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The Crystal Structure and Absolute Configuration of (+)-Methyl *p*-Tolyl Sulfoxide

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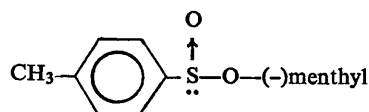
The crystal structure of (+)-methyl *p*-tolyl sulfoxide has been solved by the heavy-atom method and refined by Fourier and least-squares techniques. The absolute configuration has been determined by the anomalous phase displacement technique with the sulfur atom acting as the anomalous scatterer. The space group is $P2_12_12_1$ with four molecules per unit cell of dimensions $a = 5.826$ (6), $b = 8.621$ (8) and $c = 16.435$ (3) Å. Three-dimensional data (Cu $K\alpha$) were collected with a Picker automatic diffractometer. The final R indices obtained for the two configurations are 0.034 and 0.044 respectively, for 832 observed reflections. In the notation of Cahn, Ingold & Prelog the correct absolute configuration at sulfur is R ; the same assignment had been made earlier on the basis of chemical evidence.

Introduction

One of the most fruitful approaches to the elucidation of a specific reaction mechanism lies in the study of the reaction stereochemistry which in turn may yield clues concerning the geometry of the transition state. In general, knowledge of the dynamic stereochemistry of carbon centers has played a key role in the evolution of our present detailed picture of the reaction mechanisms of such centers. The importance of sulfur as a reaction center in biological processes is well documented; however, relative to the corresponding situation for carbon centers, fundamental mechanistic studies of sulfur centers are rare. The work reported here is part of an effort to rigorously settle the question of absolute and relative configuration for a number of optically active compounds with asymmetric sulfur centers.

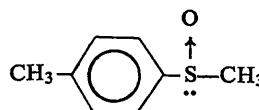
At the time this study was started the conversion of (-)-*p*-tolyl (-)-menthyl sulfinate (I) to (+)-methyl *p*-tolyl sulfoxide (II) by treatment with methyl Grignard reagent was thought to proceed *via* inversion of configuration, based on optical rotatory dispersion and

circular dichroism studies by Mislow, Green, Lauer, Melillo, Simmons & Ternay (1965).



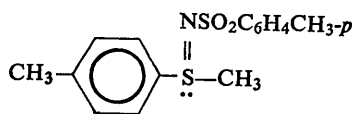
m.p. 105-106°
 $[\alpha]_D = -198^\circ$ (acetone)

(I)



m.p. 73-74.5°
 $[\alpha]_D = +146^\circ$ (acetone)

(II)



m.p. 124-125°
 $[\alpha]_D = -320^\circ$ (acetone)

(III)

The conversion of (II) to (III) by treatment with $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NSO}$ is accompanied by formation of SO_2 and is assumed by Day & Cram (1965) to proceed via a mechanism in which the entering and leaving groups form part of a quasi-6-ring transition state. For overall trigonal bipyramidal geometry at the sulfur atom, this would mean that the entering and leaving groups occupy equatorial (radial) positions. Optical rotatory dispersion data led Day & Cram to conclude that conversion of (II) to (III) also involved inversion of configuration at the asymmetric sulfur atom. Indeed, it so far appears that in organo-sulfur stereochemistry nucleophilic displacement at the asymmetric sulfur center always proceeds with inversion. However, the evidence in support of this rule is not always as rigorous as one might wish. It is therefore important that the absolute configurations of representative compounds be established unambiguously. The crystal structure and absolute configuration of the *p*-iodo analog of (I) was established by X-ray diffraction methods by Fleischer, Axelrod, Green & Mislow (1964). The absolute configuration of the molecule was determined through the known configuration of the (-)-menthyl group. These investigators were also able to relate the absolute configuration of the *p*-iodo analog to that of (I). Since a knowledge of the absolute configuration of (II) would provide unambiguous evidence for the steric course of the Grignard conversion of (I) to (II) we felt that (II) would be the most logical compound to investigate next. During the course of this work the absolute configuration of (II) was determined by chemically relating it to sulfoxides of known absolute configuration (Axelrod, Bickart, Jacobus, Green & Mislow, 1968).

Experimental

Crystals were grown from *n*-heptane solution by evaporation at room temperature. The space group was determined from symmetry and systematic absences ($h00$, $0k0$, $00l$ absent for odd indices) observed on Weissenberg and precession photographs. The cell dimensions were established from a least-squares calculation with a set of reflections measured on a Picker diffractometer. For intensity measurements a suitable crystal was ground into a sphere of radius 0.0125 cm. The high vapor pressure of the substance made it necessary to give the crystal a protective coating which

consisted of a thin layer of Eastman 910 adhesive and a further coat of 'Gluebird'. (The high solubility of the sulfoxide in water prevented the immediate use of the water-based glue.) Three-dimensional diffraction data for one octant [2θ (max) = 160°] were collected with a Picker automatic diffractometer using Ni filtered Cu $K\alpha$ radiation. In order to minimize coincidence losses, count rates were automatically held below approximately 10,000 counts.sec⁻¹ by a set of attenuators. Three check reflections which were used to monitor the condition of the crystal remained stable for the first half of the run; however, after that a gradual decrease in the intensities were observed. The maximum decrease amounted to about 7%. Because of the decay problem, and because we felt that the application of the *R* index method (Ibers & Hamilton, 1964) to the absolute configuration determination would be straightforward, we did not collect data for any Bijvoet pairs.

The data set was corrected for Lorentz, polarization and absorption ($\mu R = 0.353$) effects in the usual manner. Furthermore a decay correction based on the observed drop in intensities was applied. The standard deviations of the observed structure factors were estimated from the estimated standard deviations of the recorded scan and background counts, where each recorded number of counts *N* was assigned an e.s.d. from the expression $s(N) = N^{1/2} + 0.005N$. All reflections whose intensity was less than three times the corresponding standard deviation were treated as 'unobserved'. Out of 1046 available reflections 832 were then recorded as 'observed'. Refinement of the structure was carried out using only the 'observed' reflections.

Crystal data

(+)-Methyl *p*-tolyl sulfoxide, $\text{C}_8\text{H}_{10}\text{SO}$.

M. W. 154.09

Space group: $P2_12_12_1$ from absences and intensity symmetry

$$\begin{aligned} a &= 5.826(6) \text{ \AA} \\ b &= 8.621(8) \text{ \AA} \\ c &= 16.435(3) \text{ \AA} \\ d_m &= 1.19 \quad d_x = 1.24 \text{ g.cm}^{-3} \\ Z &= 4 \\ t &= 23^\circ\text{C}, \lambda \text{ Cu } K\alpha_1 = 1.54051 \\ \mu &= 28.3 \text{ cm}^{-1} \text{ for Cu } K\alpha \end{aligned}$$

Solution and refinement of the structure

The position of the sulfur atom was found from a three-dimensional Patterson map. A Fourier summation phased on the sulfur atom immediately revealed the location of all the carbon atoms and the oxygen atom. Two cycles of full-matrix least-squares refinement with isotropic temperature factors reduced the *R* index to 0.12 and two further cycles with anisotropic temperature factors reduced *R* to 0.077. A difference Fourier synthesis was then calculated from which the hydrogen positions were determined. All ring H atoms

were very well defined; however, the peaks corresponding to the methyl H atoms differed significantly in height, with one atom in each group being particularly poorly defined. We considered the possibility of rotational disorder, but as can be seen from Fig. 1, which shows a section through the ring methyl group, there is no real indication of such disorder. Two cycles of least-squares refinement with all atoms included, the H atoms with individual isotropic temperature factors, gave an R index of 0.045. At this stage the real and imaginary correction terms to the atomic scattering factors were introduced for sulfur and oxygen. The values $\Delta f'_S = 0.3$, $\Delta f''_S = 0.6$, $\Delta f'_O = 0.0$ and $\Delta f''_O = 0.1$ were taken from *International Tables for X-ray Crystallography* (1962). Both enantiomers were then refined to convergence. The lowest R indices for the two enantiomers were 0.044 and 0.050 respectively. The enantiomer with the lower R index was now assumed to be the correct one.

Discrepancies between F_o and F_c for some high intensity reflections indicated secondary extinction effects. Correction of the data by use of the method of Zachariasen (1963) had the immediate effect of reducing R from 0.044 to 0.038.

The weighting scheme prior to the secondary extinction correction was that proposed by Hughes (1941), and after the correction the weight of $(\Delta F)^2$ was made equal to the reciprocal of the variance of the corresponding F_o . Four additional cycles of least-squares refinement of the correct enantiomer with all hydrogen atoms included gave a final R index of 0.034. The incorrect enantiomer was also refined to convergence and gave an R of 0.044. When anomalous correction terms were omitted the structure could be refined to $R = 0.036$.

Computing procedures

All calculations were performed on an IBM 7044 computer, for the most part using programs listed elsewhere (Hope & Christensen, 1968).

The least-squares program was modified by the authors to calculate structure factors which include both the real and imaginary correction terms for anomalous scattering. The program minimizes the quantity $S = \sum w(K.F_o - G|F_c|)^2$ by full-matrix methods. G is one of the adjustable parameters, which is reset to its original value by changing K after each cycle. Estimated standard deviations were obtained from the expression $(a_{ii}S/m)^{1/2}$, where a_{ii} is the diagonal element in the inverse normal equation matrix, and m is the difference between the number of observations and the number of parameters adjusted.

The isotropic temperature factor is of the form $\exp(-B \sin^2\theta/\lambda^2)$, and the anisotropic of the form $\exp(-B_{11}a^{*2}h^2/4 - B_{22}b^{*2}k^2/4 - B_{33}c^{*2}l^2/4 - B_{12}a^*b^*hk/2 - B_{13}a^*c^*hl/2 - B_{23}b^*c^*kl/2)$. The atomic form factors for sulfur, oxygen and carbon are those given by Hanson, Herman, Lea & Skillman (1964). For hydrogen the

form factors used are those given by Stewart, Davidson & Simpson (1965).

The secondary extinction correction program, written by A.T. Christensen, was also modified by the authors to calculate structure factors with form factors which include the real and imaginary components of the anomalous scattering corrections. The program applies the correction in the form $F_{\text{corr}} = F_o(1 + C\beta J_o)^{1/2}$, where C is a constant and

$$\beta = 2(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)^2 \cdot \frac{dA^*/d\mu R}{dA_o^*/d\mu R}$$

(Zachariasen, 1963).

The R index is defined by $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ (observed F 's only).

Discussion

The difference in the R indices for the two configurations is the largest yet reported for structures with either sulfur or silicon as the anomalous scatterer. The application of Hamilton's generalized R factor method (Hamilton, 1965) to test the validity of the configurational assignments shows that the probability of the S configuration being the correct one is considerably smaller than 0.001%, so that the configuration around the sulfur atom is R in the notation of Cahn, Ingold & Prelog (1956). This is in agreement with the absolute configuration assigned by Axelrod *et al.* (1968). Since the absolute configurations of both ends of the conversion reaction of sulfinic ester to sulfoxide have now been determined rigorously, one can unambiguously conclude that this conversion occurs with inversion of configuration at the sulfur atom.

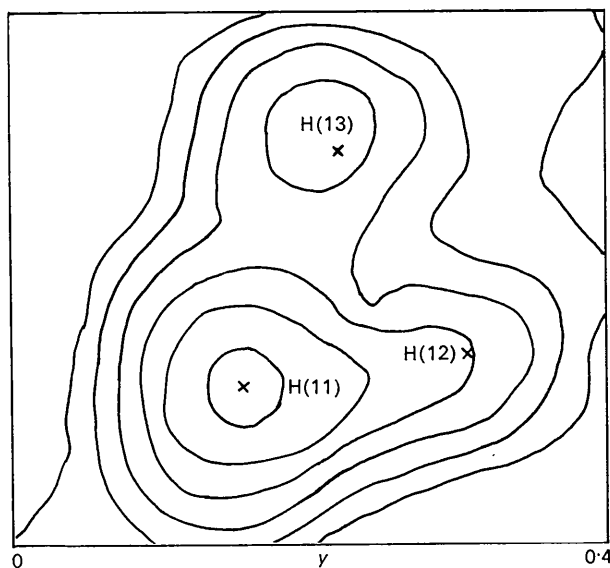
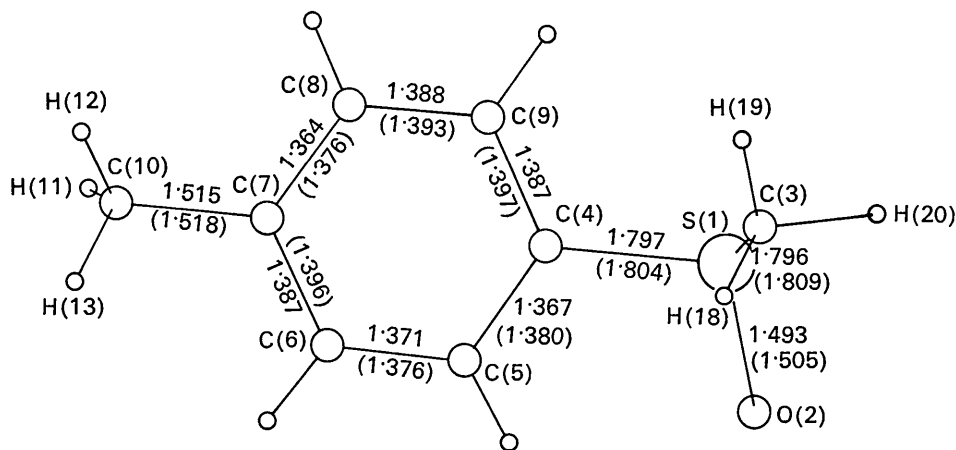


Fig. 1. Difference electron density map. Section through the plane of the ring methyl hydrogens. Contours are drawn for 0.10, 0.15, ... e.Å⁻³. Crosses indicate the positions from the least-squares refinement.

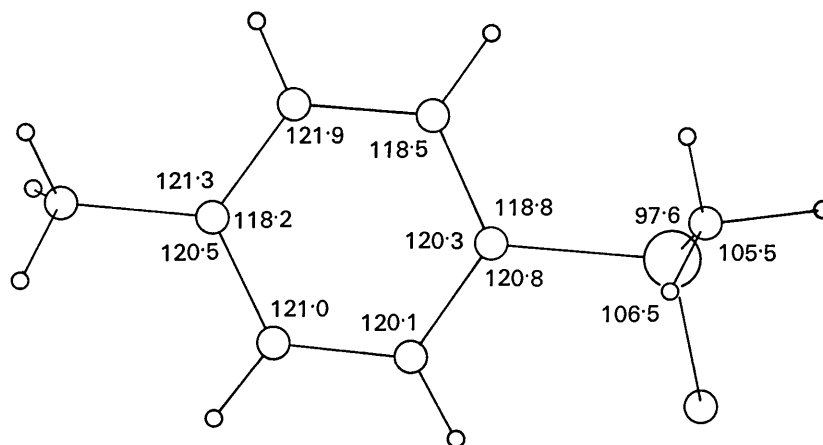
The final positional and thermal parameters for the *R* configuration together with their estimated standard deviations, are given in Tables 1, 2 and 3. A listing of the observed structure factors and those calculated from the final parameters (*R* configuration) is given in Table 4. The molecular geometry parameters not involving hydrogen are given in Fig. 2. The 'uncorrected' distances and angles were calculated from the final positional parameters while the 'corrected' distances (given in parentheses) were derived from coordinates obtained by the method of Cruickshank (1961) following an analysis of the thermal motion of the molecules (Schomaker & Trueblood, 1968).

Table 1. *Positional parameters (with estimated standard deviations) for sulfur, oxygen and carbon atoms*

	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	0.4558 (2)	0.2122 (1)	0.6073 (1)
O(2)	0.5687 (5)	0.0994 (3)	0.5512 (1)
C(3)	0.5267 (13)	0.4007 (6)	0.5682 (3)
C(4)	0.6298 (6)	0.2199 (4)	0.6976 (2)
C(5)	0.8330 (6)	0.1409 (4)	0.7018 (2)
C(6)	0.9588 (8)	0.1425 (4)	0.7723 (2)
C(7)	0.8842 (6)	0.2244 (4)	0.8400 (2)
C(8)	0.6820 (7)	0.3035 (4)	0.8346 (2)
C(9)	0.5491 (7)	0.3011 (4)	0.7646 (2)
C(10)	1.0262 (11)	0.2266 (8)	0.9172 (3)



(a)



(b)

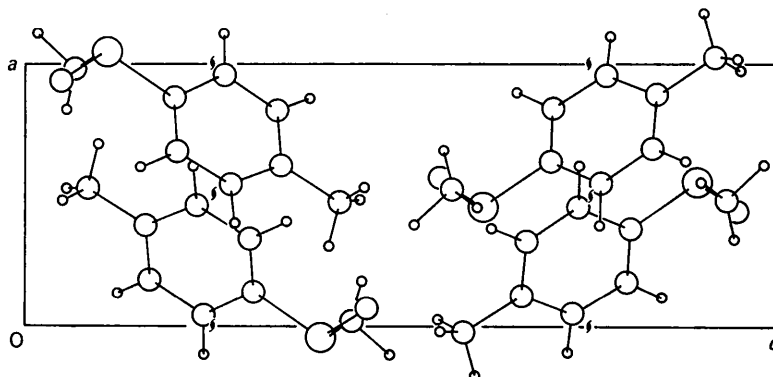
Fig. 2. (a) Interatomic distances (from parameters in Table 1), and (in parentheses) interatomic distances corrected for anisotropic thermal motion effects. E.s.d.'s are 0.003–0.006 Å. (b) Bond angles (uncorrected). E.s.d.'s are about 0.3°. The drawing represents a projection of the molecule on the plane of the benzene ring. The correct absolute configuration is shown.

Table 2. Anisotropic thermal parameters (with estimated standard deviations) for sulfur, oxygen and carbon atoms

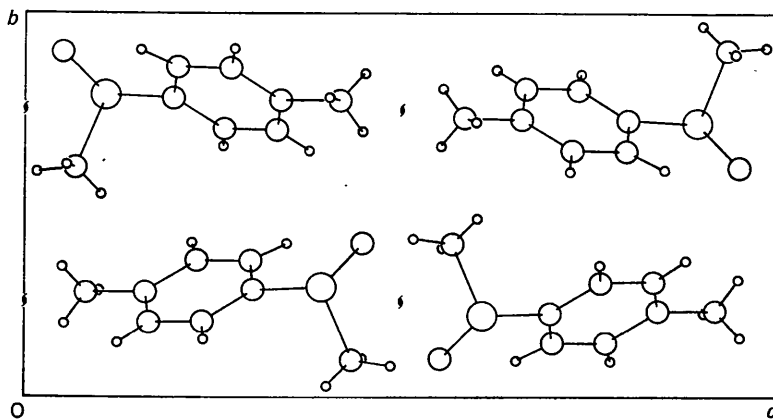
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	5.83 (4)	6.02 (4)	6.27 (4)	-1.12 (5)	0.28 (4)	-0.71 (4)
O(2)	9.42 (18)	5.96 (11)	6.28 (12)	-0.99 (15)	0.68 (15)	-1.83 (10)
C(3)	9.22 (42)	5.73 (20)	7.60 (27)	-0.43 (28)	-1.59 (30)	0.13 (20)
C(4)	4.84 (15)	4.39 (14)	5.05 (15)	-0.50 (15)	0.91 (13)	-0.28 (13)
C(5)	5.20 (19)	5.21 (18)	5.96 (19)	-0.04 (15)	1.55 (17)	-1.12 (15)
C(6)	4.93 (18)	5.53 (18)	6.68 (20)	0.98 (18)	0.36 (18)	-0.10 (15)
C(7)	6.09 (18)	4.04 (14)	5.17 (16)	-0.05 (16)	0.90 (14)	0.42 (13)
C(8)	6.79 (22)	4.62 (16)	5.05 (17)	0.65 (17)	1.58 (17)	-0.29 (15)
C(9)	5.04 (16)	4.86 (15)	6.38 (18)	0.73 (19)	1.18 (17)	-0.17 (15)
C(10)	8.71 (33)	7.77 (26)	5.91 (23)	0.44 (31)	-0.34 (23)	0.95 (22)

Table 3. Positional and isotropic thermal parameters (with estimated standard deviations) for hydrogen atoms

	x	y	z	B
H(11)	0.9705 (80)	0.1561 (45)	0.9514 (27)	9.27 (143)
H(12)	1.0183 (93)	0.3078 (46)	0.9477 (26)	9.83 (161)
H(13)	1.1934 (75)	0.2203 (54)	0.9033 (22)	10.80 (157)
H(14)	0.6320 (55)	0.3563 (35)	0.8778 (18)	6.15 (90)
H(15)	0.3902 (54)	0.3448 (35)	0.7638 (16)	5.46 (85)
H(16)	0.8944 (59)	0.0959 (39)	0.6531 (18)	7.19 (93)
H(17)	1.1051 (58)	0.0928 (36)	0.7782 (18)	5.40 (84)
H(18)	0.6733 (69)	0.3942 (55)	0.5550 (25)	7.94 (171)
H(19)	0.4599 (78)	0.4649 (45)	0.6017 (23)	9.71 (146)
H(20)	0.3885 (84)	0.4125 (53)	0.5163 (24)	12.13 (140)



(a)



(b)

Fig. 3. (a) Projection along the b axis (top view). (b) Projection along the a axis (front view).

Table 4. Observed and calculated structure factors

The five columns in each group list I , $10F_o$, $10F_c$, the phase angle ($^\circ$) and $100/\sigma(F_o)$.

I	$10F_o$	$10F_c$	Phase angle ($^\circ$)	$100/\sigma(F_o)$
2 294 157 178 90	5 105 104 182 90	20 21 26 317 84	5 21 19 196 50	15 36 37 185 63
4 288 287 184 90	6 85 67 82 21	1 31 31 317 84	6 31 31 317 84	4 103 126 338 104
4 83 87 267 137	7 111 112 185 87	1 18 18 18 46	15 32 33 276 64	8 30 30 171 74
8 154 151 177 102	8 19 19 19 46	1 323 323 77 77	11 18 18 46 82	7 111 112 185 87
10 82 82 82 82	10 23 23 35 60	2 205 270 203 87	0 19 17 169 45	8 106 107 161 -13
16 70 81 61 5	8 85 83 93 85	4 175 168 50 104	1 51 53 80 92	10 88 83 205 90
10 25 20 191 46	13 36 35 5 60	5 170 104 306 61	1 94 94 201 96	11 88 86 107 85
18 51 54 4 83	15 14 14 13 58	7 107 104 100 70	1 108 108 158 9	12 57 58 116 79
20 21 26 4 73	15 14 14 13 58	9 270 200 8 70	4 236 200 8 70	3 247 235 174 54
	1 59 63 91 76	8 148 148 336 90	5 29 26 343 57	7 48 48 176 87
	2 108 108 276 86	9 142 142 175 94	7 19 20 312 75	20 165 70 0
	3 22 21 21 95	10 13 20 95 65	7 47 45 63 74	0 103 103 273 109
	3 109 109 266 148	11 46 45 286 66	8 134 136 276 85	1 21 27 296 59
	4 83 87 267 137	0 33 32 160 56	1 41 40 92 107	2 186 187 1 94
	5 280 285 94 88	7 56 56 272 35	12 29 28 56 48	3 94 96 271 108
	6 50 50 88 116	8 85 83 93 85	3 156 151 172 115	4 425 426 62 73
	7 143 142 90 113	9 136 136 273 65	4 404 412 187 123	5 62 65 150 102
	8 40 40 78 103	10 53 50 102 78	8 187 187 102 78	6 17 120 156 6
	9 207 205 274 90	12 33 27 277 71	6 108 108 158 94	7 120 127 77 94
	10 35 35 94 74	9 24 24 272 56	7 32 26 94 73	8 40 40 256 105
	11 82 80 273 97	10 34 34 91 122	8 114 106 4 105	9 64 60 316 86
	12 43 43 92 74	0 19 18 138 51	9 205 207 92 86	10 64 63 322 93
	13 263 263 70	1 159 158 99 126	10 47 46 92 87	11 94 93 304 76
	14 54 56 271 73	1 59 56 184 77	11 78 80 93 91	12 35 34 76 59
	16 54 59 263 75	3 106 106 163 86	3 212 210 262 83	13 32 33 262 88
	16 27 26 274 52	4 38 34 4 83	4 231 230 273 86	14 26 27 39 80
	17 19 2 232 64	5 143 140 271 75	5 44 44 262 85	15 35 33 123 66
	18 19 17 271 83	6 26 25 10 51	6 104 103 200 92	16 31 30 107 86
	19 39 39 274 83	8 35 31 163 66	7 186 183 200 92	17 18 20 82 53
		9 24 24 184 70	8 80 82 101 65	18 20 20 82 53
		11 31 29 185 71	9 39 43 240 62	19 20 20 82 53
		12 14 20 17 1 93	10 226 272 84	20 26 27 22 84
			11 76 76 272 84	21 26 27 22 84
			12 65 62 273 84	22 26 27 22 84
			13 13 13 87 56	23 26 27 22 84
			14 15 14 73 50	24 26 27 22 84
			15 11 11 135 50	25 26 27 22 84
			16 11 11 135 50	26 26 27 22 84
			17 11 11 135 50	27 26 27 22 84
			18 11 11 135 50	28 26 27 22 84
			19 11 11 135 50	29 26 27 22 84
			20 11 11 135 50	30 26 27 22 84
			21 11 11 135 50	31 26 27 22 84
			22 11 11 135 50	32 26 27 22 84
			23 11 11 135 50	33 26 27 22 84
			24 11 11 135 50	34 26 27 22 84
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			26 11 11 135 50	36 26 27 22 84
			27 11 11 135 50	37 26 27 22 84
			28 11 11 135 50	38 26 27 22 84
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			31 11 11 135 50	41 26 27 22 84
			32 11 11 135 50	42 26 27 22 84
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			35 11 11 135 50	45 26 27 22 84
			36 11 11 135 50	46 26 27 22 84
			37 11 11 135 50	47 26 27 22 84
			38 11 11 135 50	48 26 27 22 84
			39 11 11 135 50	49 26 27 22 84
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			89 11 11 135 50	99 26 27 22 84
			90 11 11 135 50	100 26 27 22 84

Two different calculations were performed, one in which all ten 'heavy' atoms were incorporated in the rigid body, and one in which only the rigid body consisted of the tolyl carbon atoms plus the sulfur atom. The librational ellipsoids for the two rigid bodies are very similar, both in magnitude and orientation. The root-mean-square differences between 'observed' and calculated U_{ij} are 0.004 and 0.003 Å² respectively. The angle between the vector S-C(7) and the major librational axis is 14° for the ten-atom case and 8° for the eight-atom case. The magnitudes of the principal axes of the translational and librational tensors for the ten atom rigid-body are listed in Table 5. The screw components are all very small. The fold angle between the planes defined by the atoms C(3)-S(1)-C(4) and O(2)-S(1)-C(4), respectively, is -71.3°, and the twist angle needed to make the projection of the line S(1)-O(2) coincide with that of the line C(4)-C(5) is

+8.2°. The signs are consistent with the convention proposed by Klyne & Prelog (1960).

Table 5. Principal components of rigid body translation and libration tensors

Columns 1 and 2 contain the r.m.s. translational amplitudes (Å) and r.m.s. librational amplitudes (degrees) respectively for the 10-atom rigid body. Columns 3 and 4 are the amplitudes for the 8-atom rigid body.

0.28	7.3	0.28	7.7
0.21	4.1	0.22	4.1
0.21	3.1	0.21	3.7

Distances and angles involving hydrogen atoms are listed in Tables 6 and 7, respectively. Packing diagrams of the structure are shown in Fig. 3(a) and (b), representing views along the *b* and *a* axes respectively. No unusual intermolecular contacts were found.

Table 6. Carbon-hydrogen distances

E.s.d.'s are about 0.04 Å.

C(3)—H(18)	0.88
C(3)—H(19)	0.87
C(3)—H(20)	1.18
C(5)—H(16)	0.96
C(6)—H(17)	0.96
C(8)—H(14)	0.89
C(9)—H(15)	1.00
C(10)—H(11)	0.89
C(10)—H(12)	0.86
C(10)—H(13)	1.00

Table 7. Angles involving hydrogen atoms

E.s.d.'s are about 2° for X—X—H and about 4° for H—X—H.

S(1)—C(3)—H(18)	105
S(1)—C(3)—H(19)	104
S(1)—C(3)—H(20)	100
H(18)—C(3)—H(19)	129
H(18)—C(3)—H(20)	119
H(19)—C(3)—H(20)	96
C(4)—C(5)—H(16)	119
C(6)—C(5)—H(16)	121
C(5)—C(6)—H(17)	124
C(7)—C(6)—H(17)	115
C(7)—C(10)—H(11)	109
C(7)—C(10)—H(12)	118
C(7)—C(10)—H(13)	110
H(11)—C(10)—H(12)	100
H(11)—C(10)—H(13)	118
H(12)—C(10)—H(13)	103
C(7)—C(8)—H(14)	119
C(9)—C(8)—H(14)	119
C(4)—C(9)—H(15)	120
C(8)—C(9)—H(15)	121

Very few data on bond distances and angles are available for organic sulfoxides. Abrahams (1956) has given some data for symmetrical sulfoxides. The C—S—O angle for a series of such compounds is nearly constant at 106° while the C—S—C angle varies from 93 to 114°. Hine (1962) in a study of the structure of *S*-methyl-L-cysteine sulfoxide found the C(methyl)—S—O angle to be 107.5°; the corresponding angle in the present case is 105.5°. Our value of 97.5° for the C—S—C angle also seems to agree well with previous results.

Distances and angles in the benzene ring show some variation. Three of the bonds, C(4)—C(5), C(5)—C(6) and C(7)—C(8), are somewhat shorter than the other three which are all close to the accepted value of 1.396 Å. The internal angle at C(4), to which S is attached, is very close to 120°. Recent observations (Carter, McPhail & Sim, 1966; Hope, 1969) have suggested that electron-withdrawing substituents on a benzene ring lead to internal angles greater than 120° at the carbon atom to which they are attached. On this basis one must conclude that the sulfoxide group is not strongly electron-withdrawing, in agreement with a previously published suggestion (Schöberl & Wagner, 1955). The lack of electron-withdrawing power is pre-

sumably due to the presence of the unshared electron pair. We note with interest that this lack of electron-withdrawing power seems to be contradicted by the sign and magnitude of the Hammett 'σ' constant whose value places the electron-withdrawing power of the sulfoxide group above that of, for example, chlorine (Kosower, 1968).

The relatively small angle at C(7) presumably is due to the electron-donating effect of the methyl group. However, the similarly small angle at C(9) cannot be explained as easily.

Table 8 gives the equation of the least-squares plane through the benzene ring; also listed are the deviations from this plane for all the atoms. The benzene ring is planar, with the largest deviation found for C(9) which is displaced 0.01 Å from the plane. The ring methyl carbon is also quite close to the plane; however, the sulfur atom is tilted up from the plane by 0.06 Å. As already indicated by the C—C—S—O torsion angle, the oxygen atom lies quite close to the plane of the ring.

Table 8. Least-squares plane through benzene ring [atoms C(4)—C(9)] and deviations from plane

Normal equation of plane: $-2.827x - 7.004y + 5.315z = 0.392$.

	Deviation		Deviation
S(1)	0.062	C(9)	0.011
O(2)	0.234	C(10)	-0.004
C(3)	-1.667	H(11)	0.828
C(4)	-0.004	H(12)	-0.389
C(5)	-0.003	H(13)	-0.508
C(6)	0.004	H(14)	-0.009
C(7)	0.002	H(15)	0.150
C(8)	-0.009	H(16)	-0.120
		H(17)	-0.030

The positional parameters of a structure in a non-polar space group are not supposed to depend much on the $\Delta f''$ values (Ueki, Zalkin & Templeton, 1966; Cruickshank & McDonald, 1967). The bond lengths obtained from the *S* configuration refinement (corresponding to negative $\Delta f''$ values) indeed agree well with those for the *R* configuration. The largest difference in distances between 'heavy' atoms is about 0.01 Å, or about 2σ . The temperature factors for the two configurations differ by about one or two standard deviations.

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The Crystal and Molecular Structure of Bromdihydroacronycine

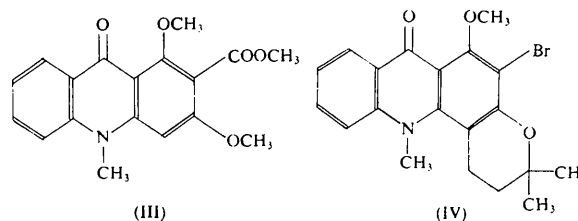
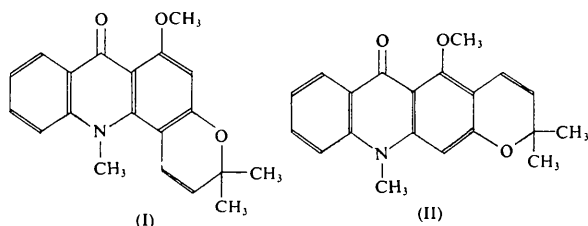
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Bromdihydroacronycine (1-methoxy-2-bromo-2',2',10-trimethyldihydropyranof[5',6'-4,3]acrid-9-one, $C_{20}H_{20}NO_3Br$) crystallizes in the monoclinic space group $P2_1/c$ with $Z=4$. The unit-cell parameters are $a=9.06$, $b=12.66$, $c=16.66$ Å, and $\beta=113.75^\circ$. 2173 reflections were recorded diffractometrically (Cu $K\alpha$ radiation) and used in the determination. The structure was solved by the heavy-atom technique and refined by the method of least squares to a final value of $R=0.059$.

Acronycine, an alkaloid from *Acronychia baueri* Schott which exhibits potent broad spectrum antitumor activity, was initially considered to have either the angular structure (I) or the linear alternative (II) (Drummond & Lahey, 1949). Since chemical degradation of acronycine produced a dimethoxy acid which was not identical with the independently synthesized dimethoxy acid (III) expected to result from degradation of structure (II), Macdonald & Robertson (1966) concluded that acronycine has structure (I). Govindachari, Pai & Subramaniam (1966) also decided in favor of the angular formulation from a consideration of the nuclear magnetic resonance spectrum of a hydrogenated derivative of acronycine.



Our three-dimensional single-crystal X-ray analysis of bromdihydroacronycine (IV), the major product from the reaction of 11,12-dihydroacronycine with *N*-bromosuccinimide,* confirms directly the structural assignment of acronycine as (I).

Slow crystallization of bromdihydroacronycine from ethyl acetate afforded yellow, acicular crystals. The cell parameters and symmetry, obtained from cali-

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