Structure of Bornane-2-spiro-2'-(6'-methyl)-1',3'-dithiane 1'-Sulfoxide*

BY N. N. DHANESHWAR, R. B. MENON, S. S. TAVALE AND T. N. GURU ROW†

Physical and Structural Chemistry Unit, National Chemical Laboratory, Pune 411008, India

Abstract. $C_{14}H_{24}OS_2$, $M_r = 272 \cdot 5$, orthorhombic, $P2_12_12_1$, $a = 10 \cdot 903$ (1), $b = 11 \cdot 004$ (1), $c = 12 \cdot 058$ (2) Å, $V = 1446 \cdot 7$ (3) Å^3, $Z = 4$, D_m(flotation in KBr solution) $= 1 \cdot 26$, $D_x = 1 \cdot 25$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1 \cdot 5418$ Å, $\mu = 3 \cdot 825$ mm^{-1}, $T = 293$ K, $F(000) = 592$, $R = 0 \cdot 049$, $S = 1 \cdot 51$ for 1157 observed reflections. The dithiane ring has a 'chair' conformation with the methyl group equatorial and the sulfoxide is axially substituted indicating a novel *cis* alkylation product.

Experimental. Optically active α-lipoic acid (Menon, Kumar & Ravindranathan, 1987) has been synthesized starting with optically active menthone as a chiral template. The same reaction sequence was attempted starting with $R(+)$-camphor as the starting ketone; however the monosulfoxide derivative failed to undergo alkylation with δ-bromovaleric acid as with menthone, which would lead to α-lipoic acid. The sulfoxide derivative, however, reacted with iodomethane under the alkylation conditions to give the methylated derivative. The stereochemistry of this methylated derivative was studied by X-ray crystallography, Crystal approx. $0 \cdot 25 \times 0 \cdot 35 \times 0 \cdot 50$ mm used, Nonius CAD-4F-11M diffractometer, Ni-filtered Cu radiation, $\omega/2\theta$ scan mode, scan speed 1° min^{-1}, $\theta < 60°$, h 0 to 12, k 0 to 12, l 0 to 13, 1326 unique reflections collected, 1157 judged significant ($|F_o| > 3\sigma|F_o|$), lattice parameters from 22 reflections ($27 < 2\theta < 57°$). Three standard reflections ($\overline{4}60$, $\overline{5}5\overline{2}$, 228) every 3600 s, 4% variation in intensity. No correction for absorption. Structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement (on F) using anisotropic thermal parameters (isotropic thermal parameters for H held fixed at the value of the non-hydrogen atoms to which they are attached, H positions calculated by stereochemistry and confirmed by difference Fourier synthesis); convergence at $R = 0 \cdot 049$, $wR = 0 \cdot 043$, $S = 1 \cdot 51$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = (3 \cdot 5 + 1 \cdot 0|F_o| + 0 \cdot 025|F_o|^2)^{-1}$, $(\Delta/\sigma)_{max} = 0 \cdot 1$, final $\Delta\rho$ excursions $< |0 \cdot 3|$ e Å^{-3}. No corrections for secondary extinction. Atomic scattering factors from *International*

Tables for X-ray Crystallography (1974). Corrections for anomalous scattering used. Program *LALS* (Gantzel, Sparks & Trueblood, 1961) used for refinement. Fig. 1 gives a *PLUTO* view of the molecule (Motherwell & Clegg, 1978). Table 1‡ gives the positional parameters and equivalent isotropic thermal parameters of the non-hydrogen atoms with their

‡ Lists of structure factors, anisotropic thermal parameters, H-atom parameters and some important torsion angles have been deposited with the British Library Document Supply Centre as Supplementary No. SUP 51669 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
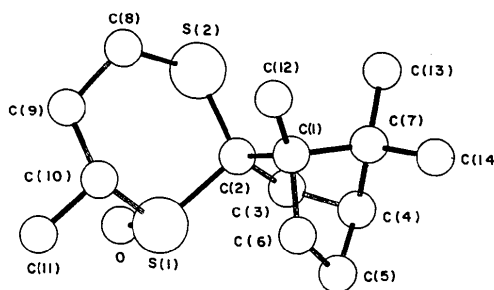

Fig. 1. *PLUTO* diagram (Motherwell & Clegg, 1978) of the molecule showing the crystallographic numbering scheme.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters for non-hydrogen atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2).$$

	x	y	z	B_{eq}(Å^2)
C(1)	−956 (7)	−241 (7)	4595 (6)	3·29 (10)
C(2)	344 (7)	361 (7)	4800 (6)	3·02 (9)
C(3)	1155 (8)	−267 (8)	3900 (7)	3·87 (10)
C(4)	241 (8)	−988 (8)	3222 (7)	3·89 (10)
C(5)	−623 (9)	−71 (10)	2619 (7)	4·67 (13)
C(6)	−1487 (7)	370 (8)	3543 (7)	4·23 (11)
C(7)	−617 (8)	−1525 (7)	4117 (7)	3·59 (11)
C(8)	334 (11)	1209 (9)	7074 (7)	5·72 (14)
C(9)	346 (11)	2511 (9)	6695 (8)	5·33 (13)
C(10)	−375 (8)	2709 (8)	5591 (8)	3·78 (10)
C(11)	−498 (10)	4053 (8)	5317 (9)	5·43 (12)
C(12)	−1846 (8)	−263 (8)	5585 (8)	4·84 (12)
C(13)	26 (10)	−2398 (9)	4929 (9)	5·16 (12)
C(14)	−1712 (9)	−2217 (8)	3617 (9)	5·01 (13)
O	1745 (5)	2390 (6)	4554 (6)	4·86 (8)
S(1)	429 (2)	2020 (2)	4435 (2)	3·17 (3)
S(2)	1089 (2)	155 (2)	6140 (2)	4·29 (3)

e.s.d.'s while Table 2 gives the bond lengths and angles for the non-hydrogen atoms.

Table 2. *Bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses*

C(1)—C(2)	1·584 (11)	C(5)—C(6)	1·537 (12)
C(1)—C(6)	1·549 (11)	C(7)—C(13)	1·540 (13)
C(1)—C(7)	1·569 (11)	C(7)—C(14)	1·539 (13)
C(1)—C(12)	1·539 (12)	C(8)—C(9)	1·504 (14)
C(2)—C(3)	1·561 (11)	C(8)—S(2)	1·814 (10)
C(2)—S(1)	1·879 (8)	C(9)—C(10)	1·562 (14)
C(2)—S(2)	1·822 (8)	C(10)—C(11)	1·521 (13)
C(3)—C(4)	1·514 (12)	C(10)—S(1)	1·813 (10)
C(4)—C(5)	1·560 (13)	O—S(1)	1·499 (6)
C(4)—C(7)	1·546 (12)		

C(2)—C(1)—C(6)	106·3 (6)	C(4)—C(5)—C(6)	103·7 (7)
C(2)—C(1)—C(7)	102·9 (6)	C(1)—C(6)—C(5)	103·2 (7)
C(2)—C(1)—C(12)	116·7 (6)	C(1)—C(7)—C(4)	93·2 (6)
C(6)—C(1)—C(7)	100·2 (6)	C(1)—C(7)—C(13)	115·8 (7)
C(6)—C(1)—C(12)	114·0 (7)	C(1)—C(7)—C(14)	114·0 (7)
C(7)—C(1)—C(12)	114·8 (7)	C(4)—C(7)—C(13)	114·0 (7)
C(1)—C(2)—C(3)	102·3 (6)	C(4)—C(7)—C(14)	112·6 (7)
C(1)—C(2)—S(1)	114·4 (5)	C(13)—C(7)—C(14)	107·1 (7)
C(1)—C(2)—S(2)	119·0 (5)	C(2)—S(2)—C(8)	105·6 (4)
C(3)—C(2)—S(1)	103·9 (5)	C(9)—C(8)—S(2)	114·6 (7)
C(3)—C(2)—S(2)	108·0 (5)	C(8)—C(9)—C(10)	112·8 (8)
S(1)—C(2)—S(2)	107·9 (4)	C(9)—C(10)—C(11)	111·5 (8)
C(2)—C(3)—C(4)	103·6 (7)	C(9)—C(10)—S(1)	110·7 (6)
C(3)—C(4)—C(5)	108·0 (7)	C(11)—C(10)—S(1)	106·4 (6)
C(3)—C(4)—C(7)	102·8 (7)	C(2)—S(1)—C(10)	101·7 (4)
C(5)—C(4)—C(7)	101·9 (7)	C(2)—S(1)—O	106·8 (4)
		C(10)—S(1)—O	106·0 (4)

Related literature. The S(1)→O bond distance is 1·499 (6) Å. Both the sulfoxide and the methyl groups are *cis*. The methyl group is equatorial while the sulfoxide is axial. The norbornane ring has a *synchro* twist (S++) (Acharya, Tavale & Guru Row, 1984). The molecules in the crystal are held together by van der Waals interactions.

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(2S,6R)-6-Carboxymethyl-2-ethyl-2-hydroxy-4,4-dimethylmorpholinium Bromide

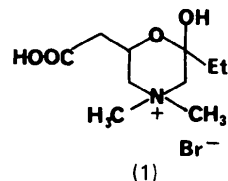BY NOELLE L. BLACKWELL, FRANK R. FRONCZEK AND RICHARD D. GANDOUR*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

Abstract. $C_{10}H_{20}NO_4^+.Br^-$, $M_r = 298·2$, orthorhombic, $P2_12_12_1$, $a = 6·976$ (2), $b = 13·603$ (2), $c = 13·674$ (4) Å, $V = 1297·7$ (8) Å^3, $Z = 4$, $D_x = 1·526$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1·54184$ Å, $\mu = 43·7$ cm^{-1}, $F(000) = 616$, $T = 298$ K, $R = 0·032$ for 1463 observations (of 1554 unique data). The molecule is a morpholinium ring in a chair conformation, containing two chiral centers with the carboxymethyl and ethyl groups *cis*. Hydrogen bonding occurs between the carboxy H atom and the Br ion with an O···Br distance of 3·218 (3) Å, and H···Br distance of 2·45 (5) Å and an angle of 158 (5)° at the H atom. A hydrogen bond also exists between the hydroxy H atom and another Br ion, with an O···Br distance of 3·323 (3) Å, and H···Br distance of 2·35 (6) Å, and an angle of 161 (4)° at the H atom.

Experimental. Colorless needles, m.p. 431–432 K, of (2S,6R)-6-carboxymethyl-2-ethyl-2-hydroxy-4,4-dimethylmorpholinium bromide [hemipropanoylcarnitinium (1)] prepared by the reaction of norcarnitine

(1)

with 1-bromo-2-butanone followed by acid hydrolysis, were crystallized from ethanol by vapor diffusion with ethyl ether. Crystal size 0·36 × 0·48 × 0·60 mm, capillary-mounted for protection from humidity, space group from systematic absences h00 with h odd, 0k0 with k odd and 00l with l odd, cell dimensions from

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