from C(11), directed perpendicular to the ring at C(5) (Fig. 2). The C(6–10) ring is unable to rotate because of a 3·86 Å in-plane repulsion between C(9) and I(2); the sulphur atom is then accommodated by an expansion of Mo–C(6–10) distances on the sulphur side: Mo–C(8) > Mo–C(6) and Mo–C(9) > Mo–C(10) (see Table 3).

The molecule cannot yield to these crystal repulsions, for it is held at the amino group by intermolecular hydrogen bonds to sulphur (3·32 Å) and to I(1) (3·64 Å). Ligand atoms C(11) and C(12) are forced nearer to the C(1–5) side of the N–Mo–S plane by a third repulsion from C(5) of another molecule acting against the chelate ring at C(11); this initiates and re-enforces the repulsions just described.

The minimum and maximum root-mean-square vibration amplitudes of the molybdenum atom are 0·125 and 0·175 Å. Maximum vibration of the I(1) ion (0·22 Å) is generally perpendicular to the N–H...I hydrogen bond. The displacement of I(2) is greater (0·30 Å)with alignment nearly normal to the C(9)... I(2) repulsion.

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Stereochemistry of Thioxanthenes and Related Folded Molecules.
I. Crystal Structure and Conformation of cis-9-Methylthioxanthene 10-Oxide*

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cis-9-Methylthioxanthene 10-oxide crystallizes in the space group *Pnma* with four molecules per unit cell of dimensions: $a = 8·609$, $b = 11·012$ and $c = 11·977$ Å. The two halves of the molecule are related by a mirror plane. The crystal structure was solved by means of the heavy atom method and refined by full-matrix least-squares on 867 observed reflections to a reliability index of 4·6%. Although the structure was also refined successfully ($R = 4·2\%$) in the wrong space group, $P2_12_12_1$, the molecular dimensions were chemically implausible. Both the 9-methyl and 10-oxygen substituents are 'boat-equatorial'. The best planes of the benzene rings make a dihedral angle of 127°. The *meso* atoms, C(9) and S, are significantly displaced from the benzene plane. The two S–C bond distances are equal (required by symmetry), $1·782 \pm 0·002$ Å, and the S–O bond distance is $1·492 \pm 0·003$ Å. The C(9)–CH₃ bond distance is $1·518 \pm 0·006$ Å, while the carbon–carbon bond involving C(9) and the benzenoid ring is $1·521 \pm 0·003$ Å. The intramolecular distance between the sulfoxide oxygen atom and the *peri* proton is 2·55 Å. The closest approach distance between the methyl proton and the *peri* proton is 2·35 Å. A comparison of the conformation of cis-9-methylthioxanthene 10-oxide with those of related folded structures indicates that the central boat ring is quite 'rigid'.

Introduction

Each of the two configurational isomers of 9-methyl-thioxanthene 10-oxide (*cis* and *trans*) could exist in two

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conformations, I to IV (Fig. 1). Spectroscopic investigations have failed to provide configurational and conformational assignments unambiguously to these various isomers (Ternay, 1968). This X-ray analysis on cis-9-methylthioxanthene 10-oxide (I) was carried out to determine whether the substituents on the 9 and 10 positions were 'boat-equatorial' (*e'*) (I) or 'boat-axial' (*a'*) (II).§ Moreover, this information would facilitate future interpretation of spectral data on these isomers and related compounds. An added reason for carrying out the present investigation was to determine accurate-

ly the C–S bond distances which have been found to be different in similar structures. In *trans*-thioxanthen-9-ol 10-oxide (Ternay, Chasar & Sax, 1967) (V), a hydrogen-bonded crystal, the S–C bond distances are 1·80 and 1·75 Å, while in *β*-thianthrene dioxide (Hosoya, 1966) (VI), a molecular crystal, they are 1·78 and 1·81 Å. However, in thianthrene (Rowe & Post, 1958) (VII), a molecular crystal with sulfur having a coordination number of only 2, and in the present structure, a molecular crystal with sulfur having a coordination of 3, no differences in the C–S bond distances are found.

Experimental

cis-9-Methylthioxanthene 10-oxide (I), $C_{14}H_{12}SO$, has a melting point of 206–7 °C. Crystals of this compound were supplied by Dr A. L. Ternay, Jr of this Department. A crystal of size $0·23 \times 0·23 \times 0·25$ mm³ was cut and mounted for X-ray analysis. The unit-cell dimensions measured on a diffractometer and the space group are given in Table 1. It should be mentioned at this point that the space group was initially erroneously assigned as $P2_12_12_1$, based on the axial extinctions alone. Interestingly, the structure analysis converged to an R of 4·2%. However, the molecular dimensions showed features that were chemically untenable. Dr R. E. Marsh (private communication) suggested to us the possibility of space group $Pnma$ ($Pn2_1a$). Indeed, a re-examination of the X-ray films clearly showed absences $h = 2n + 1$ for $hk0$, and $k + l = 2n + 1$ for $0kl$, in addition to the axial extinctions. Thus the space group of the crystal is $Pnma$ or $Pn2_1a$. The former space group was accepted from a study of Wilson (1949) statistics and confirmed by the structure analysis.

Table 1. *Crystal data on 9-methylthioxanthene 10-oxide*

Melting point,   206–207 °C
Color,   white initially, turned pale yellow after X-ray
          irradiation
$a = 8·609 \pm 0·002$ Å
$b = 11·012 \pm 0·002$
$c = 11·977 \pm 0·002$
λ Cu $K = 1·39217$ Å
Systematic
absences, $h00, h = 2n + 1; 0k0, k = 2n + 1; 00l, l = 2n + 1;$
             $0kl, k + l = 2n + 1; hk0, h = 2n + 1$
Space group, $Pnma$ or $Pn2_1a$
                $Pnma$ confirmed by intensity statistics and
                structure refinement
$D_x = 1·335$ g.cm⁻³
$D_m = 1·322$ g.cm⁻³, at 20 °C
$Z = 4$

Three-dimensional data were collected on a Picker four-circle automated diffractometer to a 2θ value of

134° with Ni-filtered Cu $K\alpha$ radiation. Attenuators of aluminum foil were automatically inserted in the diffracted beam for reflections exceeding 12,000 c.p.s. A takeoff angle of 3°, a θ–2θ scan mode, and a scan rate of 2° per minute were employed for data collection. A general background curve was determined by sixty second counts at various points throughout reciprocal space. The standard reflection (202) was checked every two to three hours. Since the standard showed only minor fluctuations, to within $\pm 0·5\%$ of its intensity, over the data collection period, no correction was applied. Anisotropy in absorption caused by inequality in the crystal cross-section was corrected by measuring a reflection at $\chi = 90°$ as a function of φ in the range used for data collection. The data were corrected for the usual Lorentz and polarization factors and for background. A reflection was considered observed if the intensity was greater than $1·9 B$, where B is the background. On this criterion, 874 reflections were considered to be observed out of the total of 1175 reflections examined.
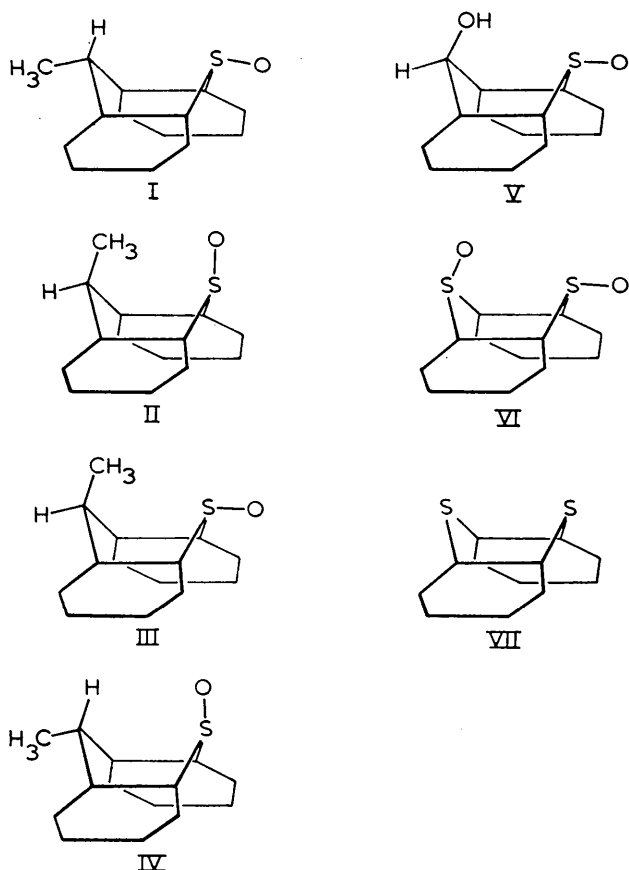
Fig. 1. The four isomers of 9-methylthioxanthene 10-oxide: *cis*-9e′,10e′ (I), *cis*-9a′,10a′ (II), *trans*-9a′,10e′ (III), *trans*-9e′,10a′ (IV). *trans*-Thioxanthen-9-ol 10-oxide (V), *β*-thianthrene dioxide (VI) and thianthrene (VII).

§ We have adopted the notations *e′* (boat-equatorial) and *a′* (boat-axial) to designate the 'equatorial' and 'axial, orientation of the substituents in the *meso* (9 and 10) positions of these systems.

Structure determination and refinement

As indicated earlier, the structure was solved by means of the heavy-atom method in the space group $P2_12_12_1$. The sulfur atom coordinates, $0{\cdot}200, 0{\cdot}248, 0{\cdot}176$ as fractions of the unit-cell edges, were derived from the Harker sections $(u, v, \frac{1}{2})$, $(u, \frac{1}{2}, w)$ and $(\frac{1}{2}, v, w)$ of a sharpened three-dimensional Patterson map. The sulfur-phased Fourier synthesis gave the positions of the oxygen atoms and several carbon atoms. Two additional rounds of structure factor Fourier calculations gave the entire molecule. Isotropic full-matrix least-squares refinement, using the *ORFLS* program of Busing, Martin & Levy (1962), gave a reliability index, R, of 14%: $R = (\Sigma|F_o - F_c|/\Sigma|F_o|) \times 100$, where F_o is the observed

and F_c the calculated structure factor. In the anisotropic least-squares refinement, the parameters for the nonhydrogen atoms and the positions of the hydrogen atoms were varied, giving a final R index of 4·2% on 867 reflections, excluding 7 intense low-order reflections which suffered large secondary extinction effects.

A modified Cruickshank *et al.* (1961) weighting scheme was used for the anisotropic least-squares refinement, with $1/\omega = (22{\cdot}4 - |F_o| + 0{\cdot}0318|F_o|^2)$. This weighting function gave lower weights to the weakest and strongest groups of reflections. The scattering factors for carbon and oxygen atoms are from Hoerni & Ibers (1954), for sulfur atoms from Dawson (1960), and for hydrogen atoms from Stewart, Davidson &

Table 2. Refinement comparison

	Pnma (correct)	$P2_12_12_1$ (incorrect)
Total reflections	867	867
Total parameters refined	98	180
Nonhydrogen atoms		
Positional parameter shifts		
Average	0·03σ	0·15σ
Range	0·001–0·26σ	0·009–0·49σ
Thermal parameter shifts		
Average	0·03σ	0·15σ
Range	0·007–0·36σ	0·004–0·57σ
Hydrogen atoms		
Positional parameter shifts		
Average	0·25σ	0·15σ
Range	0·01–1·0σ	0·001–0·43σ
R	4·6%	4·2%
Goodness of fit $[\Sigma(w\varDelta)^2/n - v]^{1/2}$*	0·96	0·97

* v = number of variables, n = number of observations, w = weight.
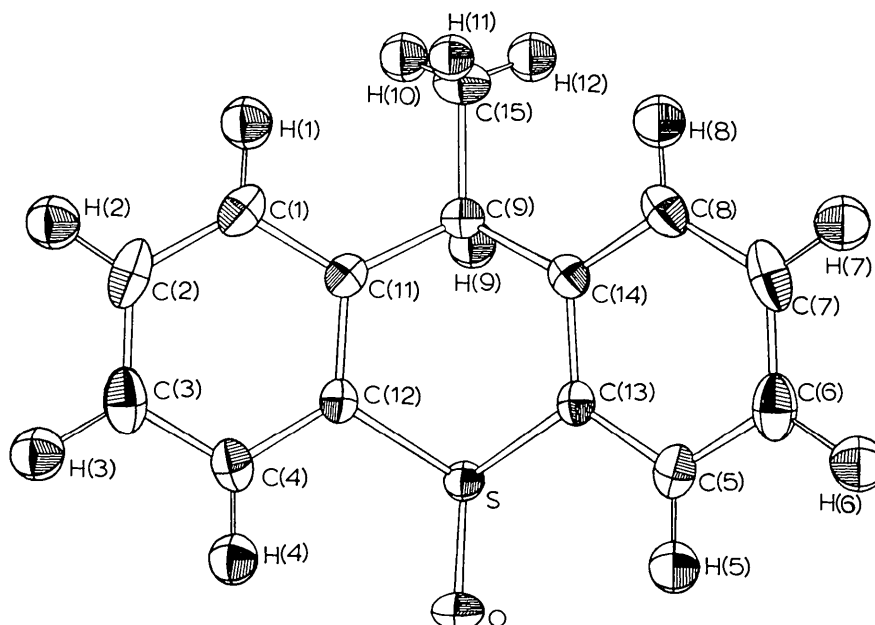

Fig. 2. A thermal ellipsoid plot of *cis*-9-methylthioxanthene 10-oxide (Johnson, 1965) showing the numbering system of the atoms.

Simpson (1965). No anomalous dispersion correction was made for sulfur.

The starting coordinates for the refinement based on the correct space group $Pnma$ were the same as those obtained for $P2_12_12_1$, except that the z coordinates were translated along the c axis by $\frac{1}{4}$.

The initial anisotropic refinement gave an R of 5.9%. The structure converged to an R of 4.6% in an additional two rounds of anisotropic refinement.

The weighting scheme used for the refinement in space group $Pnma$ was based on counting statistics, where

Table 3. *Structure factor table for cis-9-methylthioxanthene* 10-*oxide*

The columns are l, $31F_o$, $31F_c$. The seven reflections with large secondary extinctions are marked with an asterisk.

0,0,L		
2	2336	2870 *
4	1586	-1742
6	529	-561
8	837	-848
10	315	326
12	526	560
14	178	-179

(The remainder of Table 3 consists of an extensive multi-column structure factor listing of reflection indices and observed/calculated structure factors for numerous reflection groups: 0,0,L; 0,1,L; 0,2,L; 0,3,L; 0,4,L; 0,5,L; 0,6,L; 0,7,L; 0,8,L; 0,9,L; 0,10,L; 0,11,L; 0,12,L; 1,0,L; 1,1,L; 1,2,L; 1,3,L; 1,4,L; 1,5,L; 1,6,L; 1,7,L; 1,8,L; 1,9,L; 1,10,L; 2,0,L; 2,1,L; 2,2,L; 2,3,L; 2,4,L; 2,5,L; 2,6,L; 2,7,L; 2,8,L; 2,9,L; 2,10,L; 2,11,L; 2,12,L; 3,0,L; 3,1,L; 3,2,L; 3,3,L; 3,4,L; 3,5,L; 3,6,L; 3,7,L; 3,8,L; 3,9,L; 3,10,L; 3,11,L; 3,12,L; 4,0,L; 4,1,L; 4,2,L; 4,3,L; 4,4,L; 4,5,L; 4,6,L; 4,7,L; 4,8,L; 4,9,L; 4,10,L; 4,11,L; 5,0,L; 5,1,L; 5,2,L; 5,3,L; 5,4,L; 5,5,L; 5,6,L; 5,7,L; 5,8,L; 5,9,L; 5,10,L; 5,11,L; 6,0,L; 6,1,L; 6,2,L; 6,3,L; 6,4,L; 6,5,L; 6,6,L; 6,7,L; 6,8,L; 6,9,L; 6,10,L; 7,0,L; 7,1,L; 7,2,L; 7,3,L; 7,4,L; 7,5,L; 7,6,L; 7,7,L; 7,8,L; 7,9,L; 8,0,L; 8,1,L; 8,2,L; 8,3,L; 8,4,L; 8,5,L; 8,6,L; 8,7,L; 8,8,L; 9,0,L; 9,1,L; 9,2,L; 9,3,L; 9,4,L; 9,5,L; 9,6,L; 9,7,L; 10,0,L; 10,1,L; 10,2,L.)

$$\frac{1}{\sqrt{\omega}} = \sigma(F) = \frac{F_o}{2} \cdot \frac{\sigma(I)}{I} + 0.04|F_o|; \quad I = \text{intensity}$$ corrected for background, $\sigma(I) = [I + 2B + (0.01I)^2]^{1/2}$. In the least-squares refinements, the quantity minimized was $\Sigma(|F_o| - k|F_c|)^2$.

A final difference electron density map, calculated with the nonhydrogen atoms only contributing to the F_c's, showed all of the hydrogen atoms unequivocally, including those of the methyl group. The discrepancies in the hydrogen positions as determined by the least-squares refinement and the difference synthesis were within the errors of determination of the hydrogen coordinates. The small positive residual electron density $(0.4 \pm 0.07$ e.$\text{Å}^{-3})$ regions which were observed between the carbon–sulfur bonds are attributed in part to ther-

mal anisotropy of sulfur and (more likely) to the use of isolated atom scattering factors (O'Connell & Maslen, 1967). The numbering system used for cis-9-methylthioxanthene 10-oxide is given in an ORTEP (Johnson, 1965) drawing of the molecule, Fig. 2.

Table 2 compares the results of the refinements for the two space group Pnma and $P2_12_12_1$. The final observed and calculated structure factors for space group Pnma are given in Table 3. Final atomic coordinates and temperature factors for Pnma are given in Table 4.

Discussion of results

Molecular structure

The bond lengths are given in Table 5 for both space groups Pnma and $P2_12_12_1$. The bond angles for space

Table 4. *Atomic coordinates* * *and temperature factors*† *for cis-9-methylthioxanthene* 10-*oxide*

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	2206 (1)*	2500	−696 (1)	4·10 (4)†	3·33 (4)	2·46 (3)	0·00	0·41 (2)	0·00
O	3881 (3)	2500	−1019 (2)	4·46 (12)	5·60 (14)	5·52 (12)	0·00	2·42 (10)	0·00
C(1)	382 (3)	410 (3)	1708 (2)	5·51 (12)	4·36 (12)	3·74 (10)	−1·39 (10)	−0·27 (9)	0·62 (9)
C(2)	1400 (4)	−580 (2)	1714 (2)	7·48 (17)	3·56 (12)	5·14 (13)	−1·53 (12)	−2·36 (13)	1·37 (10)
C(3)	2639 (3)	−624 (3)	1000 (3)	5·62 (13)	3·52 (13)	6·33 (14)	0·20 (10)	−2·38 (12)	0·11 (11)
C(4)	2897 (3)	327 (2)	267 (2)	4·36 (11)	3·38 (11)	4·99 (12)	0·37 (8)	−0·85 (9)	−0·42 (9)
C(9)	−411 (4)	2500	935 (3)	3·63 (13)	4·12 (16)	3·73 (14)	0·00	0·34 (11)	0·00
C(11)	615 (2)	1377 (2)	990 (2)	3·85 (9)	3·55 (10)	2·81 (7)	−0·63 (7)	−0·33 (7)	−0·09 (7)
C(12)	1890 (2)	1305 (2)	280 (2)	3·76 (9)	2·88 (9)	2·99 (8)	−0·06 (7)	−0·47 (7)	−0·03 (7)
C(15)	−1748 (6)	2500	1762 (5)	5·19 (19)	6·98 (26)	7·31 (27)	0·00	2·52 (20)	0·00
H(1)	−48 (3)	46 (2)	221 (2)	5·0					
H(2)	120 (4)	124 (2)	224 (2)	5·0					
H(3)	344 (3)	−137 (3)	101 (2)	5·0					
H(4)	380 (3)	34 (3)	−27 (2)	4·7					
H(9)	−88 (4)	250	14 (3)	5·0					
H(10)	−248 (3)	183 (3)	157 (2)	5·0					
H(11)	−118 (4)	250	252 (3)	3·9					

* Estimated standard deviations (in parentheses), $\times 10^4$ for nonhydrogen atoms, $\times 10^3$ for hydrogen atoms.
† B_{ij}'s calculated from β_{ij}'s in exp$[-(h^2\beta_{11}\ldots + 2hk\beta_{12}\ldots)]$, where $B_{ij} = 4\beta_{ij}/a_ia_j$, a_i = reciprocal lattice constant.

Table 5. *Bond distances and estimated standard deviations* (*in parentheses*)

	Correct space group, Pnma		Wrong space group, $P2_12_12_1$*
	Distance (Å)	After thermal correction	Distance (Å)
S——O	1·492 (3)	1·497	1·494 (3)	
S——C(12)	1·782 (2)	1·788	1·785 (6)	1·778 (6)
C(1)—C(2)	1·399 (4)	1·402	1·435 (12)	1·362 (11)
C(1)—C(11)	1·384 (3)	1·388	1·385 (11)	1·399 (10)
C(2)—C(3)	1·368 (4)	1·375	1·323 (12)	1·410 (12)
C(3)—C(4)	1·385 (4)	1·389	1·320 (11)	1·432 (8)
C(4)—C(12)	1·382 (3)	1·386	1·388 (10)	1·391 (10)
C(9)—C(11)	1·521 (3)	1·526	1·488 (11)	1·548 (11)
C(9)—C(15)	1·518 (6)	1·523	1·518 (9)	
C(11)–C(12)	1·391 (3)	1·398	1·416 (7)	1·371 (8)
C(1)—H(1)	0·96 (3)		0·76 (6)	1·07 (5)
C(2)—H(2)	0·98 (3)		1·25 (5)	0·94 (6)
C(3)—H(3)	1·07 (3)		1·29 (5)	1·05 (6)
C(4)—H(4)	1·01 (3)		1·00 (6)	1·11 (5)
C(9)—H(9)	1·03 (4)		1·00 (4)	
C(15)–H(10)	1·00 (3)		1·24 (5)	0·85 (6)
C(15)–H(11)	1·03 (4)		1·07 (5)	

* The asymmetric structure here is the entire molecule of 9-methylthioxanthene 10-oxide. The distances of the chemically similar bonds are tabulated in pairs.

group *Pnma* are given in Table 6. Although the refinement in the wrong space group $P2_12_12_1$ appears to have converged to a satisfactory conclusion, the final structure proved to have chemically unacceptable bond distances and bond angles. In the noncentrosymmetric space group $P2_12_12_1$, about double the number of parameters were refined compared with those of the centric space group *Pnma*; hence, the R index was slightly lower in the former case. The molecular geometry is chemically reasonable in space group *Pnma* and in the following discussion only the results in this space group are considered. A rigid-body thermal analysis (Schomaker & Trueblood, 1968) of the molecule on the average increased the bond distances by about 0·005 Å, Tables 5 and 7.

The average estimated standard deviations for the various bonds are S–O, 0·003; S–C, 0·002; C–C, 0·004; C–H, 0·03 Å. The bond distances of primary interest are those of the heterocyclic ring. The sulfur–oxygen bond distance of 1·492 ± 0·003 Å is similar to that found in other known sulfoxides. The carbon–sulfur distances of 1·782 ± 0·002 Å (equal by symmetry) are in agreement with the value expected of a Csp^2–S bond. It is noteworthy that the C–S bond distance is only slightly shortened, probably not significantly, by a change in the coordination number of sulfur from three (I, V, VI of Fig. 3) to two (VI of Fig. 3), Table 8.

In dimethyl sulfoxide (DMSO), Table 8, the C–S bond distances show a larger variation at 5 °C (Thomas, Shoemaker & Eriks, 1966) than at −60° C (Viswamitra &
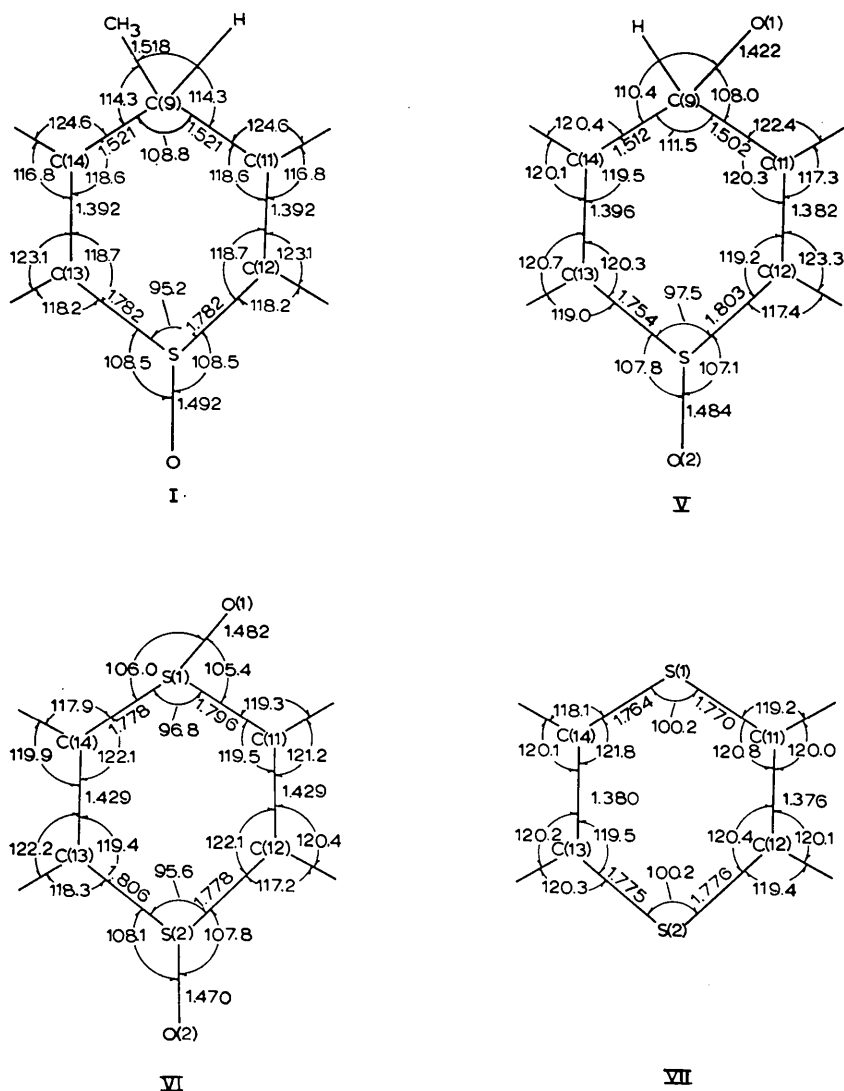

Fig. 3. Bond distances and valency angles involving the central rings of *cis*-9-methylthioxanthene 10-oxide (this work) (I), *trans*-thioxanthen-9-ol 10-oxide (Ternay, Chasar & Sax, 1967) (V), *β*-thianthrene dioxide (Hosoya, 1966) (VI), and thianthrene (Rowe & Post, 1958) (VII).

Kannan, 1965). The average value of the C–S bond distance of 1·806 ± 0·005 Å observed in the latter investigation is 0·024 Å longer than the value found in 9-methylthioxanthene 10-oxide. This difference is a conse- quence of the hybridization of the carbon atom. Whereas the carbon orbital involved in the C–S bond of DMSO is sp^3 hybridized, it is sp^2 hybridized in 9-methylthoxanthiene 10-oxide. Unexpectedly, the C–S bond

Table 6. *Interatomic angles and estimated standard deviations*

	Pnma Angle	E.s.d.		*Pnma* Angle	E.s.d.
O——S——C(12)	108·5°	0·1°	C(1)—C(2)—H(2)	117·8°	1°
S——C(12)–C(4)	118·2	0·2	C(2)—C(1)—H(1)	122·0	1
S——C(12)–C(11)	118·7	0·1	C(2)—C(3)—H(3)	121·9	1
C(12)–S——C(13)	95·2	0·1	C(3)—C(2)—H(2)	121·2	1
C(1)—C(2)—C(3)	120·9	0·2	C(3)—C(4)—H(4)	122·5	1
C(1)—C(11)–C(9)	124·6	0·2	C(4)—C(3)—H(3)	118·4	1
C(1)—C(11)–C(12)	116·8	0·2	C(9)—C(15)–H(10)	109·1	1
C(2)—C(3)—C(4)	119·6	0·2	C(9)—C(15)–H(11)	102·4	1
C(2)—C(1)—C(11)	120·8	0·2	C(11)–C(1)—H(1)	117·2	1
C(3)—C(4)—C(12)	118·8	0·2	C(11)–C(9)—H(9)	105·5	1
C(4)—C(12)–C(11)	123·1	0·2	C(12)–C(4)—H(4)	118·7	1
C(9)—C(11)–C(12)	118·6	0·2	C(15)–C(9)—H(9)	107·7	1
C(11)–C(9)—C(14)	108·8	0·2	H(10)–C(15)–H(11)	120·1	1
C(11)–C(9)—C(15)	114·3	0·2	H(10)–C(15)–H(12)	95·8	1

Table 7. **L** *and* **T** *tensors and their eigenvalues and eigenvectors*

Standard deviations are given in parentheses.

Libration tensor, **L** (°)²

$$\begin{bmatrix} 9·7\ (7) & 0·0\ (7) & 1·4\ (6) \\ & 24·9\ (13) & 0·0\ (7) \\ & & 9·0\ (6) \end{bmatrix}$$

Translation tensor, **T** (Å)

$$\begin{bmatrix} 0·042\ (1) & 0·000 & -0·007\ (1) \\ & 0·042\ (1) & 0·000 \\ & & 0·031\ (2) \end{bmatrix}$$

Principal values and components of eigenvectors

L Eigenvalue (deg²)	Direction cosines			**T** Eigenvalue (Å²)	Direction cosines		
24·9	0·000	1·000	0·000	0·0454	0·891	0·000	−0·454
10·8	0·790	0·000	0·614	0·0419	0·000	1·000	0·000
7·9	0·614	0·000	0·790	0·0276	0·454	0·000	0·891

Table 8. *Comparison of* C–S *bond distances in* DMSO (*acyclic*) *and in thioxanthene and thianthrene* (*cyclic*) *derivatives*

Compound	C-bonding	C–S distance	E.s.d.	Average C–S distance
(CH₃)₂SO (−60°)	sp^3	1·812	0·014	
(Viswamitra & Kannan, 1965)		1·801	0·010	1·806 Å
(CH₃)₂SO (5°C)	sp^3	1·771	0·008	
(Thomas *et al.*, 1966)		1·805	0·011	1·788
			Average	1·797
DMSO complexes				
Iron	sp^3	1·804	0·011	
(Bennett, Cotton & Weaver, 1967)		1·795	0·022	1·799
Palladium	sp^3	1·789	0·007	1·789
(Langs, Hare & Little, 1967)			Average	1·794
			Average Csp^3–S	1·795 Å
trans-Thioxanthen-9-ol 10-oxide	sp^2	1·80	0·012	
(Ternay *et al.*, 1967)		1·75	0·012	1·78
Thianthrene dioxide	sp^2	1·778	0·022	
(Hosoya, 1966)		1·796	0·022	
		1·806	0·022	
		1·778	0·022	1·790
Thianthrene	sp^2	1·764	0·011	
(Rowe & Post, 1958)		1·770	0·010	
		1·775	0·009	
		1·776	0·010	1·771
9-Methylthioxanthene 10-oxide				
(This work)	sp^2	1·782	0·002	1·782

distances in DMSO complexes are similar to those observed in DMSO itself, Table 8.

The carbon–carbon bond distances in the benzenoid portion of 9-methylthioxanthene 10-oxide are within the range of values found in substituted benzene derivatives. The $C(9)sp^3 - C(11)sp^2$ bond distance, $1\cdot521 \pm 0\cdot003$ Å, of the central ring appears to be longer than the normal Csp^3-Csp^2 bond distance, $1\cdot50$ Å. The exocyclic $C(9)$–$C(15)$ bond distance of $1\cdot518 \pm 0\cdot006$ Å is probably not significantly different, within the experimental error, from a saturated carbon–carbon bond distance, although it might have been expected that the widening of the exocyclic bond angle $C(11)C(9)C(15)$ would have caused a shortening of the $C(9)$–$C(15)$ bond distance (Sundaralingam, 1965).

The average C–H bond distance, $1\cdot01 \pm 0\cdot03$ Å, is in agreement with other values obtained by X-ray diffraction methods.

The interatomic angles for *cis*-9-methylthioxanthene 10-oxide (I) are presented in Table 6. Both the endocyclic and exocyclic angles involving C(9) are considerably larger than those involving the sulfur atom. Consequently, the C(9) valencies to the nonhydrogen atoms form a flattened pyramid compared with the pyramid formed by the sulfur atom. The difference between *cis*-9-methylthioxanthene 10-oxide and *trans*-thioxanthen-9-ol 10-oxide is in the nature and orientation of the substituent at C(9); while the methyl group is *boat-equatorial* in the former, the hydroxyl group is *boat-axial* in the latter, Fig. 3. The above difference in substitution is responsible for the variations in the bond angles involving C(9), *i.e.* more pyramidal character involving C(9) in (V) than in (I). Thus, the variation in hybridization of C(9) with orientation of the substituent may be used in identifying the orientation of the proton on C(9) in nuclear magnetic resonance spectroscopy. Again it is seen in β-thianthrene dioxide (VI, Fig. 3) that the exocyclic valence angle involving the *boat-axial* S–O bond is smaller than that involving the *boat-equatorial* S–O bond, while the endocyclic C–S–C angle is probably smaller for the boat-equatorially substituted sulfur atom. In the absence of a substituent on the sulfur atom, as in thianthrene (VII), the C–S–C bond angle of $100\cdot2°$ is appreciably larger than those involving the sulfoxides (I, V, VI) and smaller than the C–C–C angles involving C(9) (I, V), Fig. 3.

The valence angles in the benzenoid ring are normal, except those involving the substituted carbon atoms C(11) and C(12). The $C(1)C(11)C(12)$ valence angle of $116\cdot8°$ is considerably smaller than that of $C(11)C(12)$-$C(4)$, $123\cdot1°$. The above discrepancy is due to the fact that in the former the substituent on C(11) is a carbon atom while in the latter the substituent on C(12) is a sulfur atom. The differences in the bond angles are reversed when the exocyclic bond angles $C(9)C(11)C(1)$ and $SC(12)C(4)$ are compared. It is conceivable that steric interaction between the methyl group and the *peri* proton [H(1)] may be responsible for some of the angular distortions observed in the $C(1)$–$C(11)$–$C(9)$-

C(15) system, while van der Waals attraction between O...H(4) might be responsible for the distortions in the O–S–C(12)–C(4) system. The relevant intramolecular interactions between the aromatic protons and the substituents on the *meso* positions, Fig. 4, appear to support the above contention.

Molecular conformation and torsion angles

A view down the C(9)–C(15) bond is shown in Fig. 5. It is seen that the methyl protons are 'locked' in an almost perfectly staggered arrangement by the *peri* protons [H(1), H(8)] and the proton on C(9). The torsion angle H(9)C(9)C(15)H(10) is $51\cdot8°$.

The interactions between the methyl protons and the aromatic protons in *peri* positions are barely within the normal van der Waals contact. Therefore, a substituent larger than a methyl group in the *boat-equatorial* position or a substituent other than the protons in the *peri* positions of (I) will result in van der Waals compression favoring the *boat-axial* isomer. Similarly, substituents other than protons in the *peri* positions, C(4) and C(5),
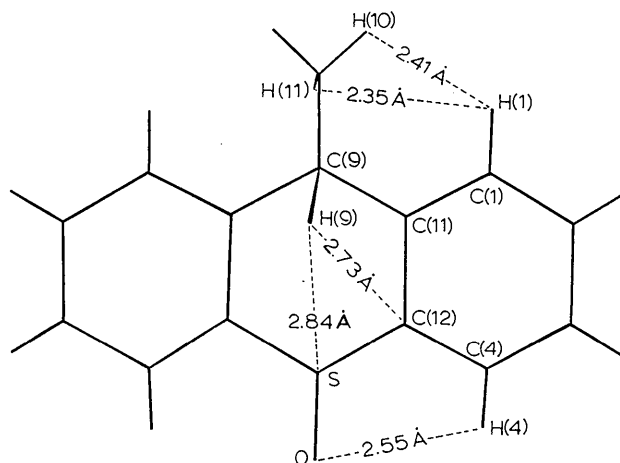

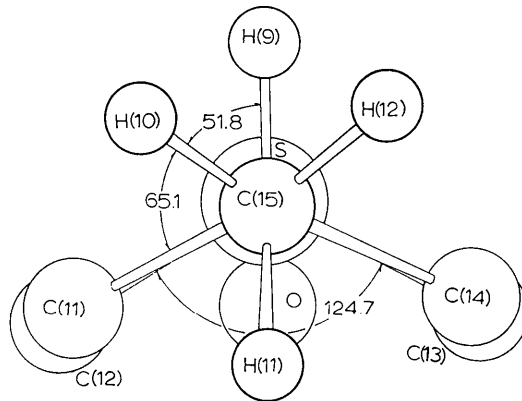Fig. 4. Relevant intramolecular distances of *cis*-9-methylthioxanthene 10-oxide.

Fig. 5. The torsion angles about the C(9)–C(15) bond of *cis*-9-methylthioxanthene 10-oxide.

of sulfoxides will tend to favor that configuration with a *boat-axial* S–O bond.

In Table 9 are presented the relevant least-squares planes in *cis*-9-methylthioxanthene 10-oxide. C(9) and S are significantly displaced on opposite sides of the benzene plane. Therefore, the molecule cannot be simply described as consisting of two planar halves folded about the C(9)–S axis. The dihedral angle between the least-squares planes through the benzene rings is 127·2°, and that between the least-squares planes through the benzene rings including the S and C(9) atoms is 126·0°. It **is** seen that the dihedral angles of I, VI and VII are significantly less than that of V (Table 10). The *boat-axial* hydroxyl substituent on C(9) is probably responsible for the increase in the dihedral angle in V compared with I. In VI and VII, although the *meso* positions are substituted by sulfur atoms, the dihedral angles are similar to those observed in the present work. When arsenic is in the 9 and 10 positions, as in 5,10-dihydro-5,10-dimethylarsanthrene (Kennard, Mann, Watson, Fawcett & Kerr, 1968), the dihedral angle is 117°, while in dihydroanthracene (Ferrier & Iball, 1954) the dihedral angle is 145°. A greater value (153·3°) for the dihedral angle is observed in phenothia-

Table 9. *Least-square planes in cis-9methylthioxanthene 10-oxide*

	Plane 1 Deviation from plane	Plane 2 Deviation from plane	Plane 3 Deviation from plane
C(1)	0·016 (3) Å	0·005 (3) Å	0·046* Å
C(2)	0·006 (3)	−0·005 (3)	0·041*
C(3)	−0·002 (3)	0·000 (3)	0·023*
C(4)	−0·011 (3)	0·004 (3)	−0·002*
C(11)	−0·001 (2)	−0·001 (2)	0·013 (2)
C(12)	−0·016 (2)	−0·003 (2)	−0·012 (2)
C(9)	−0·014 (3)	−0·014*	−0·007 (3)
S	0·022 (1)	0·051*	0·006 (1)
O	−0·543*	−0·502*	−0·567*
C(15)	−0·026*	−0·041*	−0·007*

Equation of plane 1, $-0.574x - 0.457y - 0.680z = -1.802$
R.m.s. deviation of atoms in plane 1, 0·013 Å

Equation of plane 2, $-0.568x - 0.453y - 0.688z = -1.802$
R.m.s. deviation of atoms in plane 2, 0·003 Å

Equation of plane 3, $-0.577x - 0.464y - 0.672z = -1.820$
R.m.s. deviation of atoms in plane 3, 0·010 Å

Dihedral angles between
  plane 1 and plane 2: 0·60°
  plane 3 and mirror related 3: 124·7°

* These atoms were not included in the calculation of the least-squares plane.

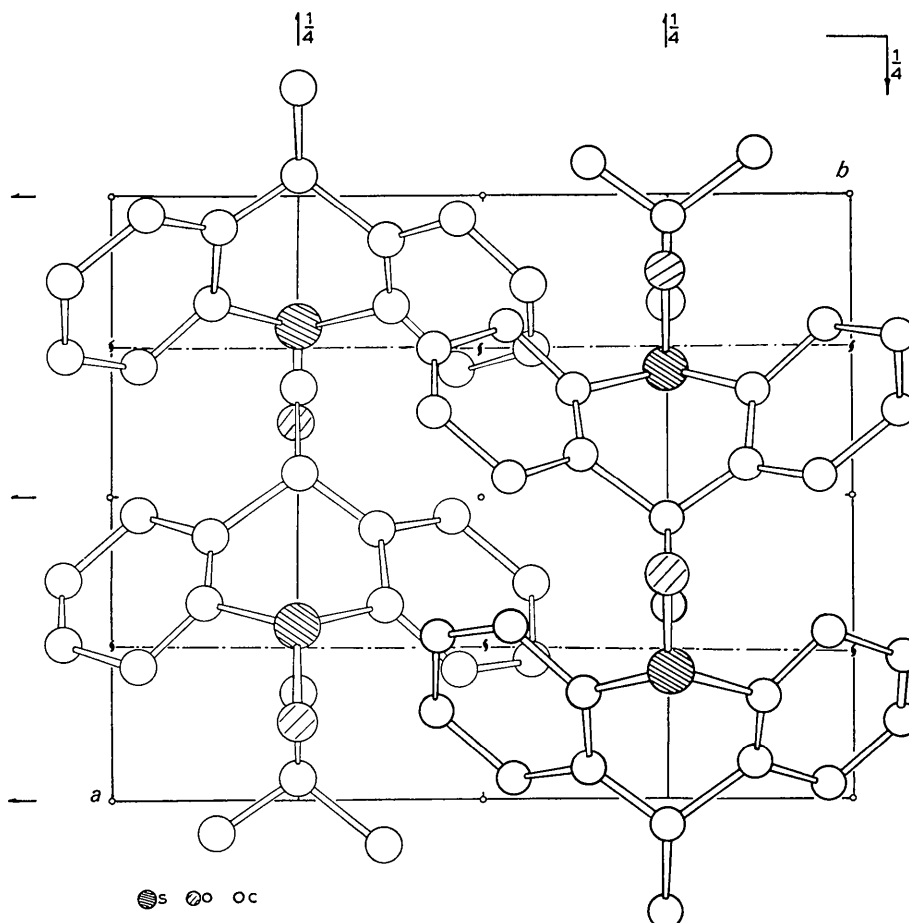

Fig.6. A packing diagram, excluding hydrogen atoms, viewed down the *c* axis of *cis*-9-methylthioxanthene 10-oxide.

zine (Bell, Blount, Briscoe & Freeman, 1968). Interestingly, in phenothiazine, the N and S atoms are significantly displaced on the same side of the benzene planes.

Table 10. Torsion angles and dihedral angles of cis-9-methylthioxanthene 10-oxide and related folded molecules

Atoms	Structure I	V[a]	VI[b]	VII[a]
9–11–12–10	−2·7[c]	−3·5[e]	−3·3[e]	0·1°
11–12–10–13	45·9	41·1	50·9	45·3
12–10–13–14	−45·9	−39·1	−48·8	−46·1
10–13–14– 9	2·7	0·1	0·3	1·7
13–14– 9–11	49·6	45·8	48·0	43·7
14– 9–11–12	−49·6	−43·5	−46·2	−44·5
14–13–10–16	−157·4[d]	−149·8	−159·6	−
5–13–10–16	24·9	28·3	24·5	−
11–12–10–16	157·4	152·4	161·9	−
4–12–10–16	−24·9	−31·4	−23·6	−
13–14– 9–15	−	−74·3	−60·2	−
8–14– 9–15	−	104·4	116·3	−
12–11– 9–15	−	78·0	62·5	−
1–11– 9–15	−	−104·0	−117·3	−
Angle between benzene rings	127·2	132·4	127·7	129·4
Angle between benzene rings, including atoms 9 and 10	126·0	132·1	124·7	128·1

[a] The coordinates for the enantiomorph were used to calculate the torsion angles. Note that the enantiomeric structures of these compounds will give the opposite signs to the torsion angles shown here.

[b] Published distances and angles do not agree with those calculated from published data.

[c] Atom 10 is the sulfur atom of Fig. 3.

[d] Atom 16 is the oxygen atom of Fig. 3.

[e] Atom 9 is sulfur (1) and atom 10 is sulfur (2) of Fig. 3.

[f] Atom 15 is oxygen atom (1) and atom 16 is oxygen atom (2) of Fig. 3.

The torsion angles in the heterocyclic rings shows some differences for the four structures studied (Table 10). These small differences are attributable to substitution effects. In general, the torsion angles indicate that the boat conformation of the central ring is quite rigid' in these folded molecules, and the boat undergoes practically no twist. In I and V, the torsion angles involving the meso carbon atoms are about 4° larger than those involving the sulfur atom. The presence of the hydroxyl group (V) at C(9), instead of the methyl group (I), appears to reduce the magnitude of the torsion angle C(12)–C(11)–C(9)–C(14).

Fig. 6 is a packing diagram down the c axis. There are no intermolecular contacts less than van der Waals

distances. The closest intermolecular contact of 2·62 Å is between the O and H(3) of adjacent molecules, thus indicating that only molecular forces determine the crystal packing.

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