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2-(2-Pyridyl)benzo[1,2-*d*;4,5-*d*′]diimidazole

Xiao-Ju Lin, Yi-Zhi Li, Hai-Jun Xu, Sheng-Gui Liu, Li Xu, Zhen Shen and Xiao-Zeng You*

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence e-mail: llyyjz@nju.edu.cn

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In the title compound, $C_{13}H_9N_5$, the dihedral angle between the pyridyl and benzodiimidazole rings is 17.76 (7)°. The molecules form a two-dimensional layer structure *via* N—H···N and C—H···N intermolecular hydrogen bonds. The layers lie parallel to the *ab* plane and are stacked along the *c* axis.

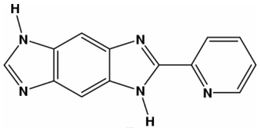
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.062
wR factor = 0.146
Data-to-parameter ratio = 16.6

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

Comment

Benzimidazole and its derivatives, as potential complexing agents, have been extensively investigated in recent years (Addison *et al.*, 1987; Sanni *et al.*, 1988; Boca *et al.*, 1998) and were found to have a broad scope for spin crossover and biological activity. Benzodiimidazole and its derivatives are potential antitumor agents as inhibitors (William & Edward, 2000) and some of their ruthenium complexes have the property of metal-to-ligand charge-transfer excited states (Ohno *et al.*, 1992). In this paper, we report the synthesis and crystal structure of the title compound, (I).



(I)

Fig. 1 shows the molecular structure of (I) along with the labeling scheme. The dihedral angle between the pyridyl and benzodiimidazole rings is 17.76 (7)°. The molecules form dimeric unit *via* N2—H2*A*···N3^{i} and C8^{i}—H8^{i}···N1 [symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}+y, z$] hydrogen bonds, and the units are further linked by an N4—H4A···N5^{ii} [symmetry code: (ii) $\frac{3}{2}-x, y-\frac{1}{2}, z$] hydrogen bond to form a two-dimensional layer structure (Fig. 2). The layers lie parallel to the *ab* plane and are stacked along the *c* axis.

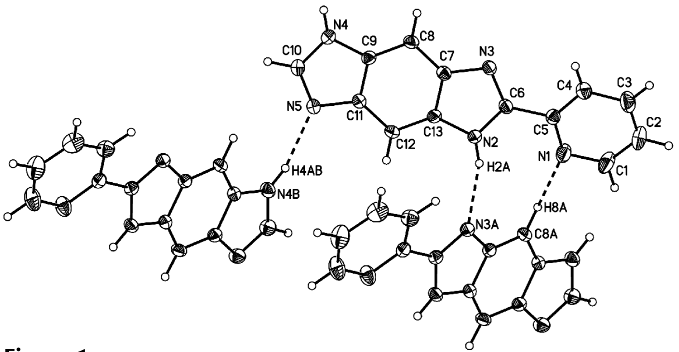


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids with the atom-numbering scheme. Dashed lines represent hydrogen bonds. [Symmetry codes: (*A*) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (*B*) $\frac{3}{2}-x, \frac{1}{2}+y, z$.]

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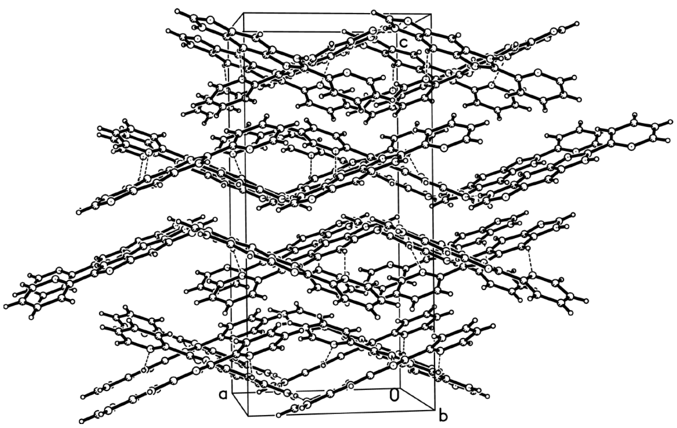

Figure 2
A packing diagram of (I). Dashed lines represent hydrogen bonds.

Experimental

The title compound, (I), was synthesized as follows: a mixture of *o*-phenylenediamine and a slight excess of formic acid was heated at the boiling temperature for 30 min to give the product, benzimidazole (Pool *et al.*, 1937). Nitration of benzimidazole gave initially 5-nitrobenzimidazole. Further nitration of this compound gave 5,6-dinitrobenzimidazole, which was reduced with tin and concentrated hydrochloric acid (Ficken & Fry, 1963). The product, 5,6-diaminobenzimidazole, was added to pyridine-2-carboxylic acid in hot polyphosphoric acid and stirred at 463 K for 3 h (Addison *et al.*, 1983). The molten product was poured into vigorously stirred cold water. When cool, the white precipitate was collected by filtration, then slurried in hot 10% aqueous sodium carbonate solution. The resulting solid was filtered off and recrystallized from ethanol–water (1/1) to obtain (I) as long colorless prisms (yield *ca* 60%). Crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a methanol solution.

Crystal data

$C_{13}H_9N_5$
$M_r = 235.25$
Orthorhombic, *Pbca*
$a = 10.3841\ (13)$ Å
$b = 10.0409\ (13)$ Å
$c = 21.911\ (3)$ Å
$V = 2284.5\ (5)$ Å^3
$Z = 8$
$D_x = 1.368$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2252 reflections
$\theta = 2.7$–$25.0°$
$\mu = 0.09$ mm^{-1}
$T = 293\ (2)$ K
Needle, colorless
$0.30 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.98$, $T_{\max} = 0.99$
12680 measured reflections

2701 independent reflections
1770 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.099$
$\theta_{\max} = 28.0°$
$h = -13 \rightarrow 11$
$k = -10 \rightarrow 13$
$l = -28 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.146$
$S = 1.03$
2701 reflections
163 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.337 (3)	C9—N4	1.386 (2)
C5—N1	1.340 (3)	C10—N5	1.316 (2)
C6—N3	1.322 (2)	C10—N4	1.343 (2)
C6—N2	1.354 (2)	C11—N5	1.398 (2)
C7—N3	1.395 (2)	C13—N2	1.381 (2)
C1—N1—C5	116.43 (19)	C10—N4—C9	106.51 (16)
C6—N2—C13	107.12 (15)	C10—N5—C11	103.82 (16)
C6—N3—C7	104.57 (15)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N3$^{\rm i}$	0.86	2.06	2.877 (2)	159
N4—H4A···N5$^{\rm ii}$	0.86	2.06	2.896 (2)	163
C8—H8···N1$^{\rm iii}$	0.93	2.50	3.317 (3)	146

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, z$.

All H atoms bonded to C atoms were placed in calculated positions, with C—H distances of 0.93 Å, and included in the refinement in the riding-model approximation, with the exception of the hydroxy group H atom, which was refined, with $U_{\rm iso} = 1.2U_{\rm eq}$ of the carrier atom. H atoms bonded to N atoms were found in difference density maps and were refined isotropically as riding, with N—H bond lengths of 0.86 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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