Structure of Cyclohexyl(4-pyridyl)methanol

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Abstract. $C_{12}H_{17}NO$, $M_r = 191.27$, monoclinic, $P2_1/c$, $a = 9.418$ (2), $b = 11.433$ (4), $c = 10.364$ (3) Å, $\beta = 101.55$ (3)°, $V = 1093.4$ (6) Å^3, $Z = 4$, $D_m = 1.16$ (by flotation), $D_c = 1.162$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.0686 mm^{-1}. $R = 0.077$ for 1077 observed reflections. The dihedral angle between the least-squares planes of the cyclohexyl ring, which is in a slightly distorted chair conformation, and the pyridine ring is 79.9 (2)°. There is no hydrogen bonding through the alcohol group.

Introduction. Bispyridinium cyclohexylcarbonyl monooximes are compounds with antidotal properties in poisoning by highly toxic organophosphorus compounds (Deljac, Bregovec, Maksimović, Rakin, Markov, Radičević & Binenfeld, 1979). It seemed of interest to find out whether a correlation exists between the structure and physiological activity in this group of compounds. For this purpose structure analysis of cyclohexyl(4-pyridyl)methanol (Bregovec, Deljac & Binenfeld, 1979), one of the intermediates in the preparation of the related compounds, has been performed.

Intensities were collected from a prismatic crystal on an automatic Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation and the ω–2θ scanning technique with a 2θ scan width of $(0.8 + 0.2 \tan \theta)°$ and a variable scan rate. Intensities of 1924 reflections were measured up to $\sin \theta/\lambda = 0.64$ Å^{-1}, 1089 of which were above the 3σ level and used in the crystal-structure analysis. Absent reflections $0k0$, $k \neq 2n$ and $h0l$, $l \neq 2n$, confirmed the space group $P2_1/c$. Corrections were made for Lorentz and polarization factors. The structure was solved by direct methods using the program *MULTAN* 80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All non-H atoms were obtained from the E

map calculated with the 256 largest E values ($E > 1.43$). All subsequent calculations were performed with the XRAY system (Stewart, 1976). Isotropic least-squares refinement of the non-H atoms gave an R of 0.176. H atoms were located from a difference map and included in the refinement with fixed isotropic temperature factors U of the corresponding C atoms increased by 0.015 Å^2 and an R of 0.135 was obtained. A full-matrix refinement with anisotropic thermal parameters for the non-H and isotropic (with fixed U_H) for the H atoms, but varying separately the parameters of the non-H and H atoms, gave an R of 0.106. Inspection of the structure factors revealed that five strong low-order reflections were subject to extinction and seven others to experimental errors (451, 661, $\bar{7}61$, 462, $\bar{1},11,2$, 673, $\bar{1}93$ reflections with observed/calculated structure factors as follows: 2.8/15.1, 4.5/24.2, 3.7/14.6, 1.8/7.6, 5.5/12.5, 3.3/10.5, 7.7/13.7). Continued refinement omitting these 12 reflections reduced R to 0.077.* An improvement was evident in the bond lengths and angles involving H atoms, while the positions of the non-H atoms were practically unchanged. The scattering factors of Cromer & Mann (1968) were used for the non-H and those of Stewart, Davidson & Simpson (1965) for the H atoms. The final atomic coordinates are listed in Table 1. All parameter shifts of the non-H atoms in the final cycle were $<0.1\sigma$. Calculations were performed on a Univac 1110 computer, at the University Computing Centre, Zagreb.

Table 1. *Fractional positional parameters* ($\times 10^4$; $\times 10^3$ *for* H) *and equivalent isotropic temperature factors of the non-hydrogen atoms* ($\times 10^2$) *computed by the expression* $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

The numbering of C atoms and their bonded H atoms is the same. Letters *A* and *E* denote axial and equatorial H atoms, respectively.

	x	*y*	*z*	U_{eq} (Å^2)
O	8189 (4)	2163 (4)	8949 (4)	6·5 (2)
N	9722 (5)	−1417 (5)	6852 (6)	6·8 (2)
C(1)	5908 (6)	1176 (5)	8284 (5)	4·8 (2)
C(2)	4908 (6)	508 (5)	7197 (6)	5·5 (2)
C(3)	3507 (6)	140 (6)	7621 (6)	6·4 (3)
C(4)	2722 (7)	1184 (7)	8005 (7)	7·7 (3)
C(5)	3703 (7)	1903 (6)	9087 (7)	7·1 (3)
C(6)	5102 (7)	2229 (5)	8675 (7)	6·4 (3)
C(7)	7331 (6)	1529 (5)	7876 (6)	5·1 (2)
C(8)	8150 (5)	489 (6)	7503 (5)	5·0 (2)
C(9)	8262 (6)	270 (6)	6219 (6)	5·9 (2)
C(10)	9033 (7)	−691 (6)	5952 (6)	6·4 (3)
C(11)	9600 (7)	−1209 (7)	8103 (7)	6·9 (3)
C(12)	8818 (6)	−287 (6)	8449 (6)	6·0 (2)
H(Ox)	855 (5)	169 (5)	942 (5)	
H(1A)	624 (5)	62 (4)	911 (4)	
H(2A)	462 (5)	98 (5)	632 (5)	
H(2E)	533 (5)	−7 (5)	700 (5)	
H(3A)	379 (5)	−31 (5)	848 (5)	
H(3E)	295 (5)	−14 (5)	688 (5)	
H(4A)	237 (6)	176 (5)	711 (5)	
H(4E)	198 (6)	110 (5)	831 (5)	
H(5A)	400 (6)	136 (5)	995 (5)	
H(5E)	321 (6)	245 (5)	944 (5)	
H(6A)	497 (6)	281 (5)	809 (5)	
H(6E)	579 (6)	275 (5)	946 (5)	
H(7)	704 (5)	215 (4)	709 (4)	
H(9)	781 (5)	93 (4)	552 (5)	
H(10)	908 (5)	−83 (5)	509 (5)	
H(11)	1000 (6)	−185 (5)	873 (5)	
H(12)	893 (5)	−12 (5)	933 (5)	

Discussion. Fig. 1 shows a perspective view of the molecule with the atomic numbering. Bond lengths and angles are listed in Table 2. Endocyclic torsion angles of the cyclohexyl ring and torsion angles relevant for the conformational situation through the bridge atom C(7) are given in Table 3.

The cyclohexyl ring has a slightly distorted chair conformation with the puckering parameters according to Cremer & Pople (1975) $Q = 0.569$ (6) Å, $\theta = 2.3$ (6), $\varphi = 57$ (16)° (described as $^1C_4$, Boeyens, 1978). The mean values of the endocyclic bond lengths,

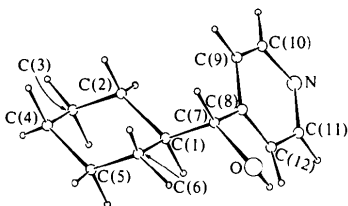Fig. 1. Perspective drawing of the molecule viewed along |010|.

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

C(1)–C(2)	1·521 (8)		C(7)–H(7)	1·07 (5)
C(2)–C(3)	1·531 (9)		O–H(Ox)	0·76 (5)
C(3)–C(4)	1·499 (10)		C(7)–C(8)	1·508 (8)
C(4)–C(5)	1·540 (9)		C(8)–C(9)	1·380 (9)
C(5)–C(6)	1·510 (10)		C(9)–C(10)	1·375 (10)
C(6)–C(1)	1·521 (9)		C(10)–N	1·319 (9)
C(1)–C(7)	1·538 (8)		N–C(11)	1·345 (10)
C(7)–O	1·434 (7)		C(11)–C(12)	1·374 (10)
			C(12)–C(8)	1·378 (8)

C(1)–C(2)–C(3)	111·5 (5)		H(7)–C(7)–O	106 (2)
C(2)–C(3)–C(4)	110·9 (5)		H(7)–C(7)–C(1)	106 (3)
C(3)–C(4)–C(5)	111·3 (5)		H(7)–C(7)–C(8)	113 (3)
C(4)–C(5)–C(6)	110·8 (6)		C(7)–O–H(Ox)	105 (4)
C(5)–C(6)–C(1)	113·0 (5)		C(7)–C(8)–C(9)	122·1 (5)
C(6)–C(1)–C(2)	109·0 (4)		C(7)–C(8)–C(12)	120·6 (5)
C(6)–C(1)–C(7)	112·0 (5)		C(8)–C(9)–C(10)	119·0 (6)
C(2)–C(1)–C(7)	111·8 (5)		C(9)–C(10)–N	124·4 (6)
C(1)–C(7)–O	107·8 (5)		C(10)–N–C(11)	116·5 (6)
C(1)–C(7)–C(8)	112·4 (5)		N–C(11)–C(12)	122·8 (6)
O–C(7)–C(8)	111·1 (4)		C(11)–C(12)–C(8)	120·0 (6)
			C(12)–C(8)–C(9)	117·2 (6)

Ranges/means of bond lengths (Å) and angles (°) involving H atoms in the cyclohexyl (cyh) and pyridine (py) rings

C–H(cyh)	0·82 (5)–1·13 (5)/0·98 (5)
C–H(py)	0·92 (5)–1·07 (5)/0·97 (5)
H–C–C(cyh)	103 (4)–120 (4)/110 (3)
H–C–H(cyh)	95 (4)–125 (5)/105 (5)
H–C–C(py)	114 (3)–125 (3)/119 (3)

Table 3. *Selected torsion angles* (°)

C(6)–C(1)–C(2)–C(3)	−56·7 (6)		C(6)–C(1)–C(7)–C(8)	179·3 (5)
C(1)–C(2)–C(3)–C(4)	57·9 (6)		C(2)–C(1)–C(7)–O	179·2 (4)
C(2)–C(3)–C(4)–C(5)	−55·5 (7)		C(6)–C(1)–C(7)–O	56·5 (6)
C(3)–C(4)–C(5)–C(6)	54·0 (8)		O–C(7)–C(8)–C(12)	50·0 (7)
C(4)–C(5)–C(6)–C(1)	−54·8 (7)		C(1)–C(7)–C(8)–C(12)	−70·9 (6)
C(5)–C(6)–C(1)–C(2)	56·0 (7)		H(Ox)–O–C(7)–C(1)	81 (4)
C(2)–C(1)–C(7)–C(8)	−58·0 (6)		H(Ox)–O–C(7)-C(8)	−42 (4)

bond angles and absolute values of torsional angles of 1·521 (7) Å, 110·9 (6) and 56·0 (6)° respectively are close to the corresponding cyclohexane values (Davis & Hassel, 1963; Altona & Sundaralingam, 1970; Kahn, Fourme, André & Renaud, 1973; Bucourt, 1974). C(7) is, as expected, in an equatorial position, and as it is chiral and the space group is centrosymmetric, the compound crystallizes as a racemic mixture.

The pyridine ring is planar within 0·015 (7) Å and the mean bond lengths and angles in it are as follows: C–C = 1·377 (5), C–N = 1·331 (15) Å, C–C–C = 118·7 (9), C–C–N = 123·6 (9)°. The bridge angle C(1)–C(7)–C(8) is 112·4 (5)°. The interplanar angle between the mean planes of both rings is 79·9 (2)°.

There is no intermolecular contact shorter than the sums of the van der Waals radii, so the hydroxyl group

does not form any O···O hydrogen bonds, on account of steric reasons.

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Structure of 4,11,17,24,29,32-Hexaoxa-1,14-diazatetracyclo[12.12.8.0⁵,¹⁰.0¹⁸,²³]-tetratriaconta-5,7,9,18,20,22-hexaene

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Abstract. $C_{26}H_{36}N_2O_6$, $M_r = 472 \cdot 6$, monoclinic, $P2_1/c$, $Z = 4$; at 138 K: $a = 11 \cdot 512$ (6), $b = 8 \cdot 493$ (4), $c = 27 \cdot 35$ (1) Å, $\beta = 112 \cdot 16$ (2)°, $V = 2476 \cdot 5$ Å³, $D_c = 1 \cdot 267$ Mg m⁻³; at 296 K: $a = 11 \cdot 565$ (7), $b = 8 \cdot 700$ (5), $c = 27 \cdot 33$ (2) Å, $\beta = 111 \cdot 62$ (3)°, $V = 2556 \cdot 4$ Å³, $D_c = 1 \cdot 228$ Mg m⁻³; $F(000) = 1016$. All intensity data were collected at 138 ± 2 K. The structure was solved by direct methods and refined by blocked-full-matrix least-squares methods to a final R value of $0 \cdot 066$ for all 5087 independent reflections with $2\theta(Cu) \leq 150°$.

Introduction. The complexation selectivity pattern of the title compound, cryptand $2_B.2_B.2$, is markedly different from that of the parent compound 2.2.2 (Dietrich, Lehn & Sauvage, 1973; Lehn, 1973; Taylor, Springer & Ott, 1981). The structure determination of cryptand $2_B.2_B.2$ was undertaken in order to determine the effects of the benzo rings on the cavity size and conformation of the ligand.

The compound was purchased from PCR Chemical Corporation and used without further purification.

Crystals were obtained from an aqueous solution in a thermal-gradient apparatus. A crystal $0 \cdot 08 \times 0 \cdot 25 \times 0 \cdot 30$ mm was used for data collection and unit-cell determination at $138 \pm 2K$ using a Nonius CAD-4 automatic diffractometer controlled by a PDP8/e computer. The space group was determined uniquely as $P2_1/c$ from systematic absences. The unit-cell dimensions were determined by a least-squares refinement of 48 reflections chosen from all octants of reciprocal space using Cu $K\alpha_1$ radiation ($\lambda = 1 \cdot 54051$ Å). A total of 5087 independent reflections with $2\theta(Cu) \leq 150°$, 3869 with $I \geq 2\sigma(I)$, were measured using θ–2θ scans and Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1 \cdot 5418$ Å). The scan angle and receiving aperture were $(0 \cdot 90 + 0 \cdot 14 \times \tan \theta)°$ and $(3 \cdot 50 + 0 \cdot 86 \tan \theta)$ mm, respectively. The receiving aperture, located 173 mm from the crystal, had a height of 4 mm. The maximum scan time per reflection was 90 s. For each reflection two thirds of the time was spent scanning the peak and the remaining one third of the time scanning the left and right backgrounds.

No significant changes were observed for the