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1,2,4,5-Tetrafluoro-3,6-diiodobenzene–4-(pyridin-4-ylsulfanyl)pyridine (1/1)

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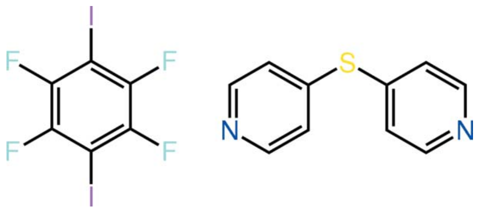
Key indicators: single-crystal X-ray study; T = 98 K; mean σ(C–C) = 0.006 Å; R factor = 0.034; wR factor = 0.073; data-to-parameter ratio = 16.0.

The asymmetric unit of the title 1:1 adduct, $C_{10}H_8N_2S\cdot C_6F_4I_2$, comprises a half-molecule of 1,2,4,5-tetrafluoro-3,6-diiodobenzene, and half a 4-(pyridin-4-ylsulfanyl)pyridine molecule. The former is completed by crystallographic inversion symmetry, the latter by twofold symmetry, with the S atom lying on the rotation axis. The almost planar 1,2,4,5-tetrafluoro-3,6-diiodobenzene molecule (r.m.s. deviation of all 12 atoms = 0.016 Å) and twisted 4-(pyridin-4-ylsulfanyl)pyridine molecule [dihedral angle between pyridyl rings = 54.88 (13)°] are connected by N···I interactions [2.838 (4) Å], generating a supramolecular chain with a step-ladder topology. These chains are connected in the crystal by C—H···F and C—H···π(pyridyl) interactions.

Related literature

For related studies on co-crystal formation, see: Broker *et al.* (2008); Arman *et al.* (2010). For background to halogen bonding, see: Metrangolo *et al.* (2008); Pennington *et al.* (2008). For the desulfurization of 4-(pyridin-4-yldisulfanyl)pyridine, see: Aragoni *et al.* (2007).



Experimental

Crystal data

$C_{10}H_8N_2S\cdot C_6F_4I_2$
M_r = 590.10
Monoclinic, $C2/c$
a = 13.804 (5) Å
b = 5.829 (2) Å
c = 22.164 (8) Å
β = 97.989 (7)°
V = 1766.1 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.72 mm^{-1}
T = 98 K
0.30 × 0.20 × 0.05 mm

Data collection

Rigaku AFC12/SATURN724 diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.757, T_{max} = 1.000
5209 measured reflections
1823 independent reflections
1733 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.073
S = 1.07
1823 reflections
114 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

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

Cg1 is the centroid of the N1,C4–C8 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···F1^{i}	0.95	2.52	3.213 (5)	130
C8—H8···Cg1^{ii}	0.95	2.82	3.557 (5)	135

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

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5647).

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supplementary materials

Acta Cryst. (2010). E**66**, o2683 [**doi:10.1107/S1600536810038316**]

1,2,4,5-Tetrafluoro-3,6-diiodobenzene-4-(pyridin-4-ylsulfanyl)pyridine (1/1)

H. D. Arman, T. Kaulgud and E. R. T. Tiekink

Comment

As a continuation of studies into the phenomenon of co-crystallization (Broker *et al.*, 2008; Arman *et al.*, 2010), including investigations of halogen bonding (Pennington *et al.*, 2008), the co-crystallization of 1,2,4,5-tetrafluoro-3,6-diiodobenzene and 4-(pyridin-4-yldisulfanyl)pyridine was investigated. This lead to the isolation of the title 1/1 co-crystal, (I), in which desulfurization of 4-(pyridin-4-yldisulfanyl)pyridine has occurred, a process that has literature precedents (Aragoni *et al.*, 2007).

The asymmetric unit in (I) comprises half a molecule of 1,2,4,5-tetrafluoro-3,6-diiodobenzene as this is situated about a centre of inversion, Fig. 1, and half a molecule of 4-(pyridin-4-ylsulfanyl)pyridine, Fig. 2, with the S atom lying on a 2-fold axis. The $C_6F_4I_2$ molecule is planar with the r.m.s. deviation of all 12 atoms being 0.016 Å. The pyridyl rings in 4-(pyridin-4-ylsulfanyl)pyridine are twisted and form a dihedral angle of 54.88 (13) °.

The components of the co-crystal are connected *via* N···I interactions [2.838 (4) Å] to form a supramolecular chain with a step-ladder topology and with a base vector 2 0 $\overline{1}$, Fig. 3. The chains are consolidated in the crystal packing by C—H···F and C—H···π(pyridyl) interactions, Table 1 and Fig. 4. The N···I interactions observed in (I) represents a further example of N···I—C halogen bonding (Metrangolo *et al.*, 2008).

Experimental

Initially 1,2,4,5-tetrafluoro-3,6-diiodobenzene (Aldrich, 0.04 mmol) and 4-(pyridin-4-yldisulfanyl)pyridine (Aldrich, 0.04 mmol) were dissolved in a THF/acetone (1/1) mixture and after evaporation of the solvent, the powder was then dissolved in ethanol. Again, crystals did not form so the powder was dissolved in a $CHCl_3$/acetone (1/1) mixture. Slow evaporation of this solution deposited yellow blocks of (I) which, after crystallographic characterization, was proven to contain 4-(pyridin-4-ylsulfanyl)pyridine, indicating that desulfurization of 4-(pyridin-4-yldisulfanyl)pyridine had occurred (Aragoni *et al.*, 2007). *M*. pt:. 423–427 K. IR assignment (cm^{-1}): 757 (m, sh); 807 (s, sh); 939 (s, sh); 1065 (s, sh); 1208 (m, sh) (C—F); 1408 (m, sh), 1456 (s, sh) C—C (aromatic); 1570 (s, sh) C═N; 2924 (*s*) C—H.

Refinement

C-bound H-atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation with U_{iso}(H) set to 1.2U_{eq}(C). The maximum and minimum residual electron density peaks of 1.34 and 0.63 e Å^{-3}, respectively, were located 1.06 Å and 0.88 Å from the S1 and I1 atoms, respectively.

Figures

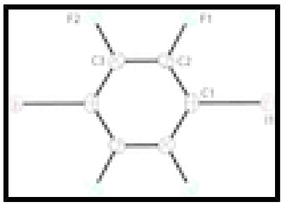

Fig. 1. Molecular structure of 1,2,4,5-tetrafluoro-3,6-diiodobenzene found in the structure of (I) showing displacement ellipsoids at the 50% probability level. Unlabelled atoms are related across a centre of inversion.

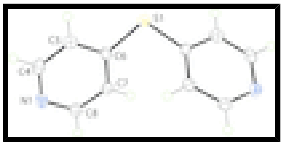

Fig. 2. Molecular structure of 4-(pyridin-4-yldisulfanyl)pyridine found in the structure of (I) showing displacement ellipsoids at the 50% probability level. Unlabelled atoms are related across a 2-fold axis.

Fig. 3. The supramolecular chain in (I) sustained by N···I halogen bonds, shown as orange dashed lines.

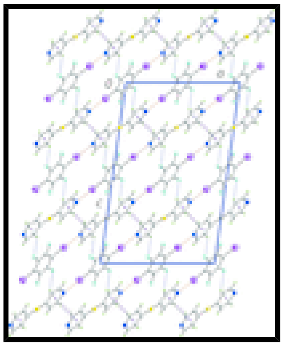

Fig. 4. A view in projection down the *b* axis showing the stacking of alternating layers of 1,2,4,5-tetrafluoro-3,6-diiodobenzene and 4-(pyridin-4-yldisulfanyl)pyridine molecules along the *c* axis. The N···I, C—H···F and C—H···π interactions are shown as orange, blue and purple dashed lines, respectively.

1,2,4,5-Tetrafluoro-3,6-diiodobenzene–4-(pyridin-4-ylsulfanyl)pyridine (1/1)

Crystal data

$C_{10}H_8N_2S\cdot C_6F_4I_2$	$F(000) = 1104$
$M_r = 590.10$	$D_x = 2.219$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 3043 reflections
a = 13.804 (5) Å	θ = 3.0–40.2°
b = 5.829 (2) Å	μ = 3.72 mm^{-1}
c = 22.164 (8) Å	*T* = 98 K
β = 97.989 (7)°	Block, yellow
V = 1766.1 (11) Å^3	0.30 × 0.20 × 0.05 mm
Z = 4	

Data collection

Rigaku AFC12K/SATURN724 diffractometer	1823 independent reflections
Radiation source: fine-focus sealed tube	1733 reflections with $I > 2\sigma(I)$

graphite

ω scans

Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.757$, $T_{\max} = 1.000$

5209 measured reflections

$R_{\rm int} = 0.027$

$\theta_{\max} = 26.5°$, $\theta_{\min} = 3.0°$

$h = -17 \rightarrow 14$

$k = -5 \rightarrow 7$

$l = -27 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.073$

$S = 1.07$

1823 reflections

114 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0202P)^2 + 21.2619P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.34$ e Å^{-3}

$\Delta\rho_{\min} = -0.63$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
I1	0.33988 (2)	0.75767 (5)	0.089898 (12)	0.02060 (11)
F1	0.4107 (2)	0.9003 (5)	−0.03751 (12)	0.0253 (6)
F2	0.5292 (2)	0.6993 (5)	−0.10663 (12)	0.0257 (6)
C1	0.4356 (3)	0.6036 (8)	0.0360 (2)	0.0186 (9)
C2	0.4540 (3)	0.6999 (7)	−0.0181 (2)	0.0180 (9)
C3	0.5168 (3)	0.5980 (8)	−0.0534 (2)	0.0205 (9)
S1	0.0000	0.4266 (3)	0.2500	0.0201 (3)
N1	0.2103 (3)	−0.0202 (7)	0.15987 (18)	0.0248 (9)
C4	0.1787 (3)	0.1842 (9)	0.1379 (2)	0.0239 (10)
H4	0.2032	0.2404	0.1028	0.029*
C5	0.1121 (3)	0.3192 (8)	0.1635 (2)	0.0215 (9)
H5	0.0905	0.4616	0.1455	0.026*

C6	0.0779 (3)	0.2417 (8)	0.2158 (2)	0.0191 (9)
C7	0.1112 (3)	0.0326 (8)	0.2401 (2)	0.0193 (9)
H7	0.0900	−0.0242	0.2763	0.023*
C8	0.1762 (3)	−0.0926 (8)	0.2104 (2)	0.0203 (9)
H8	0.1977	−0.2373	0.2268	0.024*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01922 (17)	0.02358 (17)	0.01968 (17)	0.00034 (12)	0.00505 (11)	−0.00148 (11)
F1	0.0271 (15)	0.0212 (14)	0.0285 (15)	0.0061 (12)	0.0072 (12)	0.0045 (11)
F2	0.0288 (16)	0.0283 (14)	0.0218 (14)	0.0026 (12)	0.0099 (11)	0.0084 (11)
C1	0.013 (2)	0.023 (2)	0.020 (2)	−0.0024 (17)	0.0021 (16)	−0.0062 (17)
C2	0.015 (2)	0.017 (2)	0.021 (2)	−0.0005 (17)	−0.0009 (16)	0.0016 (16)
C3	0.021 (2)	0.023 (2)	0.018 (2)	−0.0036 (19)	0.0029 (17)	0.0006 (17)
S1	0.0203 (8)	0.0166 (7)	0.0245 (8)	0.000	0.0068 (6)	0.000
N1	0.020 (2)	0.026 (2)	0.028 (2)	0.0012 (17)	0.0057 (16)	−0.0018 (17)
C4	0.017 (2)	0.031 (3)	0.023 (2)	−0.0047 (19)	0.0040 (18)	0.0002 (19)
C5	0.022 (2)	0.020 (2)	0.022 (2)	−0.0007 (18)	0.0005 (18)	0.0007 (17)
C6	0.015 (2)	0.020 (2)	0.023 (2)	−0.0012 (17)	0.0041 (17)	−0.0043 (17)
C7	0.014 (2)	0.019 (2)	0.024 (2)	−0.0025 (17)	0.0003 (17)	−0.0017 (17)
C8	0.016 (2)	0.018 (2)	0.026 (2)	−0.0010 (17)	−0.0013 (17)	−0.0009 (17)

Geometric parameters (Å, °)

I1—C1	2.101 (4)	N1—C4	1.337 (6)
F1—C2	1.355 (5)	C4—C5	1.389 (7)
F2—C3	1.352 (5)	C4—H4	0.9500
C1—C2	1.379 (6)	C5—C6	1.387 (6)
C1—C3^{i}	1.375 (6)	C5—H5	0.9500
C2—C3	1.381 (6)	C6—C7	1.385 (6)
C3—C1^{i}	1.375 (6)	C7—C8	1.392 (6)
S1—C6^{ii}	1.766 (4)	C7—H7	0.9500
S1—C6	1.766 (4)	C8—H8	0.9500
N1—C8	1.342 (6)		
C2—C1—C3^{i}	116.9 (4)	C5—C4—H4	118.0
C2—C1—I1	121.8 (3)	C6—C5—C4	118.5 (4)
C3^{i}—C1—I1	121.3 (3)	C6—C5—H5	120.7
C1—C2—F1	120.0 (4)	C4—C5—H5	120.7
C1—C2—C3	121.6 (4)	C7—C6—C5	118.6 (4)
F1—C2—C3	118.4 (4)	C7—C6—S1	124.0 (4)
F2—C3—C1^{i}	120.3 (4)	C5—C6—S1	117.3 (3)
F2—C3—C2	118.2 (4)	C6—C7—C8	118.6 (4)
C1^{i}—C3—C2	121.5 (4)	C6—C7—H7	120.7
C6^{ii}—S1—C6	104.8 (3)	C8—C7—H7	120.7
C8—N1—C4	116.7 (4)	N1—C8—C7	123.7 (4)
N1—C4—C5	123.9 (4)	N1—C8—H8	118.2

N1—C4—H4	118.0	C7—C8—H8	118.2
C3^{i}—C1—C2—F1	−179.1 (4)	N1—C4—C5—C6	1.7 (7)
I1—C1—C2—F1	0.6 (6)	C4—C5—C6—C7	−0.3 (7)
C3^{i}—C1—C2—C3	0.4 (7)	C4—C5—C6—S1	175.7 (4)
I1—C1—C2—C3	−179.9 (3)	C6^{ii}—S1—C6—C7	−34.9 (3)
C1—C2—C3—F2	178.2 (4)	C6^{ii}—S1—C6—C5	149.3 (4)
F1—C2—C3—F2	−2.3 (6)	C5—C6—C7—C8	−1.1 (6)
C1—C2—C3—C1^{i}	−0.4 (8)	S1—C6—C7—C8	−176.8 (3)
F1—C2—C3—C1^{i}	179.0 (4)	C4—N1—C8—C7	0.0 (7)
C8—N1—C4—C5	−1.5 (7)	C6—C7—C8—N1	1.3 (7)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the N1,C4–C8 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···F1^{iii}	0.95	2.52	3.213 (5)	130
C8—H8···Cg1^{iv}	0.95	2.82	3.557 (5)	135

Symmetry codes: (iii) −*x*+1/2, −*y*+3/2, −*z*; (iv) −*x*+1/2, *y*−1/2, −*z*+1/2.

Fig. 1

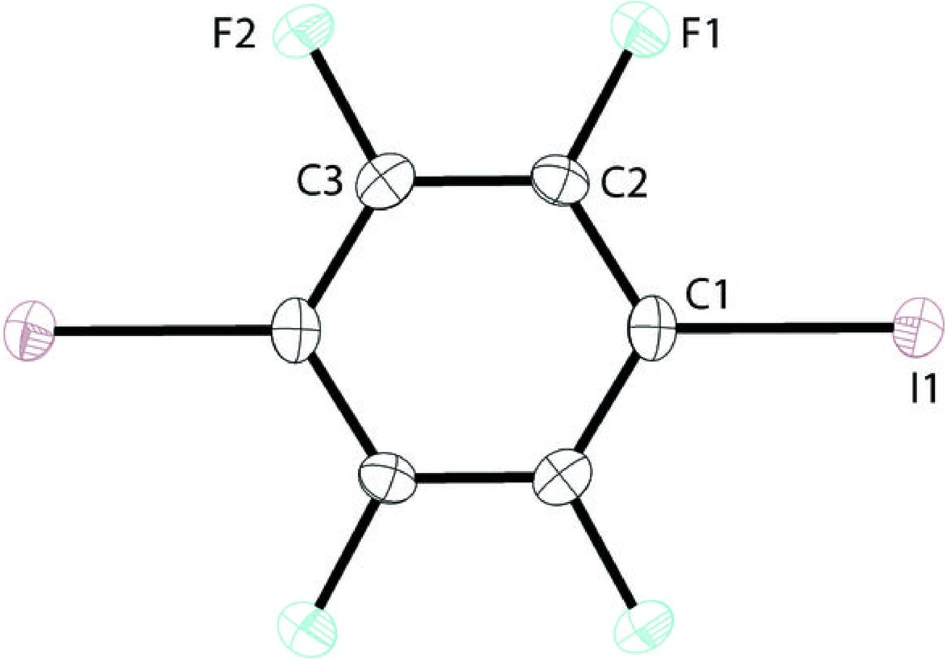

Fig. 2

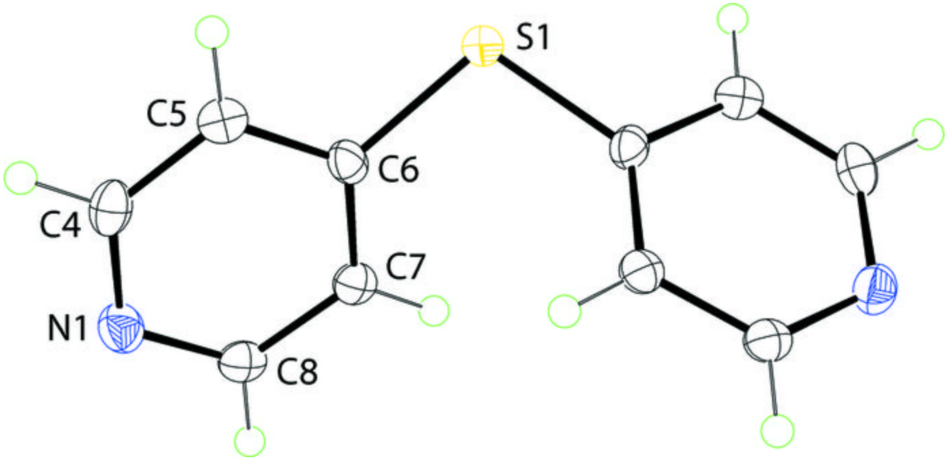

Fig. 3

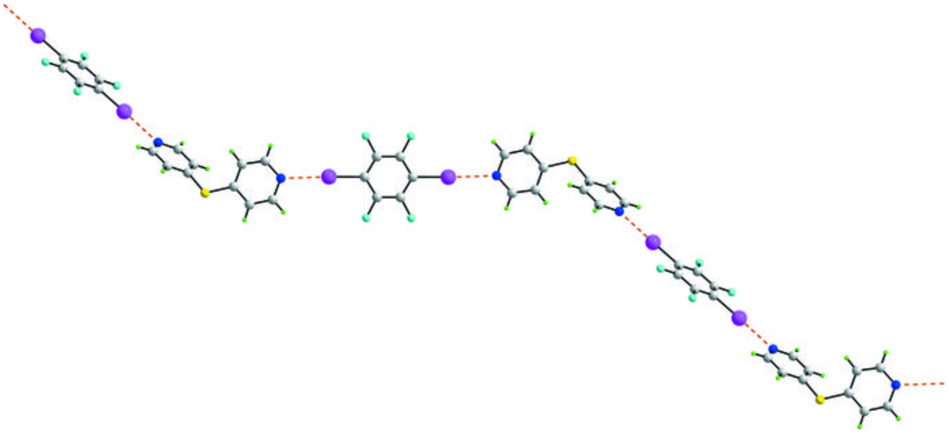

Fig. 4