

Remarkable π – π stacking of dipyrido- $[f,h]$ quinoxaline-6,7-dicarbonitrile in its ethanol solvate

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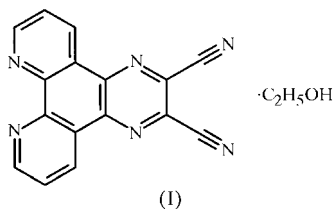
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The title compound, $C_{16}H_6N_6 \cdot C_2H_6O$, is an ethanol solvate of an aromatic phenanthroline-based flat ligand. The latter exhibits a remarkable π – π stacking in the crystal structure, with interplanar distances of 3.27 and 3.40 Å, which directs the columnar organization of the ligands. The ethanol solvent molecule is located in channels between these columns, being hydrogen bonded to one of the N-atom sites of the phenanthroline fragment.

Comment

6,7-Dicyanodipyridoquinoxaline (DICNQ) has been widely used as a coordination multidentate ligand in the synthesis of various transition metal complexes (Stephensen & Hardie, 2006; Xu *et al.*, 2002; Liu *et al.*, 2001). It has also been employed as an efficient antenna chromophore in the design of photonic and biochemical sensors (Arounagui & Maiya, 1999; Ambroise & Maiya, 2000; van der Tol *et al.*, 1998). The redox chemistry of Ru^I complexes of DICNQ has also been investigated (Kulkarni *et al.*, 2004). During our attempts to synthesize new metal–organic frameworks based on 1,10-phenanthroline and its derivatives with transition metal ions,



we synthesized DICNQ by a literature procedure (Arounagui & Maiya, 1999; van der Tol *et al.*, 1998). Surprisingly, the structure of this important ligand has not been characterized before in its uncomplexed form. We therefore report here the crystal structure at *ca* 110 K of DICNQ, which crystallized as an ethanol solvate, (I), with an emphasis on its supramolecular

self-organization. The latter is a measure of optimal ligand–ligand interactions in the absence of foreign metal ions, the coordination preference of which dominates the topology of the metal complexes of DICNQ in the previously published structures.

An *ORTEP* (Burnett & Johnson, 1996) representation of (I) is shown in Fig. 1. The molecular framework consists of

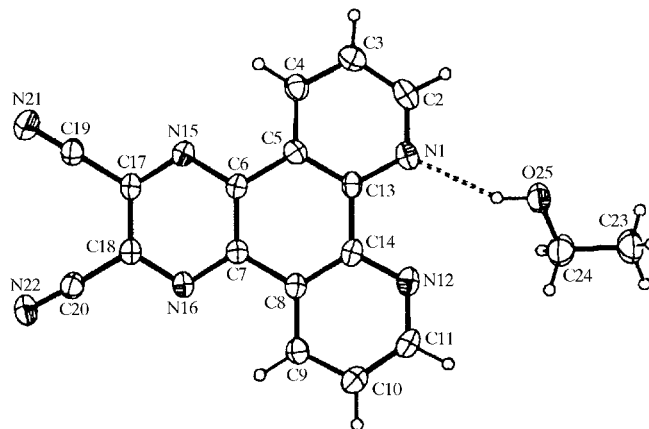


Figure 1
The molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K.

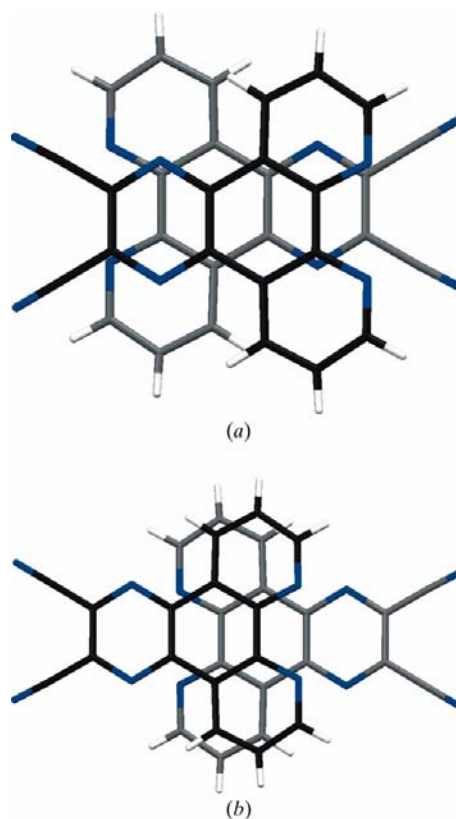


Figure 2
Modes of overlap between neighboring DICNQ molecules within the stacked arrays: (a) molecules related by inversion at (0, 0, 1), spaced at 3.269 (3) Å; (b) molecules related by inversion at ($\frac{1}{2}$, 0, 1), spaced at 3.397 (3) Å.

four fused six-membered rings and is aromatic. This 18-membered delocalized system (excluding the two $-\text{CN}$ substituents) is essentially planar, the deviations of the individual atoms from its mean plane not exceeding 0.07 \AA (with an r.m.s. deviation of the fitted atoms of 0.040 \AA). The cyano groups are bent to a minor extent with respect to this plane. As commonly observed in crystals of large aromatic molecules, the intermolecular assembly is dominated by $\pi-\pi$ stacking of overlapping flat molecular entities. Thus, the crystal structure of (I) can be best described as composed of columns of tightly stacked DICNQ ligands. The stacking direction is along the a axis, though the molecular units are slightly inclined with respect to a (the angle between the normal to the molecular plane and a is about 15°). Along the stacks, the individual species are oriented in alternating directions; the $-\text{CN}$ dipoles of adjacent overlapping units related by inversion are aligned in an antiparallel manner. Fig. 2 illustrates the two modes of intermolecular overlap along the stacks. Molecules paired around the inversion center at $x = 0, y = 0, z = 1.0$ at an interplanar distance of $3.269 (3) \text{ \AA}$ exhibit a more extensive overlap. Those paired around the $x = \frac{1}{2}, y = 0, z = 1.0$ inversion

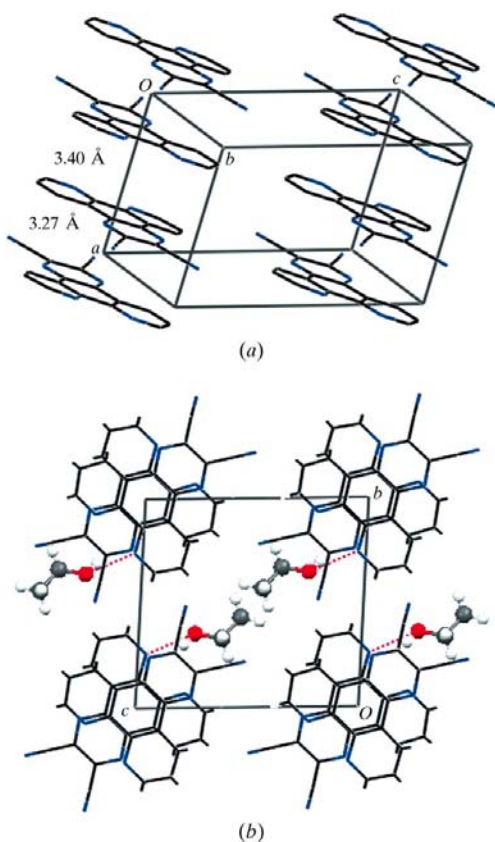


Figure 3

Two views of the crystal packing of (I). (a) An illustration of two adjacent stacks of the DICNQ species (wireframe). The alternating interplanar distances along the stacks are indicated and the ethanol solvent molecule has been omitted. (b) The intermolecular organization projected down the a axis, showing molecules of the ethanol solvent located in the channels between the stacks (DICNQ is given in wireframe and ethanol in ball-and-stick form). Hydrogen bonds are denoted by dashed lines.

with an interplanar distance of $3.397 (3) \text{ \AA}$ overlap only through their phenanthroline fragments. The almost equidistant intermolecular separation of up to 3.4 \AA along these supramolecular arrays indicates that strong $\pi-\pi$ stacking interactions assisted by the antiparallel arrangements of the polar species hold together the columnar structure (Fig. 3a).

The packing of the oval stacks in the b and c directions is stabilized mostly by dispersion, including long-range electrostatic (dipolar) interactions between the laterally oriented cyano substituents and van der Waals $\text{C}-\text{H} \cdots \text{NC}$ contacts. The packing leaves channel voids centered at $(x, \frac{1}{2}, \frac{1}{2})$. These channels contain the ethanol solvent molecules, which hydrogen bond to one of the N-atom sites of the phenanthroline fragments (Table 1 and Fig. 3b). The tight packing of DICNQ along one direction and the loose packing in another, associated with the incorporation of the solvent into the crystal structure, illustrates the significance of $\pi-\pi$ stacking as a structure-directing interaction. Similar stacking patterns have been observed in a large number of crystal structures that contain similar extended aromatic fragments (*e.g.* Gupta *et al.*, 2004; Gut *et al.*, 2002; Bergman *et al.*, 2002).

Experimental

DICNQ was synthesized according to previously reported procedures (Arounagui & Maiya, 1999; van der Tol *et al.*, 1998) and crystallized from ethanol by slow evaporation.

Crystal data

$\text{C}_{16}\text{H}_6\text{N}_6\cdot\text{C}_2\text{H}_6\text{O}$	$\gamma = 90.9640 (18)^\circ$
$M_r = 328.34$	$V = 789.48 (8) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.1090 (4) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.2326 (5) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 11.1591 (7) \text{ \AA}$	$T = 110 (2) \text{ K}$
$\alpha = 93.2852 (19)^\circ$	$0.25 \times 0.20 \times 0.10 \text{ mm}$
$\beta = 102.9380 (18)^\circ$	

Data collection

Nonius KappaCCD diffractometer	1842 reflections with $I > 2\sigma(I)$
6564 measured reflections	$R_{\text{int}} = 0.049$
2958 independent reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.155$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
$S = 1.00$	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
2958 reflections	
230 parameters	

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O25}-\text{H25} \cdots \text{N1}$	0.91 (3)	2.11 (3)	2.958 (3)	155 (3)

H atoms bound to C atoms were located in calculated positions and were constrained to ride on their parent atoms, with $\text{C}-\text{H}$ distances of 0.95, 0.98 and 0.99 \AA , and with $U_{\text{iso}}(\text{H})$ values of 1.2 and 1.5 times $U_{\text{eq}}(\text{C})$. The H atom bound to the O atom was located in a difference Fourier map and its atomic coordinates were refined freely with a $U_{\text{iso}}(\text{H})$ value of $1.5U_{\text{eq}}(\text{O})$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3061). Services for accessing these data are described at the back of the journal.

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