Crystal Engineering

Structure and Phase Behavior of a 2:1 Complex between Arene- and Fluoroarene-Based Conjugated Rigid Rods**

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Conjugated molecular materials are important[1] owing to their role in organic devices such as organic light-emitting diodes (OLEDs) and thin-film transistors (TFTs).[2] The performance of such devices depends not only on the intramolecular properties, but also on intermolecular interactions,[3] both of which can be modified by introduction of fluorine substituents.[4] Fluorinated oligomers have been utilized as electron-transporting layers in OLEDs.[5] Recently, an oligothiophene with terminal perfluorophenyl groups was used in an *n*-type TFT and shown to exhibit a high mobility, partially attributed to intermolecular arene–perfluoroarene stacking interactions.[6] The arene–perfluoroarene interaction itself has been known for over 40 years,[7] and has been shown to occur in numerous 1:1 complexes of arenes and fluoroarenes, including those of dissimilar shape,[8] as well as in partially fluorinated conjugated molecules,[9] in which it has been used to effect topological polymerizations.[10]

Phenylene–ethynylenes such as 1,4-bis(phenylethynyl)benzene (**HHH**) have attracted attention, particularly with regard to their photophysical behavior.[1,11] We have reported the crystal structure of a 1:1 complex of 1,4-bis(phenylethynyl)tetrafluorobenzene (**HFH**) and 1,4-bis(pentafluorophenylethynyl)benzene (**FHF**), which exhibits nematic liquid-crystalline (LC) phase behavior that is not present in either of the pure components.[12] Herein we report the structure and preliminary LC phase behavior of a novel[13] 2:1 arene–perfluoroarene complex formed between **HHH** and its perfluorinated analogue **FFF**.

Both components were synthesized by Sonogashira cross-coupling methodology.[14] Crystals of the 2:1 complex (2**HHH**)**FFF** were obtained reproducibly from an equimolar mixture of **HHH** and **FFF** in toluene, whereby residual **FFF** crystallized separately. The single-crystal structures of the complex and of the two pure components were determined from X-ray diffraction data.[15,16]

The complex (2**HHH**)**FFF** crystallizes in space group *Fddd*. The molecules pack in infinite stacks, in contrast to the respective herringbone and nonstacked layer arrangements found in crystals of pure **HHH** and **FFF**. In the complex, the molecules of **FFF** lie on crystallographic twofold rotation axes which pass through opposite C–C bonds of its central ring and are symmetrically sandwiched by two molecules of **HHH** (Figure 1). The molecules are essentially planar; the dihedral angles between the outer and central rings are 3.7 and 2.3° for **HHH**, and 2.0° for **FFF**, as opposed to 3.1 and 1.1° for pure **HHH** and **FFF**, respectively.

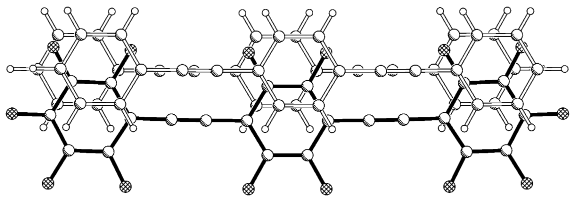

Figure 1. One **HHH-FFF-HHH** sandwich, which corresponds to twice the asymmetric unit of the crystal structure of (2**HHH**)**FFF** showing the overlap of the three molecules; filled bonds = **FFF**, hollow bonds = **HHH**.

The approximately parallel stacking of the molecules is not restricted to the (2**HHH**)**FFF** unit, but is propagated infinitely throughout the crystal structure; adjacent molecules of **HHH** are separated by 3.553 Å. Within each stack, adjacent molecules are approximately parallel, offset laterally from each other, and approximately equidistant; the mean stacking separation is 3.571 Å, typical of arene–perfluoroarene complexes. The stacks of molecules lie along directions parallel to the two *bc* diagonals of the orthorhombic unit cell,

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almost but not quite orthogonal to one another (angle of 82.7°); the two types of stacks form layers in the *bc* plane, alternating with a displacement of *a*/4 relative to each other (Figure 2).

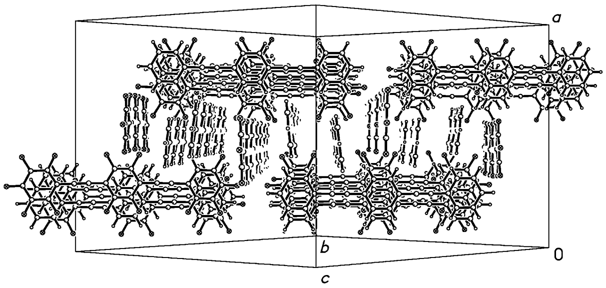

Figure 2. Packing of the triple units in the crystal structure of (2 **HHH**) **FFF**.

The principal interactions between stacks of molecules are of two types. Between stacks in a given layer, the closest contacts are F···F interactions between the fluorine atoms at the ends of the two molecules. The F···F separation of 2.528 Å compares to a sum of van der Waals (vdW) radii of 2.90 Å.[17] Between stacks in adjacent layers, there are several H···F contacts, the shortest of which are 2.515 and 2.659 Å (sum of vdW radii = 2.55 Å).[18] The near-perpendicular arrangement of stacks is proposed to arise from the unequal (2:1) ratio of H and F substituents in the stacks, which, in contrast to 1:1 complexes with parallel stacks, such as **HFH FHF**,[12] precludes the establishment of a perfectly complementary network of stabilizing edge-to-edge H···F interactions.[19]

Differential scanning calorimetry (DSC) and transmitted polarized optical microscopy were used to probe the mesomorphism of the 2:1 **HHH**:**FFF** system, which proved to be very complex. Thus, when a 2:1 mixture of **HHH** and **FFF** is cooled from the isotropic phase, surprisingly it appears to exhibit two different sequences of phase changes, with apparently no preference for either, over several samples and runs. In one pathway, the melt cools via a mesophase (ordered smectic phase S1) to a solid (X1) which, on reheating, exhibits similar thermal transitions to solution-grown cocrystals. However, in other runs, cooling leads to what appears to be a different mesophase (S2, also an ordered smectic mesophase, as judged by an optical texture different from that of S1), and then to a solid (X2), which does not have the same morphology as X1. On reheating, X2 does not behave like the solution-grown solid; instead, it first recrystallizes to a solid phase resembling X1. The DSC thermograms show subtle differences in the two cooling/heating cycles, although they also contain events which may be those of the individual components.

Solids X1 and X2 appear to be related paramorphotically to S1 and S2, respectively, and must therefore be linked to the smectic phase through particular kinetic pathways. That two different cooling pathways are found on exiting the isotropic state is highly curious, and consequently a more detailed account of the liquid-crystalline behavior of the **FFF HHH** system will be the subject of a future report, as will detailed computer-modeling studies on this system.

The 2:1 complex formed between 1,4-bis(phenylethynyl)-benzene and its perfluorinated analogue is unique in that it represents the first example of a non-1:1, hydrocarbon–perfluorocarbon:arene–perfluoroarene complex. The interstack geometry is also unusual and probably results from the lack of opportunity to maximize the stabilizing H···F edge-to-edge interactions which are generally observed in complementary 1:1 complexes. The complex phase behavior of this system suggests that alternative arrangements are close in energy.

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[13] To our knowledge, only two non-1:1 complexes have been structurally characterized: the 3:2 complex of octafluoronaphthalene (OFN) with ferrocene, which displays 1:1 stacks of alternating molecules with residual OFN filling the space between them (J. A. C. Clyburne, T. Hamilton, H. A. Jenkins, *Cryst. Eng.* **2001**, *4*, 1) and the 2:1 structure of [Cp*Co(acac)] (Cp* = C_5Me_5, acac = 2,4-pentanedione) with hexafluorobenzene of solvation, in which 1:1 stacking is precluded by the Co–acac groups (J. J. Schneider, R. Goddard, C. Kruger, *Z. Naturforsch. B* **1995**, *50*, 448).

[14] For synthetic and crystallization details, see Supporting Information.

[15] X-ray diffraction experiments were performed with SMART 1K CCD area-detector diffractometers using $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXTL; Bruker AXS Inc., Madison, WI, USA). Crystallographic data for **HHH**: $C_{22}H_{14}$, $M_r = 278.3$, triclinic, space group $P\bar{1}$, $a = 6.0202(10)$, $b = 9.662(2)$, $c = 13.692(2)$ Å, $\alpha = 90.719(4)$, $\beta = 94.732(4)$, $\gamma = 103.859(4)°$, $V = 770.2(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.200$ g cm^{-3}, $\mu = 0.068$ mm^{-1}, $T = 160$ K, R (F, $F^2 > 2\sigma$) = 0.0415, R_w (F^2, all data) = 0.1344, $S = 1.132$ for 2498 unique data ($\theta < 25.8°$) and 200 refined parameters; final difference synthesis within ±0.17 e Å^{-3}. Crystallographic data for **FFF**: $C_{22}F_{14}$, $M_r = 530.2$, monoclinic, space group $C2/m$, $a = 8.9294(7)$, $b = 7.6605(7)$, $c = 13.2005(2)$ Å, $\beta = 99.437(2)°$, $V = 890.74(13)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.977$ g cm^{-3}, $\mu = 0.219$ mm^{-1}, $T = 100$ K, R (F, $F^2 > 2\sigma$) = 0.0311, R_w (F^2, all data) = 0.1028, $S = 1.075$ for 1102 unique data ($\theta < 27.5°$) and 91 refined parameters; final difference synthesis within ±0.41 e Å^{-3}. Crystallographic data for (2**HHH**)**FFF**: $C_{22}F_{14}\cdot 2C_{22}H_{14}$, $M_r = 1086.9$, orthorhombic, space group $Fddd$, $a = 20.4645(9)$, $b = 28.5337(12)$, $c = 32.4370(14)$ Å, $V = 18940.9(14)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.525$ g cm^{-3}, $\mu = 0.126$ mm^{-1}, $T = 160$ K, R (F, $F^2 > 2\sigma$) = 0.0556, R_w (F^2, all data) = 0.1671, $S = 1.051$ for 5832 unique data ($\theta < 28.8°$) and 361 refined parameters; final difference synthesis within ±0.52 e Å^{-3}. CCDC 162387, CCDC 162389, and CCDC 161813 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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