Arene-perfluoroarene interactions in crystal engineering. Part 3. Single-crystal structures of 1 : 1 complexes of octafluoronaphthalene with fused-ring polyaromatic hydrocarbons†‡

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Molecular complexes of 1 : 1 stoichiometry of octafluoronaphthalene (OFN) with the polyaromatic hydrocarbons anthracene, phenanthrene, pyrene and triphenylene have been prepared, and their single-crystal X-ray structures determined at 120 K. All of the structures are composed of infinite stacks of alternating, almost parallel molecules of OFN and the hydrocarbons, in contrast to the herringbone or γ-type (flattened herringbone) packing of the pure components. It is clearly shown that the stacking motif does not require a close correlation between the molecular geometry of the arene and perfluoroarene species, but is stable over a wide range of differing sizes and shapes. Thus, the arene–perfluoroarene interaction is of general importance as a supramolecular synthon. The molecular geometries of the components are not affected by complexation, indicating the absence of charge transfer in the complexes. The role of close C–H···F–C and C–F···F–C intermolecular contacts between stacks is discussed. A re-determination of the single-crystal structure of triphenylene at 150 K is also reported, providing a more accurate comparison with that of the 1 : 1 OFN · triphenylene complex.

Introduction

Arene–arene ('π–π') interactions are significant in many areas of chemistry, biochemistry and materials science.[3] An important class thereof are the interactions between arenes and perfluoroarenes, which first attracted interest with the discovery that an equimolar mixture of benzene and hexafluorobenzene (HFB) forms a solid with a melting point of 24 °C, *ca.* 20 °C higher than that of either component.[4] Crystallographic studies on the complex revealed nearly parallel molecules stacked alternately in infinite columns with a parallel slip (offset) between adjacent molecules,[5] in stark contrast to the herringbone packing observed in crystals of the individual components, which are dominated by T-shaped contacts.[6]

The exact nature of arene–perfluoroarene interactions in the HFB · benzene complex still remains a subject of controversy.[7] Molecular beam studies of van der Waals complexes revealed that, even in the gas phase, the $(\text{benzene})_2$ or $(\text{HFB})_2$ dimers are T-shaped, while the HFB · benzene dimer comprises parallel molecules.[8] Thus, the effect is one of molecular recognition, rather than a cumulative result of lattice energy minimisation. Solution NMR studies have also confirmed the presence of these face-to-face dimers in liquid mixtures of HFB with benzene and naphthalene.[9] This interaction has been used as a tool for molecular recognition of aromatic molecules by catenanes.[10] The crystal structures of HFB · arene complexes predicted by lattice energy calculations with atom–atom potentials were at variance with the experimental ones,[11] showing the inadequacy of the simple van der Waals model. The hypothesis of charge transfer (CT) interactions had to be discarded for the HFB · benzene complex, as it shows no characteristic CT bands in its UV-vis absorption spectrum. The crystal packing may be significantly influenced by the interactions, particularly the H···F ones, between different stacks.[11]

The fact that both benzene and HFB have large quadrupole moments, which are of similar magnitude but opposite sign,[12] led to the suggestion that the stacking motif of the complex is dictated by electrostatic quadrupole–quadrupole interactions.[13] A schematic of how the quadrupole moments direct the packing of both the complex and pure HFB is shown in Fig. 1. This conclusion was supported by dynamic NMR studies on a series of naphthalenes having pentafluorophenyl and various substituted phenyl groups at the *peri* positions, in which the energetic barrier to their rotation was found to increase with the electron donating power of the phenyl substituent.[14] Two recent *ab initio* calculations give values of 3.7 and 4.3 kcal mol^{-1} for the interaction energy between the two components,[15] and the latest density functional calculations performed on an HFB · d_6-benzene dimer suggest that the interaction between the components is predominately van der Waals in origin, with an electrostatic component contributing around 15% of the total energy.[16]

Hexafluorobenzene is able to form complexes with numerous benzene derivatives, as can be seen in the phase diagrams of HFB–arene mixtures which exhibit congruent melting points at equimolar composition,[17] and from various thermodynamic measurements.[18] Some of these are genuine CT

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‡ Electronic supplementary information (ESI) available: experimental data for the re-determination of the crystal structure of triphenylene, tables of the average bond lengths in OFN and the polyaromatic molecules in both the complexes and pure compounds, and a table of distances and angles for intermolecular H···F contacts in the complexes which are below the sum of the van der Waals radii. See http://www.rsc.org/suppdata/nj/b1/b105502j/

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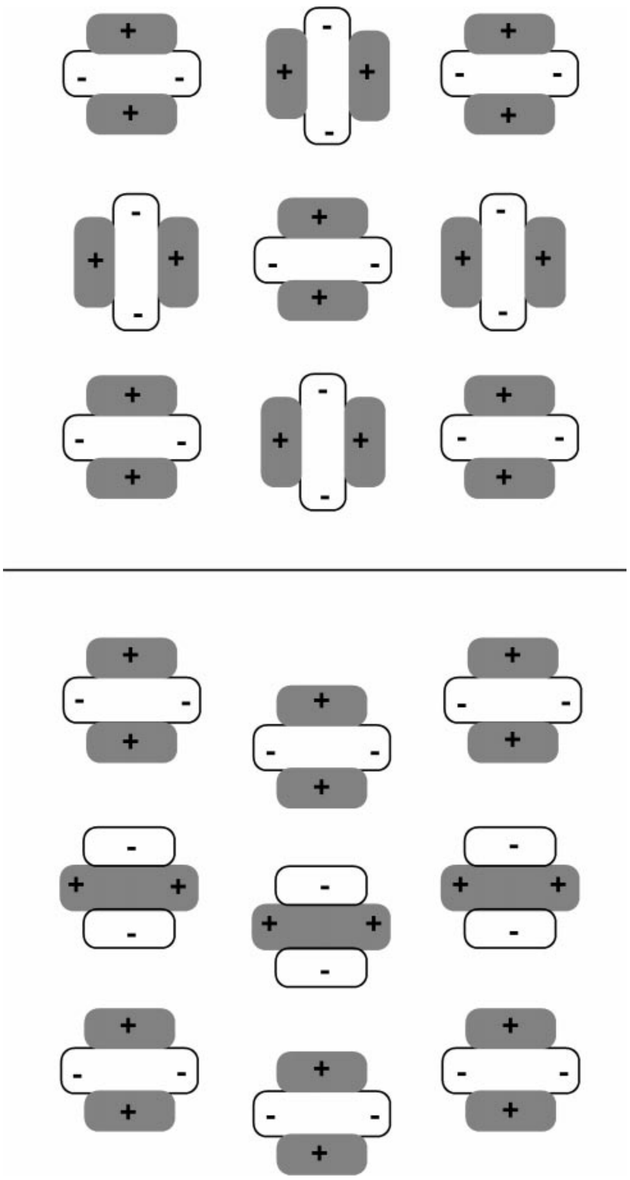

Fig. 1 Schematic representation of two possible packing modes of quadrupolar molecules. Top: the herringbone packing of hexafluorobenzene in the pure state. For benzene, reverse the charge distribution. Bottom: the stacked arrangement of the HFB · benzene complex.

complexes, *e.g.* those with aromatic amines[19] and with bis(benzene)chromium.[20] A number of crystal structures of these complexes have been obtained which also show the component molecules to be alternately π-stacked in infinite columns.[21] The same π-stacking motif has recently been observed in the solid-state packing of several fluorinated, conjugated, multiple ring molecules.[22] This demonstrates the possibility of harnessing the arene–perfluoroarene interaction for supramolecular engineering, *i.e.* influencing in a predictable way the local order in molecular packing. It has recently been used to pre-align monomers for solid-state photopolymerisation,[23] to achieve favourable packing conformations in organic conducting or electro-luminescent (EL) materials for use in devices such as field-effect transistors and light emitting diodes (LEDs),[24] and to stabilise liquid-crystal (LC) phases.[1,25]

Both experimental and theoretical studies have generally been restricted to benzene, HFB and molecules with phenyl and pentafluorophenyl groups. Much less is known about the complexes of larger, fused-ring aromatic molecules and/or perfluoroarenes. A rare example is the 1 : 1 complex formed between triphenylene and perfluorotriphenylene, which was first observed by mass spectrometry,[26] and has recently had its crystal structure solved.[25a] To our knowledge, only four crystal structures of mismatched arene–perfluoroarene systems are known, namely that of the 1 : 1 complex of naphthalene and perfluorobiphenyl,[27] and those of ferrocene and decamethylferrocene with perfluorophenanthrene,[28a,b] and octafluoronaphthalene (OFN).[28c] Recently the crystal structure of the 1 : 1 complex of HFB with an octadehydroannulene derivative containing benzene rings, has been obtained.[29] The structure is unusual in that the HFB molecules are observed to lie over the central cyclo-bis-butadiyne part of the annulene, and not over the benzene rings. Clearly, a systematic structural study of such systems, where one can vary separately the contributing factors (van der Waals, electrostatic and steric), *i.e.* the misfit between molecular shapes, is crucial for developing a comprehensive theory of arene–perfluoroarene interactions.

The present paper, devoted to the complexes of octafluoronaphthalene (OFN), represents the first part of this study. When the work was commenced, no OFN-containing crystal structure was fully characterised,[30] except that of its 1 : 1 matched complex with naphthalene.[31] This complex has also been studied by solid-state laser Raman spectroscopic techniques.[32] Comparison of the resulting Raman spectra, due to intramolecular vibrations of the naphthalene molecules in the complex, to that of naphthalene in its pure state led to the conclusion that, although intermolecular interactions in the complex are primarily van der Waals in character, electrostatic multipole–multipole interactions do exist under ambient conditions, as well as at high pressure and low temperature.[32c] However, these additional interactions were not necessary to account for the Raman spectra of complexes of OFN with 1,4-dihalonaphthalenes.[33] Luminescence studies on these complexes, plus that of OFN with durene, supported these conclusions.[34] Anthracene, phenanthrene and pyrene have been reported to produce congruently melting 1 : 1 complexes with OFN.[35] A magnetically sensitive[36] exiplex has been shown to form between anthracene and OFN, and a ground-state stabilisation energy of 1.48 kcal mol^{-1} was estimated for the complex, by comparing its fluorescence with that of pure anthracene.[37] However, none of the structures of these complexes were known. We have recently reported the crystal structure of the 1 : 1 complex formed between OFN and diphenylacetylene[2] (see also ref. 28*c*). Herein, we report the crystal structures and polymorph transformations of OFN · anthracene (**1**), OFN · phenanthrene (**2**), OFN · pyrene (**3**) and OFN · triphenylene (**4**), as well as a reinvestigation of the structure of triphenylene.

Results and discussion

The crystal structures of the four complexes **1**–**4**, shown in Fig. 2 and 3, were studied at 120 K to reduce the systematic errors caused by thermal motion. Relevant crystallographic parameters are listed in Table 1. As the structure of triphenylene had been studied only at room temperature,[38] we re-determined it at 150 K (see ESI). In all of the co-crystals, we found alternating arene–perfluoroarene π-stacking with approximately parallel molecules, as in HFB · benzene and most related complexes. Complex **1** crystallises in the monoclinic space group $P2_1/n$ with both the anthracene and OFN molecules lying at inversion centres. Complex **2** at room temperature has an *I*-centred monoclinic lattice (β-**2** phase) but, on cooling below 250 K, undergoes a phase transition into the α-**2** phase with a primitive monoclinic lattice (space group $P2_1/n$) of approximately the same parameters. In α-**2** the OFN molecule also lies at a crystallographic inversion centre, while the phenanthrene molecule is statistically disordered between two partially overlapping positions, related *via* an inversion

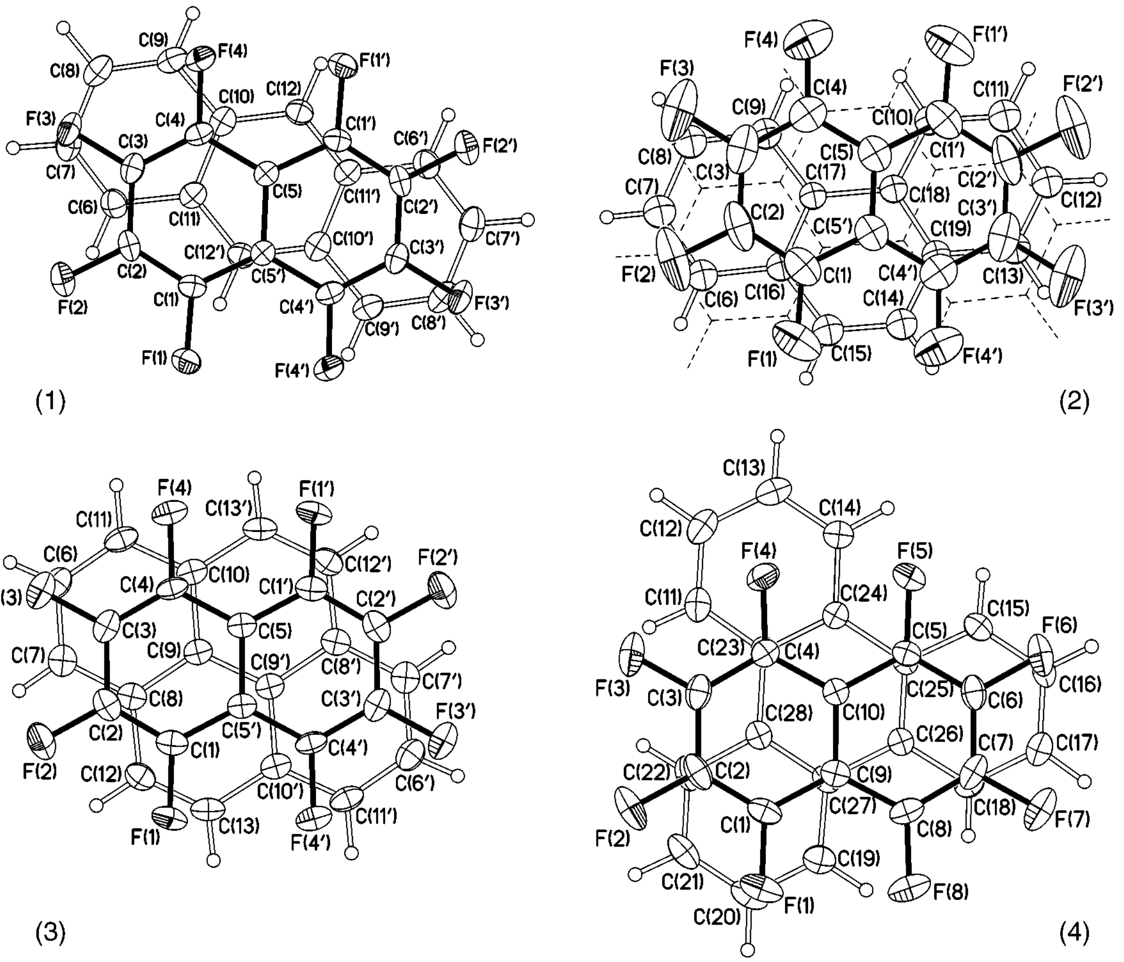

Fig. 2 ORTEP plots of the two components of complexes **1**–**4** viewed perpendicular to the OFN plane (thermal ellipsoids plotted at the 50% level).

centre. A similar mode of disorder has been found in the high-temperature phase of phenanthrene itself,[39] but there the occupancies of the two orientations are only approximately equal (55 : 45) and the structure is in fact non-centrosymmetric in the space group $P2_1$, although closely emulating $P2_1/c$.

The OFN molecule in α-**2** shows much larger atomic displacement parameters than in **1**, **3** and **4**, indicating static

Table 1 Crystal data and structure refinement parameters

Complex	**1**	α-**2**	β-**2**	**3**	**4**
Formula	$C_{10}F_8 \cdot C_{14}H_{10}$	$C_{10}F_8 \cdot C_{14}H_{10}$	$C_{10}F_8 \cdot C_{14}H_{10}$	$C_{10}F_8 \cdot C_{16}H_{10}$	$C_{10}F_8 \cdot C_{18}H_{12}$
Formula weight	450.32	450.32	450.32	474.34	500.38
T/K	120(2)	120(2)	296(2)	120(2)	120(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$I2/m$ (?)[a]	$P\bar{1}$	$P\bar{1}$
a/Å	6.810(1)	6.776(2)	6.923(2)	6.725(1)	6.732(1)
b/Å	18.326(1)	18.180(6)	17.925(3)	8.864(1)	9.365(2)
c/Å	7.390(1)	7.666(3)	8.080(3)	9.488(1)	16.550(4)
α/°	90	90	90	107.51(1)	86.44(1)
β/°	100.35(1)	102.45(1)	104.39(1)	105.23(1)	87.30(1)
γ/°	90	90	90	106.82(1)	77.30(1)
V/Å^3	907.3(2)	922.1(5)	971.3(4)	476.9(1)	1015.3(4)
Z	2	2	2	1	2
$\rho_{\text{calc.}}$/g cm^{-3}	1.648	1.622		1.652	1.637
μ/mm^{-1}	0.15	0.15		0.15	0.15
Transmission range	0.93–0.99	0.92–0.99		0.92–0.99	0.92–0.99
θ Range/°	2.2–27.5	2.2–25.0		2.4–25.0	1.2–27.5
Total reflections	6480	4586		2866	8936
Unique reflections	2083	1621		1661	4599
Parameters	165	138		174	374
R_{int}	0.061	0.051		0.047	0.042
Reflections [$I > 2\sigma(I)$]	1205	942		1106	2704
R [F, $I > 2\sigma(I)$]	0.040	0.049		0.044	0.042
wR (F^2, all data)	0.086	0.130		0.115	0.118
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$/e Å^{-3}	0.23, −0.25	0.18, −0.25		0.20, −0.20	0.26, −0.20

[a] Systematic absences agree with space groups $I2$, Im, $I2/m$; the structure was not solved.

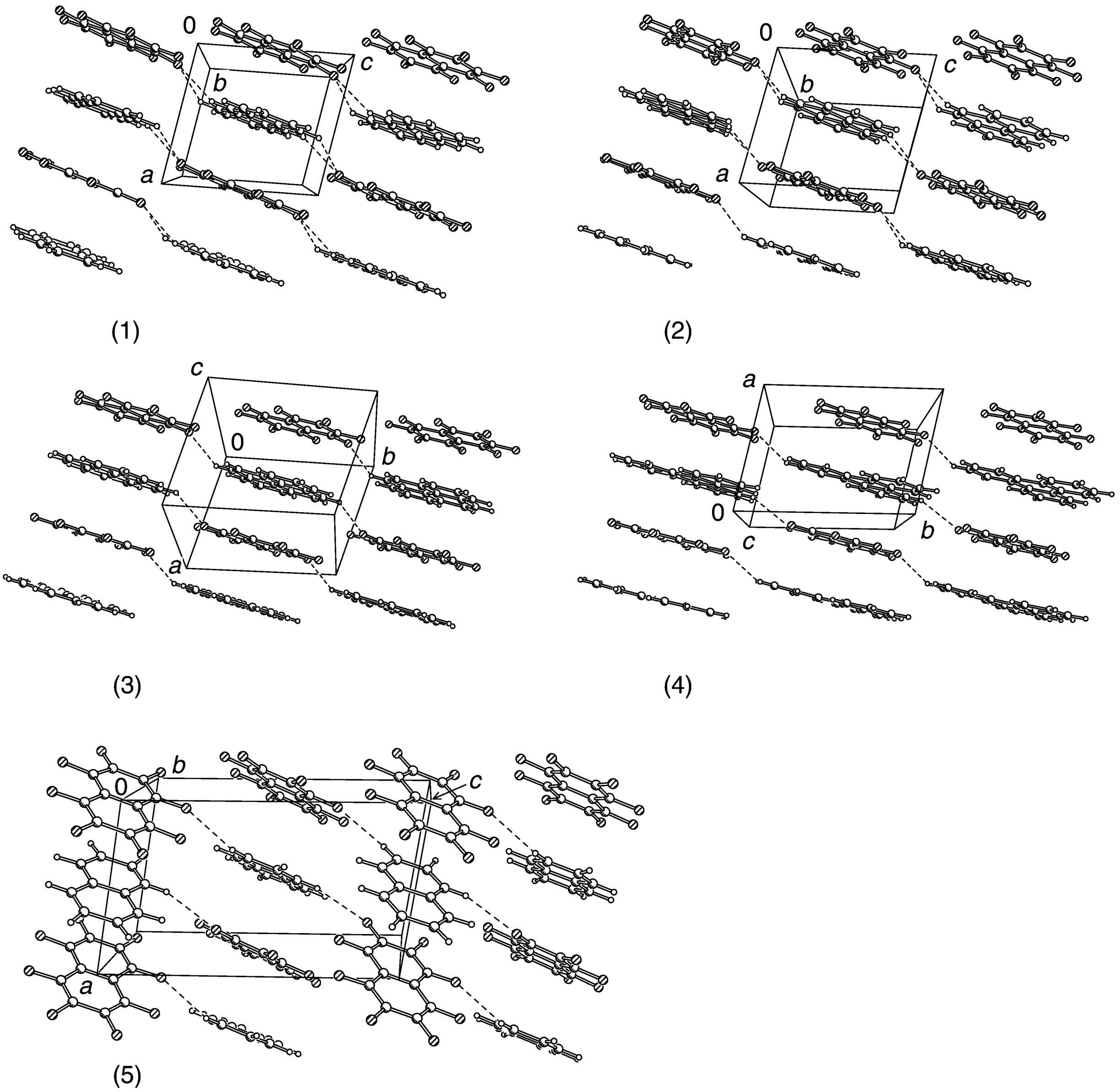

Fig. 3 Packing diagrams for complexes **1**–**4** and OFN · napthalene (**5**), showing the π-stacking of the components. The dashed lines show the intermolecular H···F distances that are below the sum of the van der Waals radii (2.67 Å).

librational disorder, which is probably correlated with the disorder of the phenanthrene molecule. Even more complicated disorder must exist in β-**2**, where the molecules have to lie on the crystallographic twofold axis, not coinciding with the molecular axis, however, we could not find any satisfactory model for this disorder. The structures of **1** and α-**2** are isomorphous, due to the similar size and steric demands of the anthracene and phenanthrene molecules. The 1 : 1 complexes of both arenes with 1,2,4,5-tetracyanobenzene are also isomorphous.[40] Complexes **3** and **4** crystallise in triclinic space group $P\bar{1}$. In **3**, as in **1**, both the OFN and the arene molecules are situated at inversion centres, while in **4** they have no crystallographic symmetry. There is no significant difference between the molecular geometry of OFN[41] and the arenes[42] in **1**–**4** and in crystals of the pure components at comparable temperatures (see ESI). This is consistent with the absence of significant charge transfer, in agreement with other properties of **1**–**4** and related complexes.

The packing mode in the complexes, however, is quite different from that of the individual components. The crystal packing of polyaromatic hydrocarbons can be classified into four types:[43] (i) herringbone, (ii) herringbone of sandwiches, (iii) flattened herringbone (γ-type) and (iv) pseudo-graphitic layered structure (β-type) (see Fig. 4). Anthracene, phenanthrene and triphenylene, as well as benzene and naphthalene, crystallise in the herringbone arrangement, where the structure-determining interactions are the T-contacts between non-parallel molecules, *i.e.* between positively charged H and negatively charged C atoms, or π-systems. HFB crystallises in the same arrangement; of course, electrostatic T-interactions in HFB are of the opposite sense, F(δ −)···C(δ +). Pyrene belongs to type (ii), where a herringbone motif is composed of face-to-face pairs of molecules, rather than separate molecules and T-interactions are complemented by stacking interactions. The same is true of type (iii), to which pure OFN belongs.

When the present work was commenced, the crystallography of OFN remained enigmatic. The disordered phase I, which exists at ambient conditions, converts into phase II at low temperature (<267 K) or high pressure (>800 bar). Although at least five crystallographic studies of phase I and three of phase II have been reported, neither structure was determined with an acceptable precision.[44] Recently, we investigated the polymorphism of OFN afresh using better-quality single crystals, obtained by sublimation rather than precipitation and solved the structures at 290 and 100 K.[41] The low-temperature phase, ordered and with a unit cell thrice that of

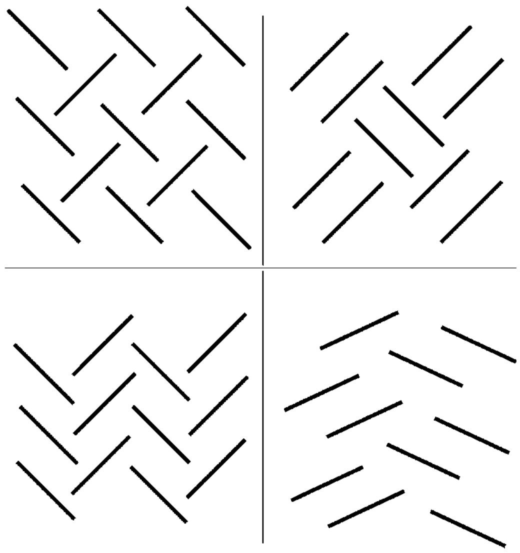

Fig. 4 Schematic illustration of the packing arrangements of polyaromatic molecules. Top left: (i) herringbone. Top right: (ii) herringbone sandwich. Bottom left: (iii) γ-type (flattened herringbone). Bottom right: (iv) β-type (pseudo graphitic).

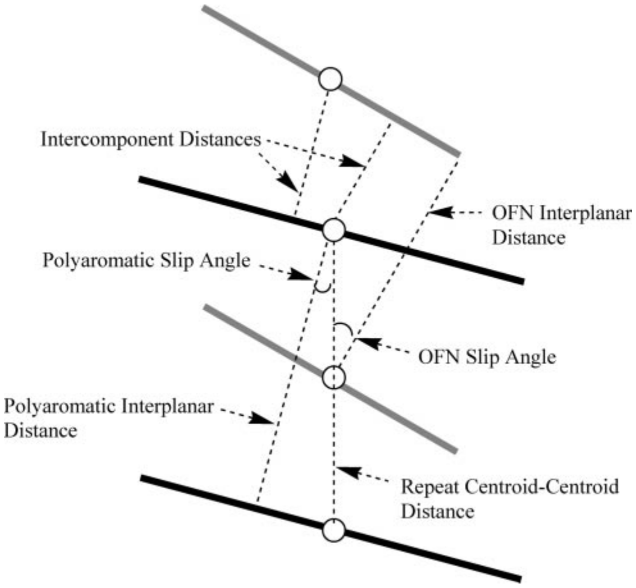

Fig. 5 Schematic showing the definition of the intermolecular parameters (see Table 2).

phase I, is different from the phase II reported earlier. We found that in both phases, OFN molecules are packed in a γ-motif, where T-contacts $F(\delta-)\cdots C(\delta+)$ between nearly perpendicular molecules (dihedral angles 81–82°) co-exist with slipped-stack interactions between parallel molecules. The stacks are obviously dominated by $F\cdots C$ attractions, resulting in some remarkably short interplanar spacings (3.17 Å) and $C\cdots C$ contacts (3.25 Å).

In contrast, structures **1**–**4** all comprise mixed stacks of alternating molecules of OFN and arene—a motif similar to that observed in HFB · arene complexes. In each structure, the planes of all the OFN molecules are strictly parallel to each other, and so are all the arene planes. The planes of the arene and OFN molecules are nearly, but not exactly, parallel, with dihedral angles of 0.4–2.7°. The geometrical parameters of the stacking arrangement are explained in Fig. 5 and summarised in Table 2. The distances between the centroids of any two nearest OFN molecules within a particular stack, and between the centroids of the polyaromatics in the stack is the same, namely the *a*-axis length, and is in the range 6.73–6.81 Å, decreasing slightly with the increasing size of the polyaromatic.

The interplanar separations between two non-parallel molecules can be defined as the distance between the mean plane of one molecule and the centroid of the other, or *vice versa.* Generally, the two distances do not coincide, therefore we quote the average of them. When both types of molecules lie at inversion centres, all interplanar separations in a stack are identical, as in **1** and **3**. The stacks of α-**2** or **4** have two alternating non-equivalent separations, which differ by 0.06 Å in **4** and practically coincide in α-**2**. In the four complexes, these distances of 3.34–3.40 Å are comparable to that in the OFN · naphthalene complex (3.42 Å)[31] and to the lower limit of the separations in HFB · arene complexes (3.39–3.56 Å), as well as to the normal 'thickness' of an aromatic molecule, 3.4 Å.

The stacks in **1**–**4** are not exactly columnar, *i.e.* the line through the centroids of identical molecules is not perpendicular to the molecular planes. The deviation can be described by the linear offset or by the slip angle (see Fig. 5). Both parameters decrease as the size of the polyaromatic molecule increases (see Table 2). Slip angles are in the range 1.2–6.4° for the OFN molecules and 1.5–9.1° for the polyaromatics.

Relative orientations (overlap modes) of the OFN and arene molecules (Fig. 2) vary widely, without any obvious general tendency. Thus, structure **3** displays a pseudo-graphitic overlap, whereas in **4**, a C–C bond of one molecule lies over the centre of an aromatic ring of another, **1** and α-**2** show even more irregular overlap.

Notwithstanding these differences, there is a remarkable similarity amongst the packings in **1**–**4**. The triclinic lattice of **4** is a distorted (by shear) analogue of **1** and α-**2**; this is obvious if a non-standard unit cell, related to the reduced one by the (−1,0,0; 0,0,1; 0,1,0) transformation, is chosen: $a = 6.732(1)$, $b = 16.550(4)$ $c = 9.365(2)$ Å, $\alpha = 86.44(1)$, $\beta = 102.70(1)$, $\gamma = 92.70(1)°$. The unit cell in **3** is approximately half the volume of those of **1**, α-**2** and **4**. However, the *I*-centred ($I\bar{1}$) lattice cell of **3**, related to the $P\bar{1}$ cell by the transformation (−1,0,0; −1,−1,−2; 0,−1,0), is also similar to the rest: $a = 6.725(1)$, $b = 16.767$, $c = 8.864(1)$ Å, $\alpha = 85.87(1)$,

Table 2 Intermolecular parameters

Complex	1	α-2	3	4
Interplanar angle/°	2.7	1.4	0.4	1.0
OFN slip angle/°	9.0	4.6	2.7	1.5
Polyaromatic slip angle/°	6.4	3.1	2.8	1.2
Repeat centroid–centroid distance/Å	6.81	6.78	6.73	6.73
OFN interplanar separation/Å	6.73	6.75	6.72	6.73
Polyaromatic interplanar separation/Å	6.77	6.77	6.72	6.73
OFN offset/Å	1.07	0.59	0.32	0.18
Polyaromatic offset/Å	0.76	0.38	0.33	0.14
Intercomponent centroid–centroid distance(s)/Å	3.41	3.39	3.36	3.45, 3.42
Mean inter-component interplanar separation(s)/Å	3.37	3.38	3.36	3.40, 3.34

Table 3 Melting points

Complex	Arene m.p./°C[a]	Complex m.p./°C	Analysis calc. (%)	Analysis found (%)
1	216	174–175	C 64.01, H 2.24	C 64.60, H 2.26
2	101	172–174	C 64.01, H 2.24	C 63.88, H 2.17
3	156	248–250	C 65.83, H 2.12	C 65.88, H 2.37
4	199	205–208	C 67.21, H 2.42	C 67.21, H 2.37

[a] For OFN, m.p. 87 °C.

$\beta = 106.82(1)$, $\gamma = 92.82(1)°$. In every case, the similarity of the lattices reflects the actual similarity of the packing.

In the triclinic structures **3** and **4**, the molecules of *each type* are strictly parallel and thus *all* the molecules are parallel within the interplanar angle of the stack, *i.e.* 0.4 (**3**) or 1.0° (**4**). In **1** and α-**2**, the molecules related by a 2_1 axis (or an n plane) need not be parallel, but the actual inclinations are small *viz.* 7.8 (OFN/OFN) and 7.0° (anthracene/anthracene) in **1**, and only 1.5 (OFN/OFN) and 1.7° (phenanthrene/phenanthrene) in α-**2**. Thus, all molecular planes in **1** and α-**2** are parallel within 10 and 3°, respectively. Note that OFN · naphthalene displays no such parallelism: although the OFN/naphthalene angle within the stack is only 3.7°, the OFN/OFN and naphthalene/naphthalene angles between the adjacent stacks are 34.5 and 31.5°, respectively (see structure **5** in Fig. 3).

Interstack H···F contacts slightly shorter than the sum of Bondi's van der Waals radii (2.67 Å),[45] down to 2.40–2.53 Å (for the C–H bonds normalised to 1.08 Å), are present in each structure (see ESI). Such distances are in fact common for intermolecular van der Waals interactions[46] (although they may be enhanced by electrostatic attraction between oppositely charged H and F atoms), the energy minimum of which has been calculated by *ab initio* methods[46b] to be −0.2 kcal mol^{-1}.

A rough estimate of the relative stability of the complexes can be derived from their melting points, compared with those of the individual components. As shown in Table 3, the m.p.s of complexes α-**2**–**4** are significantly higher than those of either component. The same is true for the OFN · naphthalene complex (m.p. 132, *cf.* 81 °C for naphthalene). Complex **1** melts at lower temperature than anthracene, but much higher than OFN. The m.p.s of **1** and **2** are similar, in accordance with close structural similarity of those complexes. The exceptional stability of **3** may be related to the absence of interstack F···F contacts shorter than 3.13 Å, while the shortest such contacts in **1** (2.82), α-**2** (2.87) and **4** (2.84 Å) are shorter than twice the van der Waals radius of fluorine (1.47 Å)[45] and, given the negative charges on these atoms, can be repulsive.

The stability of a complex may be related to the degree of geometrical matching between the component molecules. Kitaigorodsky[47] pointed out that for organic molecules, the close similarity of molecular shapes is not only necessary, but also a sufficient condition for obtaining mixed crystals, at least in the absence of hydrogen bonds and uncompensated molecular dipoles. The coefficient of geometrical similarity, known as the degree of isomorphism, is defined as

$$\varepsilon = 1 - g/G$$

where g and G are the mismatching and the overlapping volumes of the two molecules, if superimposed. Formation of a mixed crystal is likely when $\varepsilon > 0.85$ and impossible when $\varepsilon < 0.80$. For crystalline phases with short-range order, ε can be approximated as

$$\varepsilon \approx 1 - \frac{V_A - V_B}{V_A}$$

where V_A, V_B and V_{AB} are the crystal volumes per molecule for the pure components A and B and their co-crystal AB, assuming $V_A > V_B$. The change in packing density between individual components and the co-crystal,

$$\Delta \approx \frac{V_A + V_B}{V_{AB}} - 1$$

is an important indicator of the geometrical stability of a mixed crystal. Table 4 lists the molecular volumes (adjusted for thermal expansion), ε and Δ for complexes **1**–**4** and OFN · naphthalene. It is obvious that the stability of the OFN · arene complexes has no clear correlation with the relative sizes of the component molecules and must be attributed to the above-mentioned non-geometrical factors: the edge-to-edge H···F electrostatic interactions and face-to-face multipole–multipole electrostatic interactions. Indeed, ε of complex **4** lies well outside the geometrical range for co-crystallisation, as predicted by Kitaigorodsky.[47] It is noteworthy that co-crystallisation of OFN with naphthalene increases the packing density, while the opposite is true for complexes **1**–**4**, although ε of **1**–**3** is actually higher than that of OFN · naphthalene. Thus, matching bond skeletons, and hence matching but inverted charge distributions, are a better criterion of molecular similarity than formal comparison of molecular volumes.

Table 4 Parameters relating to the degree of isomorphism (see text)

Complex[a]	V_b/Å^3	ε	V_{AB}/Å^3	Δ
1	229[b]	0.94	453.7	−0.022
α-**2**	236[c]	0.91	461.1	−0.021
3	256[b]	0.84	476.9	−0.014
4	286[b]	0.75	507.7	−0.016
OFN · Naphthalene[d]	180.5	0.80	397.4[d]	0.026

[a] For OFN, $V = 215$ Å^3 at 120 K, 227 Å^3 at room temperature. [b] Adjusted for 120 K. [c] No experimental data is available below 248 K; extrapolated to 120 K proportionally to anthracene. [d] Room temperature.

Conclusions

It has been shown that octafluoronaphthalene forms π-stacked complexes with a number of fused-ring polyaromatic molecules, which have substantially different molecular geometries from each other and from OFN. In all cases, the incorporation of OFN significantly changes the packing of the polyaromatic molecules in the solid-state complex. This demonstrates the general applicability of the arene–perfluoroarene intermolecular interaction as a supramolecular synthon that appears to be relatively insensitive to the morphology of the particular aromatic molecules involved. This is a factor which could make it of considerable utility in crystal engineering. It is clear that further experimental and theoretical studies on these complexes, and related ones, are required in order to understand fully these interactions.

Experimental

The polyaromatic hydrocarbons (Aldrich) and octafluoronaphthalene (Bristol Organics) were tested for purity by

GC-MS and used without further purification. The OFN contained traces (<0.5%) of chloroheptafluoronaphthalene as detected by GC-MS. GC-MS was carried out using a Hewlett-Packard HP-5890 Series II gas chromatograph equipped with an HP-5971A mass selective detector. A 12 m fused silica (methylsilicone) capillary column was used, with UHP grade helium as the carrier gas. Elemental analyses were carried out in the Department of Chemistry at Durham University using an Exeter Analytical Inc. CE-440 elemental analyzer. Melting points were obtained using a Laboratory Devices Mel-Temp II, equipped with a Fluke 51 digital thermometer, and are uncorrected.

Co-crystals of OFN with anthracene **1**, phenanthrene **2**, pyrene **3** and triphenylene **4**, were obtained by the slow evaporation (over 2–3 days) of a solution containing 0.1 mmol of each component in 1 ml of dichloromethane. ***Caution***! Many polyaromatics are carcinogenic and should be handled accordingly. Co-crystals of **1** were obtained as large tetragonal blocks, whereas all the others formed as colourless, fine needles. The presence of both of the components in a 1 : 1 molar ratio in each of the co-crystals was verified by GC-MS and elemental analysis (see Table 3). The $C_{10}F_7Cl$ impurity in the OFN did not appear to be present in any of the co-crystals.

All X-ray diffraction experiments were carried out on a Siemens SMART 3-circle diffractometer, equipped with a 1K CCD area detector, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). The temperature of the crystal was controlled by an Oxford Cryosystems open-flow N_2 gas cryostat;[48] the temperature was calibrated on the phase transition of K_2HPO_4 at 122.5 K,[49] the possible error not exceeding ± 1 K. For each sample, a hemisphere of reciprocal space was covered by a combination of four (three for α-**2**) sets of ω scans, each set at different φ and/or 2θ angles. The structures were solved by direct methods, and refined by full-matrix least squares on F^2 of all data, using SHELXTL software.[50] All C and F atoms were refined in anisotropic approximation, H atoms in isotropic approximation, except for the disordered phenanthrene molecule in α-**2** (C atoms isotropic, H atoms 'riding'). Thermal motion analysis and bond length correction were made using PLATON-99 programs.[51] A full set of data was also collected (at room temperature) for β-**2**, the systematic absences agreeing with space groups *I*2, *Im* or *I*2/*m*, but we could not solve the structure, either by direct methods or by inference from the solved structure of the low-temperature polymorph α-**2**. The electron density maps revealed strong disorder of both components, for which no satisfactory model was found.

CCDC reference numbers 157246–157249. See http://www.rsc.org/suppdata/nj/b1/b105502j/ for crystallographic data in CIF or other electronic format.

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