# Structure of 1,2,2,4,6,6-Hexamethyl-4-piperidinol*

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**Abstract.** $C_{11}H_{23}NO$, orthorhombic, $Ccm2_1$, $a = 8.711$ (2), $b = 12.960$ (3), $c = 10.400$ (3) Å, $Z = 4$, $V = 1174.1$ Å$^3$, $D_x = 1.046$ Mg m$^{-3}$, $F(000) = 416$, $\mu r(Cu$ $K\alpha) = 0.25$. 668 independent reflexions were measured. The structure was solved by direct methods and refined to $R = 0.055$. The piperidine ring adopts a chair conformation with an axial hydroxyl group. Neighbouring molecules are joined by intermolecular $O-H\cdots N$ bonds. The influence of a substituent in position 4 on the molecular conformation is discussed.

**Introduction.** The structures of some pentamethyl-piperidine derivatives have been determined with the objective of elucidating the influence of substituents in position 4 on the molecular conformation (Cygler, Markowicz, Skolimowski & Skowroński, 1980; Cygler, 1980; Cygler, Dobrynin & Perrin, 1980). We now report our work on the title compound (PMPM), which completes this series of studies.



PMPM
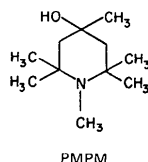
Colourless, prismatic crystals were obtained by slow sublimation. The systematic absences observed on the Weissenberg photographs (*hkl*: $h + k = 2n + 1$; 0*kl*: $l = 2n + 1$) indicated space groups $Ccm2_1$ or $Ccmm$; the latter is ruled out because the special positions in this space group with $Z = 4$ have the symmetry *mm* or $2/m$, which is impossible for this molecule. The crystal chosen for data collection, with dimensions $0.45 \times 0.28 \times 0.25$ mm, was sealed in a Lindemann capillary. Intensities were measured on a CAD-4 diffractometer at 253 K, with monochromatized Cu $K\alpha$ radiation. During the scan, the speed of the detector ($2\theta$) was $1.33$ times that of the crystal ($\omega$). Precise lattice constants were calculated from angular settings of 25

reflexions. 688 independent reflexions were measured out to $\theta = 70°$, of which 612 with $I > 2.5\sigma(I)$ were treated as observed. No absorption correction was applied.

The structure was solved by direct methods (*MULTAN*; Main, Lessinger, Woolfson, Germain & Declercq, 1976). On the best $E$ map two images of the molecule, translated by about $1.5$ Å, could be recognized. $R$ calculated for each was greater than $0.50$ and trials of successive refinement and Fourier synthesis failed. A model, constructed by averaging the positional parameters of corresponding atoms in the two images, led to $R = 0.39$. Full-matrix least-squares refinement of atomic parameters reduced $R$ to $0.13$. On the difference map all H atoms, except those (three) lying on the mirror plane, were located. Positions of the

Table 1. *Final fractional coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and mean isotropic temperature factors, with standard deviations in parentheses*

|         | $x$        | $y$       | $z$         | $U$ (Å$^2$)  |
|---------|------------|-----------|-------------|--------------|
| N(1)    | 2271 (2)   | 0         | 7586 (5)    | 0.061 (2)    |
| O(2)    | 1767 (5)   | 979 (2)   | 8220 (5)    | 0.066 (2)    |
| O(3)    | 44 (5)     | 939 (2)   | 8418 (6)    | 0.064 (2)    |
| O(4)    | −594 (5)   | 0         | 9066 (0)*   | 0.062 (3)    |
| O(41)   | −141 (4)   | 0         | 10392 (5)   | 0.084 (3)    |
| O(11)   | 3906 (8)   | 0         | 7263 (9)    | 0.137 (7)    |
| O(21)   | 2037 (10)  | 1888 (4)  | 7269 (7)    | 0.136 (5)    |
| O(22)   | 2597 (8)   | 1263 (4)  | 9477 (7)    | 0.104 (4)    |
| O(41)   | −2341 (7)  | 0         | 8958 (9)    | 0.128 (6)    |
| H(111)  | 469 (8)    | 0         | 808 (5)     | 0.123 (6)    |
| H(112)  | 406 (7)    | 63        | 682 (5)     | 0.123 (6)    |
| H(211)  | 324        | 210       | 715         | 0.123 (6)    |
| H(212)  | 165        | 179       | 637         | 0.123 (6)    |
| H(213)  | 171        | 256       | 776         | 0.123 (6)    |
| H(221)  | 245        | 61        | 1041        | 0.123 (6)    |
| H(222)  | 370        | 147       | 940         | 0.123 (6)    |
| H(223)  | 204        | 192       | 990         | 0.123 (6)    |
| H(31)   | −55 (6)    | 94 (4)    | 741 (7)     | 0.123 (6)    |
| H(32)   | −16 (7)    | 176 (3)   | 898 (5)     | 0.123 (6)    |
| H(411)  | −278 (8)   | 0         | 803 (4)     | 0.123 (6)    |
| H(412)  | −271 (6)   | 62 (2)    | 950 (4)     | 0.123 (6)    |
| H(O1)   | −101 (10)  | 0         | 1093 (10)   | 0.123 (6)    |

* Fixes the origin.

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missing H atoms were calculated from geometrical considerations and all were included in the refinement. To increase the reflexions/parameters ratio, the methyl groups in position 2 were refined as rigid bodies and a common temperature factor was assigned to all H atoms. For methyl groups in positions 1 and 4, which lie on the mirror plane, 'soft' constraints were introduced (by DFIX cards with $\sigma = 0.05$, *SHELX* program; Sheldrick, 1976). At convergence $R$ was 0.055.* The weighting scheme was $w^{-1} = \sigma^2(F) + kF^2$, with $k = 0.00002$. The highest peak on the final difference map was $0.14$ e Å$^{-3}$. The atomic parameters are listed in Table 1.

**Discussion.** In the solid state molecules of PMPM possess mirror symmetry. They adopt a chair conformation for the piperidine ring. Methyl groups at N and C(4) take equatorial positions and the hydroxyl group is axial. Distances and angles within the molecule are shown in Fig. 1 and torsion angles in Fig. 2. The ring is distorted by 2,4,6 axial interactions. The distances between axial substituents and corresponding distances in the ring are: $C_{ax}\cdots C_{ax} = 3.274$ (7); $C(2)\cdots C(2^i) = 2.538$ (4); $C_{ax}\cdots O(41) = 3.045$ (7); $C(2)\cdots C(4) = 2.572$ (5) Å. The CNC and C(2)—C(3)—C(4) angles are enlarged to $116.0$ (3) and $117.2$ (4)° respectively, the ring being flattened. The mean torsion angle in the ring is $\langle\varphi\rangle = 51.0°$. The spatial arrangement of the methyl groups at C(2) and

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35375 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
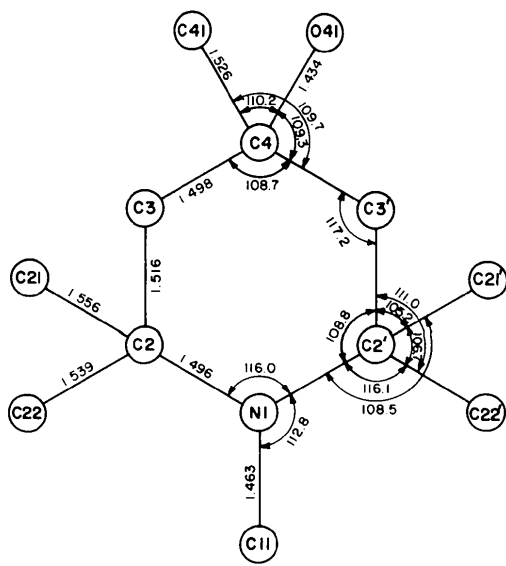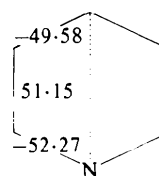
Fig. 2. Torsion angles (°) in the piperidine ring. Standard deviations were estimated to be less than 0.6°.

$C(2^i)$ is similar to that in related piperidine derivatives and is discussed in detail by Cygler, Markowicz, Skolimowski & Skowroński (1980).

The packing of the molecules is shown in Fig. 3. The neighbouring molecules related by a twofold screw axis are joined by intermolecular O—H···N hydrogen bonds. The distances and angle are: O···N = 2.941 (7), O—H = 0.94 (9), H···N = 2.04 (10) Å, ∠O—H···N = 159 (7)°. Hydrogen-bonded molecules form chains parallel to $z$. Other intermolecular interactions are normal.

A summary of the influence of equatorial substituents in position 4 on the ring distortion is given in Table 2. When the substituent changes from ethynyl through methyl and vinyl to *tert*-butyl, the axial hydroxyl group is forced more towards the ring and approaches more closely the axial methyl groups. It pushes the methyl groups outside the ring, which, in turn, causes a flattening of the ring near the N atom. It also causes a decrease of the mean torsion angle of the ring. The puckering of the ring near C(4) is similar in the first three derivatives but is larger for the *tert*-butyl one. In the latter case there is a strong interaction between the *tert*-butyl group and the H atoms of the ring methylene groups. It is clear from Table 2 that the steric effects of methyl and vinyl groups on the molecular geometry are quite similar.

In the solid state the molecules of all compounds discussed above are packed in such a way that the hydroxyl group of one molecule is directed toward the N atom of an adjacent molecule and is placed in the free space between three equatorial methyl groups. The
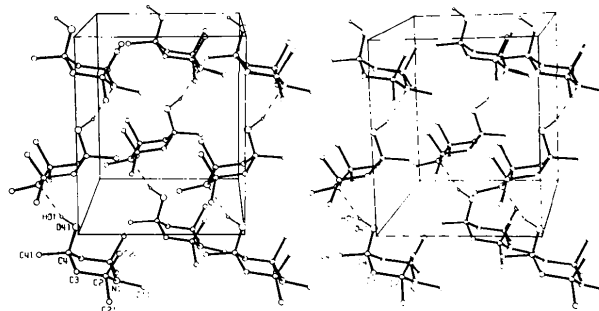
Fig. 1. Bond distances (Å) and valence angles (°). Standard deviations of bond lengths and angles are in the ranges 0.004–0.008 Å and 0.2–0.4°, respectively.

Fig. 3. Stereoview of the packing of the molecules. The origin is in the lower left-hand corner, a is horizontal, c is up the page and b is away from the reader.

Table 2. *The influence of substituents in position 4 on the distortion of the piperidine ring in pentamethyl-piperidine derivatives*

Standard deviations of individual torsion angles are in the range 0·6–0·8°.

| Compounds | Mean torsion angle | Mean CCCC angle | Mean CNCC angle | $C_{ax} \cdots C_{ax}$ | $C_{ax} \cdots O$ | $\angle CNC$ | Inter-molecular $O \cdots N$ | Number of hydrogen bonds | m.p. |
|---|---|---|---|---|---|---|---|---|---|
| PMPE[a] | 51·6° | 49·0° | 54·5° | 3·214 (5) Å | 3·14 (1) Å | 116·6 (3)° | 3·074 (5) Å | 2 | 395 K |
| PMPM[b] | 51·0 | 59·6 | 52·3 | 3·271 (7) | 3·05 (1) | 116·0 (4) | 2·941 (7) | 1 | 366 |
| PMPV[c] | 50·5 | 49·0 | 51·8 | 3·264 (6) | 3·08 (1) | 116·8 (3) | 3·240 (6) | − | 343 |
| PMPTB[d] | 50·0 | 51·6 | 48·2 | 3·383 (5) | 3·00 (1) | 118·7 (3) | 3·161 (5) | − | 324 |

(a) 4-Ethyl-1,2,2,6,6-pentamethyl-4-piperidinol (Cygler, 1980).
(b) 1,2,2,4,6,6-Hexamethyl-4-piperidinol (this paper).
(c) 1,2,2,6,6-Pentamethyl-4-vinyl-4-piperidinol (Cygler, Dobrynin & Perrin, 1980).
(d) 4-*tert*-Butyl-1,2,2,6,6-pentamethyl-4-piperidinol (Cygler, Markowicz, Skolimowski & Skowroński, 1980).

intermolecular distance between O and N atoms depends on the size and orientation of the substituent at C(4) (Table 2). In the case of ethynyl and methyl substituents this distance is close enough for the formation of a hydrogen bond. The vinyl substituent, which is intramolecularly hydrogen-bonded to the hydroxyl O atom, as well as the *tert*-butyl substituent shield the O atom, precluding a close approach by the N atom. Consequently, in these two compounds a hydrogen bond is not formed. The melting points listed in Table 2 provide a good indication of the differences in intermolecular interactions.

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# (−)-Iodolupinane Perchlorate

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**Abstract.** $C_{10}H_{19}IN^{+} \cdot ClO_{4}^{-}$, orthorhombic, $P2_{1}2_{1}2_{1}$, $a = 7\cdot961$ (2), $b = 12\cdot504$ (3), $c = 14\cdot112$ (4) Å, $Z = 4$, $D_c = 1\cdot79$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 2·5 mm$^{-1}$. The structure was solved by the heavy-atom method and refined to $R = 0\cdot047$. The iodomethyl group is axially oriented with respect to the *trans*-quinolizidine nucleus. The ammonium N atom forms hydrogen bonds with two $ClO_4^{-}$ O atoms.

**Introduction.** This work is part of a series of studies on the conformations of substituted lupinine molecules.

The protonation of bislupinine esters leads to an inversion of the *trans*-quinolizidine ring and results in a *cis* system with the $-CH_2R$ group in the equatorial position (I) (Sadykov, Aslanov & Kushmuradov, 1975). It was our interest to see whether similar configurational changes might occur on protonation of