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Structure of 4-Methyl-9-oxothioxanthene 10,10-Dioxide

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Abstract. $C_{14}H_{10}O_3S$, $M_r = 258.28$, orthorhombic, space group $Pnma$, $a = 14.384$ (12), $b = 6.882$ (3), $c = 11.705$ (1) Å, $V = 1158.7$ Å^3, $Z = 4$, $D_c = 1.48$, $D_o = 1.48$ Mg m^{-3}, $R = 0.058$ for 776 reflections with $F_o > 4\sigma(F_o)$. The thioxanthen-9-one ring is strictly planar.

Introduction. Unusual long-range coupling patterns are observed in the ^{1}H NMR spectra of methylthioxanthen-9-ones and their S,S-dioxides (Doyle, 1978). In order to try to explain this behaviour, the structures of several of these compounds are being determined. The planarity of the whole ring system is of special interest since deviations from planarity will affect the delocalization of electron density, which in turn should affect the NMR coupling constants.

Pale cream-coloured crystals were grown from warm glacial acetic acid. A single crystal $0.2 \times 0.2 \times 0.7$ mm was mounted parallel to the needle (b) axis. Weissenberg photographs showed the absence of $0kl$ reflections for $k + l$ odd and of $hk0$ reflections for h odd, consistent with space groups $Pn2_1a$ or $Pnma$. The cell dimensions were determined accurately by measurement of the high-angle axial reflections with Zr-filtered Mo $K\alpha$ radiation [$\lambda(\alpha_1) = 0.70926$ Å]. Data were collected on a manual Picker diffractometer by ω–2θ scans over a 2θ range of $2°$ at a rate of $2°$ min^{-1}. 10 s backgrounds were counted at each end of the scan range. A standard reflection was measured after every 25–50 reflections and did not vary greatly during data collection. The reflection intensities were corrected for background and converted to structure factors by applying Lorentz and polarization corrections. No correction was made for absorption ($\mu = 0.274$ mm^{-1}).

The structure was solved in space group $Pnma$ by the heavy-atom method, and subjected to full-matrix least-squares refinement with the $SHELX$ set of programs (Sheldrick, 1976). The S, carbonyl O, and all

C atoms were required to lie on crystallographic mirror planes at $y = 0.25$ and 0.75, with occupancy factors of 0.5. Scattering factors for neutral C, H, O, and S were taken from *International Tables for X-ray Crystallography* (1974). The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - |F_c|$, $w = [\sigma^2(F_o) + 0.0049|F_o|^2]^{-1}$, and $\sigma(F_o)$ is the standard deviation based on counting statistics. All non-H atoms were given anisotropic temperature factors. The ring H-atom positions were calculated ($r_{C-H} = 1.080$ Å). One of the methyl H atoms appeared on the mirror plane on a difference map, thus fixing the orientation of the methyl group. The ring H atoms were assigned an isotropic temperature factor U of 0.08 Å^2; the methyl H atoms were given $U = 0.12$ Å^2.

A total of 1105 unique reflections with $2\theta < 50°$ were collected, of which 776 had $F_o > 4\sigma(F_o)$ and were classified as observed. The weighted residual, $R_w =$

Table 1. *Atomic parameters for 4-methyl-9-oxothioxanthene 10,10-dioxide*

E.s.d.'s are in parentheses. $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq} (Å^2)
S	0.1906 (1)	0.2500	0.3968 (1)	0.0470 (5)
O(1)	−0.1154 (3)	0.2500	0.3908 (4)	0.088 (2)
O(2)	0.2425 (2)	0.0726 (5)	0.3952 (3)	0.068 (1)
C(1)	0.1177 (4)	0.2500	0.2753 (5)	0.046 (2)
C(2)	0.1630 (5)	0.2500	0.1711 (6)	0.062 (3)
C(3)	0.1123 (6)	0.2500	0.0723 (6)	0.079 (3)
C(4)	0.0166 (6)	0.2500	0.0761 (6)	0.083 (4)
C(5)	−0.0291 (5)	0.2500	0.1795 (7)	0.069 (3)
C(6)	0.0208 (4)	0.2500	0.2824 (5)	0.047 (2)
C(7)	−0.0306 (4)	0.2500	0.3919 (6)	0.055 (2)
C(8)	0.0183 (4)	0.2500	0.5038 (5)	0.050 (2)
C(9)	−0.0367 (5)	0.2500	0.6016 (6)	0.061 (2)
C(10)	0.0039 (6)	0.2500	0.7090 (6)	0.069 (4)
C(11)	0.0996 (5)	0.2500	0.7180 (5)	0.063 (3)
C(12)	0.1565 (5)	0.2500	0.6261 (5)	0.054 (2)
C(13)	0.2619 (5)	0.2500	0.6444 (6)	0.066 (3)
C(14)	0.1164 (4)	0.2500	0.5168 (5)	0.044 (2)

$(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$, was 0·062 for the observed reflections. The largest peak on the final difference map was about $\frac{1}{3}$ e Å^{-3}, located near the methyl group. No other significant features were observed.

Table 2. *Distances* (Å) *and angles* (°) *in* 4-*methyl-9-oxothioxanthene* 10,10-*dioxide*

|			
S–O(2)	1·431 (4)	C(7)–C(8)	1·486 (9)
S–C(1)	1·768 (6)	C(8)–C(9)	1·392 (9)
C(1)–C(2)	1·383 (9)	C(9)–C(10)	1·386 (11)
C(2)–C(3)	1·368 (11)	C(10)–C(11)	1·381 (11)
C(3)–C(4)	1·378 (12)	C(11)–C(12)	1·351 (9)
C(4)–C(5)	1·378 (12)	C(12)–C(13)	1·531 (10)
C(5)–C(6)	1·403 (10)	C(12)–C(14)	1·403 (9)
C(6)–C(1)	1·395 (8)	C(14)–C(8)	1·419 (8)
C(6)–C(7)	1·480 (9)	C(14)–S	1·765 (6)
C(7)–O(1)	1·220 (8)		
C(1)–C(2)–C(3)	119·6 (7)	S–C(14)–C(12)	118·5 (5)
C(2)–C(3)–C(4)	120·4 (7)	C(8)–C(14)–C(12)	120·4 (6)
C(3)–C(4)–C(5)	120·3 (7)	C(14)–C(8)–C(7)	124·4 (6)
C(4)–C(5)–C(6)	120·7 (7)	C(14)–C(8)–C(9)	118·5 (6)
C(5)–C(6)–C(1)	117·4 (6)	C(7)–C(8)–C(9)	117·1 (6)
C(5)–C(6)–C(7)	119·2 (6)	C(8)–C(7)–C(6)	121·8 (5)
C(7)–C(6)–C(1)	123·4 (6)	C(8)–C(7)–O(1)	118·8 (6)
C(6)–C(1)–C(2)	121·6 (6)	C(6)–C(7)–O(1)	119·4 (6)
C(6)–C(1)–S	123·0 (5)	C(8)–C(9)–C(10)	120·5 (7)
C(2)–C(1)–S	115·4 (5)	C(9)–C(10)–C(11)	119·2 (7)
C(1)–S–C(14)	106·4 (3)	C(10)–C(11)–C(12)	122·9 (7)
C(1)–S–O(2)	107·4 (2)	C(11)–C(12)–C(14)	118·5 (6)
O(2)–S–O(2)'	117·1 (3)	C(11)–C(12)–C(13)	119·2 (6)
O(2)–S–C(14)	109·0 (2)	C(13)–C(12)–C(14)	122·3 (6)
S–C(14)–C(8)	121·1 (5)		
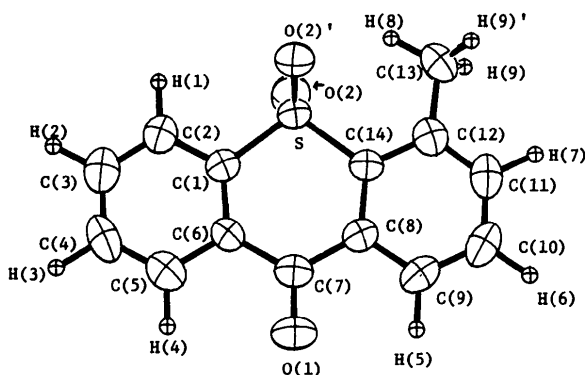
Fig. 1. *ORTEP* plot (Johnson, 1976) and numbering scheme for 4-methyl-9-oxothioxanthene 10,10-dioxide. The superscript indicates atoms related to the starting atoms by reflection through the mirror plane at $y = 0·25$.
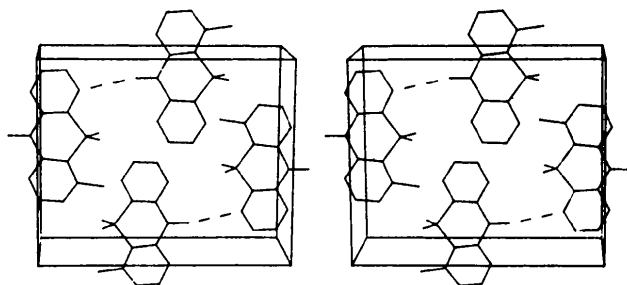

Fig. 2. Unit-cell contents of 4-methyl-9-oxothioxanthene 10,10-dioxide. The a axis is horizontal, the c axis vertical in this view.

The atomic positional parameters are presented in Table 1, and the numbering scheme is shown in Fig. 1. Bond distances and angles are reported in Table 2. The molecular packing is displayed in Fig. 2.*

Discussion. The thioxanthen-9-one ring system in the title compound is strictly planar, as all of the ring atoms are required to lie on crystallographic mirror planes. The thioxanthen-9-one system is also planar in 2-chlorothioxanthen-9-one (Chu & Yang, 1976) and in Miracil D (Neidle, 1976), but is folded about the S···C=O line in 9-oxothioxanthene 10-oxide (Chu, 1976) and hycanthone methanesulphonate (Wei & Einstein, 1978). Miracil D and hycanthone methanesulphonate both contain the thioxanthen-9-one moiety (as opposed to a 9-oxothioxanthene 10-oxide or 9-oxothioxanthene 10,10-dioxide), so planarity or lack of it in the ring system appears to be a subtle function of the substituents.

The bond angles and distances are comparable to those observed in the three thioxanthen-9-one structures and one 9-oxothioxanthene 10-oxide structure which have been determined (Chu & Yang, 1976; Chu, 1976; Neidle, 1976; Wei & Einstein, 1978). The average C–S distance and the C–S–C angle in 4-methyl-9-oxothioxanthene 10,10-dioxide are 1·767 (2) Å and 106·4°, respectively, thus lying in the range of 1·688–1·788 Å and 99·0–106·6° observed in the compounds just cited. The S–O(2) distance in 4-methyl-9-oxothioxanthene 10,10-dioxide, 1·431 (4) Å, is somewhat shorter than the S–O distance in 9-oxothioxanthene 10-oxide [1·499 (3) Å; Chu, 1976], but is typical for sulphones (*e.g.* Sime & Goodgame, 1974).

There is a short contact between the carbonyl O(1) atom and H(1^{ii}), where the superscript refers to the atom at $(0·5 + x, 0·5 - y, 0·5 - z)$. The O(1)···H(1^{ii}) and O(1)···C(2^{ii}) distances are 2·22 and 3·269 Å, respectively, and the C(2^{ii})–H(1^{ii})···O(1) angle is 163°. These parameters are in agreement with those reported by Hamilton & Ibers (1968) for C–H···O hydrogen bonds. These weak hydrogen bonds link the molecules in chains. There are no other short C–H contacts to either O(1) or O(2). The overall packing arrangement is a layered one (Fig. 2), but the ring systems in one layer do not stack above the ring systems in an adjoining layer.

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α,α'-Dimethyl-α,α'-azinodi-p-cresol Monohydrate

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Abstract. $C_{16}H_{16}N_2O_2 \cdot H_2O$, $M_r = 286 \cdot 33$, monoclinic, $P2_1/c$, $a = 15 \cdot 871$ (4), $b = 8 \cdot 300$ (2), $c = 11 \cdot 496$ (4) Å, $\beta = 94 \cdot 42$ (3)°, $U = 1509 \cdot 9$ (7) Å^3, $Z = 4$, $D_c = 1 \cdot 260$ Mg m^{-3}, final $R = 0 \cdot 068$ for 1088 observed reflexions. Mo $K\alpha$ radiation ($\lambda = 0 \cdot 71069$ Å). A torsional angle of 148 (1)° through the azine chain makes the molecule non-planar. No face-to-face close-packing of molecules occurs. The molecules are held together through hydrogen bonds of types O–H⋯O and O–H⋯N, involving a nitrogen atom of the azine chain, both molecular hydroxy groups and the water molecule.

Introduction. This analysis has been performed in connection with studies on nitrogen-containing aromatic compounds (Fayos, Martínez-Ripoll, García-Mina, Gonzalez-Martínez & Arrese, 1980; Meléndez & Serrano, 1982). The aim was to determine the dependence of structural features of these compounds, like molecular planarity and crystal packing, on solid-state properties such as thermochromism and photochromism.

A pale yellow prismatic single crystal was used to collect the intensities of 2041 independent reflexions up to $\theta = 26°$ using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0 \cdot 71069$ Å) on a four-circle automatic diffractometer. The data collection process used a rather fast $\omega/2\theta$ scan, as an intensity decay of ~ 40% was observed after 30 h of experiment. After Lorentz–polarization and intensity-decay corrections, 1088 reflexions were tagged as observed with $I > 3\sigma(I)$.

The structure was solved by *MULTAN* (Main *et al.,* 1980) and successive Fourier syntheses. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). H atoms were located on a difference map calculated with those reflexions with sin $\theta/\lambda < 0 \cdot 5$ Å^{-1}. Refinement was performed by least-squares analysis using anisotropic thermal coefficients for non-H atoms and an isotropic fixed contribution for H atoms. A weighting scheme was chosen to obtain flat dependence of $\langle w\Delta^2 F \rangle$ *vs* $\langle F_o \rangle$ and *vs* $\langle \sin \theta/\lambda \rangle$ (Martínez-Ripoll & Cano, 1975). Final disagreement indices are $R = 0 \cdot 068$ and $R_w = 0 \cdot 087$. Table 1 shows the final atomic parameters.*