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cis-2,4,9-Trimethylthioxanthene 10-Oxide

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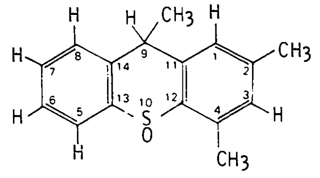
Abstract. $C_{16}H_{16}OS$, monoclinic, Cc, $Z = 4$, $M_r = 256{\cdot}36$, $a = 12{\cdot}122$ (1), $b = 14{\cdot}654$ (2), $c = 7{\cdot}734$ (1) Å, $\beta = 102{\cdot}94$ (1)°, $V = 1339{\cdot}0$ (3) Å^3, $D_x = 1{\cdot}272$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 1{\cdot}950$ mm^{-1}; final residual $R = 0{\cdot}039$. The 9-methyl and 10-oxide groups are both in the boat–axial conformation with respect to the central thioxanthene ring.

Introduction. Single crystals of *cis*-2,4,9-trimethylthioxanthene 10-oxide (I) were prepared by oxidation of the corresponding sulfide followed by recrystallization from a 1:1 mixture of benzene:hexane solution.† The unit-cell parameters were obtained by measuring the 2θ values of 15 reflections. The space group, Cc or $C2/c$, was deduced from systematic absences (hkl absent with $h + k$ odd and $h0l$ absent with l odd). The intensity data were collected on a Syntex $P2_1$ automatic diffractometer with a crystal approximately $0{\cdot}18 \times 0{\cdot}24 \times 0{\cdot}75$ mm. A $\theta/2\theta$ scanning mode with graphite-monochromated Cu $K\alpha$ radiation was used to measure 1118 independent reflections with 2θ values below 130°; of these, 1105 reflections were considered as observed by the criterion $I > 3{\cdot}0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, but no absorption corrections were applied.



(I)

The structure was determined by the application of direct methods with the weighted multisolution tangent-refinement program *MULTAN* (Germain, Main & Woolfson, 1971). The space group was deduced to be Cc, since there are four molecules in a unit cell and the molecule does not possess any center of symmetry or twofold axis. The normalized structure factors were also shown to have a noncentrosymmetric distribution; the ratios between $\langle E\rangle$, $\langle E^2\rangle$, and $\langle E^2 - 1\rangle$ are $0{\cdot}894$, $1{\cdot}000$, and $0{\cdot}707$ respectively. The E map

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† Details will be published elsewhere.

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showed the positions of all non-hydrogen atoms. The refinement was carried out by the full-matrix least-squares method (Busing, Martin & Levy, 1962) with isotropic temperature factors and by the block-diagonal least-squares method (Shiono, 1971) with anisotropic temperature factors. Most of the H positions were located on a difference Fourier synthesis, and the rest were calculated with reasonable bond lengths and bond angles with respect to the atoms to which they are bonded. The isotropic temperature factors were used for the H atoms in the refinement. The weight of a reflection was assigned as $1/[\sigma(F)]^2$, where $\sigma(F)$ was calculated from counting statistics. The quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. The final R index $(\sum ||F_o| - |F_c||/\sum |F_o|)$ was 0·039.* The magnitude of $[\sum w(F_o - F_c)^2/(m - n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 0·85, which indicated that the weights of all reflections were systematically low. The atomic scattering factors used for the N and C atoms were those from *International Tables for X-ray Crystallography* (1962). For H, the values given by Stewart, Davidson & Simpson (1965) were used. The final positional parameters are given in Table 1.

Discussion. *cis*-2,4,9-Trimethylthioxanthene 10-oxide (I) is one of a series of thioxanthene derivatives under study in this laboratory. 9-Alkylthioxanthene 10-oxides can exist as *cis* and *trans* isomers. It has been shown that the 10-oxide group prefers the boat–equatorial conformation when the size of the 9-alkyl substituent is small (Evans & Ternay, 1974; Jackobs & Sundaralingam, 1969; Ternay, Chasar & Sax, 1967), and the sulfinyl O governs the stereochemistry of these isomers. Unlike other thioxanthene sulfoxides, three 'forms' of 2,4,9-trimethylthioxanthene 10-oxide with melting points of 480 K (form *A*), 377 K (form *B*) and 399 K (form *C*) have been isolated. Since the solution spectra (NMR and IR) of forms *B* and *C* are identical, they cannot be configurational isomers of one another. However, they have markedly different solid-state (Nujol) spectra, particularly in the S–O stretching region (1100–1000 cm^{-1}). The absorption-spectra bands of form *B* are at 1073 and 1027 cm^{-1} while those of form *C* are at 1088, 1060, 1038, and 1010 cm^{-1}. The purpose of the present study is to assign unequivocally the configuration and conformation of form *A*, (I), and

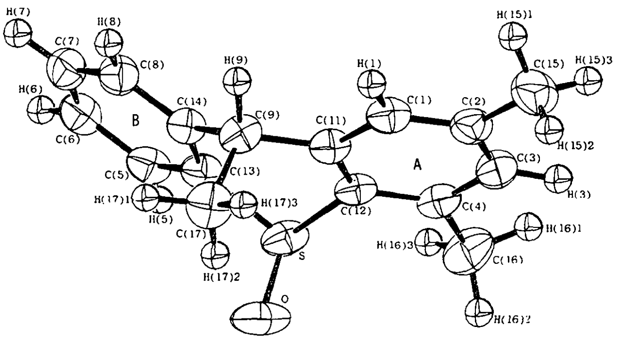

Fig. 1. *ORTEP* drawing (Johnson, 1965) of one molecule of *cis*-2,4,9-trimethylthioxanthene 10-oxide.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *for non-hydrogen atoms and fractional coordinates* ($\times 10^3$) *and thermal parameters for hydrogens*

The estimated standard deviations are given in parentheses and refer to the last positions of respective values.

	x	*y*	*z*		*x*	*y*	*z*	*B* (Å²)
S	7125 (1)	2571 (1)	211 (2)	H(1)	963 (4)	487 (3)	340 (6)	3·7 (9)
O	7173 (3)	1863 (2)	1629 (6)	H(3)	1098 (4)	326 (3)	0 (6)	3·9 (9)
C(1)	9548 (4)	4375 (3)	2563 (6)	H(5)	488 (4)	279 (3)	−128 (6)	4·0 (9)
C(2)	10457 (3)	4141 (3)	1841 (6)	H(6)	342 (4)	387 (3)	−101 (7)	4·5 (11)
C(3)	10321 (4)	3450 (3)	581 (6)	H(7)	388 (4)	506 (3)	100 (6)	4·8 (11)
C(4)	9296 (4)	2994 (3)	55 (6)	H(8)	576 (4)	523 (3)	278 (6)	5·0 (11)
C(5)	5041 (3)	3317 (3)	−523 (5)	H(9)	773 (4)	489 (3)	338 (6)	3·7 (9)
C(6)	4206 (3)	3936 (3)	−340 (6)	H(15)1	1147 (5)	534 (4)	274 (9)	9·6 (18)
C(7)	4473 (4)	4642 (3)	863 (6)	H(15)2	1206 (5)	461 (4)	157 (8)	7·6 (14)
C(8)	5552 (4)	4728 (3)	1890 (6)	H(15)3	1209 (5)	435 (4)	339 (9)	9·7 (16)
C(9)	7572 (3)	4210 (2)	2962 (5)	H(16)1	986 (6)	236 (4)	−197 (10)	9·1 (18)
C(11)	8515 (3)	3938 (2)	2074 (5)	H(16)2	941 (7)	160 (4)	−86 (10)	11·7 (21)
C(12)	8397 (3)	3240 (2)	825 (5)	H(16)3	836 (4)	217 (4)	−208 (7)	6·6 (13)
C(13)	6137 (3)	3415 (3)	520 (5)	H(17)1	699 (5)	384 (4)	533 (7)	6·6 (13)
C(14)	6405 (3)	4119 (2)	1756 (5)	H(17)2	757 (3)	304 (3)	443 (6)	3·8 (9)
C(15)	11581 (4)	4626 (4)	2426 (8)	H(17)3	841 (5)	378 (4)	548 (7)	6·7 (13)
C(16)	9197 (5)	2207 (4)	−1271 (8)					
C(17)	7639 (4)	3652 (4)	4684 (6)					

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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 34535 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

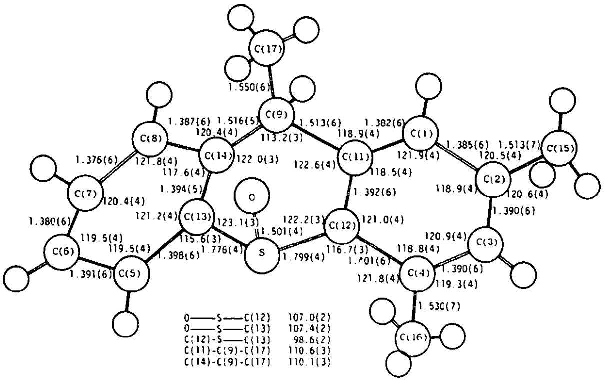

Fig. 2. Bond lengths (Å) and bond angles (°) of *cis*-2,4,9-trimethylthioxanthene 10-oxide with e.s.d.'s in parentheses.

Table 2. *Torsion angles around the central ring*

C(13)–S–C(12)–C(11)	31·0 (4)°
S–C(12)–C(11)–C(9)	−2·2 (6)
C(12)–C(11)–C(9)–C(14)	−34·3 (5)
C(11)–C(9)–C(14)–C(13)	36·0 (5)
C(9)–C(14)–C(13)–S	−0·8 (5)
C(14)–C(13)–S–C(12)	−29·5 (4)

to determine the comparative effects of the *para* methyl and the 9-axial methyl substituents on the conformation of the sulfinyl oxygen.

The identification of the atoms and the configuration of the molecule are shown in Fig. 1. Both the 9-methyl and the 10-oxide groups are in a boat–axial conformation. This is contrary to the boat–equatorial conformation found in the *cis* isomer of 9-methylthioxanthene 10-oxide (Jackobs & Sundaralingam, 1969). The boat–axial conformation of the 10-oxide was also observed in 1,4-dimethylthioxanthene 10-oxide (Chu & Chung, 1974). This demonstrates that the boat–axial conformation of the sulfinyl O is preferred, apparently due to the nonbonded interaction between the O and the *para* methyl substituent.

The bond lengths and bond angles with their standard deviations are shown in Fig. 2. There is a slight lengthening of one C–S bond, apparently due to the effect of the nonbonded interaction between the *meso* and *para* substituents. This effect has been observed in 1,4-dimethyl-9-isobutylthioxanthene 10,10-dioxide (Chu, Kou & van der Helm, 1978). Otherwise the C–S and S–O bond lengths and the C–S–O bond angles are in good agreement with those observed in other thioxanthene 10-oxides (Chu & Chung, 1974; Chu, 1975). The C–H bond lengths range from 0·92 to 1·09 Å (mean 1·01 Å) with a r.m.s. standard deviation of 0·06 Å. The C–C–H bond angles involving benzene rings range from 117 to 123° (mean 120°), and the C–C–H and H–C–H bond angles involving tetrahedral C atoms range from 98 to 120° (mean 109°). The standard deviation of these bond angles is 4°.

Fig. 3. The molecular packing of *cis*-2,4,9-trimethylthioxanthene 10-oxide in a unit cell.

The equations of the least-squares planes of the two benzene rings are $-0{\cdot}1403x + 0{\cdot}6704y - 0{\cdot}6787z = 1{\cdot}328$ and $0{\cdot}4143x + 0{\cdot}5784y - 0{\cdot}7777z = 5{\cdot}658$ (where x, y, and z are in Å) for rings *A* and *B* (Fig. 1) respectively. The deviations of atoms from the planes are less than 0·006 Å. The folding angle between the planes of the two benzene rings is 147·3°, which is considerably larger than the folding angle of 127·2° in *cis*-9-methylthioxanthene 10-oxide (Jackobs & Sundaralingam, 1969), and slightly larger than that of 143·6° in 1,4-dimethylthioxanthene 10-oxide (Chu & Chung, 1974). This is apparently due to a nonbonded interaction between the 9-methyl and 10-oxide groups, both being in axial conformations. The central ring is in a boat conformation as shown by the ring torsion angles given in Table 2. The Cremer & Pople (1975) puckering parameters for the central ring are $q_2 = 0{\cdot}518$ Å, $q_3 = -0{\cdot}033$ Å, $Q = 0{\cdot}519$ Å, $\varphi_2 = 182{\cdot}0°$, and $\theta = 93{\cdot}7°$. These parameters indicate that the central ring is near an ideal boat conformation since $q_2 \simeq Q$, $q_3 \simeq 0$ Å, $\varphi_2 \simeq 180°$, and $\theta \simeq 90°$. A stereoscopic diagram of the packing of the molecules in the crystal is shown in Fig. 3. The closest intermolecular contact is 3·218 Å between O and C(6)

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Prochlorperazine–Methanesulphonic Acid (1:2), a Phenothiazine Derivative

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Abstract. $C_{20}H_{24}ClN_3S.2CH_4O_3S$, 2-chloro-10-[3-(4-methyl-1-piperazinyl)propyl]phenothiazine–methanesulphonic acid (1:2), monoclinic, $C2/c$, a = 39·106 (2), b = 5·966 (2), c = 25·314 (2) Å, β = 115·73 (8)°, D_m = 1·423, D_c = 1·414 Mg m^{-3}, Z = 8; final R_w = 0·112. In the tricyclic group, C—S—C is 99·4 (9)°, C—S (mean) = 1·76 (2), C—N (mean) = 1·43 (2) and C—Cl = 1·55 (2) Å. The angle between the planes of the benzene rings is 136·1°. The piperazine ring has the chair conformation.

Introduction. The material was supplied by Maybaker. Colourless transparent needles were grown at a low temperature from a solution in *n*-propyl alcohol. The crystals tended to vaporize at room temperature. Systematic absences noted on Weissenberg photographs were hkl, $h + k \neq 2n$ and $h0l$, $l \neq 2n$, indicating space groups Cc or $C2/c$. Faint layer lines between the normal lines were observed in all oscillation films taken about **b**, but the corresponding Weissenberg photographs did not exhibit discrete reflexions. Intensities were collected on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ (λ = 0·7107 Å) radiation at 293 K. The ω-scan mode was used with a scan rate of 0·033° s^{-1} and a scan width of 1·0° in θ. Background counts of 15 s on each side of the reflexion were taken. 2785 reflexions, including 315 systematically extinct and 825 rated as unobserved [$I < 1{\cdot}65\sigma(I)$], were measured within a sphere θ_{max} = 20°. The lattice constants were obtained by least squares from the 2θ, χ and φ angles for 25 reflexions. Only Lorentz–polarization corrections were applied as μr for the crystal (0·15 × 0·3 × 0·6 mm) was <0·15.

Analysis of the $|E|$ statistics and distribution indicated the space group $C2/c$. With *SHELX* 76 (Sheldrick, 1976), which incorporates a multi-solution tangent-formula phasing procedure, five reflexions were hand-selected from 442 with $E_{min} \geq 1{\cdot}2$. 31 of the non-H atoms were located from the E map with the highest figure of merit. In addition, a strong peak was indicated 1·7 Å from C(10); this peak, designated Cl(2), was apparent in all subsequent Fourier syntheses and had to be accounted for. The first Fourier map located the remaining four non-H atoms, and full-matrix least-squares refinement of coordinates and individual isotropic B's of non-H atoms brought R to 0·294. The programs used were from *SHELX* 76 and the XRAY system (1976); $R = \sum||F_o| - |F_c||/\sum |F_o|$; the function minimized, $R_w = \sum w(hkl)[|F_o(hkl) - F_c(hkl)|]^2$, where $w(hkl)$ = the weighting factor. Scattering factors of Cromer & Mann (1968) were used for Cl, S, O, N and C, and those of Stewart, Davidson & Simpson (1965) for H.

Most of the H atoms were found on a difference synthesis, but futher refinement with all 67 atoms did not reduce R substantially. However, when Cl(2) was included, and Cl(1) and Cl(2) were each assigned site-occupation factors of 0·5, six cycles with anisotropic β's of non-H atoms converged to a final R for 2470 reflexions of 0·115 [R_w = 0·112, with $w(hkl) = \sin\theta/A \times C/F_o$ with A = 0·23 and C = 40·0]. When allowed to refine freely, the H atoms of the methyl groups tended to drift; therefore, with the exception of the H atoms of the tricyclic group, the remaining H atoms were placed in idealized positions and constrained to ride on the C or O atoms to which they were attached; they were assigned isotropic thermal parameters derived from those of the carrier atoms. The site-occupancy factors of Cl(1) and Cl(2) refined to 0·53 and 0·49 respectively.

The presence of the two half-Cl atoms was not considered satisfactory and several trials were carried out on the assumption that some regular arrangement of

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