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Interplay of phenyl–perfluorophenyl stacking, C–H···F, C–F···π and F···F interactions in some crystalline aromatic azines†

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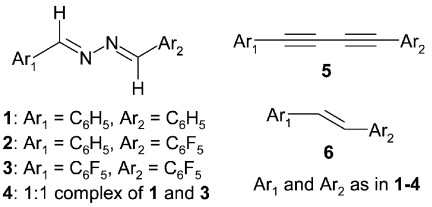
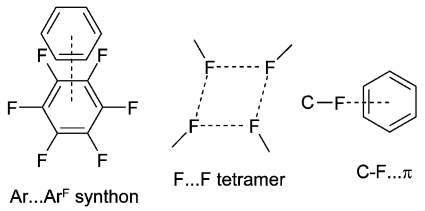
Analysis of phenyl–perfluorophenyl stacking synthon, C–H···F, C–F···π interactions, and F···F tetramer in three closely related azine crystal structures shows the dominance of Ar–Ar^F synthon while other interactions are turned on/off depending on the H/F stoichiometry in the molecule.

Intermolecular interactions in hydroaromatic and fluoroaromatic molecules, such as aryl–perfluoroaryl stacking synthon (Ar–Ar^F), C–H···F, C–F···π and F···F interactions have been the focus of recent structural, photophysical, topochemical, and DSC studies.[1–4] The Ar–Ar^F synthon, stabilised by quadrupole–quadrupole interaction between electron-rich and electron-deficient aromatic rings, has emerged as an important steering group in crystal engineering.[1] Among the intermolecular interactions of fluorine, C–H···F hydrogen bonds are directional and stabilised by electrostatic forces,[2] the C–F···π interaction is considered as destabilising,[3] and while F···F interactions are ubiquitous their exact structural role is not yet clear.[4] These studies no doubt improve our understanding of crystal packing in fluorinated molecules and shed light on structure–property relationship, but the fact that they have been carried out on diverse molecular skeletons makes a proper analysis of various intermolecular interactions somewhat tenuous. Against this background, we reasoned that if these F-based interactions are ideally examined in a family of crystal structures by gradually increasing the extent of fluorination in molecules, then their structural role and interplay might be analysed on an invariant molecular scaffold.



Unsymmetrical and symmetrical fluoroaromatic azines **2** and **3** were synthesised[5] and their structures were determined by single crystal X-ray diffraction at low temperature.‡ These molecules are almost flat in the azine tether moiety with torsion angles of $< 5°$. The crystal structure of C_6H_5–C_6F_5 azine **2** contains planar molecules stacked in a head-to-tail fashion such that the phenyl ring of one molecule is π-stacked on the perfluorophenyl group of another at a centre-to-centre distance (D_{cent}) of 3.78, 3.73 Å; the mean perpendicular distance between centroid and ring plane of adjacent phenyl rings (D_{perp}) is 3.38, 3.45 Å (Fig. 1). The D_{cent} separation in **2** is comparable to distances noted in the Ar–Ar^F stacking synthon (3.4–3.8 Å, Ph_{vdW} 1.75 Å).[1,6] The structure of **2** is further stabilised by C–H···F hydrogen bonds from phenyl and imine C–H donors (d/Å, θ/°: 2.50, 125.5; 2.57, 159.1; 2.49, 121.8). The crystal structure of C_6F_5–C_6F_5 azine **3** contains a tetramer arrangement of F-



atoms between screw axis and glide related molecules (F···F 2.80 Å; F_{vdW} 1.47 Å), (imine)C–H···F bond (2.65 Å, 146.7°) and a C–F···π interaction to the C_6F_5 ring centroid (3.07 Å, 150.9°). There is some π–π overlap between C_6F_5 rings[7] but the distance is too long to be of energetic significance (D_{cent} 4.67 Å). Crystal packing in the 1:1 complex, **4**, of bis-phenyl and bis-perfluorophenyl azines **1** and **3** was examined next. Recrystallisation of an equimolar mixture of **1** and **3** from benzene–hexane afforded yellow plate-like crystals of **4** at ambient temperature. The structure of molecular complex **4** is very similar to C_6H_5–C_6F_5 azine **2** in that the Ar–Ar^F synthon is present here with good overlap between the electron-rich and electron-deficient aromatic rings (D_{cent} 3.60, 3.75 Å; D_{perp} 3.42, 3.42 Å). Numerous weak C–H···F interactions complete the crystal packing (2.5–2.7 Å, 115–125°; Fig. 2). As reference, X-ray crystal structure of the parent benzalazine **1**[8] was analysed (*Pbcn*). Surprisingly, there is little π–π overlap (D_{cent} 4.78 Å) between the planar aromatic molecules. The structure is stabilised by chains of C–H···N and C–H···π(centroid) interactions[9] (2.62, 136.5; 2.87 Å, 139.8°) together with an overall herringbone packing of aromatic groups.

A comparison of these four crystal structures is instructive. The unsymmetrical azine **2** and the 1:1 complex **4** have similar packing features: almost complete overlay of molecular skeletons, dominance of Ar–Ar^F stacking synthon, and auxiliary C–

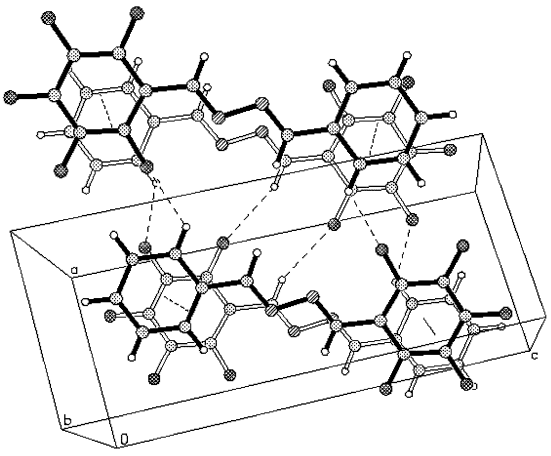


Fig. 1 Crystal packing in unsymmetrical C_6H_5–C_6F_5 azine **2**. Note the stacking of phenyl and perfluorophenyl rings (Ar–Ar^F synthon, D_{cent} 3.73, 3.78 Å) and the support from C–H···F hydrogen bonds. Adjacent molecules are shaded differently.

† Electronic supplementary information (ESI) available: experimental powder X-ray diffraction spectra. See http://www.rsc.org/suppdata/cc/b2/b202181a/

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H···F interactions. In the crystal structures of bis-phenyl and bis-perfluorophenyl azines **1** and **3**: π-stacking motif is absent, C_6H_5 or C_6F_5 rings adopt a herringbone T-geometry, and C–H···N and C–H···π interactions in **1** are replaced by F-tetramer and C–F···π interactions in **3**. A notable feature of this structural analysis is that the entire range of F-based intermolecular interactions are observed and compared in this family of four structures, making it possible to evaluate trends. Only one or more of these interactions have been identified in previous studies:[1–7] *e.g.* C–H···F; F···F; Ar–Ar^F, C–H···F; C–F···π. In such situations, an overall assessment of these intermolecular interactions in self-assembly is complicated because they are present in very different crystalline environments.

The fact that the single component crystal **2** and the molecular complex **4** are stabilised by Ar–Ar^F synthon and have the same space group ($P1$), the extent of isostructurality in these two crystals was calculated by the unit cell similarity index, Π.[10] A value of Π close to zero implies similar unit cells. The calculated value of Π, after symmetric orthogonalisation of triclinic cells,§ [11] for crystals **2** and **4** is 0.030 suggesting near identity. This value may be compared with that calculated for unsymmetrical monomolecular crystal and symmetrical bimolecular complex of diacetylene **5** and stilbene **6** reported by Coates *et al.*[1,6] (in space group $P1$, Π 0.028, 0.015). The identity of unit cell and supramolecular synthon in crystals of **2** and **4** led to a comparison of their powder X-ray diffraction spectra. There is excellent overlap in the experimental PXRD traces of **2** and **4** (see Supplementary data†) suggesting that there is local similarity (*i.e.* synthomorphism)[12] in the internal arrangement of atoms in these structures. Given these similarities, identity in the melting points of **2** and **4** (117, 118 °C) may be traced to their crystal packing.

To conclude, analysis of four closely related crystal structures with varying H/F ratio shows the turning on/off of intermolecular interactions and packing features: (1) Dominance of Ar–Ar^F synthon when both phenyl and perfluorophenyl groups are present; (2) isostructurality of unsymmetrical monomolecular and symmetrical bimolecular crystals; (3) herringbone motif of phenyl or perfluorophenyl rings in symmetrical structures; (4) occurrence of F···F and C–F···π interactions in F-rich structure; (5) stabilisation from electrostatic C–H···F hydrogen bonds through activated donors. Lastly, it may be noted that polarisation in the C–F$^{\delta-}$···π(C_6F_5) interaction is analogous to the C≡N$^{\delta-}$···π(C_6F_4) interaction noted recently.[13] The dipole–quadrupole interaction between the electronegative donor atom and the positive quadrupole moment of perfluorophenyl ring is stabilising. The concept of synthomorphism, that is different molecular components having similar crystal packing, is important not only in crystal engineering but also in the patenting of drugs and pigments. Our preliminary results also have implications in the supramolecular chemistry of fluoroaromatic enzyme inhibitors.[14]

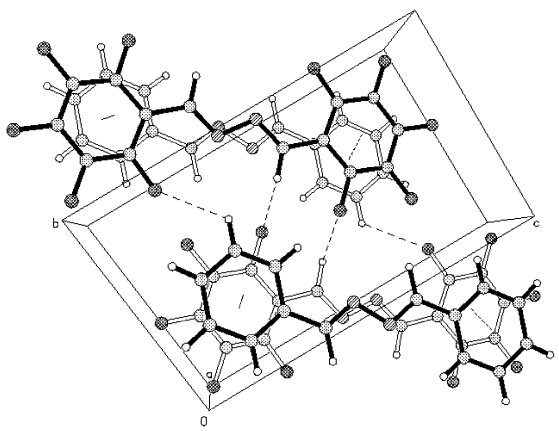

Fig. 2 Crystal packing in the 1 : 1 complex **4**. Note the stacking of phenyl and perfluorophenyl rings of symmetrical molecules **1** and **3** (Ar–Ar^F synthon, D_{cent} 3.60, 3.75 Å), and the identity with structure **2**.

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Notes and references

‡ *Crystal data.* **2**: C_6H_5–CH=N–N=CH–C_6F_5 ($C_{14}H_7F_5N_2$, M = 298.22); triclinic, space group $P1$, a = 5.9053(2), b = 7.4709(3), c = 14.3540(5) Å, α = 102.927(2), β = 92.143(2), γ = 91.222(2)°, V = 616.50(4) Å^3, Z = 2, D_c = 1.606 Mg m^{-3}, μ = 0.15 mm^{-1}, 2736 unique reflections, 2172 with $Fo > 4\sigma(Fo)$, Final R = 0.0416, wR = 0.1013. **3**: C_6F_5–CH=N–N=CH–C_6F_5 ($C_{14}H_2F_{10}N_2$, M = 388.18) monoclinic, space group $P2_1/n$, a = 6.6570(1), b = 7.9005(2), c = 13.1424(3) Å, β = 103.680(1), V = 671.60(3) Å^3, Z = 2, D_c = 1.920 Mg m^{-3}, μ = 0.213 mm^{-1}, 1977 unique reflections, 1496 with $Fo > 4\sigma(Fo)$, Final R = 0.0381, wR = 0.0946. **4**: **1**·**3** (1 : 1) ($C_{28}H_{14}F_{10}N_4$, M = 596.43) triclinic, space group $P1$, a = 7.2820(2), b = 7.9073(2), c = 11.9305(4) Å, α = 93.052(2), β = 93.590(2), γ = 113.310(1)°, V = 627.37(3) Å^3, Z = 2, D_c = 1.579 Mg m^{-3}, μ = 0.147 mm^{-1}, 2836 unique reflections, 1819 with $Fo > 4\sigma(Fo)$, Final R = 0.0526, wR = 0.1174. For all data collection, λ (Mo-Kα) = 0.7107 Å, T = 153 K, Nonius Kappa CCD area detector, structure solution and refinement with SHELX97, H-atoms refined isotropically. CCDC 181039–181041. See http://www.rsc.org/suppdata/cc/b2/b202181a/ for crystallographic data in .cif or other electronic format.

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