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9-Methyl-9-isopropylthioxanthene

BY SHIRLEY S. C. CHU AND MARGARET MANGION

Institute of Technology, Southern Methodist University, Dallas, Texas 75275, U.S.A.

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Abstract. $C_{17}H_{18}S$, monoclinic, $P2_1/n$, $Z=8$, M.W. 254.4, $a=12.676(1)$, $b=18.839(1)$, $c=11.819(1)$ Å, $\beta=93.96(1)^\circ$, $D_x=1.20$, $D_m=1.21$ g cm $^{-3}$ (by flotation), $\lambda(\text{Cu } K\alpha)=1.5418$ Å, $\mu(\text{Cu } K\alpha)=17.92$ cm $^{-1}$. Final residual $R=0.049$.

Introduction. Samples of 9-methyl-9-isopropylthioxanthene were obtained through the courtesy of Dr A. 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 ethyl alcohol solution. The space group, $P2_1/n$, was deduced from systematic absences ($h0l$ absent with $h+l$ odd and $0k0$ absent with k odd). Three-dimensional X-ray diffraction data were collected on a Datex-Syntex automatic diffractometer in the Biophysics and Biochemistry Department of the Texas A & M University, College Station, Texas. A crystal approximately $0.45 \times 0.31 \times 0.30$ mm was mounted along the a axis. A $\theta/2\theta$ time variable scanning mode with Cu $K\alpha$ radiation was used to measure 2883 independent reflections with 2θ values below 100° , of which 2556 reflections were considered as observed. A reflection was considered as observed if its intensity was greater than $3\sigma(I)$, 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. There are two crystallographically independent molecules in one asymmetric unit of the crystal. The refinement was carried out by the full-matrix least-squares method with isotropic temperature factors and block-diagonal least-squares method with anisotropic temperature factors. All the hydrogen atoms were located on two successive difference Fourier syntheses. Their positional parameters were refined; however, their thermal parameters were assigned the same values as those of the atoms to which they are bonded. 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 index ($\sum |F_o| - |F_c| / \sum |F_o|$) was 0.049. 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 1.32. There were 21 low-order strong reflections, whose calculated structure amplitudes were much higher than the observed values owing

to extinction. The observed values of these reflections were substituted from the data collected with Mo $K\alpha$ radiation and were scaled with common standard reflections. The atomic scattering factors used for sulfur and carbon atoms were those from *International Tables for X-ray Crystallography* (1962) and for hydrogen, the values given by Stewart, Davidson & Simpson (1965). The final positional and thermal parameters are given in Table 1.*

The computer programs used in this analysis were *ORFLS* (Busing, Martin & Levy, 1962), a block-diagonal least-squares program (Shiono, 1971), and Zalkin's 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 Computing Laboratory at Southern Methodist University.

Discussion. The determination of this crystal structure is a continuation of studies on a series of thioxanthene derivatives. There are two crystallographically independent molecules in an asymmetric unit of the crystal. The configuration of the two independent molecules of 9-methyl-9-isopropylthioxanthene, (I) and (II), and the identification of the atoms are shown in the *ORTEP* (Johnson, 1965) drawing, Fig. 1, which also shows the bond lengths and bond angles with their standard deviations for the two molecules.

The mean value of the four C-S bond lengths is 1.763 ± 0.004 Å and the mean value of the two C-S-C bond angles is $100.3 \pm 0.2^\circ$. These values are in good agreement with those of other thioxanthene derivatives when the coordination number of the sulfur atom is two (Chu, 1975). The C-H bond lengths range from 0.86 to 1.09 Å with a mean value of 1.01 Å and a root-mean-square standard deviation of 0.03 Å. The C-C-H bond angles involving the benzene rings range from 112 to 128° with a mean value of 120° , and the C-C-H and H-C-H bond angles involving tetrahedral carbon atoms range from 98 to 121° with a mean value of 109° . The root-mean-square standard deviation of these bond angles is 2° .

* A table of calculated and observed structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31023 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The dihedral angles between the least-squares planes of the two benzene rings are 143.0 and 144.2° for molecules I and II, respectively. The 9-methyl substituent is in 'boat equatorial' conformation, and the 9-isopropyl substituent is in a 'boat axial' conformation. These

results are the same as those obtained by the n.m.r. spectroscopic study of the thioxanthene derivatives in solution (Evans & Ternay, 1974). Within experimental errors, the two independent molecules possess the same configuration and exhibit a 'pseudo' mirror plane

Table 1. Fractional atomic coordinates and thermal parameters (all $\times 10^4$)

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 β values is $-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

Molecule I	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	-2845 (1)	4037 (1)	765 (1)	80 (1)	39 (0)	52 (1)	7 (1)	12 (1)	6 (1)
C(1)	-3937 (3)	4928 (2)	3555 (3)	65 (3)	32 (1)	79 (4)	-6 (2)	-4 (3)	-8 (2)
C(2)	-4530 (3)	5478 (2)	3084 (4)	70 (3)	30 (2)	127 (5)	0 (2)	3 (3)	-19 (2)
C(3)	-4586 (3)	5596 (2)	1940 (4)	70 (3)	26 (1)	140 (5)	6 (2)	-4 (3)	-1 (2)
C(4)	-4064 (3)	5149 (2)	1265 (3)	62 (3)	34 (2)	86 (4)	-7 (2)	-9 (3)	15 (2)
C(5)	-2819 (3)	2617 (2)	883 (3)	90 (4)	40 (2)	84 (4)	4 (2)	11 (3)	-18 (2)
C(6)	-2775 (4)	1969 (2)	1414 (4)	99 (4)	29 (2)	152 (5)	4 (2)	16 (4)	-26 (2)
C(7)	-2734 (4)	1934 (2)	2558 (4)	94 (4)	28 (2)	150 (5)	5 (2)	11 (4)	12 (2)
C(8)	-2739 (3)	2545 (2)	3201 (3)	84 (4)	29 (1)	89 (4)	-1 (2)	4 (3)	6 (2)
C(9)	-2603 (3)	3899 (2)	3406 (3)	56 (3)	29 (1)	50 (3)	-3 (2)	-2 (2)	1 (2)
C(11)	-3353 (3)	4471 (2)	2900 (3)	48 (3)	25 (1)	64 (3)	-6 (2)	-1 (2)	-4 (2)
C(12)	-3453 (3)	4586 (2)	1734 (3)	49 (3)	24 (1)	68 (3)	-2 (2)	1 (2)	1 (2)
C(13)	-2795 (3)	3232 (2)	1524 (3)	59 (3)	31 (1)	70 (3)	3 (2)	4 (3)	-1 (2)
C(14)	-2737 (3)	3213 (2)	2715 (3)	50 (3)	27 (1)	66 (3)	2 (2)	2 (2)	2 (2)
C(15)	-2807 (3)	3768 (2)	4657 (3)	72 (3)	42 (2)	57 (3)	-4 (2)	-7 (3)	4 (2)
C(16)	-1426 (3)	4161 (2)	3327 (3)	55 (3)	37 (2)	78 (4)	-7 (2)	-7 (3)	3 (2)
C(17)	-1229 (3)	4888 (2)	3862 (5)	73 (4)	38 (2)	207 (7)	-14 (2)	-30 (4)	-3 (3)
C(18)	-605 (3)	3647 (2)	3803 (4)	60 (3)	49 (2)	98 (4)	5 (2)	-7 (3)	4 (2)
Molecule II									
S'	1236 (1)	2241 (1)	2533 (1)	56 (1)	34 (0)	91 (1)	-14 (0)	11 (1)	-3 (1)
C'(1)	4325 (3)	2073 (2)	2024 (3)	63 (3)	34 (2)	92 (4)	-2 (2)	1 (3)	-8 (2)
C'(2)	4501 (3)	1360 (2)	2230 (4)	83 (4)	37 (2)	109 (5)	5 (2)	-9 (3)	-12 (2)
C'(3)	3705 (4)	933 (2)	2561 (4)	113 (4)	26 (1)	105 (4)	8 (2)	-26 (3)	-9 (2)
C'(4)	2713 (3)	1216 (2)	2649 (3)	103 (4)	26 (1)	71 (4)	-12 (2)	-11 (3)	-5 (2)
C'(5)	229 (3)	3132 (3)	1037 (3)	61 (3)	62 (2)	75 (4)	-2 (2)	-3 (3)	-6 (2)
C'(6)	134 (4)	3686 (3)	301 (4)	83 (4)	78 (3)	83 (4)	25 (3)	-14 (3)	4 (3)
C'(7)	1020 (4)	4066 (3)	63 (4)	105 (4)	64 (2)	89 (4)	16 (3)	-7 (3)	23 (3)
C'(8)	1986 (3)	3889 (2)	578 (3)	79 (4)	46 (2)	86 (4)	4 (2)	3 (3)	12 (2)
C'(9)	3168 (3)	3185 (2)	2037 (3)	49 (3)	27 (1)	67 (3)	-7 (2)	6 (2)	1 (2)
C'(11)	3350 (3)	2387 (2)	2136 (3)	52 (3)	30 (1)	49 (3)	-5 (2)	0 (2)	-7 (2)
C'(12)	2537 (3)	1929 (2)	2426 (3)	64 (3)	30 (1)	52 (3)	-6 (2)	-1 (2)	-10 (2)
C'(13)	1213 (3)	2956 (2)	1567 (3)	64 (3)	35 (2)	58 (3)	-2 (2)	-2 (2)	-5 (2)
C'(14)	2123 (3)	3339 (2)	1366 (3)	59 (3)	33 (1)	58 (3)	-2 (2)	5 (2)	1 (2)
C'(15)	4091 (3)	3553 (2)	1475 (3)	66 (3)	38 (2)	106 (4)	-8 (2)	9 (3)	10 (2)
C'(16)	3106 (3)	3482 (2)	3279 (3)	63 (3)	25 (1)	78 (4)	-10 (2)	-4 (3)	-2 (2)
C'(17)	4093 (3)	3337 (2)	4033 (4)	87 (4)	40 (2)	98 (4)	-11 (2)	-25 (3)	-6 (2)
C'(18)	2802 (4)	4262 (2)	3323 (4)	129 (5)	28 (2)	129 (5)	2 (2)	-7 (4)	-17 (2)

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

Molecule I	x	y	z	Molecule II	x	y	z
H(1)	-385 (2)	483 (2)	434 (2)	H'(1)	493 (2)	237 (2)	182 (3)
H(2)	-497 (2)	576 (2)	355 (3)	H'(2)	525 (2)	118 (2)	228 (3)
H(3)	-502 (2)	597 (2)	154 (3)	H'(3)	387 (3)	43 (2)	267 (3)
H(4)	-416 (2)	517 (2)	47 (2)	H'(4)	211 (3)	90 (2)	278 (2)
H(5)	-286 (3)	267 (2)	5 (3)	H'(5)	-36 (2)	282 (2)	131 (3)
H(6)	-279 (3)	158 (2)	95 (3)	H'(6)	-59 (3)	380 (2)	-13 (3)
H(7)	-272 (3)	154 (2)	295 (3)	H'(7)	98 (3)	441 (2)	-54 (3)
H(8)	-266 (3)	251 (2)	393 (3)	H'(8)	259 (3)	416 (2)	45 (3)
H(15)1	-265 (2)	422 (2)	508 (2)	H'(15)1	477 (2)	346 (2)	197 (3)
H(15)2	-233 (2)	345 (2)	498 (2)	H'(15)2	397 (2)	410 (2)	140 (3)
H(15)3	-349 (2)	358 (2)	474 (2)	H'(15)3	410 (2)	337 (2)	66 (3)
H(16)	-133 (2)	420 (2)	254 (2)	H'(16)	249 (2)	323 (1)	353 (2)
H(17)1	-166 (3)	523 (2)	345 (3)	H'(17)1	441 (3)	281 (2)	400 (3)
H(17)2	-42 (3)	501 (2)	372 (3)	H'(17)2	402 (3)	347 (2)	483 (3)
H(17)3	-127 (3)	482 (2)	476 (3)	H'(17)3	462 (3)	359 (2)	387 (3)
H(18)1	12 (2)	380 (2)	373 (3)	H'(18)1	278 (3)	444 (2)	409 (3)
H(18)2	-69 (2)	311 (2)	346 (3)	H'(18)2	208 (3)	435 (2)	280 (3)
H(18)3	-58 (2)	363 (2)	458 (3)	H'(18)3	331 (3)	455 (2)	298 (3)

passing through S, C(9), C(15), and C(16). The packing of the molecules in the crystal, projected down the *c* axis, is shown in Fig. 2. There is no intermolecular distance less than the van der Waals interaction.

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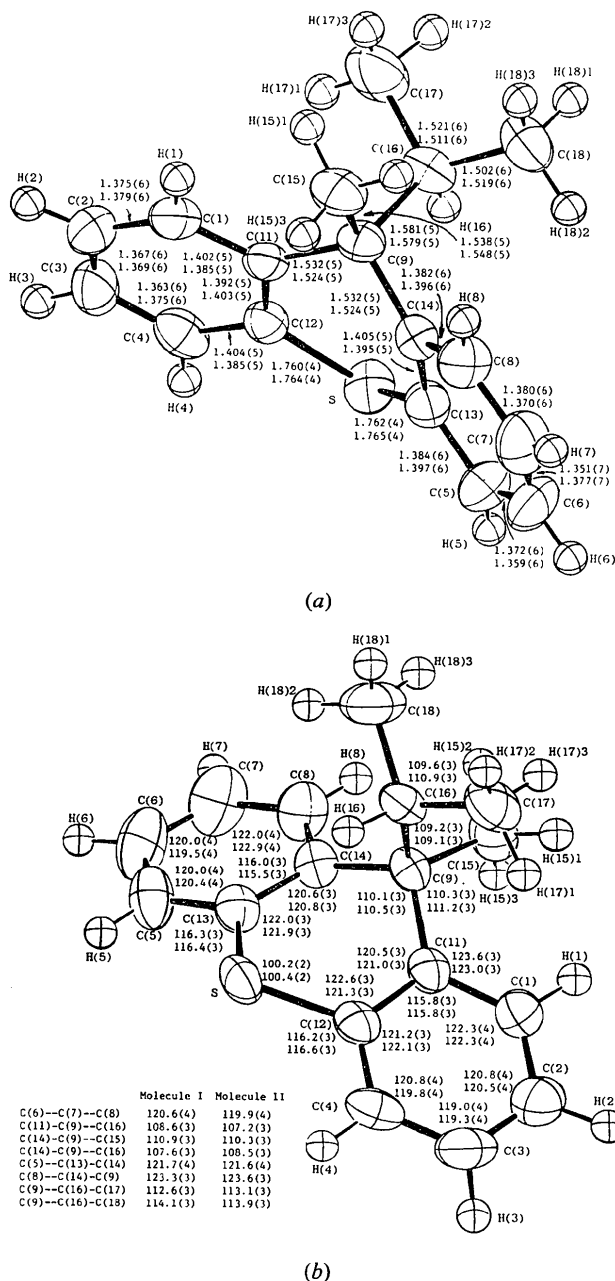


Fig. 1. The structure of the two independent molecules of 9-methyl-9-isopropylthioxanthene and their bond lengths (Å) and bond angles (°). Upper numbers refer to molecule I, lower to molecule II; e.s.d.'s in parentheses. (a) Configuration of molecule I with bond lengths. (b) Configuration of molecule II with bond angles.

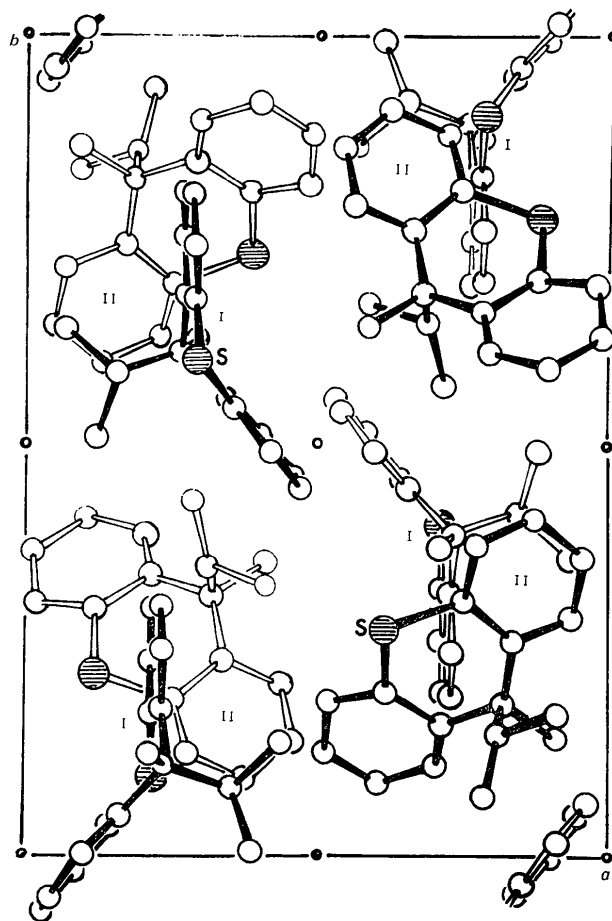


Fig. 2. The molecular packing diagram, excluding hydrogen atoms, viewed down the *c* axis of 9-methyl-9-isopropylthioxanthene.

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