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Hydrogen bonding and halogen bonding co-existing in the reaction of heptafluorobenzyl iodide with *N*,*N*,*N*′,*N*′-tetramethylethylene diamine

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Abstract—Two novel assembling systems **3** and **4**, with the structures of $C_6F_5CF_2^{-}\cdots H^{+}N(Me)_2CH_2CH_2(Me_2)N^{+}H\cdots{}^{-}CF_2C_6F_5$ and $C_6F_5CF_2I\cdots N(Me)_2CH_2CH_2(Me)_2N\cdots ICF_2C_6F_5$, respectively, have been generated from the solution of heptafluorobenzyl iodide **1** and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine **2** in dichloromethane. Their structures have been characterized by X-ray diffraction analysis, NMR and IR spectroscopy. Intermolecular N···I halogen bond and F···H hydrogen bond are revealed to be the driving forces for their formation.

The attractive intermolecular interaction between fluorocarbon iodides R_FI (working as Lewis acids) and heteroatom substituted hydrocarbons (working as Lewis bases) had been observed in early 1950s by Haszeldine who also first emphasized the effectiveness of fluorine in strengthening this kind of noncovalent interaction.[1] This unique I···D (R_F = perfluoroalkyl, D = N, O or S) interaction between R_FI and various functionalized organic bases had been rationalized as a $n \rightarrow \delta^*$ donation process[2] and recently called as ‘halogen bonding’ to stress its similarity with hydrogen bonding.[3] In recent years, several co-crystals with infinite chain structures have been assembled by using the N···I halogen bond between bidentate acceptors and donors, such as diiodo-PFCs and dinitrogen-HCs.[4] The O···I halogen bond-driven co-complexes of endless chains has also been engineered from α,ω-diiodoperfluoroalkanes $I(CF_2CF_2)_nI$ and 1,4-dioxane or HPMA.[5]

Hydrogen bonding has been most frequently applied to assemble organic supramolecular systems in solid, liquid or gas phase because of its strength and directivity.[6] Recently, Resnati and co-workers had devised a competitive experiment to directly compare the role of halogen bond and hydrogen bond in driving the assembling process between 1,4-diiodotetrafluorobenzene and 1,2-bis(4-pyridyl)ethane and hydroquinone and found that halogen bond is more effective than hydrogen bond in controlling the construction of programmed supramolecular architectures of this system.[7] In this paper, we describe that two different intermolecular noncovalent interactions, that is, the N···I halogen bond and $^{+}N\text{–}H\cdots F$ hydrogen bond can also occur simultaneously in the self-assembly of new supramolecular systems from monoiodoperfluorocarbon $C_6F_5CF_2I$ **1** and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) **2**.

When a 2:1 solution of **1** and **2** in dichloromethane was slowly evaporated, two solid products were isolated,[8] both of which are white crystalline solid and are stable in the air at room temperature (Scheme 1).

The first solid that was isolated from the above reaction was characterized as the salt $C_6F_5CF_2^{-}\cdots H^{+}N(Me)_2CH_2CH_2(Me)_2N^{+}H\cdots{}^{-}CF_2C_6F_5$ **3** (mp 134 °C). Such a product should have been generated by the attack of the nitrogen atom of **2** on the iodine of **1**, followed with a hydrolysis process due to the moisture in the air. These processes could be illustrated as in Scheme 2.

Keywords: Perfluoroalkyl iodide; Diamine; Hydrogen bond; Halogen bond; Co-crystal.

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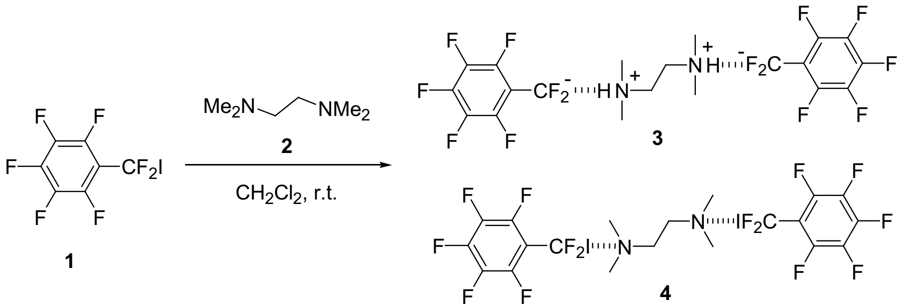

Scheme 1.

$$C_6F_5CF_2I + Me_2NCH_2CH_2NMe_2 \xrightarrow[r.t.]{CH_2Cl_2} C_6F_5CF_2^-\ IN^+(Me)_2CH_2CH_2(Me)_2N^+I\ {}^-CF_2C_6F_5$$

$$\xrightarrow[r.t.]{moisture} C_6F_5CF_2^-\ HN^+(Me)_2CH_2CH_2(Me)_2N^+H\ {}^-CF_2C_6F_5 + 2\,HOI$$

$$2\,HOI \longrightarrow I_2 + H_2O + 0.5\,O_2$$

Scheme 2.

Single crystal X-ray diffraction analysis of **3** revealed that strong hydrogen bond existed between N_1–$H_9\cdots F_2$ (Fig. 1).[9] The distance between H_9 and F_2 is 1.795 Å, while the distance between N_1 and F_2 is 2.660 Å. The N_1–$H_9\cdots F_2$ bond is nearly linear (the angle is approximately 176.9°). In contrast, the distance between H_9 and F_1 is 2.844 Å and the angle of N_1–$H_9\cdots F_1$ is about 105°. These observations indicate that no important interaction occurred between H_9 and F_1. The bond length of C_1–F_1 (1.220 Å) is slightly shorter than the C_1–F_2 (1.239 Å), which is hydrogen bonded. However, both are pronouncedly shorter than the normal C–F bond length (1.35 Å) (Table 1).

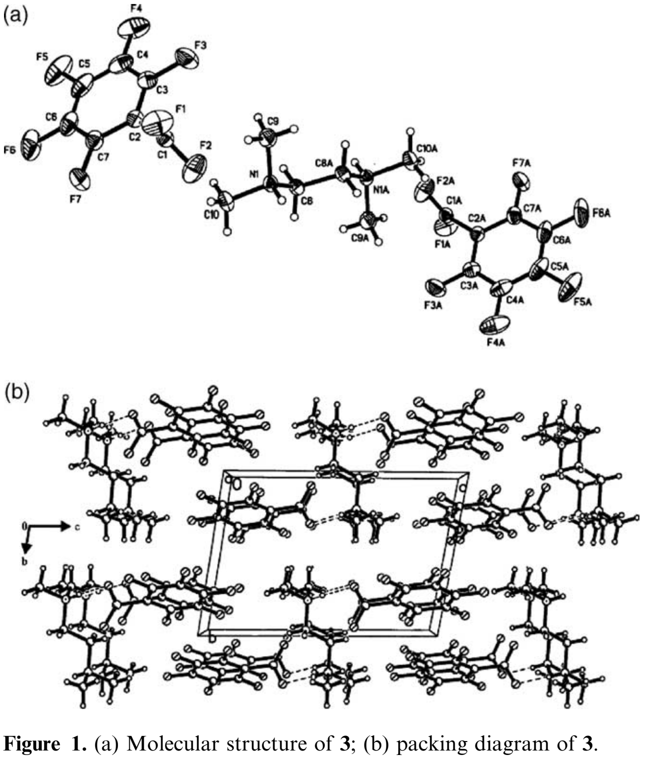

Figure 1. (a) Molecular structure of **3**; (b) packing diagram of **3**.

The ^{19}F NMR spectrum of **3** showed large difference, as compared to that of heptafluorobenzyl iodide **3**. All the signals shifted upfield (Table 2) due to the perfluorobenzyl group being negatively charged. The two fluorine atoms of the difluoromethylene group also became chemically unequivalent ($\delta_{F(1)}$ −156.3 ppm, $\delta_{F(2)}$ −140.2 ppm) due to the F_2 atom, which was hydrogen bonded.

Another solid product, which was precipitated after 2 days from the solution, was characterized to be the 2:1 co-crystal $C_6F_5CF_2I\cdots N(Me)_2CH_2CH_2(Me)_2N\cdots ICF_2C_6F_5$ **4**. The crystal melts at 39–40 °C, while both starting materials **1** and **2** are liquid at room temperature (**1**: bp 152 °C, **2**: bp 120 °C). Single crystal X-ray analysis of **4** revealed strong N···I halogen bond existing in the complex. The N···I–C bond distance is 2.799 Å, which is substantially shorter than the sum of the Van der Waals radii of nitrogen (1.55 Å) and iodine

Table 1. Selected bond lengths (Å) and angles (°) of **3** and **4**

Compound	Bond length (Å)	Angle (°)
3	F(2)···H(9) 1.795(2)	N(1)–H(9)···F(2) 176.8(9)
	F(1)···H(9) 2.844(2)	N(1)–H(9)···F(1) 105.4(2)
	C(1)–F(1) 1.220(3)	F(1)–C(1)–F(2) 127.5(2)
	C(1)–F(2) 1.239(3)	F(1)–C(1)–C(2) 117.2(2)
	C(3)–F(3) 1.343(3)	F(2)–C(1)–C(2) 115.3(2)
4	N(1)···I(1) 2.799(1)	N(1)···I(1)–C(7) 177.5(8)
	C(7)–I(1) 2.177(6)	I(1)–C(7)–C(1) 111.6(4)
	C(1)–C(7) 1.508(10)	F(6)–C(7)–C(1) 110.6(6)
	C(7)–F(6) 1.345(8)	F(7)–C(7)–C(1) 111.4(6)
	C(7)–F(7) 1.347(9)	F(6)–C(7)–F(7) 105.8(6)

Table 2. ^{1}H NMR and ^{19}F NMR spectra data of the compounds **1**, **3** and **4**

Compound	^{1}H NMR		^{19}F NMR			
	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(CF_2)$	δ(*o*-F)	δ(*m*-F)	δ(*p*-F)
1			−36.93	−139.50	−148.53	−159.62
2	2.23	2.39				
3			−140.20(1F) to −156.30(1F)	−144.30	−164.10	−164.13
4	2.25	2.42	−37.64	−140.30	−149.10	−160.46
1+5[a]			−37.12	−139.80	−148.75	−159.93
1+5[b]			−37.58	−139.98	−149.06	−160.01

[a] The ratio of **1** and **5** is 2:1 in ($CDCl_3+CCl_4$).
[b] The ratio of **1** and **5** is 1:1 in ($CDCl_3+CCl_4$).

(1.98 Å). The N···I–CF$_2$ angle is 177.5 (8)°, indicating that the contact of N with I is nearly 'head on'. The linearity of N···I–C moiety[10] is consistent with the n → δ* electron donation from nitrogen to iodine (Fig. 2).[2,11] Co-crystal **4** represents the first example of solid aggregates from fluorinated benzyl iodides, although many co-crystals have been reported, which are assembled from diiodoperfluoroalkanes or dibromoperfluoroalkanes or arenes and bidentate electron donors.[4]

IR and NMR studies provided further evidences for the formation of the noncovalent interaction in the new solid systems. For example, the $\nu_{C\text{–}H}$ absorptions appeared at 2972 and 2766 cm^{-1} for **2**,[12] but shifted to 2980 and 2872 cm^{-1} in co-crystal **4**. This result is correlated with the higher positive charge on the H atoms in **4** than in pure **2**. The difference in the chemical shifts in the ^{1}H and ^{19}F NMR spectra between adduct **4** and the starting modules **1** and **2** is another sensitive parameter for probing the relative strength of the two interactions. The observed differences, $\Delta\delta_F$: $[\Delta\delta_{F(1)} - \Delta\delta_{F(4)}] > 0.6$ ppm and $\Delta\delta_H$: $[\Delta\delta_{H(4)} - \Delta\delta_{H(2)}] > 0.02$ ppm confirmed the donor–acceptor property if the halogen bond and proved that the N···I–R$_F$ interactions also existed in solution (see Table 2).

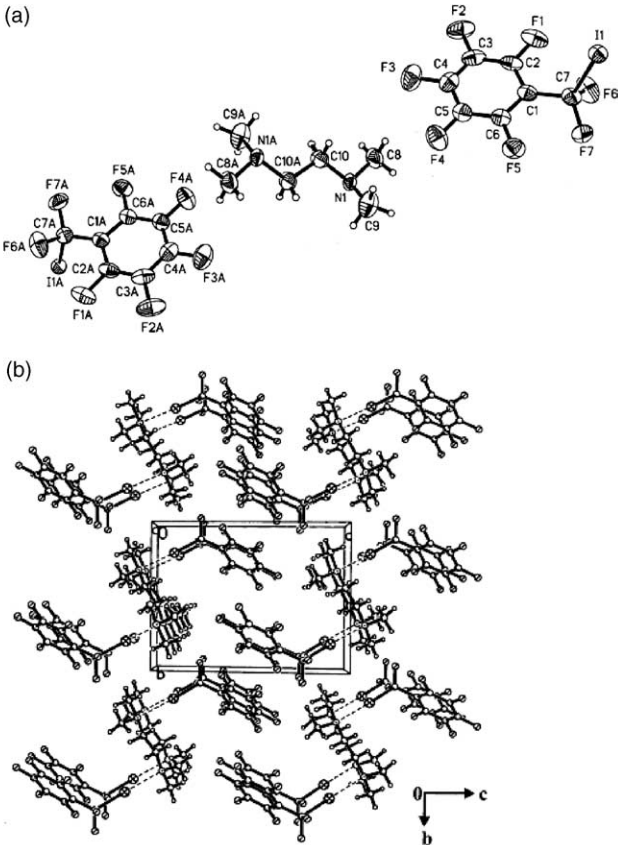

Figure 2. (a) Molecular structure of **4**; (b) packing diagram of **4**.

Previously, it has been reported that pyrazine **5** could interact with α,ω-diiodoperfluoroalkanes to afford distinct co-crystals.[4] Mixing **5** with **1** did not yield any solid product, although ^{19}F NMR spectra indicated the (sp^2) N···I interaction occurred. This result demonstrates that this noncovalent interaction is not strong enough to afford isolated halogen bonded product.

In conclusion, the results described in this paper demonstrate how *N*,*N*,*N*′,*N*′-tetramethylethlene diamine **2** is involved in the halogen bonding and hydrogen bonding driven recognition process, respectively, with heptafluorobenzyl iodide **1**. Both the N···I and N$^+$H···F interactions are strong enough to overcome the affinity existing between **1** and **2** to give co-crystals **3** and **4**, respectively. These results offer new opportunities in the design and manipulation of molecular aggregation processes and may be useful in many fields.

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8. A solution of **1** (1.72 g, 5.00 mmol), **2** (0.29 g, 2.50 mmol) and dichloromethane (8 mL) in a 25 mL flask was stirred at room temperature for 20 min, the volatile solvent was allowed to diffuse. After 1 day, some light red solid **3** (0.62 g) was formed, which was filtered out, washed with *n*-hexane, and re-crystallized from chloroform, to give white fine crystal (mp 134 °C), which was suitable for X-ray diffraction analysis. After 2 days, light red solid **4** (0.6 g) was precipitated, it was crystallized from chloroform and hexane (1:1), to give needle crystal (mp 39–41 °C). Elemental analysis for **3**: calcd for $C_{20}H_{18}F_{14}N_2$: C, 43.49; H, 3.28; N, 5.07; F, 48.15. Found: C, 43.20; H, 3.41; N, 4.89; F, 47.88. Elemental analysis for **4**: calcd for $C_{20}H_{16}F_{14}N_2I_2$: C, 29.87; H, 2.01; N, 3.48; F, 33.08. Found: C, 29.49; H, 1.71; N, 3.36; F, 32.86.
9. Crystal data for co-crystal **3**: CCDC: 215348, Formula: $C_{10}H_9F_7N_1$; $M_r = 276.18$; crystal system triclinic, space group $P1$; temperature 293 K; $a = 6.0089(10)$ Å, $b = 8.3298(13)$ Å, $c = 11.6566(18)$ Å, $\alpha = 98.641(3)°$, $\beta = 93.199(3)°$, $\gamma = 102.216(3)°$, $V = 561.44(15)$ Å^3; $Z = 2$, $D_c = 1.634$ g/cm^{-3}, μ (Mo-Kα) 0.178 mm^{-1}, $F(000) = 278$, 2962 collection reflections, 2061 independent, 199 refined parameters, $[I > 2\sigma(I)]$ $R_1 = 0.0604$, $wR_2 = 0.1782$.
10. Crystal data for co-crystal **4**: CCDC: 215347, Formula: $C_{20}H_{16}F_{14}N_2I_2$; $M_r = 804.15$; crystal system triclinic, space group $P1$; temperature 293 K; $a = 6.0496(11)$ Å, $b = 9.1935(17)$ Å, $c = 12.236(2)$ Å, $\alpha = 89.282(4)°$, $\beta = 81.713(3)°$, $\gamma = 88.829$ (2)°, $V = 673.3(2)$ Å^3; $Z = 1$, $D_c = 1.983$ g/cm^{-3}, μ (Mo-Kα) 2.445 mm^{-1}, $F(000) = 382$, 4147 collection reflections, 2988 independent, 175 refined parameters, $[I > 2\sigma(I)]$ $R_1 = 0.0516$, $wR_2 = 0.1051$.
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