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1,5-Diaminonaphthalene

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.118
Data-to-parameter ratio = 11.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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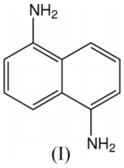
The title compound, $C_{10}H_{10}N_2$, crystallizes with one and a half molecules in the asymmetric unit, one lying on a general position and the other on an inversion centre. The dihedral angle between these two molecules is 73.30 (4)°.

Comment

Aromatic diamines are valuable building units for the design of interesting ligands, allowing the preparation of a wide array of Schiff bases, which are used in coordination chemistry (Togni & Venanzi, 1994). We have recently focused our attention on the preparation of chiral diimines (Vázquez García *et al.*, 2000; Vázquez García, 2002). While attempting to synthesize the compound resulting from the condensation of 1,5-diaminonaphthalene with camphor, the former starting material, (I), was recovered from the reaction mixture (see *Experimental*). We report here its structure.



(I)

The asymmetric unit of (I) contains one molecule in a general position and one-half molecule lying close to an inversion centre (Z' = 1.5). The former molecule possesses a non-crystallographic inversion centre at the mid-point of the C9—C10 bond (Fig. 1), while the latter has a crystallographic inversion centre at the mid-point of the bond common to both rings. A similar situation was observed in the related compound *N,N'*-bis(2-pyridyl)-1,5-diaminonaphthalene (Bensemann *et al.*, 2002).

Both independent molecules in (I) have essentially the same geometry (Table 1). The r.m.s. deviation between the non-H atoms of the molecule containing atom N1 and that containing atom N11 is 0.034 Å. This geometry is identical to that reported for related secondary amines, such as *N,N'*-diisopropyl-1,5-diaminonaphthalene (Casarini *et al.*, 1988). Furthermore, (I) has been used as a donor in the molecular charge-transfer complex chloranil-1,5-diaminonaphthalene (Tamura & Ogawa, 1977). When comparing the geometry for the amine moieties in both structures (fit carried out on non-H atoms), no significant differences are observed: r.m.s. deviations are 0.059 and 0.037 Å for the molecules containing atoms N1 and N11, respectively.

An interesting structural feature observed for (I) concerns the amine groups. The dihedral angles between the NH_2 groups and the planes of the naphthalene rings are 29 (2)° for the N1-amine group, 44 (2)° for the N5-amine group and

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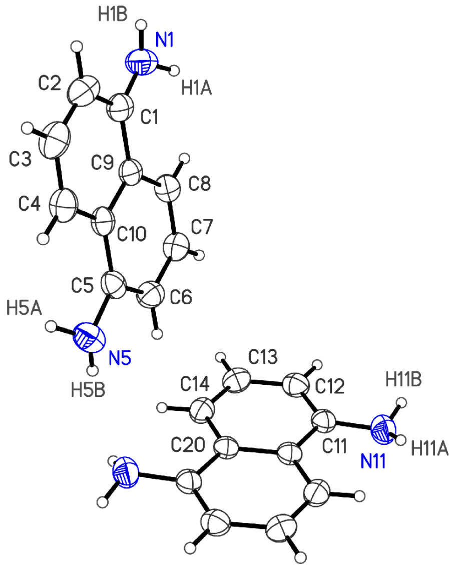

Figure 1
The structure of (I), with displacement ellipsoids drawn at the 30% probability level and showing the atom-labelling scheme for the asymmetric unit. The unlabelled part of the second molecule is related to the labelled part by the symmetry operator ($2 - x, 1 - y, 1 - z$).

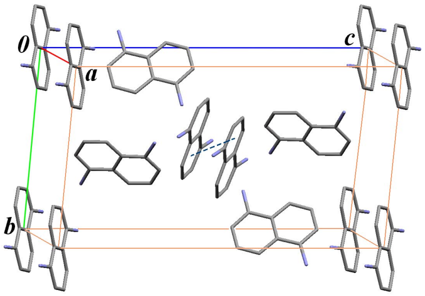

Figure 2
A packing diagram for (I), viewed almost down the a axis. H atoms have been omitted for clarity. The closest π–π intermolecular contact in the unit cell is represented by a dashed line.

33 (2)° for the N11-amine group. These angles, significantly different from 0°, reflect a partial delocalization of the lone pair on the N atoms with the extended aromatic π system of the naphthalene rings. In other words, the N atoms achieve significant sp^2 character. This is also reflected in the C=N bond lengths, which range from 1.385 (3) to 1.407 (3) Å. These bond lengths may be compared with models containing sp^3- or sp^2-N atoms (March, 1992). Thus, the Nsp^2 atoms in oximes and imines exhibit a C=N distance of 1.28 Å, while the Nsp^3 atom of methylamine has a C—N distance of 1.47 Å. On the other hand, for both molecules of (I), one amine group is oriented towards one face of the naphthalene, while the other is oriented towards the opposite face. This observation is in agreement with the fact that naphthalene has a homotopic character, but is also capable of a possible rapid interconversion of the pyramidal geometry at the N atoms. In the case of 1,5-dinitronaphthalene (Trotter, 1960), a very different configuration is observed for the NO$_2$ substituents. There, the N atom is almost trigonal, *i.e.* formally sp^2. Free rotation around the formal σ C—N bond is expected and the conformation observed for the NO$_2$ group in the solid state should be determined by steric rather than electronic effects.

Finally, an unexpected packing arrangement is observed for (I) (Fig. 2). The dihedral angle between independent naphthalene moieties in the asymmetric unit is 73.30 (4)°, very far from 0°. This 'poor' packing is reflected in the lack of π–π intermolecular contacts. The closest distance between symmetry-related six-membered rings is 4.9872 (14) Å, between the ring containing the atom sequence C11–C14/C20/C20$^{\text{i}}$ [symmetry code: (i) $2 - x, 1 - y, 1 - z$] and the same ring generated through the operator ($1 - x$, $1 - y$, $1 - z$). However, despite the lack of intermolecular contacts in (I), this crystal cannot be considered as a not-densely packed sample, as evidenced by its packing index (Spek, 2003) of 0.704.

Experimental

Crystals of the title compound were recovered from the attempted condensation of 1,5-diaminonaphthalene (83 mg, 0.52 mmol) with camphor (80 mg, 0.52 mmol) in CH$_2$Cl$_2$ (10 ml) at room temperature, following a reported procedure of Sandler & Karo (1986). Single crystals of (I) were obtained by slow evaporation of a CH$_2$Cl$_2$–hexane (1:1) solution.

Crystal data

$C_{10}H_{10}N_2$
$M_r = 158.20$
Monoclinic, $P2_1/c$
$a = 5.1790$ (7) Å
$b = 11.0081$ (18) Å
$c = 21.238$ (3) Å
$\beta = 90.679$ (10)°
$V = 1210.7$ (3) Å^3
$Z = 6$
$D_x = 1.302$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 75 reflections
$\theta = 5.1$–11.9°
$\mu = 0.08$ mm^{-1}
$T = 296$ (1) K
Plate, brown
0.65 × 0.18 × 0.08 mm

Data collection

Bruker *P*4 diffractometer
ω scans
3277 measured reflections
2117 independent reflections
1259 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.023$
$\theta_{\max} = 25.0°$
$h = -6 \rightarrow 2$
$k = -1 \rightarrow 13$
$l = -25 \rightarrow 25$
3 standard reflections every 97 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.118$
$S = 1.01$
2117 reflections
188 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.11$ e Å^{-3}
$\Delta\rho_{\min} = -0.13$ e Å^{-3}
Extinction correction: *SHELXTL-Plus* (Sheldrick, 1998)
Extinction coefficient: 0.017 (3)

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.385 (3)	N5—H5*B*	0.86 (2)
N1—H1*A*	0.90 (2)	N11—C11	1.388 (3)
N1—H1*B*	0.85 (2)	N11—H11*A*	0.84 (3)
C5—N5	1.407 (3)	N11—H11*B*	0.93 (3)
N5—H5*A*	0.91 (2)		
C1—N1—H1*A*	119.7 (15)	H5*A*—N5—H5*B*	123 (2)
C1—N1—H1*B*	113.7 (16)	C11—N11—H11*A*	113.1 (17)
H1*A*—N1—H1*B*	114 (2)	C11—N11—H11*B*	114.8 (14)
C5—N5—H5*A*	108.9 (16)	H11*A*—N11—H11*B*	118 (2)
C5—N5—H5*B*	109.6 (17)		

H atoms bonded to C atoms were placed in idealized positions and H atoms bonded to N atoms were found in difference maps. H atoms bonded to C atoms were refined using a riding model, with C—H distances constrained to 0.93 Å and $U_{\rm iso}$(H) set equal to 1.2$U_{\rm eq}$(C). H atoms bonded to N atoms were freely refined (positions and isotropic displacement parameters).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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