

Structure of 1-[1-(1-Phenylethyl)cyclohexyl]piperidine

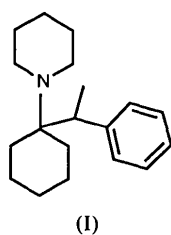
BY PHIRTU SINGH AND LOUIS A. JONES

Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

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Abstract. $C_{19}H_{29}N$, $M_r = 271.45$, monoclinic, $P2_1/n$, $a = 6.371(1)$, $b = 16.085(3)$, $c = 15.704(4)$ Å, $\beta = 94.27(2)^\circ$, $V = 1604.9(6)$ Å³, $Z = 4$, $D_x = 1.12$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.60$ cm⁻¹, $F(000) = 600$, $T = 298$ K, $R = 0.0499$ for 1307 reflections with intensities $I \geq 1.5\sigma(I)$. The conformation of the molecule is similar to the previously reported conformation of PCP [1-(1-phenylcyclohexyl)piperidine] with the piperidine ring occupying the axial site on the cyclohexane ring in both molecules. It is different, however, from that observed in PCP hydrochloride where an inversion of the cyclohexane ring from one chair conformation to another puts the piperidine ring in an equatorial position. As in PCP, the exocyclic N—C bond, N(1)—C(6) [1.489(4) Å], is slightly longer than the endocyclic N—C bonds [N(1)—C(1) = 1.465(3) and N(1)—C(5) = 1.457(4) Å].

Experimental. 1-[1-(1-Phenylethyl)cyclohexyl]piperidine (ethyl PCP), (I), was synthesized as reported elsewhere (Jones, Beaver, Schmoeger, Ort & Leander, 1981) and crystallized by slow evaporation of a concentrated methanol solution. A crystal



fragment measuring approximately $0.42 \times 0.35 \times 0.30$ mm was used for X-ray data collection by using Mo $K\alpha$ radiation on a Nicolet R3m/ μ diffractometer equipped with a graphite crystal monochromator. Unit-cell dimensions were obtained by a least-squares refinement of the setting angles of 22 reflections in the range $20 \leq 2\theta \leq 30^\circ$. The intensity data were collected by the $\theta/2\theta$ scan technique in the range $3 \leq 2\theta \leq 43^\circ$ at variable scan speeds between 4 and $29.3^\circ \text{ min}^{-1}$ depending on intensity; range in hkl : $h, 0 \rightarrow 6$; $k, 0 \rightarrow 16$; $l, -16 \rightarrow 16$. Stationary backgrounds were measured for half of scan time on each

side of a peak. Two standards (020, 004) measured after every 48 reflections to monitor the instrument and crystal stability showed very little variation ($\pm 1.7\%$); 2133 reflections were measured which yielded 1307 reflections with intensities $I \geq 1.5\sigma(I)$, $R_{\text{int}} = 0.008$. The intensities were corrected for background and Lorentz and polarization effects.

The structure was solved by direct methods and difference Fourier techniques and refined by the blocked-cascade least-squares refinement technique (Sparks, 1961). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma_F^2 + 0.0006F^2)$. The non-H atoms were refined with anisotropic thermal parameters; the H atoms, except for those belonging to the methyl group, were placed in expected positions and allowed to move in the riding mode. The methyl hydrogens were located from a difference Fourier calculation and refined isotropically. The final $R = 0.0499$, $wR = 0.0566$, goodness-of-fit $S = 1.42$, maximum $\Delta/\sigma = 0.06$, difference electron density excursion in the final ΔF map = $\pm 0.15 \text{ e } \text{Å}^{-3}$. An extinction correction was applied to the amplitudes in the form $F' = F_c/(1 + gF_c^2/\sin 2\theta)^{0.25}$, where F' is the corrected amplitude, and g is the extinction coefficient whose final value is $7.4(1) \times 10^{-6}$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974,

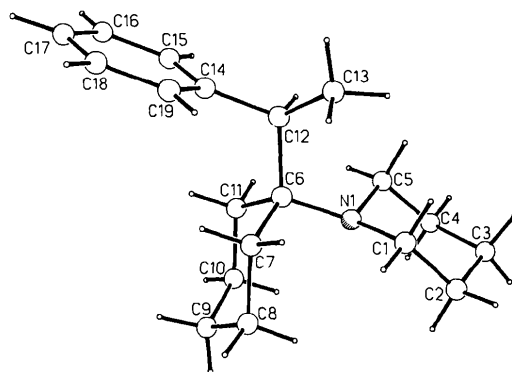


Fig. 1. Configuration of ethyl PCP showing the atom-numbering scheme and the axial and equatorial substituents on the cyclohexane ring.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N(1)	1714 (3)	8204 (1)	158 (1)	41 (1)
C(1)	3731 (4)	8131 (2)	-227 (2)	52 (1)
C(2)	3397 (4)	7764 (2)	-1114 (2)	60 (1)
C(3)	1895 (5)	8284 (2)	-1676 (2)	62 (1)
C(4)	-118 (5)	8428 (2)	-1250 (2)	58 (1)
C(5)	328 (4)	8767 (2)	-347 (2)	54 (1)
C(6)	1620 (4)	8238 (2)	1101 (2)	40 (1)
C(7)	3181 (4)	7616 (2)	1529 (2)	44 (1)
C(8)	2786 (4)	6716 (2)	1237 (2)	54 (1)
C(9)	575 (5)	6444 (2)	1396 (2)	64 (1)
C(10)	-1057 (4)	7051 (2)	1002 (2)	56 (1)
C(11)	-579 (4)	7931 (2)	1309 (2)	46 (1)
C(12)	1966 (4)	9141 (2)	1474 (2)	44 (1)
C(13)	3985 (5)	9556 (2)	1222 (2)	59 (1)
C(14)	1761 (4)	9209 (2)	2430 (2)	46 (1)
C(15)	-97 (5)	9470 (2)	2747 (2)	57 (1)
C(16)	-289 (5)	9536 (2)	3617 (2)	71 (1)
C(17)	1376 (6)	9338 (2)	4188 (2)	74 (2)
C(18)	3246 (5)	9097 (2)	3884 (2)	69 (1)
C(19)	3450 (5)	9035 (2)	3020 (2)	57 (1)

Table 2. Bond lengths (\AA), bond angles and selected torsion angles ($^\circ$)

N(1)—C(1)	1.465 (3)	N(1)—C(5)	1.457 (4)
N(1)—C(6)	1.489 (4)	C(1)—C(2)	1.514 (4)
C(2)—C(3)	1.506 (4)	C(3)—C(4)	1.508 (4)
C(4)—C(5)	1.526 (4)	C(6)—C(7)	1.531 (4)
C(6)—C(11)	1.543 (4)	C(6)—C(12)	1.574 (4)
C(7)—C(8)	1.532 (4)	C(8)—C(9)	1.514 (4)
C(9)—C(10)	1.524 (4)	C(10)—C(11)	1.519 (4)
C(12)—C(13)	1.527 (4)	C(12)—C(14)	1.520 (4)
C(14)—C(15)	1.383 (4)	C(14)—C(19)	1.395 (4)
C(15)—C(16)	1.385 (5)	C(16)—C(17)	1.375 (5)
C(17)—C(18)	1.371 (5)	C(18)—C(19)	1.377 (5)
C(1)—N(1)—C(5)	109.9 (2)	C(1)—N(1)—C(6)	121.0 (2)
C(5)—N(1)—C(6)	116.8 (2)	N(1)—C(1)—C(2)	110.1 (2)
C(1)—C(2)—C(3)	111.2 (3)	C(2)—C(3)—C(4)	110.5 (3)
C(3)—C(4)—C(5)	111.2 (2)	N(1)—C(5)—C(4)	110.2 (2)
N(1)—C(6)—C(7)	109.8 (2)	N(1)—C(6)—C(11)	107.7 (2)
C(1)—C(6)—C(11)	105.6 (2)	N(1)—C(6)—C(12)	112.9 (2)
C(7)—C(6)—C(12)	111.8 (2)	C(11)—C(6)—C(12)	108.7 (2)
C(6)—C(7)—C(8)	113.6 (2)	C(7)—C(8)—C(9)	111.0 (2)
C(8)—C(9)—C(10)	111.3 (3)	C(9)—C(10)—C(11)	110.7 (2)
C(6)—C(11)—C(10)	113.3 (2)	C(6)—C(12)—C(13)	113.9 (2)
C(6)—C(12)—C(14)	114.4 (2)	C(13)—C(12)—C(14)	111.1 (2)
C(12)—C(14)—C(15)	121.1 (2)	C(12)—C(14)—C(19)	121.5 (3)
C(15)—C(14)—C(19)	117.4 (3)	C(14)—C(15)—C(16)	121.3 (3)
C(15)—C(16)—C(17)	120.3 (3)	C(16)—C(17)—C(18)	119.2 (3)
C(17)—C(18)—C(19)	120.8 (3)	C(14)—C(19)—C(18)	121.0 (3)
N(1)—C(6)—C(12)—C(13)	-53.9 (3)	N(1)—C(6)—C(12)—C(14)	176.8 (2)
C(7)—C(6)—C(12)—C(13)	70.5 (3)	C(7)—C(6)—C(12)—C(14)	-58.8 (3)
C(11)—C(6)—C(12)—C(13)	-173.3 (2)	C(11)—C(6)—C(12)—C(14)	57.4 (3)
C(6)—C(12)—C(14)—C(15)	-97.4 (3)	C(13)—C(12)—C(14)—C(15)	132.0 (3)
C(7)—C(6)—N(1)—C(1)	-41.1 (3)	C(7)—C(6)—N(1)—C(5)	-179.5 (2)
C(11)—C(6)—N(1)—C(1)	-155.5 (2)	C(11)—C(6)—N(1)—C(5)	66.1 (3)

Vol. IV, pp. 72–102). Computations were performed on a Data General Microclipse computer using Sheldrick's crystallographic program package *SHELXTL* (Sheldrick, 1985). The refined structure was plotted by using the *SHELXTL* graphics package with the aid of a Tektronix terminal and a Zeta-8 plotter. A perspective drawing of the molecule is shown in Fig. 1. The fractional coordinates for non-H atoms are given in Table 1 and the bond distances and angles involving non-H atoms are given in Table 2.*

Related literature. Crystal structures of the following compounds related to ethyl PCP have been reported previously: 1-(1-phenylcyclohexyl)piperidine, commonly known as PCP (Singh, Jones & Couch, 1988), PCP hydrochloride (Argos, Barr & Weber, 1970), 1-piperidine-1-benzylcyclohexane (Ducruix & Pascard-Billy, 1974), 1-(1-phenyl-*t*-4-*tert*-butyl-*r*-cyclohexyl)piperidine (Briard, Roques, Kamenka, Geneste, Declercq & Germain, 1982; Geneste, Kamenka, Roques, Declercq & Germain, 1981), 2-phenyl-2-piperidinoadamantane (Eaton, Houk, Watkins & Fronczek, 1983), *cis*-1-phenyl-3-piperidinocyclohexane-1-ol hydrochloride (Kimura & Okabayashi, 1986) and *cis*-3-phenyl-3-piperidiniumbicyclo[3.1.0]hexane 2,4-dinitrobenzenesulfonate (de Costa, George, Burke, Rafferty, Contreras, Mick, Jacobsen & Rice, 1988). In addition,

the Cambridge Crystallographic Database (Allen *et al.*, 1979) lists two PCP salts containing CuCl_4^{2-} and NiCl_4^{2-} anions, respectively (Nelson & Simonsen, 1981), and a number of compounds containing the cyclohexane-piperidine moiety embedded in a more complex molecular structure.

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* Lists of anisotropic thermal parameters, H-atom coordinates and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53293 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Complexation of Water by a 4-Phenylpyridohemispherand

BY PIETER JELLE DIJKSTRA, HERMAN JOHANNES DEN HERTOOG JR AND DAVID NICOLAAS REINHOUT

Laboratory of Organic Chemistry, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

AND SYBOLT HARKEMA

Laboratory of Chemical Physics, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

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Abstract. 25,26-Dimethoxy-9,23-dimethyl-4-phenyl-13,16,19-trioxa-27-azoniatetracyclo[19.3.1.1^{2.6}.1^{7.11}]-heptacosa-1(25),2,4,6(27),7,9,11(26),21,23-nonaene perchlorate-ethanol-water (1/1/1), $C_{33}H_{36}NO_5^+ \cdot ClO_4^- \cdot C_2H_5OH \cdot H_2O$, $M_r = 690.2$, orthorhombic, $Pca2_1$, $a = 27.747$ (5), $b = 9.572$ (3), $c = 12.866$ (4) Å, $V = 3417$ (3) Å³, $Z = 4$, $D_x = 1.39$ g cm⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å, $\mu = 1.69$ cm⁻¹, $F(000) = 1464$, $T = 100$ (5) K, final $R = 6.5\%$ for 2915 observed reflections. The water molecule is complexed in the cavity of the macrocycle with hydrogen bonds to the polyethylene oxy atoms adjacent to the outer phenyl rings of the terphenyl unit. The O atom of the water molecule accepts hydrogen bonds from the pyridinium proton and the OH proton of the ethanol molecule. The HClO₄ proton is transferred to the pyrido nitrogen.

Experimental. The title compound was prepared by dissolving 50 mg (0.09 mmol) of the 4-phenylpyridohemispherand (Dijkstra, den Hertog, van Steen, Zijlstra, Skowronska-Ptasinska, Reinhoudt, van Eerden & Harkema, 1987) in 2 ml of ethanol and the slow addition of 0.5 ml of 70% HClO₄. Slow evaporation of solvent afforded colorless crystals of the complex suitable for X-ray diffraction, m.p. 496 K (dec.).

Intensities were measured at 100 (5) K on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Lattice parameters determined by least squares from 25 centered reflections $6 < \theta < 13^\circ$. A total of 2915 independent reflections up to $\theta = 25^\circ$ ($0 \leq h \leq 33$, 0

$\leq k \leq 12$, $0 \leq l \leq 16$) were measured in the $\theta/2\theta$ scan mode [scan speed 0.046° s⁻¹, scan width (θ) 1.5°]; 2021 considered observed [$F_o^2 > 2\sigma(F_o^2)$]. The intensity loss of three standard reflections measured every hour was less than 1.3%, correction for which was applied. No absorption correction.

H atoms of the macrocycle were placed in calculated positions and treated as riding on their parent atoms (bond distance 0.95 Å, $B_{iso} = 4.0$ Å²), with the exception of the methyl hydrogens. These atoms and the H atoms of the water molecule were found from a difference Fourier synthesis. Positions of these atoms were refined. Hydrogens of the ethanol group could not be located (probably due to the large thermal motions). These hydrogens were not included in the refinement. In order to fix the origin in the c direction, the z parameter of the Cl atom has been fixed.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares. Weights for each reflection in the refinement (on F) were calculated from $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$; the value of the instability factor p was determined as 0.04. The number of parameters refined was 457: scale factor, isotropic extinction factor [final value 2.4 (7) $\times 10^{-9}$], positional and anisotropic thermal parameters for the non-H atoms positional parameters of some H atoms.

Refinement converged at $R = 6.5\%$, $wR = 6.3\%$, $S = 1.64$, $(\Delta/\sigma)_{max} = 0.2$. Largest peak on the final difference Fourier map 0.54 e Å⁻³ (in the perchlorate ion). All calculations were performed using *SDP*