$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2]$
where $P (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.330 (2)	C5—C10	1.447 (2)
N1—C9	1.361 (2)	N6—C7	1.360 (2)
C2—C3	1.399 (2)	C7—C8	1.405 (2)
C3—C4	1.376 (2)	C8—C9	1.427 (2)
C4—C10	1.420 (2)	C9—C10	1.417 (2)
C5—N6	1.323 (2)		
N14—C7—C8	125.02 (13)	C4—C10—C5	126.81 (12)

Atoms C16 and C17 of the pyrrolidine ring were found to be disordered, suggesting conformational disorder. The occupancies of the disordered positions C16*A*, C16*B*, C17*A* and C17*B* were initially refined and later fixed at 60 and 40% for the major (*A*) and minor (*B*) conformations, respectively. The corresponding C—C distances in the major and minor conformers were restrained to be equal, with an effective standard deviation of 0.02 Å. The anisotropic displacement parameters of the disordered positions were also restrained. 17 H atoms were located from a difference Fourier map and refined isotropically; the remaining four (belonging to the disordered atoms C16 and C17) were geometrically fixed and allowed to ride on their attached atoms.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1213). Services for accessing these data are described at the back of the journal.

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2-(1-Naphthoyl)-5,8-dihydronaphthalen-1-ol†

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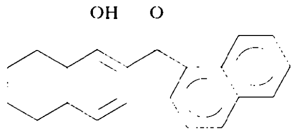
Abstract

In the title molecule, $C_{21}H_{16}O_2$, the naphthalene ring system is planar and the dihydronaphthalene ring is distorted from planarity. The dihydrobenzene ring adopts a flattened-boat conformation. The dihedral angle between the naphthalene and dihydronaphthalene ring systems is 64.13 (5)°. The hydroxyl and carbonyl O atoms are involved in O—H···O intramolecular hydrogen bonding.

Comment

Dihydronaphthalene derivatives generally serve as useful intermediates for the synthesis of several cyclic polymethylene phenols, which are useful antifibrillatory agents, disinfectants and water softeners (Hauck *et al.*, 1977). Furthermore, hydroxyketone derivatives of naphthalene are very useful in synthesizing subunits of daunomycinone and adiramycin, which are important anticancer drugs (Crouse *et al.*, 1981).

Bond lengths and angles in the naphthalene ring system of the title compound, (I), agree with the reported values (Allen *et al.*, 1987). In the dihydronaphthalene moiety, the C_{sp^2}—C_{sp^3} distances C19—C20 [1.493 (3) Å] and C16—C21 [1.507 (3) Å] are longer than the C18—C19 [1.481 (3) Å] and C16—C17 [1.470 (4) Å] distances due to steric interactions. The length of the C17—C18 [1.306 (3) Å] bond shows it to have double-bond character. Similar features are observed in 2-acetyl-5,8-dihydronaphthalen-1-ol (Chinnakali *et al.*, 1998). The naphthalene ring system is planar, with the maximum deviation of 0.027 (2) Å oc-



(I)

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† IUPAC name: 1-hydroxy-5,8-dihydro-2-naphthyl 1-naphthyl ketone.

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curring for the C2 atom. The dihydronaphthalene ring is distorted from planarity due to a slight puckering of the dihydrobenzene ring. This permits relief of steric eclipsing interactions between the H atoms. The dihydrobenzene ring adopts a flattened-boat conformation, with atoms C16 and C19 deviating from the C17, C18, C20, C21 plane by 0.026 (3) and 0.095 (3) Å, respectively. The α values (dihedral angle of the plane defined by the sp^2-C atoms and the plane defined by C18, C19, C20 or C17, C16, C21), which describe the conformation of the dihydrobenzene ring (Marshall *et al.*, 1977), are 6.6 (3) and 2.1 (3)°. The naphthalene and dihydronaphthalene ring systems form a dihedral angle of 64.13 (5)° with one another. The hydroxyl and carbonyl O atoms are involved in O—H···O intramolecular hydrogen bonding (Table 2). In the crystal, the dihydronaphthalene rings are stacked along the **c** direction, 4.386 (5) Å apart. The crystal structure is stabilized by weak C—H···O intermolecular hydrogen bonding (Table 2).

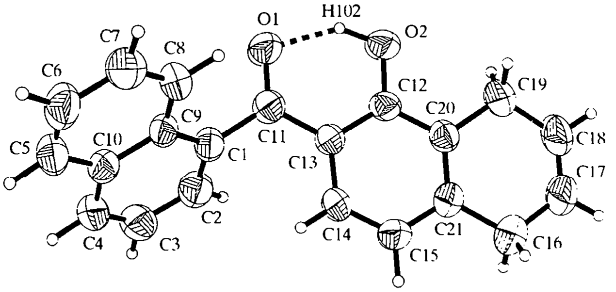

Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

Experimental

A solution of 1-naphthoyl chloride (1.9 g, 0.01 mol) in benzene (20 ml) was added dropwise to a stirred solution of 5,8-dihydronaphthalen-1-ol (1.4 g, 0.01 mol) and pyridine (0.78 g, 0.01 mol) in dry benzene (50 ml). After completion of the reaction, the solution was washed with water, dilute HCl, sodium bicarbonate solution and finally with water again before being dried over anhydrous $MgSO_4$. After removal of the solvent, the resulting residue was chromatographed over silica gel to obtain 5,8-dihydronaphthyl 1-naphthoate (70–80%; m.p. 373–375 K); this compound (1 g) was then irradiated at 254 nm using benzene as solvent. After completion of the reaction (followed by TLC), the solvent was removed and the residue chromatographed over silica gel, whereupon the title compound, 2-(1-naphthoyl)-5,8-dihydronaphthalen-1-ol (40%), and 4-(1-naphthoyl)-5,8-dihydronaphthalen-1-ol were separated and identified. Single crystals of the former were grown by slow evaporation from a solution in methanol–chloroform (1:1).

Crystal data

$C_{21}H_{16}O_2$
$M_r = 300.34$
Monoclinic
$P2_1/c$
$a = 13.409\ (3)$ Å
$b = 12.6654\ (9)$ Å
$c = 8.9671\ (11)$ Å
$\beta = 90.308\ (12)°$
$V = 1522.9\ (4)$ Å^3
$Z = 4$
$D_x = 1.310$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 5.45–12.32°$
$\mu = 0.083$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.66 × 0.36 × 0.10 mm
Yellow

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4503 measured reflections
3490 independent reflections
1173 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$

$\theta_{\rm max} = 27.50°$
$h = -17 \rightarrow 17$
$k = -16 \rightarrow 1$
$l = -1 \rightarrow 11$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.079$
$S = 0.727$
3490 reflections
273 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0132P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.13$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.11$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0049 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O2—C12	1.347 (2)	C16—C21	1.507 (3)
C12—C13	1.409 (2)	C17—C18	1.306 (3)
C13—C14	1.407 (3)	C18—C19	1.481 (3)
C14—C15	1.358 (3)	C19—C20	1.493 (3)
C15—C21	1.399 (3)	C20—C21	1.380 (2)
C16—C17	1.470 (4)		
C21—C16—C17—C18	3.5 (5)	C18—C19—C20—C21	8.2 (4)
C16—C17—C18—C19	1.3 (5)	C19—C20—C21—C16	−3.9 (4)
C17—C18—C19—C20	−7.0 (5)	C17—C16—C21—C20	−2.0 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1O2···O1	1.00 (2)	1.68 (2)	2.560 (2)	144 (2)
C2—H2···O2$^{\rm i}$	0.96 (2)	2.57 (2)	3.397 (3)	144 (1)

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

The title structure was solved by direct methods and refined by full-matrix least squares. All H atoms were located from a difference Fourier map and refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1218). Services for accessing these data are described at the back of the journal.

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2-(1-Methyl-1,2-dihydro-2-pyridylidene-aminomethylene)propanedinitrile

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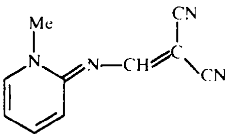
Abstract

The title compound, $C_{10}H_8N_4$, belongs to a series of conjugated molecules that offer potential utilization as organic dyes. As indicated by the planarity of the molecule and the pattern of bond lengths and angles, a considerable amount of π-electron density is transferred from the dihydropyridineimine portion of the molecule to the cyano groups. The principal packing interaction seems to be π–π stacking of the heterocyclic rings.

Comment

This work is part of our continuing study on the relationship between molecular and electronic structures, and absorption properties of polarized molecules having electron-releasing and electron-accepting groups bonded to an ethylene skeleton. These molecules absorb in the near-ultraviolet and visible regions due to delocalization of π electrons, and exhibit pronounced colour changes depending on the nature of the substituents attached to the ethylene-type C atoms. Consequently, it is of interest to examine the extent of conjugation in these molecules by combined use of theoretical and experimental methods. We report herein the crystal structure of the title compound, (I), a derivative having a dihydropyridineimine chromophore and two cyano groups bonded to an ethylene skeleton.



(I)

Bond lengths and angles within the 1,2-dihydropyridine-2-imine moiety are affected by conjugation. The bonds N1—C2 and N1—C6 have partial double-bond character (Burke-Laing & Laing, 1976) and hence are much shorter than the essentially single bond N1—C14. The N1 atom is sp^2 hybridized, as evidenced by the sum of the valence angles around this atom [360.1 (2)°], with the lone-pair electrons available for π bonding. The intra-ring C—C bond distances, perhaps with the exception of the C5—C6 bond which approximates to a double bond, are equivalent. These facts indicate π-electron delocalization within the heterocyclic ring. A similar pattern of bond distances and angles has been observed in two other compounds containing the 1-methyl-1,2-dihydropyridine-2-imine substructure (Rodier *et al.*, 1986; Hammen *et al.*, 1989), as revealed by a search of the Cambridge Structural Database (Allen *et al.*, 1983).

Considering the exocyclic bonds, the formally double bond C2═N7 is even longer than the formally single bond N7—C8, the ethylene double bond C8═C9 is considerably longer than the reported value of 1.314 (6) Å in unpolarized ethylene (van Nes & Vos, 1977), and the C9—C10 and C9—C12 bond lengths [1.411 (3) and 1.412 (3) Å, respectively] are shorter than the value expected for a pure C_{sp^2}—C_{sp} single bond (Hummel & Procher, 1986). There is, therefore, an indication that π density concentrated in the dihydropyridineimine chromophore is transferred, at least in part, to the acceptor (cyano) groups.

Due to conjugation, the dihydropyridine ring is planar within experimental error [r.m.s. deviation 0.007 (2) Å] and atoms N7 and C14 are displaced from this plane on opposite sides, with respective out-of-plane displace-