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Structures of Two 2-(2-Hydroxyaryl)piperidines: 2-(2-Hydroxy-1-naphthyl)-1-methyl-4-piperidinecarbonitrile, $C_{17}H_{18}N_2O$, and 2-(2-Hydroxy-5-methylphenyl)-1-methyl-4-piperidinecarbonitrile, $C_{14}H_{18}N_2O$

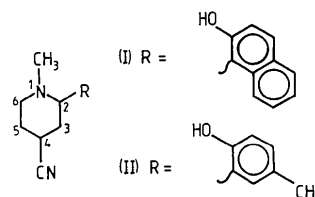
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Abstract. $C_{17}H_{18}N_2O$ (I), $M_r = 266.3$, monoclinic, $P2_1/c$, $a = 10.359$ (1), $b = 12.919$ (1), $c = 11.410$ (2) Å, $\beta = 108.61$ (1)°, $U = 1447.1$ (3) Å³, $D_m = 1.22$ (1), $D_x = 1.222$ Mg m⁻³, $Z = 4$, $F(000) = 568$, $\mu(\text{Cu } K\alpha) = 0.53$ mm⁻¹, $T = 291$ K. $C_{14}H_{18}N_2O$ (II), $M_r = 230.3$, monoclinic, $C2/c$, $a = 18.583$ (3), $b = 11.824$ (2), $c = 12.010$ (1) Å, $\beta = 99.00$ (1)°, $U = 2606.4$ (5) Å³, $D_m = 1.17$ (1), $D_x = 1.174$ Mg m⁻³, $Z = 8$, $F(000) = 992$, $\mu(\text{Cu } K\alpha) = 0.52$ mm⁻¹, $T = 291$ K. Both structures were solved by direct methods with diffractometer data measured with Cu $K\alpha$ radiation. Full-matrix least-squares refinement converged at $R = 0.055$ (I) and $R = 0.054$ (II). In (I), the methyl, cyano and aryl substituents are equatorial, while in (II) the cyano group is axial. In both structures there is an intramolecular hydrogen bond between the ring nitrogen and aryl hydroxyl group, the N...O distances being 2.612 (3) and 2.678 (3) Å in (I) and (II) respectively.

Introduction. The title compounds (I) and (II) have resulted from reaction of 1-methyl-4-piperidinecarbonitrile with 2-naphthol and *p*-cresol respectively in the presence of sodium (Butt, Deady, Mackay & Sadek, 1982). Two geometrical isomers, which differ in having an equatorial or axial cyano group, have been separated, and (I) and (II) provide an example of each isomer. The X-ray results have confirmed that the nucleophile is attached to C(2) rather than to C(3), and have defined the configuration in the piperidine moieties. A brief report of the results has been presented (Butt, Deady, Mackay & Sadek, 1982).



Experimental. Weissenberg photographs showed that the tabular crystals grown from ethanol were monoclinic, and systematic extinctions indicated space groups $P2_1/c$ and $C2/c$ for crystals of (I) and (II) respectively. Cell parameters determined by least squares from 2θ values for 25 strong reflections, Cu $K\alpha$, Rigaku-AFC four-circle diffractometer; crystal densities determined by flotation; integrated intensities measured with Cu $K\alpha$ radiation (graphite-crystal monochromator, $\lambda = 1.5418$ Å), crystals *ca* 0.18 × 0.40 × 0.38 mm (I) and 0.10 × 0.40 × 0.40 mm (II), ω - 2θ scan, 2θ scan rate 2° min⁻¹, scan range ($\Delta\omega$) 1.2° + 0.5° tan θ , 10s stationary background counts; three reference reflections monitored every 50 reflections showed no significant variation in intensity during the data-collection periods; $2\theta_{\max} = 130^\circ$; of the 2450 non-equivalent terms for (I), the 2103 with $|F_o| > 2\sigma|F_o|$ were used for the structure refinement, and of the 2205 (II), the 1601 with $|F_o| > 3\sigma|F_o|$ were used; no corrections for absorption; scattering factors for O, N, and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections for non-H atoms from Cromer & Liberman (1970); direct methods [*SHELX* 76 (Sheldrick, 1976)], full-matrix least-squares refinement with anisotropic temperature factors for C, N and O atoms,

H atoms located on difference maps; for (I) the final refinement (positional coordinates and isotropic temperature factors of the H atoms allowed to vary) converged at $R = 0.055$ and $R_w = 0.063$; mean parameter shift-to-error ratios at convergence 0.06:1 for the H atoms and 0.02:1 for all other parameters; largest peaks on the final difference map 0.18 and $-0.25 \text{ e } \text{Å}^{-3}$; for (II) the final refinement (positional coordinates of the H atoms were allowed to vary) converged at $R = 0.054$ and $R_w = 0.048$; methyl and non-methyl H atoms were given common isotropic temperature factors which refined to the respective values $B = 9.5$ (4) and 5.3 (2) Å^2 ; mean parameter shift-to-error ratios at convergence 0.07:1 for the H atoms and 0.04:1 for all other parameters; largest peaks on the final difference map 0.15 and $-0.19 \text{ e } \text{Å}^{-3}$; function minimized $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma^2|F_o| + m|F_o|^2)^{-1}$ with $m = 3 \times 10^{-4}$ and 5×10^{-5} for (I) and (II) respectively. During the analyses, examination of $|F_o|$ and $|F_c|$ terms indicated that five of the most intense reflections for each structure were significantly affected by extinction, and they were omitted from the refinements.

Discussion. Final atomic coordinates are given in Tables 1 and 2;* Figs. 1 and 2 were prepared with ORTEP (Johnson, 1965). The molecular conformations are illustrated in Fig. 1 with the numbering schemes, while bond lengths and angles are given in Table 3 and torsional angles associated with the piperidine rings are given in Table 4.

As expected, the piperidine rings adopt almost regular chair conformations with the aryl and methyl substituents in equatorial positions. The cyano group in the 2-naphthol derivative (I) is equatorial whilst in the *p*-cresol derivative (II) it is axial. The torsional angles in the piperidine rings have the mean values $\pm 56.6^\circ$ (mean deviation 1.3°) in (I) and $\pm 55.2^\circ$ (mean deviation 2.1°) in (II) compared to the value $\pm 54.7^\circ$ for an ideal chair conformation. C(2), C(3), C(5) and C(6) are coplanar within ± 0.009 (2) Å in (I) and the plane makes an angle of 129.7 (3) $^\circ$ with the C(2), N(1), C(6) plane and an angle of 129.6 (3) $^\circ$ with the C(3), C(4), C(5) plane. In (II) the four atoms are coplanar within ± 0.010 (3) Å and the comparable interplanar angles are 128.5 (4) and 132.5 (4) $^\circ$. Similar dimensions have been observed in other piperidine systems; for example in 4-hydroxy-3-piperidinecarboxylic acid (Brehm, Schaumburg & Krogsgaard-Larsen, 1979) the piperidine ring adopts a nearly ideal chair conformation with the ring torsional angles having a mean value $\pm 54.3^\circ$ (mean deviation 1.7°).

* Lists of structure amplitudes, anisotropic thermal parameters, coordinates of H atoms, and intermolecular separations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38338 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates of the non-hydrogen atoms ($\times 10^4$) and equivalent isotropic temperature factors for structure (I)*

E.s.d.'s are included in parentheses. $B_{\text{eq}} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} \rho_i^* \rho_j^* a_i a_j$.

	x	y	z	B_{eq} (Å^2)
N(1)	3641 (2)	-47 (1)	2208 (2)	3.4 (1)
C(2)	4368 (2)	963 (1)	2477 (2)	3.1 (1)
C(3)	4015 (2)	1626 (2)	1295 (2)	3.4 (1)
C(4)	2480 (2)	1763 (2)	721 (2)	3.6 (1)
C(5)	1810 (2)	701 (2)	448 (2)	4.1 (1)
C(6)	2168 (2)	79 (2)	1633 (2)	3.9 (1)
C(7)	3876 (3)	-648 (2)	3357 (2)	4.7 (1)
C(8)	2151 (2)	2387 (2)	-412 (2)	4.5 (1)
C(9)	5898 (2)	799 (1)	2944 (2)	3.1 (1)
C(10)	6492 (2)	20 (2)	2459 (2)	3.5 (1)
C(11)	7908 (2)	-118 (2)	2822 (2)	4.0 (1)
C(12)	8743 (2)	521 (2)	3681 (2)	4.1 (1)
C(13)	8202 (2)	1323 (2)	4227 (2)	3.5 (1)
C(14)	9063 (2)	1956 (2)	5177 (2)	4.3 (1)
C(15)	8547 (2)	2734 (2)	5697 (2)	4.5 (1)
C(16)	7146 (2)	2927 (2)	5283 (2)	4.1 (1)
C(17)	6279 (2)	2320 (2)	4387 (2)	3.5 (1)
C(18)	6772 (2)	1478 (1)	3850 (2)	3.1 (1)
N(2)	1887 (2)	2852 (2)	-1308 (2)	6.2 (1)
O(1)	5736 (2)	-652 (1)	1581 (1)	4.5 (1)

Table 2. *Final atomic coordinates of the non-hydrogen atoms ($\times 10^4$) and equivalent isotropic temperature factors for structure (II)*

E.s.d.'s are included in parentheses. $B_{\text{eq}} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} \rho_i^* \rho_j^* a_i a_j$.

	x	y	z	B_{eq} (Å^2)
N(1)	2820 (1)	-801 (2)	5942 (2)	3.6 (1)
C(2)	2596 (1)	391 (2)	6102 (2)	3.0 (2)
C(3)	3139 (1)	1211 (2)	5708 (2)	3.8 (1)
C(4)	3927 (2)	993 (2)	6257 (2)	4.3 (2)
C(5)	4117 (2)	-248 (3)	6106 (3)	5.0 (1)
C(6)	3567 (2)	-1015 (3)	6519 (3)	4.5 (2)
C(7)	2316 (2)	-1594 (3)	6379 (3)	5.2 (2)
C(8)	4033 (1)	1292 (2)	7459 (3)	4.7 (1)
C(9)	1850 (1)	596 (2)	5438 (2)	3.0 (1)
C(10)	1666 (10)	216 (2)	4327 (2)	3.6 (1)
C(11)	1001 (2)	492 (2)	3705 (2)	4.4 (1)
C(12)	498 (2)	1106 (2)	4186 (3)	4.4 (1)
C(13)	652 (1)	1471 (2)	5302 (2)	3.8 (1)
C(14)	99 (2)	2126 (3)	5830 (3)	5.4 (1)
C(18)	1332 (1)	1212 (2)	5899 (2)	3.4 (1)
N(2)	4111 (1)	1500 (3)	8395 (2)	6.5 (1)
O(1)	2146 (1)	-429 (2)	3831 (2)	4.5 (1)

Table 3. *Bond lengths (Å) and angles ($^\circ$) with e.s.d.'s in parentheses*

	(I)	(II)
N(1)-C(2)	1.489 (2)	1.491 (3)
N(1)-C(6)	1.465 (2)	1.471 (4)
N(1)-C(7)	1.476 (2)	1.480 (4)
C(2)-C(3)	1.540 (2)	1.528 (3)
C(2)-C(9)	1.517 (2)	1.504 (3)
C(3)-C(4)	1.524 (2)	1.529 (4)
C(4)-C(5)	1.524 (3)	1.527 (4)
C(4)-C(8)	1.468 (3)	1.469 (4)
C(5)-C(6)	1.514 (3)	1.508 (5)
C(8)-N(2)	1.141 (3)	1.137 (4)
C(9)-C(10)	1.384 (2)	1.398 (3)
C(9)-C(18)	1.435 (2)	1.391 (3)
C(10)-O(1)	1.367 (2)	1.379 (3)

Table 3 (cont.)

	(I)	(II)
C(10)—C(11)	1.403 (3)	1.377 (4)
C(11)—C(12)	1.360 (3)	1.381 (5)
C(12)—C(13)	1.414 (3)	1.394 (4)
C(13)—C(14)	1.422 (3)	1.505 (4)
C(13)—C(18)	1.419 (2)	1.384 (3)
C(14)—C(15)	1.360 (3)	—
C(15)—C(16)	1.398 (3)	—
C(16)—C(17)	1.371 (3)	—
C(17)—C(18)	1.421 (2)	—
O(1)—H(O1)	1.00 (3)	0.99 (3)
C(2)—N(1)—C(6)	112.4 (1)	111.3 (2)
C(2)—N(1)—C(7)	110.4 (1)	110.4 (2)
C(6)—N(1)—C(7)	108.0 (2)	109.1 (2)
N(1)—C(2)—C(3)	110.1 (1)	110.4 (2)
N(1)—C(2)—C(9)	110.7 (1)	109.6 (2)
C(3)—C(2)—C(9)	108.3 (1)	109.4 (2)
C(2)—C(3)—C(4)	111.4 (1)	113.2 (3)
C(3)—C(4)—C(5)	109.1 (2)	109.5 (2)
C(3)—C(4)—C(8)	111.1 (1)	110.8 (2)
C(5)—C(4)—C(8)	110.6 (2)	110.5 (2)
C(4)—C(5)—C(6)	109.2 (2)	111.0 (3)
N(1)—C(6)—C(5)	112.5 (2)	112.3 (2)
N(2)—C(8)—C(4)	178.4 (3)	178.5 (3)
C(2)—C(9)—C(10)	120.6 (2)	121.4 (2)
C(2)—C(9)—C(18)	121.0 (1)	120.7 (2)
C(10)—C(9)—C(18)	118.3 (2)	117.9 (2)
O(1)—C(10)—C(9)	122.1 (2)	120.8 (2)
O(1)—C(10)—C(11)	115.9 (2)	118.8 (2)
C(9)—C(10)—C(11)	122.1 (2)	120.3 (2)
C(10)—C(11)—C(12)	120.0 (2)	120.4 (3)
C(11)—C(12)—C(13)	120.8 (2)	121.0 (3)
C(12)—C(13)—C(14)	121.1 (2)	120.9 (3)
C(12)—C(13)—C(18)	119.5 (2)	117.5 (2)
C(14)—C(13)—C(18)	119.4 (2)	121.6 (3)
C(13)—C(14)—C(15)	121.3 (2)	—
C(14)—C(15)—C(16)	119.6 (2)	—
C(15)—C(16)—C(17)	120.8 (2)	—
C(16)—C(17)—C(18)	121.3 (2)	—
C(9)—C(18)—C(13)	119.3 (2)	122.9 (2)
C(9)—C(18)—C(17)	123.2 (2)	—
C(13)—C(18)—C(17)	117.5 (2)	—

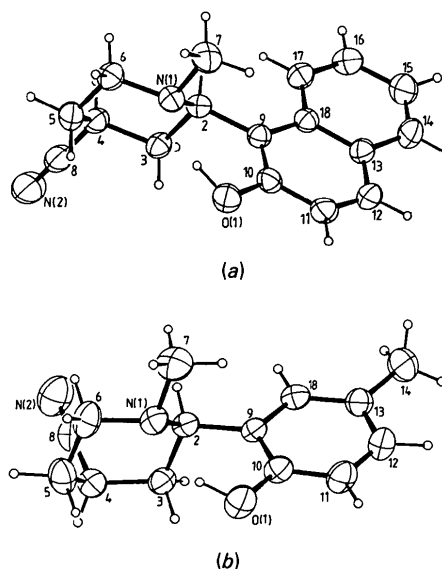


Fig. 1. Perspective views of the molecules with thermal ellipsoids scaled to 40% probability. The C atoms are denoted by numerals only. (a) Compound (I), (b) compound (II).

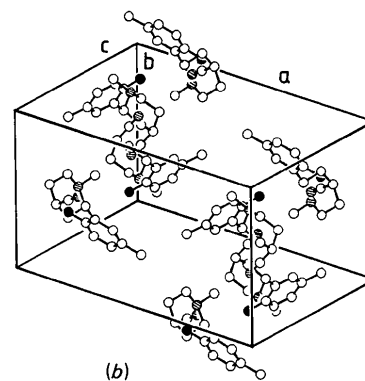
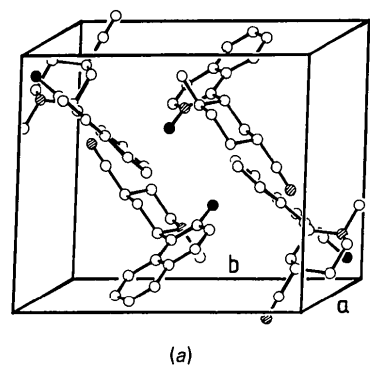


Fig. 2. The molecular packing in the crystals. (a) Compound (I), (b) compound (II).

Table 4. Torsional angles associated with the piperidyl moiety ($^{\circ}$)

The e.s.d.'s range from 0.2 to 0.4 $^{\circ}$.

	(I)	(II)
N(1)—C(2)—C(3)—C(4)	55.0	53.8
C(2)—C(3)—C(4)—C(5)	-57.3	-52.4
C(3)—C(4)—C(5)—C(6)	57.6	53.1
C(4)—C(5)—C(6)—N(1)	-58.3	-57.5
C(5)—C(6)—N(1)—C(2)	57.2	58.8
C(6)—N(1)—C(2)—C(3)	-54.2	-55.7
C(2)—C(3)—C(4)—C(8)	-179.4	69.7
C(3)—C(2)—N(1)—C(7)	-174.9	-177.0
C(4)—C(3)—C(2)—C(9)	176.1	174.5
C(5)—C(6)—N(1)—C(7)	179.2	-179.2
C(6)—N(1)—C(2)—C(9)	-174.0	-176.3
C(6)—C(5)—C(4)—C(8)	180.0	-69.2
C(7)—N(1)—C(2)—C(9)	65.3	62.4
C(2)—C(9)—C(10)—O(1)	-2.4	-4.6
N(1)—C(2)—C(9)—C(10)	37.4	44.8

In the 2-(2-hydroxyaryl)piperidine structures reported here, the orientation of the piperidine ring relative to the aryl moieties is given by the torsional angle N(1)—C(2)—C(9)—C(10), which is 37.4 (3)° in (I) and 44.8 (3)° in (II). Consequently, the hydroxyl group lies adjacent to the ring nitrogen with which it forms an intramolecular hydrogen bond. In (I), N(1)⋯O(1), N(1)⋯H(O1) and O(1)—H(O1) are 2.612 (2), 1.68 (2) and 1.00 (3) Å respectively with ∠N(1)⋯H(O1)—O(1) 155 (1)°. The analogous dimensions in (II) are 2.683 (3), 1.79 (3), 0.99 (3) Å and 148 (1)°. C(2) and O(1) are not quite planar with their associated aromatic rings as is illustrated by the torsional angles C(2)—C(9)—C(10)—O(1) of -2.4 (2) and -4.6 (3)° in (I) and (II) respectively.

The bond lengths and angles in (I) and (II) are in good agreement, and similar to values observed in comparable compounds. N(1)—C(6) is of mean length 1.468 (3) Å. This is significantly shorter than N(1)—C(2) of mean length 1.490 (3) Å, which compares well with the value 1.494 (4) Å reported for 4-hydroxy-3-piperidinecarboxylic acid; ∠C(2)—N(1)—C(6), mean value 111.9 (2)°, is close to 112.6 (2)° in the structure referred to above. In the cyano group, C(8)—N(2) and C(4)—C(8) bonds have mean lengths 1.139 (4) and 1.468 (4) Å respectively, and the C(4)—

C(8)—N(2) angle of 178.4 (3)° is almost linear. These values can be compared with the analogous lengths 1.135 (2) and 1.437 (2) Å and angle 177.93 (7)° observed in tetracyanoethylene (Becker, Coppens & Ross, 1973). The C—H lengths of the methyl groups range from 0.91 (4) to 1.07 (4) Å while the remainder vary between 0.97 (3) and 1.07 (3) Å.

The molecular packing is illustrated in Fig. 2. Both crystals are racemates, the molecules having asymmetric centres at C(2) and C(4). There are no unusually short intermolecular approaches in either structure.

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Methyl β-D-Glucoseptanoside, C₇H₁₄O₆

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Abstract. $M_r = 194.2$, monoclinic, $P2_1$, $a = 6.742$ (2), $b = 7.227$ (2), $c = 9.116$ (3) Å, $\beta = 104.49$ (2)°, $V = 430.0$ Å³, $Z = 2$, $D_m = 1.50$ (2) (by flotation in carbon tetrachloride/light petroleum), $D_x = 1.50$ (1) Mg m⁻³, $\mu(\text{Cu } K\alpha_1) = 1.096$ mm⁻¹, $F(000) = 212$, $T = 293$ K, $R = 0.027$ for 884 reflexions (including unobserveds). The septanose ring is close to a chair (²C_{5,6}) conformation and all of the hydroxyl groups are involved in hydrogen bonding, including two bifurcated bonds, one hydrogen bond involving the glycosidic oxygen, and a weak intramolecular hydrogen bond.

Introduction. The title compound (1) is the first unsubstituted septanoside to be examined by X-ray

diffraction and it was chosen for study in order to compare its molecular conformation with that of the di-*O*-isopropylidene derivative and a mono-*O*-isopropylidene derivative (studies in hand).

Experimental. Crystals of (1) (Stevens, 1975), m.p. 397–399 K, obtained from an ethanol solution; a colourless plate crystal, 0.6 × 0.16 × 0.04 mm, was used for data collection and determination of the parameters (nine high-order reflexions); intensities of all 884 symmetry-independent reflexions ($\theta < 70^\circ$) measured on a Siemen's automatic single-crystal diffractometer using Ni-filtered Cu $K\alpha_1$ radiation with θ - 2θ scans (Arndt & Willis, 1966); Lorentz,