

1-(Piperidinoacetyl)piperidine (PACp)

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Abstract. $C_{12}H_{22}N_2O$, $M_r = 210.4$, tetragonal, $P4_21c$, $a = 15.505$ (2), $c = 10.477$ (1) Å, $V = 2518$ Å³, $Z = 8$, $D_c = 1.11$ g cm⁻³, m.p. 65.5°C, $\mu(\text{Cu } K\alpha) = 5.6$ cm⁻¹. $R = 0.074$ for 663 observed counter reflexions. Both piperidyl rings are in chair conformations and the torsion angle N(1)–C(1)–C(2)–N(2) of the dicarbon bridge is 65.1°. Conformations of the title molecule and its protonated cation are compared.

Introduction. PACp is a parent compound for a series of derivatives containing two piperidyl rings joined by a dicarbon bridge. These compounds have been extensively investigated by Professor M. Wiewiórowski in his studies on conformational effects and intramolecular catalysis. These studies are supported by X-ray structure investigations and the present work is part of this programme.

Crystals of PACp for X-ray analysis were obtained by recrystallization from diethyl ether solution. From symmetry and from systematic absences on X-ray photographs the space group was established as $P4_21c$. Unit-cell constants were determined by a least-squares fit of the setting angles of 15 diffractometer reflexions. A Syntex $P2_1$ computer-controlled diffractometer was used to measure the intensity data for a single crystal ground* to $0.44 \times 0.23 \times 0.19$ mm and sealed in a glass capillary. Graphite-monochromatized Cu $K\alpha$ radiation and a variable θ – 2θ scan were applied in a 2θ range up to 115° to collect 952 reflexions of which 665 had $I \geq 1.96\sigma(I)$ and were considered observed. Structure factors and normalized structure factors were derived from the intensities in the usual way, the absorption and extinction corrections being neglected. The structure was solved with *MULTAN* using 111 E 's ≥ 1.42 for which 1316 Σ_2 relationships were generated. 16 phase sets were derived using one special and two general multiresolution phases, and an E map calculated for the set with the best figures of merit revealed the

* For this purpose a 'wet grinding' technique was applied. The crystal was put on a watch glass, several drops of appropriate solvent (water in this case) were added and the watch glass was set in rapid vibrational motion. When it reached the desired dimensions, the crystal was extracted from the solvent and dried with a piece of filter paper.

positions of all non-hydrogen atoms. Full-matrix least-squares refinement of their positional and isotropic thermal parameters converged at $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.158$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with counter weights $w = \sigma^{-2}$. The vibrational model was then changed to an anisotropic one and a similar least-squares refinement was attempted. The refinement, however, could not be advanced: the R factor oscillated around 0.155, the shift/ σ values did not converge, and the model became chemically unreasonable. At this point the weighting scheme was changed to: $w = (|F_o|/F_{low})^2$ for $|F_o| < F_{low}$; $w = 1$ for $F_{low} \leq |F_o| \leq F_{high}$; $w = (F_{high}/|F_o|)^2$ for $|F_o| > F_{high}$; with $F_{low} = 6.6$ and $F_{high} = 17.8$. The refinement then converged at $R = 0.114$. H atom coordinates were generated on the assumption of tetrahedral angles and C–H distances of 1.05 Å; the contri-

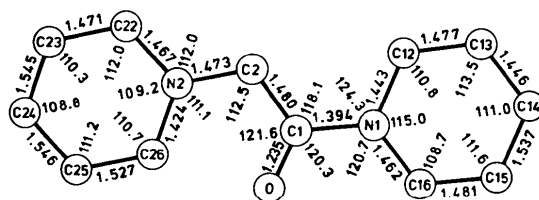


Fig. 1. Non-hydrogen atom bond distances (Å) and angles (°). E.s.d.'s for bonds and angles are 0.011–0.018 Å and 0.7–1.0° respectively.

Table 1. Final fractional non-hydrogen atom coordinates ($\times 10^4$)

	x	y	z
N(1)	1344 (5)	2018 (5)	1914 (7)
C(12)	1248 (7)	2016 (7)	3284 (9)
C(13)	671 (7)	1310 (7)	3696 (11)
C(14)	–148 (9)	1303 (8)	3036 (12)
C(15)	–19 (8)	1332 (8)	1583 (10)
C(16)	537 (7)	2064 (7)	1197 (10)
C(1)	2133 (7)	1950 (6)	1282 (9)
O	2164 (5)	1994 (5)	106 (7)
C(2)	2920 (7)	1832 (6)	2060 (9)
N(2)	2925 (5)	1005 (5)	2752 (8)
C(22)	3697 (7)	906 (6)	3548 (11)
C(23)	3647 (8)	140 (7)	4371 (10)
C(24)	3546 (7)	–682 (9)	3552 (15)
C(25)	2784 (7)	–553 (6)	2620 (12)
C(26)	2870 (7)	296 (7)	1892 (10)

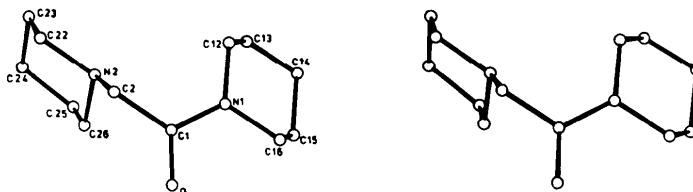


Fig. 2. Stereoscopic view of the PAcP molecule.

butions of the H atoms (with $B_{\text{iso}} = 6 \text{ \AA}^2$) were allowed for in subsequent cycles of full-matrix refinement although no attempt was made to refine their parameters. Final full-matrix least-squares refinement carried out with the two most intense reflexions excluded from the data set led to $R = 0.074$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.104$. The number of observations per parameter in the final refinement was 4.88.

All calculations were performed using original (*Syntex XTL Operation Manual*, 1973) and locally modified Syntex XTL programs on a Nova 1200 mini-computer.

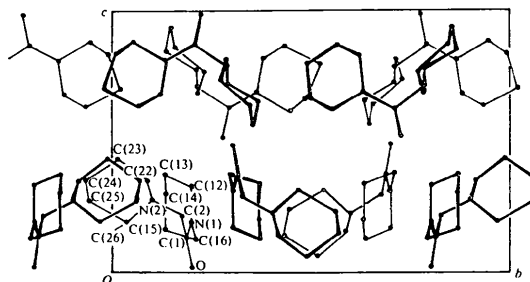
Fractional non-hydrogen atom coordinates are given in Table 1.*

Discussion. Bond lengths and angles in the PAcP molecule are shown in Fig. 1. Their values are comparable with those found in PAcP.H⁺ (Jaskólski, Gdaniec & Kosturkiewicz, 1977) and the differences may be attributed to the bond-length errors due to librational effects and to the lower accuracy of the present results. The latter in turn may be accounted for by the small number of observed data (note: m.p. 65.5°C) and their poor quality (glass capillary). The mean piperidyl C—C and C—N distances are 1.504 and 1.449 Å respectively. The molecular conformation can be seen from Fig. 2, which is an ORTEP (Johnson, 1965) stereodrawing of the PAcP molecule, and from Table 2 which gives the values of selected torsion angles: both piperidyl rings have chair conformations; the set of atoms C(2), C(1), O, N(1), C(12), and C(16) is roughly planar; the conformation around the N(2)—C(2) bond is staggered with the C(2)—C(1) bond *trans* to one of the N—C piperidyl bonds and the N(2)—C(2) bond itself is in an equatorial position. All these findings are similar to those encountered in PAcP.H⁺. The conformational differences between the PAcP.H⁺ cation and the PAcP molecule (Table 2) are limited to small ($\sim 10^\circ$) rotations around the N(1)—C(1) and N(2)—C(2) bonds and primarily to a rotation of about 132° around the C(1)—C(2) bond. The conformation

* Lists of structure factors, anisotropic thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33762 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Comparison of selected torsion angles ($^\circ$) in PAcP and PAcP.H⁺

	PAcP	PAcP.H ⁺
C(13)—C(12)—N(1)—C(1)	-122.4	-118.0
C(15)—C(16)—N(1)—C(1)	120.9	117.1
C(12)—N(1)—C(1)—O	-176.3	172.9
C(12)—N(1)—C(1)—C(2)	2.7	-9.5
C(16)—N(1)—C(1)—O	5.6	-1.9
C(16)—N(1)—C(1)—C(2)	-175.0	175.7
N(1)—C(1)—C(2)—N(2)	65.1	-161.6
O—C(1)—C(2)—N(2)	-115.5	16.1
C(22)—N(2)—C(2)—C(1)	-178.4	-168.7
C(26)—N(2)—C(2)—C(1)	59.2	67.8
C(23)—C(22)—N(2)—C(2)	172.1	-179.1
C(25)—C(26)—N(2)—C(2)	-174.3	178.9

Fig. 3. Projection of the structure down the *a* axis.

around the C(1)—C(2) bond observed in the case of PAcP.H⁺ facilitates hydrogen-bonded-dimer formation while the corresponding conformation in the free-base molecule enables the lone pair at N(2) to be moved away from O and the molecule as a whole to be more compact.

The molecular packing scheme is presented in Fig. 3. All intermolecular non-hydrogen atom distances are greater than the sums of the appropriate van der Waals radii.

I wish to thank Professor M. Wiewiórowski for suggesting the problem and Mgr D. Mickiewicz for supplying the crystals.

References

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