

## The Crystal Structure of 9-Isobutylthioxanthene 10,10-dioxide\*

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The crystal structure of 9-isobutylthioxanthene 10,10-dioxide,  $C_{17}H_{18}O_2S$ , 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 0.050 for 2283 reflections. The space group is  $P2_1/c$  with  $Z=4$ , and the unit-cell dimensions are  $a=12.973 \pm 0.004$ ,  $b=9.121 \pm 0.003$ ,  $c=12.645 \pm 0.004$  Å,  $\beta=98.96 \pm 0.03^\circ$ . The crystal contains both enantiomorphs in equal amounts. The distances and angles in the benzenoid rings are normal, and the best planes of the benzene rings make a dihedral angle of  $141.8^\circ$ . The *meso* atoms, C(9) and S, are not significantly displaced from the planes of the benzene rings. The isobutyl group is 'boat-axial' with respect to the central thioxanthene ring. The sulfur-carbon bond distance is  $1.757 \pm 0.002$  Å. The average carbon-carbon bond distance is  $1.527 \pm 0.006$  Å for carbon-carbon single bonds,  $1.386 \pm 0.004$  Å for carbon-carbon bonds in benzenoid rings and  $1.515 \pm 0.003$  Å for carbon-carbon bonds involving C(9) and the benzenoid ring. The packing of the molecules in the crystal is determined by the van der Waals interactions.

### Introduction

9-Isobutylthioxanthene 10,10-dioxide is one of a series of thioxanthene derivatives under study in this laboratory by the X-ray diffraction method. This compound is the first thioxanthene sulfone derivative studied by X-ray diffraction and is closely related to 9-isobutylthioxanthene (Chu, 1973). A comparison of the C-S bond distance, C-S-C bond angle, and the dihedral angle between the best planes of the benzene rings with other thioxanthene derivatives is of interest for understanding the bonding characteristics of the sulfur atom.

### Experimental

Single crystals of 9-isobutylthioxanthene 10,10-dioxide were obtained by courtesy of Dr A. L. Ternay of the Chemistry Department of the University of Texas at Arlington. The crystals are transparent prisms, elongated along the  $a$  axis. The accurate cell parameters were measured with  $Cu K\alpha$  radiation on a Picker FACS-1 automatic diffractometer. The density of the crystals was determined by the flotation equilibrium method in a mixture of carbon tetrachloride and toluene. The crystal data is summarized in Table 1.

The integrated intensity data were collected on a Picker FACS-1 automatic diffractometer in the Department of Crystallography of the University of Pittsburgh. The crystal was cut to approximately  $0.22 \times 0.43 \times 0.25$  mm and was mounted along the  $b$  axis. A  $\theta/2\theta$  scanning mode with  $Cu K\alpha$  radiation was used to measure 2483 independent reflections with  $2\theta$  values below  $130^\circ$ , of which 2283 were considered as observed. The total time for the background counts re-

Table 1. *Crystal data of 9-isobutylthioxanthene 10,10-dioxide*

Chemical formula $C_{17}H_{18}O_2S$	Molecular weight 270.40
Monoclinic, space group $P2_1/c$ from the systematic extinctions: $h0l$ absent when $l=2n+1$ and $0k0$ absent for $k=2n+1$ ;	
$a=12.973 \pm 0.004$ Å	$Z=4$
$b=9.121 \pm 0.003$	$D_m=1.273$ g cm $^{-3}$
$c=12.645 \pm 0.004$	$D_x=1.286$
$\beta=98.96 \pm 0.03^\circ$	$\mu(Cu K\alpha)=18.73$ cm $^{-1}$
	$\lambda(Cu K\alpha)=1.5418$ Å

corded at the limits of each scan was 20 sec. A reflection was considered observed if its intensity was greater than  $3\sigma(I)$ , where  $\sigma(I)$  was determined from counting statistics. Three standard reflections were repeated in intervals of every 100 reflections, and their intensities showed fluctuations of less than 6% over the data collection period. Scale factors, based on the variation of the standard reflections, were applied to the intensity data to compensate for this fluctuation. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors, and no absorption corrections were applied.

### Determination and refinement of the structure

The structure was solved by the heavy-atom method. The position of the sulfur atom was obtained from the Harker peaks  $(u, v, w)$ ,  $(0, v, \frac{1}{2})$ , and  $(u, \frac{1}{2}, w)$  of the  $E^2-1$  Patterson synthesis. All carbon and oxygen atoms were located in two successive Fourier syntheses. The structure-factor calculations for all atoms except hydrogen has yielded an  $R$  value of 0.29 for three-dimensional data. Two cycles of full-matrix least-squares refinement with isotropic temperature factors reduced the  $R$  value to 0.13. Two cycles of full-matrix least-squares refinement with anisotropic temperature fac-

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Table 2. Fractional atomic coordinates and thermal parameters

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  $\beta$  values is:

$$-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl).$$

Values for non-hydrogen atoms are  $\times 10^4$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S	1749 (0)	-300 (1)	-1543 (0)	66 (0)	114 (1)	45 (0)	-3 (0)	7 (0)	-4 (0)
O(1)	2658 (1)	317 (2)	-1899 (1)	89 (1)	153 (3)	69 (1)	-15 (2)	33 (1)	5 (2)
O(2)	893 (1)	-712 (2)	-2354 (1)	92 (2)	174 (3)	59 (1)	-3 (2)	-13 (1)	-20 (2)
C(1)	2831 (2)	-2845 (3)	962 (2)	68 (2)	121 (4)	84 (2)	14 (2)	15 (2)	20 (2)
C(2)	2724 (2)	-4231 (3)	528 (3)	90 (2)	114 (4)	114 (3)	14 (2)	31 (2)	20 (3)
C(3)	2320 (2)	-4421 (3)	-542 (3)	90 (2)	97 (4)	128 (3)	-4 (2)	41 (2)	-10 (3)
C(4)	2007 (2)	-3218 (3)	-1178 (2)	69 (2)	122 (4)	93 (2)	-10 (2)	26 (2)	-23 (2)
C(5)	493 (2)	1861 (3)	-1028 (2)	61 (2)	135 (4)	62 (2)	4 (2)	-1 (1)	9 (2)
C(6)	159 (2)	2877 (3)	-339 (2)	57 (2)	133 (4)	82 (2)	15 (2)	6 (1)	7 (2)
C(7)	612 (2)	2907 (3)	717 (2)	59 (2)	131 (4)	75 (2)	9 (2)	14 (1)	-9 (2)
C(8)	1409 (2)	1938 (3)	1101 (2)	56 (2)	129 (3)	59 (2)	1 (2)	11 (1)	-9 (2)
C(9)	2668 (2)	-98 (3)	848 (2)	52 (1)	111 (3)	53 (1)	6 (2)	2 (1)	2 (2)
C(11)	2532 (2)	-1606 (3)	348 (2)	48 (1)	107 (3)	66 (2)	1 (2)	13 (1)	4 (2)
C(12)	2128 (2)	-1825 (2)	-724 (2)	55 (2)	97 (3)	67 (2)	-4 (2)	14 (1)	-1 (2)
C(13)	1307 (2)	921 (2)	-638 (2)	54 (2)	98 (3)	52 (1)	0 (2)	6 (1)	1 (2)
C(14)	1781 (2)	933 (2)	427 (2)	48 (1)	102 (3)	51 (1)	-4 (2)	6 (1)	3 (2)
C(15)	3750 (2)	532 (3)	713 (2)	51 (2)	143 (4)	75 (2)	-1 (2)	4 (1)	-13 (2)
C(16)	4065 (2)	1926 (3)	1346 (2)	57 (2)	124 (4)	101 (2)	-3 (2)	5 (2)	-19 (2)
C(17)	4277 (3)	1676 (4)	2539 (3)	125 (3)	249 (7)	98 (3)	-40 (4)	-11 (2)	-39 (4)
C(18)	5016 (3)	2604 (4)	963 (3)	99 (3)	211 (6)	168 (4)	-59 (3)	37 (3)	-46 (4)

Table 2 (cont.)

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

	<i>x</i>	<i>y</i>	<i>z</i>
H(C1)	310 (3)	-266 (4)	178 (3)
H(C2)	293 (3)	-513 (4)	97 (3)
H(C3)	230 (3)	-545 (4)	-80 (3)
H(C4)	169 (3)	-334 (4)	-196 (3)
H(C5)	16 (3)	176 (4)	-184 (3)
H(C6)	-45 (3)	357 (4)	-61 (3)
H(C7)	35 (3)	363 (4)	122 (3)
H(C8)	170 (3)	198 (4)	187 (3)
H(C9)	266 (2)	-23 (3)	167 (2)
H(C15)1	431 (3)	-32 (4)	97 (3)
H(C15)2	376 (3)	72 (4)	-3 (3)
H(C16)	344 (3)	265 (4)	121 (3)
H(C17)1	491 (4)	89 (5)	262 (3)
H(C17)2	439 (4)	252 (5)	303 (4)
H(C17)3	370 (4)	111 (5)	285 (3)
H(C18)1	523 (3)	352 (5)	139 (4)
H(C18)2	564 (4)	184 (5)	117 (4)
H(C18)3	487 (4)	287 (5)	17 (4)

tors reduced *R* to 0.082. All hydrogen atoms were clearly revealed in the difference Fourier synthesis with reasonable bond lengths and bond angles with respect to the atoms to which they are bonded. Two more cycles of least-squares refinement with anisotropic temperature factors, including all hydrogen atoms, gave the final *R* value of 0.050. The positional parameters of the hydrogen atoms were refined, but their thermal parameters were assigned the same as those of the atoms to which they are bonded. Cruickshank's (1961) weighting scheme was used in order to make  $[\sum w(F_o - F_c)^2 / (\text{no. of reflections} - \text{no. of parameters})]^{1/2}$  approximately equal to unity, and the average  $w(F_o - F_c)^2$  is approximately constant for different magnitudes of  $|F_o|$  and  $\sin \theta$ . The weight of the reflections was calculated according to the formula  $1/w = (1.75 - 0.15|F_o|$

+ 0.0045 $|F_o|^2$ ). The final positional and thermal parameters are listed in Table 2, and the corresponding structure factors are given in Table 3.

The computer programs used in this analysis were the *ORFLS* program (Busing, Martin & Levy, 1962) modified by Shiono (1970), a modified Zalkin Fourier synthesis program (Shiono, 1967), a data reduction program (Shiono, 1971), and a number of structure interpretation programs (Shiono, 1971; Chu, 1971). All calculations were carried out on a UNIVAC 1108 computer.

### Description of the structure

The configuration of a 9-isobutylthioxanthene 10,10-dioxide molecule and the identification of the atoms are shown in the *ORTEP* (Johnson, 1965) drawing shown in Fig. 1. Since the crystal belongs to a centrosymmetric space group, both enantiomorphs are present in the crystal.

The bond lengths and bond angles with their standard deviations are shown in Fig. 2. The mean value of carbon-carbon bond lengths within the benzene rings is  $1.386 \pm 0.004$  Å. The carbon-carbon bond lengths in the central ring involving C(9) are  $1.512 \pm 0.003$  and  $1.517 \pm 0.003$  Å. The mean value of exocyclic carbon-carbon bond lengths is  $1.527 \pm 0.004$  Å. All of these bond lengths are in good agreement with the results obtained in methixene (Chu, 1972) and 9-isobutylthioxanthene (Chu, 1973). The average carbon-hydrogen bond length is  $1.03 \pm 0.04$  Å, in agreement with the values obtained in other X-ray crystal structure analyses.

The mean value of the two carbon-sulfur bond lengths is  $1.757 \pm 0.002$  Å with a coordination number

of four for the sulfur atom. This is significantly shorter than the  $C(sp^2)$ -S bond lengths with a sulfur coordination number of two or three. A comparison of C-S bond lengths in tricyclic compounds with accurate structure data is shown in Table 4.

The mean value of the two sulfur-oxygen bond lengths is  $1.440 \pm 0.002$  Å. This value is in good agreement with S-O bond lengths found in the other sulfone structures (Klug, 1968; Preuss, Hoppe, Hecht-fischer & Zechmeister, 1971). However, it is signifi-

Table 3. *Observed and calculated structure factors*

Columns are: index,  $10|F_o|$ ,  $10|F_c|$ . For unobserved reflections are marked with an asterisk.

h	k	l	$10 F_o $	$10 F_c $	...
1	0	0	113	102	...
2	0	0	118	108	...
3	0	0	121	112	...
4	0	0	125	116	...
5	0	0	129	120	...
6	0	0	133	124	...
7	0	0	137	128	...
8	0	0	141	132	...
9	0	0	145	136	...
10	0	0	149	140	...
11	0	0	153	144	...
12	0	0	157	148	...
13	0	0	161	152	...
14	0	0	165	156	...
15	0	0	169	160	...
16	0	0	173	164	...
17	0	0	177	168	...
18	0	0	181	172	...
19	0	0	185	176	...
20	0	0	189	180	...
21	0	0	193	184	...
22	0	0	197	188	...
23	0	0	201	192	...
24	0	0	205	196	...
25	0	0	209	200	...
26	0	0	213	204	...
27	0	0	217	208	...
28	0	0	221	212	...
29	0	0	225	216	...
30	0	0	229	220	...
31	0	0	233	224	...
32	0	0	237	228	...
33	0	0	241	232	...
34	0	0	245	236	...
35	0	0	249	240	...
36	0	0	253	244	...
37	0	0	257	248	...
38	0	0	261	252	...
39	0	0	265	256	...
40	0	0	269	260	...
41	0	0	273	264	...
42	0	0	277	268	...
43	0	0	281	272	...
44	0	0	285	276	...
45	0	0	289	280	...
46	0	0	293	284	...
47	0	0	297	288	...
48	0	0	301	292	...
49	0	0	305	296	...
50	0	0	309	300	...
51	0	0	313	304	...
52	0	0	317	308	...
53	0	0	321	312	...
54	0	0	325	316	...
55	0	0	329	320	...
56	0	0	333	324	...
57	0	0	337	328	...
58	0	0	341	332	...
59	0	0	345	336	...
60	0	0	349	340	...
61	0	0	353	344	...
62	0	0	357	348	...
63	0	0	361	352	...
64	0	0	365	356	...
65	0	0	369	360	...
66	0	0	373	364	...
67	0	0	377	368	...
68	0	0	381	372	...
69	0	0	385	376	...
70	0	0	389	380	...
71	0	0	393	384	...
72	0	0	397	388	...
73	0	0	401	392	...
74	0	0	405	396	...
75	0	0	409	400	...
76	0	0	413	404	...
77	0	0	417	408	...
78	0	0	421	412	...
79	0	0	425	416	...
80	0	0	429	420	...
81	0	0	433	424	...
82	0	0	437	428	...
83	0	0	441	432	...
84	0	0	445	436	...
85	0	0	449	440	...
86	0	0	453	444	...
87	0	0	457	448	...
88	0	0	461	452	...
89	0	0	465	456	...
90	0	0	469	460	...
91	0	0	473	464	...
92	0	0	477	468	...
93	0	0	481	472	...
94	0	0	485	476	...
95	0	0	489	480	...
96	0	0	493	484	...
97	0	0	497	488	...
98	0	0	501	492	...
99	0	0	505	496	...
100	0	0	509	500	...



the  $\pi$  bond character arising from the  $2p$  orbitals of the carbon atom and the  $3p$  and  $3d$  orbitals of the sulfur atom. The near tetrahedral configuration of the four S-C and S-O bonds in sulfones indicates that  $sp^3$  hybridization characterizes the bonding in tetravalent sulfur compounds. The short S-C and S-O bond lengths in sulfones can adequately be explained by the contribution of ionic bond character due to electrical effects resulting from a strong positive charge on the sulfur and by the capability of the  $3d$  orbitals of positively charged sulfur of accepting some share of one or more electrons from adjacent  $2p$  orbitals (Price & Oae, 1962).

The least-squares planes in 9-isobutylthioxanthene

10,10-dioxide are shown in Table 5. The central ring is in a boat conformation. The C(9) and S are not significantly displaced from the planes of the benzene rings, and the slight displacements are in the same side of the benzene planes. These are contrary to the results found in thioxanthenes (Chu, 1972, 1973) and thioxanthene sulfoxide (Jackobs & Sundaralingam, 1969). The dihedral angle between the least-squares planes of the two benzene rings is  $141.8^\circ$  as compared with  $138.9^\circ$  in 9-isobutylthioxanthene (Chu, 1973). The larger dihedral angle in 9-isobutylthioxanthene 10,10-dioxide is presumably due either to the different bonding characteristic of the sulfur atom or to the interaction between the 9-isobutyl group and the oxygen

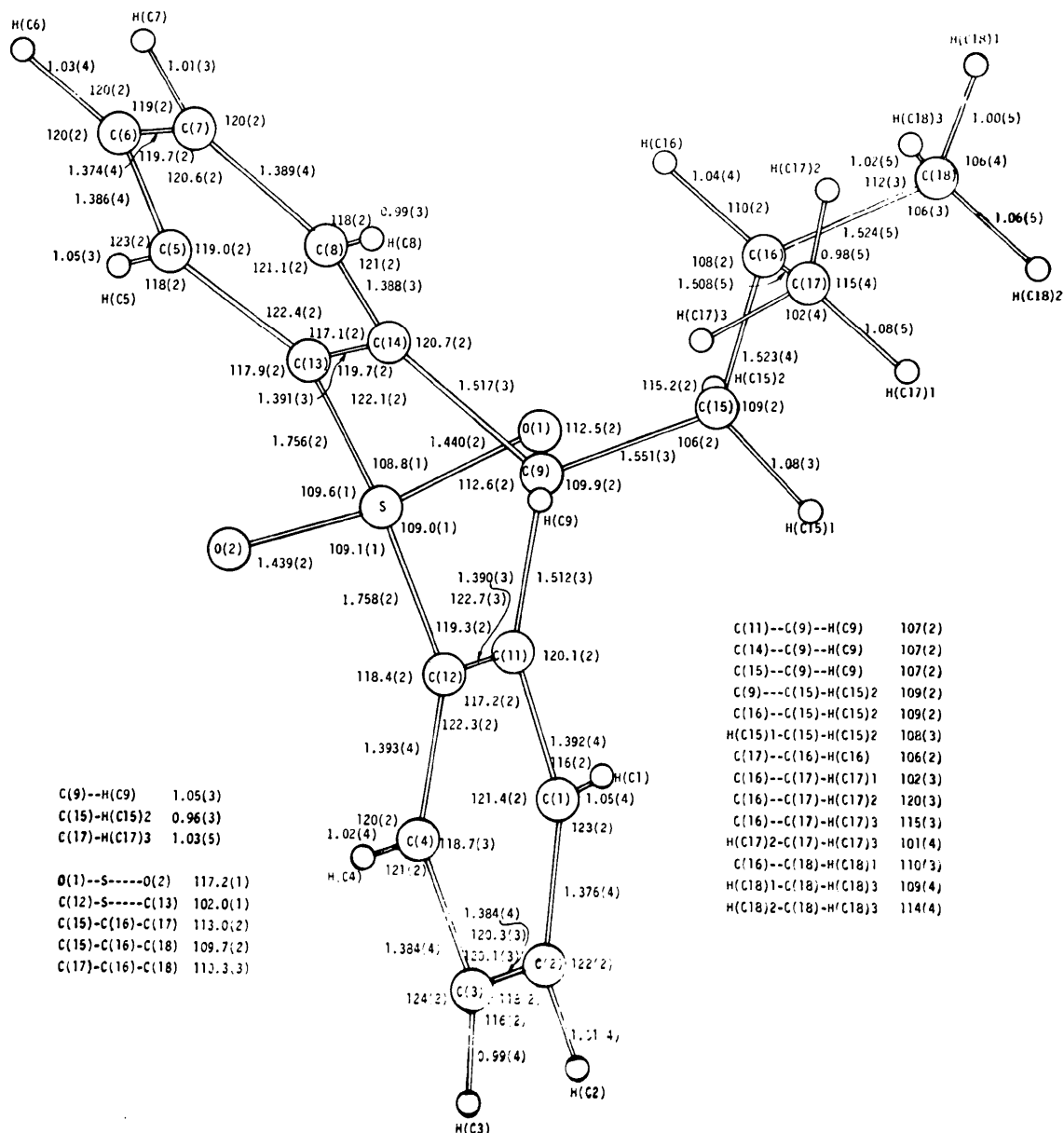


Fig. 2. Bond lengths (Å) and bond angles (°) of 9-isobutylthioxanthene 10,10-dioxide.

atom, both being in 'boat-axial' conformation. The 'boat-axial' conformation of the isobutyl group is also predicted by nuclear magnetic resonance studies in solution (Ternay & Evans, 1973). The torsion angles of the isobutyl group are shown in Fig. 3; this group is in a staggered arrangement which was also found in 9-isobutylthioxanthene. The torsion angles were calculated from the coordinates for the enantiomorph given in Table 2.

The packing of the molecules in the crystal, projected down the *c* axis, is shown in Fig. 4. There are no intermolecular contacts less than van der Waals distances. The closest intermolecular distances between C(5) and O(2) are 3.285 and 3.343 Å, that between C(2) and O(1) is 3.416 Å, and that between C(4) and C(7) is 3.548 Å.

### Analysis of thermal motion

The rigid-body thermal analysis of the 20 non-hydrogen atoms was carried out by the method of Schomaker & Trueblood (1968). The values of **T**, **L**, and **S** tensors together with their standard deviations are shown in Table 6. The r.m.s. amplitude of the principal axes of **T**, **L**, and **S** and their direction cosines with respect to orthogonal axes *a*, *b*, and *c*\* are also given in Table 6. The r.m.s. value of  $\Delta U_{ij}$ , the difference between observed  $U_{ij}$  and calculated  $U_{ij}$  based on the rigid-body model, is 0.0056 Å<sup>2</sup>. A comparison of this value with the mean  $\sigma(U_{ij})$  value of 0.0015 Å<sup>2</sup>, calculated from the estimated standard deviation of the  $\beta_{ij}$  of the least-squares refinement, indicates that the rigid-body model is only moderately satisfactory.

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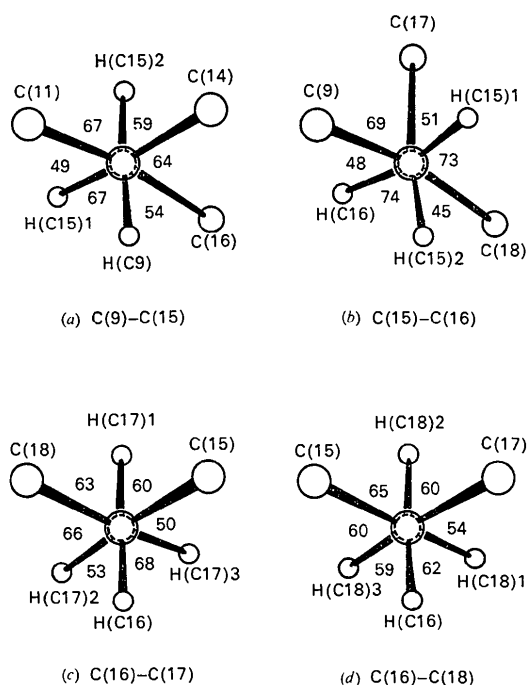


Fig. 3. The torsion angles ( $^{\circ}$ ) about the (a) C(9)-C(15), (b) C(15)-C(16), (c) C(16)-C(17), and (d) C(16)-C(18) bonds.

Table 5. Least-squares planes and the displacements of atoms from the planes

Equation of planes:  $Ax + By + Cz = D$ , where *x*, *y*, *z* are in Å.

Plane	A	B	C	D
(a)	0.9686	0.0642	-0.3882	2.9180
(b)	0.9692	0.0605	-0.3869	2.9314
(c)	0.7121	0.6659	-0.3307	2.0278
(d)	0.7073	0.6727	-0.3246	2.0373
(e)	0.8808	0.3902	-0.4020	2.1475

Displacements in Å from the least-squares planes.

	Benzene ring		Central ring				
	(a)	(b)	(c)	(d)	(e)		
C(1)	0.000	0.000	C(5)	-0.012	-0.021	C(11)	-0.003
C(2)	-0.002	0.002	C(6)	0.008	0.013	C(12)	0.002
C(3)	0.005	0.007	C(7)	0.003	0.013	C(13)	-0.002
C(4)	-0.006	-0.008	C(8)	-0.010	-0.007	C(14)	0.003
C(11)	-0.001	-0.007	C(13)	0.005	-0.011	S	0.529*
C(12)	0.004	-0.003	C(14)	0.006	-0.006	C(9)	0.435*
S	0.019*	-0.006	S	0.051*	0.017		
C(9)	0.012*	-0.003	C(9)	0.023*	0.003		

Dihedral angles between the least-squares planes

Planes	Dihedral angle
(a) and (c)	141.8°
(b) and (d)	141.1
(a) and (b)	0.2
(c) and (d)	0.6

\* Indicates atoms excluded from the calculation of the least-squares planes.

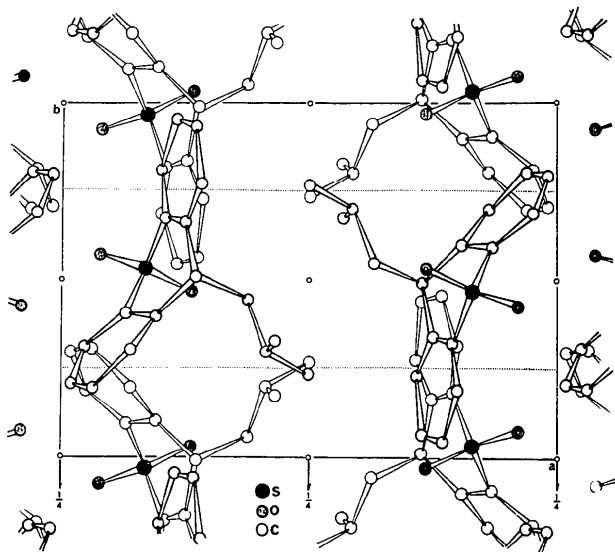


Fig. 4. The molecular packing diagram, excluding hydrogen atoms, viewed down the  $c$  axis of 9-isobutylthioxanthene 10,10-dioxide.

tallography Department, Dr R. Shiono of the University of Pittsburgh for making the *ORTEP* plot and the rigid-body thermal analysis calculation, and Dr A. L. Ternay Jr of the University of Texas at Arlington for kindly supplying the crystals and for numerous discussions.

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Table 6. Rigid-body thermal parameters refer to orthogonal axes,  $a$ ,  $b$ ,  $c$ \*

Estimated standard deviations of the elements of the  $T$ ,  $L$ , and  $S$  tensors are given in parentheses.  $T$  is in  $\text{\AA}^2$ ,  $L$  in  $(^\circ)^2$ , and  $S$  in  $[\text{\AA}]$ .

$$T(\times 10^3) = \begin{pmatrix} 38(2) & -4(2) & 3(2) \\ & 43(2) & 1(2) \\ & & 39(2) \end{pmatrix}$$

$$L = \begin{pmatrix} 9.8(9) & -1.7(9) & -2.5(7) \\ & 16.4(13) & 2.1(9) \\ & & 7.1(8) \end{pmatrix}$$

$$S(\times 10^3) = \begin{pmatrix} -4(36) & -30(24) & -78(24) \\ -13(26) & 21(43) & -122(34) \\ -41(19) & 48(24) & -17(353)^* \end{pmatrix}$$

Principal axes of  $T$

Eigenvalues ( $\text{\AA}^2$ )	Direction cosines ( $\times 10^3$ )		
0.212	-533	830	-163
0.201	-334	-388	-859
0.185	-777	-404	483

Principal axes of  $L$

Eigenvalues ( $^\circ$ )	Direction cosines ( $\times 10^3$ )		
4.20	281	-926	-251
3.22	828	363	-429
2.35	476	-98	874

Principal axes of  $S$

Eigenvalues ( $^\circ \text{\AA}$ )	Direction cosines ( $\times 10^3$ )		
0.057	723	-117	-687
0.006	52	-974	231
-0.063	-669	-168	-716

\* The trace of  $S$  has been set equal to zero; the e.s.d. of deleted  $S(3,3)$  is given.