it was observed that the 020 and 040 reflections had large negative ΔF's. They appeared to be suffering from extinction and were removed from further refinement. Scattering factors for H from Stewart, Davidson & Simpson (1965), for non-H atoms from *International Tables for X-ray Crystallography* (1974). The program used to calculate the least-squares planes was supplied by Cordes (1983); other computer programs are listed in reference (11) of Gadol & Davis (1982).

Discussion. The final atomic positional and thermal parameters are given in Table 2.* Bond distances with the atom-labelling scheme and bond angles for the non-H atoms are shown in Figs. 1 and 2 respectively. A stereoview of the unit-cell packing is shown in Fig. 3. The molecule found on a general position will be referred to as *G* while the molecule lying around the twofold axis will be referred to as *B*. The atom-labelling scheme is the same for the two molecules except that those atoms from *B* will be so designated.

The geometry around the S atoms is similar to that found in diphenyl sulphone (Sime & Woodhouse, 1974) and can be described as a distorted tetrahedron. Although the bond angles deviate from ideality, the average dihedral angle between the plane defined by the SO_2 functionality and the plane defined by the S atom

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* Lists of structure-factor amplitudes, anisotropic thermal parameters, bond distances and angles for the H atoms and a table of least-squares planes and dihedral angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39332 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters with equivalent isotropic thermal parameters for the non-*H *atoms and isotropic thermal parameters for the* H *atoms of thianthrene* 5,5,10,10-*tetraoxide*

	x	y	z	U_{eq}*/U_{iso}(Å^2)
S(10)	0·37531 (4)	0·04121 (6)	0·32104 (5)	0·0218 (2)
S(5)	0·29483 (4)	0·05097 (6)	0·51854 (5)	0·0229 (2)
S(5)*B*	−0·04304 (4)	−0·03895 (6)	0·34673 (5)	0·0201 (2)
C(1)	0·2592 (2)	0·1250 (3)	0·2483 (2)	0·0238 (9)
C(2)	0·1916 (2)	0·1602 (3)	0·2523 (3)	0·0278 (10)
C(3)	0·1578 (2)	0·1665 (3)	0·3356 (3)	0·0286 (10)
C(4)	0·1902 (2)	0·1368 (3)	0·4181 (2)	0·0255 (9)
C(4A)	0·25681 (15)	0·0980 (2)	0·4140 (2)	0·0189 (8)
C(5A)	0·38048 (14)	0·0947 (2)	0·5080 (2)	0·0188 (8)
C(6)	0·4132 (2)	0·1313 (3)	0·5872 (2)	0·0234 (9)
C(7)	0·4819 (2)	0·1606 (3)	0·5825 (3)	0·0272 (10)
C(8)	0·51631 (15)	0·1560 (3)	0·4988 (3)	0·0272 (10)
C(9)	0·4830 (2)	0·1221 (3)	0·4187 (3)	0·0247 (9)
C(9A)	0·41502 (15)	0·0899 (2)	0·4239 (2)	0·0195 (8)
C(10A)	0·29106 (15)	0·0923 (2)	0·3293 (2)	0·0178 (8)
O(1)	0·29314 (12)	−0·0670 (2)	0·5192 (2)	0·0340 (8)
O(2)	0·26461 (12)	0·1091 (2)	0·5951 (2)	0·0379 (8)
O(3)	0·37287 (13)	−0·0770 (2)	0·3233 (2)	0·0314 (7)
O(4)	0·40723 (12)	0·0933 (2)	0·2428 (2)	0·0367 (8)
C(1)*B*	0·1483 (2)	−0·1139 (2)	0·2583 (2)	0·0227 (9)
C(2)*B*	0·1800 (2)	−0·1381 (2)	0·3424 (3)	0·0243 (9)
C(3)*B*	0·1430 (2)	−0·1376 (2)	0·4243 (2)	0·0245 (9)
C(4)*B*	0·0740 (2)	−0·1123 (2)	0·4244 (2)	0·0220 (9)
C(4A)*B*	0·04266 (15)	−0·0834 (2)	0·3416 (2)	0·0188 (8)
C(10A)*B*	0·07952 (15)	−0·0843 (2)	0·2586 (2)	0·0188 (8)
O(1)*B*	−0·04319 (12)	0·0797 (2)	0·3466 (2)	0·0279 (7)
O(2)*B*	−0·07594 (12)	−0·0949 (2)	0·4222 (2)	0·0315 (7)
H(C1)	0·282 (2)	0·128 (3)	0·194 (3)	0·039 (11)
H(C2)	0·170 (2)	0·184 (3)	0·202 (3)	0·031 (10)
H(C3)	0·111 (2)	0·199 (3)	0·339 (2)	0·038 (10)
H(C4)	0·170 (2)	0·146 (3)	0·469 (3)	0·038 (12)
H(C6)	0·391 (2)	0·134 (3)	0·639 (3)	0·040 (11)
H(C7)	0·505 (2)	0·190 (3)	0·636 (3)	0·054 (13)
H(C8)	0·569 (2)	0·178 (3)	0·492 (2)	0·030 (9)
H(C9)	0·507 (2)	0·128 (3)	0·362 (3)	0·034 (10)
H(C1)*B*	0·172 (2)	−0·114 (3)	0·203 (3)	0·035 (11)
H(C2)*B*	0·225 (2)	−0·165 (3)	0·346 (2)	0·036 (10)
H(C3)*B*	0·163 (2)	−0·154 (3)	0·481 (3)	0·042 (12)
H(C4)*B*	0·049 (2)	−0·117 (3)	0·474 (3)	0·036 (11)

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$, where A_{ij} is the dot product of the ith and jth direct-space unit-cell vectors.

and the two S-bound C atoms is 90·0 ± 0·4° for both *G* and *B*. The pseudo-axial O atoms are separated by a distance of 3·233 (4) and 3·264 (4) Å for *G* and *B* respectively, with two SO_2 groups being coplanar in each molecule. The S···S intramolecular distance is 3·2610 (11) Å for *G* and 3·263 (2) Å for *B* which is slightly greater than the 3·1926 (8) Å found in thianthrene (Larson *et al.*, 1984). Unlike thianthrene, the S—C—C angles of the central ring system are significantly larger than 120° which may be the result of steric interactions between the sulphone groups. The S—C bond distances in the title compound are equivalent to those found in thianthrene which is in contrast to the thioxanthene system where the S—C distances generally decrease upon oxidation to the sulphone (Chu, 1975). The C—S—C bond angles in *G* and *B* are larger than those found in thianthrene with the result that the dihedral angles are larger than the 127·14 (3)° observed for thianthrene.

The bond distances and angles for molecules *B* and *G* are essentially equivalent except for the C—S—C bond angles. The difference in bond angles is reflected in the observed difference in the dihedral angles with the flatter molecule (larger dihedral angle), *B*, having the larger C—S—C bond angles. The difference in dihedral angles for *B* and *G* can only be due to different packing environments which would imply that the two unique

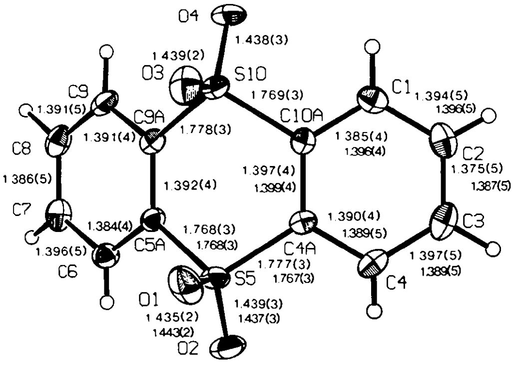
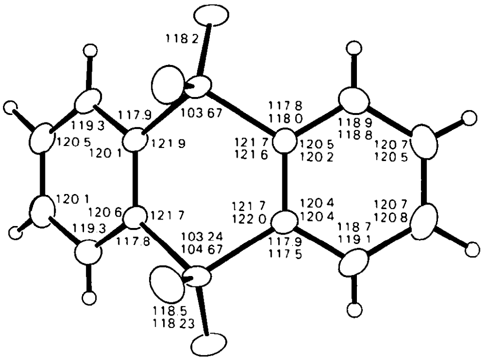


Fig. 1. View of *G* showing bond distances (Å) with e.s.d.'s in parentheses. Values for *B* are shown below those for corresponding atoms of *G*. Ellipsoids are scaled to the 50% probability level.



C(4A)—S(5)—O(1)	108·49 (107·94)	C(9A)—S(10)—O(3)	109·19
—O(2)	108·73 (108·31)	—O(4)	108·55
C(5A)—S(5)—O(1)	108·84 (108·07)	C(10A)—S(10)—O(3)	108·54
—O(2)	108·03 (108·80)	—O(4)	107·76

Fig. 2. Bond angles (°) for *B* are shown below those for *G*. E.s.d.'s are in the range 0·14 to 0·3°. Atoms are identical to the labelled atoms in Fig. 1. For the tabulated angles, those involving corresponding atoms of *B* are shown in parentheses.

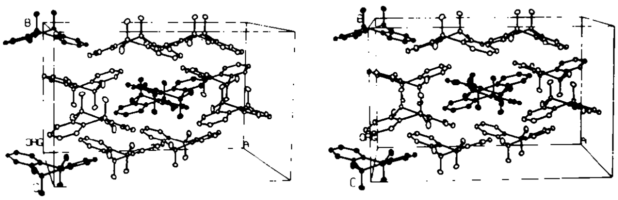


Fig. 3. Stereoview of the unit-cell packing. *B* has been darkened for contrast.

molecules differ little in total energy. That packing forces can influence the dihedral angle has been observed in analogous compounds (Chu, 1975; Chu & Mangion, 1975; Chu & Yang, 1977; Hoffschwelle, Simonsen & Martin, 1981; Phelps & Cordes, 1974) with the observed differences in the dihedral angle between the crystallographically distinct molecules ranging from 1·3 to 9·2°. An examination of the intermolecular contacts reveals no unusually close non-H interactions. The closest non-H contacts are between atoms C(10A) and C(2)*B* $(\frac{1}{2}+x, \frac{1}{2}-y, z)$ at a distance of 3·334 (4) Å and between C(3) and O(3) $(\frac{1}{2}-x, \frac{1}{2}+y, z)$ at a distance of 3·182 (4) Å. There are no O···O contacts less than 3·50 Å. There are, however, some short O···H contacts. These short contacts all involve the pseudo-equatorial O atoms. Atom O(2) is 2·39 (4) Å from atom H(C1)*B* at $x, -y, \frac{1}{2}+z$ while atom O(4) is 2·31 (4) Å from atom H(C9) at $1-x, y, \frac{1}{2}-z$. Atom O(2)*B* is 2·50 (4) Å from atom H(C4) at $-x, -y, 1-z$. Because the pharmacological activity of some members of the phenothiazine ring system (obtained by replacement of one S by a N in thianthrene) has been ascribed, in part, to the dihedral angle (Martin, Korp, Turley & Bernal, 1978), it is important to understand how substituents affect the geometry of these heterocycles. Because crystal-packing forces can mask the effects of these substituents, the interpretation of results from a single structural investigation can be misleading. As a result systematic studies such as the one in which we are currently involved are necessary for a fuller understanding of these compounds.

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Crystal Form II of Cycloamanide A, *cyclo*(-L-Prolyl-L-valyl-L-phenylalanyl-L-phenylalanyl-L-alanyl-glycyl-)–Water–Ethanol (1/1/3), $C_{33}H_{42}N_6O_6.H_2O.3C_2H_6O$, Containing an Unusual β-Bend

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(*Received* 22 *September* 1983; *accepted* 21 *December* 1983)

Abstract. $M_r = 618\cdot7 + 156\cdot2$, orthorhombic, $P2_12_12_1$, $a = 16\cdot716$ (2), $b = 24\cdot007$ (3), $c = 10\cdot918$ (1) Å, $Z = 4$, $V = 4381\cdot4$ Å^3, $D_x = 1\cdot175$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 3\cdot34$ cm^{-1}, $F(000) = 1672$, $R_F = 7\cdot2\%$ for 4007 data with $|F_o| > 0$. Cycloamanide A, isolated from *Amanita phalloides*, occurs in more than one crystalline pseudo polymorph. Form I [Chiang, Karle & Wieland (1982). *Int. J. Pept. Protein Res.* **20**, 414–420] has four H_2O solvent molecules while form II has one H_2O and three C_2H_5OH solvent molecules. The crystals are not isomorphous, although the peptide molecules are isostructural. The unusual intramolecular hydrogen bond in the β-bend encompassing the

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