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An ion-pair complex composed of one 1-(4-fluorobenzyl)pyridinium cation, one 7,7,8,8-tetracyanoquinodimethanide anion and a neutral 7,7,8,8-tetracyanoquinodimethane molecule

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In the title salt, 1-(4-fluorobenzyl)pyridinium 7,7,8,8-tetracyanoquinodimethanide 7,7,8,8-tetracyanoquinodimethane, $C_{13}H_{13}FN^{+}\cdot C_8H_4(CN)_4^{-}\cdot C_8H_4(CN)_4$, the asymmetric unit contains one cation, one anion and a neutral molecule. Intramolecular C—H···N and intermolecular C—H···N and C—H···F hydrogen bonds and $\pi-\pi$ stacking interactions seem to be effective in the stabilization of the crystal structure.

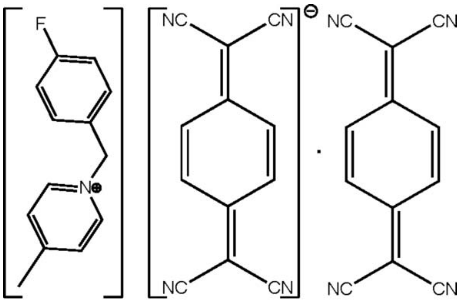
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.003 Å
R factor = 0.044
wR factor = 0.087
Data-to-parameter ratio = 12.6

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

Comment

The search for new compounds with promising electronic, magnetic and photomagnetic properties has prompted chemists to combine different spin carriers within the same molecular or supramolecular entity (Madalan *et al.*, 2002). One of the most extensively used radicals in these studies has been the planar organic molecule 7,7,8,8-tetracyanoquinodimethane, $[C_8H_4(CN)_4]$, TCNQ, since it shows a low reduction potential which makes it a suitable acceptor in charge-transfer processes. Another significant feature of this acceptor is its tendency to overlap its π-delocalized system with those of neighbouring molecules to form stacks with different degrees of electron delocalization (Alonso *et al.*, 2005). Previous work has shown that molecular stacks of ion-pair complexes exhibit low-dimensional properties in some cases, which have intriguing anisotropic magnetic, electronic and structural characteristics (Ren, Meng *et al.*, 2002; Ren *et al.*, 2003; Liu *et al.*, 2005). Furthermore, the size and shape of the counter-cations play an important role in determining the ground-state properties of the resulting materials (Ren, Chen *et al.*, 2002; Wang *et al.*, 2006). As a result, ion-pair complexes consisting of the TCNQ anion and benzylpyridinium cations could offer the possibility of systematically studying the fundamental relationship between the stack structure and the size and steric properties of substituent groups. In this communication, we report the crystal structure of the title complex, (I).



(I)

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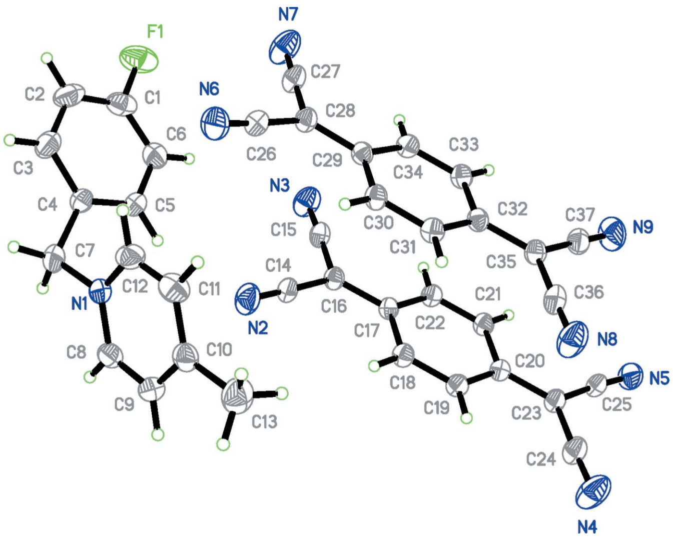

Figure 1
The asymmetric unit, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

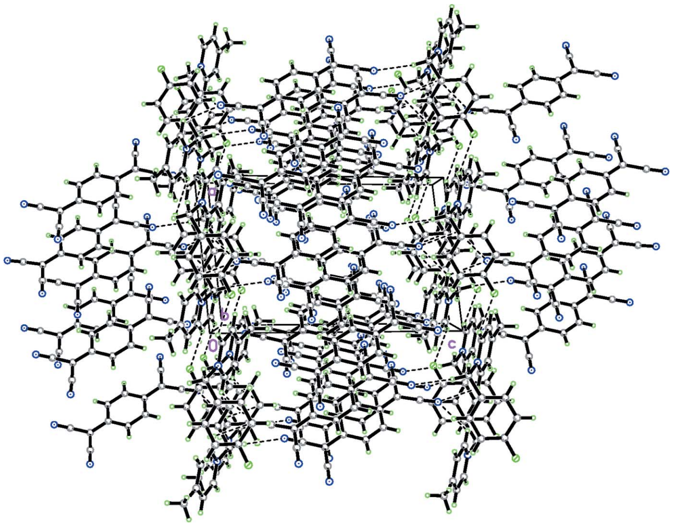

Figure 2
A packing diagram for (I). Hydrogen bonds are shown as dashed lines.

The asymmetric unit of (I) contains one $(C_{13}H_{13}FN)^+$ cation, one $[C_8H_4(CN)_4]^-$ anion and a neutral $[C_8H_4(CN)_4]$ molecule (Fig. 1). It stacks into completely segregated columns of TCNQ anions/molecules and 1-(4-fluorobenzyl)pyridinium cations, as illustrated by the projection along the crystallographic *b* axis in Fig. 2. The cation and anion columns are linked by hydrogen-bonding interactions (Table 1). Within an anionic column, a strongly bound unit of $[(TCNQ)_2]^-$ is formed, and adjacent units are displaced relative to each other along the direction of the shorter molecular axis of TCNQ. The benzene rings are parallel to each other. The centroid-to-centroid distances between adjacent aromatic rings [symmetry codes: (i) x, y, z (ii) $2 - x, 1 - y, 1 - z$] are 3.957 and 3.982 Å (Fig. 3), indicating weak π–π stacking interactions.

The $(C_{12}H_{11}NF)^+$ cation has a Λ-shaped conformation, and the dihedral angles formed by the C4/C7/N1 plane with the benzene and pyridinium rings are 55.25 (16) and 50.31 (14)°, respectively.

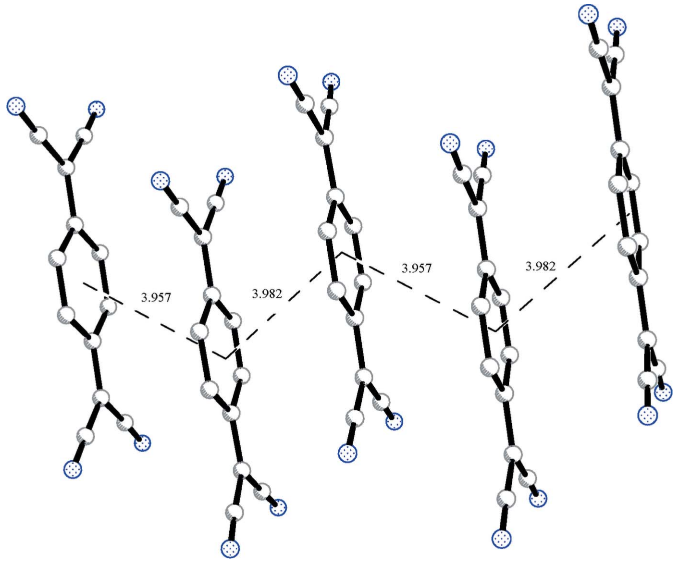

Figure 3
A side-view of the one-dimensional anionic chain of (I). Centroid-to-centroid distances are in Å.

Experimental

N-(4-Fluorobenzyl)pyridinium iodide was prepared by the direct combination of 1:1 molar equivalents of *N*-(4-fluorobenzyl)pyridinium chloride and NaI in a warm solution in acetone at 313 K. A white precipitate was formed (NaCl), which was filtered off, and a white microcrystalline product was obtained by evaporating the filtrate. 1:2 Molar equivalents of *N*-(4-fluorobenzyl)pyridinium iodide and TCNQ were mixed directly in a solution in methanol, and the mixture was refluxed for 12 h. The dark-green microcrystalline product which formed was filtered off, washed with MeOH and dried *in vacuo*. Single crystals of (I) suitable for structure analysis were obtained by diffusing diethyl ether into a MeCN solution of (I) (yield 0.46 g, 75%; m.p. 464–466 K).

Crystal data

$C_{13}H_{13}FN^+ \cdot C_{12}H_4N_4^- \cdot C_{12}H_4N_4$
$M_r = 610.63$
Triclinic, $P\overline{1}$
$a = 9.5476\ (13)$ Å
$b = 10.8917\ (14)$ Å
$c = 15.346\ (2)$ Å
$\alpha = 101.203\ (2)^\circ$
$\beta = 94.189\ (2)^\circ$
$\gamma = 100.215\ (2)^\circ$
$V = 1531.1\ (3)$ Å^3
$Z = 2$
$D_x = 1.325$ Mg m$^{-3$}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 294\ (2)$ K
Block, dark green
0.20 × 0.16 × 0.12 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.983$, $T_{\max} = 0.990$
7803 measured reflections
5336 independent reflections
2529 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 25.0^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.087$
$S = 1.01$
5336 reflections
425 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···N2	0.93	2.62	3.380 (3)	139
C7—H7*A*···N9^{i}	0.97	2.42	3.366 (3)	165
C8—H8···F1^{ii}	0.93	2.53	3.190 (3)	128
C12—H12···N6	0.93	2.56	3.177 (4)	124
C12—H12···N6^{iii}	0.93	2.62	3.189 (3)	120

Symmetry codes: (i) $x, y, z-1$; (ii) $x+1, y, z$; (iii) $-x+1, -y, -z$.

H atoms were positioned geometrically, with C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.5$ for methyl H and $x = 1.2$ for all other H atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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