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Structure of 4-Isopropyl-6-methoxymethyl-1-methyl-7-phenylthiobicyclo[3.2.1]oct-6-en-8-ol

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Abstract. $C_{20}H_{28}O_2S$, $M_r = 332{\cdot}4$, triclinic, $P\bar{1}$, $a = 10{\cdot}29$ (2), $b = 9{\cdot}66$ (2), $c = 10{\cdot}95$ (2) Å, $\alpha = 110{\cdot}0$ (1), $\beta = 79{\cdot}7$ (1), $\gamma = 112{\cdot}2$ (1)°, $V = 946$ (6) Å^3, $Z = 2$, $D_m = 1{\cdot}15$ (2), $D_x = 1{\cdot}17$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 1{\cdot}47$ mm^{-1}, $F(000) = 360$, $T = 293$ K, final $R = 0{\cdot}055$ for 1558 observed reflections. The study establishes the regiochemistry of the cyclopentene double bond with respect to the cyclohexane ring, the isopropyl group in the *exo* configuration with respect to the bicyclo[3.2.1] framework, and the bridge hydroxyl and the cyclopentene double bond *anti* relative to the cyclohexane ring. The six-membered ring has a chair conformation. The five-membered ring exists in an envelope conformation with a 46·6° angle of pucker, *i.e.* $q_2 = 0{\cdot}465$ (6) Å and $\varphi_2 = -36{\cdot}6$ (8)° [Cremer & Pople (1975). *J. Am. Chem. Soc.* **97**, 1354–1358]. An intermolecular hydrogen bond is observed: O(1)—O(2) = 2·90 (1) Å, O(1)—H(28) = 1·00 Å (fixed) and H(28)···O(2) = 1·96 Å with O(2) at $1-x, 1-y, 1-z$.

Experimental. The title compound was prepared in the course of a project aimed at the synthesis of helminthosporal derivatives (Gray, 1983). Colourless crystals were grown from petroleum ether b.p. 333:353 K. Density by flotation. Crystal size was approximately 0·20 × 0·20 × 0·20 mm. Data were collected photographically and corrected for Lorentz–polarization effects, absorption ignored. Equi-inclination multi-film Weissenberg exposures of layers 0–2*kl*, *h*0–5*l* and *hk*0–2 were scanned by use of a microdensitometer (SERC Service, Daresbury Laboratory, England). $2\theta_{max} = 156°$. 2149 reflections; merging $R = 0{\cdot}046$ for 1558 unique data. Structure solved and refined using *SHELX*76 program system (Sheldrick, 1976). Direct-methods subprograms *EEES* and *TANG* failed to show unambiguous molecular fragments but S atom was located from Patterson synthesis and structure expanded by Fourier syntheses. Difference map at $R = 0{\cdot}087$ after anisotropic refinement of S, C, O atoms showed all H atoms near calculated positions; the weaker H peaks and stronger 'noise' peaks were of similar strength, so H atoms were included at 'riding' positions in the last cycles of block-diagonal least-squares refinement on F with U_{iso} arbitrarily set at 0·07 Å^2. Final $R = 0{\cdot}055$, $wR = 0{\cdot}083$, 208 parameters, $w = 0{\cdot}162(1 + 0{\cdot}0243F^2)^{-1}$, max. Δ/σ ratio in last cycle 0·51, max., min. heights of final difference map +0·23, −0·30 e Å^{-3}. Atomic scattering factors those of *SHELX*76.

Atomic coordinates are listed in Table 1.† Fig. 1 shows the molecule and gives the atom-numbering scheme.

† Lists of bond lengths and angles, structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43770 (14 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 and equivalent isotropic thermal parameters* (×10^3) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å^2)
S(1)	0·2341 (1)	0·0854 (1)	0·0898 (1)	50·3 (1)
O(1)	0·2767 (3)	0·5931 (4)	0·4885 (3)	60·3 (1)
O(2)	0·6646 (3)	0·3371 (4)	0·2436 (3)	56·3 (1)
C(1)	0·2132 (4)	0·3604 (5)	0·3000 (4)	45·4 (1)
C(2)	0·2013 (5)	0·4633 (5)	0·2248 (4)	53·8 (1)
C(3)	0·3433 (5)	0·5423 (6)	0·1598 (4)	57·1 (1)
C(4)	0·4701 (4)	0·6133 (5)	0·2467 (4)	44·5 (1)
C(5)	0·4565 (4)	0·5021 (5)	0·3258 (4)	40·9 (1)
C(6)	0·4376 (4)	0·3403 (5)	0·2321 (4)	57·2 (1)
C(7)	0·3001 (4)	0·2602 (5)	0·2166 (4)	41·3 (1)
C(8)	0·3160 (4)	0·4640 (5)	0·4063 (4)	48·4 (1)
C(9)	0·0681 (5)	0·2702 (6)	0·3507 (5)	63·3 (1)
C(10)	0·4945 (5)	0·7860 (5)	0·3285 (5)	54·6 (1)
C(11)	0·5472 (7)	0·8893 (6)	0·2368 (6)	80·7 (2)
C(12)	0·5989 (6)	0·8453 (6)	0·4331 (6)	69·5 (1)
C(13)	0·5581 (4)	0·2924 (5)	0·1576 (4)	46·4 (1)
C(14)	0·7820 (5)	0·2958 (6)	0·1767 (5)	66·3 (1)
C(15)	0·1283 (4)	−0·0521 (5)	0·1718 (4)	45·0 (1)
C(16)	0·0014 (5)	−0·1594 (6)	0·1212 (5)	60·6 (1)
C(17)	−0·0800 (6)	−0·2713 (6)	0·1827 (7)	87·0 (2)
C(18)	−0·0375 (6)	−0·2779 (6)	0·2926 (6)	71·0 (2)
C(19)	0·0874 (6)	−0·1723 (6)	0·3401 (5)	71·1 (1)
C(20)	0·1719 (5)	−0·0597 (6)	0·2817 (5)	57·4 (1)

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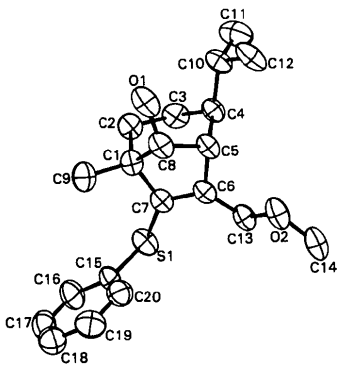

Fig. 1. *ORTEP*II diagram (Johnson, 1976) illustrating numbering scheme. Non-H ellipsoids at 50% probability level.

Related literature. Crystal structures containing the bicyclo[3.2.1] framework have been reported by Van Meerssche, Germain & Declercq (1979); Murthy, Venkatesan, Reddy & Kasturi (1982); Mehta, Rao, Suri, Cameron & Chan (1980); Duc, Fetizon, Hanna, Olesker, Pascard & Prange (1980); Yonemitsu, Nakai, Kanaoka, Karle & Witkop (1970).

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References

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
DUC, D. K. M., FETIZON, M., HANNA, I., OLESKER, A., PASCARD, C. & PRANGE, T. (1980). *J. Chem. Soc. Chem. Commun.* pp. 1209–1210.
GRAY, B. D. (1983). PhD Thesis. Univ. of Dundee, Scotland.
JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
METHA, G., RAO, K. S., SURI, S. C., CAMERON, T. S. & CHAN, C. (1980). *J. Chem. Soc. Chem. Commun.* pp. 650–652.
MURTHY, P. S., VENKATESAN, K., REDDY, S. M. & KASTURI, T. R. (1982). *Acta Cryst.* B**38**, 2055–2057.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge.
VAN MEERSSCHE, M., GERMAIN, G. & DELCERCQ, J.-P. (1979). *Acta Cryst.* B**35**, 491–493.
YONEMITSU, O., NAKAI, H., KANAOKA, Y., KARLE, I. L. & WITKOP, B. (1970). *J. Am. Chem. Soc.* **92**, 5691–5700.

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Structure of 2,2′-Biimidazole*

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Abstract. $C_6H_6N_4$, $M_r = 134{\cdot}14$, monoclinic, $P2_1/c$, $a = 5{\cdot}067$ (2), $b = 10{\cdot}786$ (3), $c = 11{\cdot}490$ (3) Å, $\beta = 102{\cdot}58$ (3)°, $V = 612{\cdot}88$ Å^3, $Z = 4$, $D_x = 1{\cdot}453$ g cm^{-3}, λ(Mo $K\alpha_1$) $= 0{\cdot}70926$ Å, $\mu = 0{\cdot}92$ cm^{-1}, $F(000) = 280$, room temperature, final $R = 0{\cdot}054$ for 578 observed reflections [$I > 3\sigma(I)$] out of 806 independent reflections. There are ribbons of hydrogen-bonded molecules parallel to the a axis and the length of this axis is equal to the width of the molecule. Each molecule is joined to its neighbors by two hydrogen bonds on each side. The hydrogen-bond distances are N(1)···N(2) = 2·865 (5) and N(3)···N(4) = 2·879 (8) Å. This rigid arrangement accounts for the low solubility of 2,2′-biimidazole in anything but an acid solution. The five atoms in each ring are coplanar within 0·002 Å but the two rings are rotated 4·6° about the central C–C bond.

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Experimental. 2,2′-Biimidazole prepared by a modification of a method reported by Debus (1958) and by Fieselmann, Hendrickson & Stucky (1978). Anhydrous ammonia was bubbled through a 20% solution of glyoxal, carefully keeping the solution temperature below 293 K. After 3–4 h a copious light-tan precipitate was obtained. Precipitate collected by vacuum filtration and washed with water and acetone. Crystallization from water or 0·1% NaOH (1 g l^{-1}) gives a white material. Crystals for the X-ray structure determination obtained by slow cooling of an aqueous solution. Long needle parallel to a axis, dimensions 0·06 × 0·08 × 1·3 mm. CAD-4 diffractometer, θ–2θ scans. θ-scan range (1·2 + 0·34tanθ)°. Scan speed