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Thioxanthone 10-Oxide

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Abstract. $C_{13}H_8O_2S$; orthorhombic, $Pca2_1$, $Z=4$; M.W. 228·27, $a=21·087$ (3), $b=4·753$ (1), $c=10·227$ (2) Å; $D_x=1·479$, $D_m=1·47$ g cm^{-3} (by flotation); λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 25·56 cm^{-1}. Final residual $R=0·040$.

Introduction. Single crystals of thioxanthone 10-oxide (I) were obtained in the form of transparent prisms through the courtesy of Dr Andrew L. Ternay of the Chemistry Department of the University of Texas at Arlington.

(I)
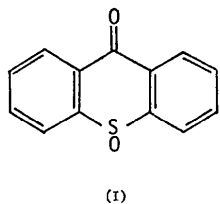
The unit-cell parameters were obtained by measuring '+' and '−' 2θ values of 15 reflections. The space group, $Pca2_1$ or $Pcam$, was deduced from systematic absences ($h0l$ absent with h odd and $0kl$ absent with l odd). The intensity data were collected on a Syntex $P\bar{1}$ automatic diffractometer at 3 °C with a crystal approximately $0·10 \times 0·20 \times 0·35$ mm. A $\theta/2\theta$ scanning mode with graphite-monochromated Cu $K\alpha$ radiation was used to measure 746 independent reflections with 2θ values below 116°, of which 721 were considered as observed by the criterion $I>2·0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors; no absorption corrections were applied.

The structure was determined by the heavy-atom method, and the correct space group was proved to be $Pca2_1$, as also shown by the noncentrosymmetric distribution of normalized structure factors. The ratios be-

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *except* $\times 10^3$ *for hydrogens*) *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 B values in Å^2 is:

$$-\tfrac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23}).$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	1356 (0)	1774 (2)	5000 (0)	2·78 (3)	3·01 (3)	2·91 (3)	0·07 (2)	−0·29 (3)	0·72 (4)
O(1)	1342 (1)	−1321 (6)	4720 (4)	3·76 (12)	2·73 (10)	5·73 (23)	−0·11 (9)	−0·23 (12)	−2·13 (14)
O(2)	1664 (1)	7932 (6)	8085 (4)	4·77 (14)	4·19 (14)	5·15 (17)	0·07 (12)	−0·35 (15)	−2·62 (13)
C(1)	516 (2)	5013 (8)	8258 (5)	4·05 (19)	3·22 (17)	3·45 (18)	0·32 (14)	0·50 (16)	−0·09 (16)
C(2)	−59 (2)	3630 (10)	8236 (5)	3·46 (17)	3·85 (19)	4·50 (24)	1·07 (16)	0·93 (18)	0·73 (19)
C(3)	−190 (2)	1648 (9)	7279 (6)	2·75 (17)	3·46 (19)	5·77 (28)	0·06 (14)	0·60 (18)	1·05 (20)
C(4)	254 (2)	1059 (9)	6325 (5)	3·24 (17)	3·34 (17)	4·40 (22)	0·05 (17)	−0·23 (19)	−0·23 (19)
C(5)	2621 (2)	1378 (7)	5166 (5)	2·72 (16)	3·49 (14)	3·84 (20)	−0·26 (13)	0·04 (16)	−1·15 (18)
C(6)	3221 (2)	2103 (9)	5615 (5)	2·89 (16)	4·00 (19)	4·67 (22)	0·34 (14)	0·44 (17)	−0·45 (20)
C(7)	3290 (2)	3981 (10)	6615 (5)	2·87 (16)	3·94 (18)	4·43 (22)	−0·69 (15)	−0·72 (18)	−0·04 (18)
C(8)	2769 (2)	5236 (8)	7181 (5)	3·41 (17)	3·08 (16)	3·59 (20)	−0·89 (13)	−0·52 (15)	−0·63 (16)
C(9)	1602 (2)	5819 (9)	7414 (4)	3·56 (17)	3·09 (15)	2·74 (17)	0·56 (15)	−0·29 (16)	−0·33 (15)
C(11)	982 (2)	4385 (7)	7318 (4)	2·87 (16)	2·24 (13)	2·95 (18)	0·64 (12)	−0·03 (15)	−0·02 (14)
C(12)	843 (2)	2429 (7)	6355 (4)	2·82 (14)	2·43 (14)	2·91 (16)	0·60 (13)	0·20 (13)	−0·11 (16)
C(13)	2099 (2)	2606 (8)	5755 (4)	2·50 (14)	2·31 (13)	2·32 (15)	−0·23 (12)	−0·14 (12)	−0·02 (15)
C(14)	2159 (2)	4544 (7)	6747 (4)	2·98 (14)	2·05 (14)	2·92 (17)	−0·05 (12)	−0·06 (14)	0·20 (14)

Table 1 (cont.)

	x	y	z	B
H(1)	62 (2)	650 (9)	885 (5)	5·4 (11)
H(2)	−33 (2)	403 (9)	888 (6)	4·1 (10)
H(3)	−61 (2)	100 (8)	722 (5)	4·2 (10)
H(4)	20 (2)	−34 (8)	561 (5)	4·3 (11)
H(5)	251 (3)	−26 (6)	439 (5)	5·4 (10)
H(6)	356 (2)	134 (11)	521 (7)	6·7 (12)
H(7)	372 (2)	448 (8)	687 (6)	3·5 (10)
H(8)	281 (2)	664 (8)	776 (5)	4·0 (10)

tween $\langle E \rangle$, $\langle E^2 \rangle$ and $\langle E^2 - 1 \rangle$ are 0·865, 0·980 and 0·751, respectively. The crystal belongs to space group $Pca2_1$ rather than $Pcam$, the molecule of thioxanthone 10-oxide is not situated in any special position although the molecule itself has a mirror-plane symmetry. The refinement was carried out by the full-matrix least-squares method with isotropic temperature factors and the block-diagonal least-squares method with anisotropic temperature factors. The z coordinate of the sulfur atom was held constant during the refinement. All the hydrogen atoms were located on a difference Fourier synthesis. The isotropic temperature factors were used for hydrogen atoms in the final refinements. 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 $(\sum ||F_o| - |F_c||/\sum |F_o|)$ was 0·040. The magnitude of $[\sum w(F_o - F_c)^2/(m-n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 1·35. The atomic scattering factors used for the sulfur, oxygen, and carbon atoms were those from *International Tables for X-ray Crystallography* (1962). For hydrogen, the values given by Stewart, Davidson & Simpson (1965) were used. The final positional and thermal parameters are given in Table 1.*
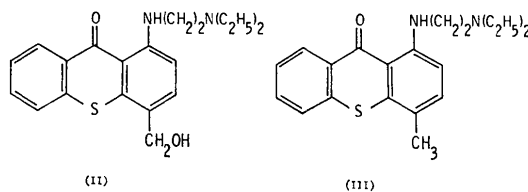
The crystal of thioxanthone 10-oxide belongs to a polar space group, and its polarity was determined by the refinement of atomic parameters with positive and negative z values for $+h+k+l$ data (Ibers & Hamilton, 1964). The refinement of the atomic parameters of the molecule reported in Table 1 gave an R value of 0·040, and the refinement for the atomic parameters with opposite z values gave an R value of 0·045. Therefore, the crystal with the reported atomic parameters

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31652 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(Table 1) has the correct polarity at the greater than 99·5% confidence level using Hamilton's (1965) R-value significance test.

The computer programs used in this analysis were the *ORFLS* program (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). All calculations were carried out on a CDC CYBER 72 computer in the Bradfield Computing Laboratory at the Southern Methodist University.

Discussion. The determination of this crystal structure is a continuation of studies on a series of thioxanthene derivatives, and this is the first study on a thioxanthone compound. Thioxanthone is the basic ring system for many pharmacological compounds; for example, hycanthone (II) and lucanthone (III) are used as antischistosomal agents, and their sulfoxides act as metab-

olite in the biological systems (Michaelis, Schindler & Signer, 1966). Therefore, the study of the conformation of thioxanthone 10-oxide will play an important role in understanding the effect of substituents on the conformation and configuration of the thioxanthone ring system.

A stereoscopic view of the configuration of a thioxanthone 10-oxide molecule is shown in Fig. 1 (Johnson, 1965). The identification of the atoms and the bond lengths and bond angles with their standard deviations are shown in Fig. 2. The S–O group is in 'boat equatorial' conformation, the same as in *cis*-9-methylthioxanthene 10-oxide (Jackobs & Sundaralingam, 1969) and *trans*-thioxanthen-9-ol 10-oxide (Ternay, Chasar & Sax, 1967) where the size of the C(9) substituent is also small.

The mean value of the two C–S bond lengths is $1·788 \pm 0·003$ Å, and the C–S–C bond angle is $99·0 \pm 0·2°$. The S–O bond length is $1·499 \pm 0·003$ Å, and the mean value of the two C–S–O bond angles is $108·2 \pm$
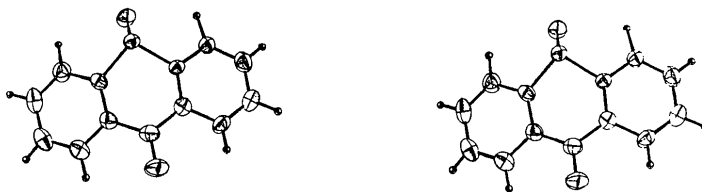

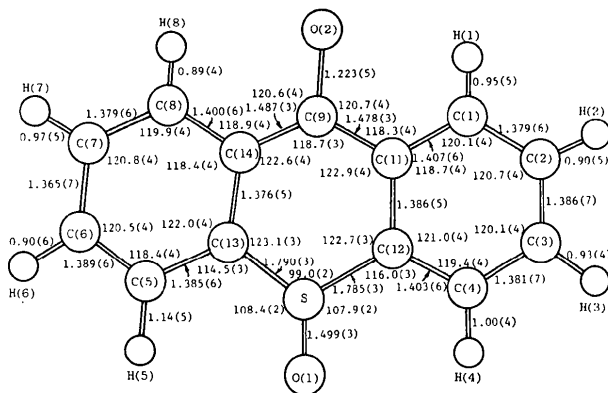Fig. 1. The stereoscopic drawing of one molecule of thioxanthone 10-oxide.

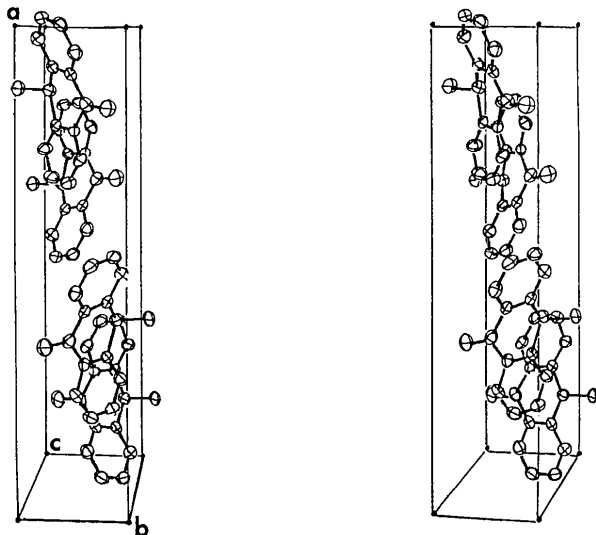Fig. 2. Bond lengths (Å) and bond angles (°) of thioxanthone 10-oxide with e.s.d.'s in parentheses.

Fig. 3. The stereoscopic drawing of molecular packing of thioxanthone 10-oxide, excluding hydrogen atoms, in the unit cell.

0·2°. Except for the significantly larger C–S–C bond angle, these values are in good agreement with those found in the other thioxanthene sulfoxides (Chu, 1975).

The dihedral angle between the best planes of the two benzene rings is 155·7°. This is larger than thioxanthene derivatives with tetrahedrally bonded C(9) (Chu, 1975). The dihedral angles are 141·6 and 152° for α-chlorprothixene (Post, Kennard & Horn, 1974) and α-flupenthixol (Post, Kennard, Sheldrick & Horn, 1975), respectively. C(9) is sp^2 hybridized in these two compounds as in thioxanthone 10-oxide. Therefore, the magnitude of the dihedral angle depends on the nature of the substituents.

The packing of the molecules in the crystal is shown

in the stereoscopic drawing in Fig. 3. With the exception of the 3·08 Å separation between O(2) and C(5) $(\frac{1}{2}-x, 1+y, \frac{1}{2}+z)$, there are no other intermolecular contacts less than van der Waals distances. This contact is common for structures involving carbonyl oxygen and benzene ring carbon atoms (Chu, Jeffrey & Sakurai, 1962; Meresse, Courseille & Chanh, 1974).

The rigid-body thermal analysis of the 16 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 0·0036 Å². A comparison of this value with the mean $\sigma(U_{ij})$ value of 0·0021 Å², calculated from the estimated standard deviation of the β_{ij} of the least-squares refinement, indicates that the rigid-body model is moderately satisfactory.

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