

4,4'-Bipyridine–2,4,5,6-tetrafluoro-1,3-diiodobenzene (1/1)

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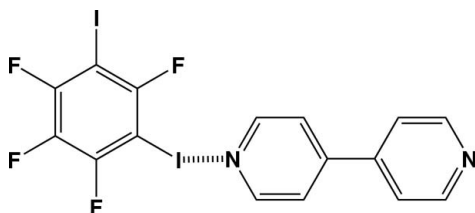
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Key indicators: single-crystal X-ray study; $T = 297$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.030; wR factor = 0.074; data-to-parameter ratio = 15.4.

The self-assembly of 1,3-diiodotetrafluorobenzene (13DITFB) and bipyridine (44BPY), $\text{C}_{10}\text{H}_8\text{N}_2 \cdot \text{C}_6\text{F}_4\text{I}_2$, is driven by halogen bonding. It results in infinite wave-like chains, with the two molecules in a 1:1 mole ratio. Both molecules lie on crystallographic mirror planes, bisecting the central 44BPY C–C bond and passing through two opposite CF groups of 13DITFB. The $\text{N} \cdots \text{I}$ halogen-bonding interaction is 2.902 (4) Å, and the $\text{C}-\text{I} \cdots \text{N}$ angle is almost linear [175.6 (2)°]. The chain $\cdots 13\text{DITFB} \cdots 44\text{BPY} \cdots$ is polar, with all 13DITFB on the wave crest and all 44BPY at the bottom. This is in contrast to similar complexes obtained on self-assembly of 44BPY with 1,3-dibromotetrafluorobenzene (13DBrTFB), 1,4-diiodotetrafluorobenzene (14DITFB) or 1,2-diiodotetrafluorobenzene (12DITFB), where centrosymmetric wave-like chains are observed.

Related literature

For related literature, see: Altomare *et al.* (1994); De Santis *et al.* (2003); Liantonio *et al.* (2002); Messina *et al.* (2001); Metrangolo & Resnati (2001); Metrangolo *et al.* (2005, 2007); Neenan & Whitesides (1988); Walsh *et al.* (2001).



Experimental

Crystal data

$\text{C}_{10}\text{H}_8\text{N}_2 \cdot \text{C}_6\text{F}_4\text{I}_2$	$V = 850.6$ (2) Å ³
$M_r = 558.04$	$Z = 2$
Orthorhombic, $Pmn2_1$	Mo $K\alpha$ radiation
$a = 18.069$ (3) Å	$\mu = 3.74$ mm ⁻¹
$b = 8.2939$ (12) Å	$T = 297$ (2) K
$c = 5.6759$ (8) Å	$0.28 \times 0.20 \times 0.06$ mm

Data collection

Bruker SMART 1000 CCD diffractometer	7436 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	2020 independent reflections
$T_{\min} = 0.785$, $T_{\max} = 1.000$	1710 reflections with $I > 2\sigma(I)$
(expected range = 0.627–0.799)	$R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	All H-atom parameters refined
$wR(F^2) = 0.074$	$\Delta\rho_{\text{max}} = 0.77$ e Å ⁻³
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.30$ e Å ⁻³
2020 reflections	Absolute structure: Flack (1983)
131 parameters	Flack parameter: 0.02 (4)
15 restraints	

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SIR2002 (Burla *et al.*, 2003); 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 and figures for this paper are available from the IUCr electronic archives (Reference: FJ2045).

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supplementary materials

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4,4'-Bipyridine-2,4,5,6-tetrafluoro-1,3-diiodobenzene (1/1)

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Comment

The construction of supramolecular architectures by XB is a topic of current interest due to the efficiency and reliability of the interaction (Metrangolo & Resnati, 2001; Metrangolo *et al.*, 2005; Metrangolo *et al.*, 2007). In the present study, we report the first use of 1,3-diiodotetrafluorobenzene (Neenan & Whitesides, 1988) in crystal engineering. Both molecules in the co-crystal lie on a crystallographic mirror (Figure 1). When interacting each other the perfluoroarene acts as a bidentate electron acceptor and 4,4'-bipyridine as a bidentate donor. An halogen bonded system in which the modules alternate is formed (Figure 2). The two rings connected by halogen bonding are twisted each other by an angle of 64.9 (2)°, while 44BPY and 13DITFB, related by the *n* glide, are nearly parallel. The bipyridine core shows a bent conformation, being 9.2 (2)° the angle between the two pyridine rings. The crystallographic analysis revealed that the N1...I1 distance is 2.902 (4) Å. This value is shorter than those found in the complex between of 12DITFB and bipyridine (2.909–2.964) Å. The C2—I1...N1 angle slightly deviates from linearity (175.6 (2)°). The 4,4'-bipyridine gives an unlimited 1:1 chain also in the presence of 1,2-diiodotetrafluorobenzene and 1,4-diiodotetrafluorobenzene. The XB properties of the chain in the three complexes are quite similar, the N...I length and N...I—C angles being 2.909–2.964 Å and 172.1–176.2° for the complex 44BPY-12DITFB (four independent values, Liantonio *et al.*, 2002), 2.851–2.864 Å and 176.9–177.3° for 44BPY-14DITFB (Walsh *et al.*, 2001; Messina *et al.*, 2001). Also in these two complexes the 44BPY and the DITFB mean planes are nearly orthogonal. In these two structures, 44BPY, rather than bent, is slightly twisted, as shown by Figure 3, where the main differences among the waves of the three structures are evidenced. While the 44BPY-14DITFB chain is nearly linear, the 44BPY-12DITFB chain is much more winding than the 44BPY-13DITFB chain. While the structures of 44BPY-12DITFB and 44BPY-14DITFB are both centrosymmetric (as the single chains), in the complex 44BPY-13DITFB both the structure and the chain are polar. This is even more surprising if we consider that 44BPY-13DBrTFB, the complex between 44BPY and 1,3-dibromotetrafluorobenzene, that could be expected to be isomorphous to 44BPY-14DITFB, is centrosymmetric with two independent 44BPY-13DBrTFB waves, the first lying along a line of symmetry centres, and the second lined up to a 2₁ screw axis, but having a conformation very near to the first one (Figure 4, De Santis, Forni, Liantonio, Metrangolo, Pilati & Resnati, 2003).

Experimental

The starting materials were commercially available from Aldrich. 1,3-Diiodotetrafluorobenzene was prepared as already reported (Neenan & Whitesides, 1988). The 1:1 adduct was obtained by dissolving in chloroform, at room temperature and in a vial, equimolecular amounts of 1,3-diiodotetrafluorobenzene and bipyridine. The open vial was closed in a cylindrical bottle containing vaseline oil. Volatile solvents were allowed to diffuse at room temperature and, after one day, the resulting crystals were filtered. IR (cm⁻¹, selected bands): 3032, 1589, 1459, 1404, 1219, 1067, 1043, 1037, 860, 799.

Figures

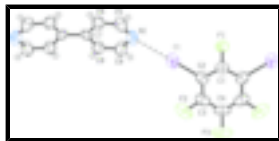


Fig. 1. Molecular plot of the complex with the numbering scheme, showing 50% probability displacement ellipsoids; H atom not to scale. Dashed lines represent the XB. The view is parallel to the crystallographic mirror planes passing through the atoms C1, C4, F1 and F3 for 1,3-diiodotetrafluorobenzene and at the middle of the N1...N1(-x,y,z) axis for bipyridine.

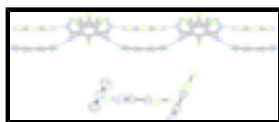


Fig. 2. Top: two waves of 44BPY...13DITFB... projected on the plane of a 44BPY; H atoms omitted for clarity; bottom: the same waves projected along the *a* axis.

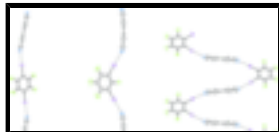


Fig. 3. Single waves of the complexes 44BPY...14DITF (top), B44BPY...13DITFB (middle), and 44BPY...12DITFB (bottom), showed in the plane defined by the normal to 44BPY and the wave elongation axis.



Fig. 4. The two independent waves of the complexes 44BPY...14DBrTF both projected parallel to a 44BPY plane. Top: this wave is formed by molecules correlated by centres of symmetry. Bottom: a wave formed by molecules along a screw axis; it may easily be seen that this wave is nearly centro-symmetric.

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Crystal data

C₁₀H₈N₂·C₆F₄I₂

M_r = 558.04

Orthorhombic, *Pmn*2₁

Hall symbol: P 2ac -2

a = 18.069 (3) Å

b = 8.2939 (12) Å

c = 5.6759 (8) Å

V = 850.6 (2) Å³

Z = 2

*F*₀₀₀ = 520

D_x = 2.179 Mg m⁻³

Melting point: 368 K

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 934 reflections

θ = 2.5–23.2°

μ = 3.74 mm⁻¹

T = 297 (2) K

Tabular, yellow

0.28 × 0.20 × 0.06 mm

Data collection

Bruker SMART 1000 CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 297(2) K

ω and φ scans

Absorption correction: multi-scan (SADABS; Bruker, 1999)

*T*_{min} = 0.785, *T*_{max} = 1.000

7436 measured reflections

2020 independent reflections

1710 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.037

θ_{max} = 27.5°

θ_{min} = 2.3°

h = -23→23

k = -10→10

l = -7→7

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.0579P]$
$wR(F^2) = 0.074$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\max} = 0.005$
2020 reflections	$\Delta\rho_{\max} = 0.77 \text{ e } \text{\AA}^{-3}$
131 parameters	$\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$
15 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983)
Secondary atom site location: difference Fourier map	Flack parameter: 0.02 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

H atoms were refined by *SHELX97* with the following restraints: FLAT C5 C6 C7 C8 C9 N1 H5 H6 H8 H9; SADI C5 H5 C6 H6 C8 H8 C9 H9; SADI H5 H6 H8 H9;

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.333096 (14)	0.22991 (3)	0.34245 (12)	0.06844 (14)
F1	0.5000	0.2934 (6)	0.4760 (9)	0.0691 (11)
F2	0.3712 (2)	0.0212 (4)	-0.1240 (7)	0.0933 (11)
F3	0.5000	-0.0625 (6)	-0.3226 (8)	0.1003 (17)
C1	0.5000	0.2039 (8)	0.2766 (11)	0.0526 (17)
C2	0.4325 (3)	0.1604 (5)	0.1831 (8)	0.0560 (10)
C3	0.4346 (3)	0.0699 (6)	-0.0198 (8)	0.0637 (12)
C4	0.5000	0.0246 (8)	-0.1196 (11)	0.0668 (18)
N1	0.1965 (2)	0.3500 (6)	0.5460 (8)	0.0679 (11)
C5	0.1578 (3)	0.2874 (7)	0.7222 (12)	0.0699 (14)
H5	0.181 (3)	0.232 (4)	0.830 (11)	0.071 (14)*
C6	0.0820 (3)	0.2952 (6)	0.7403 (9)	0.0611 (11)
H6	0.054 (3)	0.251 (4)	0.848 (11)	0.081 (16)*

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C7	0.0410 (2)	0.3727 (5)	0.5671 (7)	0.0451 (9)
C8	0.0815 (3)	0.4426 (7)	0.3889 (8)	0.0607 (13)
H8	0.063 (3)	0.498 (5)	0.274 (9)	0.078 (19)*
C9	0.1586 (3)	0.4285 (8)	0.3845 (12)	0.0740 (18)
H9	0.190 (3)	0.460 (7)	0.275 (11)	0.17 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
II	0.05658 (18)	0.0705 (2)	0.0783 (2)	0.00068 (10)	-0.0055 (4)	0.0075 (4)
F1	0.062 (3)	0.077 (3)	0.068 (3)	0.000	0.000	-0.027 (2)
F2	0.108 (2)	0.0919 (19)	0.080 (3)	-0.0149 (16)	-0.038 (2)	0.000 (2)
F3	0.162 (5)	0.089 (3)	0.050 (2)	0.000	0.000	-0.017 (2)
C1	0.066 (4)	0.042 (3)	0.051 (5)	0.000	0.000	0.002 (2)
C2	0.061 (3)	0.050 (2)	0.057 (3)	0.001 (2)	-0.009 (2)	0.0050 (19)
C3	0.089 (4)	0.050 (2)	0.052 (2)	-0.007 (2)	-0.015 (3)	0.005 (2)
C4	0.110 (5)	0.057 (3)	0.033 (4)	0.000	0.000	-0.002 (3)
N1	0.048 (2)	0.075 (3)	0.081 (3)	0.000 (2)	-0.008 (2)	-0.002 (2)
C5	0.061 (3)	0.076 (3)	0.073 (3)	0.004 (2)	-0.016 (3)	0.011 (3)
C6	0.058 (3)	0.071 (3)	0.054 (2)	-0.004 (2)	-0.005 (2)	0.007 (2)
C7	0.049 (2)	0.045 (2)	0.042 (2)	-0.0041 (16)	-0.0069 (17)	-0.0112 (16)
C8	0.053 (2)	0.073 (3)	0.056 (3)	0.0057 (19)	-0.001 (2)	0.014 (2)
C9	0.052 (2)	0.088 (3)	0.082 (5)	-0.003 (2)	0.013 (3)	0.006 (3)

Geometric parameters (\AA , $^\circ$)

II—C2	2.092 (5)	N1—C5	1.326 (8)
F1—C1	1.353 (8)	C5—C6	1.375 (8)
F2—C3	1.350 (5)	C5—H5	0.88 (4)
F3—C4	1.360 (7)	C6—C7	1.388 (6)
C1—C2	1.378 (5)	C6—H6	0.88 (5)
C1—C2 ⁱ	1.378 (5)	C7—C8	1.377 (6)
C2—C3	1.375 (6)	C7—C7 ⁱⁱ	1.482 (8)
C3—C4	1.364 (6)	C8—C9	1.398 (7)
C4—C3 ⁱ	1.364 (6)	C8—H8	0.87 (4)
N1—C9	1.316 (8)	C9—H9	0.88 (5)
F1—C1—C2	117.8 (3)	N1—C5—H5	119 (4)
F1—C1—C2 ⁱ	117.8 (3)	C6—C5—H5	117 (4)
C2—C1—C2 ⁱ	124.5 (6)	C5—C6—C7	120.0 (5)
C3—C2—C1	116.2 (5)	C5—C6—H6	127 (4)
C3—C2—II	122.4 (4)	C7—C6—H6	112 (4)
C1—C2—II	121.4 (4)	C8—C7—C6	115.6 (4)
F2—C3—C4	118.1 (4)	C8—C7—C7 ⁱⁱ	122.1 (3)
F2—C3—C2	120.5 (5)	C6—C7—C7 ⁱⁱ	122.2 (3)
C4—C3—C2	121.4 (5)	C7—C8—C9	120.5 (5)
F3—C4—C3	119.9 (3)	C7—C8—H8	124 (4)
F3—C4—C3 ⁱ	119.9 (3)	C9—C8—H8	115 (4)

C3—C4—C3 ⁱ	120.2 (6)	N1—C9—C8	123.1 (6)
C9—N1—C5	116.4 (5)	N1—C9—H9	108 (5)
N1—C5—C6	124.3 (5)	C8—C9—H9	129 (5)
F1—C1—C2—C3	179.8 (5)	F2—C3—C4—C3 ⁱ	-179.5 (4)
C2 ⁱ —C1—C2—C3	-1.2 (9)	C2—C3—C4—C3 ⁱ	-0.5 (9)
F1—C1—C2—I1	0.0 (7)	C9—N1—C5—C6	2.3 (8)
C2 ⁱ —C1—C2—I1	179.0 (4)	N1—C5—C6—C7	-0.1 (8)
C1—C2—C3—F2	179.8 (5)	C5—C6—C7—C8	-2.2 (6)
I1—C2—C3—F2	-0.4 (6)	C5—C6—C7—C7 ⁱⁱ	174.7 (4)
C1—C2—C3—C4	0.8 (7)	C6—C7—C8—C9	2.3 (7)
I1—C2—C3—C4	-179.4 (4)	C7 ⁱⁱ —C7—C8—C9	-174.6 (4)
F2—C3—C4—F3	2.2 (8)	C5—N1—C9—C8	-2.2 (9)
C2—C3—C4—F3	-178.8 (5)	C7—C8—C9—N1	-0.1 (9)

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

Fig. 1

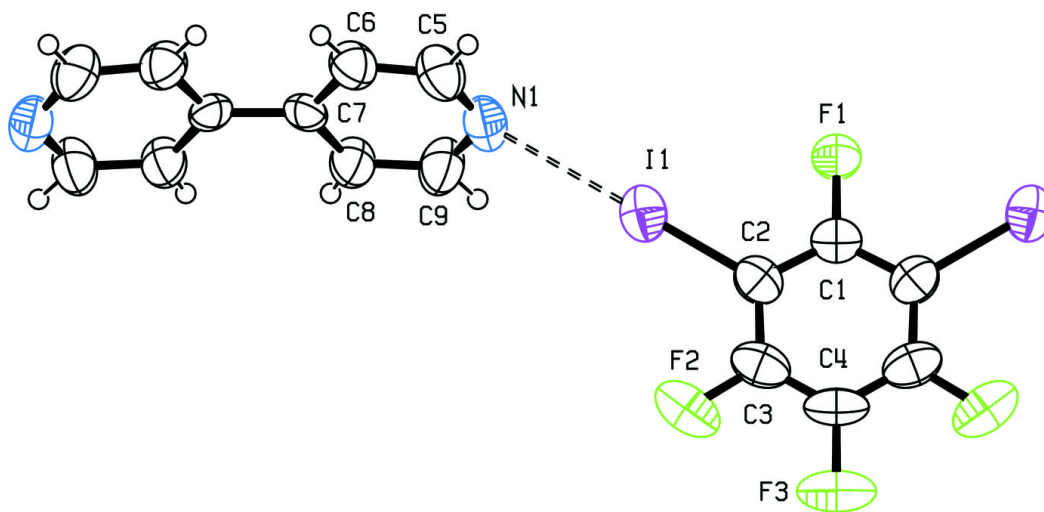


Fig. 2

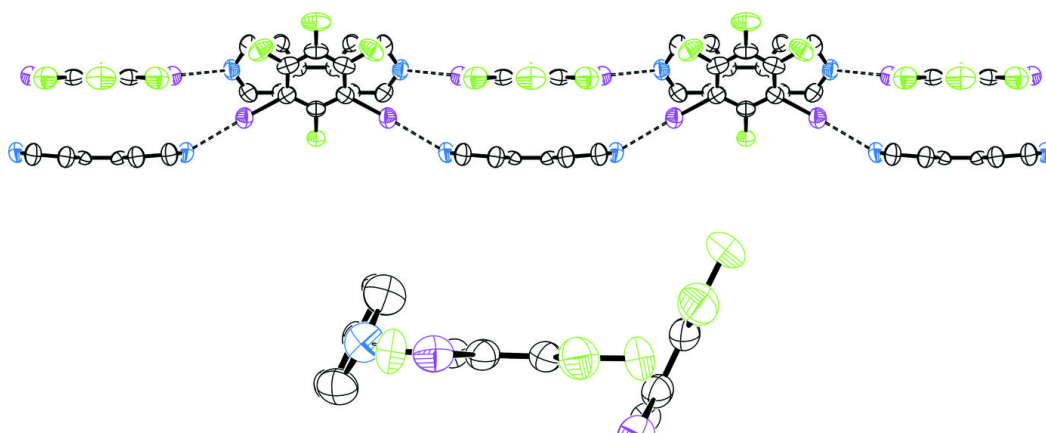


Fig. 3

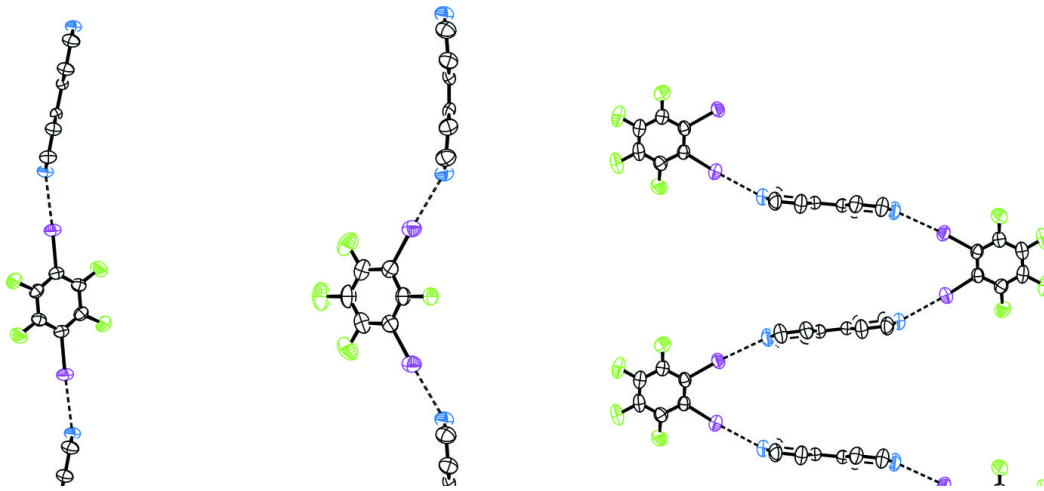


Fig. 4

