

cis-9-Ethyl-2,4-dimethylthioxanthene 10-Oxide

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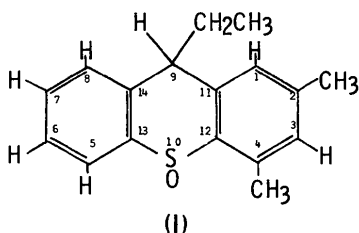
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Abstract. C₁₇H₁₈OS, monoclinic, $P2_1/n$, $Z = 4$, $M_r = 270.40$, $a = 8.237$ (1), $b = 14.352$ (1), $c = 12.342$ (1) Å, $\beta = 100.04$ (1)°, $V = 1436.7$ (2) Å³, $D_x = 1.250$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 1.844$ mm⁻¹; final $R = 0.078$ for 2149 observed reflexions. The 9-ethyl and 10-oxide groups are both in the 'boat-axial' conformation with respect to the central ring of the thioxanthene ring system.

Introduction. The compound (I) was prepared by the *m*-chloroperoxybenzoic acid oxidation of the corresponding sulfide and was separated from its stereoisomer by recrystallization from ethanol after an initial mechanical separation using a binocular microscope. 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 from 60 to 84°. The space group $P2_1/n$ was deduced from systematic absences ($0k0$ absent with k odd, $h0l$ absent with $h + l$ odd). The intensity data were collected on a Syntex $P2_1$ automatic diffractometer with a crystal approximately $0.61 \times 0.22 \times 0.28$ mm with the a axis along the ϕ axis of the diffractometer. A $\theta/2\theta$ scanning mode with graphite-monochromated Cu $K\alpha$ radiation was used to measure 2395 independent reflections with 2θ values below 130°, of which 2149 were considered as observed by the criterion $I > 3.0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, and no absorption corrections were applied.



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

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>	B_{eq}^\dagger (Å ²)
S	4349 (1)	2624 (1)	3912 (1)	4.77 (4)
O	2954 (4)	3284 (2)	3958 (2)	6.78 (17)
C(1)	2480 (5)	692 (3)	1624 (3)	4.65 (17)
C(2)	3185 (5)	945 (3)	720 (3)	5.02 (18)
C(3)	4231 (5)	1703 (3)	820 (3)	5.52 (21)
C(4)	4587 (5)	2221 (3)	1787 (3)	4.88 (18)
C(5)	5286 (5)	1808 (3)	5896 (3)	4.94 (18)
C(6)	5217 (5)	1158 (3)	6703 (3)	5.20 (19)
C(7)	4150 (5)	422 (3)	6510 (3)	5.04 (19)
C(8)	3122 (4)	318 (3)	5490 (3)	4.56 (17)
C(9)	2014 (4)	866 (3)	3565 (3)	4.30 (16)
C(11)	2801 (4)	1180 (3)	2604 (3)	4.10 (16)
C(12)	3858 (4)	1941 (3)	2677 (3)	4.41 (17)
C(13)	4231 (4)	1715 (3)	4872 (3)	4.26 (16)
C(14)	3153 (4)	968 (3)	4660 (3)	4.12 (15)
C(15)	2759 (6)	402 (4)	-334 (3)	6.81 (26)
C(16)	5687 (6)	3063 (4)	1823 (4)	6.94 (26)
C(17)	365 (4)	1383 (3)	3597 (3)	5.30 (20)
C(18)	-976 (5)	1166 (4)	2614 (4)	6.39 (23)

	<i>x</i>	<i>y</i>	<i>z</i>	B (Å ²)
H(1)	175 (4)	14 (3)	162 (3)	4.8 (8)
H(3)	485 (4)	188 (3)	20 (3)	5.4 (9)
H(5)	610 (5)	236 (3)	599 (3)	5.9 (9)
H(6)	583 (5)	119 (3)	741 (3)	6.4 (10)
H(7)	402 (5)	-6 (3)	708 (3)	5.8 (9)
H(8)	235 (4)	-19 (2)	536 (3)	4.5 (8)
H(9)	171 (4)	19 (2)	346 (3)	4.5 (8)
H(15)1	345 (5)	62 (3)	-76 (3)	7.7 (11)
H(15)2	299 (6)	-28 (4)	-27 (4)	11.2 (16)
H(15)3	159 (8)	56 (4)	-73 (5)	14.0 (21)
H(16)1	667 (6)	300 (4)	239 (4)	12.3 (16)
H(16)2	611 (6)	315 (4)	110 (4)	10.2 (15)
H(16)3	515 (6)	359 (4)	203 (4)	12.1 (17)
H(17)1	59 (5)	206 (3)	365 (3)	6.7 (10)
H(17)2	-5 (4)	115 (3)	432 (3)	6.4 (10)
H(18)1	-201 (5)	142 (3)	275 (3)	8.0 (12)
H(18)2	-58 (5)	138 (3)	192 (3)	6.7 (10)
H(18)3	-112 (5)	51 (3)	253 (4)	8.1 (12)

† B_{eq} is calculated from the relation; $B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$.

The structure was determined by the application of direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). The *E* map showed the positions of all non-hydrogen atoms. The refinement was carried out by the block-diagonal least-squares method (Shiono, 1971) with anisotropic temperature factors. Most of the H positions were located in 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. 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 by $\sigma(F) = \sigma(I)(Lp^{-1})/2|F_o|$. The quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. The final *R* index ($\sum |F_o| - |F_c| / \sum |F_o|$) was 0.078,* and the weighted disagreement index, R_w , was 0.090. The magnitude of $[\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$ was 0.94. The atomic scattering factors used for S, O and C were those from *International Tables for X-ray Crystallography* (1962). For hydrogen, the values given by Stewart, Davidson & Simpson (1965) were used. The final positional parameters are given in Table 1.*

Discussion. The title compound is one of a series of thioxanthene derivatives under study by crystal structure determination in this laboratory. The objectives of these studies are to determine the conformations of these compounds and to examine the effects of different substituents on the conformation and configuration of the thioxanthene ring system. Preliminary results, based on the structure studies and on NMR and IR analyses, indicated that the *m*-chloro-peroxybenzoic acid oxidation of 2,4,9-trialkylthioxanthenes generally affords an excess of the *cis*-sulfoxide. Thus, *cis*-2,4,9-trimethylthioxanthene 10-oxide (m.p. 478 K) is produced in a 4:1 excess relative to the *trans* isomer (m.p. 377 K/400 K)† (Chu, Rosenstein & Ternay, 1979). Similarly, the *cis* isomer (m.p. 413 K) of the title compound is produced in a 4:1 excess relative to the *trans* isomer (m.p. 475 K). The C(9)—H resonances occur at 2.24 δ and 1.55 δ for the *cis* and *trans* isomers, respectively.

The identification of the atoms and the configuration of the molecule are shown in Fig. 1. The central ring is in a boat conformation and the ring torsion angles are also shown in Fig. 1. The Cremer & Pople (1975) puckering parameters for the central ring are $q_2 =$

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35805 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† This isomer exists in two different crystalline forms which, however, have the same ¹H NMR spectra. The C(9)—H resonance of the major isomer occurs at 1.84 δ while that of the minor isomer occurs at 1.61 δ .

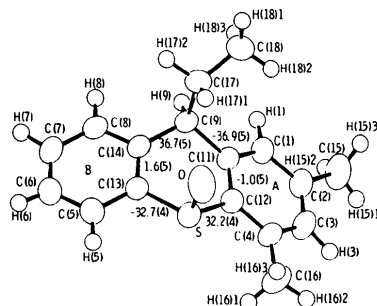


Fig. 1. ORTEP drawing (Johnson, 1965) of one molecule of *cis*-9-ethyl-2,4-dimethylthioxanthene 10-oxide.

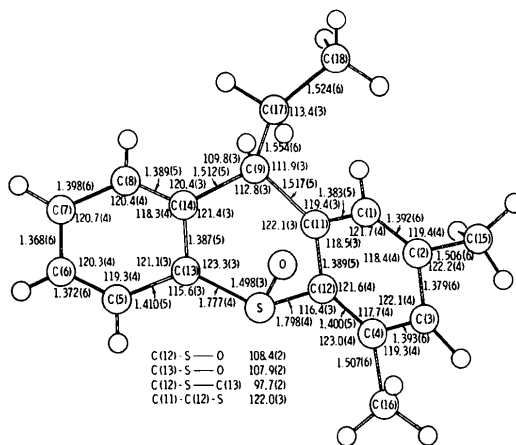


Fig. 2. Bond lengths (Å) and bond angles (°) of *cis*-9-ethyl-2,4-dimethylthioxanthene 10-oxide with e.s.d.'s in parentheses.

0.550, $q_3 = -0.039$, $Q = 0.551$ Å, $\varphi_2 = 359.9$ and $\theta = 94.0^\circ$. These values are very similar to those in *cis*-2,4,9-trimethylthioxanthene 10-oxide (Chu, Rosenstein & Ternay, 1979). Both the 9-ethyl and 10-oxide groups are in a boat-axial conformation. The conformation of the 9-ethyl group is similar to that in *cis*-9-ethyl-9-methylthioxanthene 10-oxide (Chu & Rosenstein, 1980), as indicated by the torsion angles. The torsion angle C(11)—C(9)—C(17)—C(18) in the title compound is 65.0 (4)°.

The bond lengths and bond angles with their standard deviations are shown in Fig. 2. As observed in other *para*-substituted thioxanthene derivatives (Chu, Kou & van der Helm, 1978; Chu, Rosenstein & Ternay, 1979), there is a slight lengthening of one C—S bond. All bond lengths and bond angles are in good agreement with those observed in other thioxanthene 10-oxides (Chu, 1975; Chu, Rosenstein & Ternay, 1979). The C—H bond lengths range from 0.90 to 1.06 Å (mean 0.99 ± 0.04 Å). The C—C—H bond angles involving benzene rings range from 113 to 124° (mean $119 \pm 2^\circ$) and the C—C—H and H—C—H bond angles involving tetrahedral C atoms range from 104 to 117° (mean $109 \pm 3^\circ$). The packing of the molecules

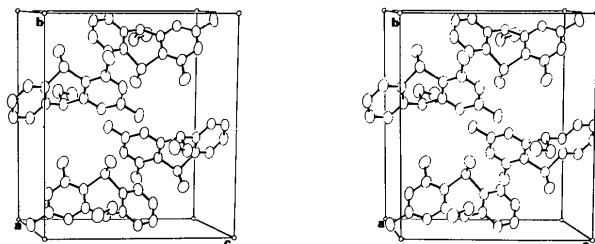


Fig. 3. The molecular packing of *cis*-9-ethyl-2,4-dimethylthioxanthene 10-oxide in a unit cell.

in the crystal is shown in Fig. 3. There are no intermolecular contacts shorter than van der Waals distances.

The equations of the least-squares planes of the two benzene rings are $0.7339x - 0.5991y + 0.1872z = 1.280$ and $-0.7749x + 0.5358y + 0.4653z = 1.410$ (where x , y , and z are in Å) for rings *A* and *B* (Fig. 1), respectively. The deviations of atoms from the planes range from 0.001 to 0.007 Å. The deviations of the two methyl substituents on the benzene ring, C(15) and C(16), from plane *A* are 0.03 and 0.05 Å, respectively. The folding angle between the planes of the two benzene rings is 141.5° , compared with 147.3° in *cis*-2,4,9-trimethylthioxanthene 10-oxide (Chu, Rosenstein & Ternay, 1979). The difference in the folding angle is apparently due to the effect of the

different 9 substituent since the C—S—C and C—C—C bond angles involving the *meso* atoms within the central ring are both smaller in the title compound.

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Structure of *p*-Cyanobenzoic Acid

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Abstract. $C_8H_5NO_2$, triclinic, $P\bar{1}$, $a = 13.000$ (2), $b = 7.406$ (3), $c = 3.831$ (1) Å, $\alpha = 101.68$ (4), $\beta = 89.93$ (2), $\gamma = 101.69$ (3)°, $Z = 2$, $D_x = 1.382$ Mg m⁻³; final $R = 0.086$ for 1050 reflections collected photographically. The molecule has approximate twofold symmetry with normal molecular dimensions, and the carboxyl group is disordered. The crystal structure consists of layers of molecules parallel to (201). The molecules are linked by hydrogen bonds forming dimers, which are gathered together *via* antiparallel contacts of the cyano groups. In addition, the short intermolecular contacts suggest some contribution of Coulombic interaction in the crystal.

Introduction. As part of a study on the molecular packing of benzonitriles, the crystal structure of *p*-cyanobenzoic acid has been determined. Colourless wedge-shaped crystals were grown in ethanol solution by slow evaporation.

Intensity data were measured on a Syntex AD1 autodensitometer from equi-inclination Weissenberg photographs about the b ($h0l-h4l$) and c axes ($hk0-hk2$), with Ni-filtered Cu $K\alpha$ radiation. 1050 reflection data were obtained by application of the usual corrections. An absorption correction [$\mu(Cu K\alpha) = 0.808$ mm⁻¹] was also applied, taking into consideration the irregular shape of the crystal used for the data