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cis-9-Ethyl-9-methylthioxanthene 10-Oxide

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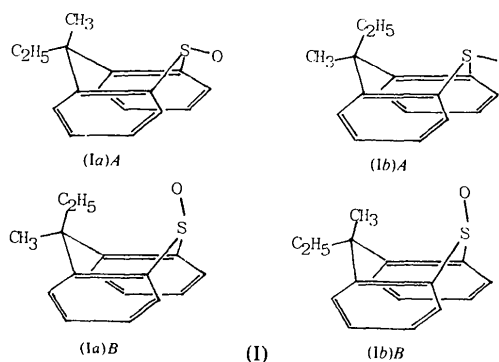
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Abstract. C₁₆H₁₆OS, orthorhombic, *Pnam*, *Z* = 4, *M_r* = 256.35, *a* = 11.249 (1), *b* = 9.693 (1), *c* = 11.797 (2) Å, *V* = 1286.3 (2) Å³, *D_x* = 1.322 Mg m⁻³, λ(Cu *Kα*) = 1.5418 Å, μ(Cu *Kα*) = 2.027 mm⁻¹, final *R* = 0.063. In the *cis* isomer of the title compound, the 9-ethyl and 10-oxide groups have a *cis* relation, and both are in a 'boat-equatorial' conformation with respect to the central ring. The two halves of the molecule are related by a mirror plane.

Introduction. Single crystals of the title compound (I) were obtained through the courtesy of Dr Andrew L. Ternay Jr of the Chemistry Department of the University of Texas at Arlington. The crystals are transparent prisms. The unit-cell parameters were obtained from a least-squares analysis of 15 reflections with *2θ* values in the range of 20–65°. The space group, *Pna*2₁ or *Pnam*, was deduced from systematic absences (*Ok**l* absent with *k* + *l* odd, *h*0*l* absent with *h* odd). The intensity data were collected on a Syntex P2₁ automatic diffractometer with a crystal approximately 0.54 × 0.18 × 0.11 mm. The crystal was mounted with the *a* axis approximately along the φ axis of the diffractometer. A θ/2θ scanning mode with graphite-monochromated Cu *Kα* radiation was used to measure 1128 independent reflections with *2θ* values below 130°; of these, 1006 reflections were considered as

observed by the criterion *I* > 3.0σ(*I*), where σ(*I*) was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, and no absorption corrections were applied.



The structure was determined by the application of direct methods with the weighted multisolution tangent-refinement program *MULTAN* (Germain, Main & Woolfson, 1971). The correct space group was proved to be *Pnam* by the structure determination, and the normalized structure factors were also shown to have centrosymmetric distributions. The ratios between ⟨*E*⟩, ⟨*E*²⟩, and ⟨*E*² - 1⟩ are 0.815, 1.000, and 0.922, respectively. The *E* map showed the positions of all non-hydrogen atoms. The refinement was carried out by the full-matrix least-squares method (Busing, Martin

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& 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 the 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 0.063* and the weighted disagreement index, R_w , was 0.067. Two low-order strong reflections (200, 110), whose calculated structure amplitudes were much higher than the observed values, were given zero weight in the least-squares refinement and were excluded from the calculation of the disagreement index. 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 approximately unity. The atomic scattering factors used for C, O and S 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*-9-Ethyl-9-methylthioxanthene 10-oxide is one of a series of tricyclic compounds under study in this laboratory. It has been shown by NMR and X-ray crystal structure studies that in the *cis* isomer of 9-alkylthioxanthene 10-oxide, the 10-oxide group prefers the 'boat-equatorial' conformation and that the 10-oxide group governs the stereochemistry of these

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34999 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

isomers when the size of the 9-alkyl substituent is small (Ternay & Evans, 1974; Jackobs & Sundaralingam, 1969; Ternay, Chasar & Sax, 1967). The NMR data have indicated that the 'boat-axial' conformation of both the 9-alkyl and 10-oxide groups becomes significant when the 9-alkyl substituent is an ethyl group. Furthermore, *cis*-9-isopropylthioxanthene 10-oxide appears to be conformationally homogeneous in solution with both groups in the 'boat-axial' conformation (Evans, 1970; Evans & Ternay, 1975), and this conformation has been confirmed by the crystal structure determination in the solid state (Chu, 1975). The objectives of the present study are (1) to determine the conformation of the title compound, (2) to determine whether the 9-ethyl or 9-methyl group has the *cis* relation with the 10-oxide, (Ia) or (Ib), and (3) to determine whether the 9-alkyl or 10-oxide group governs the stereochemistry of this isomer in the solid state (*A* or *B*).

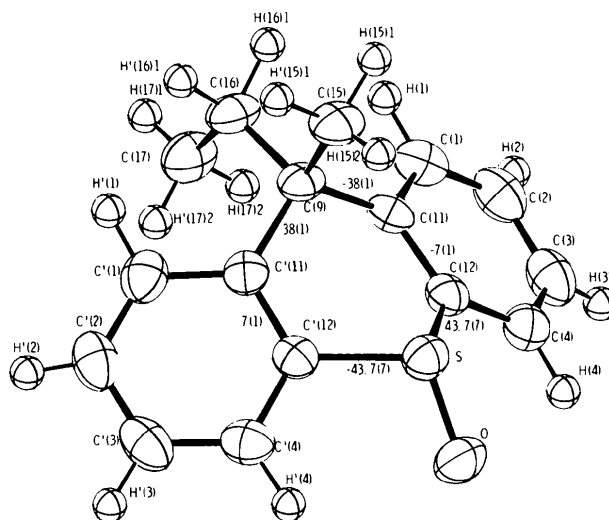


Fig. 1. ORTEP drawing (Johnson, 1965) of one molecule of the title compound with torsion angles ($^{\circ}$) around the central ring.

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

The estimated standard deviations are given in parentheses and refer to the last positions of respective values.								
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)	
S	4192 (2)	5422 (3)	2500 (0)	H(1)	510 (8)	124 (9)	454 (7)	8 (3)
O	3120 (8)	6318 (8)	2500 (0)	H(2)	368 (8)	191 (10)	609 (9)	8 (3)
C(1)	4571 (7)	2123 (9)	4546 (7)	H(3)	275 (7)	393 (8)	612 (7)	5 (2)
C(2)	3906 (8)	2517 (10)	5484 (7)	H(4)	292 (8)	555 (9)	453 (7)	6 (2)
C(3)	3300 (8)	3743 (10)	5486 (7)	H(15)1	705 (7)	289 (8)	322 (6)	6 (2)
C(4)	3382 (7)	4612 (9)	4558 (7)	H(15)2	656 (11)	414 (14)	250 (0)	7 (4)
C(9)	5310 (9)	2477 (11)	2500 (0)	H(16)1	616 (7)	64 (8)	314 (6)	5 (3)
C(11)	4630 (6)	2928 (7)	3569 (6)	H(17)1	454 (15)	-103 (18)	250 (0)	12 (6)
C(12)	4040 (6)	4194 (8)	3619 (6)	H(17)2	387 (11)	26 (12)	314 (9)	11 (4)
C(15)	6535 (9)	3182 (13)	2500 (0)					
C(16)	5540 (9)	897 (12)	2500 (0)					
C(17)	4430 (12)	-11 (13)	2500 (0)					

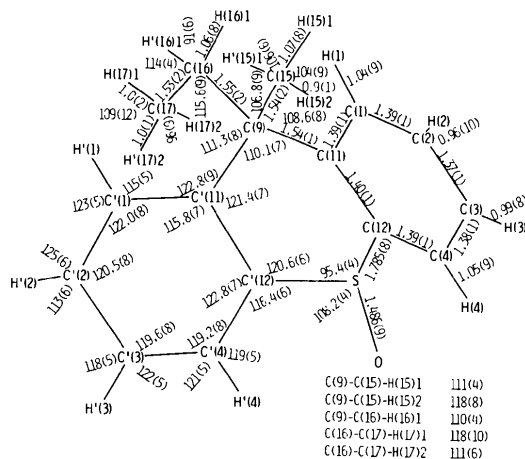


Fig. 2. Bond lengths (Å) and bond angles (°) of the title compound with e.s.d.'s in parentheses. Note that the two halves of the molecule are related by a mirror plane.

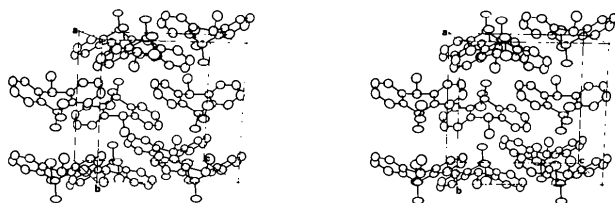


Fig. 3. The molecular packing of the title compound in a unit cell.

The identification of the atoms and the configuration of the molecule are shown in Fig. 1. The two halves of the molecule are related by a mirror plane as required by the space group. The central ring is in a boat conformation, as shown by the ring torsion angles in Fig. 1, and by the Cremer & Pople (1975) puckering parameters, which are $q_2 = 0.673$, $q_3 = 0.095$, $Q = 0.680$ Å, $\varphi_2 = 0.0$, and $\theta = 98.0^\circ$. The 9-ethyl and 10-oxide groups have the *cis* relation and both are in equatorial conformations. This demonstrates that the 10-oxide group governs the stereochemistry of the thioxanthene isomers when the 9-alkyl substituent is an ethyl group. The equation of the least-squares plane of the benzene ring is $0.8098x + 0.4450y + 0.3823z = 7.1169$, with deviations of atoms from the plane to 0.02 Å. The folding angle between the planes of the two mirror-related benzene rings is 135.0° , which is similar to that in *cis*-9-isopropylthioxanthene 10-oxide (Chu, 1975).

The bond lengths and bond angles with their standard deviations are shown in Fig. 2. The C—S and S—O bond lengths and the C—S—C and C—S—O bond angles have values similar to those found in other thioxanthene 10-oxides (Chu, 1975). The C atoms of both the methyl and ethyl groups lie on the mirror plane. The torsion angle C(11)—C(9)—C(16)—C(17) is $62 \pm 1^\circ$. The packing of the molecules in the crystal is shown in Fig. 3. The closest intermolecular contact is 2.68 Å between O and H(2). There are no intermolecular contacts less than the van der Waals distances.

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