Perfluorocarbon−Hydrocarbon Self-Assembling. 1D Infinite Chain Formation Driven by Nitrogen···Iodine Interactions

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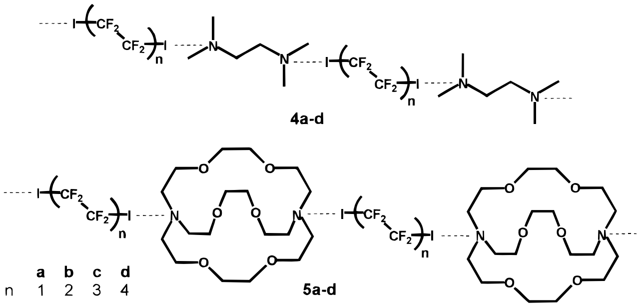
The importance of exploring specific interactions that may drive an intermolecular recognition process derives from the relevance of these interactions in quite different fields such as crystal engineering, supramolecular chemistry, and drug design. This is particularly true if such interactions are of substantial stability and if they effectively involve a class of molecules of high technological relevance such as perfluorocarbon (PFC) compounds.[1]

Numerous analytical techniques consistently show that carbon-bound halogens (C−X, X = Cl, Br, or I) can be involved in attractive interactions (C−X···El) with electronegative atoms (El = N, O, or S).[4] If the environment around the halogen is sufficiently electron-withdrawing, the resulting interaction becomes strong enough to influence the crystal packing in the solid as shown by the X-ray structure of chlorocyanoacetylene.[5] Calculations performed on the dimer of this compound estimated the energy of the N···Cl−C interaction as 10 kJ·mol^{-1}.[6] The strength of the C−X···El interaction increases on moving from chlorine to bromine to iodine.

Here our aim is the molecular recognition between the PFC and HC units driven by an interaction between nitrogen as a donor (i.e., base) and iodine as an acceptor (i.e., acid).[7] *We describe the first case of PFC−HC self-assembling to give cocrystals*. From an equimolar mixture of 1,2-diiodotetrafluoroethane (bp 112−113 °C, **1a**) and *N,N,N′,N′*-tetramethylethylenediamine (bp 120−122 °C, **2**) in chloroform, the complex **4a** is isolated as white crystals which can be handled and stored at room temperature and in air (Scheme 1). Compounds **4b**−**d** and **5a**−**d** have been obtained similarly.[11,12]

Scheme 1



From the crystal structures of **4a** (Figure 1) and **5a** (Figure 2),[13] it is clear that the interaction between the nitrogen and iodine atoms is largely responsible for keeping the perfluorinated diiodide in place. The value of the N···I distance, very close to 2.80 Å in both cocrystals, is clearly longer than the average covalent N−I bond length (2.07 Å)[16] but less than 0.8 times the sum of van der Waals radii (1.98 Å for iodine and 1.55 Å for nitrogen).[17] It compares well with the values reported for the crystalline complexes that I_2 forms with heteroaromatics containing nitrogen atoms as electron donors (2.27−3.07 Å).[18] The similarity between

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(1) PFC derivatives show a unique combination of physical properties, and they usually have a low affinity for their analogous hydrocarbon (HC) parents. Heat of solution and cohesive pressures of PFCs are quite different from those of HCs. Enthalpies of interaction between PFCs and HCs are smaller than interaction enthalpies between HCs (ref 2). Perfluorinated alkanes, ethers, and tertiary amines are practically insoluble in water, and their miscibility with many organic solvents is limited (ref 3). Specifically tailored patterns of intermolecular interactions are thus required if the PFC−HC recognition process is pursued to the point of triggering the self-assembling of the two species into cocrystals.

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(7) The N···I interaction has been observed between iodotrifluoromethane and various monoamines. The discrete molecular complexes formed have a 1:1 stoichiometry, and they have been studied in the gas phase at room temperature and in the solid phase in the cold (80 K) (ref 8). The first X-ray crystallographic study of a molecular addition compound between a halogen molecule and an electron-pair donor molecule was reported in the mid fifties (ref 9) and the crystal structures of several 1:1 complexes involving carbon-bound halogens have successively been reported (for reviews, see refs 4 and 10).

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(11) Compounds **4a**−**d** and **5a**−**d** were obtained by crystallization from chloroform of equimolar amounts of *N,N,N′,N′*-tetramethylethylenediamine (**2**) or 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane (kryptofix 2.2.2., **3**) with 1,2-diiodotetrafluoroethane (**1a**), 1,4-diiodooctafluorobutane (**1b**), 1,6-diiodoperfluorohexane (**1c**), 1,8-diiodoperfluorooctane (**1d**). Elemental analyses expected for a 1:1 ratio between **1a**−**d** and **2**, **3** were obtained (C, H, N, F, I ± 0.44%). ^{1}H and ^{19}F NMR spectra of highly diluted solutions of **4** and **5** were identical to those shown by pure **1**−**3**. ^{19}F NMR spectra of concentrated solutions of **4a** and **5a** showed for the CF_2I group a high-field shift of several ppm relative to pure **1a**. These observations are consistent with a rapid association equilibrium which gives dimeric, trimeric, ... adducts. The shifts of the difluoromethylene groups of compounds **4b**−**d** and **5b**−**d** decrease with increasing distance from the iodine atom. This supports the hypothesis that the specific N···I intermolecular interaction observed in the solid state also exists in solution.

(12) Solid cocrystals (1:1 ratio) have also been obtained starting from perfluorocarbon diiodides and dibromides with other secondary and tertiary diamines, bifunctional heteroaromatics, and diethers. The formation of infinite 1D coordination chains reiterating indefinitely the C−X···El interaction (X = I, or Br; El = N(sp^3), N (sp^2), or O (sp^3) seems quite general.

(13) Crystal data for **4a**: $C_8H_{16}F_4I_2N_2$, M_w = 470.03, triclinic, space group $P\bar{1}$, a = 6.380(1) Å, b = 6.808(1) Å, c = 9.242(1) Å, α = 109.20(3)°, β = 96.86(1)°, γ = 94.95(1)°, V = 373.0(1) Å^3, Z = 1; colorless prismatic crystals, 1937 reflections (1380 unique) were collected and corrected for decay. **5a**: $C_{20}H_{36}F_4I_2N_2O_6$, M_w = 730.31, monoclinic, space group $C2/c$, a = 15.917(2) Å, b = 23.778(2) Å, c = 8.714(1) Å, β = 123.17(1)°, V = 2760.6(4) Å^3, Z = 4; colorless prismatic crystals, 5458 reflections (2299 unique) were collected (no significant decay). For both structures, data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structures were solved by direct methods, using SIR92 (ref 14) and refined by full-matrix least squares on F^2 using SHELXL97 (ref 15). Final disagreement factors, **4a**: $R_1 = 0.0653$ (data with $I > 2\sigma(I)$ and $R_1 = 0.0954$ (all data). **5a**: $R_1 = 0.0703$ (data with $I > 2\sigma(I)$ and $R_1 = 0.0887$ (all data). The electron densities of the diiodide moiety in both compounds and the amine molecule in **4a** were modeled using rigid body restraints. For both compounds, hydrogen atoms were placed at calculated positions and refined in the riding mode.

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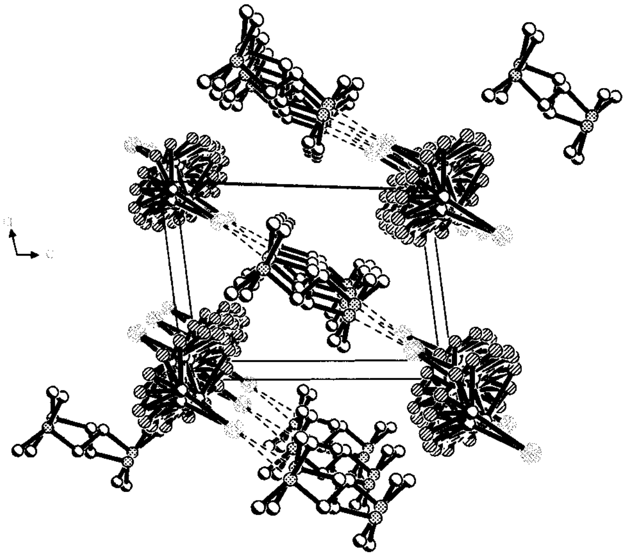

Figure 1. Crystal packing of cocrystal **4a** viewed down the *b* axis. Molecules segregate into distinct layers joined by N···I−C interactions (dotted lines). The disorder of both species was modeled using rigid body restraints. The amine is adequately represented by two images of equal occupancy, the diiodide moiety was described by splitting the carbon and the fluorine atoms over four locations. The average N···I distance is 2.84(0.03) Å, and the average value of the N···I−C angle is 166.2(0.7)°.

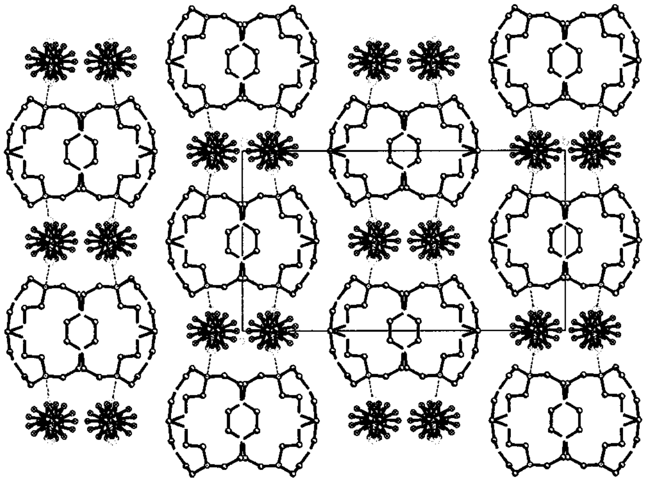

Figure 2. Crystal packing of cocrystal **5a** viewed down the *c* axis. The diiodide moiety was modeled using rigid body restraints. The disorder involving carbon atoms was described by splitting each atom over two locations with occupancy 0.5, while the disorder involving fluorine atoms was described by splitting each atom over four locations. The N···I distance is 2.796(0.008) Å, and the N···I−C angle is 168.6(0.7)°.

perfluoroalkyliodides and iodine in cocrystal formation also holds for the N···I−C angle, which is close to 180° for both **4a** and **5a**.

In both cocrystals **4a** and **5a**, the perfluorinated diiodoethane moiety of **1a** exhibits dramatic rotational disorder around the axis joining the two iodines, these two atoms being the only nondisordered atoms of **1a**. In the crystal of **4a**, all of the atoms of the diamine, including the nitrogens, also exhibit disorder over two positions corresponding to distinct conformers or to different molecular orientations. Both PFC and HC units **1a** and **2**, respectively, are liquids as pure compounds at room temperature, and in cocrystal **4a** they are highly disordered; thus, the N···I interaction must be indeed largely responsible for crystal cohesion. Note that in **4a**, the hydrocarbon amine and the perfluorinated diiodide segregate into layers (perpendicular to the *c* crystallographic axis) which are joined by N···I interactions running roughly along the (111) direction. A qualitative measure of the importance of the interaction between **1a** and **2** results from the fact that the molar volumes of the liquids **1a** and **2** are reduced by 21% in the cocrystallization process to give **4a**. These data seem particularly significant since in the cocrystals the PFC and the HC components segregate and the volume reduction must result at the interface between the two components. The general reluctance of PFC and HC moieties to mix is apparent also from the structure of **5a** (Figure 2). Because of the different steric requirements of the two cocrystallizing species, the structure is not characterized by layers, the diamine **3** forms in the cocrystal a 3D network of ordered molecules interacting through dispersive forces, and the disordered perfluorinated diiodide **1a** gives rise to pairs of segregated and parallel columns linked to the diamine by the N···I interactions.[19]

Differential scanning calorimetry analyses of networks **4** and **5** also proved that a specific binding is occurring between the HC and the PFC “bricks”. After pure **1a** and **2** are cooled, exothermic transitions of crystallization are observed at −28 °C ($\Delta H = -11.0$ kJ·mol^{-1}) and at −64 °C ($\Delta H = -12.3$ kJ·mol^{-1}), respectively. Both these exotherms are missing in the cooling curve of **4a** which shows instead a characteristic exothermic transition at −76 °C ($\Delta H = -1.3$ kJ·mol^{-1}) related to an ordering process of both the hydrocarbon and fluorocarbon components as confirmed by X-ray studies at different temperatures to be discussed elsewhere.[21]

Results described in this paper show that the nitrogen−iodine interaction is strong enough to overcome the low affinity existing between PFC and HC compounds. These results offer new opportunities in the design and manipulation of molecular aggregation processes and may be useful in many fields. For instance, this interaction can drag hydrocarbon reagents/catalysts into fluorocarbon solvents, thus offering an alternative to the “perfluorinated ponytail” approach.[22] Perfluorinated compounds, for example, do not dissolve hydrocarbon porphyrins, but addition of perfluoro *n*-heptyliodide to the suspensions has been found to induce porphyrin dissolution.[23]

Supporting Information Available: Tables of crystallographic data, selected IR absorption bands, ^{19}F NMR chemical shifts, and DSC analyses (31 pages, print/PDF). An X-ray crystallographic file, in CIF format, for **4a** and **5a** is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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(19) Other proofs of the interaction between PFC diiodides **1** and HC diamines **2** and **3** come from vibrational spectra of networks **4** and **5** (KBr pellets, 500−4000 cm^{-1}). These spectra were not the sum of the absorption bands of precursors **1**−**3**, and since the N···I interaction is weaker than that of covalent or ionic bonds, it is reasonable to discuss spectra of **4** and **5** in terms of modified modes of **1**−**3**. The C−H stretching modes of donor amines **2** and **3** in the 2760−2950 cm^{-1} region shifted to higher frequencies in chains **4** and **5** (ref 20) and as for the acceptor iodides **1**, the C−F stretching modes in the 1100−1220 cm^{-1} region moved to lower frequencies.

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(23) Other useful applications can be anticipated in the field of bioactive compounds. The interaction of iodine atoms of thyroid hormones with donor sites in the target protein has been suggested (ref 24) and the occurrence of similar C−X···El interactions can be proposed to explain some stereospecific bindings (ref 25) between chiral volatile anaesthetics and proteins in the brain.

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