

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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