Crystal Engineering

Supramolecular Assemblies of Hydrogen-Bonded Carboxylic Acid Dimers Mediated by Phenyl–Pentafluorophenyl Stacking Interactions

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Stacking between aryl and perfluoroaryl units is an important class of aromatic–aromatic interactions that has been attracting rapidly growing interest in recent years.[1–7] This phenomenon has been studied extensively since Patrick and Prosser demonstrated in 1960 that a 1:1 mixture of benzene and hexafluorobenzene forms a solid complex that melts at 24 °C.[1] In contrast to the crystals of the individual components, which show a herringbone packing, this complex consists of face-to-face stacks of alternating benzene and hexafluorobenzene molecules. Crystallographic studies of several 1:1 complexes of perfluorinated aromatic compounds with non-fluorinated arenes have revealed similar stacking motifs of alternating component molecules.[2–7] This kind of arrangement can be attributed to a quadrupolar interaction between electron-rich and electron-deficient aromatic rings.[8] The calculated binding energy between two aromatic rings (benzene and hexafluorobenzene) ranges from 3.7 to 4.7 kcal mol^{-1}.[9] Thus, this interaction has emerged as a very important synthon in crystal engineering that has a utility comparable to that of many robust hydrogen-bonding synthons. For example, the aryl–perfluoroaryl stacking interaction has been used to induce the crystal packing of monomers suitable for solid-state photopolymerization[2] and to stabilize liquid-crystalline phases.[3] It also seems to offer new possibilities for the modification of biologically important structures including peptides and oligonucleotides.[10]

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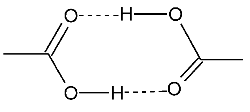
We were particularly interested as to whether the aryl–perfluoroaryl interaction could be effectively used in the construction of supramolecular aggregates from discrete hydrogen-bonded assemblies instead of covalently bonded units. Herein we report the structures of cocrystals obtained from benzoic acids, the self-assembly of which is controlled by phenyl–pentafluorophenyl π-stacking interactions. Since aromatic carboxylic acids are known to assemble through formation of the cyclic motif **I**,[11] we anticipated that cocrystallization of pentafluorobenzoic acid (**1**) with benzoic (**2**) or 2,4,6-trimethylbenzoic acid (**3**, Scheme 1) should afford the corresponding homo- or heterodimers that assemble into face-to-face stacks with alternating phenyl and pentafluorophenyl rings. Cocrystallization of the acids **1** and **2** from water as well as from CH_2Cl_2/heptane gave colorless plates that proved to be the 1:1 complex **1**·**2**. X-ray structural analysis of the complex revealed that two types of symmetry-independent heterodimers are formed in these monoclinic crystals (space group *Cc*): one with a nearly planar arrangement of the aryl rings and the carboxylic dimer system **I** (the corresponding dihedral angle is 8.9°) and a second one with system **I** twisted by 30.9° out of the plane of the neighboring aryl rings.[12] More importantly, the heterodimers are assembled into infinite stacks in a head-to-tail fashion such that the phenyl rings interact with the pentafluorophenyl moieties (Figure 1 a). These rings are not completely parallel (dihedral angles A/D 7.8° and B/C 4.6°) but, as usual for such systems, the aryl rings show offset face-to-face stacking. The slip angles of the stacks[13] are in the range of 19.7–27.7°.



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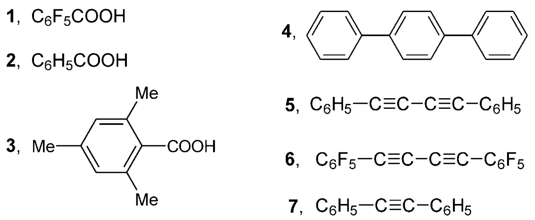

Scheme 1. Chemical structures of the substrates.

A remarkably similar assembly of carboxylic acid molecules was observed for the 1:1 complex **1**·**3** that crystallized from water (triclinic, $P\bar{1}$; Figure 1 b).[12] Again, the acid heterodimers are packed in well-ordered columns with the 2,4,6-trimethylphenyl and pentafluorophenyl residues stacked in an alternating fashion. The creation of heterodimers is not unexpected in both of the above cases since it has been shown that a heterodimer is favored over either of the two homodimers by about 1 kcal mol^{-1} for a pair of aromatic carboxylic acids with substituents of different electronegativities.[14] This observation remains in accordance with the principle that the strongest proton donor forms hydrogen bonds with the strongest proton acceptor.[15] It is important to note that the homodimers of **1**–**3** do not form π stacks in the crystals of the pure acids.[16]

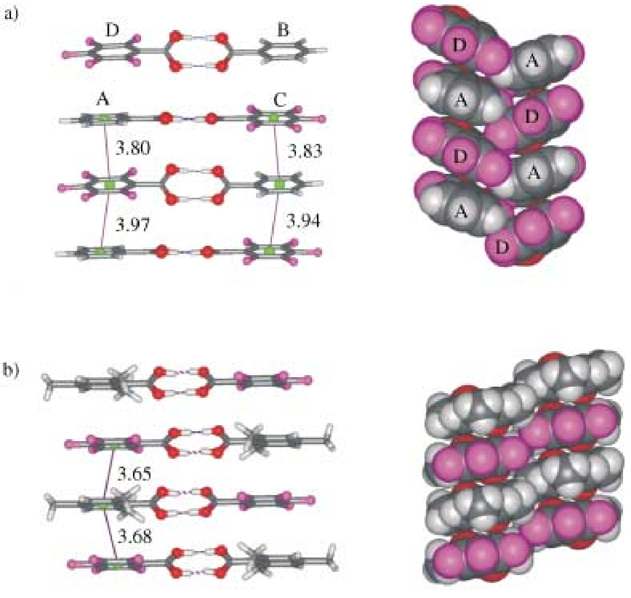

Figure 1. Stacking of carboxylic acid heterodimers and space-filling models of the adjacent binary stacks observed in a) the monoclinic cocrystal **1**·**2** and b) the triclinic cocrystal **1**·**3**. The distances between the phenyl-ring centroids are given in Å. The carboxylic hydrogen atoms are disordered.

Since the benzoic acid dimer can be regarded as a supramolecular analogue of *p*-terphenyl (**4**),[17] we tried to cocrystallize **1** with **4**. However, no cocrystals formed, probably because the size of the ring **I** does not match that of the central benzene ring in **4**; that is, the distance between the carboxylic carbon atoms in **I** is 3.81 Å, whereas the C-1 and C-4 atoms in the *p*-substituted benzene unit are separated by 2.80 Å, which makes interaction between the phenyl and pentafluorophenyl units in **4** and **1**, respectively, ineffective. Therefore, we used 1,4-diphenylbutadiyne (**5**),[18] where the separation of the phenyl rings almost exactly matches that in the benzoic acid dimer (the length of the diacetylene spacer is 3.78 Å). Cocrystallization of equimolar amounts of **1** (m.p. 101–102 °C) and **5** (m.p. 87–88 °C) from CH_2Cl_2/heptane produced colorless needles that melted at 136–137 °C. Interestingly, when a solution of **1** was mixed with a solution of **5** in the same solvent, precipitation of the 1:1 adduct **1**·**5** occurred spontaneously. The sharp and higher melting point of **1**·**5** compared to either of the two pure compounds indicated a possible phenyl–pentafluorophenyl interaction. X-ray structural analysis of **1**·**5** revealed that the dimers of **1** are sandwiched between the molecules of the diacetylene **5** which leads to formation of regular columns (Figure 2).[12] Analogously, the combination of acids **2** and **3** with 1,4-bis(pentafluorophenyl)butadiyne (**6**)[19] gave 1:1 cocrystals **2**·**6** and **3**·**6**, respectively, which are nearly isostructural with the complex **1**·**5**. Here again, the aryl–perfluoroaryl interaction mediates formation of infinite stacks similar to those

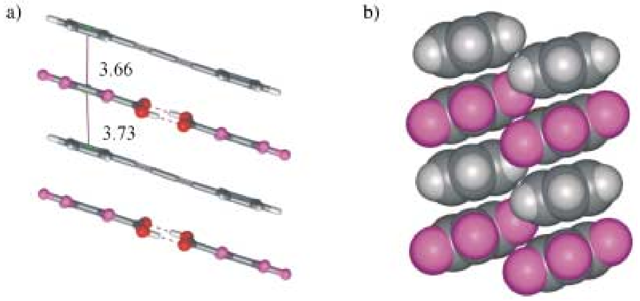

Figure 2. a) π Stacks of the homodimers of **1** and the diyne **5** in **1·5** and b) space-filling models of the adjacent binary stacks. The distances between phenyl-ring centroids are given in Å. The interplanar angle between the aromatic rings of the two components is 5.7° and the stack slip angles are 35 and 31°.

observed in **1·5**. The homodimer **2** remains nearly planar in the complex **2·6** as well as in the crystals of the pure acid **2**. However, complexation of **1** and **3** with 1,4-bisarylbutadiynes leads to a significant flattening of the corresponding carboxylic homodimers. Thus, the system **I** in **1·5** and **3·6** is twisted out of the plane of the neighboring aryl rings by 10.7 and 32.6°, respectively, whereas the corresponding dihedral angles found in the crystals of the pure acids **1** and **3** are 29.8 and 48.4°, respectively.[16]

The component molecules in all the complexes described above are arranged in a columnar fashion with the strongest intermolecular interactions within the infinite columns (Figure 3). Thus, we became interested in the possibility of constructing 2D assemblies stabilized by aryl–perfluoroaryl interactions in combination with hydrogen-bonding interactions between the carboxylic acid groups. Since **4** did not form a complex with **1**, we looked for molecules with a shorter spacer between the phenyl rings. For this purpose we studied the complexation of **1** with diphenylacetylene (**7**), where the spacer length is only 1.20 Å. We expected that the stacking between the phenyl and pentafluorophenyl units in these mismatching systems would lead to a "brick-wall" structure constructed of rows of alternating acid dimers **1** and acetylene **7** "bricks". The 1:1 prismatic crystals of the complex **1·7** were obtained from hexane, and X-ray structure analysis revealed that, indeed, the dimer **1** and the acetylene **7** aggregate in a simple brick-wall motif (Figure 4) with the carboxylic dimer **I** units located in a row just over the gap between the molecules of **7** in the row below.[12] The aryl rings within the wall are nearly parallel (dihedral angle 2.9°): they show an usual offset face-to-face stacking with an aryl–perfluoroaryl stack slip angle of 21.4°.

In conclusion, our results demonstrate that the phenyl–pentafluorophenyl interaction is a useful synthon, which in cooperation with hydrogen-bonding interactions, may enable supramolecular architectures to be controlled in a predictable way. Furthermore, as illustrated by the complexation of the carboxylic acid dimers with diphenylacetylene (**7**) and 1,4-bisarylbutadiynes **5** and **6**, these interactions allow the assembly of systems with extremely different chemical functionalities. However, some degree of size and shape compatibility between the supramolecular substrates is necessary to allow effective aryl–perfluoroaryl stacking within the molecular complexes.

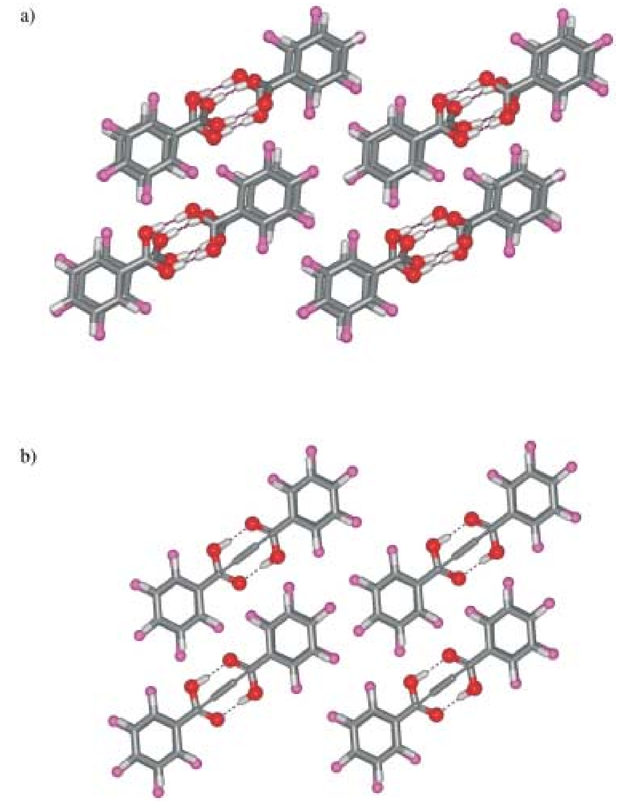

Figure 3. Projection of the crystal packing viewed along the stack axis in a) **1·2** and b) **1·5.**

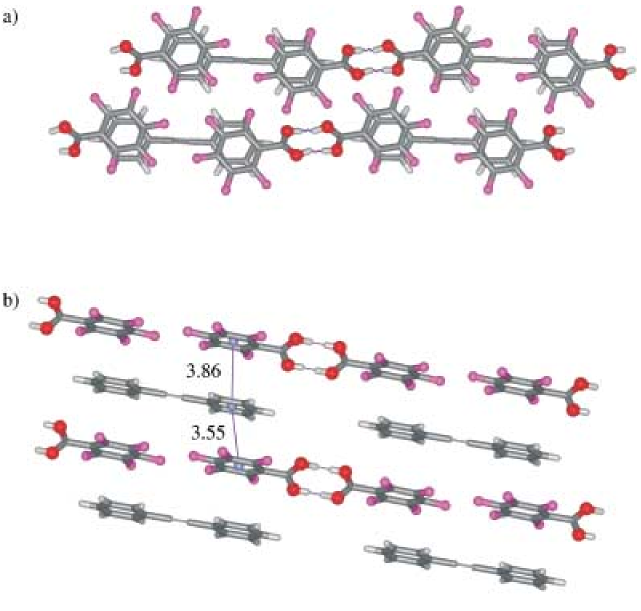

Figure 4. a) Projection of the crystal packing viewed along the stack axis in **1·7** and b) side view of the brick-wall construction in this complex**.** The distances between the phenyl-ring centroids are given in Å. The carboxylic hydrogen atoms are disordered.

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[12] X-ray crystal structure analyses: Kuma Diffraction KM4CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), Lorentz and polarization corrections, no absorption correction; the structures were solved by direct methods with SHELXS-97 and refined against F^2 with SHELXL-97. Hydrogen atoms were located on the ΔF maps and their positional and isotropic displacement parameters included in the refinement. a) Crystal structure data for **1·2**: $C_6H_5CO_2H\cdot C_6F_5CO_2H$, crystal size $0.5\times0.5\times0.2$ mm, $M_r = 334.20$, monoclinic, space group *Cc* (no. 9), $a = 24.7871(15)$, $b = 7.7160(3)$, $c = 14.3292(9)$ Å, $\beta = 108.571(4)°$, $V = 3741.0(9)$ Å^3, $T = 120$ K, $Z = 8$, $\mu(Mo_{K\alpha}) = 0.17$ mm^{-1}, $\theta_{max} = 26.37°$, 6923 reflections measured, 3349 unique ($R_{int} = 0.021$) which were used in all calculations. Final $R_1 = 0.0336$ and $wR(F^2) = 0.0890$ (all data). The carboxylic hydrogen atoms are disordered over two positions. b) Crystal structure data for **1·3**: $C_6F_5CO_2H\cdot C_9H_{11}CO_2H$, crystal size $0.45\times0.45\times0.25$ mm, $M_r = 376.27$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.1521(7)$, $b = 8.1727(8)$, $c = 15.2499(12)$ Å, $\alpha = 99.337(8)$, $\beta = 99.018(7)$, $\gamma = 107.234(9)°$, $V = 820.01(13)$ Å^3, $T = 293$ K, $Z = 2$, $\mu(Mo_{K\alpha}) = 0.144$ mm^{-1}, $\theta_{max} = 26.37°$, 5578 reflections measured, 3240 unique ($R_{int} = 0.027$) which were used in all calculations. Final $R_1 = 0.0675$ and $wR(F^2) = 0.1494$ (all data). The carboxylic hydrogen atoms are disordered over two positions. c) Crystal structure data for **1·5**: $(C_6F_5CO_2H)_2\cdot C_{16}H_{10}$, crystal size $0.6\times0.6\times0.6$ mm, $M_r = 626.40$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.3812(9)$, $b = 7.9939(8)$, $c = 11.6725(12)$ Å, $\alpha = 98.775(8)$, $\beta = 92.169(9)$, $\gamma = 112.861(11)°$, $V = 623.63(12)$ Å^3, $T = 130$ K, $Z = 1$, $\mu(Mo_{K\alpha}) = 0.160$ mm^{-1}, $\theta_{max} = 26.37°$, 5123 reflections measured, 2525 unique ($R_{int} = 0.026$) which were used in all calculations. Final $R_1 = 0.0445$ and $wR(F^2) = 0.1168$ (all data). d) Crystal structure data for **2·6**: $(C_6H_5CO_2H)_2\cdot C_{16}F_{10}$, crystal size $0.8\times0.3\times0.05$ mm, $M_r = 626.40$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.2876(10)$, $b = 7.6086(11)$, $c = 12.5006(13)$ Å, $\alpha = 94.933(10)$, $\beta = 90.670(10)$, $\gamma = 111.319(13)°$, $V = 642.63(14)$ Å^3, $T = 130$ K, $Z = 1$, $\mu(Mo_{K\alpha}) = 0.155$ mm^{-1}, $\theta_{max} = 26.37°$, 5804 reflections measured, 2616 unique ($R_{int} = 0.041$) which were used in all calculations. Final $R_1 = 0.0675$ and $wR(F^2) = 0.1370$ (all data). The carboxylic hydrogen atoms are disordered over two positions. e) Crystal structure data for **3·6**: $(C_9H_{11}CO_2H)_2\cdot C_{16}F_{10}$, crystal size $0.4\times0.4\times0.3$ mm, $M_r = 710.55$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.2150(4)$, $b = 8.1122(5)$, $c = 14.3128(6)$ Å, $\alpha = 97.488(4)$, $\beta = 100.135(4)$, $\gamma = 105.863(5)°$, $V = 779.04(7)$ Å^3, $T = 130$ K, $Z = 1$, $\mu(Mo_{K\alpha}) = 0.138$ mm^{-1}, $\theta_{max} = 26.37°$, 8805 reflections measured, 3123 unique ($R_{int} = 0.023$) which were used in all calculations. Final $R_1 = 0.0467$ and $wR(F^2) = 0.11508$ (all data). One of the methyl groups is disordered. f) Crystal structure data for **1·7**: $(C_6F_5CO_2H)_2\cdot C_{14}H_{10}$, crystal size $0.4\times0.4\times0.2$ mm, $M_r = 602.38$, triclinic, space group $P\bar{1}$ (no. 2), $a = 6.3760(5)$, $b = 7.3009(5)$, $c = 13.9240(11)$ Å, $\alpha = 104.681(6)$, $\beta = 101.092(6)$, $\gamma = 91.897(7)°$, $V = 613.00(8$ Å^3, $T = 125$ K, $Z = 1$, $\mu(Mo_{K\alpha}) = 0.159$ mm^{-1}, $\theta_{max} = 26.37°$, 4923 reflections measured, 2483 unique ($R_{int} = 0.016$) which were used in all calculations. Final $R_1 = 0.0435$ and $wR(F^2) = 0.1081$ (all data). The carboxylic hydrogen atoms are disordered over two positions. g) CCDC-199913–199917 and CCDC-205458 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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