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Hydrogen-bonding *versus* π–π stacking interactions in dipyrido[*f*,*h*]quinoxaline-6,7-dicarbonitrile and 6,7-dicyanodipyrido[*f*,*h*]quinoxalin-1-ium chloride dihydrate

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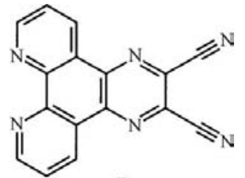
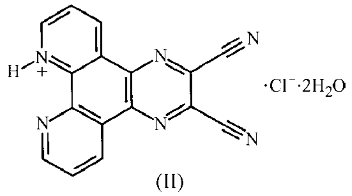
The solvent-free title compound, $C_{16}H_6N_6$, is an aromatic derivative of phenanthroline with an extended π system. It exhibits a remarkable π–π columnar stacking in the crystal structure, with interplanar distances of 3.229 (3) and 3.380 (3) Å, the shorter spacing being between the two molecules within the asymmetric unit. Adjacent units along the stacked arrays are rotated in-plane with respect to one another by approximately 120°. The hydrochloride derivative, $C_{16}H_7N_6^+\cdot Cl^-\cdot 2H_2O$, in which one of the phenanthroline N atoms has been protonated, crystallized as a dihydrate. The supramolecular organization in this compound is characterized by continuous hydrogen bonding between the component species, yielding two-dimensional hydrogen-bonded networks. This study demonstrates the high significance of the π–π stacking interactions in the solvent-free aromatic system and how they can be undermined by introducing hydrogen-bonding capacity into the ligand.

Comment

The dipyrido[*f*,*h*]quinoxaline-6,7-dicarbonitrile ligand (DICNQ) is an attractive building block for the formation of complexes with diverse metal ions. It has several pyridyl and cyano coordination sites for potential coordination of the latter. Moreover, it has an extended π-electron system, which may engage in effective π–π stacking interactions to direct the supramolecular organization of the molecular entities. The synthesis and chemical reactivity of various transition metal complexes with DICNQ have been reported (Kozlov & Goldberg, 2008; Stephenson & Hardie, 2006; Xu *et al.*, 2002; Liu *et al.*, 2001; Kulkarni *et al.*, 2004). Attempts to employ DICNQ in the fabrication of sensing devices have also been described (Arounaguiri & Maiya, 1999; Ambroise & Maiya, 2000; van der Tol *et al.*, 1998). However, the structure of this important ligand has not been characterized before in its uncomplexed form, although such a structure determination would provide information about the dominant π–π stacking interactions that characterize the preferred self-organization features inherent in this compound. Recently, we were able to describe the remarkable π–π stacking that dominates the crystal structure of the ethanol solvate of DICNQ (Kozlov *et al.*, 2008). During our attempts to synthesize new metal–organic frameworks (rather than discrete complexes) of this ligand, we have now obtained (as a by-product) for the first time X-ray quality crystals of the solvent-free ligand, (I). In an additional experiment, the hydrochloride derivative of DICNQ crystallized as the dihydrate, (II). Correspondingly, we report in this paper on the structures of (I) and (II), with an emphasis on the supramolecular self-organization observed in the crystals of the two compounds. In most of the previously published structures, the coordination preference of foreign metal ions dominates both the topology of the metal complexes and, in part, the intermolecular organization.



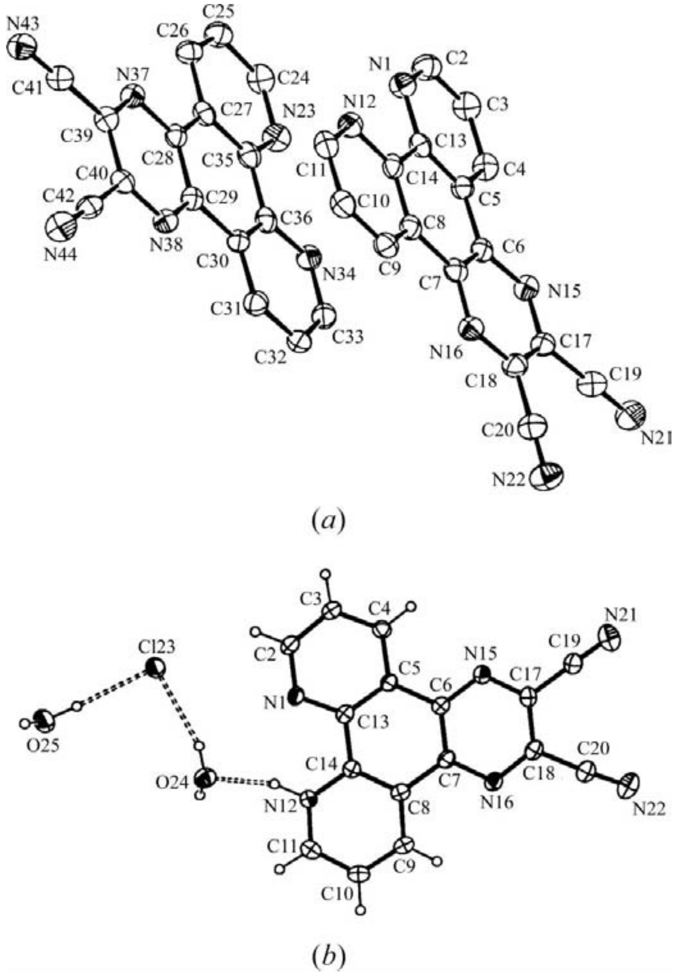
(I)



(II)

ORTEPIII (Burnett & Johnson, 1996) representations of (I) and (II) are shown in Fig. 1. The asymmetric unit in (I) consists of two crystallographically independent molecules (X1–X22 and X23–X44, X = C or N). The two phenanthroline fragments therein, *viz.* N1/C2–C11/N12/C13/C14 and N23/C24–C33/N34/C35/C36 (hereafter N1–C14 and N23–C36), are essentially planar. These two planes are nearly parallel to one another, with a dihedral angle between them of 2.48 (6)°. A significant bending of the cyano groups from the respective planes of the phenanthroline residues has been observed, with atom N21 deviating by 0.345 (6) Å from the N1–C14 plane and atom N44 deviating by 0.374 (6) Å from the N23–C36 plane.

As already observed in the crystal structure of the ethanol solvate of DICNQ (Kozlov *et al.*, 2008), the intermolecular assembly of these ligand species is dominated by π–π stacking of overlapping phenanthroline fragments of adjacent molecules (Fig. 2). Thus, the crystal structure of (I) can be best described as composed of columns of tightly stacked DICNQ ligands. The interplanar distance between the phenanthroline rings in the two molecules of the asymmetric unit is 3.229 (3) Å. This is a remarkably short distance between uncharged overlapping aromatic fragments, which may explain the outward deviations of the cyano groups from the respective phenanthroline plane in order to minimize repulsion between the electron-rich N-atom sites of the overlapping entities. The corresponding interplanar distance between such neighboring pairs displaced along the *b* axis of the crystal is 3.380 (3) Å [*e.g.* between the N1–C14 plane and the N23–C36 plane at (x, $y - 1$, z)], also indicative of significant π–π interactions. These observations are consistent with earlier findings in the structure of the ethanol solvate of DICNQ (Kozlov *et al.*, 2008). However, in the former case, the overlapping ligands are related to one another by inversion, with an antiparallel alignment of the –CN dipoles, the attractive electrostatic interaction between them adding the stabilizing contribution of the columnar organization. In the present case, the π–π stacking arrangement of the DICNQ species is preserved, even though the individual units are oriented differently. For example, the angle between the C13—C14 and C35—C36 central bonds of the phenanthroline rings is 60.5 (3)°, and the –CN dipoles of neighboring species thus form an angle of about 120° between them rather than the angle of 180° observed in the earlier study. The resulting columnar organization of the DICNQ species in (I) is illustrated in Fig. 3. The centrosymmetric space symmetry of the entire crystal structure dictates an antiparallel arrangement of adjacent columns related by inversion. Therefore, intermolecular dipolar interactions add to the intercolumnar dispersion forces in stabilizing the overall structure. Molecular modeling calculations are currently being carried out in order to characterize the relative stabilization enthalpies of the different intermolecular organizations in (I) and in the ethanol solvate of DICNQ (Kozlov *et al.*, 2008).



(*a*)

(*b*)

Figure 1
The molecular structures of (*a*) (I) (H atoms omitted) and (*b*) (II) (dashed lines denote hydrogen bonds), showing the atom-labeling scheme. The atom ellipsoids represent displacement parameters at the 50% probability level at *ca* 110 (2) K. H atoms have been omitted.

Protonation of the DICNQ ligand in (II) occurs on one of the phenanthroline N-atom sites (N12), without affecting to a considerable extent the planarity of the molecular framework. A more subtle inspection of the molecular conformation reveals that the protonated ring (C8–C11/N12/C14) is bent slightly with respect to the other pyridyl ring (N1/C2–C5/C13) and the remaining aromatic residue (N1/C2–C8/C13/C14/N15/N16/C17/C18). The corresponding dihedral angles between the mean planes of these fragments are 5.86 (9) and 4.35 (8)°, respectively. The intermolecular organization in (II) is dominated by hydrogen-bonding interactions (Table 1) and is characterized by minimal overlap between neighboring DICNQ species. The hydrogen bonds propagate from the protonated DICNQ unit (N12—H12) to an adjacent water molecule, from there to two neighboring chloride ions, and then again to a water molecule, forming a continuous hydrogen-bonded layer of the different species (Fig. 4). A view of the crystal structure (Fig. 5) shows that these layers are parallel to the *bc* plane of the crystal and centered around

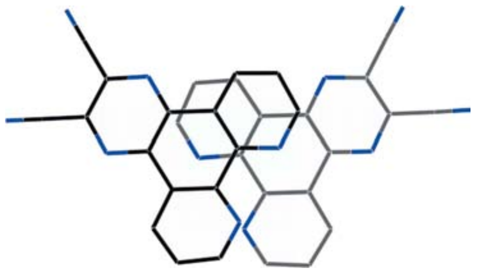


Figure 2
An illustration of the overlapping mode between the two DICNQ units in the asymmetric unit.

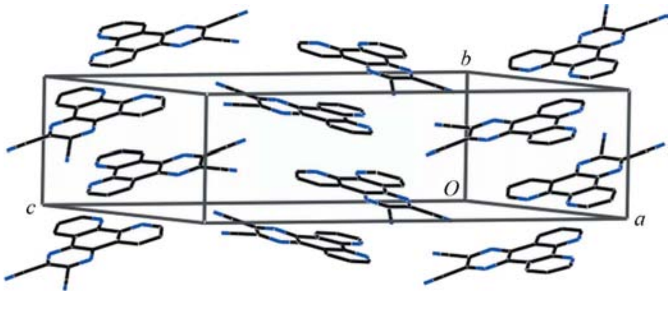


Figure 3
The crystal packing of (I), illustrating the columnar organization of the DICNQ molecules, as well as their side packing in the crystal structure. H atoms have been omitted.

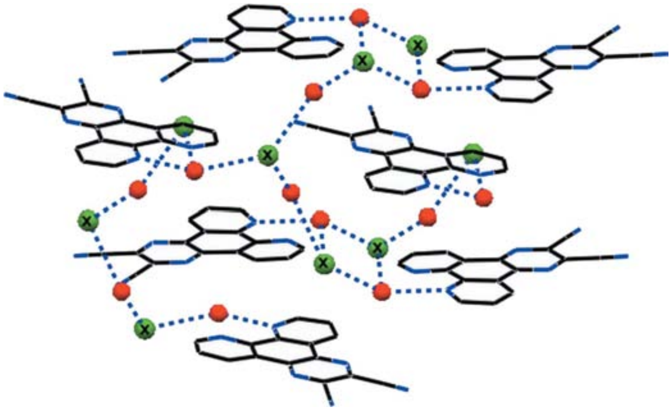


Figure 4
A perspective view of the continuous hydroden-bonding scheme in (II). The hydrogen bonds are denoted by dashed lines. H atoms have been omitted. The chloride ions and water molecules are indicated by small spheres, the former being crossed. See Table 1 for geometric details.

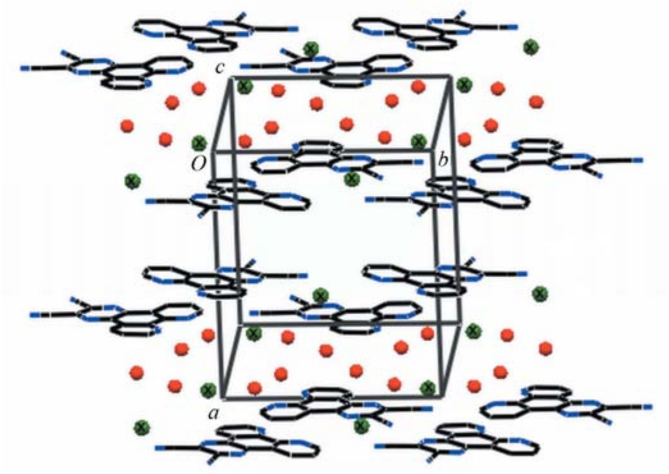


Figure 5
The crystal packing in (II). The polar, charged and hydrophilic entities, interconnected into hydrogen-bonded layers, are centered at $x = 0$ and $x = 1$. A lipophilic surface centered around $x = \frac{1}{2}$ characterizes the interface between neighboring layers. H atoms have been omitted. The chloride ions and the water molecules are indicated by small spheres, the former being crossed.

$x = 0$. The layers are stacked along the *a* axis with a lipophilic interface between them around $x = \frac{1}{2}$.

The above-described observations indicate that the N-atom sites of the phenanthroline fragment of DICNQ are reactive not only to coordination of metal ions but also to protonation, as well as hydrogen-bonding interactions. In its ethanol solvate (Kozlov *et al.*, 2008), the ethanol molecule was found to hydrogen bond to one of the N atoms. However, owing to the small size of the solvent molecule this had little disrupting effect on the π–π stacking organization of the neutral DICNQ ligand. The high significance of the stacking interactions to the supramolecular organization of DICNQ has been confirmed by elucidation of the solvent-free compound, (I), which is consistent with similar stacking patterns observed in a large number of phenanthroline-derived aromatic compounds (*e.g.* Gupta *et al.*, 2004; Gut *et al.*, 2002; Bergman *et al.*, 2002). On the other hand, this study shows also that the π–π stacking can be disrupted when an extended hydrogen-bonding scheme is introduced into the system by converting the neutral DICNQ ligand to its hydrochloride derivative, as in (II). It appears that the co-operative charge-assisted hydrogen bonding has in this case a more significant enthalpic contribution than the tight π–π stacking interactions, providing in (II) a dominant structure-directing force.

Experimental

The two title compounds were obtained as by-products of our studies of the coordination chemistry of DICNQ with various metal ions. DICNQ was synthesized according to previously reported procedures (Arounaguiri & Maiya, 1999; van der Tol *et al.*, 1998) from commercially available reagents (Aldrich). We attempted the formation of its palladium complex by reacting DICNQ (8 mg) with dichloridobis(triphenylphosphine)palladium(II) (12 mg) dissolved in acetonitrile (4 ml) and dichloromethane (15 ml). After 3 h of reflux and filtration of the resulting solution, followed by one week of slow evaporation, solvent-free crystals of DICNQ were obtained as thin yellow plates. Reaction of DICNQ (8 mg) with lanthanum(III) chloride (14 mg) dissolved in methanol (2 ml) and carbon tetrachloride (15 ml) yielded, after 1 h of reflux and filtration of the resulting solution, followed by three months of slow evaporation, crystalline brown pyramids suitable for X-ray diffraction analysis.

Compound (I)

Crystal data

$C_{16}H_6N_6$
$M_r = 282.27$
Monoclinic, $P2_1/c$
$a = 15.0150\ (14)$ Å
$b = 6.9620\ (6)$ Å
$c = 24.5189\ (16)$ Å
$\beta = 104.224\ (5)^\circ$
$V = 2484.5\ (4)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 110\ (2)$ K
0.35 × 0.30 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
13248 measured reflections
4340 independent reflections
2660 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.084$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.081$
$wR(F^2) = 0.169$
$S = 1.08$
4340 reflections
397 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}

Compound (II)

Crystal data

$C_{16}H_7N_6^+\cdot Cl^-\cdot 2H_2O$
$M_r = 354.76$
Monoclinic, $P2_1/c$
$a = 13.9417\ (4)$ Å
$b = 12.0846\ (4)$ Å
$c = 9.6350\ (3)$ Å
$\beta = 100.452\ (2)^\circ$
$V = 1596.37\ (9)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.26$ mm^{-1}
$T = 110\ (2)$ K
0.35 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
10352 measured reflections
3123 independent reflections
2381 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.064$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.115$
$S = 1.03$
3123 reflections
226 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N12—H12$\cdots$O24	0.95	1.79	2.706 (3)	160
O24—H24$A\cdots$Cl23	0.86	2.39	3.2277 (18)	162
O24—H24$B\cdots$Cl23^{i}	0.93	2.28	3.2119 (18)	176
O25—H25$A\cdots$Cl23^{ii}	0.92	2.36	3.2140 (19)	154
O25—H25$B\cdots$Cl23	0.95	2.27	3.177 (2)	160

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

In (II), H atoms bound to C atoms were located in calculated positions and were constrained to ride on their parent atoms, with C—H distances of 0.95 Å and $U_{\rm iso}$(H) values of 1.2$U_{\rm eq}$(C). All other H atoms were located from difference Fourier maps [C—H = 0.87–1.03 Å in (I); see Table 1 for other distances], but their atomic positions were not refined. For them also, the $U_{\rm iso}$(H) values were set at 1.2$U_{\rm eq}$(C,N,O). Crystals of (I) exhibited high mosaicity and relatively poor diffraction. The diffraction experiment at 110 K was affected also to some extent by the accumulation of ice on the diffracting sample. Correspondingly, the resulting structural model is characterized by relatively high R factors. No better crystals could be found to improve the experimental data, yet all the H atoms could be clearly located in the difference Fourier map, and the molecular structure seems to be rather precise.

For both compounds, 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, 2008); 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: FA3158). Services for accessing these data are described at the back of the journal.

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