and may explain the stability of crystals of urocanic acid dihydrate when exposed to ultraviolet irradiation.

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9-Isopropylxanthene

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Abstract. $C_{16}H_{16}O$, orthorhombic, $Pca2_1$, $Z = 4$, $M_r = 224.30$, $a = 16.389$ (2), $b = 5.789$ (1), $c = 13.005$ (4) Å, $D_x = 1.207$, $D_m = 1.22$ g cm^{-3} (by flotation); λ(Mo $K\alpha$) $= 0.7107$ Å, μ(Mo $K\alpha$) $= 0.786$ cm^{-1}; final $R = 0.065$. The isopropyl substituent is in the boat–axial conformation.

Introduction. Samples of 9-isopropylxanthene (I) were obtained through the courtesy of Dr Andrew L. Ternay Jr of the Chemistry Department of the University of Texas at Arlington. Single crystals in the form of clear prisms were grown from an ethanol solution. The unit-cell parameters were obtained by measuring the 2θ values of 10 reflections. The space group, $Pca2_1$ or $Pcam$, was deduced from systematic absences ($0kl$ absent with l odd and $h0l$ absent with h odd). The intensity data were collected on a Picker FACS-1 automatic diffractometer at the Lyndon B. Johnson Space Center, NASA, Houston, Texas, with a crystal approximately $0.37 \times 0.75 \times 0.37$ mm. A $\theta/2\theta$ scanning mode, with graphite-monochromated Mo $K\alpha$ radiation, was used to measure 1145 independent reflections with 2θ values below 50°; of these, 699 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.

(I)   (II)
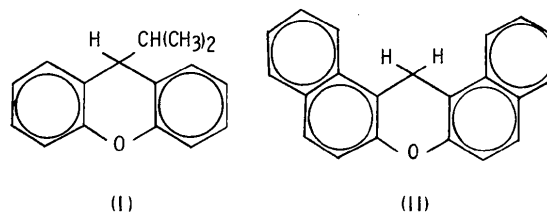
The structure was determined by the application of direct methods with the weighted multisolution tangent-refinement technique (Germain, Main & Woolfson, 1971). The correct space group was shown to be $Pca2_1$, as was also shown by the noncentrosymmetric distribution of normalized structure factors. The ratios between $\langle E \rangle$, $\langle E^2 \rangle$, and $\langle E^2 - 1 \rangle$ are 0.872, 1.010, and 0.810 respectively. The E map calculated from 132 reflections with $|E| \geq 1.5$ showed the positions of all non-hydrogen atoms. The refinement was carried out by the full-matrix least-squares method with isotropic temperature factors, and by the block-diagonal least-squares method with anisotropic temperature factors. The z coordinate of the O atom was held constant during the refinement. Only four of the H positions were located on a difference Fourier synthesis and the rest were calculated with reasonable bond lengths and bond angles with respect to the atoms to which they are bonded. In the final refinements, the positional parameters of the H atoms were refined, but their

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *except* $\times 10^3$ *for* H)

The estimated standard deviations are given in parentheses and refer to the last positions of respective values.

	x	y	z
O	2343 (2)	31 (7)	5000 (0)
C(1)	1193 (3)	932 (11)	6032 (5)
C(2)	574 (3)	2347 (11)	6290 (5)
C(3)	459 (3)	4423 (11)	5751 (5)
C(4)	959 (3)	5003 (11)	4986 (5)
C(5)	3668 (3)	3636 (10)	3389 (4)
C(6)	4356 (3)	2393 (11)	3446 (5)
C(7)	4375 (3)	355 (12)	4005 (5)
C(8)	3695 (3)	−388 (10)	4509 (5)
C(9)	2125 (3)	4141 (8)	3766 (4)
C(11)	1719 (3)	1505 (10)	5214 (4)
C(12)	1600 (3)	3594 (10)	4668 (4)
C(13)	2931 (3)	2923 (8)	3872 (4)
C(14)	2983 (3)	890 (10)	4445 (5)
C(15)	1670 (3)	3638 (9)	2747 (4)
C(16)	1581 (4)	973 (10)	2584 (5)
C(17)	2099 (4)	4711 (12)	1821 (5)
H(1)	125 (2)	−50 (8)	638 (4)
H(2)	26 (3)	199 (8)	684 (4)
H(3)	1 (3)	530 (8)	592 (4)
H(4)	87 (3)	643 (9)	466 (4)
H(5)	371 (3)	505 (8)	302 (4)
H(6)	482 (2)	289 (8)	306 (4)
H(7)	489 (3)	−50 (9)	406 (4)
H(8)	372 (3)	−182 (9)	495 (4)
H(9)	226 (2)	594 (7)	384 (4)
H(15)	110 (3)	445 (7)	276 (4)
H(16)1	122 (3)	37 (8)	323 (4)
H(16)2	215 (3)	23 (8)	255 (4)
H(16)3	125 (3)	71 (8)	187 (4)
H(17)1	212 (3)	650 (9)	184 (4)
H(17)2	192 (3)	421 (10)	119 (4)
H(17)3	272 (3)	431 (9)	188 (4)

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 $1/w = (0\cdot49 - 0\cdot045|F_o| + 0\cdot0041|F_o|^2)$. The unobserved reflections, as well as five low-order strong reflections showing extinction effects, were given a zero weight in the least-squares refinement and were excluded from the calculations of the R value. The quantity $\Sigma w(||F_o| - |F_c||)^2$ was mimimized. The final R index $(\Sigma||F_o| - |F_c||/\Sigma |F_o|)$ was 0·065.* The magnitude of $[\Sigma w(F_o - F_c)^2/(m - n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 0·84. There was no residual electron density above 0·28 e Å^{-3}. The atomic scattering factors used for O and C atoms were those from *International Tables for X-ray Crystallography* (1962). For H, the values given by Stewart, Davidson & Simpson (1965) were used. The final positional parameters are given in Table 1.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32546 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The computer programs used in this analysis were *ORFLS* (Busing, Martin & Levy, 1962); a block-diagonal least-squares program (Shiono, 1971); the Zalkin Fourier synthesis program modified by Dr R. Shiono of the University of Pittsburgh; *MULTAN* (Germain, Main & Woolfson, 1971); 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 Southern Methodist University.

Discussion. This determination of the crystal structure of 9-isopropylxanthene (one of the tricyclic compounds currently under study in this laboratory) is a continuation of a series of studies on the effect of different substituents on the configuration and conformation of the tricyclic ring system. The conformation of 9-isopropylxanthene and the packing of the molecules in the crystal are shown in the stereoscopic drawing (Fig. 1). The identification of the atoms, and the bond lengths and bond angles with their standard deviations are shown in Fig. 2. The mean value of the two C—O bond lengths is $1\cdot364 \pm 0\cdot007$ Å, and the C—O—C bond angle is $117\cdot2 \pm 0\cdot4°$. However, the two C—O bond lengths are significantly different [$1\cdot347$ (5) and $1\cdot422$ (5) Å] in 14-dibenzo[*aj*]xanthene [(II), Andreetti, Bocelli & Sgarabotto, 1974]. The C—H bond lengths range from 0·91 to 1·08 Å (mean 1·00 Å) with a r.m.s. standard deviation of 0·05 Å. The C—C—H bond angles involving benzene rings range from 116 to 122° (mean 120°), and the C—C—H and H—C—H bond angles involving tetrahedral C atoms range from 101 to 116° (mean 109°). The r.m.s. standard deviation of these bond angles is 3°. There are no intermolecular contacts less than van der Waals distances. The closest intermolecular distance is 3·59 Å between C(11) and C(17).

The folding angle between the best planes of the two benzene rings in 9-isopropylxanthene is 158·1°, which is larger than that in similar thioxanthene derivatives (Chu, 1975) and the corresponding phenothiazine derivative (Chu & van der Helm, 1976). The molecule of dibenzoxanthene is essentially planar, apparently because of the interaction between the dibenzo groups and the *meso* hydrogens.

The isopropyl substituent in 9-isopropylxanthene is in a boat–axial conformation, and the torsion angles of C(12)—C(9)—C(15)—C(16), C(13)—C(9)—C(15)—C(16), and C(13)—C(9)—C(15)—C(17) about the C(9)—C(15) bond are 71·4, 53·2, and 69·3° respectively. The conformation of this isopropyl substituent is similar to that in *N*-isopropylphenothiazine (Chu & van der Helm, 1976); however, it is different from that in 9-isopropylthioxanthene 10-oxide (Chu, 1975) in which the isopropyl substituent is symmetrical with respect to a plane passing through the *meso* atoms of the central ring. It is apparent that the conformation of the isopropyl substituent in 9-isopropylxanthene and *N*-
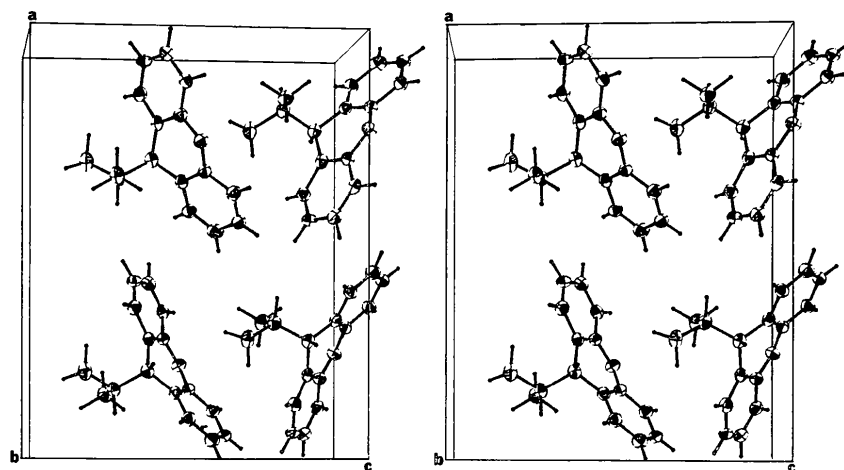
Fig. 1. A stereoscopic drawing of the molecular packing of 9-isopropylxanthene in the unit cell (*ORTEP*, Johnson, 1965).
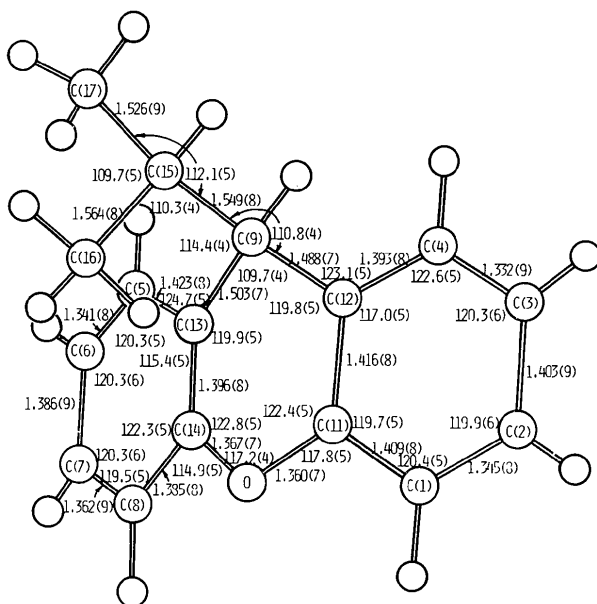

Fig. 2. Bond lengths (Å) and bond angles (°) of 9-isopropyl-xanthene with e.s.d.'s in parentheses.

isopropylphenothiazine is preferable, and the different conformation in 9-isopropylthioxanthene 10-oxide is a result of the interactions between the 9-isopropyl group and the sulfinyl oxygen, both being in the boat–axial conformation.

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