



Fig. 2. A stereoview of the molecular packing of the title compound in a unit cell.

closest contacts between the iodide and the main molecule are 3.87 Å [$I^- \cdots C(19)(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$] and 3.93 Å [$I^- \cdots C(21)(2-x, \frac{1}{2}+y, \frac{1}{2}-z)$], and the distances between the iodide ion and quaternary ammonium ion are 4.40 Å [$I^- \cdots N^+(x,y,z)$] and 4.37 Å [$I^- \cdots N^+(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$].

This research was supported by the Robert A. Welch Foundation, Houston, Texas. The authors wish to thank Dr R. Shiono of the University of Pittsburgh for making the *ORTEP* plots.

Acta Cryst. (1981). **B37**, 1948–1950

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

BY SHIRLEY S. C. CHU,* WILLIAM K. GRANT AND VERA NAPOLEONE

School of Engineering and Applied Science, Southern Methodist University, Dallas, Texas 75275, USA

AND ANDREW L. TERNAY JR AND FARHAD MASSAH

Department of Chemistry, University of Texas at Arlington, Arlington, Texas 76019, USA

(Received 13 January 1981; accepted 22 April 1981)

Abstract. C₁₆H₁₆OS, triclinic, $P\bar{1}$, $Z = 2$, $M_r = 256.36$, $a = 8.002$ (1), $b = 9.260$ (1), $c = 9.411$ (1) Å, $\alpha = 103.39$ (1), $\beta = 100.94$ (1), $\gamma = 90.58$ (1)°, $V = 665.0$ (1) Å³, $D_x = 1.280$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 1.950$ mm⁻¹. The final $R = 0.047$ for 1792 reflections. The 9-methyl group is in a 'boat-equatorial' conformation and the 10-oxide group is in a 'boat-axial' conformation with respect to the central thioxanthene ring.

Introduction. 9-Alkylthioxanthene 10-oxides can exist as *cis* and *trans* isomers. Unlike other thioxanthene sulfoxides, it appears that three 'forms' of 2,4,9-trimethylthioxanthene 10-oxide (I) have been isolated,

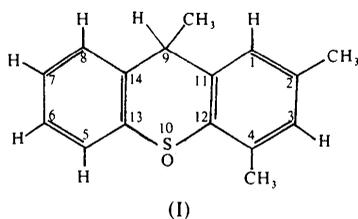
and the crystal structure of one, form *A* (the *cis* isomer), has been determined by X-ray diffraction (Chu, Rosenstein & Ternay, 1979). Form *B* (m.p. 374–377 K) and form *C* (m.p. 397–400 K) are both *trans* isomers and they have the same NMR spectra in CDCl₃ (CH_3 : 1.61 δ , *d*, $J = 7$ Hz; CH_3 : 2.33 δ , *s*; CH_3 : 2.74 δ , *s*; CH : 4.67 δ , *q*, $J = 7$ Hz; ArH: 6.92–7.54 δ , *m*, 5H; 7.81–7.97 δ , *m*, 1H) and, therefore, the same conformation in solution. However, their structures are different in the solid state since they have different melting points and solid-state IR spectra. Form *C* is a polycrystalline material, and it transforms into form *B* upon recrystallization from methanol solution. The lower melting form *B* appears to be more stable. The purpose of the present study is to determine the conformation and configuration of form *B* (I) in the solid state. The study of form *C* will be carried out

* To whom correspondence should be addressed.

References

- BOLSHUTKIN, D. N., GASAN, V. M., PROKHVATILOV, A. I. & ERENBURG, A. I. (1972). *Acta Cryst.* **B28**, 3542–3547.
 CHU, S. S. C. & CHUNG, B. (1976). *Acta Cryst.* **B32**, 836–842.
 CHU, S. S. C. & ROSENSTEIN, R. (1979). *J. Chem. Soc. Chem. Commun.* pp. 491–492.
 CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 DELAPLANE, R. G., LUNDGREN, J.-O. & OLOVSSON, I. (1975). *Acta Cryst.* **B31**, 2202–2207.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 JONES, R. D. G. (1976). *Acta Cryst.* **B32**, 1224–1227.
 SHIONO, R. (1971). Tech. Rep. 49. Crystallography Department, Univ. of Pittsburgh.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 ZIRKLE, C. L. & KAISER, C. (1979). Private communication.

when a suitable single crystal of this form can be obtained.



The unit-cell parameters of the title compound were obtained from a least-squares analysis of 15 reflections with 2θ values in the range of 32 to 65° . The crystal is triclinic and belongs to space group $P\bar{1}$. The intensity data were collected on a Syntex $P2_1$ automatic diffractometer with a crystal of approximately $0.39 \times 0.12 \times 0.09$ mm in size. The crystal was mounted with the $[011]$ direction approximately along the φ axis of the diffractometer. A $\theta/2\theta$ scanning mode with graphite-

monochromated Cu $K\alpha$ radiation was used to measure 2201 independent reflections with 2θ values below 130° , of which 1792 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.

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-H 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 for some H atoms associated with methyl groups. The positions of these H atoms were calculated by using the C—H bond length of 1.0 \AA and ideal tetrahedral bond angles. 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 0.047 , and the weighted disagreement index, R_w , was 0.046 . The magnitude, $\{\sum w(F_o - |F_c|)^2 / (m - n)\}^{1/2}$, was 1.15 . 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.*

Table 1. Fractional atomic coordinates ($\times 10^4$) for non-H atoms and ($\times 10^3$) for H atoms and thermal parameters with e.s.d.'s in parentheses

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

	x	y	z	B_{eq} (\AA^2)
S	616 (1)	8587 (1)	1106 (1)	4.25 (3)
O	1816 (3)	9873 (2)	2007 (3)	5.29 (11)
C(1)	2337 (4)	5581 (3)	3436 (3)	4.34 (14)
C(2)	3089 (4)	4565 (3)	2435 (4)	4.51 (14)
C(3)	3006 (4)	4774 (4)	1015 (4)	4.58 (15)
C(4)	2195 (4)	5958 (3)	559 (3)	4.19 (13)
C(5)	-2693 (4)	9019 (4)	1206 (4)	5.02 (16)
C(6)	-4140 (5)	9077 (4)	1826 (5)	6.10 (19)
C(7)	-4026 (5)	8727 (4)	3194 (5)	6.30 (20)
C(8)	-2501 (5)	8341 (4)	3949 (4)	5.49 (17)
C(9)	704 (4)	7910 (3)	4120 (3)	4.34 (14)
C(11)	1517 (4)	6779 (3)	3041 (3)	3.89 (12)
C(12)	1470 (4)	6962 (3)	1597 (3)	3.79 (12)
C(13)	-1194 (4)	8601 (3)	1957 (3)	4.19 (14)
C(14)	-1025 (4)	8268 (3)	3345 (3)	4.31 (14)
C(15)	3962 (5)	3260 (4)	2900 (5)	5.97 (19)
C(16)	2113 (5)	6117 (4)	-1012 (4)	5.51 (18)
C(17)	699 (5)	7505 (4)	5611 (4)	5.98 (20)
H(1)	245 (4)	540 (3)	448 (3)	4.4 (7)
H(3)	360 (4)	405 (4)	26 (4)	6.9 (9)
H(5)	-269 (4)	930 (4)	22 (4)	6.0 (8)
H(6)	-535 (4)	948 (4)	126 (4)	6.5 (9)
H(7)	-512 (5)	874 (4)	355 (4)	8.3 (10)
H(8)	-234 (4)	804 (3)	495 (3)	5.2 (7)
H(9)	147 (4)	883 (3)	433 (3)	5.2 (7)
H(15)1	499 (5)	298 (5)	249 (5)	10.1 (12)
H(15)2	449 (5)	345 (5)	411 (5)	10.3 (13)
H(15)3	309 (5)	238 (5)	265 (5)	9.5 (12)
H(16)1	285 (6)	532 (6)	-163 (6)	13.1 (16)
H(16)2	280 (5)	703 (4)	-102 (4)	8.8 (11)
H(16)3	88 (5)	613 (4)	-153 (4)	9.1 (11)
H(17)1	198 (4)	739 (4)	610 (4)	6.9 (9)
H(17)2	13 (5)	825 (4)	626 (4)	7.8 (10)
H(17)3	-4 (4)	654 (4)	543 (4)	6.2 (8)

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 as shown by the ring torsion angles in Fig. 1, and by the Cremer & Pople (1975) puckering parameters, which are $q_2 = 0.712$, $q_3 = 0.057$, $Q = 0.715 \text{ \AA}$, $\varphi_2 = 2.3$, and $\theta = 85.4^\circ$. For the ideal boat conformation, these parameters are $q_2 = Q$, $q_3 = 0 \text{ \AA}$, $\varphi_2 = 0$, and $\theta = 90^\circ$. The 9-methyl group is in a 'boat-equatorial' conformation and the 10-oxide group is in a 'boat-axial' conformation. The 'boat-equatorial' conformation of the 9-methyl group was also found by NMR spectra in solution. Therefore, form *B* is the *trans* isomer which exists in solution. Presumably, form *C* is a *trans* isomer with the 9-methyl group in a 'boat-axial' conformation and the 10-oxide group in a 'boat-equatorial' conformation.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36133 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

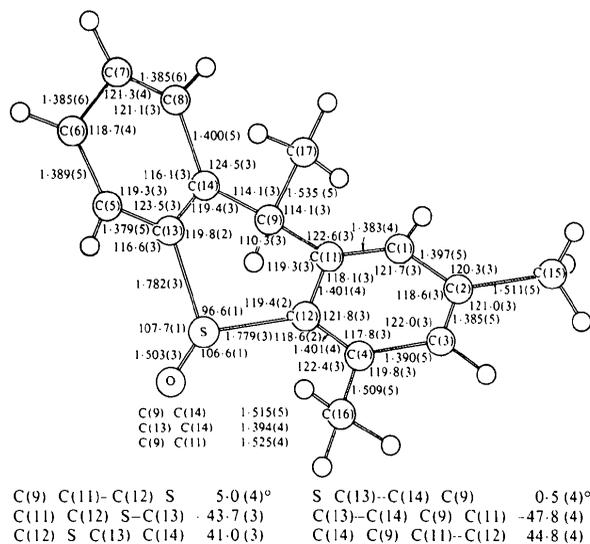


Fig. 1. Bond lengths (Å) and bond angles (°) of the title compound with e.s.d.'s in parentheses. The torsion angles around the central ring are shown above.

The bond lengths and bond angles with their standard deviations are also shown in Fig. 1. The two C—S bond lengths are equal within standard deviations. This is contrary to the *cis* isomers of 2,4,9-trimethylthioxanthene 10-oxide (Chu *et al.*, 1979) and 9-ethyl-2,4-dimethylthioxanthene 10-oxide (Chu, Napoleone, Massah & Ternay, 1981) in which the two C—S bond lengths are significantly different. The C(12)—S—C(13) and C(11)—C(9)—C(14) bond angles within the central ring are 96.6(1) and 110.3(3)^o respectively, both smaller than the corresponding bond angles of 98.6(2) and 113.2(3)^o in the *cis* isomer of 2,4,9-trimethylthioxanthene 10-oxide. Since the folding angle between the planes of the two benzene rings is correlated with the bond angles involving the *meso* atoms of the central ring, the folding angle of 134.2^o in the *trans* isomer is smaller than that of 147.3^o in the *cis* isomer. The larger folding angle in the *cis* isomer is due presumably to the nonbonded interaction between the 9-methyl substituent and the 10-oxide group, both being in 'boat-axial' conformations, and the intermolecular interaction in the solid state. The equations of the least-squares planes of the two benzene rings are $0.8105x + 0.4861y + 0.0304z = 4.1264$ and $0.1479x$



Fig. 2. ORTEP drawing (Johnson, 1965) of the molecular packing of the title compound in a unit cell.

+ 0.8754y + 0.2031z = 7.2159 (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 0.000 to 0.007 Å and the deviations of the two methyl substituents on the benzene ring, C(15) and C(16), from plane A are 0.007 and 0.032 Å respectively.

The C—H bond lengths range from 0.98 to 1.13 Å (mean 1.03 ± 0.04 Å). The C—C—H bond angles involving benzene rings range from 114 to 125^o (mean 120 ± 2 ^o) and the C—C—H and H—C—H bond angles involving tetrahedral C atoms range from 97 to 115^o (mean 109 ± 3 ^o). The packing of the molecules in the crystal is shown in Fig. 2. There are no intermolecular contacts less than van der Waals distances.

This research was supported by the Robert A. Welch Foundation, Houston, Texas, through grants N-495 (to SSCC) and Y-484 (to ALT). The authors wish to thank Dr R. Shiono of the University of Pittsburgh for making the ORTEP plots.

References

- CHU, S. S. C., NAPOLEONE, V., MASSAH, F. & TERNAY, A. L. JR (1981). *Acta Cryst.* **B37**, 775–777.
 CHU, S. S. C., ROSENSTEIN, R. & TERNAY, A. L. JR (1979). *Acta Cryst.* **B35**, 2430–2433.
 CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 SHIONO, R. (1971). Tech. Rep. 49, Crystallography Department, Univ. of Pittsburgh.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.