Structure of (+)-(2*S*,3*S*,5*S*)-3-Hydroxy-5-isopropenyl-2-methylcyclohexanone

BY A. L. SPEK AND A. J. M. DUISENBERG

Vakgroep Algemene Chemie, afdeling Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

AND H. L. A. VAN DEN HEUVEL, R. BOER ROOKHUIZEN AND R. BOSCH

Department of Internal Medicine, Clinical Research Group for Bonemetabolism, University of Utrecht, Catharijnesingel 101, 3511 GV Utrecht, The Netherlands

Abstract. $C_{10}H_{16}O_2$, $M_r = 168\cdot24$, orthorhombic, $P2_12_12_1$, $a = 6\cdot407$ (1), $b = 8\cdot954$ (1), $c = 16\cdot865$ (1) Å, $U = 967\cdot5$ (2) Å^3, $Z = 4$, $D_x = 1\cdot155$ g cm^{-3}, λ(Mo $K\alpha$) = $0\cdot71073$ Å, $\mu = 0\cdot7$ cm^{-1}, $F(000) = 368$, $T = 295$ K, $R = 0\cdot048$ for 1769 reflections with $I \geq 2\cdot5\sigma(I)$. The cyclohexanone ring has a chair conformation with the isopropenyl and methyl groups in equatorial and the hydroxyl group in axial positions. The molecules are hydrogen bonded into infinite chains running in the **a** direction.

Introduction. The title compound was synthesized as part of the study on the stereochemical outcome of the selective reduction of α,β-epoxyketones with reducing agents. The structure of the product was characterized initially with conventional spectroscopic techniques. However, neither NMR nor IR results appeared to be unambiguous with respect to the stereochemistry of the 2-methyl substituent. An X-ray study was undertaken to establish the conformational details of the six-membered ring and its substituents as a basis for future research.

Experimental. Crystals were obtained by recrystallization from purified *n*-hexane. X-ray data for a plate-shaped colourless crystal ($0\cdot14 \times 0\cdot65 \times 0\cdot75$ mm), glued on top of a glass fibre, were collected on an Enraf–Nonius CAD-4F diffractometer using Zr-filtered Mo $K\alpha$ radiation. Lattice parameters and their estimated standard deviations were derived from the setting angles of 25 SET4 (de Boer & Duisenberg, 1984) reflections ($8\cdot6 < \theta < 13\cdot5°$). The space group was determined from the observed systematic absences as $P2_12_12_1$. A total of 4725 reflections $\{\theta < 27\cdot5°;\ \omega/2\theta$ scan; $\Delta\omega = [0\cdot55 + 0\cdot35\tan(\theta)]°;\ -8 < h < 8,\ 0 < k < 11,\ -21 < l < 21\}$ were scanned. Two reference reflections (223, $\overline{2}2\overline{3}$) showed a small linear decay of 3% during the 25 h of X-ray exposure time. The intensities were corrected for Lp and the small decay but not for

absorption, and merged ($R_{int} = 0\cdot02$) into a set of 2220 unique reflections. Variance $\sigma^2(I)$ was calculated based on counting statistics plus a term $(PI)^2$, where $P (= 0\cdot01)$ is the instability constant as derived from the excess variance in the reference reflections (McCandlish, Stout & Andrews, 1975). The 1769 reflections with $I > 2\cdot5\sigma(I)$ were used in the subsequent analysis. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1986). Refinement was carried out by full-matrix least-squares techniques on F with *SHELX*76 (Sheldrick, 1976) on a MicroVAX-II. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms, except for those on the methyl group, could be located from a difference Fourier map, and their positions refined. Methyl hydrogen atoms were refined with fixed geometry with respect to their carrier atom. Two separate isotropic thermal parameters were used for the two groups of hydrogen atoms. Convergence was reached at $R = 0\cdot048$ ($wR = 0\cdot065$), $w^{-1} = \sigma^2(F) + 0\cdot0016F^2$, 1769 reflections, 153 parameters, $S = 0\cdot34$; $(\Delta/\sigma)_{max} = 0\cdot076$, $0\cdot41 > \Delta\rho > -0\cdot27$ e Å^{-3}. Residual peaks near the methyl group C(10) indicate some rotational disorder of the hydrogen atoms. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Scattering factors of Cromer & Mann (1968) were used. Geometrical calculations and illustrations were performed with the programs *PLATON* and *PLUTON* of the *EUCLID* package (Spek, 1982).

Discussion. Fig. 1 shows the molecule with atom numbering. Bond lengths and angles have been

---

Table 1. *Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms, with their e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

|	x	y	z	$U_{eq}(\text{Å}^2)$
O(1)	0·7164 (2)	0·3773 (2)	0·2739 (1)	0·0541 (5)
O(2)	1·2833 (3)	0·3373 (2)	0·2305 (1)	0·0500 (5)
C(1)	0·8405 (3)	0·4503 (2)	0·2346 (1)	0·0409 (6)
C(2)	1·0305 (3)	0·5227 (3)	0·2706 (1)	0·0441 (6)
C(3)	1·2266 (3)	0·4915 (2)	0·2201 (1)	0·0459 (6)
C(4)	1·1918 (3)	0·5257 (3)	0·1332 (1)	0·0476 (7)
C(5)	1·0068 (3)	0·4374 (3)	0·0994 (1)	0·0440 (6)
C(6)	0·8092 (3)	0·4751 (3)	0·1469 (1)	0·0491 (7)
C(7)	1·0584 (4)	0·4868 (4)	0·3572 (2)	0·0633 (9)
C(8)	0·9704 (3)	0·4613 (3)	0·0118 (1)	0·0521 (7)
C(9)	0·9531 (5)	0·3431 (4)	−0·0370 (2)	0·067 (1)
C(10)	0·9535 (6)	0·6159 (4)	−0·0173 (2)	0·078 (1)
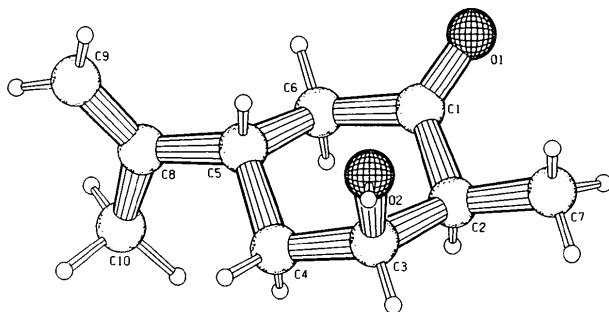
Fig. 1. View of the molecule with atom numbering.

assembled in Table 2. The cyclohexanone ring exhibits a chair conformation (Boeyens, 1978) with puckering parameters $Q = 0·543$ (2) Å, $\theta = 7·9$ (2) and $\varphi = 205$ (2)° (Cremer & Pople, 1975). The methyl group assumes an equatorial position, making an angle of 71·1 (2)° with the normal to the Cremer & Pople plane. The molecules are linked *via* a hydrogen bond [O(2)—H(1)···O(1), with O(2)··· O(1) = 2·892 (2), O(2)—H(1) = 0·74 (3), H(1)···O(1)

Table 2. *Bond lengths (Å) and bond angles (°)*

O(1)—C(1)	1·224 (3)	C(3)—C(4)	1·514 (3)
O(2)—C(3)	1·438 (2)	C(4)—C(5)	1·535 (3)
C(1)—C(2)	1·507 (3)	C(5)—C(6)	1·536 (3)
C(1)—C(6)	1·508 (3)	C(5)—C(8)	1·512 (3)
C(2)—C(3)	1·543 (3)	C(8)—C(9)	1·345 (4)
C(2)—C(7)	1·506 (4)	C(8)—C(10)	1·472 (4)
O(1)—C(1)—C(2)	122·4 (2)	C(3)—C(4)—C(5)	111·7 (2)
O(1)—C(1)—C(6)	121·5 (2)	C(4)—C(5)—C(6)	109·3 (2)
C(2)—C(1)—C(6)	116·0 (2)	C(4)—C(5)—C(8)	114·2 (2)
C(1)—C(2)—C(3)	111·0 (2)	C(6)—C(5)—C(8)	110·6 (2)
C(1)—C(2)—C(7)	113·2 (2)	C(1)—C(6)—C(5)	111·7 (2)
C(3)—C(2)—C(7)	113·5 (2)	C(5)—C(8)—C(9)	120·0 (3)
O(2)—C(3)—C(2)	108·2 (2)	C(5)—C(8)—C(10)	118·0 (2)
O(2)—C(3)—C(4)	110·4 (2)	C(9)—C(8)—C(10)	122·0 (2)
C(2)—C(3)—C(4)	112·2 (2)		

= 2·200 (3) Å and O(2)—H(1)···O(1) = 156 (3)°] into an infinite chain running in the *a*-axis direction.

References

BOER, J. L. DE & DUISENBERG, A. J. M. (1984). *Acta Cryst.* **A40**, C410.
BOEYENS, J. A. C. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.
CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
McCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). *SHELXS86.* Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.
SPEK, A. L. (1982). *The EUCLID Package.* In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.

Structure of α-D-Mannosido-naphtho-18-crown-6:* A Potent Host for Chiral Recognition

BY KINGA SUWIŃSKA

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01 224 Warsaw, Poland

Abstract. (Methyl 2,3-dideoxy-4,6-O-isopropylidene-mannopyranosido)-naphtho-18-crown-6, $C_{28}H_{38}O_{10}$,

---
* IUPAC name: methyl 4,6-O-isopropylidene-2,3-O-{2,3-naphthylenebis(oxyethyleneoxyethylene)}mannopyranoside.

$M_r = 534·6$, monoclinic $P2_1$, $a = 11·606$ (2), $b = 8·126$ (4), $c = 14·977$ (2) Å, $\beta = 102·38$ (2)°, $V = 1379$ (2) Å^3, $Z = 2$, $D_x = 1·287$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 0·909$ cm^{-1}, $F(000) = 572$, $T = 298$ K, final $R = 0·035$ for 2108 reflections. In its