DOI: 10.1002/chem.200700267

# Synthesis, X-ray Diffraction and Computational Study of the Crystal Packing of Polycyclic Hydrocarbons Featuring Aromatic and Perfluoroaromatic Rings Condensed in the Same Molecule: 1,2,3,4-Tetrafluoronaphthalene, -anthracene and -phenanthrene

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*Dedicated to Professor Hans-Beat Bürgi on the occasion of his 65th birthday*

**Abstract:** We have synthesised some planar polycyclic compounds, in which unsubstituted aromatic rings are condensed with perfluorinated aromatic rings, and have carried out a combined X-ray diffraction and computational study to analyse their self-recognition behaviour in crystalline phases. We compare our results with the parent hydrocarbons and with other compounds that have a variable degree of fluorination. Whereas the molecular planes in crystals of hydrocarbons with mono- or difluorinated aromatic rings or of perfluorinated compounds arrange themselves in V-shaped configurations, our present results show that perfluorinated rings tend to stack over unsubstituted rings even when these two moieties coexist in a condensed system, producing crystalline materials with parallel molecular layers with the arene–perfluoroarene recognition pattern. Our analysis shows that the packing energy of all these crystals is dispersion-dominated and that coulombic terms are selective rather than quantitatively predominant in crystals with arene–perfluoroarene interactions. No compelling proof of a special role of C−H⋯F interactions has been found.

**Keywords:** arenes • crystal engineering • fluoroaromatic synthesis • intermolecular interactions • PIXEL calculations

## Introduction

The chemistry of intermolecular interactions has nowadays at its disposal a series of empirical correlations between molecular constitution and recognition patterns. Examples range from obvious cases, like the O−H⋯O hydrogen bond, to cases in which the consistency and robustness of the correlation has been questioned, like the weak C−H⋯X hydrogen bond or the halogen–halogen attraction.[1] A widely recognised and undisputed correlation is the arene–perfluoroarene interaction arising from the tendency of perfluorinated and plain hydrogenated (that is, otherwise unfunctionalised) aromatic rings to form parallel-stacked recognition patterns. It has been demonstrated that a parallel-stacked structure of alternating Ar(H) and Ar(F) molecules is invariably adopted in co-crystals made not only of arenes and perfluoroarenes, but also of any kind of planar molecule containing aromatic and perfluoroaromatic residues.[2]

The interaction between plain unsubstituted and fully fluorinated aromatic rings in different molecules is well

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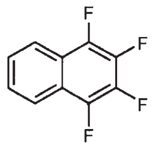
documented and we have previously investigated some of its structural and energetic properties.[3] Much less information is available on molecules in which perfluorinated and plain aromatic rings coexist in a planar, rigid, condensed aromatic system, which may be called a hydrofluoroaromatic (HFA) system. These HFA molecules should be strong auto-assemblers without the need for conformational adaptation or the formation of heteromolecular complexes and, as such, they could constitute a robust synthon for the design of one-component organic materials. In particular, it is not known if the coulombic driving forces in the arene–fluoroarene interaction, sometimes approximately described as stabilisation/attraction between reversed quadrupoles, may survive in the electron charge distribution of such condensed HFA systems. The most obvious examples of HFAs are 1,2,3,4-tetrafluoronaphthalene (**1**), 1,2,3,4-tetrafluoroanthracene (**2**) and 1,2,3,4-tetrafluorophenanthrene (**3**). Accordingly, we have synthesised these three molecules, carried out X-ray structure determinations, analysed the molecular recognition and molecular packing in their crystals and compared the results with crystals of selected partially fluorinated or perfluorinated compounds.



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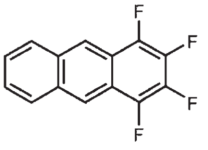

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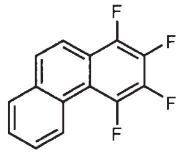


**3**

## Computational Methods

The Cambridge Structural Database was searched for crystal structures of pure compounds containing only carbon and fluorine atoms with three-dimensional coordinates fully determined and no disorder. This search yielded only 35 independent hits, some of which corresponded to small molecules crystallised in peculiar conditions of temperature and crystal isolation (e.g., at very low temperatures, in situ crystallisation from liquid). This very limited number further testifies to the difficulties associated with the crystallisation of perfluorinated compounds. Another search was conducted for crystals of compounds containing only carbon, hydrogen and fluorine atoms with the same limitations as described above, yielding 129 independent hits. These two databases were used for systematic studies of crystal packing by using the OPiX[4] computer program package. In addition, temperature-dependent crystal structure determinations for naphthalene (NAPHTA[5,6]) and anthracene (ANTCEN[7]), and the only structure for phenanthrene (PHENAN08[8]), were retrieved for comparison with their partially fluorinated counterparts whose crystal structures were determined in this work. A synopsis of the crystal properties is presented in Table 1.

Table 1. Summary of the crystal properties of unsubstituted and fluorinated condensed aromatics.

| Compound | CSD refcode | Space group | *Z* | Comments |
|---|---|---|---|---|
| naphthalene[a] | NAPHTA | $P2_1/a$ | 2 | variable-*T* study |
| anthracene[b] | ANTCEN | $P2_1/a$ | 2 | variable-*T* study |
| phenanthrene[c] | PHENAN08 | $P2_1$ | 2 | – |
| 2-fluoronaphthalene[d] | FNAPTH | $P2_1/a$ | 2 | *F* disorder over 4 β positions |
| 1,5-difluoronaphthalene[e] | DFNAPH | $P2_1/c$ | 2 | – |
| 1,8-difluoronaphthalene[e] | FLNAPH | $P2_1/c$ | 4 | – |
| tetrafluoronaphthalene **1** | present study | $P2_1/n$ | 4 | variable-*T* study |
| perfluoronaphthalene[f] | OFNAPH05 | $P2_1/c$ | 6 | 1.5 molecules in asymmetric unit |
| perfluoronaphthalene[g] | OFNAPH01 and present study | $P2_1/c$ | 2 | total disorder |
| tetrafluoroanthracene **2** | present study | $P\bar{1}$ | 2 | – |
| tetrafluorophenanthrene **3** | present study | $C2/c$ | 4 | total disorder |

[a] Ref. [5,6]. [b] Ref. [7]. [c] Ref. [8]. [d] Ref. [13]. [e] Ref. [14]. [f] Ref. [16]. [g] Ref. [15].

Distributions of atom–atom distances in crystals were studied by using density distribution functions (DDF; for a description, see ref. [1]). All atom–atom distances between atomic species *i* and *j* in a given database of crystal structures were calculated up to a certain limit $R_{\max}$. $N_k(R)^{ij}$ is the number of atom–atom distances within the *k*-th distance bin defined by a separation $R_k$, a radial increment d$R$ and a volume d$V_k$. Let $(R^\circ)^{ij}$ be the separation below which no contacts are observed (the exclusion radius). The DDF normalisation factor, $F_N$, can then be estimated as the total number of contacts divided by the volume of the explored space, that is, the spherical shell between the exclusion radius and the maximum distance considered (usually, 8 Å) [Eqs. (1) and (2)].

$$F_N^{ij} = \frac{\sum_k N_k(R)^{ij}}{4\pi/3\{(R_{\max})^3 - [(R^\circ)^{ij}]^3\}} \tag{1}$$

$$\mathrm{DDF} = g_k(R)^{ij} = \frac{(1/F_N^{ij})N_k(R)^{ij}}{\mathrm{d}V_k} \tag{2}$$

$F_N$ represents the condition of uniform distribution of the observed contacts over the available contact space, while $g_k$ is larger than unity if many contacts populate the *k*-th distance bin. A DDF is very similar to a true radial distribution function (RDF), but the meaning is different: a RDF refers to a distribution of many identical molecules within one molecular ensemble, like a portion of liquid, whereas a DDF refers to sampling different molecules over many different systems, the crystal structures. The DDF gives a representation of the frequency with which nuclei of two atomic species are brought into close contact within the considered database of crystal structures.

The lattice energies of all the crystals considered herein were calculated by standard atom–atom potentials using a parameter set that has been shown[3] to reproduce rather accurately the few available enthalpies of sublimation of fluorinated compounds. Although these parameters do not require the addition of coulombic terms to reproduce lattice energies, atom–atom coulombic energies were also calculated by using point-charge parameters from a previously described procedure;[9] although changing the total lattice energies by only small amounts, these supplementary terms increase the structural selectivity of the potential functions. The force-field parameters are collected in Table 2. For some selected samples, the cohesion energies were also calculated by using the PIXEL method,[10] which allows a rigorous calculation of coulombic/polarisation energies and a parametric estimation of the dispersion contribution. The dispersion energy contribution from two electron charge pixels *i* and *j* separated by $R_{ij}$ in different molecules is calculated by using Equation (3):

$$E(\mathrm{disp},i,j) = \frac{(-{}^3\!/_4)f(R)(I_iI_j)^{1/2}\alpha_i\alpha_j}{(4\pi\varepsilon^\circ)^2(R_{ij})^6} \tag{3}$$

in which $f(R)$ is a damping function, $f(R) = \exp[-(D/R_{ij}-1)^2]$, for $R_{ij} < \mathrm{D}$,

Table 2. Force-field parameters[3,9] for the atom–atom energies.[a]

| Atoms | | $A$ | $B$ | $C$ | $R°$ | $\varepsilon$ |
|---|---|---|---|---|---|---|
| H | F | 64257.8 | 4.110 | 248.36 | 3.29 | −0.110 |
| F | F | 170916.4 | 4.220 | 564.84 | 3.20 | −0.293 |
| H | H | 24158.4 | 4.010 | 109.20 | 3.36 | −0.042 |
| C | C | 226145.2 | 3.470 | 2418.35 | 3.89 | −0.387 |
| H | C | 120792.1 | 4.100 | 472.79 | 3.29 | −0.205 |
| C | F | 196600.9 | 3.840 | 1168.75 | 3.50 | −0.350 |

[a] Atom–atom energies given in the form $E = A\exp(-BR) - CR^{-6}$, with distances $R$ in Å and energies in kJ mol$^{-1}$. $R°$ is the minimum energy distance and $\varepsilon$ is the well depth in kJ mol$^{-1}$. Supplementary charge assignments for coulombic terms (electrons): for aromatic C–H groups: H +0.10, C −0.10; for C–F groups: C +0.20, F −0.20; for remaining C atoms: 0.0.

where $D$ is an adjustable empirical parameter, $I_i$ is the ionisation potential of pixel $i$ and is also damped according to $I_i = I°\exp(-\beta R_i)$, where $I°$ is the atomic ionisation potential of the atom the pixel belongs to and $\beta$ is an adjustable parameter (between 1.0 and 0.4), and $\alpha_i$ is the polarisability at pixel $i$. In this respect, perfluoroaromatic compounds pose a parameterisation problem because the dispersion energies are systematically underestimated, as also systematically happens for crystals of aromatic molecules with electron-withdrawing substituents. One possible explanation for this is that in the latter case the carbon atoms of the rings are in fact electron-deficient to a point at which their ionisation potential becomes higher than it is in the neutral atom. Dispersion energies calculated using Equation (3) are consequently too small. The simple remedy, which has been applied earlier in calculations on crystals of nitro derivatives[11] and is applied here to perfluoro compounds, is to decrease the damping parameter $D$. In this work it was changed from the usual value of 3.0 to 2.4 Å to provide a better match between the calculated and experimental lattice energies of perfluoronaphthalene. Electron densities for the PIXEL calculations were calculated by using the Gaussian 03 software package at the MP2/6-31G** level.[12]

Table 3. Crystal data for compounds studied in this work.

| $T$ [K] | $\rho_x$ [g cm$^{-3}$] | $V_{\text{cell}}$ per molecule [Å$^3$] | $a$ [Å] | $b$ [Å] | $c$ [Å] | $\alpha$ [°] | $\beta$ [°] | $\gamma$ [°] |
|---|---|---|---|---|---|---|---|---|
| tetrafluoronaphthalene **1**: $P2_1/n$, $Z = 4$ | | | | | | | | |
| 90 | 1.745 | 190.4 | 7.416 | 8.050 | 12.767 | – | 92.13 | – |
| 120 | 1.736 | 191.4 | 7.437 | 8.057 | 12.788 | – | 92.05 | – |
| 160 | 1.724 | 192.7 | 7.464 | 8.063 | 12.817 | – | 91.91 | – |
| 200 | 1.709 | 194.5 | 7.499 | 8.074 | 12.854 | – | 91.77 | – |
| 240 | 1.693 | 196.3 | 7.535 | 8.084 | 12.896 | – | 91.58 | – |
| 295 | 1.665 | 199.6 | 7.600 | 8.108 | 12.959 | – | 91.33 | – |
| tetrafluoroanthracene **2**: $P\bar{1}$, $Z = 2$ | | | | | | | | |
| 295 | 1.584 | 262.3 | 7.413 | 7.833 | 10.397 | 101.3 | 98.81 | 113.53 |
| 90 | 1.647 | 252.2 | 7.315 | 7.806 | 10.421 | 102.0 | 97.23 | 116.5 |
| tetrafluorophenanthrene **3**: $C2/c$, $Z = 4$, disorder | | | | | | | | |
| 123 | 1.592 | 261.0 | 7.852 | 20.208 | 6.801 | – | 104.7 | – |
| octafluoronaphthalene, $P2_1/c$, $Z = 2$, disorder | | | | | | | | |
| | 2.002 | 225.7 | 7.593 | 5.004 | 11.965 | – | 96.8 | – |
| | 1.997 | 226.2 | 7.613[a] | 5.002 | 11.968 | – | 96.9 | – |

[a] See ref. [15].

The computational generation of crystal structures was used to help in the interpretation of disordered crystal structures. For octafluoronaphthalene, the *Prom* module of the OPiX package[4] was used and only space group $P2_1/c$ was considered with a molecular model built from naphthalene by replacing each hydrogen atom with a fluorine atom. For tetrafluorophenanthrene, space groups $C2$ and $Cc$ were explored by using the *Pro-many* version of the *Prom* module, which allows much more freedom than the standard automatised version, but requires more expert control. The planar molecular model was built from phenanthrene by replacing four hydrogen atoms with fluorine atoms on the bisector of the C-C-C angle. In all cases the C–F distances were taken as 1.34 Å. All lattice energies at this stage were calculated by using the empirical atom–atom scheme of Table 2.

## Results and Discussion

**Crystallography**: All the molecules in our determinations (Table 3) are planar with bond distances in the usual ranges and an average C–F separation of 1.34 Å. Figure 1 shows the variation of cell volumes per molecule as a function of temperature. Figure 2 shows the isotropic expansion coefficients, $\beta = 1V(\mathrm{d}V/\mathrm{d}T)$, as determined by finite differences over the X-ray cell volumes $V$. All expansion coefficients are in the usual range for organic crystals and show the expected increase with increasing temperature. The expansion coefficients decrease in the order naphthalene > tetrafluoronaphthalene > anthracene, although the limited data available do not allow a safe comparison with the coefficient for the disordered crystal of 2-fluoronaphthalene. The reasons why the tetrafluorinated material is more cohesive than its hydrocarbon counterpart are open to speculation and could simply be related to a decrease in librational amplitudes due to increasing molecular mass and surface. In fact, anthra-

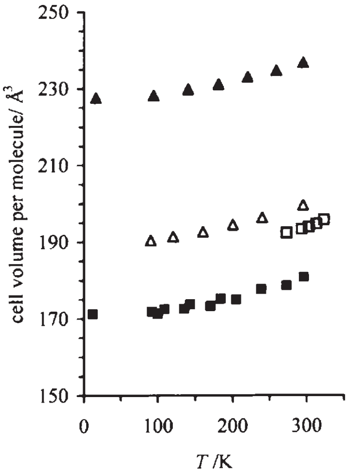


Figure 1. The variation in cell volume [Å$^3$] with temperature for the crystals of some condensed aromatic molecules: naphthalene[5] (■), anthracene[7] (▲), 2-fluoronaphthalene[13] (□) and tetrafluoronaphthalene (△).

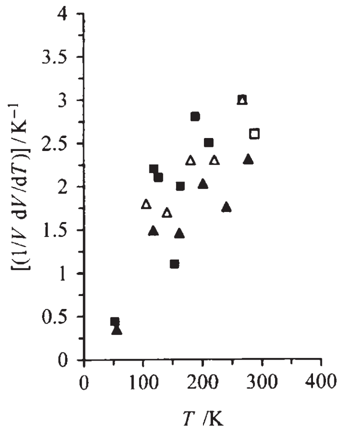


Figure 2. Isotropic expansion coefficients [$K^{-1}$]: naphthalene[5] (■), anthracene[7] (▲), 2-fluoronaphthalene[13] (□) and tetrafluoronaphthalene (△).

cene has a smaller expansion coefficient than naphthalene. Another factor that influences the expansion coefficient of a material is of course the cohesive potential energy, but correlations between crystal structure, crystal energy and expansion coefficients are uncertain for very weakly bound materials like our crystals.

In the crystal structures of mono- and difluorinated naphthalenes (2-fluoronaphthalene,[13] 1,5- and 1,8-difluoronaphthalene[14]) the molecular planes are not parallel, but assume the so-called V-shaped arrangement, as also found in the crystals of naphthalene and anthracene (Figure 3a,c). For octafluoronaphthalene, the literature reports one determination at room temperature (CSD refcode OFNAPH01[15]), revealing a single "average molecule" matching what must have been a diffuse electron density (*R* factor 0.35), and a determination at 203 K (CSD refcode OFNAPH05[16]), interpreted by a model with 1.5 molecules in the asymmetric unit (*R* factor 0.048). Detailed analysis shows that the exact screw or translation operations in OFNAPH01 deform slightly into almost screw or translation interactions between molecules in the asymmetric unit in OFNAPH05. Thus, OFNAPH05 is a refined modulation of the approximate crystal structure OFNAPH01 with the formal loss of two symmetry elements, but the crystal packing is essentially identical. The results of our present analysis are similar to those of OFNAPH01. In any case, nearest-neighbour molecules are in a V-shaped arrangement, as in the hydrocarbon or in the mono- and difluoronaphthalenes.

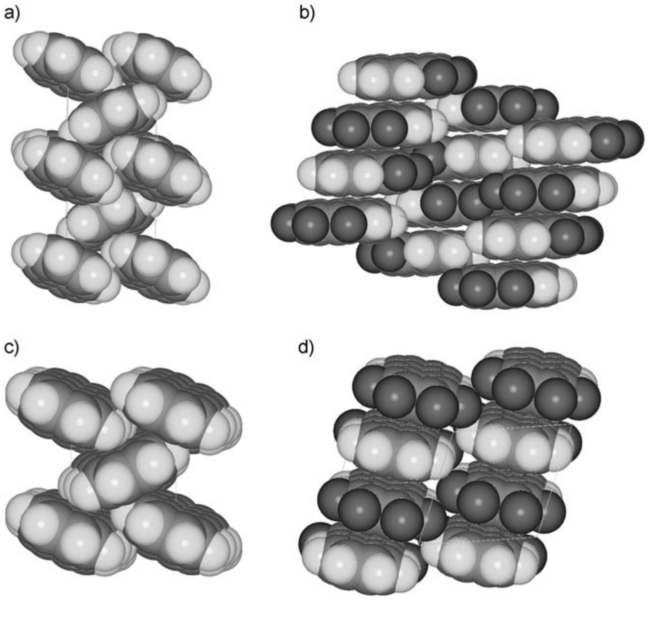


Figure 3. Crystal packing in a) naphthalene, b) tetrafluoronaphthalene, c) anthracene and d) tetrafluoroanthracene. The crystals of 2-fluoronaphthalene, and 1,5- and 1,8-difluoronaphthalene show V-shaped arrangements similar to the pattern on the left. Darker spheres represent fluorine atoms.

As soon as one ring is fully fluorinated, however, the packing switches to planar parallel layers, taking advantage of the extra stabilisation that results from overlapping arene and fluoroarene rings (Figure 3b,d). This finding is a further confirmation of the selective coulombic stabilisation due to arene–perfluoroarene stacking and confirms the hypothesis that arene and perfluoroarene moieties tend to stack even if they belong to a condensed polycyclic system within the same molecule.

The case of tetrafluorophenanthrene is more complex. The X-ray experiment reveals a disordered crystal structure. Therefore the driving influence of arene–tetrafluoroarene stacking is not sufficient to cause the material to assume long-range order and comparison with tetrafluoroanthracene indicates that this uncertainty must somehow be due to the bent molecular shape. These difficulties in aggregation are presumably of kinetic origin and must be encountered at the nucleation and growth stages because computer simulation (see below) shows that stable, ordered crystals of both octafluoronaphthalene and tetrafluorophenanthrene are possible.

**Crystal structure generation**: The crystal structure generator-predictors readily supply a large number of ordered, perfectly stable ("acceptable", as defined on p. 225 of ref.[1], in terms of being within average limits of crystal density and lattice energy) crystal structures for octafluoronaphthalene in the $P2_1/c$ space group and for tetrafluorophenanthrene in the $P2_1/c$, $C2$ and $Cc$ space groups (Table 4). No doubt, many other structures could have been found in other closely packed space groups, as is invariably the case (see, for example, p. 392 of ref. [1]). For octafluoronaphthalene, one of the most stable crystal structures found by the *Prom* module coincides with the structure obtained when the experimental data of OFNAPH01 were subjected to lattice energy optimisation.

For tetrafluorophenanthrene, the most stable structure generated in space group *Cc* appears within a few seconds of computing time and its cell parameters are almost identical to the experimental ones found in space group $C2/c$. The

Table 4. Results of the crystal structure generation experiments for tetrafluorophenanthrene **3**.

| Crystal | Space group | *Z* | *E*(6-exp)[a] | *E*(pc)[b] | *a* [Å] | *b* [Å] | *c* [Å] | *β* [°] |
|---|---|---|---|---|---|---|---|---|
| experimental | *C*2/*c* | 4 (disorder) | – | – | 7.852 | 20.208 | 6.801 | 104.7 |
| simulation | *Cc* | 4 | −103 | −12 | 7.89 | 20.11 | 7.21 | 61.5 |
|  | *C*2 | 4 | −96 | −4 | 8.11 | 19.98 | 6.37 | 90.0 |
|  | $P2_1/c$ | 4 | −104 | −11 | 11.02 | 5.97 | 17.07 | 60.9 |

[a] 6-exp potential energy, parameters are given in Table 1. [b] Coulombic energy estimated using point charges (pc's) on atomic nuclei (see Table 2).

molecular planes are perpendicular to the *c* axis, as also results from the approximate treatment of experimental diffraction data. When a refinement of the crystal structure was attempted using the computational *Cc* model as a starting point, no satisfactory results were obtained but a difference Fourier map showed a distribution of peaks more or less coinciding with missing fluorine atoms where hydrogen atoms had been postulated and missing carbon atoms in correspondence with a two-fold axis rotation of the molecule along its longest axis. Joint consideration of the limited information from X-ray diffraction and of the very clear-cut result from the computer simulation strongly suggests that the real crystal structure consists of a superimposition of rotated molecules or of layers with alternating orientation, resulting in an object of overall *mm*2 symmetry and justifying the space group change from *Cc* to *C*2/*c*. Incidentally, this result shows that crystal structure generators can very often be better used for help when partial or incomplete diffraction data are available rather than as problematic polymorph "predictors".

Figure 4 allows the ordered *Cc* crystal structure of tetrafluorophenanthrene to be compared with that of phenanthrene. In this case too the arene–perfluoroarene interaction between separate moieties within the same molecule causes a structural change from V-shaped neighbouring dimers to planar stacking.

**Crystal packing analysis**: The PIXEL calculations offer more insight into the nature of the crystal packing of organic compounds. Figure 5 (left) shows the behaviour of the components of the crystal lattice energy as a function of temperature. At lower temperatures, the cohesive terms, coulombic, polarisation and dispersion, become more stabilising and the repulsive term becomes more destabilising, as is expected on the basis of increased overlap between molecular electron clouds. The PIXEL calculation gives a very realistic picture of this temperature dependence. The total energy shows the expected stabilisation with decreasing temperature (see Figure 5, right).

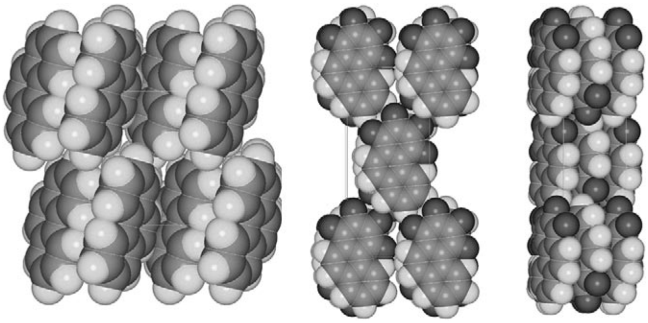


Figure 4. Crystal structure of phenanthrene showing the V-shaped molecular association mode (left). The *ab* projection (centre) and the *bc* projection (right) of the ordered model for the crystal structure of tetrafluorophenanthrene showing the stacking of flat layers perpendicular to the *c* axis. The disorder is such that the molecular object in the *ab* plane has an effective *mm*2 symmetry.

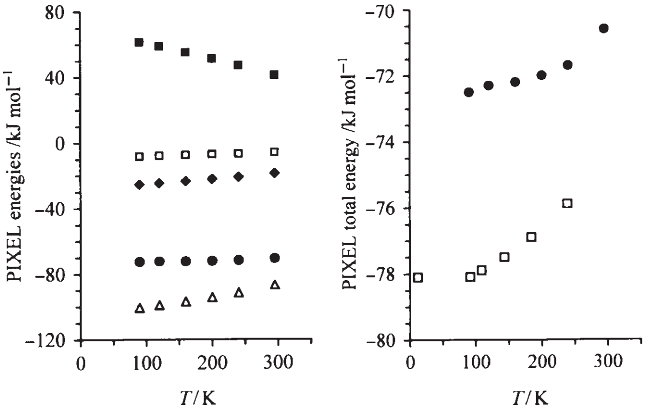


Figure 5. Left: Tetrafluoronaphthalene: lattice energy components determined by the PIXEL method (top to bottom: repulsion, polarisation, coulombic, total, dispersion) as a function of the temperature of the X-ray crystal structure determination. Right: Total PIXEL lattice energies for tetrafluoronaphthalene (●) and naphthalene (□).

The general conclusion that can be drawn from a comparative analysis of our structures is that fluorination of one ring in a condensed aromatic molecule is sufficient to generate the arene–fluoroarene stacking motif in the crystal. The energetic foundations of this structural effect can also be analysed by using PIXEL calculations. As the PIXEL lattice energies are sensitive to the temperature at which the crystal structure determination was carried out (see Figure 5), comparisons between crystal structures determined at different temperatures may be misleading. To obviate this difficulty, a set of crystal structures (naphthalene, NAPHTA06; tetrafluoronaphthalene; anthracene, ANTCEN09; tetrafluoroanthracene; phenanthrene, PHENAN08) were energy-optimised by using the *Minop* module of the OPiX package.[4] The crystal structure of tetrafluorophenanthrene (in space group *Cc*) obtained from the crystal structure generation procedure described above is already energy-optimised. As optimisation of the potential energy alone removes the effect of thermal vibration, the lattice energy components of these optimised structures are directly comparable as they are all referred to formally zero-temperature (i.e., vibrationless) structures.

The energy contributions of this group of structures are compared in Table 5. All the crystals in this series are bound mainly by dispersive forces with nearly constant contributions in the range of 100–115 kJ mol$^{-1}$ for the naphthalenes and 130–150 kJ mol$^{-1}$ for the anthracenes and phenanthrenes. The lattice energies of the anthracenes are slightly more stabilising than those of the phenanthrenes, as expected in view of the more favourable molecular shape of the former compounds. Coulombic/polarisation energies contribute no more than 20 % of the total cohesive power and are as large in the hydrocarbon crystals as in the fluorinated crystals or even larger in the former. Thus, the success of the arene–perfluoroarene stacking motif is not due to a larger coulombic stabilisation of the whole crystal, but to a preferential, local orientation effect between first-neighbour molecules. Previous analyses[3,10] have shown that the physical basis of this effect is a selective coulombic stabilisation from the inverted polarities of C–H and C–F bonds.

Part of this success might also be due to favourable lateral interactions between hydrogen- and fluorine-rich rim regions in coplanar molecules within layers. In a typical calculation on tetrafluoronaphthalene, however, the arene—fluoroarene stacked pairs interact with a PIXEL stabilising energy of about −35 kJ mol$^{-1}$, whereas even for neighbouring coplanar molecular pairs showing short H···F contacts (2.40 Å) the stabilising energies are no more than −4 kJ mol$^{-1}$. This result tends to classify lateral H···F interactions as just permissive or non-detrimental, rather than as structure-defining.

The existence or necessity of C–H···F special interactions, sometimes labelled "hydrogen bonds", has also been examined by a statistical observation of the density distribution functions (DDF) of atom–atom distances in the databases of crystal structures collected as described in the Computational Methods section. Figure 6 shows the DDFs for the sample of 35 perfluoro compounds and for the sample of 129 CHF compounds. A prominent peak appears in the F···F curves, but one does not see an opportunity for defining a F···F intermolecular bond, but rather attributes the peak to unavoidable contacts between peripheral atoms of planar rings. Defining a C–H···F bond apparently requires the assumption that the concomitant H···F peak (Figure 6, right) instead has an electronic origin and necessity. Such an assumption seems unjustified in the absence of separate evidence and is at odds with the above-mentioned PIXEL results. The position of the peak at 2.6–2.7 Å does not particularly encourage defining it as a short and strong bond.

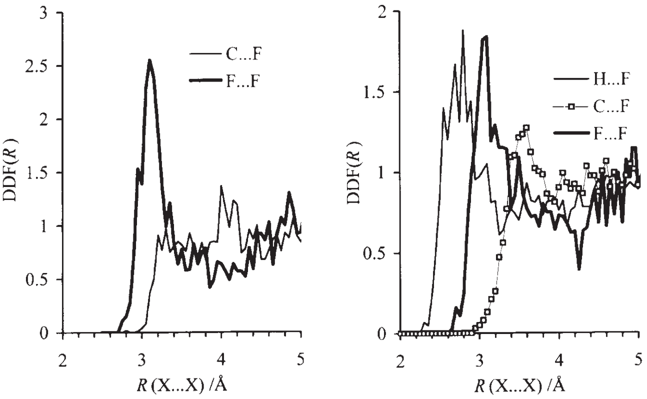


Figure 6. Density distribution functions [DDFs, see Eq. (2)] for atom–atom distances in the databases of crystal structures: left: perfluorinated compounds; right: CHF compounds.

## Conclusion

In crystals of planar, polycyclic, condensed aromatic hydrocarbons or of their sparingly fluorinated derivatives, molecules tend to pack in V-shaped arrangements. The presence of a tetrafluorinated ring in the condensed system enables the crystal packing to switch to layered structures with overlapping of unsubstituted and fluorinated molecular moieties in the arene–fluoroarene stacking synthon. We suggest that this finding could be exploited in improving our ability to control the crystal packing of organic compounds without recourse to complexation of separate hydrocarbon and perfluorohydrocarbon molecules. This conclusion has been reached without invoking a special role of contacts between hydrogen- and fluorine-rich regions at the rim of coplanar molecules, that is, special C–H···F interactions, for which our analysis and a statistical consideration of databases of related crystal structures do not support a compelling role in stabilisation. These conclusions are in keeping with detailed analyses of the interactions between organic fluorine and hydrocarbons.[17,18]

Table 5. PIXEL-partitioned lattice energies [kJ mol$^{-1}$]. Energy-optimised (formally zero-temperature) structures.

| Compound | $E_{coul}$[a] | $E_{pol}$[b] | $E_{disp}$[c] | $E_{rep}$[d] | $E_{tot}$[e] | $E_{FF}$[f] |
|---|---|---|---|---|---|---|
| naphthalene | −26 | −12 | −114 | 73 | −79 | −74 |
| 1,5-difluoronaphthalene | −21 | −8 | −103 | 56 | −76 | −77 |
| 1,8-difluoronaphthalene | −26 | −12 | −107 | 63 | −81 | −77 |
| tetrafluoronaphthalene **1** | −24 | −8 | −100 | 59 | −72 | −78 |
| anthracene | −33 | −15 | −153 | 91 | −110 | −102 |
| tetrafluoroanthracene **2** | −29 | −11 | −136 | 78 | −99 | −104 |
| phenanthrene | −32 | −15 | −148 | 94 | −101 | −98 |
| tetrafluorophenanthrene **3** | −26 | −10 | −129 | 74 | −92 | −101 |

[a] Coulombic energy. [b] Polarisation energy. [c] Dispersion energy. [d] Repulsion energy. [e] Total PIXEL lattice energy. [f] Lattice energy estimated by the atom–atom force field in Table 2.

As a cautionary attitude is always recommended in such inferences on prediction and control of crystal packing in weakly bound organic crystals, we plan to extend the analysis to crystals of compounds that contain other well-recognised association linkers, like hydrogen-bonding groups. In this way the proposed synthon would be placed in competition and its reliability tested.

## Experimental Section

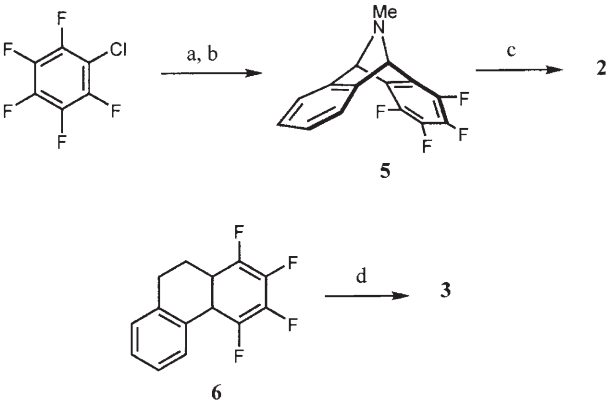
**General**: $^1$H NMR spectra were recorded at 400 MHz in $CDCl_3$ unless otherwise stated and were referenced to tetramethylsilane (TMS) at $\delta = 0.00$ ppm. $^{13}$C NMR spectra were recorded at 100 MHz and were referenced to $\delta = 77.0$ ppm in $CDCl_3$. $^{19}$F NMR spectra were recorded at 376 MHz in $CDCl_3$ and were referenced to hexafluorobenzene at $\delta = 0.0$ ppm. NMR spectra were recorded by using a Varian INOVA-400 spectrometer equipped with a Varian 5 mm ATB $^1$H/$^{19}$F{$^{13C}$-$^{31}$P} PFG Probe. All chemicals and solvents were used as purchased or after standard purification. Reactions were monitored by TLC on silica gel plates. Flash chromatography was performed on silica gel (particle size 40—63 μm) with PRA-grade solvents.

Tetrafluoronaphthalene **1**, tetrafluoroanthracene **2** and tetrafluorophenanthrene **3** were obtained following reported procedures or modifications thereof.

**Synthesis**

*Tetrafluoronaphthalene 1* (m.p. 107 °C; lit.:[19] 107–109 °C) was obtained as white needles by recrystallisation from hexane of a sample obtained following a literature procedure[19] and preliminarily purified by sublimation (80 °C/1 torr).

*Tetrafluoroanthracene 2* (pale yellow needles by recrystallisation from EtOH, m.p. 173–174 °C; lit.:[20] 174–175 °C) was obtained in two steps as described in Scheme 1.



Scheme 1. Synthesis of **2** and **3**: a) *n*BuLi, $Et_2O$, −78 °C, 30 min; b) *N*-methylisoindole (**4**), −78 °C to RT, 6 h; c) 3-chloroperbenzoic acid, $CHCl_3$, 0 °C to RT, 15 h; d) DDQ, toluene, 115 °C, 40 h.

*Adduct 5*: *n*BuLi (2 mL of a 1.5 M solution in hexane) was added dropwise over 2 min to a stirred solution of pentafluorochlorobenzene (0.607 g, 3 mmol) in dry $Et_2O$ (6 mL) cooled to −78 °C and kept under nitrogen. The resulting colourless solution was stirred at −78 °C for 30 min and a solution of *N*-methylisoindole (**4**)[21] (0.393 g, 3 mmol) in $Et_2O$ (9 mL) was slowly added. The resulting dark yellow solution was allowed to warm to room temperature. After a total reaction time of 6 h, the reaction mixture was poured into water, the organic layer was separated and the aqueous layer was extracted twice with $CH_2Cl_2$ (10 mL). The combined organic phases were dried with $Na_2SO_4$, filtered and concentrated under vacuum to afford the crude product (0.700 g) as a thick brown oil. $^1$H NMR analysis of this material showed signals at $\delta = 2.25$ and 5.20 ppm ascribable to the N−Me group and the bridgehead hydrogen of adduct **5**, respectively, by analogy with the spectrum of a structurally related product.[22]

*Oxidative deamination of adduct 5*:[20] A stirred solution of crude adduct **5** (0.280 g, ≈1 mmol) in $CHCl_3$ (5 mL), cooled to 0 °C, was treated with 3-chloroperbenzoic acid (70 %, 0.500 g, 2 mmol). The solution turned colourless in about 15 min and after another 15 min a white precipitate formed. The mixture was stirred at room temperature overnight, filtered on a Buchner funnel and the solid washed with $CH_2Cl_2$ (10 mL). The filtrate was washed with a saturated aqueous solution of $K_2CO_3$ and the separated organic phase was dried and concentrated under vacuum. The resulting crude product was purified by flash chromatography with hexane as the eluent. The first eluted fraction afforded pale yellow needles by slow evaporation of the solvent. These were recrystallised from ethanol to afford the product (0.150 g, 20 % overall yield from **4**).

*Tetrafluorophenanthrene 3* was obtained by aromatisation of 9,10-dihydro-1,2,3,4-tetrafluorophenanthrene (**6**) (m.p. 86–88 °C; lit.:[23] 87–88.5 °C) as follows (Scheme 1). A stirred solution of compound **6** (0.070 g, 0.2 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.273 g, 1.2 mmol) in toluene (3 mL) was heated at reflux for 40 h. The solvent was then evaporated under vacuum and the crude product was triturated with cyclohexane (3 mL). The solid was filtered off and the filtrate purified by flash chromatography with cyclohexane as the eluent. The resulting white solid (0.042 g, 60 %) was crystallised from EtOH to afford the product as white needles (m.p. 165 °C; lit.:[23] 164–165 °C). This aromatisation procedure was preferred to the one described in ref. [23] that involves the use of Pd/C at 250 °C.

**X-ray crystallography**: Structure determination of tetrafluoronaphthalene could be carried out without problems, except for partial sublimation at room temperature, on the single crystals obtained in prismatic or pyramidal forms. Tetrafluoroanthracene afforded thin prismatic crystals: data collection, crystal structure solution and refinement using the one suitable single crystal retrieved from the crystallisation batch proceeded without difficulty at room temperature. That crystal was later mechanically damaged and data collection at low temperatures could not be carried out systematically. Later, another very small single crystal was found which only allowed a determination of cell parameters at 90 K. By using a specimen of octafluoronaphthalene retrieved from a batch of monoclinic tabular crystals, we confirmed the crystal cell of OFNAPH01 and a disordered structure at room temperature, but when the temperature was lowered, the crystal shattered and data collection had to be discontinued. Tetrafluorophenanthrene gave elongated monoclinic tabular crystals: diffraction data collected at 123 K indicate a disordered structure with electron density concentrating in parallel planes perpendicular to the *c* axis, presumably with multiple orientation of molecular objects in their planes, but all attempts at fitting the observed density with reasonable molecular models led to unsatisfactory results.

Data collection was performed with a Bruker Smart Apex diffractometer equipped with temperature control. No absorption corrections were applied. No intensity decay was detected during data collection. The structures were solved by direct methods[24] and refined by full-matrix least-squares cycles on $F^2$ (SHELXL-97).[25] Anisotropic thermal parameters were assigned to all non-hydrogen atoms and hydrogen atoms were placed in calculated positions and refined using a riding model.

Crystallographic data are collected in Table 6. CCDC-633067 (octafluoronaphthalene), CCDC-633068 (**2**, 90 K), CCDC-633069 (**2**, 295 K), CCDC-633076 (**3**), CCDC-633075 (**1**, 90 K), CCDC-633070–633074 (**1**: 120, 160, 200, 240, 295 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Figures 3 and 4 were drawn by using the Schakal program.[26]

Table 6. Selected crystallographic and data collection parameters.

| | Tetrafluoronaphthalene **1**[a] | Tetrafluoroanthracene **2** | Octafluoronaphthalene[b] |
|---|---|---|---|
| formula | $C_{10}H_4F_4$ | $C_{14}H_6F_4$ | $C_{10}F_8$ |
| $M_r$ | 200.13 | 250.19 | 272.10 |
| dimensions [mm] | 0.30×0.20×0.18 | 0.18×0.12×0.09 | 0.52×0.18×0.05 |
| $T$ [K] | 90(2) | 90(2) | 295(2) |
| system | monoclinic | triclinic | monoclinic |
| space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/c$ |
| $Z$ | 4 | 2 | 2 |
| $\rho_{calcd}$ [g cm$^{-1}$] | 1.745 | 1.648 | 2.002 |
| $\mu(Mo_{K\alpha})$ [mm$^{-1}$] | 0.170 | 0.147 | 0.233 |
| $2\theta_{max}$ [°] | 77.18 | 50.00 | 51.20 |
| data collected | 21398 | 4528 | 2458 |
| unique data | 4209 | 1758 | 738 |
| $R_{int}$ | 0.0417 | 0.0509 | 0.0501 |
| $[I_o>2\sigma(I_o)]$ | 3365 | 1130 | 326 |
| parameters | 143 | 163 | 64 |
| restraints | 0 | 0 | 84 |
| $R_{all}$ | 0.0450 | 0.1015 | 0.1792 |
| $R_{obsd}$ | 0.0362 | 0.0683 | 0.1155 |
| $wR_{all}$ | 0.1057 | 0.1797 | 0.4294 |
| $wR_{obsd}$ | 0.1021 | 0.1642 | 0.3816 |
| goodness-of-fit | 1.006 | 0.970 | 1.335 |
| $\Delta\rho_{min}$ [e Å$^{-3}$] | −0.35 | −0.38 | −0.24 |
| $\Delta\rho_{max}$ [e Å$^{-3}$] | 0.61 | 0.39 | 0.36 |

[a] Data collected at 90 K. [b] A model with two half-molecules with an equal population factor was assumed to interpret the disorder. Isotropic refinement was carried out. Constraints and strong restraints both on geometry and displacement parameters were adopted.

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Received: February 15, 2007