

Fig. 2 shows the packing in the unit cell.

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References

- DE TITTA, G. T., EDMONDS, J. W., LANGS, D. A. & HAUPTMAN, H. (1975). *Acta Cryst.* **A31**, 472–479.
 FRAY, G. I. & SAXTON, R. G. (1978). *The Chemistry of Cyclooctatetraene and its Derivatives*. Cambridge Univ. Press.
 GIACOVAZZO, C. (1976). *Acta Cryst.* **A32**, 74–82.

- HAUPTMAN, H. & GREEN, E. A. (1976). *Acta Cryst.* **A32**, 45–49.
 HELLWINKEL, D. & HAAS, G. (1979). *Justus Liebigs Ann. Chem.* pp. 145–149.
 HELLWINKEL, D., REIFF, G. & NYKODYM, V. (1977). *Justus Liebigs Ann. Chem.* pp. 1013–1025.
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210–213.
 IRNGARTINGER, H. & REIBEL, W. R. K. (1981). *Acta Cryst.* **B37**, 1724–1728.
 KAY, M. I., OKAYA, Y. & COX, D. E. (1971). *Acta Cryst.* **B27**, 26–33.
 MARTIN, R. H. (1974). *Angew. Chem.* **86**, 727–738.
 THULIN, B. & WENNERSTRÖM, O. (1977). *Tetrahedron Lett.* pp. 929–930.

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Structure of 4-Ethynyl-1,2,2,6,6-pentamethyl-4-piperidinol*

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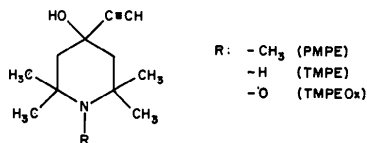
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Abstract. $C_{12}H_{21}NO$, monoclinic, $P2_1/c$, $a = 13.744$ (3), $b = 7.477$ (2), $c = 11.477$ (3) Å, $\beta = 76.68$ (5)°, $V = 1147.3$ Å³, $D_x = 1.131$ Mg m⁻³, $Z = 4$, $F(000) = 432$, $\mu(Cu K\alpha) = 0.15$. The structure was solved by direct methods and refined to $R = 0.053$ for 1489 independent reflexions with $I > 3\sigma(I)$. The molecule exists in a distorted chair conformation with the methyl group equatorial at the N atom and with an equatorial ethynyl group. Two weak intermolecular O—H...N and $\equiv C-H...O$ hydrogen bonds are formed.

Introduction. 2,2,6,6-Tetramethylpiperidine derivatives form simple overcrowded systems with strong steric interactions. Substituents in position 4 lead to additional strain and cause a decrease of the energy barrier between chair and twist or boat conformations of the ring. The hydroxyl substituent in position 4 may form an intramolecular O—H...N bond and in that way stabilize the non-chair conformation of the ring. However, the existence of such a conformation stabilized by an intramolecular hydrogen bond was established only in solution (Lyle, 1957; Brière, Lemaire, Rasset & Dunand, 1970; Cygler, Markowicz, Skolimowski & Skowroński, 1980).

In our earlier studies we have investigated 4-ethynyl-2,2,6,6-tetramethyl-4-piperidinol, TMPE (Cygler, Grabowski, Skolimowski & Skowroński, 1978), and 4-ethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, TMPEOx (Cygler, 1979). Both molecules exist in the solid state in a chair conformation. The ring is more distorted than in the case of 2,6-diaxial interactions only (*e.g.*, Ruben, Zalkin & Templeton, 1974; De Camp, Mićović & Pelletier, 1974) and shows the greatest flexibility at the methylene groups (positions 3 and 5). In both compounds the hydroxyl groups adopt equatorial positions and form strong intermolecular hydrogen bonds, which have some influence on the ring distortion (Cygler *et al.*, 1978).

To elucidate the effect of substituents at the N atom on the ring conformation we have studied the title compound (PMPE) with a methyl group in position 1.



Colourless, prismatic crystals were obtained by slow sublimation. The crystal (0.3 × 0.2 × 0.2 mm) chosen for X-ray measurements was sealed in a Lindemann capillary. Intensities were measured on a CAD-4 diffractometer at 253 K with monochromatized $Cu K\alpha$

* The Conformation of the Piperidine Ring. III. Part II: Cygler (1979).

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

	x	y	z	$U_{eq}^*/U(\text{\AA}^2)$
C(11)	8662 (3)	95 (6)	5099 (4)	0.050 (2)
N(1)	7904 (1)	-968 (3)	4695 (2)	0.033 (1)
C(2)	7166 (2)	189 (3)	4268 (2)	0.035 (2)
C(3)	6336 (2)	-1026 (4)	4022 (3)	0.037 (2)
C(4)	6683 (2)	-2595 (4)	3174 (2)	0.033 (1)
C(5)	7507 (2)	-3595 (4)	3593 (3)	0.037 (2)
C(6)	8356 (2)	-2484 (4)	3888 (2)	0.036 (1)
C(21)	7606 (3)	1395 (5)	3172 (3)	0.047 (2)
C(22)	6668 (3)	1429 (5)	5290 (3)	0.048 (2)
C(61)	9130 (3)	-1929 (6)	2758 (3)	0.046 (2)
C(62)	8894 (3)	-3754 (5)	4584 (3)	0.051 (2)
C(41)	5820 (2)	-3823 (4)	3236 (3)	0.042 (2)
C(411)	5135 (2)	-4787 (5)	3315 (3)	0.055 (2)
O(41)	7001 (1)	-1911 (3)	1984 (2)	0.039 (1)
H(111)	834 (3)	99 (5)	574 (3)	0.065 (12)
H(112)	923 (2)	78 (5)	435 (3)	0.068 (10)
H(113)	911 (3)	-63 (6)	551 (4)	0.077 (14)
H(31)	593 (2)	-160 (3)	480 (2)	0.031 (7)
H(32)	579 (2)	-28 (4)	383 (2)	0.047 (7)
H(51)	715 (2)	-425 (4)	432 (3)	0.029 (8)
H(52)	788 (2)	-457 (4)	294 (2)	0.040 (8)
H(211)	789 (2)	67 (4)	246 (3)	0.062 (9)
H(212)	706 (3)	218 (5)	300 (3)	0.064 (11)
H(213)	824 (3)	214 (5)	322 (3)	0.055 (10)
H(221)	649 (3)	74 (5)	600 (4)	0.079 (12)
H(222)	598 (2)	200 (4)	511 (3)	0.052 (10)
H(223)	711 (2)	235 (5)	556 (3)	0.060 (9)
H(611)	953 (3)	-299 (5)	227 (3)	0.071 (11)
H(612)	964 (3)	-123 (6)	294 (4)	0.113 (16)
H(613)	883 (3)	-129 (6)	219 (4)	0.094 (14)
H(621)	919 (2)	-489 (3)	404 (2)	0.038 (6)
H(622)	841 (3)	-412 (4)	538 (3)	0.058 (9)
H(623)	955 (3)	-327 (5)	470 (3)	0.061 (11)
H(411)	451 (2)	-562 (3)	337 (2)	0.051 (6)
H(O1)	724 (2)	-283 (4)	140 (3)	0.063 (10)

* For non-hydrogen atoms $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

radiation. The cell parameters were determined by least squares from angular settings of 25 reflexions. Of the 2291 independent reflexions measured out to $\theta = 75^\circ$, with the counter (2θ) moving at the same speed as the crystal (ω), 1489 had $I > 3\sigma(I)$ and were treated as observed. No absorption correction was applied.

The structure was solved by direct methods (Sheldrick, 1976). The E map with the highest figure of merit revealed all the nonhydrogen atoms. The structure was refined by full-matrix least squares. A difference Fourier map clearly showed all the H atoms. Refinement continued with isotropic temperature factors for the H atoms and converged with $R = 0.053$.* The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35968 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

weighting scheme $w^{-1} = \sigma^2(F) + kF^2$ was used, with $k = 0.0001$ in the last few cycles ($R_w = 0.053$). The highest peak on the final difference map was 0.2 e \AA^{-3} . All calculations were performed with the program *SHELX* (Sheldrick, 1976). Neutral-atom scattering factors were taken from Cromer & Mann (1968). Final atomic parameters are given in Table 1.

Discussion. PMPE exists in the crystal in a chair conformation. The methyl group at N(1) and the ethynyl group at C(4) are equatorial, while the hydroxyl group is axial. The bond lengths and valence angles are shown in Fig. 1 and the torsion angles in Fig. 2. The ring is distorted by 2,4,6 axial interactions, similarly as in TMPE and TMPEOx. The distances between axial substituents and the corresponding distances in the ring are as follows: $C(21) \cdots C(61) = 3.214 (6)$, $C(2) \cdots C(6) = 2.556 (4)$; $C(21) \cdots O(41) = 3.030 (4)$, $C(2) \cdots C(4) = 2.596 (4)$; $C(61) \cdots O(41) = 3.247 (4)$, $C(6) \cdots C(4) = 2.615 (4) \text{ \AA}$. The asymmetry parameter (Duax & Norton, 1975) of the ring relative to the plane of symmetry through N(1) and C(4) is $C_s^N = 3.51^\circ$. The ring is flattened as compared to the ideal chair form. The puckering near N(1) is similar to

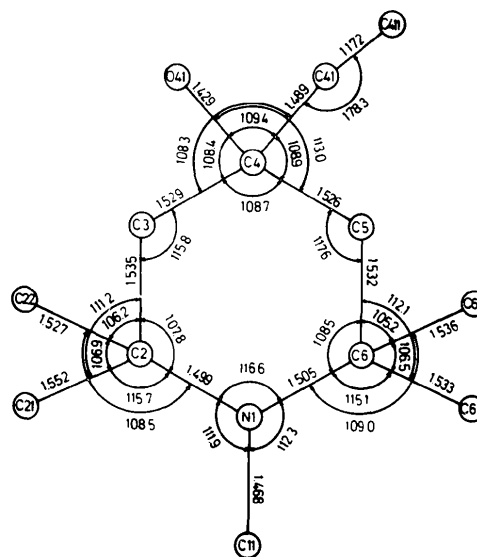


Fig. 1. Bond lengths (\AA) and valence angles ($^\circ$). The standard deviations are in the ranges $0.004\text{--}0.006 \text{ \AA}$ and $0.1\text{--}0.3^\circ$ respectively.

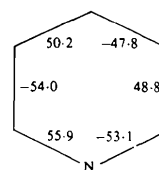


Fig. 2. Torsion angles ($^\circ$) in the piperidine ring. Standard deviations are estimated to be less than 0.6° .

that found in the *N,N'*-bis(2,2,6,6-tetramethyl-4-piperidyl)succinamide dihydrate molecule with an equatorial H atom at the N (DTMP; Ruben, Zalkin & Templeton, 1974), while in the case of axial substituents (TMPE, DTMP molecules with axial H atoms) the torsion angles in that part of the ring are about 10° smaller.

The change of the substituent at the N atom has an effect on the positions of the methyl groups at C(2) and C(6). The equatorial methyl groups move away from the N atom with increasing bulkiness of the substituent [$\angle C_{eq}-C-N = 105.7(5)^\circ$ in TMPE, $107.6(3)^\circ$ in TMPEOx and $108.7(3)^\circ$ in PMPE]. The positions of the axial methyl groups seem to be dependent on the position of the substituent rather than on its bulkiness.

The interaction of the methyl group at N(1) with the surrounding methyl groups in PMPE is responsible for the decrease of about 3° of the C(2)-N(1)-C(6) angle in comparison with the TMPE and DTMP molecules. The packing of the molecules in the unit cell is shown in Fig. 3. The distances between the hydroxyl group and the N atom of a molecule related by a *c* glide plane [$O \cdots N = 3.075(3)$, $H \cdots N = 2.16(3)$ Å, $\angle O-H \cdots N = 159(3)^\circ$] indicate the formation of a weak hydrogen bond.

Closer approach of the molecules is hindered by the interaction of the hydroxyl group with the equatorial methyl groups [shortest $H \cdots H$ contacts are 2.29 (5) and 2.49 (5) Å]. The O atom is also in close contact with the $\equiv C-H$ group of a molecule related by a twofold screw axis. The corresponding distances and the angle are: $C \cdots O = 3.424(4)$, $H \cdots O = 2.41(3)$ Å, $\angle C-H \cdots O = 162(2)^\circ$. However, the $H \cdots O$ distance is close to the sum of the van der Waals radii, so the interaction is rather weak. In both TMPE and TMPEOx the same type of interaction has been found with $H \cdots O$ distances slightly shorter [2.20 (9) and 2.29 (3) Å respectively], definitely indicating hydrogen bonds. Similar interactions of the $\equiv C-H \cdots O$ type are often found in nucleosides, where an $H \cdots O$ distance as long as 2.41 Å was reported (Hillen, Egert, Lindner & Gassen, 1978).

The conformation of the hydroxyl and ethynyl groups found in this structure, where the influence of hydrogen bonds seems to be of secondary importance, shows a preference of the ethynyl group for the equatorial position. This preference is, however, not pronounced and the conformation may easily change, as was found in the crystal structures of TMPE and TMPEOx. These molecules can form strong hydrogen bonds in the equatorial direction where the steric hindrance of the methyl groups is much lower. The

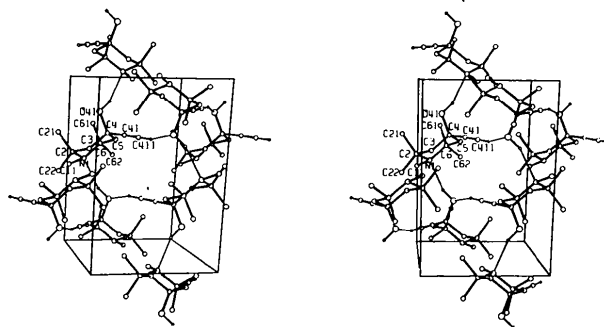


Fig. 3. Stereoview of the packing of the molecules. The origin is at the lower left-hand corner; *b* is horizontal, *c* is up the page and *a* towards the reader.

hydroxyl groups are forced to take equatorial positions and $N \cdots H-O$ bonds are formed with $N \cdots O \sim 2.8$ Å. In TMPE the H atom at the N is also forced to assume the axial position. Such a possibility is blocked in PMPE by the methyl group at N(1), which strongly prefers an equatorial position.

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References

- BRIÈRE, R., LEMAIRE, H., RASSAT, A. & DUNAND, J. J. (1970). *Bull. Soc. Chim. Fr.* p. 4220.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
 CYGLER, M. (1979). *Acta Cryst.* B35, 195–197.
 CYGLER, M., GRABOWSKI, M. J., SKOLIMOWSKI, J. & SKOWROŃSKI, R. (1978). *Acta Cryst.* B34, 2327–2331.
 CYGLER, M., MARKOWICZ, T., SKOLIMOWSKI, J. & SKOWROŃSKI, R. (1980). *J. Mol. Struct.* 68, 161–171.
 DE CAMP, W. H., MIĆOVIĆ, I. V. & PELLETIER, S. W. (1974). *Cryst. Struct. Commun.* 3, 427–431.
 DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*. Vol. 1, p. 18. London: Plenum.
 HILLEN, W., EGERT, E., LINDNER, H. Y. & GASSEN, H. G. (1978). *Biochemistry*, 17, 5314–5320.
 LYLE, R. E. (1957). *J. Org. Chem.* 22, 1280.
 RUBEN, H., ZALKIN, A. & TEMPLETON, D. H. (1974). *Acta Cryst.* B30, 334–337.
 SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.