Table 3. *Deviations* (Å) *of the atoms from the least-squares planes*

The imide ring

$-0\cdot0533X + 0\cdot9015Y - 0\cdot4295Z = 4\cdot9315$

C(1)	0·004 (5)	*O(2)	−0·052 (4)
C(2)	0·003 (5)	*C(4)	0·591 (6)
C(7)	−0·013 (6)	*C(5)	−0·209 (6)
C(8)	−0·010 (5)	*C(10)	−0·016 (5)
N(9)	0·008 (4)	*C(13)	−0·136 (7)
*S(3)	0·039 (2)	$\chi^2 = 13\cdot69$	
*S(6)	−0·025 (2)	$p < 0\cdot01$	
*O(1)	−0·057 (5)		

The phenyl ring

$-0\cdot6554X - 0\cdot5650Y - 0\cdot5013Z = -8\cdot9313$

C(10)	0·000 (5)	C(15)	−0·005 (5)
C(11)	0·005 (5)	*N(9)	0·016 (4)
C(12)	−0·007 (6)		
C(13)	0·000 (6)	$\chi^2 = 4\cdot03$	
C(14)	0·006 (6)	$0\cdot10 < p < 0\cdot50$	

* Not included in the calculation of the plane.

bond length and bond order is assumed, the present C—N bonds possess 35 and 45% double-bond character. This may be due to the different contribution of resonance structures (II) and (III) (Fig. 1). The C—O bond lengths correspond to this scheme, the shorter C(7)—O(1) = 1·193 (7) Å bond is adjacent to the longer C(7)—N(9) = 1·403 (6) Å bond and the longer C(8)—O(2) = 1·206 Å is adjacent to the shorter C(8)—N(9) = 1·377 (6) Å. The phenyl ring is perfectly planar within the observed errors. The dihedral angle between the phenyl and imide rings is 75°. The maximum difference between C—H bond lengths is 0·035 Å, with a mean value of 1·02 Å.

The only noteworthy intermolecular contact is S(6)···O(2) = 3·149 (3) Å between molecules related by the *a* glide.

We would like to thank Professor W. Hahn and Dr B. Rybczyński for supplying the crystals.

This research was supported by Project MR I-9 from the Polish Academy of Sciences.

References

Bukowska-Strzyżewska, M. & Pniewska, B. (1979*a*). *Acta Cryst.* B**35**, 633–639.

Bukowska-Strzyżewska, M. & Pniewska, B. (1979*b*). *Acta Cryst.* B**35**, 640–643.

Dobrowolska, W. & Bukowska-Strzyżewska, M. (1980). *Acta Cryst.* B**36**, 890–893.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure.* New York, Washington, London: Plenum.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Hahn, W. E. & Rybczyński, B. (1971). *Soc. Sci. Łódź. Acta Chim.* **16**, 123–128.

Hahn, W. E. & Rybczyński, B. (1976). *Rocz. Chem.* **50**, 1523–1533.

Kirfel, A., Will, G. & Fickentscher, K. (1975). *Acta Cryst.* B**31**, 1973–1975.

Pauling, L. (1960). *The Nature of the Chemical Bond*, pp. 224–250. Ithaca: Cornell Univ. Press.

Acta Cryst. (1980). B**36**, 2478–2480

Structure of 1,2,2,6,6-Pentamethyl-4-vinyl-4-piperidinol*

By M. Cygler and K. Dobrynin

Department of Crystallography, Institute of Chemistry, University of Łódź, 91–416 *Łódź, Nowotki* 18, *Poland*

and M. Perrin

Université Claude Bernard Lyon I, *Laboratoire de Minéralogie–Cristallographie associé au CNRS* (*ERA* 600), 43 *boulevard du* 11 *Novembre* 1918, 69621 *Villeurbanne, France*

(*Received* 9 *October* 1979; *accepted* 22 *May* 1980)

Abstract. $C_{12}H_{23}NO$, orthorhombic, $P2_12_12_1$, $a = 7\cdot860$ (2), $b = 10\cdot935$ (3), $c = 14\cdot407$ (3) Å, $Z = 4$, $V = 1238\cdot3$ Å^3, $D_x = 1\cdot06$ Mg m^{-3}, $F(000) = 440$, $\mu r(\mathrm{Cu}\ K\alpha) = 0\cdot15$. 1514 independent reflexions were measured on a CAD-4 diffractometer. The structure was solved by direct methods and refined to $R = 0\cdot054$ for 999 reflexions with $I > 3\sigma(I)$. The piperidine ring adopts a chair conformation with an axial hydroxyl group. The formation of an intramolecular =C—H···O bond is suggested. Between molecules there are only van der Waals contacts.

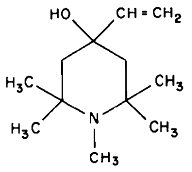
Introduction. In molecules with bulky ring substituents, steric interactions strongly influence the conformation of the molecular skeleton. 2,2,6,6-

---

* The Conformation of the Piperidine Ring. IV.

Tetramethylpiperidine derivatives belong to this group. The greatest attention has been paid to the nitroxyl derivatives, which form stable radicals (*e.g.* Lajzérowicz-Bonneteau, 1976; Guseinova & Mamedov, 1978), but other derivatives have also been studied (Rees & Weiss, 1971; Sato, Yoshioka & Tamura, 1975; Ruben, Zalkin & Templeton, 1974; Golovina, Klitskaya, Medzhidov & Atovmian, 1975). In most of the compounds investigated, 2,4 diaxial interactions of methyl groups were responsible for the deformation of the piperidine ring. A systematic study of other derivatives with 2,4,6 axial interactions has been undertaken in our laboratory (Cygler, Grabowski, Skolimowski & Skowroński, 1978; Cygler, 1979; Cygler, Markowicz, Skolimowski & Skowroński, 1980).

We now report our work on the title compound, PMPV.



PMPV

Colourless, prismatic crystals were obtained by recrystallization from *n*-hexane; they sublime easily. The crystal chosen for data collection had dimensions 0·30 × 0·20 × 0·16 mm and was sealed in a Lindemann capillary. Intensities were measured on a CAD-4 diffractometer at 258 K, with monochromatized Cu $K\alpha$ radiation. During the scan, the speed of the detector (2θ) was the same as that of the crystal (ω). Precise lattice constants were calculated from angular settings of 25 reflexions. 1514 independent reflexions out to $\theta = 75°$ were measured, of which 999 with $I > 3\sigma(I)$ were treated as observed and used in the refinement. No absorption correction was made.

The structure was solved by direct methods (*MULTAN*, Main, Lessinger, Woolfson, Germain & Declercq, 1976) and refined by full-matrix least squares (*SHELX*, Sheldrick, 1976). All H atoms were located on difference maps. Refinement converged to R = 0·054.* Eight reflexions with low θ and high F_o values appeared to be strongly affected by extinction and were excluded from refinement. Neutral-atom scattering factors were taken from Cromer & Mann (1968). Final atomic parameters are listed in Table 1.

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)	3512 (5)	481 (3)	3460 (2)	0·050 (2)
C(2)	5038 (6)	1278 (4)	3598 (3)	0·056 (3)
C(3)	6016 (6)	1355 (4)	2690 (3)	0·053 (3)
C(4)	5025 (6)	1698 (4)	1828 (3)	0·051 (2)
C(5)	3446 (4)	894 (4)	1788 (3)	0·052 (2)
C(6)	2373 (5)	788 (4)	2659 (3)	0·055 (2)
C(11)	2537 (12)	283 (6)	4324 (5)	0·094 (5)
C(21)	6271 (10)	644 (6)	4295 (5)	0·088 (4)
C(22)	4638 (10)	2580 (5)	3993 (4)	0·080 (4)
C(61)	1135 (7)	−304 (5)	2503 (5)	0·082 (4)
C(62)	1241 (7)	1949 (5)	2783 (5)	0·077 (4)
O(41)	4430 (5)	2949 (3)	1853 (3)	0·059 (2)
C(41)	6097 (8)	1461 (6)	968 (4)	0·083 (4)
C(411)	6154 (10)	2098 (6)	223 (5)	0·105 (6)
H(31)	648 (5)	52 (3)	263 (3)	0·05 (1)
H(32)	698 (5)	182 (4)	278 (3)	0·08 (1)
H(51)	269 (5)	118 (4)	122 (3)	0·06 (1)
H(52)	419 (6)	−1 (4)	174 (3)	0·09 (2)
H(111)	191 (7)	110 (4)	454 (4)	0·11 (2)
H(112)	163 (6)	−39 (5)	420 (4)	0·11 (2)
H(113)	351 (6)	2 (5)	476 (4)	0·13 (2)
H(211)	760 (7)	110 (7)	426 (6)	0·20 (4)
H(212)	642 (8)	−19 (5)	392 (4)	0·15 (3)
H(213)	584 (8)	55 (6)	499 (3)	0·14 (2)
H(221)	383 (6)	314 (4)	351 (3)	0·09 (2)
H(222)	588 (6)	285 (5)	410 (4)	0·13 (2)
H(223)	401 (8)	255 (6)	465 (3)	0·15 (2)
H(611)	65 (7)	−14 (5)	178 (3)	0·13 (2)
H(612)	196 (6)	−112 (4)	251 (4)	0·11 (2)
H(613)	10 (5)	−24 (4)	302 (3)	0·09 (2)
H(621)	40 (5)	195 (4)	225 (3)	0·07 (1)
H(622)	68 (7)	195 (5)	347 (3)	0·12 (2)
H(623)	202 (5)	273 (4)	283 (3)	0·02 (1)
H(41)	719 (11)	91 (7)	115 (6)	0·23 (4)
H(*V*1)	723 (8)	187 (6)	−29 (4)	0·18 (3)
H(*V*2)	558 (9)	302 (5)	38 (4)	0·18 (3)
H(O1)	504 (6)	338 (4)	205 (3)	0·09 (2)

Discussion. The molecules of PMPV adopt a chair conformation for the piperidine ring. The methyl group at the N atom and the vinyl group at C(4) take equatorial positions, while the hydroxyl group is axial. Values of bond distances and valence angles are shown in Fig. 1 and torsion angles in Fig. 2. The piperidine ring is distorted as in related derivatives (Cygler, Skarżyński, Skolimowski & Thozet, 1980). The axial substituents interact with each other and are bent away from the ring. The corresponding distances are as follows: C(22)···C(62) = 3·263 (9); C(2)···C(6) = 2·550 (6); C(22)···O(41) = 3·114 (7); C(2)···C(4) = 2·591 (6); C(62)···O(41) = 3·045 (7); C(6)···C(4) = 2·602 (6) Å. The asymmetry parameter of the ring (Duax & Norton, 1975) with respect to the plane of symmetry through N(1) and C(4) is $C_s^N = 0{\cdot}74°$. The arrangement of methyl groups in the N part of the ring is similar to that found in other pentamethylpiperidine derivatives and no significant dependence on the substituent in position 4 is observed.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35374 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

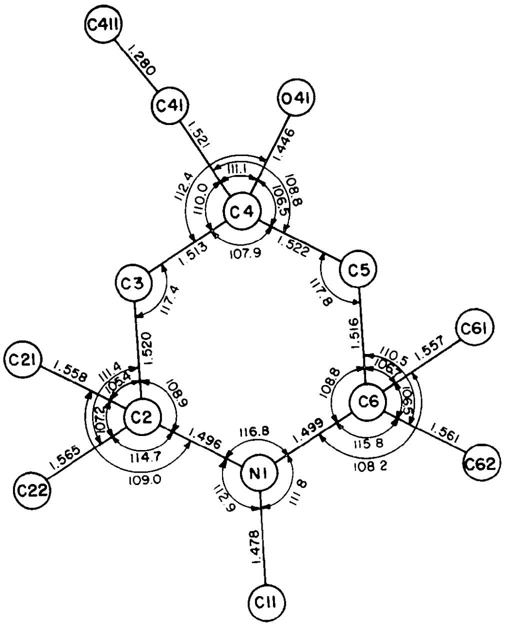


Fig. 1. Bond lengths (Å) and valence angles (°). The standard deviations are in the ranges 0·004–0·008 Å and 0·3–0·4°, respectively.

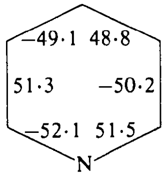


Fig. 2. Torsion angles (°) in the piperidine ring. Standard deviations are estimated to be less than 0·7°.

The hydroxyl and vinyl groups are in *gauche* conformation with respect to the C(4)–C(41) bond. To minimize interatomic interactions between the vinyl group and the rest of the molecule one would expect the value of the O(41)–C(4)–C(41)–C(411) torsion angle to be about 60°. The actual value found in the structure is, however, 18·1 (6)°, which brings one of the vinyl protons, H(*V*2), into close contact with the O atom [2·30 (6) Å]. The low value of the H(*V*2)–C(411)–C(41) angle, 108 (3)°, indicates a movement of H(*V*2) toward O(41). Despite the low C(411)–H(*V*2)···O(41) angle [108 (4)°], these facts suggest the formation of an intramolecular =C–H···O hydrogen bond which closes a quasi five-membered ring. A similar low =C–H···O angle was recently observed in an intramolecular hydrogen bond in 2′-deoxy-5-hydroxymethyluridine (Birnbaum, 1980).

The packing of the molecules is shown in Fig. 3. The molecules are located in such a way that the quasi five-membered ring of one molecule is placed between three equatorial methyl groups of a molecule related by a twofold screw axis. The distances between the hydroxyl group and the N atom of a neighbouring molecule are N(1)···O(41) = 3·328 (5), N(1)···H(O1) = 2·67 (4) Å, and ∠O(41)–H(O1)···N(1) = 137 (4)°. A closer approach is hindered by the interaction of the vinyl group with one of the equatorial methyl groups [H(*V*2)···H(113) = 2·31 (8) Å]. The N···H distance is very close to the sum of the van der Waals radii. The hydrogen bond, if any, is a very weak one. All other intermolecular interactions are of van der Waals type.

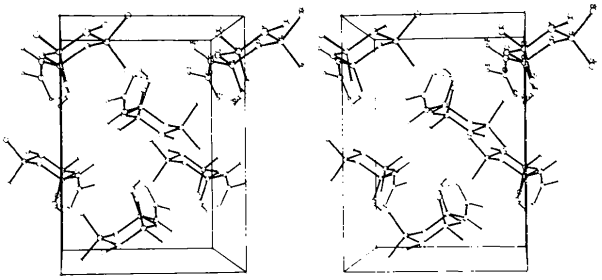


Fig 3. Stereoview of the packing of the molecules. The origin is at the lower left-hand corner, **a** is horizontal, **b** is up the page and **c** towards the reader.

The authors wish to thank Dr J. Skolimowski for supplying the crystals and Mr S. Lecocq for collecting the diffraction data. This work was supported by grant MR.I.12 from the Polish Academy of Sciences, which is hereby gratefully acknowledged.

References

Birnbaum, G. I. (1980). *J. Am. Chem. Soc.* **102**, 4236–4241.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Cygler, M. (1979). *Acta Cryst.* B**35**, 195–197.
Cygler, M., Grabowski, M. J., Skolimowski, J. & Skowroński, R. (1978). *Acta Cryst.* B**34**, 2327–2331.
Cygler, M., Markowicz, T., Skolimowski, J. & Skowroński, R. (1980). To be published.
Cygler, M., Skarżyński, T., Skolimowski, J. & Thozet, A. (1980). *Acta Cryst.* B**36**, 2481–2483.
Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure.* Vol. 1, p. 18. London: Plenum.
Golovina, N. I., Klitskaya, G. A., Medzhidov, A. A. & Atovmian, L. O. (1975). *Zh. Strukt. Khim.* **16**, 145–147.
Guseinova, M. K. & Mamedov, C. D. (1978). *Zh. Strukt. Khim.* **19**, 702–710.
Lajzérowicz-Bonneteau, J. (1976). In *Spin Labeling. Theory and Applications*, edited by L. J. Berliner. New York: Academic Press.
Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J. P. (1976). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Rees, B. & Weiss, R. (1971). *Acta Cryst.* B**27**, 932–940.
Ruben, H., Zalkin, A. & Templeton, D. H. (1974). *Acta Cryst.* B**30**, 334–337.
Sato, S., Yoshioka, T. & Tamura, C. (1975). *Acta Cryst.* B**31**, 1385–1392.
Sheldrick, G. M. (1976). *SHELX* 76. A program for crystal structure determination. Univ. of Cambridge, England.