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The Crystal Structure of *cis*-9-Isopropylthioxanthene 10-Oxide

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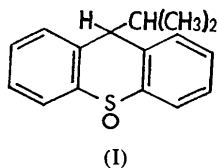
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The crystal structure of *cis*-9-isopropylthioxanthene 10-oxide, C₁₆H₁₆OS, has been determined by the heavy-atom method. The refinement was carried out by the least-squares method with anisotropic temperature factors based on three-dimensional data to give a final *R* value of 0.039 for 2677 reflections. The space group is *P*2₁/*c* with *Z*=8, and the unit-cell dimensions are *a*=14.356 (3), *b*=8.235 (2), *c*=24.263 (4) Å, β=106.77 (3)°. There are two independent molecules in one asymmetric unit of the crystal; however, the two molecules have the same configuration. The distances and angles in the benzenoid rings are normal, and the best planes of the benzene rings make a dihedral angle of 138.8 and 135.5° for the two crystallographically independent molecules. Both the 9-isopropyl and 10-oxide groups are in 'boat-axial' conformation with respect to the central thioxanthene ring. The average sulfur-carbon bond distance is 1.782 (3) Å, and the average sulfur-oxygen bond distance is 1.499 (3) Å. The carbon-sulfur-carbon bond angle is 97.0 (1)°. All these values agree well with those found in other thioxanthene derivatives where the coordination number of the sulfur atom is three. The packing of the molecules in the crystal is determined by the van der Waals interaction.

Introduction

This paper reports the determination of the crystal structure of *cis*-9-isopropylthioxanthene 10-oxide (I)



and is a continuation of the studies on a series of thioxanthene derivatives. The *cis*-isomer of 9-alkylthioxanthene 10-oxide could exist in two conformations; 9-alkyl and 10-oxide groups are both in 'boat equatorial' or in 'boat axial' conformation (Fig. 1). It has been shown that in thioxanthene sulfoxides, the 10-

oxide group prefers the 'boat equatorial' conformation by proton magnetic resonance spectroscopic studies (Evans & Ternay, 1974) and by crystal structure determinations on *cis*-9-methylthioxanthene 10-oxide (Jacobs & Sundaralingam, 1969) and *trans*-thioxanthene-9-ol 10-oxide (Ternay, Chasar & Sax, 1967). The sulfinyl oxygen group governs the stereochemistry of these isomers when the size of the *meso*-substituent is small. However, n.m.r. investigations of *cis*-9-alkylthioxanthene 10-oxides, employing the nuclear Overhauser effect, have shown that the conformation in which the 9-alkyl and sulfinyl oxygen groups are both in the 'boat axial' position becomes significant when the 9-substituent is an ethyl group. Furthermore, *cis*-9-isopropylthioxanthene 10-oxide appears to be conformationally homogeneous in solution (Evans, 1970; Evans, Davenport & Ternay, 1974*a, b*). The purpose of the present study is to determine the conformation of

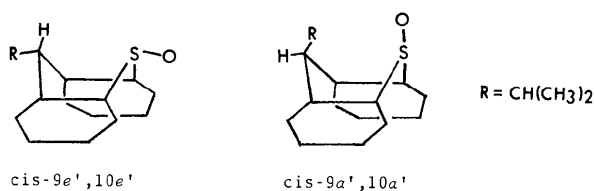
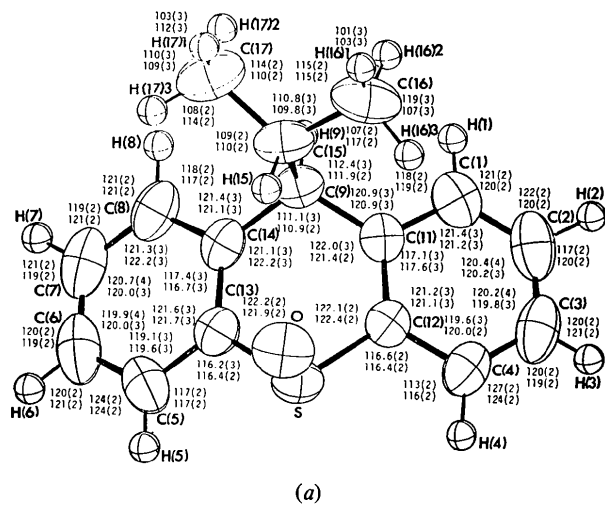


Fig. 1. Conformation of the two *cis*-isomers of 9-isopropylthioxanthene 10-oxide.



	Molecule I	Molecule II		Molecule I	Molecule II
0.....S-----C(12)	108.6(11)	108.8(11)	C(11)-C(9)-H(9)	107(2)	107(2)
0.....S-----C(13)	107.9(11)	108.3(11)	C(14)-C(9)-H(9)	108(2)	107(2)
0.....S-----C(13)	97.1(17)	96.9(11)	C(15)-C(9)-H(9)	107(2)	108(2)
C(14)-C(9)-C(15)	111.1(13)	110.9(2)	C(16)-C(15)-H(15)	106(2)	107(2)
C(9)-C(15)-C(16)	111.4(3)	110.9(3)	C(16)-C(15)-H(15)	107(2)	108(2)
C(9)-C(15)-C(17)	110.3(13)	111.7(3)	C(17)-C(15)-H(15)	109(2)	110(2)
			C(15)-C(16)-H(16)	109(2)	109(2)
			H(16)-C(16)-H(16)	108(3)	104(3)
			C(15)-C(17)-H(17)	110(2)	108(2)
			H(17)-C(17)-H(17)	112(3)	104(3)

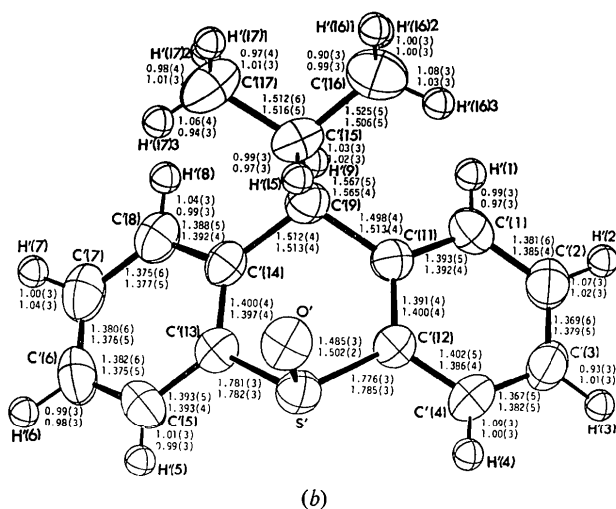


Fig. 2. The structure of the two independent molecules of *cis*-9-isopropylthioxanthene 10-oxide and their bond lengths (Å) and bond angles (°). Upper numbers refer to molecule I, lower to molecule II; e.s.d. in parentheses. (a) Configuration of molecule I with bond angles. (b) Configuration of molecule II with bond lengths.

cis-9-isopropylthioxanthene 10-oxide in the solid state, and to determine whether the 9-isopropyl group governs the conformation of this derivative in solid state as in solution. It has been shown that most biologically active thioxanthene derivatives require a large substituent on the C(9) position (Gallant & Bishop, 1967; Zirkle & Kaiser, 1970) and their sulfoxides act as metabolite in the biological system (Schindler, Lehner, Michaelis & Schmutz, 1963; Michaelis, Schindler & Signer, 1966). Therefore, the study of the conformation of 9-alkylthioxanthene sulfoxides must play a critical role in understanding the structural requirements for their pharmacological activities.

Experimental

Single crystals of *cis*-9-isopropylthioxanthene 10-oxide were obtained through the courtesy of Dr A. L. Ternay of the Chemistry Department of the University of Texas at Arlington. The crystals are transparent prisms. The accurate cell parameters were measured with Mo $K\alpha$ radiation on a Picker FACS-1 automatic diffractometer. The crystal data are summarized in Table 1.

Table 1. Crystal data of *cis*-9-isopropylthioxanthene 10-oxide

Chemical formula:	$C_{16}H_{16}OS$	M.W.	256.37
Crystal system:	monoclinic		
Space group:	$P2_1/c$ from the systematic extinctions: $h0l$ absent with l odd and $0k0$ absent with k odd		
a	$14.356(3)$ Å	b	$8.235(2)$ Å
c	$24.263(4)$ Å	β	$106.77(3)^\circ$
V	2746.5 Å ³	Z	8
D_x	1.24 g cm ⁻³	$F(000)$	1088
D_m	1.23 g cm ⁻³ (in a mixture of toluene and carbon tetrachloride)		
λ (Mo $K\alpha$)	0.7107 Å		
μ (Mo $K\alpha$)	2.19 cm ⁻¹		

The integrated intensity data were collected on a Picker FACS-1 automatic diffractometer in NASA, Houston, Texas. The crystal was cut to approximately $0.21 \times 0.68 \times 0.26$ mm in dimensions and was mounted along the b axis. A $\theta/2\theta$ scanning mode with graphite monochromatic Mo $K\alpha$ radiation was used to measure 3420 independent reflections with 2θ values below 45° , of which 2677 reflections were considered as observed. The total time for the background counts recorded at the limits of each scan was 20 s. A reflection was considered observed if its intensity was greater than $3\sigma(I)$, where $\sigma(I)$ is determined from counting statistics. Scale factors, based on the variation of the standard reflections, were applied to the intensity data to compensate for the fluctuations during the data collection period. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors, and no absorption corrections were applied.

Structure determination

The presence of eight molecular units of *cis*-9-isopropylthioxanthene 10-oxide in a unit cell in space group $P2_1/c$ requires that there are two crystallogra-

phically independent molecules in an asymmetric unit. The positions of the two sulfur atoms were obtained from the Harker peaks (u, v, w), $(0, v, \frac{1}{2})$, $(u, \frac{1}{2}, w)$, and the vectors between the two sulfur atoms of the E^2-1 Patterson synthesis. However, the carbon and oxygen

Table 2. Fractional atomic coordinates and thermal parameters (all $\times 10^4$)

The estimated standard deviations are given in parentheses and refer to the last positions of respective values. The expression for the temperature factor exponent consistent with β values is $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Molecule I	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	-1663 (1)	391 (1)	1036 (0)	65 (1)	168 (1)	21 (0)	0 (1)	3 (0)	-6 (0)
O	-2166 (2)	1595 (3)	594 (1)	86 (2)	259 (5)	20 (1)	16 (2)	-5 (1)	4 (1)
C(1)	-1867 (3)	2228 (5)	2542 (2)	71 (2)	249 (7)	23 (1)	24 (3)	10 (1)	4 (2)
C(2)	-2565 (3)	1225 (6)	2651 (2)	68 (2)	356 (10)	30 (1)	42 (4)	21 (1)	28 (3)
C(3)	-2981 (3)	17 (5)	2272 (2)	53 (2)	2272 (2)	40 (1)	18 (4)	18 (1)	41 (3)
C(4)	-2701 (2)	-216 (4)	1785 (2)	51 (2)	189 (6)	32 (1)	8 (3)	6 (1)	15 (2)
C(5)	231 (3)	128 (5)	1073 (2)	89 (3)	232 (7)	27 (1)	30 (4)	24 (1)	9 (2)
C(6)	1205 (3)	543 (6)	1249 (2)	77 (3)	312 (10)	40 (1)	45 (4)	32 (1)	38 (3)
C(7)	1523 (3)	1773 (6)	1645 (2)	59 (2)	328 (10)	37 (1)	-1 (4)	15 (1)	39 (3)
C(8)	880 (2)	2593 (5)	1868 (2)	63 (2)	237 (7)	26 (1)	-18 (3)	7 (1)	25 (2)
C(9)	-819 (2)	3154 (4)	1931 (1)	62 (2)	155 (5)	18 (1)	-7 (3)	1 (1)	-1 (2)
C(11)	-1563 (2)	2039 (4)	2050 (1)	51 (2)	175 (6)	19 (1)	11 (3)	6 (1)	8 (2)
C(12)	-1980 (2)	780 (4)	1678 (1)	48 (2)	161 (6)	22 (1)	12 (3)	4 (1)	10 (2)
C(13)	-417 (2)	971 (4)	1298 (1)	62 (2)	169 (6)	20 (1)	1 (3)	9 (1)	14 (2)
C(14)	-106 (2)	2229 (4)	1697 (1)	56 (2)	182 (6)	18 (1)	-5 (3)	5 (1)	17 (2)
C(15)	-1293 (3)	4591 (4)	1522 (1)	87 (2)	146 (6)	20 (1)	-1 (3)	-2 (1)	-2 (2)
C(16)	-2148 (3)	5324 (5)	1690 (2)	103 (3)	190 (7)	35 (1)	46 (4)	-3 (1)	-10 (2)
C(17)	-539 (3)	5872 (5)	1523 (2)	123 (4)	177 (7)	35 (1)	-18 (4)	5 (2)	14 (2)

Molecule II

S'	4712 (1)	4246 (1)	1596 (0)	58 (1)	155 (1)	15 (0)	5 (1)	4 (0)	4 (0)
O'	3963 (2)	3310 (3)	1787 (1)	81 (2)	180 (4)	19 (0)	-10 (2)	15 (1)	10 (1)
C'(1)	3305 (2)	8271 (4)	803 (1)	54 (2)	165 (5)	19 (1)	18 (3)	11 (1)	4 (2)
C'(2)	3703 (2)	9459 (4)	1205 (1)	63 (2)	153 (6)	24 (1)	-3 (3)	14 (1)	-5 (2)
C'(3)	4385 (2)	9054 (4)	1715 (1)	68 (2)	161 (6)	24 (1)	-16 (3)	10 (1)	-18 (2)
C'(4)	4677 (2)	7457 (4)	1821 (1)	64 (2)	180 (6)	17 (1)	-19 (3)	7 (1)	-6 (2)
C'(5)	5378 (2)	2562 (4)	829 (1)	58 (2)	155 (5)	26 (1)	18 (3)	13 (1)	8 (2)
C'(6)	5369 (3)	2008 (4)	293 (2)	77 (2)	150 (6)	32 (1)	3 (3)	27 (1)	-14 (2)
C'(7)	4654 (3)	2518 (4)	-187 (2)	83 (2)	184 (6)	25 (1)	-17 (3)	22 (1)	-19 (2)
C'(8)	3951 (2)	3591 (4)	-130 (1)	69 (2)	176 (6)	18 (1)	-13 (3)	11 (1)	-9 (2)
C'(9)	3150 (2)	5361 (4)	455 (1)	50 (2)	161 (5)	14 (1)	0 (2)	5 (1)	0 (1)
C'(11)	3579 (2)	6650 (4)	900 (1)	42 (2)	152 (5)	15 (1)	-1 (2)	9 (1)	-1 (1)
C'(12)	4279 (2)	6267 (4)	1419 (1)	51 (2)	141 (6)	15 (1)	-4 (2)	9 (1)	1 (1)
C'(13)	4654 (2)	3622 (3)	883 (1)	54 (2)	133 (5)	17 (1)	-8 (2)	10 (1)	4 (1)
C'(14)	3923 (2)	4170 (3)	404 (1)	52 (2)	132 (5)	16 (1)	-15 (2)	10 (1)	-3 (1)
C'(15)	2258 (2)	4494 (4)	576 (1)	54 (2)	209 (6)	17 (1)	-21 (3)	6 (1)	-1 (2)
C'(16)	1467 (3)	5696 (6)	575 (2)	55 (2)	319 (9)	40 (1)	-3 (4)	17 (1)	-11 (3)
C'(17)	1854 (3)	3159 (5)	142 (2)	76 (3)	282 (8)	27 (1)	-56 (4)	11 (1)	-17 (2)

Hydrogen atomic coordinates ($\times 10^3$)

Molecule I	x	y	z	Molecule II	x	y	z
H(1)	-156 (2)	310 (4)	282 (1)	H'(1)	286 (2)	857 (3)	43 (1)
H(2)	-284 (2)	139 (4)	302 (1)	H'(2)	350 (2)	1063 (3)	112 (1)
H(3)	-343 (2)	-68 (4)	236 (1)	H'(3)	472 (2)	992 (3)	200 (1)
H(4)	-300 (2)	-109 (4)	144 (1)	H'(4)	515 (2)	708 (3)	219 (1)
H(5)	-5 (2)	-73 (4)	78 (1)	H'(5)	585 (2)	218 (3)	119 (1)
H(6)	168 (2)	-9 (4)	111 (1)	H'(6)	584 (2)	120 (3)	25 (1)
H(7)	223 (2)	205 (4)	179 (1)	H'(7)	465 (2)	208 (4)	-59 (1)
H(8)	112 (2)	351 (4)	217 (1)	H'(8)	344 (2)	400 (3)	-47 (1)
H(9)	-43 (2)	367 (3)	232 (1)	H'(9)	291 (2)	593 (3)	7 (1)
H(15)	-156 (2)	416 (3)	113 (1)	H'(15)	249 (2)	403 (4)	96 (1)
H(16)1	-240 (2)	623 (4)	150 (1)	H'(16)1	87 (2)	523 (4)	63 (1)
H(16)2	-192 (2)	573 (4)	209 (1)	H'(16)2	122 (2)	621 (4)	17 (1)
H(16)3	-272 (2)	444 (4)	158 (1)	H'(16)3	164 (2)	660 (4)	86 (1)
H(17)1	-84 (3)	679 (4)	129 (1)	H'(17)1	126 (2)	269 (4)	23 (1)
H(17)2	-24 (3)	637 (4)	190 (1)	H'(17)2	170 (2)	362 (4)	-26 (1)
H(17)3	-1 (3)	534 (4)	135 (1)	H'(17)3	230 (2)	232 (4)	14 (1)

atoms were not revealed distinctly from the Fourier synthesis. The direct method was used with the program *MULTAN* (Germain, Main & Woolfson, 1971) from the 495 reflections with E greater than 1.5. The E map confirmed the two sulfur positions but did not show the other atoms clearly. By careful examination

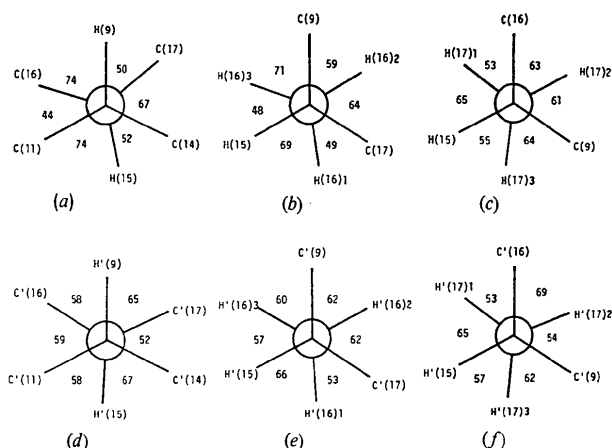


Fig. 3. The torsion angles ($^{\circ}$) about (a) C(9)–C(15), (b) C(15)–C(16), and (c) C(15)–C(17) for molecule I, and about (d) C'(9)–C'(15), (e) C'(15)–C'(16), and (f) C'(15)–C'(17) for molecule II.

of the Fourier and E maps with the considerations of obtaining reasonable packing of the molecules, two oxygen and four carbon atoms were located. The positions of all other carbon atoms were obtained from three successive Fourier syntheses. Two cycles of full-matrix least-squares refinements with isotropic temperature factors reduced R , the disagreement index, to 0.135. Two cycles of full-matrix least-squares refinements with anisotropic temperature factors reduced R to 0.123. All hydrogen atoms were clearly revealed in two successive difference Fourier syntheses with reasonable bond lengths and bond angles with respect to the atoms to which they are bonded. Three cycles of block-diagonal least-squares refinements with anisotropic temperature factors, including all the hydrogen atoms, gave the final R value of 0.039. The positional parameters of the hydrogen atoms were refined, but their thermal parameters were made the same as those of the atoms to which they are bonded. Cruickshank's (1965) weighting scheme was used, and the weight of the reflections was calculated according to the formula $1/w = (1.75 - 0.10|F_o| + 0.0025|F_o|^2)$. The quantity $\sum w\{|F_o| - |F_c|\}^2$ was minimized. The final goodness-of-fit, $[\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 0.974. The atomic scattering factors used for sulfur, oxygen, and carbon atoms were those from *International Tables for X-ray Crystallog-*

Table 3. Comparison of C–S and S–O bond lengths, C–S–C and C–S–O bond angles, and dihedral angles in thioxanthene derivatives

The estimated standard deviations are given in parentheses and refer to the last decimal positions

Compound	Coordination number of S	Mean bond lengths		Bond angles		Dihedral angle ($^{\circ}$)	References
		C–S (\AA)	S–O (\AA)	C–S–C ($^{\circ}$)	C–S–O ($^{\circ}$)		
Thioxanthene	2	1.770 (6)		99.2 (3)		135.3	Gillean, Phelps & Cordes (1973)
Methixene	2	1.765 (3)		100.5 (2)		137.9	Chu (1972)
9-Isobutylthioxanthene	2	1.768 (3)		100.9 (2)		138.9	Chu (1973a)
9-Methyl-9-isopropylthioxanthene	2	1.761 (4)		100.2 (2)		143.0	Chu & Mangion (to be published)
(molecules I & II)		1.765 (4)		100.4 (2)		144.2	
	Mean value*	1.766 (1)		100.37 (4)			
<i>cis</i> -9-Methylthioxanthene 10-oxide	3	1.782 (2)	1.492 (3)	95.2 (1)	108.5 (1)	127.2	Jackobs & Sundaralingam (1969)
<i>trans</i> -Thioxanthene-9-ol 10-oxide	3	1.775 (12)	1.484 (8)	97.5 (7)	107.5 (8)	132.4	Ternay, Chasar & Sax (1967)
1,4-Dimethylthioxanthene 10-oxide	3	1.780 (3)	1.502 (3)	98.7 (2)	106.5 (1)	143.6	Chu & Chung (1974a)
<i>cis</i> -9-Isopropylthioxanthene 10-oxide (molecules I & II)	3	1.779 (3)	1.485 (3)	97.1 (1)	108.3 (1)	138.8	This work
		1.784 (3)	1.502 (2)	96.9 (1)	108.6 (1)	135.5	
	Mean value	1.781 (1)	1.497 (1)	96.58 (7)	107.97 (7)		
Thioxanthene 10,10-dioxide	4	1.751 (3)	1.441 (2)	101.4 (1)	109.1 (1)	133.9	Chu & Chung (1974b)
9-Isobutylthioxanthene 10,10-dioxide	4	1.757 (2)	1.440 (2)	102.0 (1)	109.1 (1)	141.8	Chu & Chung (1973)
9-(Cyclohexylmethyl)thioxanthene 10,10-dioxide	4	1.756 (3)	1.437 (2)	101.0 (1)	109.4 (1)	133.7	Chu & Mangion (to be published)
	Mean value	1.755 (1)	1.439 (1)	101.47 (3)	109.20 (3)		

* The mean values are calculated from $l = \frac{\sum_i \left(\frac{1}{\sigma_i^2} l_i \right)}{\sum_i \left(\frac{1}{\sigma_i^2} \right)}$.

raphy (1962). For hydrogen, the values given by Stewart, Davidson & Simpson (1965) were used. The final positional and thermal parameters are given in Table 2.*

The computer programs used in this analysis were *ORFLS* (Busing, Martin & Levy, 1962), the block-diagonal least-squares program (Shiono, 1971), the Zalkin Fourier synthesis program modified by Dr R. Shiono of the University of Pittsburgh, and a number of structure interpretation programs (Shiono, 1971; Chu, 1973*b*). All calculations were carried out on a CDC CYBER 72 computer in the Computing Laboratory at Southern Methodist University.

Discussion of structure

The configuration of the two crystallographically independent molecules of *cis*-9-isopropylthioxanthene 10-oxide, I and II, and the identification of the atoms are shown in the *ORTEP* (Johnson, 1965) drawing, Fig. 2. The bond lengths and bond angles with their standard deviations of the two molecules are also shown in Fig. 2. The mean value of carbon-carbon bond lengths within the benzene rings is 1.386 (5) Å, and that of carbon-carbon bond lengths in the central ring involving C(9) is 1.509 (4) Å. The mean value of exocyclic carbon-carbon bond lengths is 1.532 (5) Å. All of these bond lengths are in good agreement with other thioxanthene derivatives (Chu & Chung, 1973, 1974). The average carbon-hydrogen bond length is 1.00 (3) Å, in agreement with the values obtained in other X-ray crystal structure analyses.

The mean value of the four carbon-sulfur bond lengths is 1.781 (3) Å, and that of the two sulfur-oxygen bond lengths is 1.494 (2) Å. The mean value of the two C-S-C bond angles is 97.0 (1)°, and that of the four C-S-O bond angles is 108.4 (1)°. These values are in good agreement with those found in the other thioxanthene sulfoxides when the coordination number of the sulfur atom is three. A correlation of the coordination number of the sulfur atom with the C-S and S-O bond lengths, and C-S-C and C-S-O bond angles in thioxanthene derivatives with accurate structure data are summarized in Table 3.

The distances and angles in the benzenoid rings of the *cis*-9-isopropylthioxanthene 10-oxide are normal and the C(9) and S are not significantly displaced from the planes of the benzene rings. The central ring is in a boat conformation. The dihedral angle between the least-squares planes of the two benzene rings for molecule I is 138.8° and that for molecule II is 135.5°. A comparison of the dihedral angles in thioxanthene derivatives is also given in Table 3. It can be shown

that the dihedral angle does not depend on the coordination number of sulfur but varies with the nature of substituents. Both the 9-isopropyl and S-O groups are in 'boat axial' conformation, in contrast to the conformation observed in *cis*-9-methylthioxanthene 10-oxide (Jackobs & Sundaralingam, 1969). This confirms the n.m.r. spectroscopic study which indicates that the sulfinyl oxygen atom prefers the 'boat equatorial' conformation and that this oxygen atom governs the conformation when the 9-substituent is not larger than the methyl group (Evans & Ternay, 1974). However, the alkyl group governs the conformation of *cis*-9-alkylthioxanthene 10-oxide when the alkyl group is an isopropyl substituent. The torsion angles of the isopropyl group for both molecules are shown in Fig. 3. Within experimental errors, the two independent molecules possess the same configuration. The dihedral angles between the plane passing through S, O, C(9), and C(15) atoms and the planes of the two benzene rings in molecule I are 68.7 and 70.1°, and those in molecule II are 67.5 and 68.0°. Therefore, the molecule exhibits a 'pseudo' mirror plane passing through S, O, C(9), and C(15).

The packing of the molecules in the crystal, projected down the *b* axis, is shown in Fig. 4. Molecules I and molecules II form alternate layers along the *bc* plane. There are no intermolecular contacts less than van der Waals distances. The intermolecular distances less than 3.5 Å are those between O and C'(1), O and C'(6), O' and C(3), and O' and C'(4), and they are 3.313, 3.418, 3.321 and 3.449 Å, respectively. The rigid-body thermal analysis of the 18 non-hydrogen atoms was carried out by the method of Schomaker & Trueblood (1968). The r.m.s. value of ΔU_{ij} , the difference between observed U_{ij} and calculated U_{ij} based on the rigid-body model, is 0.0041 Å² for molecule I and 0.0045 Å² for molecule II. A comparison of this value with the mean $\sigma(U_{ij})$

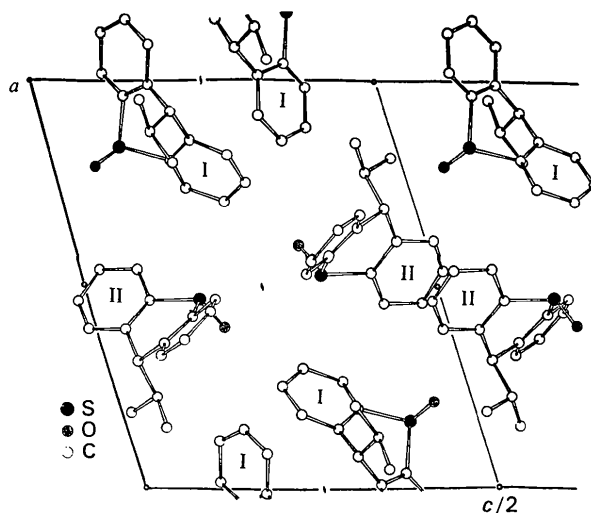


Fig. 4. The molecular packing diagram, excluding hydrogen atoms, viewed down the *b* axis of *cis*-9-isopropylthioxanthene 10-oxide.

* A table of calculated and observed structure factors has been deposited with the British Library Lending Division, as Supplementary Publication No. SUP 30799 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

value of 0.0020 \AA^2 , calculated from the estimated standard deviation of the β_{IJ} of the least-squares refinement, indicates that the rigid-body model is only moderately satisfactory.

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The Crystal Structure of $\text{Bi}_6\text{O}_7\text{FCl}_3$

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The structure of $\text{Bi}_6\text{O}_7\text{FCl}_3$ has been determined by symbolic addition and Fourier methods and refined to $R=0.055$ for 1214 independent counter intensities. The crystals are orthorhombic, space group *Pnma*, with $a=20.105$ (6), $b=3.892$ (2), $c=15.432$ (5) Å, $Z=4$. The Bi atoms are of two types, one four-coordinated by O or O and F which form a nearly square plane, the other five-coordinated by two F and three O, all on one side of Bi. The Bi–O, F distances range between 2.19 and 2.51 Å. The fourfold coordination can be described as a square pyramid with the lone pair of electrons at its apex, and the five-coordination as an octahedron with the lone pair at one corner. The coordination polyhedra are linked by sharing edges and corners to form infinite layers parallel to [010]. Between the nets, trigonal prism columns of chloride ions run in the same direction.

Introduction

By heating BiOCl in air above 600°C , it was totally transformed into a new well defined phase, $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$

(Sillén & Edstrand, 1942). The substitution of O^{2-} by F^- in BiOCl is useful in preparing compounds with simple and predictable structures, related to the above phase. These substances can serve as models for the