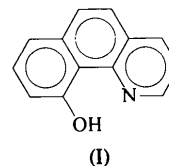Riche, C. (1992). *ACTACIF. Logiciel de Préparation des Fichiers CIF.* Institut de Chimie des Substances Naturelles du CNRS, France.

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10-Hydroxybenzo[*h*]quinoline

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Abstract

The crystal structure of 10-hydroxybenzo[*h*]quinoline, $C_{13}H_9NO$, has been determined. The asymmetric part of the unit cell comprises two almost planar molecules. A strong intramolecular O—H$\cdots$N hydrogen bond closes the six-membered ring. The geometrical features of the molecule suggest that it can be regarded as a 2-phenylpyridine with a fused double bond. In the crystal structure there are alternate layers of the two symmetry-independent molecules.

Comment

The results of the studies on *o*-phenanthroline (Nishigaki, Yoshioka & Nakatsu, 1978) show that from the point of view of geometrical features and MO calculations, it could be regarded as 2,2′-bipyridyl containing a fused C=C double bond. Examination of the Cambridge Structural Database (CSD) (Allen, Kennard & Taylor, 1983) encouraged us to extend this conclusion to a wider class of compounds, *e.g.* phenanthrene and benzo[*h*]-quinoline derivatives, which therefore, can be treated as biphenyl and 2-phenylpyridine derivatives, respectively. For example, there is a significant difference between two crucial bond lengths: the 'central' and the 'peripheral' (analogues of C10a—C10b and C5—C6 in Fig. 1). For 45 phenanthrene fragments in the CSD, the mean

values are 1.458 (3) and 1.340 (3) Å, respectively, and for 83 *o*-phenanthroline fragments, the mean values are 1.436 (3) and 1.335 (2) Å. Therefore, we performed an X-ray diffraction study on 10-hydroxybenzo[*h*]quinoline (I) as part of our studies into 2-phenylpyridine deriva-

(I)

tives, which are model compounds for the surprisingly easy deoxygenation of orellanine (Antkowiak & Gessner, 1984; Kubicki, Borowiak, Antkowiak & Antkowiak, 1990). The title compound contains crucial structural features of orelline (double-deoxidated orellanine): it is planar and has a hydroxy group and an N atom in *ortho* positions with respect to the central C—C bond.
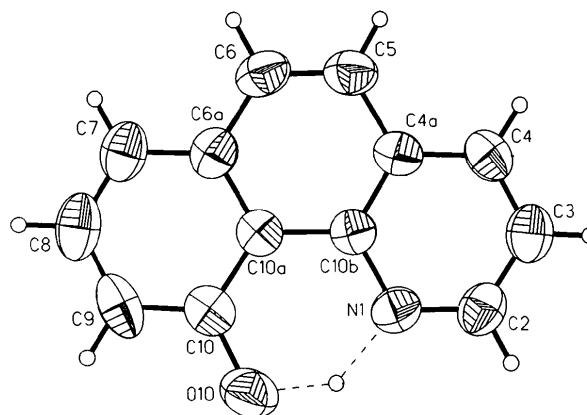

Fig. 1. The displacement-ellipsoid representation of molecule *A* with the labelling scheme. The ellipsoids are drawn at the 50% probability level, the H atoms are drawn as spheres of arbitrary radii.

There are two symmetry-independent molecules in the asymmetric part of the unit cell. The geometries of both are similar; however, inspection of a normal probability plot suggests that the differences may be statistically significant. Both molecules are almost planar, with a maximum deviation from the least-squares plane of 0.045 (4) Å for molecule *A* and 0.015 (4) Å for molecule *B*. The dihedral angles between the terminal ring planes are 2.3 (2) and 1.0 (3)° for *A* and *B*, respectively. Similar values of this angle were observed in 7,8-benzoquinoline in complex with TCNQ [2.5 (2)°; Shaanan & Shmueli, 1980], in *o*-phenanthroline [2.9 (3) and 3.4 (2)° for the two symmetry-independent molecules; Nishigaki, Yoshioka & Nakatsu, 1978] and in phenanthrene [2.4°; Kay, Okaya & Cox, 1971]. A strong intramolecular O—H$\cdots$N hydrogen bond closes the almost planar six-

membered rings [maximum deviations of 0.10 (3) and 0.02 (1) Å, for molecules A and B, respectively]. The H10 atoms are almost an equal distance from both N and O atoms, and the O—H· · ·N angle becomes smaller in order to close the intramolecular ring.

Bond-length and angle patterns are typical, the long C10a—C10b bond and short C5—C6 bond support the validity of our assumption (see above). The hydroxyl substituent changes the bond-angle pattern in agreement with the results of Domenicano & Murray-Rust (1979). In the crystal structure, there are separate layers of molecules A and B, connected by 2_1 axes. A similar motif was observed for two independent molecules of *o*-phenanthroline (Nishigaki, Yoshioka & Nakatsu, 1978). The dihedral angle between the planes of both molecules is 73.65 (5)°, while in *o*-phenanthroline this angle is *ca* 88°.

Experimental

Crystal data

$C_{13}H_9NO$
$M_r = 195.21$
Orthorhombic
$Pbc2_1$
$a = 4.6530 (4)$ Å
$b = 15.1910 (10)$ Å
$c = 26.902 (2)$ Å
$V = 1901.5 (2)$ Å^3
$Z = 8$
$D_x = 1.364$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 15 reflections
$\theta = 19.35$–$37.54°$
$\mu = 0.695$ mm^{-1}
$T = 293 (2)$ K
Prism
$0.35 \times 0.20 \times 0.15$ mm
Colorless
Crystal source: crystallized from a CH$_2$Cl$_2$–benzene system

Data collection

Syntex $P2_1$ diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1312 measured reflections
1312 independent reflections
1076 observed reflections
  $[I > 2\sigma(I)]$

$\theta_{max} = 57.34°$
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 29$
2 standard reflections
  monitored every 100
  reflections
  intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0383$
$wR(F^2) = 0.0767$
$S = 1.260$
1306 reflections
280 parameters
H-atom parameters not refined except H10A and H10B, which were refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0150P)^2 + 0.9500P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.117$ e Å^{-3}
$\Delta\rho_{min} = -0.131$ e Å^{-3}
Extinction correction: SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.0048 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1A	1.0034 (9)	1.0843 (2)	0.19974 (14)	0.0568 (10)
C2A	1.1949 (11)	1.0912 (3)	0.2364 (2)	0.0637 (13)
C3A	1.2955 (11)	1.0195 (4)	0.2626 (2)	0.0684 (14)
C4A	1.1979 (10)	0.9372 (3)	0.2512 (2)	0.0624 (13)
C4aA	0.9963 (10)	0.9272 (3)	0.2129 (2)	0.0516 (11)
C5A	0.8866 (11)	0.8426 (3)	0.1987 (2)	0.0636 (13)
C6A	0.6899 (11)	0.8364 (3)	0.1622 (2)	0.0656 (14)
C6aA	0.5831 (10)	0.9113 (3)	0.1357 (2)	0.0558 (12)
C7A	0.3734 (11)	0.9023 (4)	0.0990 (2)	0.0671 (14)
C8A	0.2742 (12)	0.9748 (4)	0.0746 (2)	0.0745 (15)
C9A	0.3794 (11)	1.0571 (4)	0.0849 (2)	0.0690 (15)
C10A	0.5907 (10)	1.0688 (3)	0.1210 (2)	0.0571 (12)
O10A	0.6961 (8)	1.1515 (2)	0.12983 (14)	0.0762 (10)
C10aA	0.6929 (9)	0.9956 (3)	0.1483 (2)	0.0486 (11)
C10bA	0.9016 (9)	1.0025 (3)	0.1878 (2)	0.0480 (11)
N1B	0.0295 (9)	0.3704 (2)	0.39230 (15)	0.0621 (10)
C2B	−0.1629 (11)	0.4246 (3)	0.4131 (2)	0.0723 (15)
C3B	−0.2514 (12)	0.4181 (4)	0.4617 (2)	0.077 (2)
C4B	−0.1385 (11)	0.3533 (3)	0.4909 (2)	0.0669 (13)
C4aB	0.0618 (10)	0.2947 (3)	0.4714 (2)	0.0541 (12)
C5B	0.1861 (11)	0.2256 (3)	0.4993 (2)	0.0634 (13)
C6B	0.3795 (12)	0.1703 (3)	0.4792 (2)	0.0634 (13)
C6aB	0.4708 (10)	0.1782 (3)	0.4284 (2)	0.0533 (12)
C7B	0.6763 (11)	0.1209 (3)	0.4080 (2)	0.0643 (13)
C8B	0.7608 (11)	0.1317 (3)	0.3596 (2)	0.0715 (15)
C9B	0.6460 (11)	0.1974 (3)	0.3305 (2)	0.0658 (13)
C10B	0.4467 (10)	0.2542 (3)	0.3490 (2)	0.0576 (12)
O10B	0.3330 (8)	0.3175 (3)	0.31866 (13)	0.0848 (11)
C10aB	0.3530 (9)	0.2464 (3)	0.3991 (2)	0.0491 (10)
C10bB	0.1455 (10)	0.3050 (3)	0.4211 (2)	0.0494 (11)

Table 2. *Selected geometric parameters* (Å, °)

N1A—C2A	1.332 (6)	N1B—C2B	1.339 (6)
N1A—C10bA	1.368 (5)	N1B—C10bB	1.371 (5)
C2A—C3A	1.380 (6)	C2B—C3B	1.373 (8)
C3A—C4A	1.365 (6)	C3B—C4B	1.365 (7)
C4A—C4aA	1.403 (6)	C4B—C4aB	1.391 (6)
C4aA—C10bA	1.400 (5)	C4aB—C5B	1.415 (6)
C4aA—C5A	1.435 (6)	C4aB—C10bB	1.417 (6)
C5A—C6A	1.347 (7)	C5B—C6B	1.344 (7)
C6A—C6aA	1.431 (6)	C6B—C6aB	1.436 (6)
C6aA—C7A	1.394 (6)	C6aB—C7B	1.405 (6)
C6aA—C10aA	1.421 (6)	C6aB—C10aB	1.412 (6)
C7A—C8A	1.363 (7)	C7B—C8B	1.368 (7)
C8A—C9A	1.372 (7)	C8B—C9B	1.377 (7)
C9A—C10A	1.394 (7)	C9B—C10B	1.362 (6)
C10A—O10A	1.368 (5)	C10B—O10B	1.367 (5)
C10A—C10aA	1.415 (6)	C10B—C10aB	1.422 (5)
C10aA—C10bA	1.442 (6)	C10aB—C10bB	1.440 (6)
C2A—N1A—C10bA	118.5 (4)	C2B—N1B—C10bB	118.2 (4)
N1A—C2A—C3A	123.0 (5)	N1B—C2B—C3B	123.7 (5)
C4A—C3A—C2A	119.7 (5)	C4B—C3B—C2B	118.9 (5)
C3A—C4A—C4aA	119.1 (5)	C3B—C4B—C4aB	120.2 (5)
C10bA—C4aA—C4A	118.5 (4)	C4B—C4aB—C5B	123.2 (5)
C10bA—C4aA—C5A	119.5 (4)	C4B—C4aB—C10bB	118.3 (5)
C4A—C4aA—C5A	122.0 (4)	C5B—C4aB—C10bB	118.5 (4)
C6A—C5A—C4aA	119.9 (5)	C6B—C5B—C4aB	121.6 (4)
C5A—C6A—C6aA	123.0 (4)	C5B—C6B—C6aB	121.9 (5)
C7A—C6aA—C10aA	120.6 (4)	C7B—C6aB—C10aB	120.0 (4)
C7A—C6aA—C6A	121.2 (5)	C7B—C6aB—C6B	121.4 (4)
C10aA—C6aA—C6A	118.2 (4)	C10aB—C6aB—C6B	118.6 (4)
C8A—C7A—C6aA	120.0 (5)	C8B—C7B—C6aB	119.5 (5)
C7A—C8A—C9A	121.2 (5)	C7B—C8B—C9B	121.1 (5)
C8A—C9A—C10A	120.6 (5)	C10B—C9B—C8B	121.0 (5)
O10A—C10A—C9A	119.4 (4)	C9B—C10B—O10B	119.4 (4)
O10A—C10A—C10aA	120.7 (4)	C9B—C10B—C10aB	120.2 (5)
C9A—C10A—C10aA	119.9 (5)	O10B—C10B—C10aB	120.4 (4)
C10A—C10aA—C6aA	117.7 (4)	C6aB—C10aB—C10B	118.2 (4)
C10A—C10aA—C10bA	123.4 (4)	C6aB—C10aB—C10bB	119.0 (4)

C6aA—C10aA—C10bA	118.9 (4)	C10B—C10aB—C10bB	122.9 (4)		
N1A—C10bA—C4aA	121.3 (4)	N1B—C10bB—C4aB	120.7 (4)		
N1A—C10bA—C10aA	118.2 (4)	N1B—C10bB—C10aB	118.7 (4)		
C4aA—C10bA—C10aA	120.5 (4)	C4aB—C10bB—C10aB	.120.5 (4)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O10A—H10A···N1A	1.36 (6)	1.45 (5)	2.573 (5)	132 (4)
O10B—H10B···N1B	1.34 (4)	1.41 (4)	2.562 (5)	138 (3)

The background and integrated intensity for each reflection were obtained by the profile-analysis method of Lehmann & Larsen (1974).

Data collection: *P*2₁ diffractometer software. Cell refinement: *P*2₁ diffractometer software. Data reduction: *PRADIR* (Jaskólski, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989). Software used to prepare material for publication: *SHELXL*93.

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The Effect of Substituents on the Crystal Structure of β-Amino Alcohols. 2-[(3,4-Dimethoxybenzyl)(methyl)amino]-2-phenylethanol

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Abstract

The crystal structure of 2-[(3,4-dimethoxybenzyl)-(methyl)amino]-2-phenylethanol, $C_{18}H_{23}NO_3$, (I), has been determined. The influence of the type and size of the groups bonded to the N atom in the crystal structure of (I) was studied and compared with the influence of such groups on the crystal structure of 2-[(3,4-dimethoxybenzyl)(p-toluenesulfonyl)amino]-2-phenylethanol, (II). The N atom of compound (I) shows sp^3 character and is synclinal to the OH group, while the N atom of compound (II) shows sp^2 character and is antiperiplanar to the OH group.

Comment

β-Amino alcohols constitute an interesting class of substances with pharmaceutical and other biological activities (Reetz, 1991). They can also be used as intermediates in the synthesis of nitrogen heterocycles with potential pharmacological activity, such as 3-arylisoquinoline derivatives (Venkov & Vodenicharov, 1990). These facts have prompted us to begin crystallographic studies of β-amino alcohols (Arriortua *et al.*, 1995). We have also found it interesting to determine the effects of the substituents on these crystal structures. In this context, we decided to study the arrangement of