

Octafluoronaphthalene–diphenyl-
acetylene (1/1)Jonathan C. Collings, Andrei S. Batsanov,* Judith A. K.
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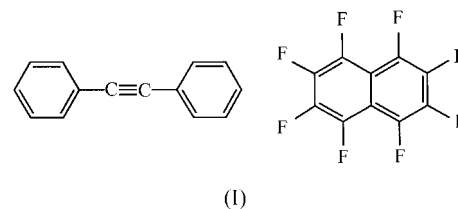
The structure of the title complex, $C_{10}F_8 \cdot C_{14}H_{10}$, comprises mixed stacks of alternating diphenylacetylene and octafluoronaphthalene molecules, both lying at inversion centres and parallel to within $8.6 (1)^\circ$, in contrast with the herring-bone packing observed in crystals of either pure component.

Comment

It has been known for a long time that geometrically matching arenes and perfluoroarenes form stable 1:1 molecular complexes with higher melting points than either of the components (Patrick & Prosser, 1960). The crystal structures of these complexes, *e.g.* hexafluorobenzene–benzene (Williams *et al.*, 1992) or octafluoronaphthalene–naphthalene (Potenza & Mastropaolo, 1975), comprise mixed stacks of approximately parallel arene and perfluoroarene molecules, in contrast with the herring-bone structures of the pure components. Recently, there has been a remarkable increase of interest in arene–perfluoroarene interactions, which have been recognized as an important supramolecular synthon (Dai *et al.*, 1999) with potential applications for solid-state chemistry, molecular electronics, liquid crystals, *etc.* For the most important recent experimental and theoretical work and for references to earlier results, see West *et al.* (1997), Hernandez-Trejillo *et al.* (1997), Parks *et al.* (1998), Beck *et al.* (1998), Coates *et al.* (1998), Aspley *et al.* (1999), Weck *et al.* (1999), Bunz & Enkelmann (1999), Blanchard *et al.* (2000), Lorenzo *et al.* (2000), Ponzini *et al.* (2000), Bartholomew *et al.* (2000) and Feast *et al.* (2001).

In the course of our studies on such systems, we found that a perfect geometrical match between the arene and the perfluoroarene is not a necessary condition of equimolar complexation; complexes of octafluoronaphthalene (OFN) with anthracene, phenanthrene, pyrene and triphenylene have been isolated and all were shown by X-ray crystallography to contain mixed stacks (Collings *et al.*, 2001). In order to examine the limits of stability of this motif, we attempted to co-

crystallize OFN with increasingly disparate aromatic hydrocarbons. In the course of this work, we prepared the stable 1:1 title complex, (I), formed between OFN and diphenylacetylene (tolan), and its crystal structure is presented here.



Both molecules in complex (I) are located at crystallographic inversion centres (Fig. 1). Thus, both phenyl rings in the tolan molecule are parallel, albeit not exactly coplanar; their planes are separated by 0.06 \AA . The OFN molecule is planar within experimental error. The geometry of both molecules is essentially the same as in the crystals of pure OFN (Batsanov & Collings, 2001) and tolan (Mavridis & Moustakali-Mavridis, 1977; Abramnikov *et al.*, 1988; Zanin *et al.*, 1991). This indicates the absence of intermolecular charge transfer, as is usual for most arene–perfluoroarene systems.

The packing motif in (I) is one of mixed stacks of alternating OFN and tolan molecules (Fig. 2), quite different from the herring-bone packing of pure tolan and the flattened herring-bone (γ) motif of pure OFN. Within the stack, mean planes of adjacent molecules form a dihedral angle of $8.6 (1)^\circ$, with a uniform interplanar separation of $3.39 (7) \text{ \AA}$. The direction of the stack is parallel to the crystallographic z axis. Adjacent stacks are shifted relative to each other by approximately $c/2$, hence the tolan molecules of one stack lie against the OFN molecules of another. Four out of five symmetry-independent H atoms participate in intrastack $H \cdots F$ contacts of 2.61 – 2.73 \AA (calculated for the idealized $C-H$ bond length of 1.08 \AA), while H12 forms a shorter $H12 \cdots F4$ contact of 2.43 \AA . Although these contacts are not particularly short compared with the standard van der Waals contact distance, variously estimated as 2.55 (Pauling, 1960),

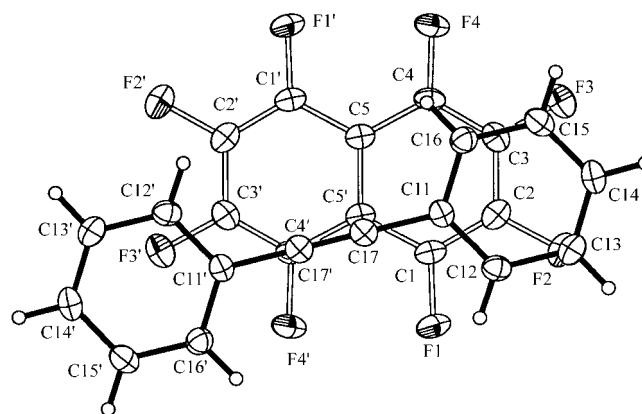


Figure 1

The molecules of OFN and tolan in (I) shown projected on the OFN mean plane. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Primed atoms are symmetrically dependent *via* inversion centres.

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2.67 (Bondi, 1964) or 2.54 Å (Zefirov & Zorkii, 1995; Rowland & Taylor, 1996), they may play a significant role in stabilizing the structure (Dahl, 1990; Thalladi *et al.*, 1998). Interstack contacts between F1 atoms [2.838 (2) Å] are shorter than the standard distance of 2.90 Å (Rowland & Taylor, 1996). The contacting atoms are related *via* an inversion centre, an orientation which is characteristic of repulsive contacts (Thalladi *et al.*, 1998).

The molecules of each type, which are symmetrically related by a 2_1 axis and belong to adjacent stacks (Fig. 2), are not parallel; the interplanar angle between OFN molecules is 28.5 (1)° and that between tolan molecules is 24.4 (1)°. A similar arrangement was observed in OFN–naphthalene (Potenza & Mastropaolo, 1975), where the OFN/naphthalene dihedral angle within the stack is only 3.7°, but the OFN/OFN and naphthalene/naphthalene angles between adjacent stacks



Figure 2
The crystal packing of (I). H atoms have been omitted for clarity.

are 34.5 and 31.5°, respectively. Both structures can be described as laminar with a residual herring-bone perturbation. However, in the mixed-stack structures of OFN–anthracene, OFN–phenanthrene, OFN–pyrene and OFN–triphenylene, all molecules are parallel to within 10, 3, 0.4 and 1°, respectively (Collings *et al.*, 2001). Thus, there is no simple correlation between the degree of non-coplanarity of the stacks and the geometrical mismatch between the arene and perfluoroarene molecules.

The molecular volume of crystalline OFN at 100 K is 214 Å³ (Batsanov & Collings, 2001), and that of tolan (extrapolated for 100 K) is *ca* 250 Å³. The volume per formula unit in (I) is 470 Å³ at the same temperature, indicating an insignificant (1%) decrease of packing density compared with that of the pure components.

The most electron-rich bond of tolan, C17–C17', is practically eclipsed by the C4'–C5' bond of OFN (and by the corresponding bond of its inversion equivalent). These bonds are nearly parallel, diverging by 13.6 (2)°, and the resulting contacts C17···C5' [3.370 (2) Å] and C17'···C4' [3.321 (2) Å] are slightly shorter than twice the van der Waals radius of carbon (3.40–3.59 Å). However, the acetylene moiety remains linear and there is no evidence of electron transfer. Generally, the mode of overlap between the OFN and tolan molecules permits no obvious interpretation in terms of electrostatic interactions.

Experimental

Crystals of (I) were grown by the slow evaporation over 3 d at room temperature of a solution of tolan (0.1 mmol, 0.018 g) and OFN (0.1 mmol, 0.027 g) in previously distilled CH₂Cl₂ (2 ml) (m.p. 389–391 K). Analysis, found: C 63.85, H 2.24%; calculated for C₂₄H₁₀F₈: C 64.01, H 2.24%.

Crystal data

C₁₀F₈·C₁₄H₁₀
M_r = 450.32
Monoclinic, $P2_1/n$
 a = 6.3867 (5) Å
 b = 20.9583 (17) Å
 c = 7.1413 (6) Å
 β = 100.272 (5)°
 V = 940.57 (13) Å³
 Z = 2

D_x = 1.590 Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 552 reflections
 θ = 12–26°
 μ = 0.15 mm⁻¹
 T = 100 (2) K
Plate, colourless
0.55 × 0.34 × 0.03 mm

Data collection

Siemens SMART 1 K CCD area-detector diffractometer
 ω scans
5480 measured reflections
2153 independent reflections
1790 reflections with $I > 2\sigma(I)$

R_{int} = 0.033
 θ_{max} = 27.5°
 h = -8 → 7
 k = -27 → 24
 l = -9 → 9

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.038
 $wR(F^2)$ = 0.089
 S = 1.07
2153 reflections
165 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 0.4264P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max}$ = 0.001
 $\Delta\rho_{max}$ = 0.26 e Å⁻³
 $\Delta\rho_{min}$ = -0.21 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1–F1	1.3480 (16)	C5–C5 ⁱ	1.439 (3)
C1–C2	1.359 (2)	C11–C16	1.402 (2)
C1–C5 ⁱ	1.417 (2)	C11–C12	1.405 (2)
C2–F2	1.3399 (17)	C11–C17	1.438 (2)
C2–C3	1.404 (2)	C12–C13	1.387 (2)
C3–F3	1.3392 (17)	C13–C14	1.391 (2)
C3–C4	1.358 (2)	C14–C15	1.391 (2)
C4–F4	1.3483 (16)	C15–C16	1.386 (2)
C4–C5	1.413 (2)	C17–C17 ⁱⁱ	1.201 (3)
C17 ⁱⁱ –C17–C11	179.4 (2)		

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

The range of refined C–H distances is 0.950 (18)–0.965 (18) Å.

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: FG1634). Services for accessing these data are described at the back of the journal.

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