Table 3. *Torsion angles* (°)

S–C(1)–C(2)–C(3)	−64·4 (3)	S–C(5)–C(6)–C(7)	−64·0 (3)
C(1)–C(2)–C(3)–C(4)	50·6 (3)	C(5)–C(6)–C(7)–C(8)	50·6 (3)
C(2)–C(3)–C(4)–C(5)	−46·2 (3)	C(6)–C(7)–C(8)–C(1)	−46·7 (3)
C(3)–C(4)–C(5)–S	56·8 (3)	C(7)–C(8)–C(1)–S	56·4 (3)
C(3)–C(4)–C(5)–C(6)	−64·9 (3)	C(7)–C(8)–C(1)–C(2)	−64·3 (3)
C(4)–C(5)–S–C(1)	63·1 (2)	C(8)–C(1)–S–C(5)	−61·9 (2)
C(4)–C(5)–S–O(1)	51·2 (2)	C(8)–C(1)–S–O(2)	53·3 (2)
C(4)–C(5)–S–O(2)	−178·2 (2)	C(8)–C(1)–S–O(1)	−176·1 (2)
C(5)–S–C(1)–C(2)	66·2 (2)	C(1)–S–C(5)–C(6)	65·5 (2)
O(1)–S–C(1)–C(2)	48·0 (2)	O(2)–S–C(5)–C(6)	−49·7 (2)
O(2)–S–C(1)–C(2)	−178·6 (2)	O(1)–S–C(5)–C(6)	179·7 (2)
Cl(1)–C(2)–C(1)–S	171·9 (1)	Cl(2)–C(6)–C(5)–S	173·3 (1)
Cl(1)–C(2)–C(1)–C(8)	−66·0 (3)	Cl(2)–C(6)–C(5)–C(4)	−64·1 (3)
Cl(1)–C(2)–C(3)–C(4)	174·0 (2)	Cl(2)–C(6)–C(7)–C(8)	172·4 (2)
C(8)–C(1)–C(2)–C(3)	57·7 (3)	C(4)–C(5)–C(6)–C(7)	58·6 (3)

C(8)—C(7) and S—C(5)—C(6)—C(7). Accordingly, the symmetry of the carbon framework is lowered from C_{2v} and approximates closely to C_2. Within the rings, the C—C—C angles at C(2) and C(6) are 115·8 (2) and 115·1 (2)° whereas those at C(4) and C(8) are slightly larger, 116·8 (2) and 117·0 (2)°. The angles at C(3) and C(7) are rather smaller, 113·3 (2) and 113·9 (2)°, and the S—C—C angles at C(1) and C(5) are substantially smaller, 105·9–108·7, mean 107·5°.

The C(3)···C(7) and H(3_2)···H(7_2) separations obtained from the final coordinates are 3·120 (4) and 1·96 (4) Å. However, the C(3)—H(3_2) and C(7)—H(7_2) lengths of 1·00 Å are shorter than the normal spectroscopic value for C(sp^3)—H bonds, a recognized artifact of the X-ray diffraction method, and when H(3_2) and H(7_2) are displaced along the C—H vectors to make these C—H distances 1·10 Å the H···H transannular distance becomes 1·85 Å. Some molecular-mechanics calculations estimate the H···H 3,7 separation in bicyclo[3.3.1]nonane to be greater than 2 Å and clearly exaggerate the transannular repulsion. The C(3)···C(7) separation reported here differs slightly from the value of 3·10 Å obtained for bicyclo[3.3.1]-nonane in an electron diffraction study (Osina, Mastryukov, Vilkov & Belikova, 1976).

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Structure of (+)-*cis*-9-(3-Dimethylaminopropyl)-10-methyl-2-(trifluoromethyl)-9,10-dihydroanthracene Methyliodide Benzene Solvate at 168 K

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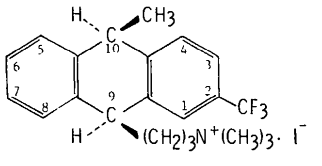
Abstract. $C_{21}H_{24}F_3N.CH_3I.C_6H_6$, orthorhombic, $P2_12_12_1$, $Z = 4$, $M_r = 567·49$, $a = 8·026$ (2), $b = 11·623$ (2), $c = 29·389$ (4) Å, $V = 2741·6$ (8) Å^3, $T = 168$ K, $D_x = 1·375$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 9·40 mm^{-1}, final $R = 0·047$ for 1621 observed reflections. Both the *meso* substituents are in the 'boat–axial' conformation with respect to the central ring of the dihydroanthracene ring system. The absolute configuration of the title molecule was determined by using the anomalous-scattering effect and is the same as that determined from room-temperature data.

Introduction. Single crystals of the methyliodide of *cis*-9-(3-dimethylaminopropyl)-10-methyl-2-(trifluoromethyl)-9,10-dihydroanthracene (I) (assigned as

0567-7408/81/101945-04$01.00

SKF-d-28175 by Smith Kline and French Laboratories) were obtained through the courtesy of Dr C. L. Zirkle of Smith Kline and French Laboratories.



(I)

The crystal structure of the hydrochloride of SKF-d-28175 was determined by X-ray diffraction (Chu & Chung, 1976). However, the absolute configuration of the molecule cannot be determined due to the presence of a pseudocentre of symmetry between the two crystallographically independent molecules. Since the different optical enantiomers show considerable difference in neuroleptic activity (Zirkle & Kaiser, 1979), the determination of the absolute configuration of the title compound is of interest in the understanding of the structure–activity relationship. The absolute configuration of SKF-d-28175 was determined with diffraction data obtained at room temperature from its methyliodide derivative which crystallizes in the form of its benzene solvate (Chu & Rosenstein, 1979). However, the agreement between the observed and calculated structure factors was relatively poor especially for several zones of high-order reflection. This was due apparently to the large thermal effect of the trifluoromethyl group. In this work, the crystal structure of the title compound was refined by using the intensity data collected at low temperature with the objectives of confirming the room-temperature structure and obtaining more accurate structural data. A Syntex LT-1 low-temperature device was used to maintain the crystal at 168 K. No evidence of phase transition was found by comparing the unit-cell parameters obtained at room temperature and at 168 K. The unit-cell parameters of the crystal at 168 K were determined from a least-squares analysis of 15 reflections with 2θ values ranging from 26 to 56°. The intensity data were measured with a crystal approximately 0·67 × 0·27 × 0·24 mm in size and with the a axis of the crystal oriented along the φ axis of the diffractometer. A $\theta/2\theta$ scanning mode with graphite-monochromated Cu $K\alpha$ radiation was used to measure 1649 independent reflections with 2θ values below 100° by maintaining the crystal at 168 K, from which 1621 reflections were considered as observed by the criterion $I > 3{\cdot}0\ \sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors; no absorption corrections were applied.

The refinement of the structure was carried out by the block-diagonal least-squares method (Shiono, 1971) from the non-H atomic parameters determined at room temperature (Chu & Rosenstein, 1979). Most of the H positions were located in 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. Isotropic temperature factors with $B = 3{\cdot}0$ Å^2 were used for the H atoms and were not refined. The weight of the reflection was assigned as $1/[\sigma(F)]^2$, where $\sigma(F)$ was calculated according to the relation $\sigma(F) = \sigma(I).(\mathrm{Lp})^{-1/2}|F_o|$. The quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. The final R index $(\sum||F_o| - |F_c||/\sum|F_o|)$ was 0·047, and the weighted disagreement index, R_w, was 0·052. The magnitude $[\sum w(F_o - F_c)^2/(m - n)]^{1/2}$ was approximately equal to 1·0. The atomic scattering factors used for C, N, F, and I 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.* The absolute configuration of the molecule determined at room temperature (Chu & Rosenstein, 1979) was confirmed in this work by refining the parameters with the application of anomalous-scattering factors for I. The refinement converged at $R = 0{\cdot}047$ for the configuration shown in Fig. 1 and at $R = 0{\cdot}077$ for its mirror-related structure.

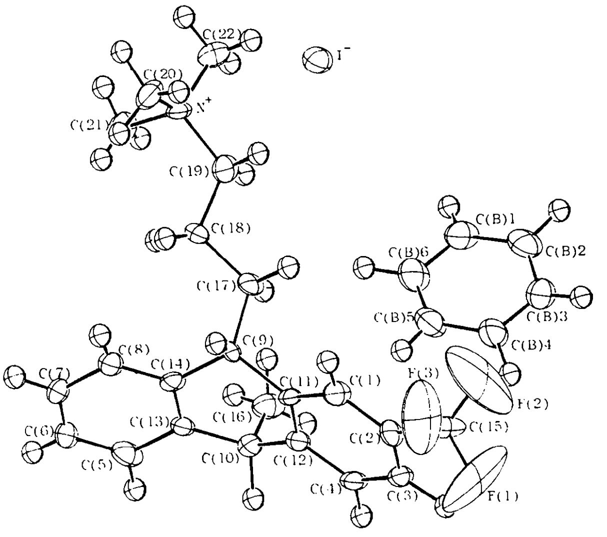


Fig. 1. *ORTEP* drawing (Johnson, 1965) of one molecule of the title compound.

Discussion. The absolute configuration of the molecule and the identification of the atoms are shown in Fig. 1. Even at 168 K the trifluoromethyl group still showed

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* Lists of structure factors, anisotropic thermal parameters, and the bond lengths and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36071 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$ *for non*-H, $\times 10^3$ *for* H) *and thermal parameters for non*-H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
I	8012 (1)	3487 (1)	2266 (1)	4·0 (1)
F(1)	6041 (24)	3649 (8)	5327 (4)	18·2 (10)
F(2)	5520 (24)	3166 (7)	4680 (5)	17·8 (11)
F(3)	7748 (15)	3625 (8)	4864 (4)	11·4 (7)
N	6612 (13)	7136 (7)	2154 (2)	3·1 (4)
C(1)	6623 (15)	5626 (9)	4435 (3)	3·0 (5)
C(2)	5799 (17)	5121 (8)	4792 (3)	3·3 (5)
C(3)	4585 (16)	5687 (9)	5038 (3)	3·0 (5)
C(4)	4202 (16)	6808 (9)	4920 (3)	3·0 (5)
C(5)	6032 (18)	10411 (10)	4234 (4)	3·7 (5)
C(6)	7273 (18)	10997 (9)	4015 (3)	3·5 (5)
C(7)	8471 (16)	10415 (10)	3766 (3)	3·5 (6)
C(8)	8417 (17)	9220 (9)	3729 (3)	3·6 (6)
C(9)	7067 (18)	7297 (8)	3901 (3)	3·1 (5)
C(10)	4505 (16)	8553 (10)	4430 (3)	3·5 (5)
C(11)	6197 (16)	6763 (8)	4307 (3)	2·8 (5)
C(12)	4997 (17)	7353 (9)	4553 (3)	2·8 (5)
C(13)	5915 (18)	9191 (9)	4198 (3)	3·0 (5)
C(14)	7114 (17)	8632 (9)	3942 (3)	3·1 (5)
C(15)	6119 (23)	3895 (9)	4915 (4)	5·4 (7)
C(16)	2910 (17)	8608 (10)	4143 (3)	3·6 (5)
C(17)	6171 (17)	6894 (8)	3459 (3)	3·1 (5)
C(18)	6934 (18)	7347 (9)	3024 (3)	3·5 (5)
C(19)	6093 (18)	6758 (9)	2629 (4)	3·7 (5)
C(20)	6393 (21)	8446 (10)	2103 (4)	5·2 (6)
C(21)	8451 (18)	6861 (10)	2068 (4)	4·1 (6)
C(22)	5512 (19)	6563 (13)	1823 (4)	5·4 (7)
C(*B*)1	−5 (19)	4977 (10)	3388 (4)	4·4 (6)
C(*B*)2	−508 (19)	3970 (11)	3584 (4)	4·6 (7)
C(*B*)3	267 (19)	3623 (10)	3994 (4)	4·8 (6)
C(*B*)4	1497 (18)	4288 (11)	4192 (4)	4·5 (7)
C(*B*)5	1971 (21)	5279 (10)	3977 (4)	4·8 (6)
C(*B*)6	1243 (20)	5638 (10)	3583 (4)	4·7 (7)
H(1)	766 (16)	523 (10)	424 (4)	
H(3)	393 (15)	522 (10)	532 (4)	
H(4)	326 (15)	722 (10)	513 (4)	
H(5)	508 (15)	1079 (10)	444 (4)	
H(6)	737 (15)	1167 (10)	406 (4)	
H(7)	941 (15)	1081 (11)	362 (4)	
H(8)	954 (15)	886 (10)	355 (4)	
H(9)	849 (15)	703 (10)	389 (4)	
H(10)	404 (16)	901 (10)	475 (4)	
H(16)1	197 (15)	830 (10)	433 (4)	
H(16)2	320 (14)	827 (10)	384 (4)	
H(16)3	245 (15)	932 (10)	400 (4)	
H(17)1	481 (15)	716 (11)	345 (4)	
H(17)2	618 (16)	616 (10)	346 (4)	
H(18)1	840 (15)	751 (10)	304 (4)	
H(18)2	711 (15)	817 (10)	295 (4)	
H(19)1	621 (16)	598 (10)	263 (4)	
H(19)2	476 (16)	701 (10)	264 (3)	
H(20)1	683 (14)	880 (10)	229 (3)	
H(20)2	505 (15)	869 (10)	217 (4)	
H(20)3	653 (14)	852 (10)	180 (4)	
H(21)1	873 (15)	712 (10)	173 (4)	
H(21)2	899 (16)	625 (10)	211 (4)	
H(21)3	928 (15)	739 (10)	228 (4)	
H(22)1	595 (15)	671 (10)	152 (4)	
H(22)2	568 (15)	577 (10)	181 (4)	
H(22)3	428 (15)	679 (10)	185 (4)	
H(*B*)1	−50 (14)	523 (10)	316 (4)	
H(*B*)2	−137 (14)	349 (10)	344 (4)	
H(*B*)3	13 (15)	302 (10)	410 (4)	
H(*B*)4	179 (15)	405 (10)	454 (4)	
H(*B*)5	291 (16)	565 (10)	414 (4)	
H(*B*)6	170 (14)	636 (10)	343 (4)	

Table 2. *Torsion angles* (°)

The standard deviation of the torsion angles is 1°.

Around the central ring		About the 9-(3-dimethylaminopropyl) group	
C(14)–C(9)–C(11)–C(12)	27·0	C(11)–C(9)–C(17)–C(18)	−178·9
C(9)–C(11)–C(12)–C(10)	0·0	C(14)–C(9)–C(17)–C(18)	58·0
C(11)–C(12)–C(10)–C(13)	−27·7	C(9)–C(17)–C(18)–C(19)	172·3
C(12)–C(10)–C(13)–C(14)	29·0	C(17)–C(18)–C(19)–N	176·9
C(10)–C(13)–C(14)–C(9)	−2·3	C(18)–C(19)–N–C(20)	−55·2
C(13)–C(14)–C(9)–C(11)	−25·4	C(18)–C(19)–N–C(21)	63·6
		C(18)–C(19)–N–C(22)	−173·3

relatively large thermal vibration. There is no indication that the trifluoromethyl group is disordered. The large thermal vibration is due apparently to the high degree of libration of the trifluoromethyl group about the C(2)—C(15) bond. This can be supported by the short C—F bond length. The mean value of the C—F bond length is 1·25 Å in the title compound as compared with 1·322 Å (at 85 K) in trifluoromethanesulphonic acid (Delaplane, Lundgren & Olovsson, 1975), 1·312 Å in thenoyltrifluoroacetone (Jones, 1976), and 1·325 Å in carbon tetrafluoride (Bolshutkin, Gasan, Prokhvatilov & Erenburg, 1972). There are two crystallographically independent molecules in the structure of the hydrochloride of SKF-d-28175 and the two molecules have slightly different conformations (Chu & Chung, 1976). The structure obtained in this work has the same conformation as one of the molecules (molecule *A*) determined previously. The bond lengths and bond angles are not significantly different from accepted values.

The tricyclic ring system is folded with the central ring in a boat conformation as shown by the ring torsion angles in Table 2, and by the Cremer & Pople (1975) puckering parameters, which are: $q_2 = 0{\cdot}397$, $q_3 = 0{\cdot}005$, $Q = 0{\cdot}387$ Å, $\varphi_2 = 181{\cdot}4$, and $\theta = 89{\cdot}3°$. For the ideal boat conformation, these parameters are: $q_2 = Q$, $q_3 = 0$ Å, $\varphi_2 = 180°$, and $\theta = 90°$. The 9-(3-dimethylaminopropyl) and 10-methyl groups are both in the 'boat–axial' conformation. The folding angle between the least-squares planes of the two benzo rings is 151·4°, as compared with 154·4° for the molecule *A* in the hydrochloride of SKF-d-28175 (Chu & Chung, 1976). The torsion angles of the 9-(3-dimethylaminopropyl) group are also shown in Table 2. The benzene molecule is planar and there is no close contact between benzene and the main molecules. The packing of the molecules in the crystal is shown in Fig. 2. The

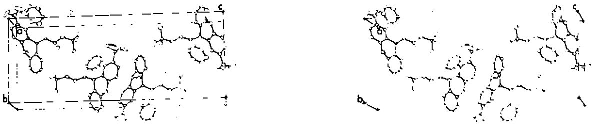

Fig. 2. A stereoview of the molecular packing of the title compound in a unit cell.

closest contacts between the iodide and the main molecule are 3·87 Å$[I^-\cdots C(19)(1-x, \frac{1}{2}+y, \frac{1}{2}-z)]$ and 3·93 Å $[I^-\cdots C(21)(2-x, \frac{1}{2}+y, \frac{1}{2}-z)]$, and the distances between the iodide ion and quaternary ammonium ion are 4·40 Å $[I^-\cdots N^+(x,y,z)]$ and 4·37 Å $[I^-\cdots N^+(1-x, \frac{1}{2}+y, \frac{1}{2}-z)]$.

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trans-2,4,9-Trimethylthioxanthene 10-Oxide

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Abstract. $C_{16}H_{16}OS$, triclinic, $P\bar{1}$, $Z = 2$, $M_r = 256·36$, $a = 8·002$ (1), $b = 9·260$ (1), $c = 9·411$ (1) Å, $\alpha = 103·39$ (1), $\beta = 100·94$ (1), $\gamma = 90·58$ (1)°, $V = 665·0$ (1) Å^3, $D_x = 1·280$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 1·950 mm^{-1}. The final R = 0·047 for 1792 reflections. The 9-methyl group is in a 'boat–equatorial' conformation and the 10-oxide group is in a 'boat–axial' conformation with respect to the central thioxanthene ring.

Introduction. 9-Alkylthioxanthene 10-oxides can exist as *cis* and *trans* isomers. Unlike other thioxanthene sulfoxides, it appears that three 'forms' of 2,4,9-trimethylthioxanthene 10-oxide (I) have been isolated, and the crystal structure of one, form *A* (the *cis* isomer), has been determined by X-ray diffraction (Chu, Rosenstein & Ternay, 1979). Form *B* (m.p. 374–377 K) and form *C* (m.p. 397–400 K) are both *trans* isomers and they have the same NMR spectra in $CDCl_3$ (CH_3: 1·61δ, *d*, J = 7 Hz; CH_3: 2·33δ, *s*; CH_3: 2·74δ, *s*; CH: 4·67δ, *q*, J = 7 Hz; ArH: 6·92–7·54δ, *m*, 5H; 7·81–7·97δ, *m*, 1H) and, therefore, the same conformation in solution. However, their structures are different in the solid state since they have different melting points and solid-state IR spectra. Form *C* is a polycrystalline material, and it transforms into form *B* upon recrystallization from methanol solution. The lower melting form *B* appears to be more stable. The purpose of the present study is to determine the conformation and configuration of form *B* (I) in the solid state. The study of form *C* will be carried out

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