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Hydrogen bonding in 1*H*-naphth[2,3-*d*]imidazole

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Key indicators

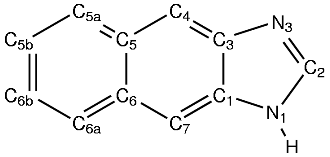
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.007 Å
R factor = 0.046
wR factor = 0.110
Data-to-parameter ratio = 6.1

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

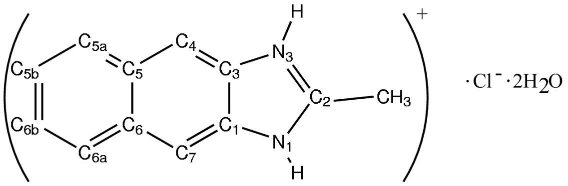
The title compound, $C_{11}H_8N_2$, contains two essentially planar molecules (*A* and *B*) in the asymmetric unit. Molecules of type *B* exhibit π–π stacking and form infinite zigzag chains along the *a* axis. *A* and *B* molecules are linked by $N_{amine}—H\cdots N_{imine}$ hydrogen bonds and form polymeric –*A*–*B*–*A*–*B*– criss-crossed chains approximately along the [110] and [$\bar{1}$10] directions. The *A* molecules show little evidence of π stacking and, in addition to the hydrogen bonds, appear to be held in the crystal structure primarily by $C—H\cdots\pi$ interactions. The geometric parameters of molecules *A* and *B* agree well with each other and, where comparisons are appropriate, with those of a naphthimidazolium cation.

Comment

The title compound, (I), $C_{11}H_8N_2$, whose structure we report here, was prepared as a synthetic intermediate for part of a project designed to extend our exploration of the chemistry of bisimidazoles and bisbenzimidazoles to bisnaphthimidazoles. Previously, we have utilized species containing bisimidazoles as agents to study electron self-exchange (Knapp *et al.*, 1990), whilst species containing bisbenzimidazoles have been shown to behave as catalysts (Patil *et al.*, 2003; Stibrany *et al.*, 2003; Stibrany, 2001), as geometrically constraining ligands (Stibrany *et al.*, 2004) and as proton sponges (Stibrany *et al.*, 2002).



(I)



(II)

The structure contains two approximately planar molecules of (I) in the asymmetric unit (Fig. 1). A search of the Cambridge Structural Database (Version 5.24; Allen, 2002) reveals only one entry, the salt 2-methylnaphthimidazolium chloride dihydrate, (II) (REFCODE GEYMAY; Zhan *et al.*, 1988), for a species containing the naphthimidazole substructure. Consequently, the present structure appears to

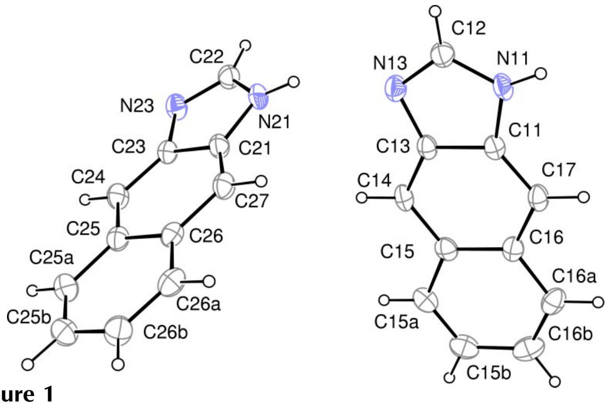


Figure 1
View of molecules *A* and *B* in (I), showing 25% probability displacement ellipsoids and the atom-numbering scheme.

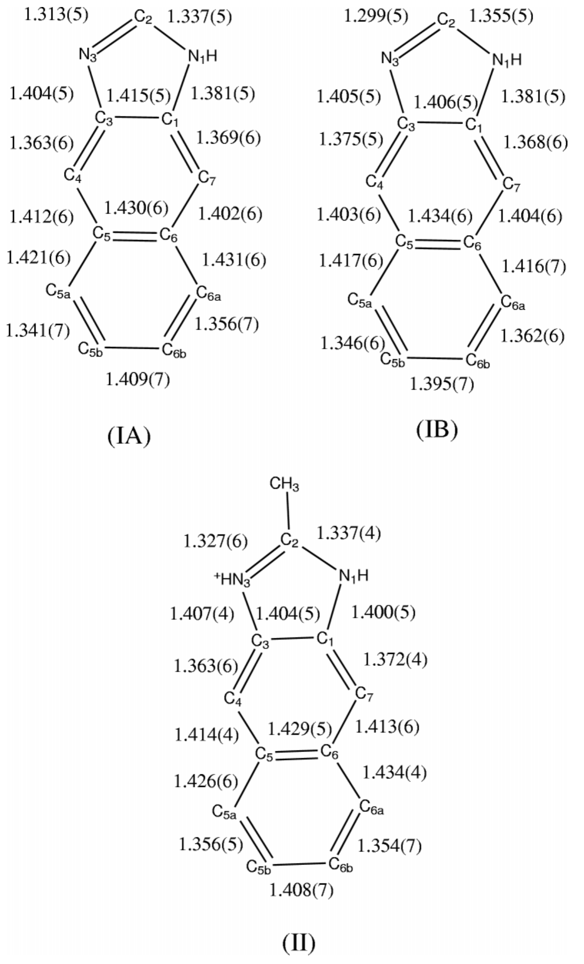


Figure 2
Bond distances (Å) in molecules *A* and *B* of (I), and in (II).

provide the first example of a neutral naphthimidazole characterized structurally by X-ray diffraction techniques.

Metric parameters for the cation (II) and for the two unique molecules in (I), labeled *A* and *B*, respectively, for the molecules containing N11 and N21, compare favorably in general (Fig. 2); in particular, in all three molecules, the pattern of long and short C—C distances is maintained. Variation in C—C bond lengths of the magnitude reported here is consistent with variations observed for a variety of polycyclic aromatic hydrocarbons (Li & Jiang, 1995). As expected, the cation exhibits more nearly equal C—N_{imine} and C—N_{amine} distances than do the neutral molecules, consistent with greater electron delocalization over the $N_1—C_2—N_3$ fragment in (II), resulting from protonation at the N_{imine} site.

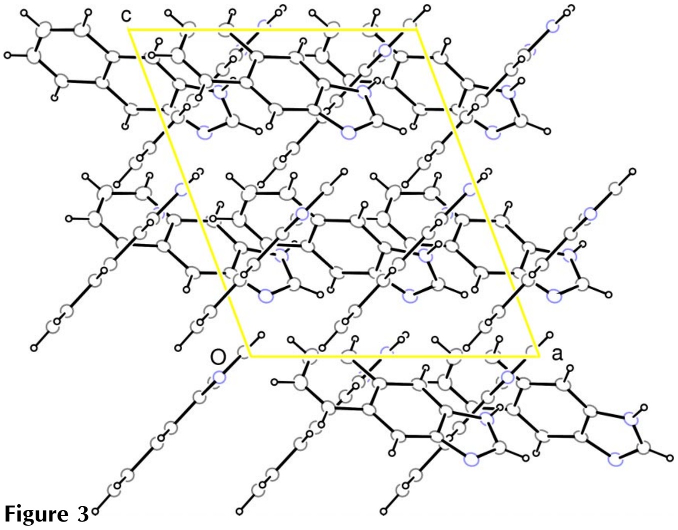
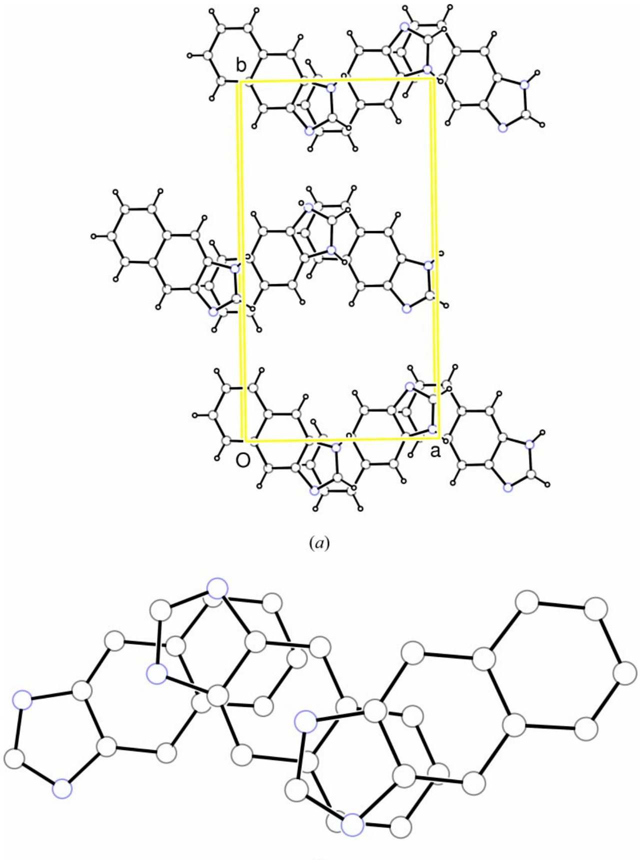


Figure 3
Projection, along the *b* axis, of the structure. *B* molecules are seen edge-on.

In the crystal structure, molecules *B* of (I) are arranged with their planes approximately parallel to the *c* axis, while molecules *A* appear more nearly face on (Fig. 3); both *A* and *B* molecules related by *a*-glide plane symmetry operations form columns along the *a* axis. When viewed along the *c* axis (Fig. 4*a*), the *B* molecules appear as zigzag chains propagating in the *a* direction, within which a given molecule exhibits 17 unique interatomic contacts of between 3.445 (7) and 3.782 (7) Å with its neighbors (Table 2), all within the range (3.3–3.8 Å; Janiak, 2000) generally accepted to indicate π–π interactions. A view of a portion of the zigzag chain, showing the ring overlap explicitly, is given in Fig. 4(*b*). Molecules *A* and *B* are linked by strong $N_{amine}—H\cdots N_{imine}$ hydrogen bonds (Table 1) to form polymeric –*A*–*B*–*A*–*B*– criss-crossed chains parallel to the [110] and [$\bar{1}$10] directions (Fig. 5). In contrast to molecules *B*, molecules *A* show little, if any, evidence of π stacking and, in addition to the hydrogen bonds, appear to be held in the crystal structure primarily by C—H$\cdots\pi$ interactions with adjacent *A*- and *B*-type molecules. Different parameters have been used in the literature to describe C—H$\cdots\pi$ interactions involving aromatic rings (Desiraju & Steiner, 1999). For Table 3, we have used one of these, the H$\cdots$C distances in the C—H$\cdots C_{aromatic}$ fragments, with a cutoff of 3.25 Å, to summarize these interactions in the present structure.

Experimental

The title compound was prepared by following a published procedure (Fries *et al.*, 1935). Crystals were obtained by slow evaporation of a concentrated solution of (I) in dry dimethyl sulfoxide (m.p. 519 K, decomposed).



(*a*)

(*b*)

Figure 4
(*a*) View, approximately along the *c* axis, showing the zigzag chains of molecules *B*. Molecules *A* are not shown. (*b*) View of three *B* molecules, approximately normal to the molecular planes, showing the pattern of ring overlap of the *B* molecules.

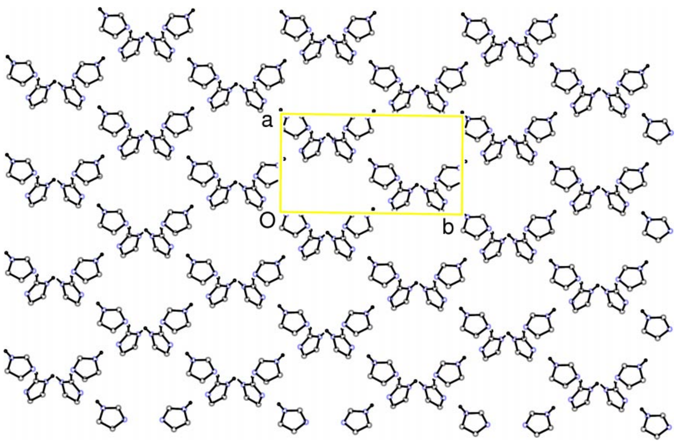


Figure 5
View, along the *c* axis, of the imidazole fragments of (I).

Crystal data

$C_{11}H_8N_2$
$M_r = 168.19$
Monoclinic, *Ia*
$a = 9.4503$ (6) Å
$b = 16.3882$ (8) Å
$c = 11.4770$ (9) Å
$\beta = 110.502$ (4)°
$V = 1664.90$ (19) Å^3
$Z = 8$
$D_x = 1.342$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 730 reflections
$\theta = 2.3$–20.8°
$\mu = 0.08$ mm^{-1}
$T = 295$ (2) K
Plate, pale yellow
0.47 × 0.22 × 0.02 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.778$, $T_{\max} = 1.00$
5846 measured reflections
1480 independent reflections
1145 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\max} = 25.1°$
$h = -11 \rightarrow 10$
$k = -19 \rightarrow 19$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.110$
$S = 1.00$
1480 reflections
243 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.13$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N11—H11$\cdots$N23$^{\rm i}$	0.83 (5)	2.12 (5)	2.888 (5)	155 (5)
N21—H21$\cdots$N13	0.85 (5)	2.13 (5)	2.919 (5)	154 (5)

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

Table 2
Interatomic N$\cdots$C and C$\cdots$C distances (Å) for molecules of type *B*, which lie within the range generally accepted for π–π interactions.

N21$\cdots$C25$^{\rm ii}$	3.562 (6)	C22$\cdots$C26$a^{\rm ii}$	3.596 (7)
N21$\cdots$C26$^{\rm ii}$	3.515 (6)	C22$\cdots$C27$^{\rm ii}$	3.673 (7)
N21$\cdots$C27$^{\rm ii}$	3.734 (7)	C23$\cdots$C25$a^{\rm ii}$	3.714 (7)
N23$\cdots$C26$^{\rm ii}$	3.752 (6)	C23$\cdots$C25$b^{\rm ii}$	3.618 (7)
N23$\cdots$C26$a^{\rm ii}$	3.445 (7)	C23$\cdots$C26$b^{\rm ii}$	3.659 (7)
N23$\cdots$C26$b^{\rm ii}$	3.637 (6)	C24$\cdots$C25$b^{\rm ii}$	3.523 (8)
C21$\cdots$C25$^{\rm ii}$	3.486 (6)	C27$\cdots$C25$^{\rm ii}$	3.782 (7)
C21$\cdots$C25$a^{\rm ii}$	3.588 (6)	C27$\cdots$C25$a^{\rm ii}$	3.655 (7)
C22$\cdots$C26$^{\rm ii}$	3.465 (7)		

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

Table 3
Interatomic C$\cdots$H distances less than 3.25 Å between an *A* molecule and its nearest neighbors.

C11$\cdots$H24	3.10$^{\rm i}$	C15$a\cdots$H25a	2.95$^{\rm vii}$
C11$\cdots$H25b	2.94$^{\rm ii}$	C15$b\cdots$H25a	2.75$^{\rm vii}$
C11$\cdots$H16a	3.24$^{\rm iii}$	C16$\cdots$H27	3.20$^{\rm viii}$
C12$\cdots$H15b	3.12$^{\rm iv}$	C16$a\cdots$H25a	3.06$^{\rm vii}$
C12$\cdots$H17	3.04$^{\rm iii}$	C16$a\cdots$H26a	3.15$^{\rm ix}$
C12$\cdots$H26b	3.22$^{\rm v}$	C16$a\cdots$H27	2.95$^{\rm ix}$
C13$\cdots$H15a	3.04$^{\rm vi}$	C16$b\cdots$H25a	2.81$^{\rm vii}$
C13$\cdots$H16a	2.90$^{\rm iii}$	C16$b\cdots$H26a	3.15$^{\rm ix}$
C13$\cdots$H25b	3.20$^{\rm ii}$	C17$\cdots$H24	3.15$^{\rm i}$
C14$\cdots$H15a	3.22$^{\rm vi}$	C17$\cdots$H25b	3.20$^{\rm ii}$
C15$\cdots$H25a	3.23$^{\rm vii}$	C17$\cdots$H26b	3.16$^{\rm ii}$
C15$a\cdots$H22	3.10$^{\rm viii}$		

Symmetry codes: (i) $x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x+1, y, z+1$; (iii) $x, -y+\frac{1}{2}, -\frac{1}{2}+z$; (iv) $x+1, y, z$; (v) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, -y, z$; (vii) $x+\frac{1}{2}, -y, z+1$; (viii) $x-\frac{1}{2}, -y, z$; (ix) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

The structure was originally refined in space group *Cc*, with $\beta = 116.801$ (4)°, but was converted to *Ia* to reduce correlation among *x*- and *z*-related parameters. The $N_{\rm amine}$ H atoms, which are involved in hydrogen bonding, were refined isotropically; the remaining H atoms

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were positioned geometrically and treated as riding, with Csp^2—H distances set to 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). In the absence of anomalous dispersion effects, Friedel pairs were merged.

Data collection: *SMART-WNT*/2000 (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *ORTEP*-32 (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

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