organic papers

2,3-Dihydro-4-phenyl-1,4-benzoxazine-6,7-dicarbonitrile

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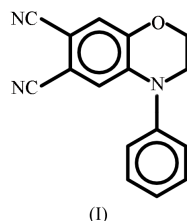
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The title molecule, $C_{16}H_{11}N_3O$, contains a benzene ring fused to an oxazine ring and one phenyl ring bound to the N atom. The two aromatic rings are not coplanar because of steric hindrance, the shortest H···H contact being 2.45 (4) Å. The dihedral angles between these two rings is 52.28 (1)°.

Comment

Phthalocyanine compounds are used in electrochromism, batteries, photodynamic therapy, semiconductive materials, liquid crystal and non-linear optics (Moser & Thomas, 1983; Leznoff & Lever, 1996). The title compound, (I), was isolated as a reaction precursor during the preparation of a phthalocyanine. Compound (I) has a very similar structure to previously reported compounds (Öztürk et al., 1999, 2000; Işık et al., 1999; Karadayı et al., 2003).

(I)

The molecular structure of (I) is shown in Fig. 1. In the structure, C10—C15—N2 = 179.2 (2)° and C9—C16—N3 = 177.6 (2)°, i.e. near to the value of 180°, since atoms C15 and C16 are in the sp state. The N1—C7 bond distance is 1.378 (2) Å and agrees with literature values (Vergeer et al., 1999; Chen et al., 2003; Olmstead et al., 2003). The bond distances and angles for (I) are listed in Table 1. The C1—C6 and C7—C12 rings are not coplanar, the dihedral angle between the least-squares planes through them being 55.28 (1)°. This lack of coplanarity is caused by steric hindrance, as shown by the H1···H8 = 2.45 (4) Å contact and the asymmetry of the two exocyclic angles at N1 (Table 1). For
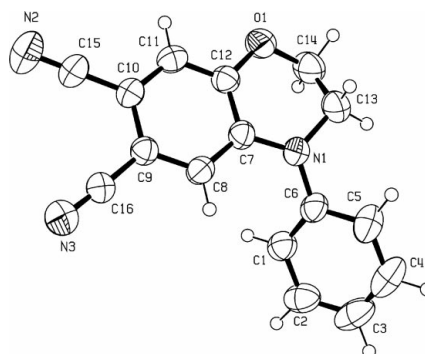

Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-labelling scheme.

the oxazine ring, the Cremer & Pople (1975) total puckering amplitude Q_T = 0.468 (3) Å. According to Duax *et al.* (1976), the conformation is a half-chair, with a local pseudo-twofold axis running along the mid-points of the C7—C12 and C13—C14 bonds.

There is one weak intermolecular C11—H11···N3[i] hydrogen bond (see Table 2 for details).

Experimental

N-(hydroxyethyl)aniline (5.48 g, 40 mmol) was dissolved in dry DMSO (150 ml) under nitrogen and 1,2-dichloro-4,5-dicyanobenzene (3.94 g, 20 mmol) was added. After stirring for 10 min at 353 K, finely ground anhydrous K_2CO_3 (5.52 g, 320 mmol) was added portionwise over 2 h with vigorous stirring. After stirring for 8 h at 353 K, the reaction mixture was poured into ice–water (250 g). The precipitate was filtered off, washed with water to remove inorganic residues, and recrystallized from ethanol (yield: 1.2 g, 42%). The compound is soluble in ethanol, ethyl acetate, chloroform, DMSO and DMF. IR (KBr, ν, cm^{-1}): 3080–2860 (Ar–H and CH), 2225 (C≡N). ^{1}H NMR (CDCl$_3$): δ 7.6–6.4 (7H, *m*, Ar), 3.8–3.1 (4H, *m*, CH$_2$).

Crystal data

$C_{16}H_{11}N_3O$	D_x = 1.338 Mg m^{-3}
M_r = 261.28	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8295
a = 14.3699 (14) Å	reflections
b = 7.5806 (4) Å	θ = 1.7–28.3°
c = 13.1208 (14) Å	μ = 0.09 mm^{-1}
β = 114.879 (7)°	T = 293 (2) K
V = 1296.6 (2) Å^3	Prism, colourless
Z = 4	0.35 × 0.22 × 0.10 mm

Data collection

Stoe IPDS-2 diffractometer	2264 independent reflections
ω scans	1449 reflections with $I > 2\sigma(I)$
Absorption correction: by	R_{int} = 0.050
integration (*X-RED*32;	θ_{max} = 25.0°
Stoe & Cie, 2002)	$h = -17 \rightarrow 17$
T_{min} = 0.980, T_{max} = 0.993	$k = -8 \rightarrow 8$
15978 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.059P)^2]$
$R[F^2 > 2\sigma(F^2)]$ = 0.038	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.098	$(\Delta/\sigma)_{max}$ = 0.025
S = 0.91	$\Delta\rho_{max}$ = 0.18 e Å^{-3}
2264 reflections	$\Delta\rho_{min}$ = −0.16 e Å^{-3}
226 parameters	Extinction correction: *SHELXL*97
All H-atom parameters refined	Extinction coefficient: 0.031 (4)

Table 1
Selected geometric parameters (Å, °).

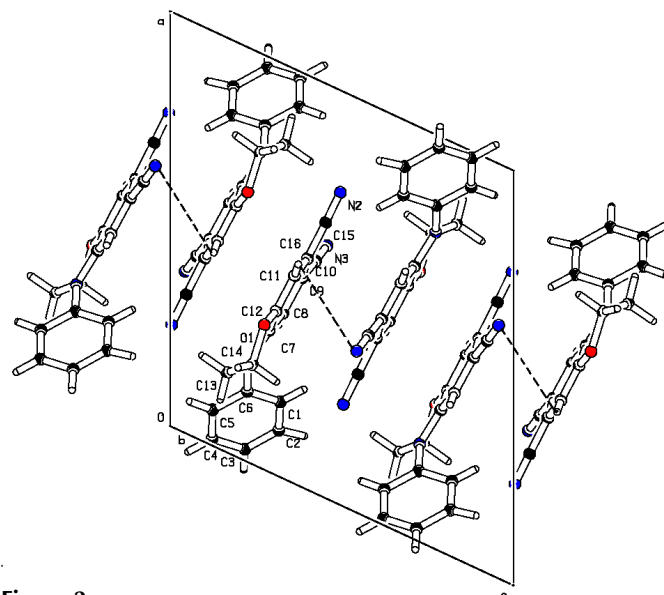|			
C14—O1	1.434 (3)	C10—C15	1.403 (3)
C14—C13	1.486 (4)	C15—N2	1.154 (3)
O1—C12	1.360 (2)	C9—C16	1.388 (2)
C6—N1	1.416 (3)	C16—N3	1.163 (3)
N1—C13	1.465 (3)		
C12—O1—C14	115.36 (18)	C6—N1—C13	119.27 (17)
C7—N1—C6	124.51 (18)	C15—C10—C9	120.55 (18)
C7—N1—C13	116.16 (18)	C16—C9—C10	119.02 (17)
C14—O1—C12—C11	−167.9 (2)	C6—N1—C13—C14	133.2 (2)
C14—O1—C12—C7	14.0 (3)	C6—N1—C7—C8	19.4 (3)

Figure 2
PLUTON plot (Spek, 1997), viewed down the *b* axis, showing part of the stacking of molecules.

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···N3[i]	0.94 (2)	2.52 (2)	3.425 (3)	163 (2)

Symmetry code: (i) $x, 1 + y, z$.

The H atoms were refined isotropically. Refined distances: CH = 0.94 (2)–1.02 (3) Å and CH$_2$ = 0.96 (3)–1.05 (3) Å. The U_{iso} values for the H atoms were in the range 0.055 (5)–0.104 (10) Å^2.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *PLUTON* (Spek, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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