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### Perfluorocarbon-Hydrocarbon Discrete Intermolecular Aggregates: An Exceptionally Short N...I Contact

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# Perfluorocarbon–Hydrocarbon Discrete Intermolecular Aggregates: An Exceptionally Short N···I Contact\*

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**1-Iodoperfluoroheptane (1a) and tetramethylethylenediamine (2, TMEDA) form the 2:1 ratio stable aggregate 3a and a similar behaviour is shown by 1-iodoperfluoroalkanes 1b–e and iodopentafluorobenzene 1f. These aggregates have been characterised in solution by <sup>1</sup>H/<sup>19</sup>F-NMR spectroscopy and in the solid state through IR and single crystal X-ray diffraction. The determined structure of 3a (triclinic, *a* = 6.2283(10), *b* = 9.250(2), *c* = 15.098(3) Å,  $\alpha$  = 81.369(5),  $\beta$  = 81.397(5),  $\gamma$  = 86.010(5), *V* = 849.3(3) Å<sup>3</sup>, *T* = 175(3) K, space group P-1 (No. 2), *Z* = 1; *d*(calc) = 2.167 g cm<sup>-3</sup>; 4121 independent reflections, 3665 with *I*<sub>o</sub> > 2(*I*<sub>σ</sub>); final refinement gave *R*1 = 0.0400, *wR*2 = 0.0901) showed the second shortest N···I interaction found in the crystallographic literature [2.762(3) Å] and the interdigitation of perfluorocarbon and hydrocarbon modules due to co-operative –C–H···F–C– interactions. Calculations to quantify these latter interactions have been also performed.**

**Keywords:** Halogen bonding; Perfluoroalkyl chains; Thin films; –C–H···F–C– contacts

## INTRODUCTION

It is well known that perfluoroalkyl compounds adopt a twisted, helical structure while the corresponding hydrocarbon parents prefer a zigzag chain arrangement. It has been proposed that this helical structure is responsible, among others, for

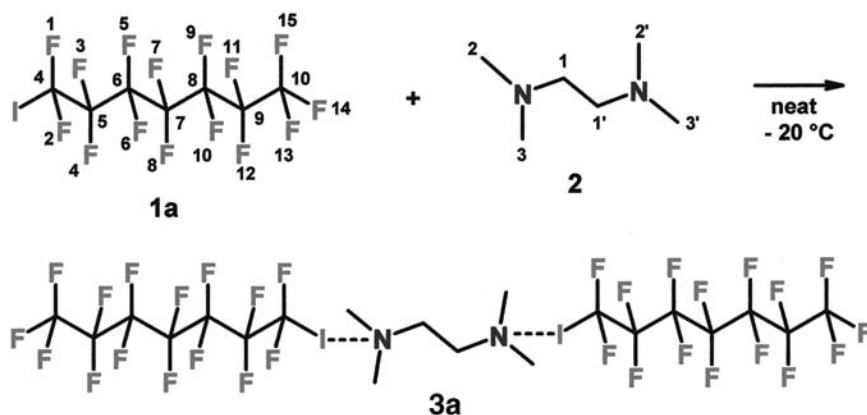
the very rich phase behaviour and properties of the chemically quite simple polymer polytetrafluoroethylene (PTFE) [1].

Due to their unique combination of chemical and physical properties [2], e.g. low frictional character, high compressibilities, high surface activity, low cohesive pressures, perfluorocarbon compounds in pure form are not convenient candidates for a detailed solid state analysis through single crystal X-rays diffraction. Consistent with the great tendency of perfluoro derivatives to form waxes and the related difficulty to grow suitable crystals, a careful survey of the Cambridge Structural Database has revealed that a quite limited number of perfluoroalkyl chains with more than four CF<sub>2</sub> units has been characterised and until now a single example of perfluoroheptyl residue has been reported [3].

In the recent years the search for fluorine-phase [4–6] soluble reagents and catalysts prompted the synthesis of numerous compounds bearing fluoroalkyl appendages or “pony tails” such as (CH<sub>2</sub>)<sub>*y*</sub>(CF<sub>2</sub>)<sub>*x*</sub>CF<sub>3</sub>. These solid and crystalline compounds, where the perfluoroalkyl chain is covalently bound to the hydrocarbon moiety which is responsible for the compound crystallinity, have become the derivatives most frequently used by the structural chemist in order to study perfluoroalkyl chain peculiar properties [7–9].

\*Perfluorocarbon–hydrocarbon self-assembly. Part 13. For part 12 see Ref [10].

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SCHEME 1 Schematic diagram representing the formation of trimer **3a** starting from 1-iodoperfluoroheptane (**1a**) and *N,N,N',N'*-tetramethylethylenediamine (**2**). The single atom numbering adopted in the X-ray structure discussion of co-crystal **3a** has been indicated on starting modules **1a** and **2**.

In the present work we explore single non-covalent bonds as an alternative approach to connect organic and fluoroorganic components.

## RESULTS AND DISCUSSION

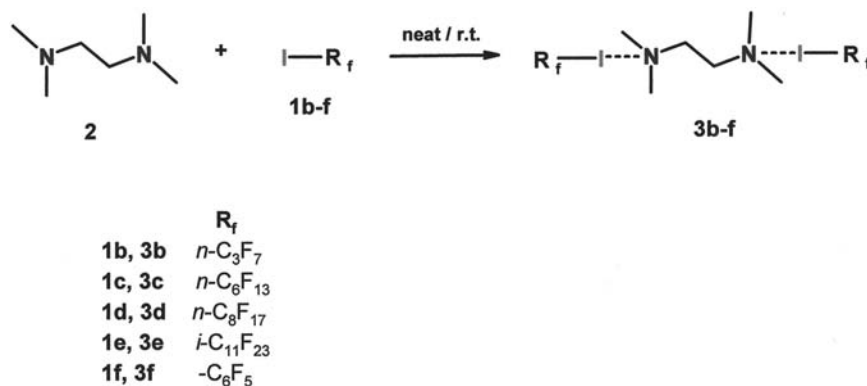
$\alpha,\omega$ -Diiodoperfluoroalkanes (acidic modules) form solid non-covalent co-polymers when interacting with bidentate electron donors (basic modules) such as aliphatic diamines [10–13]. The formation of the supramolecular architecture is driven by  $N \cdots I - R_f$  intermolecular halogen bonds [14–18]. The low affinity between the hydrocarbon and perfluorocarbon modules [2] is overcome in these self-assembled systems by the strength of this interaction which experimental measurements [19,20] and theoretical calculations [21,22] prove to be of *ca.* 7 kcal mol<sup>-1</sup>.

The ability of monoiodo-perfluorocarbons to behave similarly giving solid and discrete co-crystals is here shown by using iodoperfluorocarbons (**1a–f**) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, **2**).

## Synthesis and NMR Studies

On standing in the cold ( $-20^\circ\text{C}$ ), a 2:1 mixture of 1-iodoperfluoroheptane (**1a**) and TMEDA **2**, (m.p.  $-8$  and  $-64^\circ\text{C}$ , respectively), affords the co-crystal **3a** which melts slightly over room temperature ( $52$ – $53^\circ\text{C}$ ) (Scheme 1). In this co-crystal the 2:1 ratio of the iodoperfluoroalkane and hydrocarbon diamine modules was established by microanalysis (C, H, F, N, I) and peak integration of the  $^1\text{H}/^{19}\text{F}$ -NMR spectra in the presence of  $(\text{CF}_3\text{CH}_2)_2\text{O}$  as internal standard. Upfield shift of the  $\text{CF}_2$  group geminal to the iodine atom was observed in the  $^{19}\text{F}$ -NMR spectrum of the co-crystal **3a** compared to the pure iodide **1a**. The magnitude of the shift decreased on dilution but increased when TMEDA **2** was added to the solution thus confirming that perfluorocarbon and hydrocarbon modules interact through an halogen bonding which gives rise to association equilibria which are rapid on the NMR time scale [23–25].

Electron donation from nitrogen to iodine was shown in the solid by IR spectroscopy (KBr pellets). Most of the bands of the acid and basic modules, **1a** and **2**, respectively, are present in the co-crystal **3a**



SCHEME 2

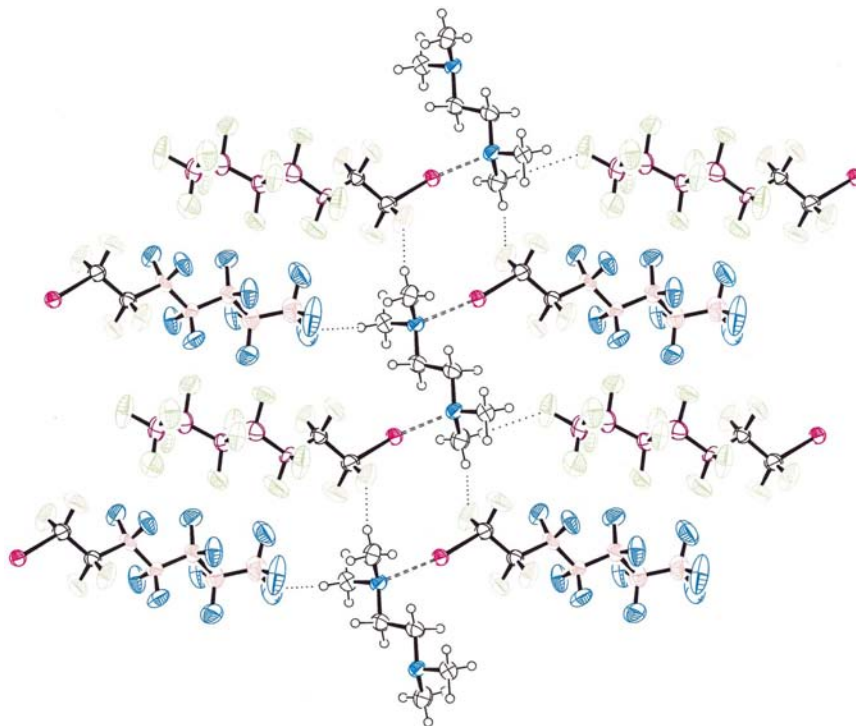


FIGURE 1 Packing draw of co-crystal **3a** along *b* axis showing the N···I bond (dashed lines) and the H···F interactions shorter than 2.75 Å (dotted lines). Due to the structural disorder, we draw an artificially simplified plot: Only the molecules  $T_1^+$  and  $T_2^+$  (see text) are drawn, assuming space group *P1*, to emphasize all possible intermolecular interaction without clearness loss. Ellipsoids at 50% probability level; H atoms not to scale. Colours are as follows: Blu, nitrogen; red, iodine; black: hydrogen and ordered carbons; olive green, ordered and unseparated fluorines; orange and dark green: disordered carbons and fluorines of  $T_1^+$  conformation; brown and light green, disordered carbons and fluorines of  $T_2^+$  conformation.

and the expected [26,27] modifications of the absorptions of the pure modules on co-crystal formation are also observed. For instance, the C–H stretching mode of pure electron donor **2** (2700–3000  $\text{cm}^{-1}$  region) are shifted to higher frequencies in trimer **3a** and a similar behaviour has already been observed when the same base or other secondary and tertiary amines formed electron donor–acceptor complexes with halogens, interhalogens, haloperfluorocarbons [28,29].

The halogen bonding effectiveness in forming trimers which melt higher than single modules is emblematically shown by the trimer **3b** which melts at  $-2^\circ\text{C}$  while the starting 1-iodoperfluoropropane (**1b**) melts at  $-95^\circ\text{C}$  (Scheme 2). Similarly, co-crystals **3c–f** all melt higher than starting 1-iodoperfluoroalkanes **1c–e** and iodoperfluorobenzene **1f** (e.g. **1d** and **3d** melt at 25 and  $56^\circ\text{C}$ , respectively). While the correlation between intermolecular interaction strength and melting point cannot be quantified, this thermal behaviour is consistent with the formation of well-defined molecular aggregates on interaction of iodides **1** and amine **2** and points to the occurrence of strong non-covalent bindings. In general, it can thus be stated that halogen bonding driven self-assembly of perfluorocarbon iodides and hydrocarbon diamines forms aggregates which are solid at room temperature not only when one

dimensional infinite chains are produced, but also when discrete intermolecular complexes are formed.

### Crystallography

The molecular parameters and the lattice organisation of co-crystal **3a** were firmly established through single crystal X-ray diffraction study obtained at 175 K (Fig. 1). The key structural unit in the packing is the  $\text{CF}_3(\text{CF}_2)_6\text{–I}\cdots\text{TMEDA}\cdots\text{I}(\text{CF}_2)_6\text{CF}_3$  trimer which lies on a centre of symmetry of the crystal lattice. In this trimer two 1-iodoperfluoroheptane molecules are bound to one TMEDA molecule through halogen bonding between the nitrogen and iodine atoms. Consistent with the  $n \rightarrow \sigma^*$  character of the interaction, the C–I···N angle in co-crystal **3a** is  $172.4(1)^\circ$ , a value slightly larger than in structurally related infinite chains given by TMEDA and other diamines with various  $\alpha,\omega$ -diiodoperfluoroalkanes [10–13]. The value of the N···I–R<sub>f</sub> distance is 2.762(3) Å, namely longer than the average N–I covalent bond (2.07 Å) [30], approximately 0.8 times the sum of the van der Waals radii for nitrogen and iodine [31], comparable with the N···I distance shown by numerous complexes formed by  $\text{I}_2$  [32–35]. Indeed, the N···I–C intermolecular distance here observed is only 0.05 Å longer than the shortest N···I–C interaction reported in the crystallographic

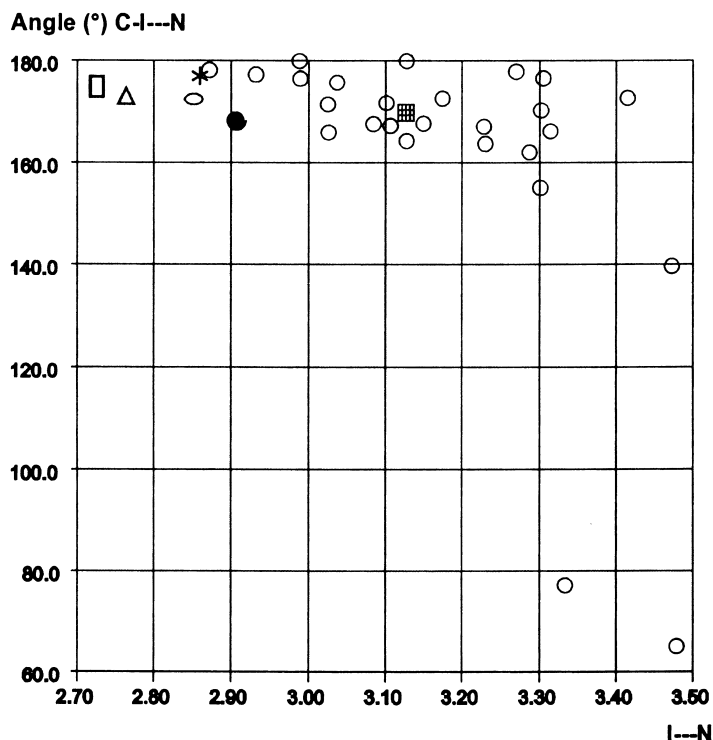


FIGURE 2 Scatterplot of C-I...N angles versus N...I distances for intermolecular C-I...N interactions: Only error free and non-polymeric structures showing no disorder and with  $R < 0.06$  are reported. (□) Co-crystal between 1-iodo-2-phenylacetylene and morpholine (Ref. [36]); co-crystal between 1-iodoperfluoroheptane and TMEDA (this paper). (\*) co-crystal between 1,4-diiodotetrafluorobenzene and 4,4'-bipyridine (Ref. [22]). (○) Co-crystal between 1,8-diiodoperfluorooctane and K.2.2. (Ref. [11]). (●) Co-crystal between bis-pyridylmethyl-tetra-tert-butylcalix[4]arene and 1,4-diiodotetrafluorobenzene (Ref. [13]). (▨) Co-crystal between 4'-(4-methylphenyl)-2,2':6',2''-terpyridine 1,4-diiodotetrafluorobenzene (Ref. [12]).

literature [36], namely the 1-iodo-2-phenylacetylene/morpholine complex (the structure of which was determined at 150 K).

The neighbouring group effect on the electron accepting properties of a given halogen atom has been widely recognised, introduction of electron withdrawing residues resulting into stronger interactions [37] as recently shown, among others, with polynitroiodoarenes [38]. Fluorine for hydrogen substitution in alkyl halides has already been observed to enhance the halogen bonding strength in solution [39]. As shown by a Cambridge Structural Database search (CSD version 5.1.10, 1 October 2000, 224,000 crystal structures having atomic co-ordinates available, Fig. 2), iodoperfluoroalkanes routinely give rise to quite short N...I-C contacts, probably due to the quite high group electronegativity [40] of perfluorocarbon residues.

In solution [41] and when chelating metal cations [42] TMEDA 2 preferentially adopts a *gauche* conformation. Differently in co-crystal 3a the two nitrogen atoms are pinned by the halogen bonding in a *trans* arrangement, as is the case in the structurally related infinite chain formed with 1,2-diiodotetrafluoroethane [10–13].

The N...I-R<sub>f</sub> interaction is largely responsible for keeping iodoperfluorocarbon 1a and hydrocarbon diamine 2 in place in the well-defined

CF<sub>3</sub>(CF<sub>2</sub>)<sub>6</sub>-I...TMEDA...I(CF<sub>2</sub>)<sub>6</sub>CF<sub>3</sub> unit. As a result all the TMEDA atoms and the I-CF<sub>2</sub>- group atoms are ordered while the remaining -(CF<sub>2</sub>)<sub>5</sub>CF<sub>3</sub> part of the perfluoroheptyl chain exhibits dramatic rotational disorder which has been modelled by splitting atoms over two locations. The separation of the CF<sub>2</sub> group atoms β to the iodine in the two conformers is too small to be refined; but it becomes large enough to be modelled for the remaining -(CF<sub>2</sub>)<sub>4</sub>CF<sub>3</sub> part of the chain. The perfluoropentyl residue was refined with soft restraints over two equally populated locations. The two conformations have opposite winding that we designate with T<sub>1</sub><sup>+</sup> and T<sub>2</sub><sup>-</sup> in the general *x,y,z* position (T<sub>1</sub><sup>-</sup> and T<sub>2</sub><sup>+</sup> in *-x, -y, -z*). Each tail in fact deviates from the exact *trans* planar conformation as torsion angles are significantly different from 180°, being all positive in T<sub>1</sub><sup>+</sup> and all negative in T<sub>2</sub><sup>-</sup>. The torsion angles along the T<sub>1</sub><sup>+</sup> spiral, C4-C5-C6A-C7A-C8A-C9A-C10A are in the sequence 168.7(7), 170.5(9), 165.6(9), 168.6(10)° and those along the T<sub>2</sub><sup>-</sup> spiral, C4-C5-C6B-C7B-C8B-C9B-C10B are in the sequence -165.1(7), -165.8(9), -165.5(9), 166.5(10)°. This twisting probably minimises the intramolecular fluorine repulsion between 1,3-positioned difluoromethylene groups and similar behaviour has been frequently observed in long [43] and short [44] perfluoroalkyl chains despite the fact that exceptions



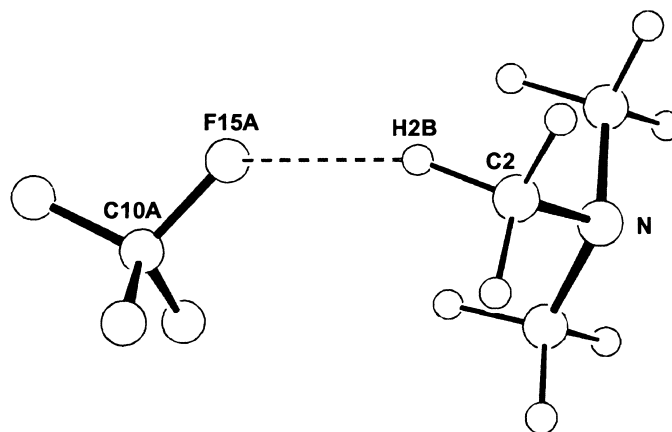


FIGURE 3 Pattern of the H $\cdots$ F interaction obtained for the CF $_4$ /N(CH $_3$ ) $_3$  model system in the first (constrained) step of the MP2/6-31G\*\* geometry optimisation.

have been recently reported [45] (for instance, three minima with C–C–C–C torsion angles of about 166, 95, and 54° have been described for an  $n$ -C $_4$ F $_9$  segment) [46].

The divergence from 180° of the torsion angles along the chain (C4–C5–C6–C7–C8–C9–C10) observed in co-crystal **3a** is significantly more pronounced than that found in the only other perfluoroheptyl chain studied by X-rays [3] (where the torsion angles range from 175.6 to 178.9°); however a detailed comparison can hardly be made due to the high atomic displacement parameters reported for this literature structure, the data of which were collected at 293 K. Probably, the X-ray acquisition temperature greatly affects the possibility to detect the deviation from the exact *trans* planar conformation in perfluoroalkyl chains, since lower temperatures freeze minimum energy conformations, favouring their detection. In fact, in co-crystal **3a** the average absolute torsion angle along the cited chain is 167.0(1.8)°, as established at 175 K, and this value nicely matches with the average torsion angle of 169.0(3.4)° established at 193 K for an iridium phosphine carrying a perfluoro-hexyl chain [47]. The perfluoroheptyl chain in **3a** is anchored to the hydrocarbon part of the complex with a non-covalent bond while the perfluoro-hexyl chain is bound to the iridium-phosphine complex with a covalent bond. This definitively proves the ability of the halogen bond to lock perfluorinated chains and to favour their structural analyses by X-ray.

Segregation of the perfluorocarbon and hydrocarbon modules has been frequently found in supramolecular architectures related to the co-crystal **3a** [10–13,48], but surprisingly in this case it does not occur. While the N $\cdots$ I–R $_f$  interaction is largely responsible for the presence of the CF $_3$ (CF $_2$ ) $_6$ –I $\cdots$ TMEDA $\cdots$ I(CF $_2$ ) $_6$ CF $_3$  well-defined unit in the co-crystal, weak H $\cdots$ F interactions also play a role in determining the packing of these units

in the co-crystal as they fasten the –CF $_2$ I and –CF $_3$  ends of the perfluorinated chain to the amine methyl groups. These stabilising H $\cdots$ F interactions are preferred over H $\cdots$ H and F $\cdots$ F interactions [49] and result in the observed interdigitated structure (Fig. 1) in which halogen and hydrogen bonds cooperate in determining the relative arrangement of the perfluorocarbon and hydrocarbon modules. As depicted in Fig. 1, two different patterns of such H $\cdots$ F interactions involve the –CF $_3$  tail group of iodoperfluoroheptane **1a**. For  $T_1^+$ , a linear H $\cdots$ F hydrogen bond is implied, measuring the interaction F15A $_{x-1,y,z-1}\cdots$ H2B 2.56(6) Å and the angle F15A $_{x-1,y,z-1}\cdots$ H2B–C2 164(4)°. For  $T_2^+$ , there is a longer hydrogen interaction, namely F14B $_{x-1,y,z-1}\cdots$ H3C [2.71(5) Å] with the angle F14B $_{x-1,y,z-1}\cdots$ H3C–C3 equal to 159(4)° and another even longer hydrogen interaction, namely F15B $_{x,y,z-1}\cdots$ H3C [2.85(5) Å]. Other three H $\cdots$ F interactions in the range 2.72–2.79 Å, namely F1 $_{1-x,1-y,-z}\cdots$ H2C, F1 $_{1-x,1-y,-z}\cdots$ H3B, and F2 $_{1-x,1-y,-z}\cdots$ H3B, probably contribute to stabilise the structure by pinning the –CF $_2$ I head of **1a** in a single position.

### Molecular Modelling Studies

To better characterise the nature of these –C–F $\cdots$ H–C– interactions and to compare their relative strength with respect to the halogen bonding, *ab initio* calculations on the CF $_4$ /N(CH $_3$ ) $_3$  model system in the gas-phase were performed. The pattern of the shortest H $\cdots$ F interaction observed in the experimental structure and discussed above is shown in Fig. 3, where the C1 $_{-x,-y,-z}$  atom bonded to C1 is replaced by an H atom at the correct C–H equilibrium distance.

The geometry of the dimer reported in Fig. 3 was taken as input for an MP2/6-31G\*\* geometry optimisation. Owing to the packing forces and the greater dimensions of the real system, this input

conformation is of course expected to be very far from the minimum energy one. It should also be noted that several minima are to be expected, because of the large number of F atoms on one monomer and of H atoms on the other one.

To gain an insight about the hydrogen bonding in the experimental structure, optimisation was then performed by two steps. First, all bond distances and angles and the relative distance between the monomers were relaxed, while among the dihedral angles only those defining the positions of the H atoms not involved in the interaction were optimised. In this way, in the optimised geometry, the relative disposition of one monomer with respect to the other well reproduced the experimental one, as indicated for example by the distance between C10 and N [4.91 versus 4.94(1) Å] and the dihedral angle F15'–C10'···N–C2 [80.4 versus 82.1°(9)]. Obviously, this constrained geometry does not correspond to a true minimum on the potential energy surface (two imaginary frequencies were obtained), but it can be usefully compared with the experimental one. The F15'···H2B distance and the F15'···H2B–C2 angle measure 2.685 Å and 149.6°, respectively, in good agreement with the experimental values above reported. The interaction energy, defined here as the energy difference between the total electronic energy of the dimer and the electronic energies of the fully relaxed isolated monomers, was  $\Delta E = 0.81 \text{ kcal mol}^{-1}$ .

In the second step all co-ordinates were simultaneously optimised and a true minimum was gained, where three F atoms are faced and nearly eclipsed to three H atoms, each of them belonging to a different CH<sub>3</sub> group, giving rise to three F···H bonds. For all three hydrogen bonds F···H = 2.716 Å and the angles F···H–C are equal to 168.3, 168.6 and 168.8°. The interaction energy grows to 2.4 kcal mol<sup>-1</sup>, which, if compared with the  $\Delta E$  of the constrained geometry, should suggest for the present system a sort of additivity in the energy associated to a single F···H bond. Further optimisation of this geometry with a more accurate basis set, namely 6-311++G\*\*, gives an interaction energy of 3.3 kcal mol<sup>-1</sup>, and F···H distances = 2.932 Å and the angles F···H–C are equal to 172.5°. We can then conclude that the linear –C–F···H–C– interaction in co-crystal **3a** is a weak hydrogen bonding with an energy of approximately 1 kcal mol<sup>-1</sup>. For both the basis sets used, the C–H distances corresponding to the bonds involved in the interaction are always greater than the other ones, as is usually the case in hydrogen bonds.

Similar results were experimentally obtained on the CF<sub>2</sub>H<sub>2</sub> dimer by rotationally resolved spectroscopy [50], where a symmetrical structure with eclipsed F and H atoms was predicted to give rise to three H bonding. The binding energy associated to

each C–F···H–C linkage was estimated to be about 0.5 kcal mol<sup>-1</sup>. At variance with our results, *ab initio* calculations performed on this dimer within a similar level of theory show evidence of “anti-hydrogen bond” character, with shortening of the C–H bond length and blue shifting of the  $\nu_{\text{C-H}}$  band.

Our results are perfectly in agreement with those reported by Desiraju and others [49] which described similar H···F distances. They also observed that usually compounds containing only carbon, hydrogen, and fluorine atoms are more appropriate to assess the viability of the –C–F···H–C– interaction as, due to the weakness of the interaction, the presence of proton acceptors that are stronger and more polarisable than the C–F group usually prevents the –C–F···H–C– linkage from playing a significant structural role in crystal packing. In co-crystal **3a** nitrogen atoms are present, but the weak –C–F···H–C– interaction nevertheless occurs and plays a role in inducing module interdigitation and preventing the expected segregation, as nitrogen is involved in the formation of the strong halogen bonding. Indeed, the preferential involvement of nitrogen atoms in halogen rather than hydrogen bonds has already been observed in related systems [19]. Even if stronger interactions are on the disposal to the crystal engineer for his rational design, the structure of co-crystal **3a** confirms [49] how the sum of several of these weak –C–F···H–C– contacts in a crystalline lattice add stabilisation to the system and influence its overall packing.

## CONCLUSIONS

The formation and the properties of the solid co-crystal **3a** are described in the detail. In this co-crystal the well defined structural unit is a trimer where two molecules of 1-iodoperfluoroheptane (**1a**) and one molecule of TMEDA **2** are bound through strong N···I halogen bonds resulting in an exceptionally short N···I–C distance. The packing of these structural units into an interdigitated lattice is controlled by a network of weak –C–F···H–C– hydrogen bonds. Conformational preferences of the perfluoroheptyl chains in co-crystal **3a** are studied and the system is proposed as an experimental model [51] to study the conformational preferences and segmental motions in fluoropolymer chains, these latter properties influencing the mechanical behaviour of fluoropolymers.

The stability of the discussed discrete intermolecular aggregates **3a–f** along with the strength, specificity, and directionality of the halogen bonding allows the non-covalent deposit of fluorinous coating layers. The halogen bonding between a perfluoroalkyl iodide and an electron donor residue grafted to a metal surface can thus be pursued as an

innovative approach in thin film chemistry. There is a great interest in the deposition of perfluorinated monolayers [52] on conveniently functionalised surfaces and the obtained results make the halogen bonding driven perfluorinated monolayers deposition a feasible target.

The relevance of the reported results extends to quite different fields spanning from crystal engineering to material science. Due to their inertness to chemical attack and to their poor affinity towards non-fluorinated organics as well as aqueous solutions, perfluoroalkyl compounds have desirable properties as coating materials. A few examples of fluorinated coating of metallic surfaces have been obtained by chemisorption of fluorinated long-chain thiols onto a gold surface [53]. Possible fields of interest include chemical sensing and nanolithographic techniques [54–56], friction reduction and enhancement of water-repellent properties of surfaces [57,58]. Self-assembled and perfluoroalkylated monolayers have also been deposited onto the surface of gold colloidal particles [59,60] without any loss of stability of the colloidal dispersion; potential applications range from biosensors to optoelectronics.

## EXPERIMENTAL

### General Methods

All materials were obtained from commercial suppliers and were used without further purification. Reagent grade solvents were used without further purification. Elemental analyses were performed by Redox S.n.c., Cologne Monzese, Milano, Italy.  $^1\text{H}/^{19}\text{F}$ -NMR spectra were recorded on a Bruker AV 500 spectrometer at 25°C, chemical shifts ( $\delta$ ) are given in ppm,  $\text{CDCl}_3$  was used as solvent and tetramethylsilane and  $\text{CFCl}_3$  as internal standards.

### Co-crystal **3a** Formed by 1-iodoperfluoroheptane (**1a**) and TMEDA **2**

Crystallisation at  $-20^\circ\text{C}$  from chloroform of a 2:1 mixture of 1-iodoperfluoroheptane (**1a**) and TMEDA **2** afforded the white and crystalline solid **3a**, m.p. (neat)  $52\text{--}53^\circ\text{C}$ . Elemental analyses (%): calculated for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{I}_2\text{F}_{30}$ , C 21.67, H 1.45, N 2.53, I 22.90, F 51.44; found C 21.22, H 1.48, N 2.81, I 23.32, F 51.17.  $^{19}\text{F}$ -NMR: Pure 1-iodoperfluoroheptane (**1a**) (0.16 M)  $\delta_{\text{-CF}_2\text{I}} = -59.65$ ;  $\delta_{\text{-CF}_2\text{CF}_2\text{I}} = -113.65$ ; co-crystal **3a**:  $\Delta\delta_{\text{-CF}_2\text{I}} = \delta_{\text{pure1e}} - \delta_{\text{3e}} = 2.40$ ;  $\Delta\delta_{\text{-CF}_2\text{CF}_2\text{I}} = \delta_{\text{pure1e}} - \delta_{\text{3e}} = 0.20$ . In another experiment  $^1\text{H}$  and  $^{19}\text{F}$ -NMR spectrum were registered in the presence of 2,2,2-trifluoroethyl ether as an internal standard. On calibrating integration parameters so that in the  $^1\text{H}$ -NMR spectrum the  $\text{CH}_2\text{O}$  quartet of

2,2,2-trifluoroethyl ether was corresponding to four and in the  $^{19}\text{F}$ -NMR spectrum the  $\text{CF}_3$  triplet of 2,2,2-trifluoroethyl ether was corresponding to six, the ratio of the  $\text{-CF}_2\text{-I}$  signal area (deriving from **1a**) and the  $\text{N}(\text{CH}_3)_2$  signal area (deriving from **2**) is 1:3 thus revealing that the **1a**:**2** ratio in **3a** is 2:1 IR (KBr pellets, selected bands) 2966, 2876, 2840 1249, 1202, 1147, 644,  $560\text{ cm}^{-1}$ .

### X-ray Data of Co-crystal **3a**

$(\text{C}_6\text{H}_{16}\text{N}_2)_2 \cdot 2(\text{C}_6\text{F}_{15}\text{I})$ ,  $F_w = 1108.14$ , triclinic,  $a = 6.2283(10)$ ,  $b = 9.250(2)$ ,  $c = 15.098(3)\text{ \AA}$ ,  $\alpha = 81.369(5)$ ,  $\beta = 81.397(5)$ ,  $\gamma = 86.010(5)^\circ$ ,  $V = 849.3(3)\text{ \AA}^3$ ,  $T = 175(3)\text{ K}$ , space group  $\text{P}\bar{1}$  (No. 2),  $Z = 1$ ;  $\mu(\text{Mo-K}\alpha) = 2.035\text{ mm}^{-1}$ ;  $d_{\text{calc.}} = 2.167\text{ g cm}^{-3}$ . Because the compound shows a very high vapour pressure, a colourless crystal, cut to a cube of about 0.5 mm, was allowed to sublime in few minutes to a sphere of about 0.2 mm diameter, then dipped with a perfluorinated oil, put on a glass capillary and quickly frozen to the experiment temperature. Data were collected on a Bruker SMART diffractometer equipped with a low temperature device. Because of the risk of crystal cracking, we did not reach the lowest possible temperature;  $\omega\text{-}2\theta$  scan mode; 8760 reflection collected below  $2\theta < 58.86^\circ$ ; 4121 independent (merging  $R_{\text{av}} = 0.0234$ ), 3665 with  $I_o > 2\sigma(I_o)$ . No absorption correction was applied because of the crystal form and because an attempt to correct data with *SADABS* [61] gave a worsening of  $R_{\text{av}}$ . The structure was solved by direct methods (*SIR-92*) [62] and the refinement was carried on by full-matrix least-squares based on  $F^2$  (*SHELXL-97*) [63].

The refinement of the disordered part of the perfluoroalkyl chain was carried on by using 540 restraints, both on the geometry and on the thermal parameters. Final refinement gave  $R_1 = 0.0400$ ,  $wR_2 = 0.0901$ , goodness-of-fit = 1.041 for all data, 420 parameters using weights  $w = 1/[\sigma^2(F_o)^2 + (0.0561P)^2 + 0.4123P]$ , where  $P = (F_o^2 + 2F_c^2)$ ; the final map range was  $-0.38 < \Delta\rho < 2.20\text{ e\AA}^{-3}$ , being the maximum residue at  $0.77\text{ \AA}$  away from the iodine atom.

### Computational Studies

Calculations were performed using the PC GAMESS version [64] of the GAMESS (US) QC package [65].

### Co-crystal **3b** Formed by 1-iodoheptafluoropropane (**1b**) and TMEDA **2**

On mixing pure 1-iodoheptafluoropropane (**1b**) and TMEDA **2** in a 2:1 ratio, after a few days at  $-4^\circ\text{C}$  the white and crystalline solid **3b** precipitated, m.p. (neat)  $-2^\circ\text{C}$ .  $^1\text{H}/^{19}\text{F}$ -NMR analyses in the presence of 2,2,2-trifluoroethyl ether as internal standard (see



co-crystal **3a**) proved the 2:1 ratio of **1b** and **2** in **3b**.  $^{19}\text{F}$ -NMR: Pure 1-iodoheptafluoropropane (**1b**) (0.16 M):  $\delta_{-\text{CF}_2\text{I}} = -60.52$ ;  $\delta_{-\text{CF}_2\text{CF}_2\text{I}} = -118.21$ ; co-crystal **3e**:  $\Delta\delta_{-\text{CF}_2\text{I}} = \delta_{\text{pure1e}} - \delta_{3\text{e}(0.16\text{M})} = 2.38$ ;  $\Delta\delta_{-\text{CF}_2\text{CF}_2\text{I}} = \delta_{\text{pure1e}} - \delta_{3\text{e}(0.16\text{M})} = 0.23$ . IR (liquid film, selected bands) 2977, 2945, 2866, 2822, 2771, 1465, 1230, 1209, 1118, 1030, 815  $\text{cm}^{-1}$ .

### Co-crystal **3c** Formed by 1-iodoperfluorohexane (**1c**) and TMEDA **2**

On mixing at r.t. pure 1-iodoperfluorohexane (**1c**) and TMEDA **2** in a 2:1 ratio, immediate precipitation of the white and crystalline solid **3c** occurred, m.p. (neat) 34–36°C. Elemental analyses: (%): calculated for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{I}_2\text{F}_{26}$ , C 21.43, H 1.59, N 2.78, I 25.19, F 49.01; found C 21.02, H 1.61, N 3.05, I 25.58, F 48.67.  $^1\text{H}/^{19}\text{F}$ -NMR analyses in the presence of 2,2,2-trifluoroethylether as internal standard (see co-crystal **3a**) confirmed the 2:1 ratio of **1c** and **2** in **3c**.  $^{19}\text{F}$ -NMR: Pure 1-iodoperfluorohexane (**1c**) (0.16 M):  $\delta_{-\text{CF}_2\text{I}} = -59.68$ ;  $\delta_{-\text{CF}_2\text{CF}_2\text{I}} = -113.62$ ; co-crystal **3e**:  $\Delta\delta_{-\text{CF}_2\text{I}} = \delta_{\text{pure1e}} - \delta_{3\text{e}(0.16\text{M})} = 2.41$ ;  $\Delta\delta_{-\text{CF}_2\text{CF}_2\text{I}} = \delta_{\text{pure1e}} - \delta_{3\text{e}(0.16\text{M})} = 0.24$ .

### Co-crystal **3d** Formed by 1-iodoperfluorooctane (**1d**) and TMEDA **2**

On mixing at 25°C pure 1-iodoperfluorooctane (**1d**) and TMEDA **2** in a 2:1 ratio, immediate precipitation of the white and crystalline solid **3d** occurred, m.p. (neat) 56–58°C. Elemental analyses: (%): calculated for  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{I}_2\text{F}_{34}$ , C 21.85, H 1.32, N 2.32, I 21.03, F 53.48; found C 21.42, H 1.35, N 2.61, I 21.41, F 53.17.  $^1\text{H}/^{19}\text{F}$ -NMR analyses in the presence of 2,2,2-trifluoroethylether as internal standard (see co-crystal **3a**) confirmed the 2:1 ratio of **1d** and **2** in **3d**.  $^{19}\text{F}$ -NMR: Pure 1-iodoperfluorooctane (**1d**) (0.16 M)  $\delta_{-\text{CF}_2\text{I}} = -59.61$ ;  $\delta_{-\text{CF}_2\text{CF}_2\text{I}} = -113.67$ ; co-crystal **3e**:  $\Delta\delta_{-\text{CF}_2\text{I}} = \delta_{\text{pure1e}} - \delta_{3\text{e}(0.16\text{M})} = 2.53$ ;  $\Delta\delta_{-\text{CF}_2\text{CF}_2\text{I}} = \delta_{\text{pure1e}} - \delta_{3\text{e}(0.16\text{M})} = 0.26$ .

### Co-crystal **3e** Formed by Perfluoroisoundecyl Iodide (**1e**) and TMEDA **2**

On mixing at 25°C a chloroform solution (0.1 M) of perfluoroisoundecyl iodide (**1e**) and pure TMEDA **2** in a 2:1 ratio, after the evaporation of the solvent, the precipitation of the white and crystalline solid **3e** occurred, m.p. (neat) 57–58°C. Elemental analyses: (%): calculated for  $\text{C}_{28}\text{H}_{16}\text{N}_2\text{I}_2\text{F}_{46}$ , C 22.28, H 1.06, N 1.86, I 16.84, F 57.96; found C 21.95, H 1.10, N 2.15, I 17.21, F 57.61.  $^1\text{H}/^{19}\text{F}$ -NMR analyses in the presence of 2,2,2-trifluoroethylether as internal standard (see co-crystal **3a**) proved the 2:1 ratio of **1e** and **2** in **3e**.  $^{19}\text{F}$ -NMR: Pure perfluoroisoundecyl iodide (**1e**) (0.16 M):  $\delta_{-\text{CF}_2\text{I}} = -59.63$ ;  $\delta_{-\text{CF}_2\text{CF}_2\text{I}} = -113.61$ ;

co-crystal **3e**:  $\Delta\delta_{-\text{CF}_2\text{I}} = \delta_{\text{pure1e}} - \delta_{3\text{e}(0.16\text{M})} = 2.51$ ;  $\Delta\delta_{-\text{CF}_2\text{CF}_2\text{I}} = \delta_{\text{pure1e}} - \delta_{3\text{e}(0.16\text{M})} = 0.25$ .

### Co-crystal **3f** Formed by 1-iodopentafluorobenzene (**1f**) and TMEDA **2**

On mixing at 25°C pure 1-iodopentafluorobenzene (**1f**) and TMEDA **2** in a 2:1 ratio, immediate precipitation of the white and crystalline solid **3f** occurred, m.p. (neat) 52–53°C.  $^1\text{H}/^{19}\text{F}$ -NMR analyses in the presence of 2,2,2-trifluoroethylether as internal standard (see co-crystal **3a**) proved the 2:1 ratio of **1f** and **2** in **3f**.  $^{19}\text{F}$ -NMR: 1-iodopentafluorobenzene (**1f**) (0.16 M):  $\delta_{\text{F}_o} = -119.39$ ;  $\delta_{\text{F}_p} = -152.34$ ;  $\delta_{\text{F}_m} = -159.57$ ; co-crystal **3f**:  $\Delta\delta_{\text{F}_o} = \delta_{\text{pure1f}} - \delta_{3\text{f}} = +0.32$ ;  $\Delta\delta_{\text{F}_p} = \delta_{\text{pure1f}} - \delta_{3\text{f}(0.16\text{M})} = +0.49$ ;  $\Delta\delta_{\text{F}_m} = \delta_{\text{pure1f}} - \delta_{3\text{f}(0.16\text{M})} = +0.23$ . IR (KBr pellets, selected bands) 2963, 2872, 2836, 2792, 1482, 1079, 969, 863, 794  $\text{cm}^{-1}$ .

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