

Arene–perfluoroarene interactions in crystal engineering. 5.¹ Octafluoronaphthalene–tetrathiafulvalene (1/1)

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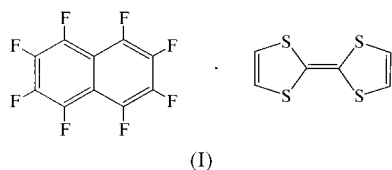
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In the title complex, $C_{10}F_8 \cdot C_6H_4S_4$, planar centrosymmetric molecules of tetrathiafulvalene and octafluoronaphthalene, inclined to each other by $9.6(1)^\circ$, form a mixed stack which does not exhibit charge transfer. Adjacent stacks pack in a herring-bone motif.

Comment

Octafluoronaphthalene (OFN) forms stable 1:1 cocrystals with a variety of fused-ring aromatic hydrocarbons (Potenza & Mastropaolo, 1975; Collings, Roscoe *et al.*, 2001) and with diphenylacetylene (Collings, Batsanov *et al.*, 2001; Clyburne *et al.*, 2001). The cocrystals comprise mixed stacks of parallel molecules and can be described as molecular complexes, showing no evidence of charge transfer (CT) either in their crystal structures or in their UV–visible spectra (CT band). On the other hand, hexafluorobenzene can form genuine CT complexes, *e.g.* with aromatic amines (Beaumont & Davis, 1967, 1968) or with bis(benzene)chromium (Aspley *et al.*, 1999), although its complexes with non-functionalized arenes also show no CT. To clarify the CT properties of OFN, we prepared its 1:1 complex, (I), with the facile electron donor tetrathiafulvalene (TTF).



The crystal of (I) has a 1:1 TTF·OFN composition. Both molecules (Fig. 1) possess crystallographic C_i symmetry and are planar within experimental error. They form an infinite stack parallel to the *a* axis of the crystal (Fig. 2). The OFN and TTF molecules within a stack are not entirely parallel, but form a dihedral angle of $9.6(1)^\circ$, with an average interplanar

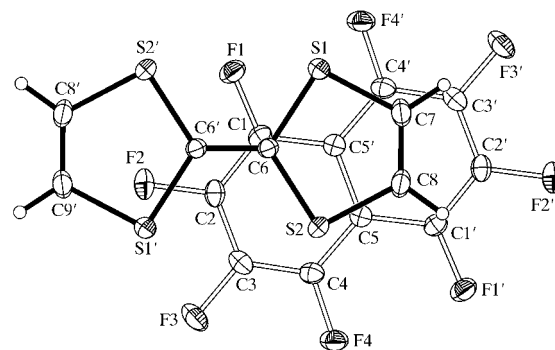


Figure 1

The molecules of TTF (solid bonds) and OFN (hollow bonds) in (I), projected onto the mean plane of OFN. Displacement ellipsoids are drawn at the 50% probability level. Primed atoms are related by inversion centres to their unprimed equivalents.

separation of 3.45 \AA . This distortion may be due to short interstack contacts [$F1 \cdots F4(x, y-1, z)$ $2.827(2) \text{ \AA}$ and $F2 \cdots F3(-x, y-\frac{1}{2}, \frac{1}{2}-z)$ $2.858(2) \text{ \AA}$, and their symmetry-related equivalents] compared with the standard van der Waals sum of 2.90 \AA (Rowland & Taylor, 1996). In each case, a more parallel alignment of molecules in a stack would generate even shorter $F \cdots F$ contacts, as illustrated in Fig. 2 for the $F2 \cdots F3$ contacts. Adjacent stacks, symmetrically related by a 2_1 axis, have the same general direction, **a**, but the orientations of the TTF planes within them differ by $33.1(1)^\circ$, and the orientations of the OFN planes differ by $48.8(1)^\circ$. No intermolecular contacts, either within or between the stacks, are significantly shorter than the sums of the relevant van der Waals radii (Rowland & Taylor, 1996).

The bond distances in (I) are essentially the same as in crystals of pure TTF (Cooper *et al.*, 1974) and OFN (Batsanov & Collings, 2001), showing the absence of CT in (I), despite the strong electron-donor ability of TTF. To our knowledge, the reduction potential of OFN has not been reported so far. Therefore, we undertook a cyclic voltammetry study of OFN,

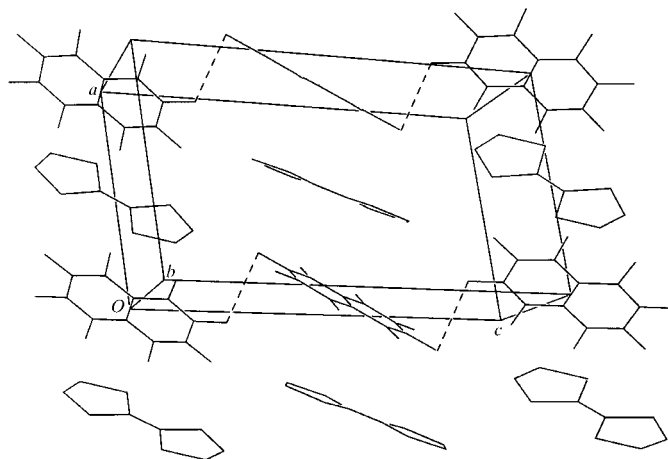


Figure 2

The crystal packing of (I). H atoms have been omitted for clarity and dashed lines indicate interstack $F2 \cdots F3$ contacts of $2.858(2) \text{ \AA}$.

¹ Part 4: Batsanov *et al.* (2001).

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but observed no redox behaviour whatsoever in the range between 1.0 and -2.0 V. Thus, OFN behaves as an exceedingly poor electron acceptor, notwithstanding the apparent abundance of electronegative atoms in the molecule.

Experimental

Slow evaporation (2–3 d) of a solution of OFN (0.027 g, 0.1 mmol) and TTF (0.020 g, 0.1 mmol) in CH_2Cl_2 (1 ml) at room temperature, in a vial capped with a needle-pierced septum, yielded yellow–brown blocks of (I) (m.p. 383–385 K; m.p. for TTF 393–396 K and m.p. for OFN 360–361 K). Gas chromatography and mass spectroscopy on a single crystal of (I) dissolved in CH_2Cl_2 showed both compounds to be present. Elemental analysis, found (calculated): C 40.05 (40.34), H 0.80 (0.40)%. Cyclic voltammetry measurements were carried out in Bu_4NPF_6 as the supporting electrolyte at 293 K in MeCN, *versus* an Ag/AgCl reference electrode.

Crystal data

$\text{C}_{10}\text{F}_8\cdot\text{C}_6\text{H}_4\text{S}_4$	$D_x = 1.919 \text{ Mg m}^{-3}$
$M_r = 476.43$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 992 reflections
$a = 8.581 (3) \text{ \AA}$	$\theta = 12.0\text{--}26.4^\circ$
$b = 6.321 (2) \text{ \AA}$	$\mu = 0.66 \text{ mm}^{-1}$
$c = 15.355 (2) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\beta = 98.16 (1)^\circ$	Plate, light brown
$V = 824.4 (4) \text{ \AA}^3$	$0.45 \times 0.40 \times 0.08 \text{ mm}$
$Z = 2$	

Data collection

SMART 1K CCD area-detector diffractometer	2196 independent reflections
ω scans	1967 reflections with $I > 2\sigma(I)$
Absorption correction: by integration (<i>XPREP</i> in <i>SHELXTL</i> ; Bruker, 1997)	$R_{\text{int}} = 0.029$
$T_{\text{min}} = 0.763$, $T_{\text{max}} = 0.962$	$\theta_{\text{max}} = 29^\circ$
9843 measured reflections	$h = -11 \rightarrow 11$
	$k = -8 \rightarrow 8$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 0.3542P]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.060$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
2196 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
135 parameters	
All H-atom parameters refined	

The value of R_{int} fell from 0.047 to 0.029 upon application of the absorption correction.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1464). Services for accessing these data are described at the back of the journal.

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