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4-Ethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl*

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Abstract. $C_{11}H_{18}NO_2$, monoclinic, $P2_1/c$, $a = 13{\cdot}327\,(4)$, $b = 7{\cdot}662\,(2)$, $c = 12{\cdot}668\,(4)$ Å, $\beta = 118{\cdot}50\,(5)°$, $V = 1136{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}147$ Mg m^{-3}, $F(000) = 428$. The structure was solved by direct methods and refined to $R = 0{\cdot}0398$ using 1453 reflexions with $I > 3\sigma(I)$ measured on a Syntex $P2_1$ diffractometer in the θ–2θ scan mode with monochromatized Cu $K\alpha$ radiation ($\mu r = 0{\cdot}1$). The molecule possesses a chair-type conformation with an axial ethynyl group and an equatorial hydroxyl group. Steric interactions cause a strong deformation of the molecule from an ideal form. The N–O$^{\bullet}$ bond forms an angle of 19·8° with the CNC plane. There are O–H···O and ≡C–H···O intermolecular hydrogen bonds.

Introduction. Tetramethyl-substituted nitroxyl derivatives of piperidine form stable radicals which are solids at room temperature. Among the few compounds of this type whose structures have been determined by X-ray diffraction methods, the majority exist in a chair-type conformation (Lajzérowicz-Bonneteau, 1976; Shibaeva & Rozenberg, 1974; Atovmian *et al.*, 1975) with a non-planar $\genfrac{}{}{0pt}{}{C}{C}\!>\!N{-}O^{\bullet}$ group. The N–O$^{\bullet}$ bond forms an angle of 15 to 20° with the CNC plane. In only one compound has a twist conformation of the molecule been found (2,2,6,6-tetramethyl-4-oxopiperidin-1-oxyl; Shibaeva, Atovmian, Neigauz, Novakovskaya & Ginzburg, 1972). The $\genfrac{}{}{0pt}{}{C}{C}\!>\!N{-}O^{\bullet}$ group is planar in this compound. The change of conformation was probably due to a different hybridization of C(4) in the piperidine ring. Because of the steric interactions and presence of the nitroxyl group, the molecules of these compounds are highly distorted from ideal conformations.

Redetermination of the structures of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (Berliner, 1970) and 2,2,6,6-tetramethyl-4-oxopiperidin-1-oxyl (Bordeaux & Lajzérowicz, 1974) shows that the comparison of molecules of different derivatives with the aim of examining the influence of substituents on molecular conformation and on the $\genfrac{}{}{0pt}{}{C}{C}\!>\!N{-}O^{\bullet}$ group configuration is sensible only for structures determined with high accuracy. Because very few structures of nitroxyl piperidine derivatives have been determined with enough accuracy, further investigations are needed.

The title compound was synthesized at the Institute of Chemistry, University of Łódź, by Professor Skowroński's group (Skolimowski, 1977). Crystals for X-ray investigation were obtained from ethanol. They are orange and equant in habit. The space group was determined by examination of Weissenberg photographs. Precise lattice constants were calculated from setting angles of 15 reflexions automatically centered

Table 1. *Final fractional coordinates with standard deviations in parentheses*

	x	*y*	*z*
O(1)	0·7026 (1)	0·5110 (2)	0·4650 (1)
N(1)	0·7261 (1)	0·6740 (2)	0·4836 (1)
C(2)	0·6270 (1)	0·7934 (2)	0·4193 (2)
C(21)	0·5298 (2)	0·7249 (3)	0·4402 (2)
C(22)	0·5895 (2)	0·7874 (3)	0·2849 (2)
C(3)	0·6595 (2)	0·9763 (2)	0·4729 (2)
C(4)	0·7757 (1)	1·0464 (2)	0·4981 (1)
C(41)	0·7805 (2)	1·0984 (2)	0·3883 (2)
C(411)	0·7838 (2)	1·1543 (3)	0·3036 (2)
O(4)	0·8014 (1)	1·1980 (2)	0·5734 (1)
C(5)	0·8662 (2)	0·9135 (2)	0·5750 (2)
C(6)	0·8480 (1)	0·7250 (2)	0·5296 (2)
C(61)	0·8805 (2)	0·6965 (3)	0·4304 (2)
C(62)	0·9213 (2)	0·6080 (3)	0·6370 (2)
H(41)	0·772 (2)	1·294 (4)	0·528 (2)
H(411)	0·784 (2)	1·194 (3)	0·233 (2)
H(31)	0·661 (3)	0·972 (3)	0·553 (2)
H(32)	0·599 (2)	1·059 (3)	0·421 (2)
H(51)	0·942 (2)	0·953 (3)	0·589 (2)
H(52)	0·867 (2)	0·911 (3)	0·655 (2)
H(211)	0·509 (2)	0·604 (4)	0·405 (2)
H(212)	0·462 (3)	0·813 (4)	0·398 (2)
H(213)	0·559 (2)	0·719 (4)	0·528 (3)
H(221)	0·579 (2)	0·667 (3)	0·259 (2)
H(222)	0·514 (2)	0·843 (3)	0·243 (2)
H(223)	0·645 (2)	0·844 (3)	0·262 (2)
H(611)	0·838 (2)	0·775 (3)	0·359 (2)
H(612)	0·862 (2)	0·572 (3)	0·401 (2)
H(613)	0·961 (2)	0·720 (3)	0·462 (2)
H(621)	1·001 (2)	0·654 (3)	0·675 (2)
H(622)	0·890 (2)	0·605 (4)	0·691 (2)
H(623)	0·921 (2)	0·481 (3)	0·610 (2)

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* Conformation of the Piperidine Ring. II.

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on a Syntex $P2_1$ diffractometer. 1889 reflexions up to $\theta = 70°$ were measured by the θ–2θ scan mode using monochromatized Cu $K\alpha$ radiation. Of these 1453 had $I > 3\sigma(I)$, and were considered observed. The Lp correction was applied but no absorption correction was made.

The structure was solved by direct methods (*MULTAN*; Main, Lessinger, Woolfson, Germain & Declercq, 1976). 150 E values $>1{\cdot}8$ were used. The E map for the solution with the highest combined figure of merit revealed all non-hydrogen atoms. Three cycles of full-matrix least-squares refinement gave an R value of 0·164. After three further cycles of anisotropic refinement ($R = 0{\cdot}097$), a difference map was calculated and on this 16 out of the 18 H atoms were located and included in the refinement with isotropic temperature factors. After two more cycles of refinement ($R = 0{\cdot}052$) a new difference map revealed the two missing H atoms, H(41) and H(411). Two further cycles of refinement including all H atoms decreased the R value to 0·0398 and R_w to 0·0522 for 1448 reflexions. During the refinement the Cruickshank weighting scheme was used with constants recalculated after each cycle. The maximum value of shift/e.s.d. in the last cycle was 0·51 and its mean value was 0·05. Five reflexions with low angles and high F_o values were probably strongly affected by extinction and were excluded from the refinement. Scattering amplitudes for C, N and O were taken from Cromer & Mann (1968) and for H from *International Tables for X-ray Crystallography* (1962). Least-squares refinement was calculated with the local version of *ORFLS* (Busing, Martin & Levy, 1962). Final atomic parameters are listed in Table 1.*

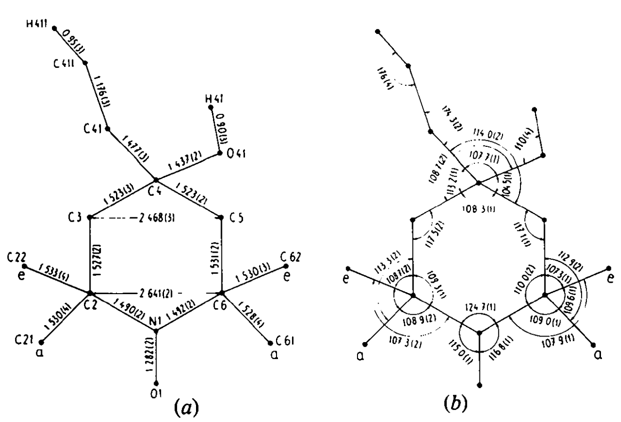

Fig. 1. (*a*) Bond lengths (Å) and (*b*) angles (°) with e.s.d.'s in parentheses.

Discussion. Molecules of the title compound exist in a chair-type conformation in the solid state. As in 4-ethynyl-2,2,6,6-tetramethyl-4-piperidinol (TMPE, Cygler, Grabowski, Skolimowski & Skowroński, 1978), the ethynyl group is axial while the hydroxyl group is equatorial. Distances and angles in the molecule are shown on Fig. 1 and ring torsion angles are shown on Fig. 2. The plane through N(1), C(4) and O(41) is a pseudo mirror plane of the molecule. The asymmetry parameter C_s^N (Duax & Norton, 1975) is equal to 0·90° for the piperidine ring and 1·14° for the whole molecule. The mean distances are: $\langle C{-}C \rangle = 1{\cdot}528$, $\langle C{-}N \rangle = 1{\cdot}491$, $\langle C{-}H \rangle_{\text{methyl}} = 1{\cdot}00$ Å. The geometry of the nitroxyl group is similar to that found in related compounds (Lajzérowicz-Bonneteau, 1976). The N–O· bond length is 1·282 Å and forms an angle of 19·7° with the CNC plane. The CNC angle in the ring is enlarged to 124·7°.

Steric interactions between axial substituents cause considerable deformation of the molecule from the ideal chair form. The piperidine ring is strongly flattened. The mean value of the ring torsion angle is 44·1°. In the N part of the ring, CNCC torsion angles are about 36° and are intermediate between values found in 2,2,6,6-tetramethylpiperidin-1-oxyl (Capiomont & Lajzérowicz-Bonneteau, 1974), 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (Berliner, 1970), a 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl derivative (McPhail, Abou-Donia & Rosen, 1976), 4,4′-suberoyldioxybis-(2,2,6,6-tetramethylpiperidin-1-oxyl) (Capiomont, 1972), 4,4′-tetramethylenebis(2,2,6,6-tetramethylpiperidin-1-oxyl) (Shibaeva & Rozenberg, 1974). In the opposite part of the ring, near atom C(4), torsion angles are about 8° smaller than in the above-mentioned compounds. The flattening of this part of the ring is caused by the interaction of the ethynyl group with axial methyl groups. A similar effect was found in TMPE. Comparison of these two molecules shows the increase of molecule deformation with the change of N hybridization from sp^3 to a mixed sp^3–sp^2. There is an increase of the CNC angle from 119·3 to 124·7° and axial C(methyl)–C(methyl) distance from 3·287 to 3·479 Å. On the other hand the distance of C(41) from the axial methyl C atoms changes slightly (3·275 and 3·242 Å in TMPE and 3·270 and 3·296 Å in the present compound) indicating a smaller deviation of the ethynyl group outside the ring in the nitroxyl derivative. The presence of an O atom instead of H linked to the N

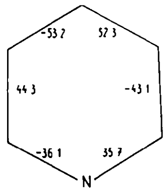

Fig. 2. Torsion angles (°) in the piperidine ring.

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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 33903 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

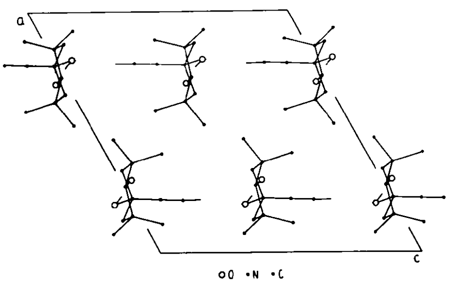

Fig. 3. A projection of the structure down the *y* axis.

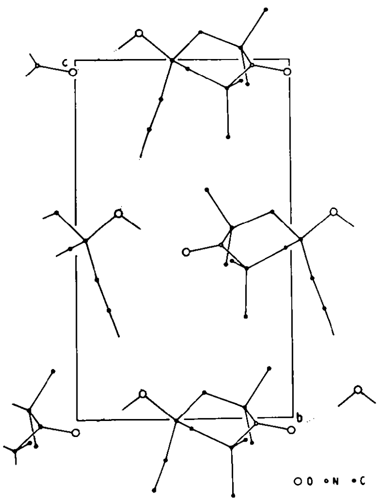

Fig. 4. A projection of the structure down the *x* axis.

atom causes an increase in the C_a—C—C_e and N—C—C_e angles of about 2° and a decrease in the C—C—C_a angle of the same amount.

The molecules in the structure are joined by hydrogen bonds to form layers parallel to the *yz* plane. Every molecule forms two hydrogen bonds: O—H···O with O—H = 0·90, H···O = 1·89, O···O = 2·765 Å, ∠O—H···O = 166° in the *y* direction and a ≡C—H···O bond between the ethynyl H and the hydroxyl O atoms with C(411)—O(4′) = 3·239 Å, H(411)···O(4′) = 2·29 Å, ∠C(411)—H(411)···O(4′) = 173° in the *z* direction.

The projections of the structure along two axes are shown in Figs. 3 and 4.

It is noteworthy that the H atoms located on the very last difference map are those forming hydrogen bonds.

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