

Tableau 3. Distances (Å) et angles (°) interatomiques

S(1)—C(2)	1,783 (5)	O(12)—C(13)	1,439 (6)
S(1)—C(8a)	1,838 (4)	C(7)—C(14)	1,500 (5)
C(2)—C(3)	1,506 (6)	C(14)—O(15)	1,187 (4)
C(3)—N(4)	1,478 (5)	C(14)—O(16)	1,318 (4)
N(4)—C(5)	1,326 (5)	O(16)—C(17)	1,451 (6)
C(8a)—N(4)	1,470 (5)	C(8)—C(18)	1,468 (5)
C(5)—C(6)	1,392 (5)	C(18)—O(19)	1,188 (5)
C(6)—C(7)	1,425 (5)	C(18)—O(20)	1,333 (5)
C(7)—C(8)	1,370 (5)	O(20)—C(21)	1,439 (6)
C(8)—C(8a)	1,510 (5)	C(8a)—C(22)	1,543 (5)
C(5)—C(9)	1,492 (6)	C(22)—O(23)	1,196 (5)
C(6)—C(10)	1,467 (5)	C(22)—O(24)	1,325 (5)
C(10)—O(11)	1,203 (5)	O(24)—C(25)	1,442 (5)
C(10)—O(12)	1,346 (5)		
C(2)—S(1)—C(8a)	90,0 (2)	C(7)—C(8)—C(8a)	116,2 (3)
S(1)—C(2)—C(3)	106,6 (3)	C(7)—C(8)—C(18)	125,8 (3)
C(2)—C(3)—N(4)	107,1 (4)	C(8a)—C(8)—C(18)	117,9 (3)
C(3)—N(4)—C(5)	123,4 (4)	S(1)—C(8a)—N(4)	104,4 (2)
C(3)—N(4)—C(8a)	115,3 (3)	S(1)—C(8a)—C(8)	115,5 (3)
C(5)—N(4)—C(8a)	121,2 (3)	N(4)—C(8a)—C(8)	109,9 (3)
N(4)—C(5)—C(6)	119,3 (3)	S(1)—C(8a)—C(22)	106,1 (2)
N(4)—C(5)—C(9)	116,5 (4)	N(4)—C(8a)—C(22)	108,4 (3)
C(6)—C(5)—C(9)	123,5 (4)	C(8)—C(8a)—C(22)	112,1 (3)
C(5)—C(6)—C(7)	118,2 (3)	C(6)—C(10)—O(12)	112,1 (4)
C(5)—C(6)—C(10)	121,9 (4)	O(11)—C(10)—O(12)	121,7 (4)
C(7)—C(6)—C(10)	119,4 (4)	C(10)—O(12)—C(13)	116,0 (4)
C(6)—C(7)—C(8)	121,0 (3)	C(7)—C(14)—O(15)	123,6 (4)
C(6)—C(7)—C(14)	117,9 (3)	C(7)—C(14)—O(16)	111,3 (5)
C(8)—C(7)—C(14)	121,1 (3)	O(15)—C(14)—O(16)	125,0 (4)
C(8)—C(18)—O(19)	125,2 (4)	C(14)—O(16)—C(17)	115,8 (4)
C(8)—C(18)—O(20)	112,9 (3)	C(8a)—C(22)—O(23)	123,6 (4)
O(19)—C(18)—O(20)	121,9 (4)	C(8a)—C(22)—O(24)	111,0 (3)
C(18)—O(20)—C(21)	117,0 (4)	O(23)—C(22)—O(24)	125,4 (4)
		C(22)—O(24)—C(25)	117,1 (4)

L'existence d'un plan de symétrie dans le groupe $P2_1/n$ permet la présence de deux énantiomères dans le cristal.

En conclusion, l'étude par rayons X du composé (1) a permis de confirmer l'hypothèse de structure basée sur l'étude des déplacements chimiques observés en RMN ^{13}C , d'établir sans ambiguïté sa structure et de préciser la conformation des cycles.

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3,4,4a,5-Tetrahydro-[1,2,4]triazino[6,1-c][1,4]benzoxazine, $C_{10}H_{11}N_3O$

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Abstract. $M_r = 189.2$, monoclinic, $P2_1/n$, $a = 6.909(1)$, $b = 15.149(2)$, $c = 9.430(2)$ Å, $\beta = 109.17(1)^\circ$, $V = 932.3(4)$ Å³, $Z = 4$, $D_x = 1.348$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, graphite mon-

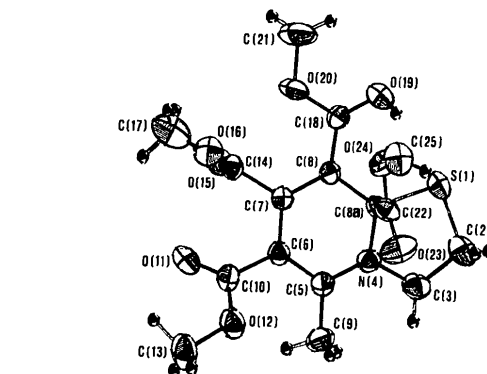


Fig. 2. Géométrie moléculaire du composé (1) obtenue à l'aide du programme ORTEP (Johnson, 1965). Les ellipsoïdes de vibration des atomes non hydrogène ont une probabilité de 50%. Les atomes d'hydrogène sont représentés par des sphères de rayon arbitraire. Afin d'avoir des éléments de comparaison avec les composés (2) et (3) nous avons gardé la même numérotation des atomes.

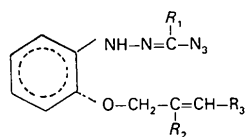
France) pour l'assistance technique qu'il nous a apportée lors de l'enregistrement des intensités diffractées.

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ochromator, $\mu = 0.09$ mm⁻¹, $F(000) = 400$, room temperature, final $R = 0.065$ for 1459 reflections. The structure proposed from spectroscopic data has been confirmed.

Introduction. The title compound and some derivatives were recently synthesized (Garanti & Zecchi, 1980) by thermal decomposition of 1-azidohydrazone.



$R_1 = \text{H, COOCH}_3$

$R_2 = \text{H, CH}_3$

$R_3 = \text{H, C}_6\text{H}_5$

The above formula was suggested on the basis of spectroscopic data. As a further proof of the proposed configuration, this X-ray analysis was undertaken.

Experimental. White prism, ground to a sphere of diameter 0.025 mm, Nonius CAD-4 diffractometer, $3 < 2\theta < 27.5^\circ$, three check reflections, one of which had an intensity decay of about 8%, 2124 reflections measured, 1459 with $I > 2\sigma(I)$ used for the analysis, Lp correction, absorption and decay ignored, direct methods (*MULTAN*, Germain, Main & Woolfson, 1971), anisotropic full matrix, H (from ΔF synthesis) isotropic, secondary extinction parameter $g = 0.77(2) \times 10^{-6}$, 172 parameters, refinement on F magnitude, $w = 1/\sigma^2(F)$, $R = 0.065$, $R_w = 0.069$, goodness-of-fit = 2.99,* maximum shift/error in the last cycle 0.1, scattering factors from Cromer & Waber (1974).

Discussion. Fractional coordinates and equivalent or isotropic thermal parameters are given in Table 1, bond distances and angles (involving heavy atoms only) are collected in Table 2. A projection of the molecule with thermal ellipsoids at the 50% probability level and the atomic numbering scheme is shown in Fig. 1. The molecules are joined in chains by means of hydrogen bonds: $\text{N}(3)\text{---H}(\text{N}3)\cdots\text{N}(2)(\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z)$. The $\text{N}(3)\cdots\text{N}(2)$ and $\text{H}(\text{N}3)\cdots\text{N}(2)$ distances are 3.184 (2) and 2.51 (2) Å respectively and the angle $\text{N}(3)\text{---H}(\text{N}3)\cdots\text{N}(2)$ is $163(1)^\circ$. The molecular geometry shows no unusual feature such as to justify anomalous chemical behaviour. From the structural viewpoint it is worthwhile noticing the short $\text{N}(3)\text{---C}(7)$ distance suggesting partial double-bond character. In fact, the H atom might migrate from $\text{N}(3)$ to $\text{N}(2)$ via a hydrogen shift in adjacent hydrogen bonds. This idea is supported by the decreased pyramidalization at $\text{N}(3)$ as compared to $\text{N}(1)$. The rings containing heteroatoms show twisted conformations.

The present work completely supports the proposed structure.

We are in debt to Professor L. Garanti for the gift of a crystalline sample.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38311 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final coordinates and isotropic thermal parameters

For non-H atoms $U_{\text{eq}} = (6\pi^2)^{-1} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$.

	x	y	z	$U/U_{\text{eq}}(\text{\AA}^2)$
C(1)	0.0267 (4)	0.6070 (2)	0.2734 (3)	0.0390 (8)
C(2)	-0.0310 (4)	0.5925 (2)	0.1214 (3)	0.0514 (10)
C(3)	-0.2358 (5)	0.5865 (2)	0.0363 (3)	0.0530 (10)
C(4)	-0.3822 (4)	0.5927 (2)	0.1051 (3)	0.0452 (9)
C(5)	-0.3252 (4)	0.6075 (2)	0.2577 (3)	0.0383 (8)
C(6)	-0.1212 (4)	0.6169 (2)	0.3440 (2)	0.0324 (7)
C(7)	-0.1388 (4)	0.7058 (2)	0.6825 (3)	0.0475 (9)
C(8)	0.2039 (4)	0.6467 (2)	0.7399 (3)	0.0506 (10)
C(9)	0.1534 (4)	0.6579 (2)	0.5715 (3)	0.0385 (8)
C(10)	0.2825 (4)	0.6006 (2)	0.5092 (3)	0.0490 (10)
N(1)	-0.0603 (3)	0.6322 (1)	0.5003 (2)	0.0351 (7)
N(2)	-0.2053 (3)	0.6818 (2)	0.5444 (2)	0.0430 (7)
N(3)	0.0436 (4)	0.6869 (2)	0.7857 (2)	0.0515 (3)
O	0.2331 (3)	0.6139 (1)	0.3509 (2)	0.0529 (7)
H(2)	0.073 (4)	0.590 (2)	0.077 (3)	0.063 (9)
H(3)	-0.276 (4)	0.578 (2)	-0.072 (3)	0.069 (9)
H(4)	-0.529 (4)	0.588 (2)	0.050 (3)	0.061 (8)
H(5)	-0.426 (4)	0.609 (2)	0.305 (3)	0.044 (7)
H(7)	-0.221 (4)	0.742 (2)	0.718 (3)	0.050 (8)
H'(8)	0.212 (4)	0.579 (2)	0.772 (3)	0.062 (9)
H''(8)	0.343 (4)	0.677 (2)	0.795 (3)	0.059 (8)
H(9)	0.166 (3)	0.721 (2)	0.545 (2)	0.038 (7)
H'(10)	0.264 (4)	0.537 (2)	0.519 (3)	0.051 (8)
H''(10)	0.419 (5)	0.610 (2)	0.536 (4)	0.094 (11)
H(N3)	0.078 (4)	0.715 (2)	0.847 (3)	0.067 (9)

Table 2. Bond distances (Å) and angles ($^\circ$)

C(1)—C(2)	1.373 (3)	C(1)—C(6)	1.399 (4)
C(1)—O	1.376 (2)	C(2)—C(3)	1.382 (3)
C(2)—H(2)	0.94 (3)	C(3)—C(4)	1.372 (4)
C(3)—H(3)	0.98 (3)	C(4)—C(5)	1.380 (3)
C(4)—H(4)	0.98 (2)	C(5)—C(6)	1.384 (3)
C(5)—H(5)	0.94 (2)	C(6)—N(1)	1.413 (2)
C(7)—N(2)	1.283 (3)	C(7)—N(3)	1.346 (3)
C(7)—H(7)	0.92 (2)	C(8)—C(9)	1.520 (3)
C(8)—N(3)	1.449 (4)	C(8)—H'(8)	1.07 (2)
C(8)—H''(8)	1.04 (2)	C(9)—C(10)	1.497 (4)
C(9)—N(1)	1.460 (3)	C(9)—H(9)	1.00 (2)
C(10)—O	1.432 (3)	C(10)—H'(10)	0.99 (2)
C(10)—H''(10)	0.91 (3)	N(1)—N(2)	1.419 (3)
N(3)—H(N3)	0.69 (2)		
C(2)—C(1)—C(6)	120.5 (2)	C(2)—C(1)—O	117.5 (2)
C(6)—C(1)—O	122.0 (2)	C(1)—C(2)—C(3)	120.5 (3)
C(2)—C(3)—C(4)	119.6 (2)	C(3)—C(4)—C(5)	120.1 (2)
C(4)—C(5)—C(6)	121.1 (2)	C(1)—C(6)—C(5)	118.1 (2)
C(1)—C(6)—N(1)	120.1 (1)	C(5)—C(6)—N(1)	121.8 (2)
N(2)—C(7)—N(3)	127.7 (2)	C(9)—C(8)—N(3)	109.2 (2)
C(8)—C(9)—C(10)	112.5 (2)	C(8)—C(9)—N(1)	107.5 (2)
C(10)—C(9)—N(1)	107.9 (2)	C(9)—C(10)—O	111.0 (2)
C(6)—N(1)—C(9)	115.6 (2)	C(6)—N(1)—N(2)	113.3 (1)
C(9)—N(1)—N(2)	115.4 (1)	C(7)—N(2)—N(1)	113.3 (2)
C(7)—N(3)—C(8)	120.0 (2)	C(1)—O—C(10)	113.2 (2)

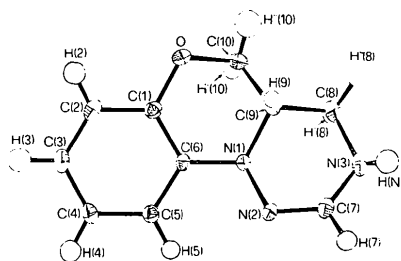


Fig. 1. A molecule of the title compound with the atomic numbering.

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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, $C_{14}H_{18}N_2O$

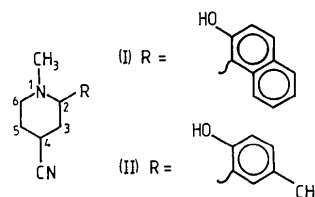
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Abstract. $C_{17}H_{18}N_2O$ (I), $M_r = 266.3$, monoclinic, $P2_1/c$, $a = 10.359$ (1), $b = 12.919$ (1), $c = 11.410$ (2) Å, $\beta = 108.61$ (1)°, $U = 1447.1$ (3) Å³, $D_m = 1.22$ (1), $D_x = 1.222$ Mg m⁻³, $Z = 4$, $F(000) = 568$, $\mu(\text{Cu } K\alpha) = 0.53$ 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 $0.18 \times 0.40 \times 0.38$ mm (I) and $0.10 \times 0.40 \times 0.40$ mm (II), ω - 2θ scan, 2θ scan rate 2° min⁻¹, scan range ($\Delta\omega$) $1.2^\circ + 0.5^\circ \tan\theta$, 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,