

Arene–perfluoroarene interactions in crystal engineering. XV. Ferrocene–decafluorobiphenyl (1/1)¹

Andrei S. Batsanov,* Jonathan C. Collings and Todd B. Marder*

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England

Correspondence e-mail: a.s.batsanov@durham.ac.uk, todd.marder@durham.ac.uk

Received 10 March 2006

Accepted 18 April 2006

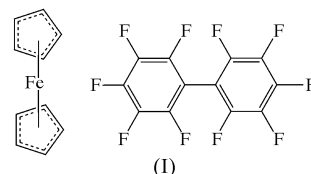
Online 16 May 2006

The title crystal, $[\text{Fe}(\text{C}_5\text{H}_5)_2] \cdot \text{C}_{12}\text{F}_{10}$, comprises infinite chains of alternating component molecules, linked through face-to-face contacts of nearly parallel cyclopentadienyl and pentafluorophenyl rings. The decafluorobiphenyl molecule has a crystallographic twofold axis and the Fe atom of the ferrocene molecule is on a crystallographic inversion centre, with both cyclopentadienyl rings disordered.

Comment

The propensity of perfluoroarenes to form 1:1 cocrystals with arenes is now well known [for references to earlier work, see Dahl (1988) and Collings, Roscoe *et al.* (2002)]. A recurrent feature of such solids is a mixed stack of alternating arene and perfluoroarene molecules, with parallel or nearly parallel planes. Contrary to original expectations, a geometric match between the components is unnecessary, and stable combinations can include molecules of very disparate size and form (Bunz & Enkelmann, 1999; Batsanov *et al.*, 2001; Collings, Roscoe *et al.*, 2002; Collings, Batsanov *et al.*, 2002; Collings *et al.*, 2005, 2006). Thus, sandwich π -complexes of transition metals can also form mixed infinite stacks with perfluoroarenes. Beck *et al.* (1998) were the first to prove this, with a 1:1 adduct of dexamethylferrocene with perfluorophenanthrene. Unlike ordinary arenes, however, π -complexes show a variety of other structural motifs. Thus, a 1:1 adduct of ferrocene with perfluorophenanthrene (Burdeniuc *et al.*, 1997) presents a sandwich of two ferrocene molecules enclosed between two perfluorophenanthrene molecules. The complex between ferrocene and octafluoronaphthalene (OFN) has an unusual 2:3 stoichiometry (Clyburne *et al.*, 2001). Nevertheless, the structure contains mixed stacks of 1:1 composition, with additional perpendicularly oriented OFN molecules inserted between the stacks. In 1:2 complexes of ferrocene or

nickelocene with $\text{Hg}_3(\text{C}_6\text{F}_4)_2$, recently reported by Haneline & Gabbai (2004), the cyclopentadienyl ring is stacked with an organomercury heterocycle rather than a tetrafluorobenzene moiety. Probably the most interesting structure is the 1:1 adduct of ferrocene with perfluorotetraphenylene, reported by Day *et al.* (2001). In this structure, a continuous chain is formed through face-to-face contacts of cyclopentadienyl and tetrafluorophenylene rings, notwithstanding substantial non-planarity of the perfluoroarene molecule.



With these examples in mind, we undertook a cocrystallization of ferrocene with decafluorobiphenyl (DFB). The latter molecule must have a twisted conformation to avoid unfavourable contacts between *peri*-F atoms. In the gas phase, the dihedral angle between the benzene rings is 70° (Almenningen *et al.*, 1968); in pure solid DFB, it decreases to 59.6° at

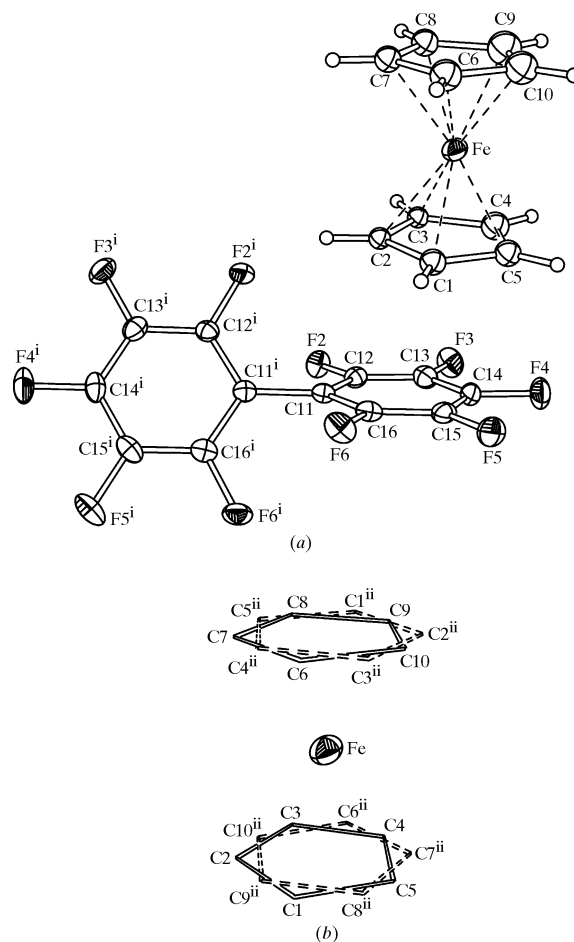


Figure 1
(a) The molecular structure of (I), not showing the disorder. (b) The disorder in the ferrocene molecule. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, y, -z + \frac{1}{2}$; (ii) $1 - x, 1 - y, 1 - z$.]

¹ For Part XIV, see Collings *et al.* (2006).

room temperature (Gleason & Britton, 1976) and 57.0° at 100 K (Batsanov & Howard, 2003), while in 1:1 cocrystals with biphenyl (Nae, 1979) and naphthalene (Foss *et al.*, 1984) it is smaller still, at 50.8 and 55.3°, respectively. Both cocrystals contain mixed stacks of alternating nearly parallel arene and perfluoroarene rings, in contrast with the herring-bone motif of pure DFB. Note that non-paranarity of both biphenyl and DFB molecules does not preclude parallel stacking of their individual rings.

The title decafluorobiphenyl–ferrocene adduct, (I), has a 1:1 stoichiometry (Fig. 1), the asymmetric unit comprising one-half of the formula unit. The DFB molecule possesses crystallographic C_2 symmetry, the twofold axis passing through the mid-point of the C11–C11ⁱ bond. The twist of this molecule [55.3 (1)°] is similar to that in other molecular complexes, as well as that in solid DFB. Such a conformation results in intramolecular contacts $F2 \cdots F2^i = 2.845$ (2) Å and $F6 \cdots F6^i = 2.841$ (2) Å, which are only moderately shorter than the normal intermolecular $F \cdots F$ contact of 3.00 Å (Rowland & Taylor, 1996). In fact, the shortest $F \cdots F$ contacts in the structure are intermolecular, *viz.* $F2 \cdots F6(1-x, 1+y, \frac{1}{2}-z)$ and its equivalents, at 2.642 (2) Å. Each DFB molecule participates in four such contacts, with two adjacent molecules related by the translations $\pm b$.

The Fe atom is situated on a crystallographic inversion centre. Each cyclopentadienyl (Cp) ring is disordered between two orientations which differ by a *ca* 32° rotation around the fivefold axis, thus creating an ambiguity as to whether the actual conformation of an individual molecule is eclipsed or staggered. We presume, by analogy with the disorder in the monoclinic phase of pure ferrocene (Seiler & Dunitz, 1979), that the actual conformation is eclipsed, as shown in Fig. 1. The Cp rings are parallel within experimental error; the Fe-to-ring plane distance [mean 1.65 (1) Å], as in other ferrocene–perfluoroarene adducts, agrees with the absence of charge transfer, in contrast with the HFB–bis(benzene)chromium(0) complex, which does show charge-transfer character (Aspley *et al.*, 1999).

The ferrocene molecule is sandwiched between two (inversion-related) pentafluorophenyl moieties. The contacting Cp and benzene rings are nearly parallel [dihedral

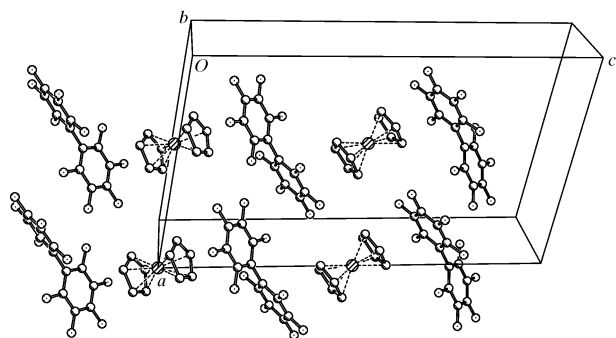


Figure 2
The crystal packing of (I). H atoms and the disorder have been omitted. Displacement ellipsoids are drawn at the 50% probability level.

angles of 9.1 (3) and 8.8 (3)° for the two Cp orientations], with an average interplanar separation of *ca* 3.3 Å. The resulting motif is a zigzag chain of alternating ferrocene and DFB molecules, running in the general direction of the *c* axis (Fig. 2). On the ‘rear’ side, the pentafluorophenyl moiety is contacted by a perfluorophenyl group of an adjacent chain, in a herring-bone manner [dihedral angle = 55.3 (1)°].

Most arene–perfluoroarene complexes are remarkable for having higher melting points than either of the components, as was first observed by Patrick & Prosser (1960) on the seminal benzene–HFB complex, which has a melting point of 296.9 K, *cf.* 278.6 K for benzene and 278.2 K for HFB (see also Collings *et al.*, 2001; Collings, Roscoe *et al.*, 2002; Collings *et al.*, 2006). Therefore, we studied the thermal behaviour of (I), the components of which have melting points of 342 (DFB) and 446 K (ferrocene) and boiling points of 479 and 522 K, respectively. Thermal gravimetric analysis (TGA) of (I) shows the loss of mass starting at 333 K and ending at 403 K, probably due to sublimation. Differential scanning calorimetry (DSC) at a rate of 5 K min^{−1} showed two sharp endotherms at 369 and 381 K, with $\Delta H = 16$ and 25 J g^{−1}, respectively (*ca* 8 and 13 kJ mol^{−1}, if we presume the original molecular weight). Both endotherms appeared on the first heating cycle only, with subsequent cycles showing a completely featureless curve in the same range, presumably due to sublimation. Transmission polarized light microscopy on a sample of (I) enclosed between two glass slides showed (I) to begin partial melting at *ca* 377 K, and to have completely evaporated by *ca* 440 K. Thus, complex (I) displays an intriguing phase behaviour which deserves further investigation.

Experimental

Single crystals of ferrocene–decafluorobiphenyl (1/1) were grown by slow evaporation of a 1:1 molar mixture of the two compounds in solution in dichloromethane. Analysis calculated for C₂₂H₁₀F₁₀Fe: C 50.80, H 1.94%; found: C 50.41, H 1.89%.

Crystal data

[Fe(C ₅ H ₅) ₂]:C ₁₂ F ₁₀	Z = 4
<i>M_r</i> = 520.15	<i>D_x</i> = 1.847 Mg m ^{−3}
Monoclinic, C2/c	Mo K α radiation
<i>a</i> = 13.3025 (12) Å	μ = 0.91 mm ^{−1}
<i>b</i> = 6.1690 (6) Å	<i>T</i> = 120 (2) K
<i>c</i> = 23.026 (2) Å	Block, yellow
β = 98.69 (1)°	0.36 × 0.22 × 0.20 mm
<i>V</i> = 1867.9 (3) Å ³	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	10117 measured reflections
ω scans	2143 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2001)	1714 reflections with <i>I</i> > 2 σ (<i>I</i>)
<i>T_{min}</i> = 0.708, <i>T_{max}</i> = 0.839	<i>R_{int}</i> = 0.045
	θ_{\max} = 27.5°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 2.913P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.098$	$(\Delta/\sigma)_{\max} = 0.002$
<i>S</i> = 1.06	$\Delta\rho_{\max} = 0.52 \text{ e \AA}^{-3}$
2143 reflections	$\Delta\rho_{\min} = -0.39 \text{ e \AA}^{-3}$
146 parameters	
H-atom parameters constrained	

Table 1

Selected bond lengths (Å).

Fe—C1	2.078 (5)	Fe—C7	2.045 (5)
Fe—C2	2.075 (5)	Fe—C8	2.036 (5)
Fe—C3	2.054 (5)	Fe—C9	2.003 (6)
Fe—C4	2.033 (5)	Fe—C10	2.013 (5)
Fe—C5	2.034 (5)	C11—C11 ⁱ	1.487 (4)
Fe—C6	2.040 (5)		

Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.

All H atoms were treated as riding on their parent C atoms, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank D. Carswell and K. Wonghan for assistance with measurements of the thermal behaviour. TBM thanks One NorthEast for funding.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3003). Services for accessing these data are described at the back of the journal.

References

- Almenningen, A., Hartmann, A. O. & Seip, H. M. (1968). *Acta Chem. Scand.* **22**, 1013–1024.
- Aspley, C. J., Boxwell, C., Buil, M. L., Higgitt, C. L., Long, C. & Perutz, R. N. (1999). *Chem. Commun.* pp. 1027–1028.
- Batsanov, A. S. & Howard, J. A. K. (2003). Private communication to the Cambridge Structural Database, No. CCDC-207400. CCDC, 12 Union Road, Cambridge, England.
- Batsanov, A. S., Howard, J. A. K., Marder, T. B. & Robins, E. G. (2001). *Acta Cryst.* **C57**, 1303–1305.
- Beck, C. M., Burdeniuc, J., Crabtree, R. H., Rheingold, A. L. & Yap, G. P. A. (1998). *Inorg. Chim. Acta*, **270**, 559–562.
- Bruker (1998). *SMART*. Version 5.049. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2001). *SAINTE* (Version 6.02a), *SADABS* (Version 2.03) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bunz, U. H. F. & Enkelmann, V. (1999). *Chem. Eur. J.* **5**, 263–266.
- Burdeniuc, J., Crabtree, R. H., Rheingold, A. L. & Yap, G. P. A. (1997). *Bull. Soc. Chim. Fr.* **134**, 955–958.
- Clyburne, J. A., Hamilton, T. & Jenkins, H. A. (2001). *Cryst. Eng.* **4**, 1–9.
- Collings, J. C., Batsanov, A. S., Howard, J. A. K., Dickie, D. A., Clyburne, J. A. C., Jenkins, H. A. & Marder, T. B. (2005). *J. Fluorine Chem.* **126**, 515–518.
- Collings, J. C., Batsanov, A. S., Howard, J. A. K. & Marder, T. B. (2002). *Cryst. Eng.* **5**, 37–46.
- Collings, J. C., Batsanov, A. S., Howard, J. A. K. & Marder, T. B. (2006). *Can. J. Chem.* **84**, 238–242.
- Collings, J. C., Roscoe, K. P., Robins, E. G., Batsanov, A. S., Stimson, L. M., Howard, J. A. K., Clark, S. J. & Marder, T. B. (2002). *New J. Chem.* **26**, 1740–1746.
- Collings, J. C., Roscoe, K. P., Thomas, R. L., Batsanov, A. S., Stimson, L. M., Howard, J. A. K. & Marder, T. B. (2001). *New J. Chem.* **25**, 1410–1417.
- Dahl, T. (1988). *Acta Chem. Scand. Ser. A*, **42**, 1–7.
- Day, M. W., Matxger, A. J. & Grubbs, R. H. (2001). Private communication to the Cambridge Structural Database, No. CCDC-130854. CCDC, 12 Union Road, Cambridge, England.
- Foss, L. I., Syed, A., Stevens, E. D. & Klein, C. L. (1984). *Acta Cryst.* **C40**, 272–274.
- Gleason, W. B. & Britton, D. (1976). *Cryst. Struct. Commun.* **5**, 483–488.
- Haneline, M. R. & Gabbai, F. P. (2004). *Angew. Chem. Int. Ed.* **43**, 5471–5474.
- Naae, D. G. (1979). *Acta Cryst.* **B35**, 2765–2768.
- Patrick, C. R. & Prosser, G. S. (1960). *Nature*, **187**, 1021.
- Rowland, B. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.
- Seiler, P. & Dunitz, J. D. (1979). *Acta Cryst.* **B35**, 2020–2032.