$C_{16}H_{24}BrNO_3$

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# 9-*tert*-Butylthioxanthene

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Abstract. $C_{17}H_{18}S$, orthorhombic, $Pmn2_1$, $Z = 2$, $M_r = 254.39$, $a = 16.096$ (2), $b = 6.002$ (1), $c = 7.133$ (1) Å, $V = 689.17$ (20) Å^3, $D_x = 1.226$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, μ(Cu $K\alpha$) = 18.33 cm^{-1}. Final residual $R = 0.045$. The *tert*-butyl group is in a boat-axial conformation with respect to the central thioxanthene ring.

Introduction. 9-*tert*-Butylthioxanthene is one of a series of thioxanthene derivatives whose crystal structures have been studied in this laboratory. The crystal structure of 9-isobutylthioxanthene (Chu, 1973) has already been determined. This work will determine the effect of a more bulky *meso* substituent, a *tert*-butyl group, on the stereochemistry of the thioxanthene ring system.

Single crystals of 9-*tert*-butylthioxanthene (I) were obtained through the courtesy of Dr Andrew L. Ternay Jr, of the Chemistry Department of the University of Texas at Arlington. The unit-cell parameters were obtained by measuring the 2θ values of 15 reflections. The space group, $Pmn2_1$, was deduced from systematic absences (*h0l* absent with $h + l$ odd). The intensity data were collected on a Syntex $P2_1$ automatic diffractometer with a crystal of approximately $0.16 \times 0.61 \times 0.32$ mm. A $\theta/2\theta$ scanning mode with graphite-monochromatized Cu $K\alpha$ radiation was used to measure 646 independent reflections with 2θ values below 130°, of which 636 reflections were considered observed by the criterion $I > 3.0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, and no absorption corrections were applied.


(I)
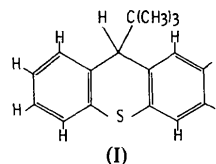
The structure was determined by the heavy-atom method. Since there are only two molecules in a unit cell with space group $Pmn2_1$, the molecule is situated at the special position with the two halves of the molecule related by a mirror plane. The refinement was carried out by the full-matrix least-squares method (Busing, Martin & Levy, 1962) with isotropic temperature factors and the block-diagonal least-squares method (Shiono, 1971) with anisotropic temperature factors. Some 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. The isotropic temperature factors were used for the H atoms in the refinement. The weight of a 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 index ($\sum ||F_o| - |F_c||/\sum |F_o|$) was 0.045.* The magnitude, $[\sum w(F_o - F_c)^2/(m - n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 0.80. The atomic scattering factors used for S and C atoms were those from *Inter-*

Table 1. *Fractional atomic coordinates* (× 10⁴) *for the non-hydrogen atoms and fractional coordinates* (× 10³) *and thermal parameters for hydrogen*

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

	x	y	z		x	y	z	B (Å²)
S	0 (0)	1565 (2)	0 (0)	H(1)	141 (2)	−520 (6)	182 (6)	3·5 (8)
C(1)	1461 (3)	−3748 (8)	1156 (7)	H(2)	268 (3)	−414 (9)	38 (10)	6·4 (15)
C(2)	2191 (3)	−3157 (9)	224 (10)	H(3)	272 (4)	−88 (13)	−173 (15)	10·1 (24)
C(3)	2249 (3)	−1118 (11)	−696 (9)	H(4)	160 (4)	193 (9)	−168 (10)	7·3 (15)
C(4)	1576 (3)	308 (9)	−732 (8)	H(9)	0 (0)	−484 (8)	245 (8)	3·1 (11)
C(9)	0 (0)	−2964 (9)	2245 (9)	H(16)1	54 (3)	103 (8)	413 (9)	6·3 (13)
C(11)	777 (2)	−2308 (7)	1212 (6)	H(16)2	0 (0)	106 (18)	609 (18)	13·0 (33)
C(12)	846 (2)	−293 (7)	209 (7)	H(17)1	136 (3)	−283 (8)	481 (9)	5·3 (12)
C(15)	0 (0)	−2259 (10)	4387 (9)	H(17)2	80 (4)	−341 (11)	663 (14)	11·4 (26)
C(16)	0 (0)	306 (10)	4617 (10)	H(17)3	83 (3)	−525 (10)	513 (11)	6·1 (17)
C(17)	771 (3)	−3219 (8)	5359 (7)					
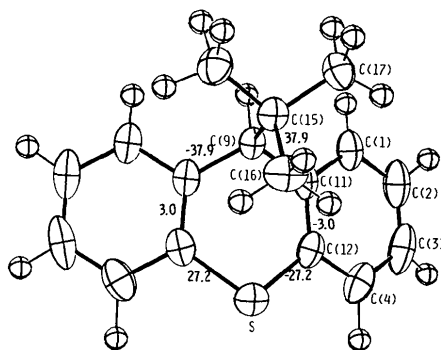
Fig. 1. *ORTEP* drawing (Johnson, 1965) of one molecule of 9-*tert*-butylthioxanthene with torsion angles around the central ring.
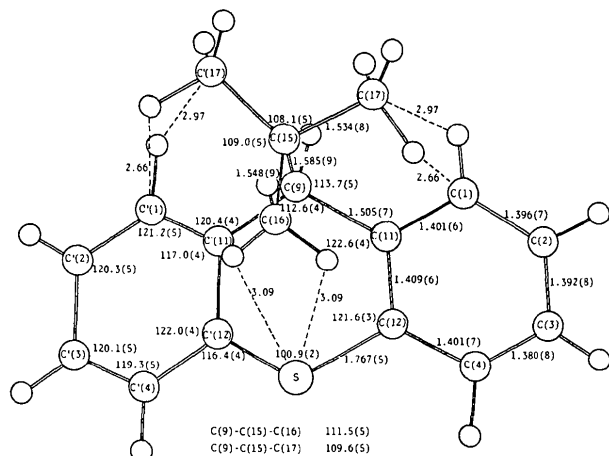
Fig. 2. Bond lengths (Å) and bond angles (°) of 9-*tert*-butyl-thioxanthene; e.s.d.'s are in parentheses. Dashed lines represent non-bonded intramolecular distances.

national 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.

Discussion. The identification of the atoms and the configuration of the molecule are shown in Fig. 1. The two halves of the molecule are related by a mirror plane as required by the space group. The bond lengths and bond angles with their standard deviations are shown in Fig. 2. The C—S bond length and C—S—C bond angle are 1·767 (5) Å and 100·9 (2)°, respectively; they are in good agreement with those determined in 9-isobutyl-thioxanthene (Chu, 1973) and other thioxanthene derivatives with a S coordination number of two (Chu, 1972; Chu & Mangion, 1975). The C(9)—C(15) bond length of 1·585 (9) Å is significantly longer than the C—C single-bond length, and this lengthening was also observed in 9-*tert*-butyl-9,10-dihydroanthracene (Brennan, Putkey & Sundaralingam, 1971). The lengthening of the C(9)—C(15) bond can be attributed to the non-bonded interaction between the *tert*-butyl group and the C atoms in *peri* positions and the lone-pair electrons of the S. The nonbonded distances (Fig. 2) are 2·66, 2·97, and 3·09 Å between C(1) and H(17)1, C(17) and H(1), and S and H(16)1 respectively.

The equation of the least-squares plane of the benzene ring is $0·3442x + 0·4360y + 0·8316z = 0·5266$ (where x,y,z are in Å) and the largest atomic displacement from the plane of the ring is 0·019 Å. The folding angle between the planes of the two mirror-related benzene rings is 139·7° which is similar to that found in 9-isobutylthioxanthene (Chu, 1973). The central ring is in an ideal boat conformation. This can be shown by the ring torsion angles given in Fig. 1, and by the Cremer & Pople (1975) puckering parameters, which are $q_2 = 0·504$, $q_3 = 0·002$, $Q = 0·504$ Å, $\varphi_2 = 180·0$, and $\theta = 89·75°$. The *tert*-butyl group is in a boat-axial conformation, and the torsion angles C(11)—C(9)—C(15)—C(16) and C(11)—C(9)—C(15)—C(17) are 65·2 and −55·5°, respectively. The packing of the molecules in the crystal is shown in Fig. 3. The closest intermolecular contact is 2·81 Å between S and H(16)2. There are no other intermolecular contacts less than the van der Waals distances.
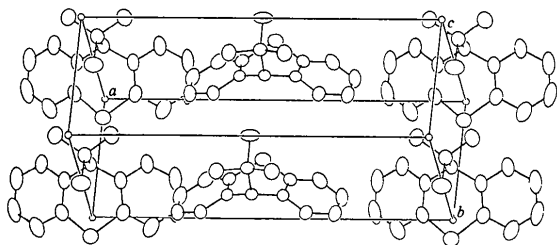
Fig. 3. The molecular packing of 9-*tert*-butylthioxanthene, excluding hydrogen atoms, in a unit cell.

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2,6-Naphthalenediacrylic Acid Bis(2,4-dichlorophenyl) Ester

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Abstract. $C_{28}H_{16}Cl_4O_4$, triclinic, $P\bar{1}$, $a = 5.897$ (2), $b = 8.799$ (4), $c = 12.784$ (4) Å, $\alpha = 69.42$ (3), $\beta = 97.14$ (3), $\gamma = 99.98$ (3)°, $Z = 1$, $D_x = 1.52$ g cm^{-3}. The distance between the double bonds in adjacent molecules is 3.76 Å.

Introduction. The title substance is of interest because it is known to polymerize in the solid state (Meyer & Wegner, 1978). This study was undertaken to assist investigation of the mechanism of this topochemical reaction. It was of special interest to know whether the molecular packing allows reaction of neighbouring molecules without large molecular motions.

Single crystals suitable for data collection were obtained by slow cooling (3° h⁻¹) of a solution in γ-butyrolactone. A crystal, 0.6 × 0.2 × 0.1 mm, was used for data collection on a Nonius automatic four-circle diffractometer with Mo Kα radiation. The θ–2θ scan mode was used. Of the 3241 accessible unique reflexions significant counts were recorded for 2974 (2θ < 60°). The structure was solved with *MULTAN*

(Declercq, Germain, Main & Woolfson, 1973). Refinement was by full-matrix least squares with unit weights. The coordinates of the H atoms were found in a
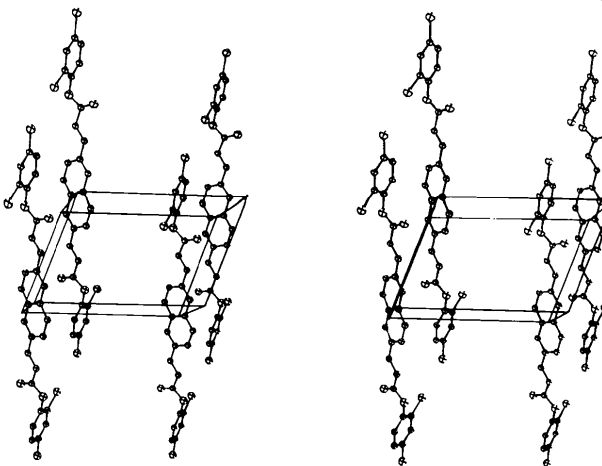

Fig. 1. Stereoscopic diagram of the packing arrangement (Johnson, 1965). The *c* axis is horizontal and *b* vertical.