

Co-crystals of iodopentafluorobenzene with nitrogen donors: 2-D molecular assemblies through halogen bonding and aryl–perfluoroaryl interactions

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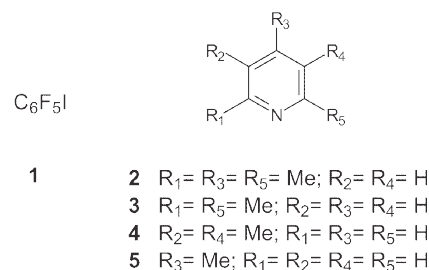
Electron deficient iodopentafluorobenzene forms heterodimers with electron rich pyridine donors stabilized by halogen bonding, that are further assembled into polar brick-wall type 2-D network via π – π stacking interactions between aryl and perfluoroaryl moieties.

The non-covalent interactions between halogen atoms and electron-pair donating heteroatoms are receiving increasing attention as a useful tool for assembling molecules in the crystal.^{1,2} They have primarily charge transfer character (n – σ^*), where carbon bound halogens work as electron acceptors (Lewis acids) and heteroatoms bearing lone pairs as electron donors (Lewis bases). To stress their analogy with hydrogen bonding the term “halogen bonding” is often used.³ The strength of the halogen bonding increases on moving from chlorine to bromine to iodine as the energy of the corresponding C–X σ^* orbital decreases. In addition strongly electronegative perfluoroalkyl residues further enhance the Lewis acid character (electron accepting ability) of halogen atoms in perfluorocarbon halides.^{1,4}

Recently Resnati and collaborators have demonstrated effectiveness of halogen bonding in construction of 1-D infinite chain structures assembled of diiodoperfluoroalkanes with various bifunctional donors.^{1,5} The remarkable feature of these assemblies is a distinct segregation of the hydrocarbon and perfluorohydrocarbon chains, being a consequence of their extreme low affinity. On the other hand, it is known that aryl and perfluoroaryl rings show attractive electrostatic quadrupole–quadrupole interactions leading to their face-to-face stacking.^{6,7} Thus we anticipated that supramolecular complexes should be simply constructed from iodopentafluorobenzene (**1**) and aromatic electron donors by linking them with use of halogen bonds into discrete heterodimeric aggregates and further assembling into stacks by aryl–perfluoroaryl interactions. This procedure is somewhat analogous to that recently described by us and is relying on combination of hydrogen bonding and π -stacking of aryl and perfluoroaryl moieties.⁸

In this contribution we report the preparation and the crystal structures of halogen-bonded complexes obtained from **1** and aromatic nitrogen donors **2–5**. The methyl substituents in these compounds enhance the electrodonor character of the aryl rings and should thus increase the electrostatic interaction with the

pentafluorophenyl moiety of **1**. Due to a large contribution to the lattice energy from halogen bonding and aryl–perfluoroaryl interactions substituted pyridines **2–5**, which are liquids in normal conditions, readily form with **1** (mp -29 °C) co-crystals with melting points far above the room temperature. In contrast, pyridine itself does not form co-crystals with **1** at ambient temperature.



The solid complexes were obtained after mixing the components in the 1 : 1 molar ratio, whereas diffraction quality crystals were grown from a small amount of hexane. The crystals started to decompose immediately when exposed to air and therefore, for X-ray diffraction experiments, they were flash cooled to 130 K. After collecting diffraction data, crystals were heated on a diffractometer up to 260 K to check for possible solid-to-solid phase transitions. Diffraction patterns of all crystalline complexes studied, except for the co-crystal **1·4**, did not show any indication of solid-phase transformations. The co-crystal **1·4** (mp 58 – 59 °C), obtained from **1** and **4** (mp -9 °C), when flash cooled to temperatures below 170 K disintegrates into polycrystalline material, indicating a phase transition accompanied by large structural changes.

The crystal structure of **1·4** (space group $C2/c$) determined at 200 K (HT-form) revealed the heterodimers located on special position of the C_2 symmetry. The dimers are formed with use of halogen bonding showing the N \cdots I distance of 2.830(4) Å, *i.e.* significantly shorter than the sum of van der Waals radii for N and I (3.53 Å),⁹ and the exactly linear N \cdots I–C arrangement resulting from the crystallographic symmetry of the heterodimer (Fig. 1). The linear geometry of halogen bonding reflects anisotropic distribution of the electrostatic potential of heavier halogens showing electrophilic character along the axis of the C–X bond and nucleophilic character in the perpendicular direction.¹⁰ The nearly planar heterodimers are further assembled into a polar “brick-wall” type structure, in which pentafluorophenyl and pyridine moieties stack in alternating fashion (Fig. 1b). The distance between the centroids of the aromatic rings

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