Fig. 4. Unit cell contents of (I) illustrating the base packing and the hydrophilic channels.

base stack (pattern II of Motherwell & Isaacs, 1972). The degree of base overlap is limited to 5·9% of the maximum as a result of (non-hydrogen-bonded) steric contact, 2·94 Å, between N(6) and O(1') of the sugar ring of the screw-related molecule.

hydrogen bonds. The adenine heterocycles are related to one another at an interplanar distance of 3·17 Å by a twofold screw axis perpendicular to the base plane, thereby placing the sugar rings on alternate sides of the

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4-Ethynyl-2,2,6,6-tetramethylpiperidin-4-ol (TMPE)*

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Abstract. C$_{11}$H$_{19}$NO, monoclinic, $P2_1/n$, a = 6·427 (2), b = 13·203 (4), c = 12·753 (3) Å, β = 91·08 (2)°, Z = 4, V = 1081·97 Å³, D_x = 1·112 g cm⁻³, $F(000)$ = 400, μr(Mo $K\alpha$) = 0·02. 1892 independent reflexions were measured on a single-crystal diffractometer. The structure was solved by the symbolic addition method and refined by full-matrix least squares to a final R = 0·0689 for 1010 reflexions with $I > \sigma(I)$. The molecule exists in a chair conformation. The ethynyl group is axial and the hydroxyl group is equatorial. The H bonded to N takes the axial position. There are strong intermolecular O–H···N hydrogen bonds. The H of the ethynyl group forms a hydrogen bond with the O of the hydroxyl group. The correlation between the flatness of the ring and the system of intermolecular hydrogen bonds in related piperidine derivatives is described.

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* Conformation of the Piperidine Ring. I.

Introduction. Very interesting problems, connected with the conformations of overcrowded systems with strong steric interactions, arise in studies on non-

aromatic cyclic compounds. In six-membered rings these interactions cause considerable deformation of the 'chair' form, or even a stabilized twist or boat conformation.

The most commonly used method in the determination of molecular conformation is NMR spectroscopy. This method, however, gives rather qualitative information about the conformation of molecules in solution and does not always lead to unequivocal answers. A quantitative determination of the shape of molecules is only possible by a diffraction method.

Relatively little attention has been paid to the X-ray investigation of conformation in overcrowded piperidine derivatives. As model compounds of this type 2,2,6,6-tetramethylpiperidine derivatives can be chosen. Only a few structures of these molecules have been reported. Most exist in a distorted chair conformation (Lajzérowicz-Bonneteau, 1976; Rees & Weiss, 1971; De Camp, Mićović & Pelletier, 1974; Sato, Yoshioka & Tamura, 1975). Different conformations have been found in only three derivatives (Shibaeva, Atovmyan, Neigauz, Novakovskaya & Ginzburg, 1972; Sato *et al.*, 1975). In these compounds C(4), opposite the N atom, is sp^2 hybridized and there are bulky substituent(s) (O· radical) causing flattening of the ring at the N atom. However, it has been found, on the basis of IR investigations, that the non-chair conformation could be stabilized by an intramolecular hydrogen bond when there are bulky substituents in position 4, *e.g.* in 1,2,2,6,6-pentamethyl-4-phenyl-piperidin-4-ol (Lyle, 1957).

The existing experimental data are not sufficient to elucidate the influence of substituents on the conformation of the piperidine ring.

Systematic X-ray studies of 2,2,6,6-tetramethylpiperidine derivatives have been undertaken in our laboratory.

The IR and NMR spectra were investigated to obtain preliminary information on the type of conformation in TMPE. The IR spectra of solutions of TMPE in CS_2 at different concentrations show an intermolecular hydrogen bond only. The lack of splitting of the methyl-protons' signal in the NMR spectrum suggested no spatial interaction between hydroxyl and methyl groups. This indicates the equatorial position of the hydroxyl. The conformation of the ring, however, could not be unequivocally determined on the basis of these investigations.

The colourless, prismatic crystals used for X-ray investigation were crystallized from ethanol solution. The space group $P2_1/n$ has been determined from systematic absences ($0k0$: $k = 2n + 1$; $h0l$: $h + l = 2n + 1$) on Weissenberg photographs. The lattice constants were refined using 25 θ values measured on a Nonius CAD-4 diffractometer. 1892 independent reflexions were measured in the θ range 1–25° with the ω scan and Mo $K\alpha$ radiation (without a mono-

chromator). 1010 reflexions with $I > \sigma(I)$ were treated as observed. No absorption correction was applied and the intensities were converted to $|F|^2$ in the usual way.

The structure was solved by the symbolic addition method (NRC crystallographic programs, Ahmed, Hall, Pippy & Huber, 1966). 157 reflexions with $E > 1.85$ were used to obtain correlations between three symbols. With the most probable set of symbols, the signs of 376 reflexions with $E > 1.3$ were calculated using the tangent formula. All nonhydrogen atoms were located on the E map. After four cycles of full-matrix least-squares refinement with isotropic and four cycles with anisotropic temperature factors R was 0.120. On the difference map, 17 of the 19 H atoms were located. After a further three cycles of full-matrix refinement with H atoms treated as isotropic (B_{iso} was assumed to be equal to the B_{iso} of the neighbouring atom and was not refined) the difference map revealed the two remaining H atoms. The refinement was terminated after another two cycles when the maximum value of the shift/e.s.d. was 0.27. Cruickshank's weighting scheme was used in all stages of refinement with constants recalculated after each cycle. The final

Table 1. *Final fractional coordinates* ($\times 10^4$, *for* H $\times 10^3$) *with standard deviations resulting from the least-squares refinement*

	x	y	z
O(41)	1117 (6)	3492 (3)	7081 (4)
N(1)	2102 (8)	6599 (4)	7528 (4)
C(2)	2460 (9)	6205 (4)	6447 (5)
C(3)	1723 (10)	5090 (4)	6343 (5)
C(4)	2387 (9)	4374 (4)	7222 (5)
C(5)	1887 (10)	4863 (5)	8281 (5)
C(6)	2648 (10)	5958 (4)	8442 (5)
C(21)	4724 (11)	6334 (6)	6140 (6)
C(22)	1120 (13)	6864 (6)	5719 (6)
C(61)	4988 (12)	6020 (5)	8696 (6)
C(62)	1483 (14)	6412 (6)	9373 (6)
C(41)	4585 (9)	4063 (5)	7170 (5)
C(411)	6291 (11)	3766 (5)	7142 (6)
H(211)	517 (12)	701 (7)	635 (6)
H(212)	487 (13)	620 (6)	530 (6)
H(213)	568 (14)	589 (7)	651 (7)
H(221)	−34 (14)	679 (7)	589 (6)
H(222)	111 (13)	653 (7)	500 (7)
H(223)	156 (14)	760 (7)	577 (7)
H(611)	535 (12)	675 (6)	875 (6)
H(612)	518 (11)	569 (6)	942 (6)
H(613)	580 (12)	561 (6)	817 (6)
H(621)	−10 (14)	637 (7)	923 (6)
H(622)	199 (13)	708 (7)	946 (7)
H(623)	171 (12)	598 (6)	999 (6)
H(11)	67 (11)	676 (5)	757 (5)
H(31)	0 (11)	508 (5)	634 (5)
H(32)	224 (11)	487 (6)	568 (6)
H(51)	25 (13)	487 (6)	830 (5)
H(52)	243 (11)	445 (6)	885 (6)
H(41)	185 (12)	294 (7)	730 (6)
H(411)	770 (12)	359 (7)	708 (5)

disagreement factor is $R = 0.0689$.* The final atomic parameters are given in Table 1. Scattering factors for neutral O, N and C atoms were taken from Cromer & Mann (1968) and those for H from *International Tables for X-ray Crystallography* (1962).

Discussion. The molecule of TMPE has an approximate plane of symmetry. The value of the asymmetry parameter, as introduced by Duax & Norton (1975), is $C_s^N = 1.02°$ for the ring and $C_s^N = 1.06°$ for the whole molecule. Distances and angles in the molecule are shown in Fig. 1. The average value of a C—C single bond, excluding the shortened C(4)—C(41), is 1.534 Å. The mean C—N distance is 1.487 Å, in good

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33426 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. Bond lengths (Å) and valence angles (°) with e.s.d.'s in parentheses.

agreement with values found in other piperidine derivatives (Lajzérowicz-Bonneteau, 1976; Rees & Weiss, 1971; Ruben, Zalkin & Templeton, 1974). The smaller value of the C—N distance in comparison with C—C is largely connected with the contribution of the N lone pair of electrons. In 2,2,6,6-tetramethylpiperidin-4-one hydrochloride (TMPH+, Rees & Weiss, 1971), where the —C—N+—C— group is found (no lone-pair), the

$$\overset{/\backslash}{\underset{\text{H \quad H}}{}}$$

C—N distance is 1.521 Å, which is very close to that of C—C. The mean C—H distance in the molecule is 1.01 Å.

In the solid state the TMPE molecule exists in a chair conformation. The OH group is equatorial and the ethynyl group axial. Torsion angles in the ring are shown in Fig. 2; the mean ring torsion angle is 47.2°. This value indicates considerable flattening of the ring when compared with the undistorted cyclohexane ring.

The steric interaction between axial ethynyl and methyl groups causes them to deviate markedly from the ring [C(2)—C(6) 2.566, C(21)$_a$—C(61)$_a$ 3.287; C(2)—C(4) 2.612, C(21)$_a$—C(41) 3.275; C(4)—C(6) 2.609, C(41)—C(61)$_a$ 3.242 Å; see also Figs. 3 and 4]. This is the main cause of ring flattening. The participation in this interaction of the ethynyl group in position 4 also influences the increase in the C—C—C angle of the ring methylene groups to 116.3° [which is about 4° larger than in 2,2,6,6-tetramethylpiperidin-4-one derivatives (Ruben et al., 1974; Rees & Weiss, 1971)].

The H bonded to N takes the axial position and the lone pair of electrons the equatorial. The reverse configuration is preferred in the free molecule in the gaseous state and in non-interacting solvents, but the energy difference of these two configurations is only 1.68 kJ mol⁻¹ (Armarego, 1977). Stabilization of the energetically less favourable configuration in the solid state results from the formation of a strong intermolecular hydrogen bond with a contribution from the equatorial lone pair of electrons on N (Fig. 3). O···N and H···N are 2.790 Å and 1.91 Å respectively, and ∠O—H···N is 164°. The dependence of the configuration of the H and the N lone pair of electrons

Fig. 2. Torsion angles (°) in the piperidine ring.

Table 2. *Comparison of torsion angles* (°) *in various 2,2,6,6-tetramethylpiperidine derivatives*

Compound	Mean ring torsion angle $\langle\varphi\rangle$	Mean torsion angle $\langle\varphi_{N-C-C-C}\rangle$	Hydrogen bond	Reference
TMPE	47·2	47·1°	Strong equatorial	This paper
DTMP, molecule (I)	47·9	47·5	Strong equatorial	Ruben *et al.* (1974)
TMP	50·8	48·4	Strong equatorial, weak axial	De Camp *et al.* (1974)
TMPH⁺, molecule (I)	51·8	49·6	Equatorial, axial	Rees & Weiss (1971)
TMPH⁺, molecule (II)	53·5	50·7	Equatorial, axial	Rees & Weiss (1971)
DTMP, molecule (II)	54·9	53·1	Strong axial	Ruben *et al.* (1974)

OO oN •C •H
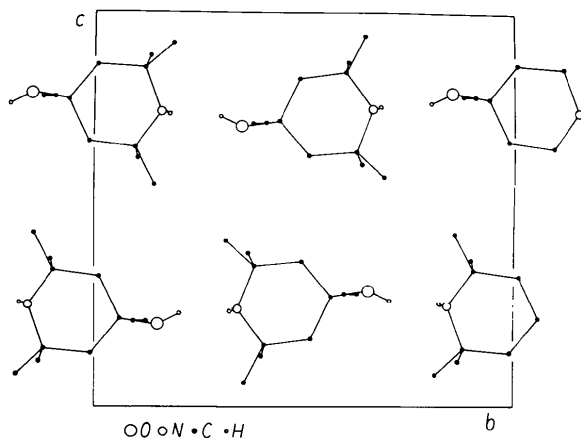
Fig. 3. A projection of the structure down the *x* axis.
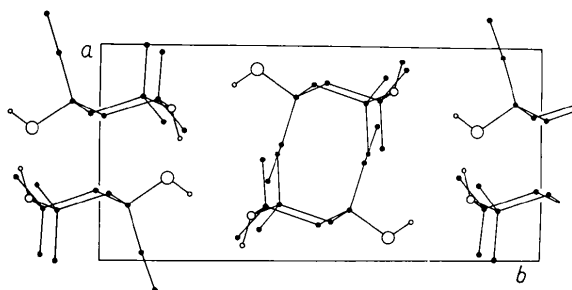
Fig. 4. A projection of the structure down the *z* axis.

on the direction of the hydrogen bond has also been found in N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-succinamide dihydrate (DTMP, Ruben *et al.*, 1974).

The next closest intermolecular contact is between the ethynyl group of one molecule and O(41') of a corresponding molecule translated along *x* [C(411)··· O(41') 3·126, H(411)···O(41') 2·20 Å, ∠C(411)—H(411)···O(41') 169°]. These values suggest the formation of a hydrogen bond. The other intermolecular distances are greater than the sum of the van der Waals radii of the corresponding atoms.

Projections of the structure down the *x* and *z* axes are shown in Figs. 3 and 4 respectively. The mean plane of the ring is nearly parallel to the *yz* plane. Molecules joined by O—H···N hydrogen bonds form

chains elongated in the *y* direction. The neighbouring chains are connected through C—H···O hydrogen bonds in the *x* direction into layers.

Comparison of the values of torsion angles in the piperidine ring for TMPE, DTMP, TMPH⁺ and TMP* (2,2,6,6-tetramethylpiperidin-4-one monohydrate, De Camp *et al.*, 1974) shows a correlation between them and the system of intermolecular hydrogen bonds (Table 2). Hydrogen bonds in TMPE cause the stretching of the piperidine ring in the direction of N(1)—C(4), which in conjunction with the above-mentioned interaction of axial substituents leads to the smallest value of the mean torsion angle of the ring. In DTMP, where there are two symmetrically independent molecules, hydrogen bonds stretch one molecule and bend another. There are also two independent molecules in TMPH⁺. Each forms two N—H···Cl hydrogen bonds (equatorial and axial) whose influences on the flattening of the ring cancel each other. Finally, in TMP there is a strong stretching equatorial hydrogen bond and a weaker axial one.

Taking into account the positions of the methyl groups in all the above-mentioned compounds, the stability of $\angle C_e$—C—N and $\angle C_a$—C—C may be stated. Their mean values are 105·5 and 111·5° respectively. $\angle C_e$—C—N is about 2° smaller than in corresponding nitroxide radicals (Lajzérowicz-Bonneteau, 1976). Values of the other angles formed by the methyl groups and neighbouring bonds in the ring depend on the flatness of the ring and on the position of the H atom bonded to N.

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* Data for this compound are less reliable because of the low precision of the atomic parameters due to disorder.

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Perchlorodiphenylnitroxide, a Free Radical

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Abstract. $(C_6Cl_5)_2NO\cdot$, $M_r = 528\cdot62$, $F(000) = 1028$, monoclinic, $C2/c$, $a = 16\cdot652$ (7), $b = 5\cdot284$ (2), $c = 19\cdot304$ (8) Å, $\beta = 90\cdot84$ (3)°, $V = 1698\cdot73$ Å^3, $Z = 4$, $D_c = 2\cdot066$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot7107$ Å, $\mu = 16\cdot3$ cm^{-1}. The structure has been solved with *MULTAN* and refined by the block-diagonal least-squares method. The final R value is 0·046 for 1964 observed reflexions. The two parts of the molecule are related by a twofold axis passing through the N and O atoms. The perchlorophenyl group and the $C_2NO\cdot$ group are both planar. The dihedral angle between these two planes is 57·2°.

Introduction. Red prismatic crystals of perchloro-diphenylnitroxide were kindly supplied by Professor M. Ballester. They were obtained by crystallization in benzene and washed with pentane.

A crystal, $0\cdot2 \times 0\cdot3 \times 0\cdot4$ mm, was used for crystal data and intensity measurements on a Nonius CAD-4 diffractometer. The unit cell was measured by automatically centring 25 independent reflexions and refining the orientation matrix and unit-cell parameters by least squares. Intensities were collected with Mo $K\alpha$ radiation, monochromatized by reflexion from a graphite crystal, at a take-off angle of 5°. The ω–2θ technique was used with scan interval $\Delta\omega = (0\cdot70 + 0\cdot35 \tan\theta)°$. The background was measured before and after each reflexion. The maximum scan time was 80 s, with 53·3 s used for the peak scanning and 13·3 s for both backgrounds. The intensity of 133 was chosen as the standard and it was measured every hour. The reflexions $2,2,\overline{12}$, $3,1,\overline{15}$ and $31\overline{3}$, chosen as an orientation control, were measured every 100 reflexions. 2537 independent reflexions were collected within the range $1 < \theta \le 30°$, 1964 of which have been considered as observed, applying the condition $I > 2\sigma(I)$. The data were collected with the crystal mounted along the long axis. Lorentz–polarization corrections were made, but none were for absorption ($\mu r < 0\cdot7$).

The observed systematic absences indicated that the possible space groups are $C2/c$ (centrosymmetric) and Cc (non-centrosymmetric). The statistical results of $\langle ||E|^2 - 1| \rangle$, $\langle |E| \rangle$, and the $N(z)$ distribution (Howells, Phillips & Rogers, 1950) indicated that the space group is $C2/c$.

The structure was solved with the *MULTAN* system of computer programs (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The overall temperature factor was 3·8 Å^2. 274 reflexions with $|E| \ge 1\cdot61$ were used in the phase-determining procedure, because at this value the experimental $N(z)$ (Howells, Phillips & Rogers, 1950) coincides with the theoretical value in centrosymmetric crystals (Solans, 1977). 2000 Σ_2 relationships were used and an E map computed with the phases from the set with the highest combined figure of merit ($= 3$) revealed peaks for all the atoms.

The structure was isotropically and anisotropically refined by means of block-diagonal least squares with the modified version of *SFLS* (Ahmed, Hall, Pippy &