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Thioxanthene 10,10-Dioxide

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Abstract. $C_{13}H_{10}O_2S$, orthorhombic, *Pbca*, $Z=8$, M.W. 230·28, $a=21·670$ (4), $b=6·763$ (1), $c=15·030$ (3) Å, $D_x=1·389$, $D_m=1·393$ g cm^{-3} (by flotation), λ(Cu $K\alpha$) $=1·5418$ Å, μ(Cu $K\alpha$) $=23·80$ cm^{-1}. Final residual $R=0·044$.

Introduction. Single crystals of thioxanthene 10,10-dioxide were obtained through the courtesy of Dr A. L. Ternay Jr of the Chemistry Department of the University of Texas at Arlington. The space group is *Pbca* as deduced from systematic absences ($0kl$ absent with k odd, $h0l$ absent with l odd, and $hk0$ absent with h odd) on Weissenberg photographs. The crystals are clear needle prisms with **b** parallel to the needle axis. Three-dimensional X-ray diffraction data were collected on a Syntex automatic diffractometer in the Molecular Structure Department of the Institute for Cancer Research, Philadelphia. A crystal approximately $0·17\times0·50\times0·17$ mm in dimensions was mounted along the b axis. A $\theta/2\theta$ scanning mode with monochromatic Cu $K\alpha$ radiation was used to measure 1968 independent reflections with 2θ values below 138°, of which 1350 reflections were considered observed. A reflection was considered observed if its intensity was greater than $\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors, and no absorption corrections were applied. The data were scaled by means of a Wilson plot.

The structure was determined by the heavy-atom method. The refinement was carried out by the full-matrix least-squares method with anisotropic temperature factors. All the hydrogen atoms were located on a difference Fourier synthesis. Their positional parameters were refined; their thermal parameters were assigned the same values as those of the atoms to which they are bonded. Cruickshank's (1965) weighting scheme was used, and the weights were calculated according to the formula $1/w=1·75-0·15|F_o|+0·005|F_o|^2$. The quantity $\sum w\{||F_o|-|F_c||\}^2$ was minimized. The final R index $(\sum||F_o|-|F_c||/\sum|F_o|)$ was 0·044. The final goodness-of-fit, $[\sum(F_o-F_c)^2/(m-n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 0·96. The atomic scattering factors used were those of *International Tables for X-ray Crystallography* (1962). The final

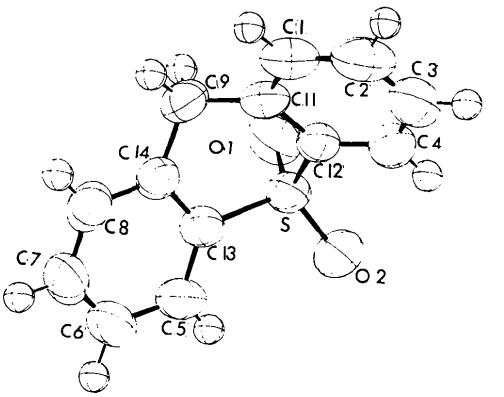

Fig. 1. The structure of one molecule of thioxanthene 10,10-dioxide.

Table 1. *Fractional atomic coordinates and thermal parameters* (*all* $\times10^4$)

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

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	1243 (0)	1789 (1)	353 (0)	20 (0)	184 (2)	55 (0)	−4 (0)	−3 (0)	6 (1)
O(1)	1782 (1)	1021 (3)	−96 (2)	26 (1)	267 (5)	68 (1)	−22 (1)	−3 (1)	24 (2)
O(2)	828 (1)	394 (3)	755 (2)	31 (1)	244 (5)	84 (1)	−30 (1)	−6 (1)	47 (2)
C(1)	1932 (1)	6637 (5)	1472 (2)	21 (1)	299 (9)	74 (2)	8 (2)	−1 (1)	−34 (4)
C(2)	1930 (2)	6181 (7)	2370 (3)	24 (1)	478 (13)	71 (2)	13 (3)	−1 (1)	−64 (5)
C(3)	1710 (2)	4362 (7)	2654 (2)	26 (1)	495 (13)	48 (2)	6 (3)	1 (1)	−20 (4)
C(4)	1479 (1)	3000 (6)	2045 (2)	22 (1)	369 (10)	54 (2)	2 (2)	3 (1)	13 (3)
C(5)	295 (1)	2681 (5)	−761 (2)	20 (1)	313 (9)	55 (2)	6 (2)	0 (1)	11 (3)
C(6)	−11 (2)	3917 (6)	−1350 (2)	21 (1)	432 (11)	53 (2)	−14 (2)	−1 (1)	−1 (4)
C(7)	229 (2)	5756 (6)	−1547 (2)	24 (1)	452 (13)	58 (2)	27 (3)	−1 (1)	−41 (4)
C(8)	778 (2)	6389 (5)	−1159 (2)	26 (1)	296 (9)	64 (2)	11 (2)	−8 (1)	−44 (3)
C(9)	1690 (1)	5817 (5)	−129 (2)	22 (1)	236 (7)	62 (2)	−12 (2)	−4 (1)	−13 (3)
C(11)	1708 (1)	5326 (4)	848 (2)	16 (1)	227 (6)	60 (2)	2 (2)	−2 (1)	−8 (3)
C(12)	1491 (1)	3498 (4)	1152 (2)	17 (1)	231 (6)	48 (1)	2 (2)	1 (1)	5 (2)
C(13)	843 (1)	3323 (4)	−387 (2)	18 (1)	245 (6)	46 (1)	−2 (2)	2 (1)	0 (2)
C(14)	1099 (1)	5164 (4)	−571 (2)	19 (1)	246 (7)	47 (1)	4 (2)	−5 (1)	−12 (2)

Table 1 (*cont.*)

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

	x	*y*	*z*
H(C1)	208 (2)	806 (6)	126 (3)
H(C2)	216 (2)	701 (6)	284 (3)
H(C3)	171 (2)	391 (7)	326 (3)
H(C4)	131 (2)	182 (6)	226 (3)
H(C5)	12 (2)	153 (6)	−64 (3)
H(C6)	−43 (2)	354 (6)	−163 (3)
H(C7)	0 (2)	674 (6)	−192 (3)
H(C8)	95 (2)	760 (7)	−131 (3)
H′(C9)	179 (2)	723 (6)	−25 (3)
H″(C9)	204 (2)	508 (6)	−40 (2)

positional and thermal parameters are given in Table 1.*

The computer programs used in this analysis were the *ORFLS* program (Busing, Martin & Levy, 1962) and Zalkin Fourier synthesis program modified by Dr R. Shiono of the University of Pittsburgh, and a

* A table of calculated and observed structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30381 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

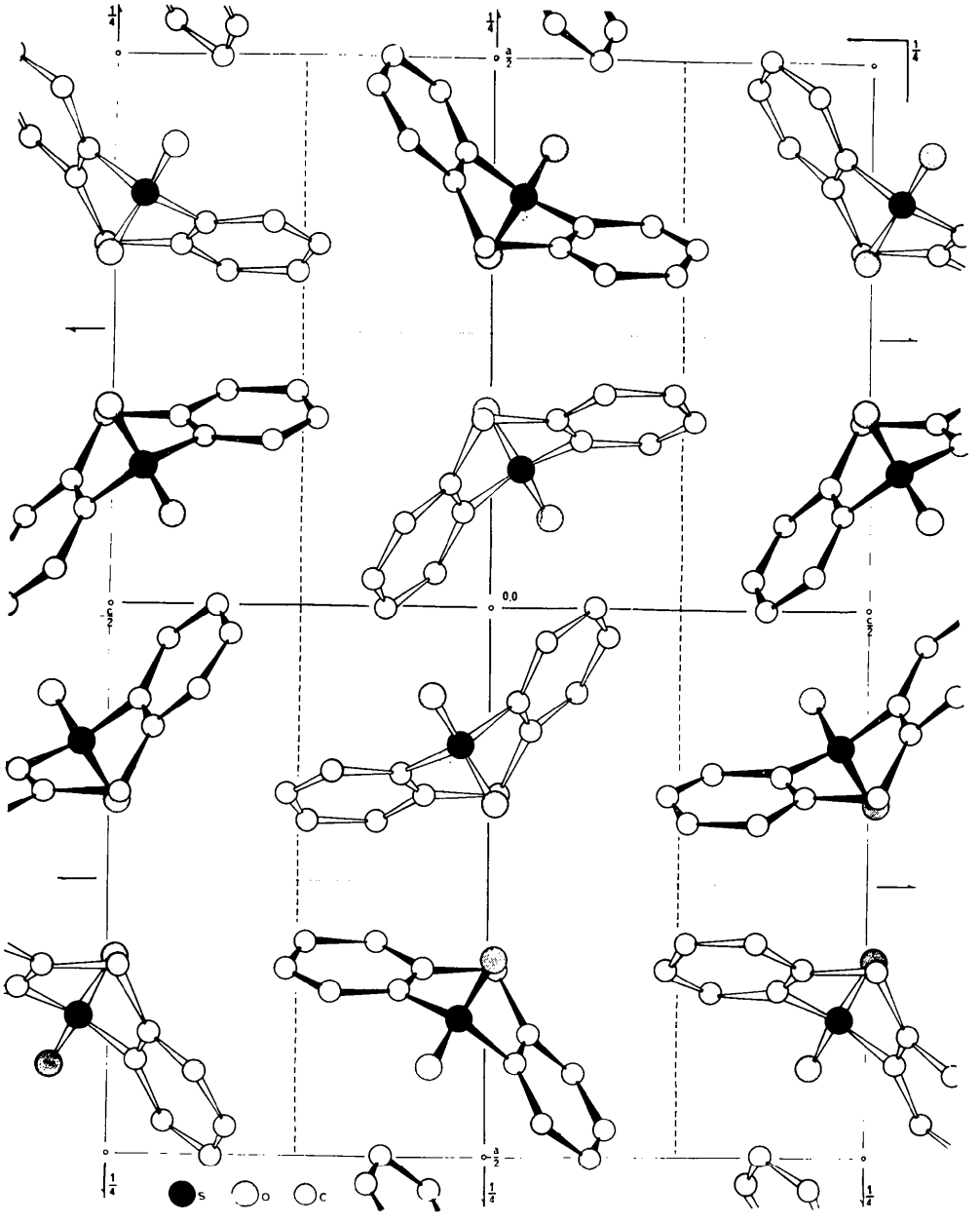

Fig. 2. The molecular packing diagram, excluding hydrogen atoms, viewed down the *b* axis of thioxanthene 10,10-dioxide.

number of structure interpretation programs (Shiono, 1971; Chu, 1971). All calculations were carried out on a CDC CYBER 72 computer in the Computing Laboratory at Southern Methodist University.

Discussion. The determination of this crystal structure is a continuation of studies on a series of thioxanthene derivatives. Fig. 1 shows the conformation of thioxanthene 10,10-dioxide in an *ORTEP* (Johnson, 1965) drawing. Bond lengths and bond angles with their standard deviations involving nonhydrogen atoms are listed in Table 2. The average carbon–hydrogen bond length is 0·98 Å with a root-mean-square standard deviation of 0·04 Å. The least-squares planes in thioxanthene 10,10-dioxide are shown in Table 3. The dihedral angle between the least-squares planes of the two benzene rings is 133·9° as compared with 141·8° in 9-isobutylthioxanthene 10,10-dioxide (Chu & Chung 1973) and 135·3° in thioxanthene (Gillean, Phelps & Cordes, 1973). The larger dihedral angle in 9-isobutylthioxanthene 10,10-dioxide is due to the interaction between the 9-isobutyl group and the oxygen atom. The S–C and S–O bond lengths and the bond angles around the S atom in thioxanthene 10,10-dioxide all agree well with those in 9-isobutylthioxanthene 10,10-dioxide where the coordination number of the sulfur atom is four.

The packing of the molecules in the crystal, projected down the *b* axis, is shown in Fig. 2. There are no intermolecular contacts less than the van der Waals distances.

Table 2. *Bond lengths and bond angles involving nonhydrogen atoms (estimated standard deviations in parentheses with respect to the last place given)*

S——O(1)	1·446 (2) Å	O(1)—S——O(2)	117·7 (1)°
S——O(2)	1·435 (2)	O(1)—S——C(12)	108·0 (1)
S——C(12)	1·751 (3)	O(1)—S——C(13)	108·4 (1)
S——C(13)	1·751 (3)	O(2)—S——C(12)	109·7 (1)
C(1)—C(2)	1·384 (5)	O(2)—S——C(13)	110·3 (1)
C(1)—C(11)	1·379 (5)	C(12)–S——C(13)	101·4 (1)
C(2)—C(3)	1·387 (6)	C(2)—C(1)—C(11)	121·2 (3)
C(3)—C(4)	1·392 (5)	C(1)—C(2)—C(3)	119·9 (4)
C(4)—C(12)	1·383 (4)	C(2)—C(3)—C(4)	120·6 (3)
C(5)—C(6)	1·386 (5)	C(3)—C(4)—C(12)	118·0 (3)
C(5)—C(13)	1·383 (4)	C(6)—C(5)—C(13)	118·7 (3)
C(6)—C(7)	1·380 (5)	C(5)—C(6)—C(7)	120·1 (3)
C(7)—C(8)	1·393 (5)	C(6)—C(7)—C(8)	120·5 (3)
C(8)—C(14)	1·397 (4)	C(7)—C(8)—C(14)	120·6 (3)
C(9)—C(11)	1·507 (4)	C(11)–C(9)—C(14)	112·7 (3)
C(9)—C(14)	1·508 (4)	C(1)—C(11)–C(9)	122·0 (3)
C(11)–C(12)	1·400 (4)	C(1)—C(11)–C(12)	117·7 (3)
C(13)–C(14)	1·391 (4)	C(9)—C(11)–C(12)	120·3 (3)
		S——C(12)–C(4)	119·9 (2)
		S——C(12)–C(11)	117·5 (2)
		C(4)—C(12)–C(11)	122·5 (3)
		S——C(13)–C(5)	119·8 (2)
		S——C(13)–C(14)	117·3 (2)
		C(5)—C(13)–C(14)	122·9 (3)
		C(8)—C(14)–C(9)	121·9 (3)
		C(8)—C(14)–C(13)	117·2 (3)
		C(9)—C(14)–C(13)	120·9 (2)

Table 3. *Least-squares planes and 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*)	0·9149	−0·3930	−0·0924	1·8579
(*b*)	0·9218	−0·3765	−0·0921	1·9399
(*c*)	0·5106	−0·3953	−0·7636	0·4874
(*d*)	0·5141	−0·3920	−0·7629	0·4996
(*e*)	0·7712	−0·4514	−0·4490	0·6504

Displacements in Å from the least-squares planes

Benzene ring

	(*a*)	(*b*)		(*c*)	(*d*)
C(1)	0·004	0·025	C(5)	−0·004	−0·009
C(2)	−0·003	0·014	C(6)	0·002	−0·003
C(3)	0·004	−0·002	C(7)	0·002	0·003
C(4)	−0·007	−0·032	C(8)	−0·005	0·002
C(11)	−0·006	−0·013	C(13)	0·003	0·010
C(12)	0·007	−0·002	C(14)	0·001	0·002
S	0·081*	0·038	S	0·004*	0·005
C(9)	−0·036*	−0·028	C(9)	−0·024*	−0·011

Central ring

	(*e*)
C(11)	0·005
C(12)	−0·005
C(13)	0·005
C(14)	−0·005
S	0·642*
C(9)	0·485*

* Atoms excluded from the calculation of the least-squares planes.

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