

Table 2. Short intermolecular contacts (Å) (H...H contacts are excluded)

Second atom at $\frac{1}{2} - x, \frac{1}{2} - y, -z$		Second atom at $x, -y, \frac{1}{2} + z$	
C(3)...O(4)	2.08 (1)	C(5)...O(3)	3.36 (1)
C(3)...N(2)	3.75 (1)	C(6)...O(2)	3.55 (1)
C(4)...C(5)	3.72 (1)	C(6)...O(3)	3.38 (1)
N(1)...O(4)	3.11 (1)	C(6)...N(1)	3.79 (1)
C(2)...O(4)	3.49 (1)	N(2)...O(3)	3.21 (1)
C(4)...C(6)	3.96 (1)		
C(5)...C(5)	3.85 (1)	Second atom at $2 - x, -y, -z$	
		C(2)...O(2)	3.35 (1)
Second atom at $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$		O(2)...H(C2)	2.53 (2)
C(4)...O(4)	3.01 (1)	Second atom at $2 - x, 1 - y, 1 - z$	
O(1)...H(C6)	2.86 (2)	C(8)...C(8)	3.42 (1)
O(5)...H(C6)	2.89 (2)		
O(5)...H(C82)	2.68 (2)	Second atom at $\frac{1}{2} - x, -\frac{1}{2} - y, -z$	
C(3)...O(4)	3.33 (1)	O(1)...O(3)	3.19 (1)
C(5)...O(4)	3.50 (1)	O(3)...O(3)	2.70 (1)
O(1)...O(4)	3.16 (1)	O(3)...H(O1)	2.57 (2)
Second atom at $x, -y, -\frac{1}{2} + z$		Second atom at $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	
O(3)...O(5)	3.06 (1)	C(8)...O(5)	3.45 (1)
O(2)...H(C81)	2.81 (1)		

and O(5) away from close contact with the —OH group, resulting in an ordered intramolecular hydrogen bond between the —OH group and O(3) of the nitro group of N(1). The O(1)...O(3) and H(O1)...O(3) distances are 2.59 (1) and 1.87 (1) Å, respectively,

and the O(1)—H(O1)...O(3) angle is 137.2 (1)°. A similar feature has been observed in the structure of the picric acid—2-amino-1-bromonaphthalene complex (Carstensen-Oeser, Götlicher & Habermehl, 1968). Picric acid also has one hydroxy group between two nitro groups. The dihedral angles of the two nitro groups adjacent to the hydroxy group are 16.5 (4) and 3.4 (4)° with respect to the phenyl-ring plane. The greater rotation of the N(2) nitro group in the present molecule is probably due to different intermolecular interactions in the two compounds.

The crystal packing, shown in Fig. 3, is through short C...O, C—H...O, O...O and hydrophobic contacts. The C(3)...O(4)( $\frac{1}{2} - x, \frac{1}{2} - y, -z$ ) distance is only 2.08 (1) Å. The intermolecular contacts are listed in Table 2.

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### *trans*-9-Ethyl-2,4-dimethylthioxanthene 10-Oxide

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**Abstract.** C<sub>17</sub>H<sub>18</sub>OS, triclinic,  $P\bar{1}$ ,  $Z = 2$ ,  $M_r = 270.40$ ,  $a = 8.019$  (1),  $b = 8.615$  (2),  $c = 11.144$  (3) Å,  $\alpha = 104.09$  (2),  $\beta = 77.30$  (2),  $\gamma = 103.75$  (2)°,  $V = 714.5$  (3) Å<sup>3</sup>,  $D_x = 1.257$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu(\text{Cu } K\alpha) = 1.844$  mm<sup>-1</sup>; final  $R = 0.049$  for 2121 observed reflections. The 9-ethyl group is in the 'boat-axial' and the 10-oxide group in the 'boat-equatorial' conformation with respect to the central ring of the thioxanthene ring system.

**Introduction.** 9-Ethyl-2,4-dimethylthioxanthene 10-oxide can exist in the form of *cis* and *trans* isomers.

The crystal structure of the *cis* isomer has been determined (Chu, Napoleone, Massah & Ternay, 1981), and the preparation and NMR data of the title compound have been reported. In the *cis* isomer, the 9-ethyl and 10-oxide groups are both in the 'boat-axial' conformation. The crystal structure of the *trans* isomer is reported in this paper, and its conformation is compared with that of the *cis* isomer.

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

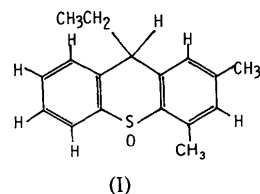
prisms. The unit-cell parameters were obtained from a least-squares analysis of 15 reflections with  $2\theta$  values ranging from 60 to 92°. The space group,  $P\bar{1}$ , assumed on the basis that there are two molecules in a unit cell, was confirmed by the structure determination. The intensity data were collected on a Syntex  $P2_1$  automatic diffractometer with a crystal approximately 0.35 × 0.24 × 0.21 mm in size with the  $a$  axis of the crystal along the  $\phi$  axis of the diffractometer. A  $\theta/2\theta$  scanning mode with graphite-monochromated Cu  $K\alpha$  radiation was used to measure 2382 independent reflections with  $2\theta$  values below 130°; of these, 2121 reflections 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.

Table 1. Fractional atomic coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) and thermal parameters

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

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$B_{eq}/B$ ( $\text{\AA}^2$ )
S(10)	6225 (1)	3711 (1)	6819 (1)	4.84 (3)
O	7759 (2)	3553 (3)	7296 (2)	7.12 (12)
C(1)	2131 (3)	5778 (3)	8706 (2)	4.48 (12)
C(2)	2811 (3)	7111 (3)	9550 (2)	4.74 (13)
C(3)	4579 (4)	7363 (3)	9601 (3)	4.91 (13)
C(4)	5655 (3)	6343 (3)	8823 (2)	4.63 (12)
C(5)	5335 (4)	448 (3)	6809 (3)	5.45 (14)
C(6)	4191 (4)	-1038 (4)	6807 (3)	6.45 (17)
C(7)	2430 (4)	-1123 (3)	6864 (3)	6.06 (16)
C(8)	1811 (4)	265 (3)	6920 (3)	5.15 (14)
C(9)	2293 (3)	3308 (3)	6981 (2)	4.26 (12)
C(11)	3129 (3)	4713 (3)	7913 (2)	4.08 (11)
C(12)	4919 (3)	5000 (3)	7984 (2)	4.21 (11)
C(13)	4688 (3)	1825 (3)	6865 (2)	4.48 (12)
C(14)	2925 (3)	1766 (3)	6920 (2)	4.28 (11)
C(15)	1708 (4)	8273 (4)	10384 (3)	6.38 (17)
C(16)	7563 (4)	6747 (4)	8952 (3)	6.25 (16)
C(17)	2555 (4)	3754 (3)	5691 (3)	5.24 (14)
C(18)	1439 (4)	2541 (4)	4816 (3)	6.61 (17)
H(1)	96 (3)	558 (3)	865 (2)	4.9 (6)
H(3)	512 (3)	832 (3)	1022 (2)	4.9 (6)
H(5)	662 (4)	58 (3)	674 (3)	6.9 (7)
H(6)	461 (3)	-204 (3)	670 (3)	6.9 (7)
H(7)	168 (3)	-222 (3)	676 (3)	6.9 (7)
H(8)	63 (3)	18 (3)	692 (3)	6.9 (7)
H(9)	110 (3)	316 (3)	730 (2)	4.2 (5)
H(15)1	66 (5)	809 (4)	1029 (3)	11.5 (11)
H(15)2	223 (4)	940 (4)	1031 (3)	11.8 (10)
H(15)3	178 (4)	834 (4)	1127 (3)	11.5 (10)
H(16)1	777 (4)	610 (4)	944 (3)	8.5 (9)
H(16)2	792 (4)	786 (4)	914 (3)	9.6 (9)
H(16)3	817 (5)	636 (5)	808 (4)	12.8 (12)
H(17)1	375 (3)	391 (3)	526 (3)	6.3 (7)
H(17)2	233 (3)	492 (3)	580 (2)	5.9 (7)
H(18)1	84 (5)	296 (5)	450 (4)	16.0 (14)
H(18)2	86 (5)	164 (5)	504 (4)	13.8 (2)
H(18)3	205 (6)	210 (5)	421 (4)	16.3 (14)



The structure was determined by the application of direct methods with the weighted multisolution tangent-refinement program, *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, except some of those associated with the methyl groups which were calculated 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. The quantity  $\sum w(|F_o| - |F_c|)^2$  was minimized. The final  $R$  index ( $\sum |F_o| - |F_c| / \sum |F_o|$ ) was 0.049, and the weighted disagreement index,  $R_w$ , was 0.051. The atomic scattering factors used for S, O 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.** 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  $q_2 = 0.698$ ,  $q_3 = 0.076$ ,  $Q = 0.703 \text{ \AA}$ ,  $\varphi_2 = 177.9$  and  $\theta = 83.8^\circ$ . The 9-ethyl group is in a 'boat-axial' and the 10-oxide group is in a 'boat-equatorial' conformation. This is in contrast to the *trans* isomer of 2,4,9-trimethylthioxanthene 10-oxide, in which the 9-methyl group is in a 'boat-equatorial' and the 10-oxide group is in a 'boat-axial' conformation. These demonstrate that the 10-oxide group governs the stereochemistry of the isomers when the size of the 9-alkyl substituent is small. However, when the size of the 9-alkyl substituent is increased to an ethyl group, the 9-ethyl group prefers the 'boat-axial' conformation, and this group governs the stereochemistry of these isomers. The conformation of the 9-ethyl substituent in the title compound is different from that in the *cis* isomer. This can be shown by the torsion angles about

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36804 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

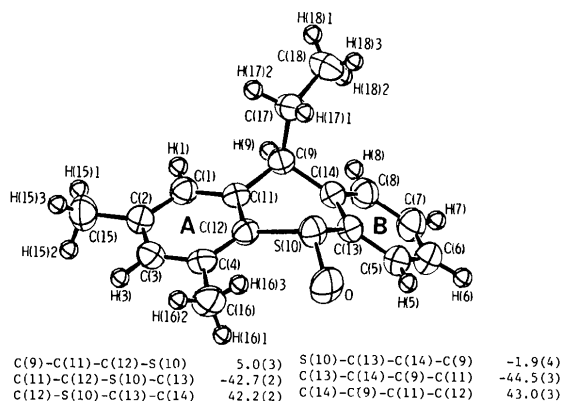


Fig. 1. ORTEP drawing (Johnson, 1965) of one molecule of the title compound. The torsion angles ( $^{\circ}$ ) around the central ring are shown.

the C(9)–C(17) bond. The torsion angles of C(11)–C(9)–C(17)–C(18) are  $-168.0(2)$  and  $65.0(4)^{\circ}$  for the *trans* and *cis* isomers, respectively.

The bond lengths and bond angles with their standard deviations are shown in Fig. 2. The effects of the nonbonded interactions between the sulfinyl O and the methyl substituent at C(4) can be shown by the lengthening of the C(12)–S(10) bond length and the larger C(12)–S(10)–O, S(10)–C(12)–C(4), and C(12)–C(4)–C(16) bond angles. These effects were also observed in other *p*-substituted thioxanthene 10-oxides (Chu, Kou & van der Helm, 1978; Chu, Rosenstein & Ternay, 1979; Chu & Rosenstein, 1980; Chu, Napoleone, Massah & Ternay, 1981). The C–H bond lengths range from 0.81 to 1.03 Å (mean  $0.94 \pm 0.03$  Å). The C–C–H bond angles involving benzene rings range from 117 to 123 $^{\circ}$  (mean  $119 \pm 2^{\circ}$ ) and the C–C–H and H–C–H bond angles involving tetrahedral C atoms range from 95 to 120 $^{\circ}$  (mean  $109 \pm 3^{\circ}$ ). There are no intermolecular contacts less than van der Waals distances.

The equations of the least-squares planes of the two benzo rings are  $0.0826x - 0.7153y + 0.8213z = 4.548$  and  $0.0441x - 0.0319y + 0.9684z = 7.524$  (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 benzo rings, C(15) and C(16), from plane A are 0.03 and 0.01 Å, respectively. The folding angle between the planes of the two benzo rings is 135.4 $^{\circ}$ , compared with 141.5 $^{\circ}$  in the *cis* isomer of 9-ethyl-2,4-dimethylthioxanthene 10-oxide (Chu, Napoleone, Massah & Ternay, 1981). As a comparison, the folding angle of 134.2 $^{\circ}$  in the *trans* isomer (Chu, Grant, Napoleone, Ternay & Massah, 1981) of 2,4,9-trimethylthioxanthene 10-oxide is also smaller than that of 147.3 $^{\circ}$  in the *cis* isomer (Chu, Rosenstein & Ternay, 1979).

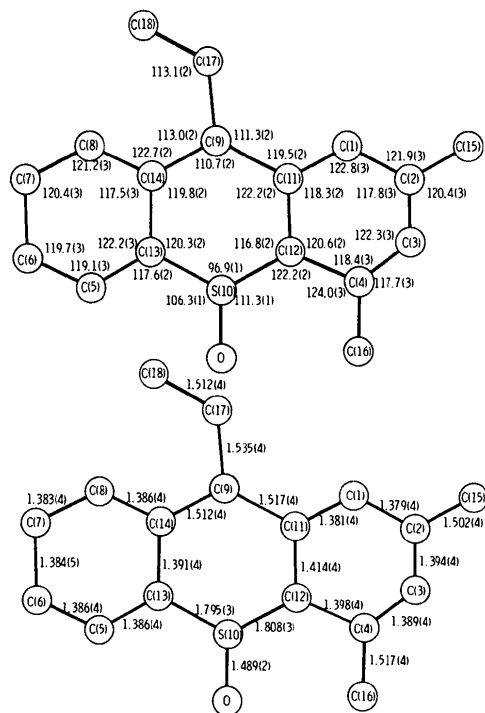


Fig. 2. Bond lengths (Å) and bond angles ( $^{\circ}$ ) of the title compound with e.s.d.'s in parentheses.

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