

Fig. 3. Packing of molecules in the unit cell. The origin is at the lower left-hand corner of the unit cell.

The puckering of the two six-membered rings, as can be seen from bond angles (Fig. 1), is due to the strain imposed by the two substituents on C(2)···C(5) and C(7)···C(10).

The discrepancies in chemically equivalent bond lengths and angles might be attributed to systematic errors in intensity measurements.

The packing of molecules in the unit cell is shown in Fig. 3. Intermolecular distances shorter than van der Waals contacts have not been found.

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1,4-Dimethyl-9-isobutylthioxanthene 10,10-Dioxide

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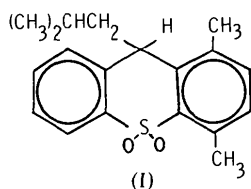
(Received 28 June 1977; accepted 24 August 1977)

Abstract. $C_{19}H_{22}O_2S$, triclinic, $P\bar{1}$, $Z = 4$, $M_r = 314.43$, $a = 9.860$ (1), $b = 18.294$ (1), $c = 14.197$ (1) Å, $\alpha = 108.71$ (1), $\beta = 111.49$ (1), $\gamma = 116.48$ (1)°, $V = 1726.81$ Å³, $D_x = 1.209$, $D_m = 1.22$ g cm⁻³ (by flotation), $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 16.48$ cm⁻¹. Final residual $R = 0.057$. The interactions

between the *meso* and *para* substituents cause the differences in bond lengths and bond angles involving the *meso* atoms.

Introduction. Single crystals of the title compound (I) were obtained through the courtesy of Dr A. L. Ternay

Jr of the Chemistry Department of the University of Texas at Arlington. The crystals are transparent prisms. The unit-cell parameters and the intensity data were measured on a Nonius CAD-4 automatic diffractometer. The size of the crystal was $0.58 \times 0.27 \times 0.21$ mm. An $\omega/2\theta$ scanning mode with Ni-filtered Cu $K\alpha$ radiation was used to measure 6570 independent reflections with 2θ values below 140° , of which 4862 reflections were considered observed. A reflection was considered observed if its intensity was greater than $2.0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. Because of the large number of reflections, only the observed reflections were used for the structure determination and for all refinements. The intensity data were reduced to structure factors, and no absorption corrections were applied.



The structure was determined by the heavy-atom method. There are two crystallographically independent molecules in one asymmetric unit of the crystal. The refinement was carried out by the full-matrix least-squares method (Busing, Martin & Levy, 1962) with isotropic temperature factors and the block-diagonal least-squares method (Shiono, 1971) with anisotropic temperature factors. All the H atoms were located by difference Fourier syntheses. 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 ($\sum w(|F_o| - |F_c|)/\sum |F_o|$) was 0.057.* The magnitude $[\sum w(F_o - F_c)^2/(m - n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 0.85. The atomic scattering factors used for S, O, and C 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 determination of the crystal structure of (I) is one of a series of studies of thioxanthene derivatives undertaken in this laboratory. The crystal structures of 9-isobutylthioxanthene (Chu, 1973) and 9-isobutylthioxanthene 10,10-dioxide (Chu & Chung, 1973) have been determined. The study of the crystal structure of (I) will determine the effect of the additional *para* substituents on the stereochemistry of the thioxanthene ring system.

The stereoscopic view (Johnson, 1965) of the configuration of one of the two crystallographically independent molecules is shown in Fig. 1. The two molecules have the same conformation. The identification of the atoms and the bond lengths and bond angles with their standard deviations are shown in Fig. 2. In all other thioxanthene derivatives, the bond lengths, and bond angles, involving the *meso* S atom are equal. When the coordination number of S is four, the mean values of C-S and S-O bond lengths are found to be 1.755 and 1.439 Å, respectively, and the mean values of the C-S-C and C-S-O bond angles are 101.5 and 109.2° respectively (Chu, 1975). It is apparent from Fig. 2 that the C-S and C-C bond lengths involving the *meso* atoms are lengthened on the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32959 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

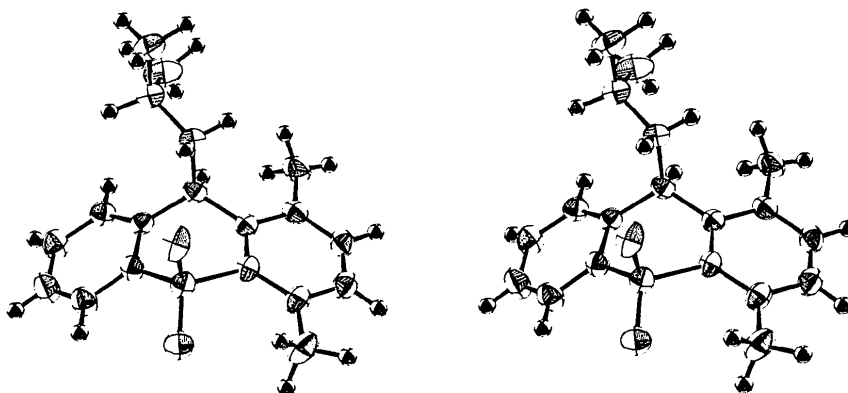


Fig. 1. A stereoscopic drawing of one of the two crystallographically independent molecules.

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

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

Molecule A	x	y	z	Molecule B	x	y	z
S	745 (1)	8617 (1)	22 (1)	S'	8890 (1)	6652 (1)	3497 (1)
O(1)	-479 (3)	8775 (2)	-618 (2)	O'(1)	10475 (3)	6866 (2)	3483 (3)
O(2)	-124 (3)	7743 (2)	39 (2)	O'(2)	9322 (4)	7342 (2)	4622 (2)
C(1)	4885 (5)	8865 (2)	-184 (3)	C'(1)	4025 (5)	5648 (3)	567 (3)
C(2)	4040 (5)	8480 (3)	-1442 (3)	C'(2)	4762 (7)	6294 (3)	249 (4)
C(3)	2254 (5)	8129 (3)	-2240 (3)	C'(3)	6669 (7)	7034 (3)	906 (4)
C(4)	1168 (5)	8147 (2)	-1835 (3)	C'(4)	7978 (6)	7191 (3)	1929 (3)
C(5)	2126 (5)	10281 (3)	2071 (3)	C'(5)	8661 (5)	5137 (3)	3546 (3)
C(6)	3478 (5)	11103 (3)	3280 (3)	C'(6)	7718 (6)	4190 (4)	3284 (4)
C(7)	5200 (5)	11347 (3)	3969 (3)	C'(7)	5787 (6)	3561 (3)	2638 (4)
C(8)	5605 (4)	10766 (2)	3443 (3)	C'(8)	4779 (5)	3866 (2)	2225 (3)
C(9)	4726 (4)	9314 (2)	1626 (3)	C'(9)	4559 (4)	5128 (2)	2023 (3)
C(11)	3854 (4)	8921 (2)	267 (3)	C'(11)	5305 (5)	5768 (2)	1594 (3)
C(12)	2048 (4)	8572 (2)	-558 (3)	C'(12)	7269 (5)	6525 (2)	2238 (3)
C(13)	2519 (4)	9689 (2)	1556 (3)	C'(13)	7634 (4)	5442 (3)	3145 (3)
C(14)	4269 (4)	9924 (2)	2226 (3)	C'(14)	5676 (4)	4814 (2)	2477 (2)
C(15)	4192 (5)	8431 (3)	1750 (3)	C'(15)	4422 (5)	5694 (2)	3021 (3)
C(16)	5246 (6)	8710 (3)	3059 (4)	C'(16)	3178 (5)	5041 (3)	3274 (3)
C(17)	4384 (10)	7743 (5)	2996 (5)	C'(17)	3585 (6)	5723 (4)	4480 (4)
C(18)	7360 (8)	9306 (5)	3710 (5)	C'(18)	1109 (6)	4351 (3)	2236 (4)
C(19)	6841 (5)	9218 (3)	627 (4)	C'(19)	1932 (6)	4877 (4)	-164 (4)
C(20)	-824 (5)	7709 (3)	-2779 (3)	C'(20)	10070 (8)	8057 (3)	2655 (5)

Molecule A	x	y	z	B (Å ²)	Molecule B	x	y	z	B (Å ²)
H(2)	483 (5)	845 (3)	-174 (3)	7.4 (9)	H'(2)	392 (5)	617 (3)	-51 (3)	7.3 (9)
H(3)	160 (5)	784 (3)	-313 (3)	8.0 (10)	H'(3)	709 (6)	748 (3)	62 (4)	9.1 (11)
H(5)	95 (5)	1011 (3)	158 (3)	7.2 (9)	H'(5)	1000 (5)	560 (3)	399 (3)	7.3 (10)
H(6)	319 (5)	1150 (3)	361 (3)	6.6 (9)	H'(6)	853 (5)	395 (3)	365 (4)	8.1 (10)
H(7)	616 (4)	1193 (2)	473 (3)	5.8 (8)	H'(7)	494 (5)	282 (3)	238 (4)	9.0 (11)
H(8)	690 (4)	1098 (2)	394 (3)	4.5 (7)	H'(8)	342 (4)	341 (2)	168 (3)	5.7 (8)
H(9)	621 (4)	978 (2)	208 (3)	4.8 (7)	H'(9)	323 (4)	450 (2)	128 (2)	3.6 (6)
H(15)1	283 (4)	798 (2)	136 (3)	4.6 (7)	H'(15)1	584 (5)	631 (3)	383 (3)	6.6 (8)
H(15)2	439 (5)	803 (3)	131 (3)	6.9 (9)	H'(15)2	375 (4)	593 (2)	264 (3)	5.0 (7)
H(16)	516 (5)	918 (3)	365 (3)	7.6 (9)	H'(16)	357 (5)	463 (3)	343 (3)	7.1 (9)
H(17)1	492 (6)	788 (3)	377 (4)	9.7 (11)	H'(17)1	291 (6)	534 (3)	463 (4)	10.7 (13)
H(17)2	465 (8)	732 (4)	258 (5)	14.7 (17)	H'(17)2	306 (6)	608 (3)	433 (4)	11.3 (12)
H(17)3	297 (7)	734 (4)	262 (5)	13.5 (16)	H'(17)3	505 (6)	633 (3)	518 (4)	10.6 (12)
H(18)1	820 (7)	983 (4)	369 (5)	14.1 (15)	H'(18)1	26 (6)	392 (3)	237 (4)	9.3 (11)
H(18)2	757 (9)	880 (5)	332 (6)	18.5 (20)	H'(18)2	78 (6)	483 (3)	223 (4)	11.1 (12)
H(18)3	794 (7)	956 (4)	467 (5)	14.8 (17)	H'(18)3	64 (6)	382 (3)	132 (4)	8.6 (11)
H(19)1	787 (5)	998 (3)	146 (4)	8.2 (10)	H'(19)1	127 (5)	480 (3)	-90 (4)	9.3 (10)
H(19)2	713 (5)	898 (3)	114 (3)	7.1 (9)	H'(19)2	149 (6)	418 (3)	-46 (4)	10.3 (12)
H(19)3	719 (7)	906 (4)	18 (4)	11.3 (14)	H'(19)3	158 (5)	501 (3)	36 (4)	8.5 (10)
H(20)1	-122 (5)	729 (3)	-366 (3)	8.1 (10)	H'(20)1	1084 (5)	846 (3)	355 (4)	9.3 (10)
H(20)2	-176 (6)	732 (3)	-266 (4)	10.0 (12)	H'(20)2	1013 (8)	862 (4)	258 (5)	14.9 (16)
H(20)3	-91 (7)	827 (4)	-275 (5)	13.5 (14)	H'(20)3	1081 (7)	786 (4)	247 (5)	11.5 (14)

side attached to the benzene ring with the *p*-dimethyl substituents. The two S—O bond lengths, and the two C—S—O bond angles, are also not equal in molecule *A*. The inequalities in bond lengths and bond angles are due apparently to the non-bonded interactions between the *meso* and *para* substituents. However, the inequalities are more pronounced in molecule *A* than in molecule *B*, presumably because of the different molecular environments in the two independent molecules. The non-bonded intramolecular distances are 2.85 and 2.89 Å, between O(1) and C(20), 2.53 and 2.75 Å between O(1) and H(20)2, 2.66 and 2.64

Å between O(1) and H(20)3, 2.56 and 2.58 Å between O(2) and H(15)1, and 2.42 and 2.47 Å between C(19) and H(9) for molecules *A* and *B* respectively. The bond angles around the S atom are similar in magnitude to those in other thioxanthene 10,10-dioxide derivatives (Chu & Chung, 1973, 1974; Chu & Mangion, 1975).

The least-squares planes of the benzene rings indicate that the benzene rings without the *para* substituents are planar; however, the benzene rings with the *p*-dimethyl substituents are slightly distorted with both methyl C atoms out of the plane on the order of 0.03–0.04 Å for C(19) and 0.08–0.09 Å for C(20).

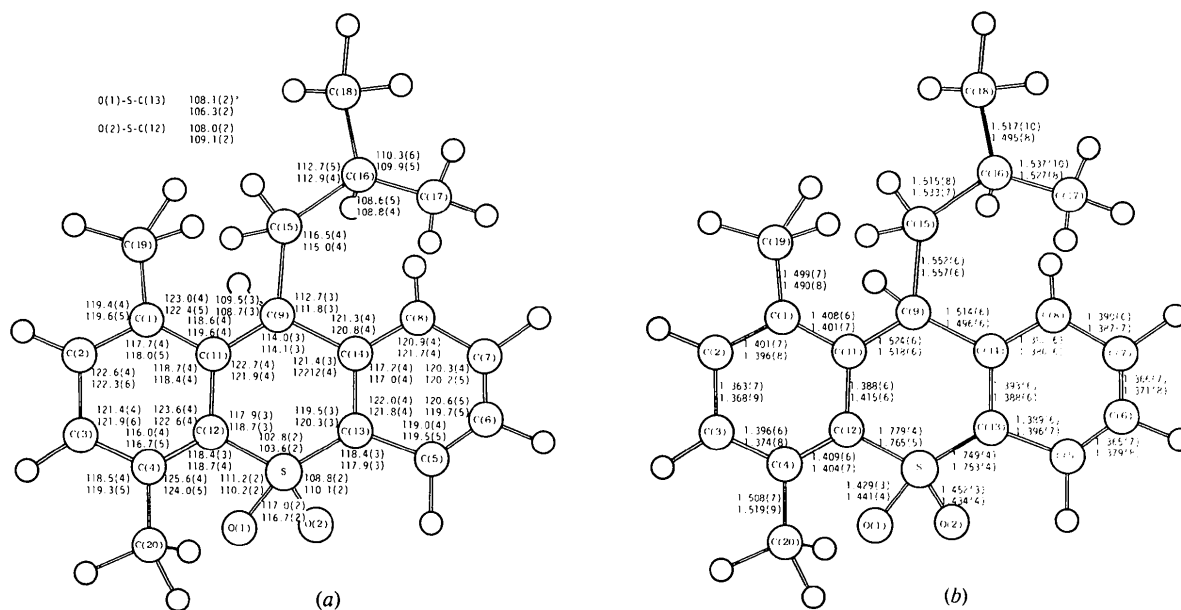


Fig. 2. (a) The bond lengths (Å) and (b) the bond angles (°) of the two independent molecules. Upper numbers refer to molecule *A*, lower numbers to molecule *B*; e.s.d.'s are in parentheses.

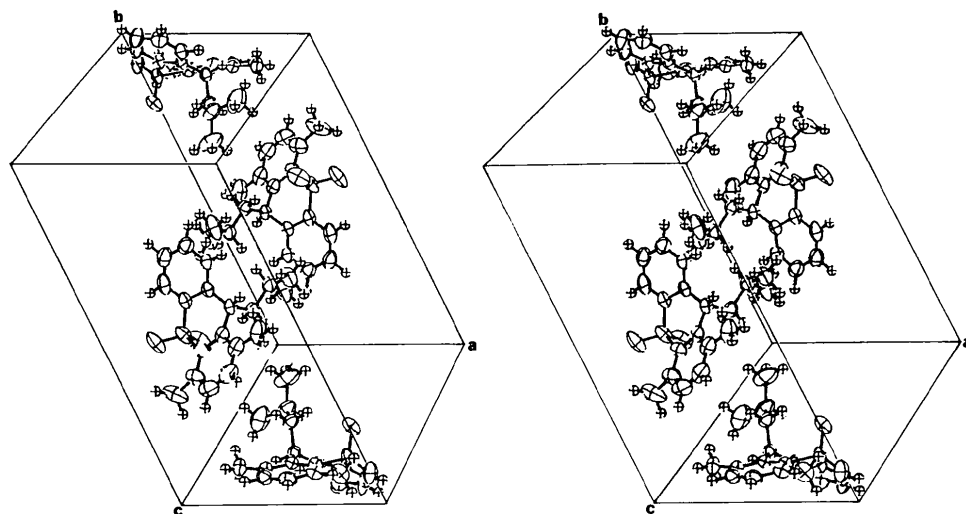


Fig. 3. A stereoscopic drawing of the molecular packing in the unit cell.

The folding angles between the best planes of the two benzene rings are 141.1 and 144.9° for molecules *A* and *B*, respectively, as compared with 141.8° in 9-isobutylthioxanthene 10,10-dioxide (Chu & Chung, 1973). The 9-isobutyl group is in a 'boat-axial' conformation. The torsion angles of this group indicate that its conformation agrees with that found in 9-isobutylthioxanthene (Chu, 1973) and in 9-isobutylthioxanthene 10,10-dioxide (Chu & Chung, 1973).

The packing of the molecules in the crystal is shown in the stereoscopic drawing in Fig. 3. There are no intermolecular contacts less than van der Waals distances. The closest intermolecular distances are 3.26 Å between O'(1) and C(7) and 3.34 Å between O(2) and C'(8).

The half-normal probability plot analysis (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972) was used to compare the two crystallographically independent

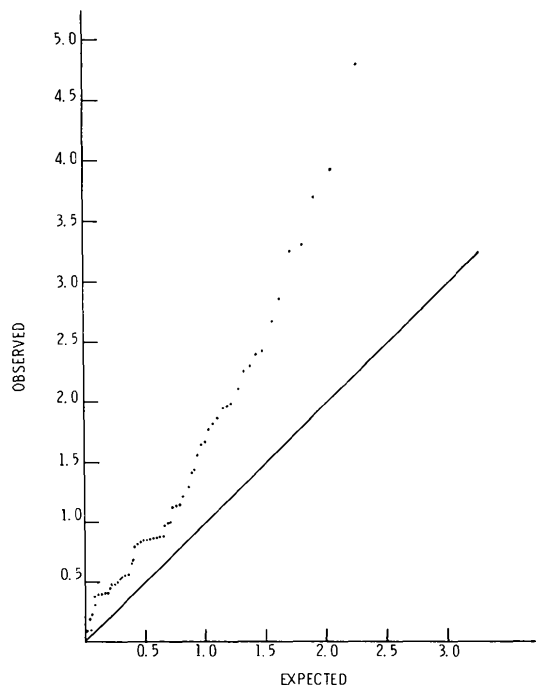


Fig. 4. Half-normal probability plot for the comparison of bond lengths and bond angles of the two crystallographically independent molecules (excluding hydrogen atoms). The solid line represents unit slope.

molecules. The comparisons of the bond lengths and bond angles are shown in Fig. 4. Results derived from data containing a random normal distribution of error should give a linear plot of zero intercept and unit slope.

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Cyan(2,2-dimethyl-1,2,4-triazol-3-yl)formylmethanid, eine zwitterionische Verbindung

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Abstract. $C_7H_8N_4O$, orthorhombic, *Pnma*, $a = 13.169(7)$, $b = 7.129(3)$, $c = 8.799(5)$ Å, $V = 826.1$ Å³, $M_r = 164.2$, $Z = 4$, $D_x = 1.320$, $D_m = 1.316$ g cm⁻³. The molecule has the symmetry *m*, occupying a special position on the crystallographic mirror plane. The bond lengths show that the bonding relations are mainly described by four zwitterionic resonance formulae. The molecular configuration

However, the slope of the least-squares line is 1.5 indicating that the bond lengths and bond angles of the two independent molecules do not agree as well as they are predicted to on the basis of the e.s.d.'s in the positional parameters.

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allows a weak intramolecular hydrogen bond, forming a five-membered chelate ring.

Einleitung. Durch Umsetzung von 1,1-Dimethylhydrazin (I) mit *N*²-(1-Chlor-2-cyan-3-oxo-1-propenyl)-*N*¹,*N*¹-dimethylformamidin (II) konnte die farblose Titelverbindung (III) synthetisiert werden (Klemm, Prüsse & Baron, 1976). Um die primär über