

Structure of 2,2,5,5-Tetramethyl-3-phenylethynyl-3-pyrrolidinol*

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Abstract. $C_{16}H_{21}NO$, monoclinic, $P2_1/c$, $a = 11.993$ (1), $b = 11.656$ (2), $c = 10.943$ (1) Å, $\beta = 106.53$ (1)°, $V = 1466.5$ Å³, $Z = 4$, $D_x = 1.03$ Mg m⁻³, $\mu(Cu K\alpha) = 0.54$ mm⁻¹. The structure was solved by direct methods and refined to $R = 0.040$ for 2261 reflexions with $I > \sigma(I)$. The pyrrolidine ring adopts a half-chair conformation with fully substituted atoms C(2) and C(3) above and below the plane of the other atoms. The hydroxyl group takes an axial position while the phenylethynyl group is equatorial. Molecules are connected by O—H...N bonds and form chains parallel to the z axis. A comparison with other pyrrolidine structures is presented.

Introduction. Tetramethyl-substituted five- and six-membered ring systems containing N have been investigated with interest focused mainly on their N -oxide derivatives, which form stable radicals. Other derivatives have also been studied, but only of six-membered rings (e.g., Cygler, Grabowski, Skolimowski & Skowroński, 1978; Cygler, 1981, and literature cited therein). The title compound was synthesized by Nazarski, Skolimowski & Skowroński (1978) as part of a study of crowded ring systems. The colourless, plate-shaped crystals were obtained by slow evaporation from hexane solution. The systematic absences of the type $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ indicated space group $P2_1/c$. The crystal chosen for data collection had dimensions $0.48 \times 0.34 \times 0.10$ mm. Cell constants were calculated from angular settings of 22 reflections measured on a CAD-4 diffractometer. An $\omega/2\theta$ scan with a scan width $\Delta\omega$ (°) = $0.8 + 0.2 \tan \theta$ was used to measure 3058 reflections up to $\theta = 76^\circ$ with Ni-filtered Cu $K\alpha$ radiation. The intensities of three control reflections, measured every 6000 s, varied in the range $\pm 5\%$ and were used for appropriate scaling of the data. A total of 2261 reflections (73%) had intensities greater than $\sigma(I)$ and were treated as observed and used in the least-squares refinement. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods (*MULTAN*; Main, 1978). The E map calculated for the set with the highest combined figure of merit revealed all the non-hydrogen atoms. Several cycles of block-diagonal least-squares refinement, followed by a difference map, led to the location of all H atoms. All atoms except for H were refined with anisotropic

Table 1. Fractional atomic coordinates ($\times 10^4$, for H $\times 10^3$) and isotropic thermal parametersFor nonhydrogen atoms $B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

	x	y	z	B_{eq}/B (Å ²)
O(1)	6495 (1)	2629 (1)	4733 (1)	4.4 (0.1)
N(1)	5966 (1)	2324 (1)	2070 (1)	3.3 (0.1)
C(2)	6979 (1)	1769 (1)	2982 (1)	3.3 (0.1)
C(3)	6506 (1)	1543 (1)	4151 (1)	3.3 (0.1)
C(4)	5266 (1)	1131 (1)	3505 (1)	3.6 (0.1)
C(5)	4873 (1)	1814 (1)	2237 (1)	3.4 (0.1)
C(21)	8014 (2)	2575 (2)	3288 (2)	5.1 (0.1)
C(22)	7293 (2)	658 (2)	2420 (1)	4.6 (0.1)
C(31)	7196 (1)	699 (1)	5058 (1)	4.0 (0.1)
C(311)	7739 (1)	-14 (1)	5764 (1)	4.2 (0.1)
C(51)	4046 (1)	2784 (2)	2308 (2)	4.8 (0.1)
C(52)	4299 (2)	1035 (2)	1116 (2)	5.0 (0.1)
C(11)	8371 (1)	-903 (1)	6583 (1)	4.0 (0.1)
C(12)	8362 (1)	-2016 (2)	6138 (2)	4.9 (0.1)
C(13)	8933 (2)	-2883 (2)	6944 (2)	5.8 (0.1)
C(14)	9532 (2)	-2642 (2)	8182 (2)	6.3 (0.1)
C(15)	9556 (2)	-1552 (2)	8624 (2)	6.9 (0.1)
C(16)	8982 (2)	-675 (2)	7843 (2)	5.7 (0.1)
H(1)	596 (1)	306 (2)	236 (2)	4.3 (0.4)
H(21,1)	867 (2)	226 (2)	394 (2)	6.5 (0.5)
H(21,2)	780 (2)	333 (2)	365 (2)	7.2 (0.5)
H(21,3)	820 (2)	276 (2)	254 (2)	6.2 (0.5)
H(22,1)	799 (2)	32 (2)	301 (2)	7.0 (0.5)
H(22,2)	661 (2)	7 (2)	223 (2)	5.8 (0.5)
H(22,3)	748 (2)	84 (2)	156 (2)	5.5 (0.4)
H(11)	625 (2)	254 (2)	538 (2)	6.2 (0.5)
H(4,1)	527 (1)	29 (1)	333 (1)	3.5 (0.3)
H(4,2)	475 (1)	129 (2)	405 (2)	4.2 (0.4)
H(51,1)	387 (2)	327 (2)	153 (2)	5.1 (0.4)
H(51,2)	326 (2)	250 (2)	238 (2)	7.4 (0.6)
H(51,3)	440 (1)	327 (2)	308 (2)	4.6 (0.4)
H(52,1)	403 (2)	150 (2)	30 (2)	5.2 (0.4)
H(52,2)	483 (2)	43 (2)	100 (2)	6.7 (0.5)
H(52,3)	361 (2)	70 (2)	122 (2)	7.7 (0.6)
H(12)	794 (2)	-219 (2)	523 (2)	5.7 (0.5)
H(13)	892 (2)	-366 (2)	665 (2)	8.1 (0.6)
H(14)	993 (2)	-325 (2)	874 (2)	7.3 (0.5)
H(15)	1002 (2)	-134 (2)	953 (2)	8.9 (0.7)
H(16)	894 (2)	12 (2)	820 (2)	6.6 (0.5)

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temperature factors. The final R values are $R = 0.040$ and $R_w = 0.064$ for observed reflections ($R = 0.067$ for all reflections). The average shift/e.s.d. ratio in the last cycle of the refinement was 0.1 and the maximum shift was 0.8σ . The weights used were $w = 1/[1.0 + (F_o - 2.85)^2/5.53^2]$. The final atomic parameters are shown in Table 1.*

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The NRC Crystallographic Programs were used for all computations (Ahmed, Hall, Pippy & Huber, 1973).

Discussion. A view of the molecule is shown in Fig. 1, and the bond lengths, valence angles and torsion angles are in Fig. 2 (*ORTEP*; Johnson, 1970). The pyrrolidine ring adopts a half-chair conformation with C(2) 0.314 (2) Å above and C(3) 0.358 (2) Å below the C(4)C(5)N(1) plane. This form is imposed by bulky substituents on neighbouring C(2) and C(3) atoms, forcing a staggered conformation along that bond, with an N(1)–C(2)–C(3)–C(4) torsion angle of 41.3 (3)° and C(21)⋯O(1) and C(22)⋯C(31) distances of 2.731 (3) and 2.923 (3) Å, respectively. The shortest distance between methyl groups [C(22)⋯C(52) = 3.494 (3) Å] is slightly longer than in the related six-membered 4-ethynyl-2,2,6,6-tetramethyl-4-piperidinol [TMPE, 3.287 (8) Å; Cygler, Grabowski, Skolimowski & Skowronski, 1978]. The deviation of the ring from twofold symmetry is relatively small. The asymmetry parameters (Duax & Norton, 1975) are $\Delta C_2^{-3} = 0.8^\circ$ (ring torsion angles only) and 3.4° (including the torsion angles of all ring substituents). The puckering parameters (Cremer & Pople, 1975) are $Q = 0.41$ Å, $\varphi = 55.9^\circ$ for the N(1), C(2), C(3), C(4), C(5) sequence ($\varphi = 54^\circ$ for the ideal half-chair conformation). The endocyclic angles vary between 101.9 (2) and 108.8 (2)°, the largest being at the N atom and the smallest at the fully substituted C(2) and C(3). Of the substituents at C(3), the hydroxyl group takes an axial position while the phenylethynyl group is equatorial.

The phenyl ring is almost perpendicular to the pyrrolidine moiety, making an angle of 85.0 (3)° with its mean plane. The O(1) atom lies nearly in the plane of the phenyl ring; the angle between the O(1)C(3)–C(31) plane and the phenyl ring is 4.9 (3)°. The average C–H bond length is 1.00 (3) Å. The C≡C bond length is slightly longer than that found in nonsubstituted ethynyl groups in related compounds [TMPE, 1.166 (9) Å; 4-ethynyl-1,2,2,6,6-pentamethyl-4-piperidinol, 1.174 (5) Å; Cygler, 1981].

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36055 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

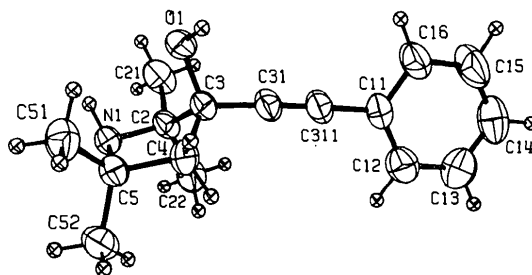


Fig. 1. Molecular structure with the atom-numbering scheme. All the nonhydrogen atoms are drawn as thermal ellipsoids at the 50% probability level.

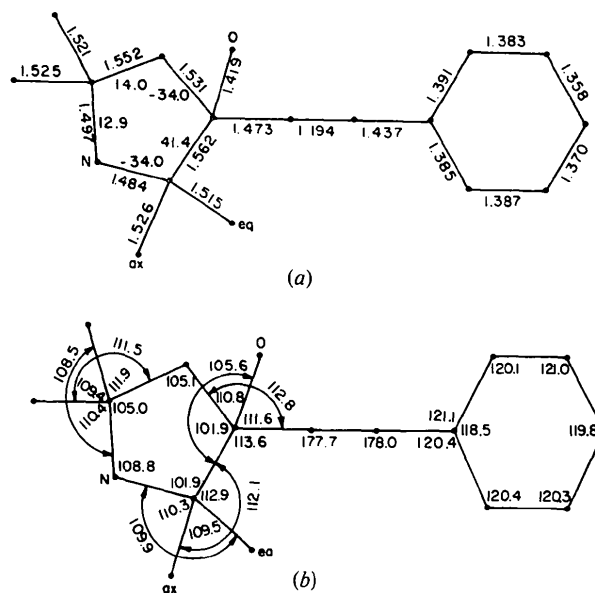


Fig. 2. (a) Bond lengths (Å) and selected torsion angles (°). The standard deviations are in the range 0.002–0.003 Å and 0.3–0.5° respectively. (b) Valence angles (°). Standard deviations are in the range 0.2–0.4°.

The phenyl ring is planar. The equation of the best plane is $0.9428X + 0.1843Y - 0.2779Z - 5.4228 = 0$ (X, Y, Z are orthogonal coordinates) and the largest deviation of an atom from that plane is 0.007 (2) Å. C(311) is slightly out of the ring plane [0.047 (2) Å] and the C(311)–C(11) bond makes an angle of 1.9 (1)° with it. The thermal vibrations of the outside atoms C(13), C(14) and C(15) are larger ($\Delta B \sim 2$ Å²) than the atoms closer to the centre of inertia of the molecule.

A very similar conformation of the pyrrolidine ring was found in spiro[4-ethyl-3a,6a-dimethylperhydrofuro[3,2-*b*]pyrrole-2,2'-1'-ethyl-3'-methyl-3'-pyrrolidinol] (Chiglien, Jaulmes & Etienne, 1978), where C(2) and C(3) are also fully substituted. The puckering parameters are $Q = 0.42$ Å, $\varphi = 51.0^\circ$, very close to those of the half-chair form.

Other reported 2,2,5,5-tetramethylpyrrolidine structures are *N*-oxide derivatives with only one substituent at C(3) (Chion, 1976; Guseinova & Mamedov, 1978, and references cited therein). The pyrrolidine ring usually exhibits the half-chair conformation [C(3) and C(4) above and below the C(5)N(1)C(2) plane], slightly distorted towards the envelope form with the substituted C(3) atom out of the plane of the other atoms, the smallest torsion angle being C(2)–N(1)–C(5)–C(4). These rings are less puckered than in the compound described above, their *Q* parameter being in the range 0.34 [(+)-3-hydroxy-2,2,5,5-tetramethylpyrrolidine *N*-oxide; Chion, Lajzërowicz, Collet & Jacques, 1976] to 0.39 Å (2,2,5,5-tetramethyl-3-pyrrolidinecarboxamide 1-oxyl; Chion & Lajzërowicz, 1975). In only one case does the tetramethyl-substituted pyrrolidine ring adopt a conformation similar to that discussed above. In 1,3-dinitro-4,6-bis[(2,2,5,5-tetramethyl-3-pyrrolidinyl *N*-oxide)amino]benzene monohydrate (Hilti, Ottersen & Seff, 1976) one of the two pyrrolidine rings exists in a conformation intermediate between a half-chair [with C(2) and C(3) out of the plane] and an envelope with C(3) out of the plane of the other atoms. The puckering parameters for this ring are $Q = 0.27 \text{ \AA}$, $\varphi = 65.2^\circ$ ($\varphi = 54^\circ$ for an ideal half-chair and 72° for an envelope conformation). The other ring exists in the usual half-chair conformation ($Q = 0.35 \text{ \AA}$, $\varphi = 84.2^\circ$). This difference could be caused by hydrogen bonds which involve the O(N) atom of the first pyrrolidine ring only.

The molecules of the title compound are packed in the crystal in the head-to-head, tail-to-tail pattern. Pyrrolidine rings related by a glide plane are joined by an intermolecular O–H...N hydrogen bond with O...N = 2.806 (2), H...N = 1.98 (2) Å and $\angle \text{O–H...N} = 165 (2)^\circ$. They form chains parallel to the *z* axis. All other interatomic distances are larger than the sum of the appropriate van der Waals radii, with shortest H...H contacts of 2.40 Å.

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