Fluorine-containing donor-acceptor complexes: crystallographic study of the interactions between electronegative atoms (N, O, S) and halogen atoms (I, Br)

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On the basis of our results, which concern $sp^3N\cdots Br–R_f$ [R_f = per(poly)fluoroalkyl], $sp^3O\cdots I–R_f$, $sp^2O\cdots I–R_f$, $sp^3N\cdots I–R_f$, $sp^2N\cdots I–R_f$ and interactions of $sp^2N\cdots I–R_f$ with different substituents, a brief profile of the interactions between electronegative atoms (N, O, S) and halogen atoms (I, Br) of fluorine-containing alkylates is determined. The first example of an aliphatic fluorine-containing donor-acceptor supramolecule that is based on the $N\cdots Br–R_f$ interaction is reported in this paper. Our X-ray structure shows that 1,2-dibromotetrafluoroethane and 1,4-dimethylpiperazine alternately form endless chains depending on the $N\cdots Br–R_f$ interactions. The distance between Br and N is 2.864(3) Å, which is considerably longer than the average covalent bond between N and Br, but it is also definitively shorter than the sum of the corresponding van der Waals radii of N and Br. From two other crystals, we successfully obtained precise data on the $sp^3O\cdots X–R_f$ and $sp^2O\cdots X–R_f$ interactions. Furthermore, an investigation of the substituent group effect is presented. We also report a valuable method to recrystallize and collect X-ray data of co-crystals that are easily disordered.

Introduction

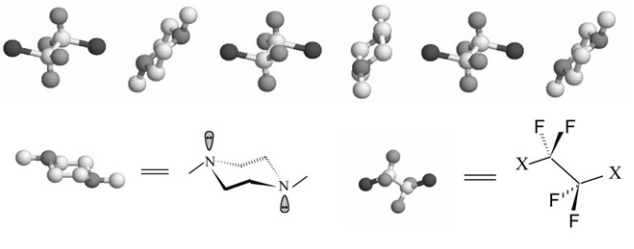
The importance of donor-acceptor (or charge-transfer) interactions has been recognized for many decades.[1–4] With the emergence of template-directed synthesis,[5] crystal engineering,[4a,6] supramolecular chemistry and self-assembly,[7] studies of all interactions between molecules are becoming more and more important. Consequently, halogen bonding,[8] which has been recognized as being similar to hydrogen bonding,[9,10] has recently become popular. One of the most attractive systems is the fluorine-containing donor-acceptor complexes.[11–15] The introduction of per(poly)fluoroalkane into complexes provides enormous opportunities to tune the physical and chemical properties of the resulting complexes.[13e,16]

Though much work has been conducted in the field,[8b,11–14] most of the literature is focused on $N\cdots I–R_f$ interactions. To understand the nature of this kind of intermolecular interaction, it is essential to investigate the whole $B\cdots X–R_f$ (B = base, X = halogen) halogen bonding family and compare them with each other. With this in mind, we report seven crystal structures that have been synthesized and analyzed in this contribution.

Results and discussion

Amongst the different halogens, the tendency to form $X\cdots B$ interactions follows the order I > Br > Cl, which parallels the order of their polarizabilities.[3b,17] Similarly, the donor-acceptor interaction in $B\cdots Br–R_f$ is weaker than that in $B\cdots I–R_f$.[8b,13b] Despite there being reports of many perfluorocarbon-hydrocarbon supramolecular self-assemblies,[11–14] few complexes containing the $B\cdots Br–R_f$ interaction have been reported and discussed.[12a] Unsuccessful attempts to achieve this kind of interaction were reported in recent work.[8b,13b]

In this contribution, we present the first case of aliphatic fluorine-containing donor-acceptor complexes based on the $N\cdots Br–R_f$ interaction (Scheme 1). From an equimolar mixture of 1,2-dibromotetrafluoroethane (**1a**) and 1,4-dimethylpiperazine (**2**) in chloroform, complex **3** was isolated as colorless crystals. The crystal packing of **3** is shown in Fig. 1. The endless chains of alternating **1a** and **2** molecules are formed by $N\cdots Br–R_f$ interactions. The distance between Br and N is 2.864(3) Å. This is considerably longer than the average covalent bond between N and Br, (1.843 Å),[18] but is also definitively shorter than 3.40 Å, the sum of the corresponding van der Waals radii of N (1.55 Å)[19] and Br (1.85 Å).[19] The interaction compares well with the $N\cdots I–R_f$ interaction in complex **4** between 1,2-diiodotetrafluoroethane (**1b**) and **2**; the structure



X = Br **3**; X = I **4**

Scheme 1

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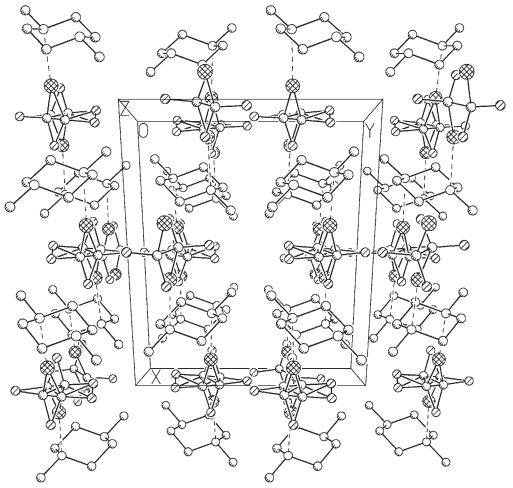


Fig. 1 Crystal packing of **3** viewed down the *c* axis. Two kinds of molecules are distinctly joined by N···Br–R_f interactions (dotted lines).

of **4** is shown in Fig. 2. Both of the endless chains of alternating 1,2-dihalogentetrafluoroethane and **2** depend on nitrogen-halogen interactions running in a direction roughly equal to the axial direction in cyclohexane. The angle of two 1,4-dimethylpiperazine molecules that are connected by a **1b** molecule is almost orthogonal.

It is interesting to notice that the bond angles of N···Br–R_f are 165.5(3)° and 168.0(3)°. These are closer to the values of the N···I–R_f angles [170.2(2)° and 167.1(2)°] in complex **4** than that of the reported N···Br–R_f [172.2(9)°] in the aromatic fluorine-containing complex **5**, which is formed of 1,2-bis(4-pyridyl)ethane and 1,4-dibromotetrafluorobenzene.[12a] Meanwhile, The Br···N distances are only marginally longer than that of N···I–R_f [2.818(3) Å] in its analog **4**, but significant shorter than the Br···N–R_f distance [3.025(9) Å] in the reported aromatic fluorine-containing interaction. It is normally assumed that bond distances may serve as indicators of bond strength with the shorter distance associated with the stronger bond. Thus, R_f–Br also can form a stable complex with the Lewis-base-like R_f–I. In addition, under the same reaction conditions, $ClCF_2CF_2Cl$ failed to give any complex with compound **2**. These results confirm the reported tendency to undergo interactions, which is R_f–I > R_f–Br > R_f–Cl.[13e]

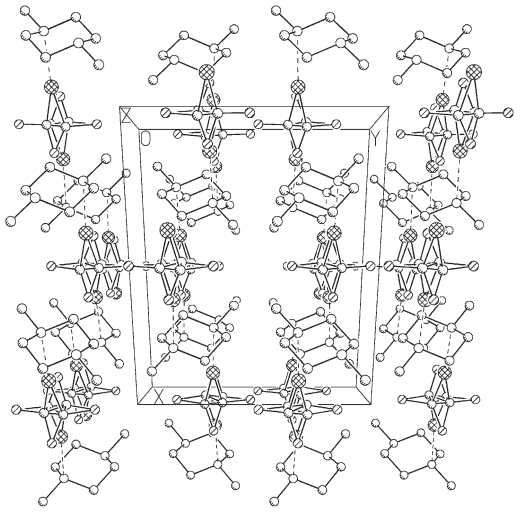


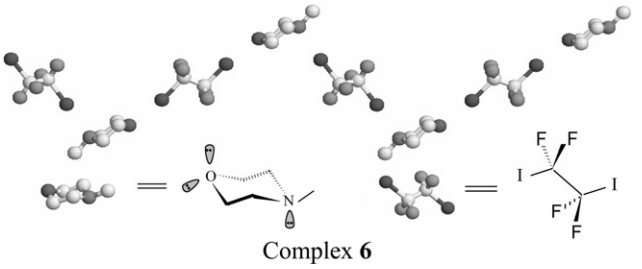
Fig. 2 Crystal packing of **4** viewed down the *c* axis. Two kinds of molecules are distinctly joined by N···I–R_f interactions (dotted lines).

After achieving the synthesis of the supramolecular complex containing the N···Br–R_f interaction, we turned to the O···I–R_f and S···I–R_f[12b] interactions. Previously, we reported two kinds of O···I–R_f interactions in a communication.[14] However, the complex formed by the sp^3O···I–R_f interaction is unstable at room temperature. At the same time another group observed a O^-···I–R_f interaction;[13a] however, to get precise X-ray data of uncharged O···I–R_f remained a problem. The reaction of 1,2-diiodotetrafluoroethane (**1b**) with an equimolecular quantity of *N*-methylmorpholine in chloroform leads to the formation of the corresponding complex **6** (Scheme 2) in quantitative yield, from which we successfully collected precise bonding length and angle data on the sp^3O···I–R_f interactions.

It is worth noting that N···I–R_f and O···I–R_f appear alternately in pairs in complex **6** (see Fig. 3). While the bond length of N···I–R_f [2.817(3) Å] is highly consistent with its analog **4**, the bond length of O···I–R_f [2.862(3) Å] is slightly, but obviously, longer than the bond length [2.814(12) Å] in its reported analog **8** (Scheme 3), which is formed by reaction of **1b** with 1,4-dioxane (**7**). Both of the sp^3O···I–R_f interactions in complexes **6** and **8** exist near to the equatorial direction. In contrast, all sp^3N···I–R_f and sp^3N···Br–R_f interactions in **3**, **4** and **6** run in a direction roughly equal to the axial direction because the methyl groups on the N atoms have taken the equatorial direction.

Interestingly, 1,2-diiodotetrafluoroethane (**1b**) reacts readily with hexamethylphosphoramide (HMPA, **9**) to give a colorless crystal of **10** (Fig. 4). In this special case, R_f–I does not interact with sp^3N but rather with sp^2O, though normally the N atom is generally a better lone electron pair donor than the O atom in donor-acceptor systems.[13e] We attribute this special case to not only the electron charge distribution[13a] but also to the molecular structure of HMPA. Thus, a selective supramolecular synthesis containing this weak interaction is realized as a consequence of these factors.

Meanwhile, from complex **10**, we also obtained precise data on the sp^2O···I–R_f interaction. The O···I distances are only



Complex **6**

Scheme 2

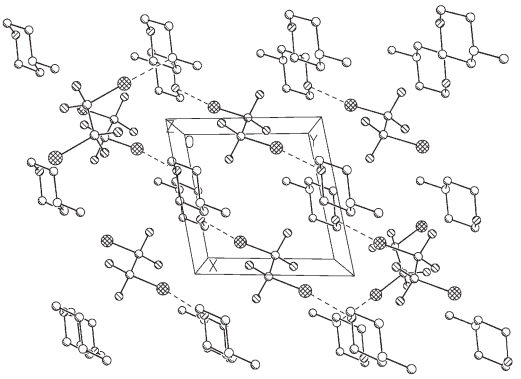
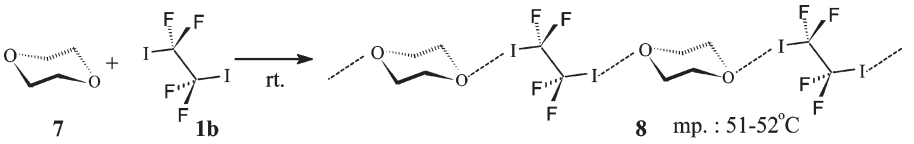


Fig. 3 Crystal packing of **6** viewed down the *c* axis. Two kinds of molecules are distinctly joined by O···I–R_f and N···I–R_f interactions (dotted lines).



Scheme 3

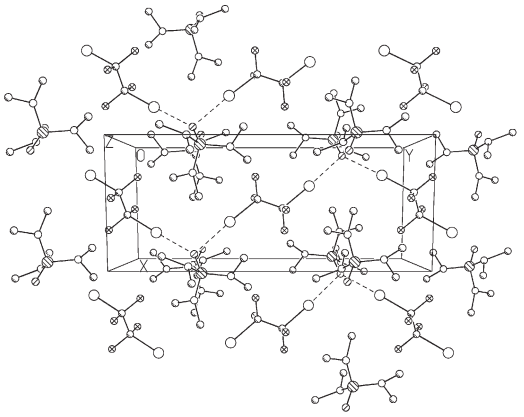


Fig. 4 Crystal packing of **10** viewed down the *c* axis. Two kinds of molecules are distinctly joined by O···I–R_f interactions (dotted lines).

2.808(5) and 2.824(5) Å, respectively, a little shorter than the ones in its HMPA···I$(CF_2CF_2)_2$I (**11**) analog.[14] The comparison illuminates that increasing the length of the CF_2 chain will decrease the strength of the sp^2O···I–R_f interaction in the system. This conclusion also agrees with the order of melting points given in Scheme 4. Furthermore, the relative strength can be quantitatively shown by *P* (distance/sum of van der Waals radii) and *Q* (distance/covalent bond length), which can be a pair of indicators of the relative strength of a certain interaction. The smaller they are the stronger is the interaction. All the *P* and *Q* values of complex **10** are smaller than those of complex **11** (Table 1).

Based on ^{19}F NMR chemical shift differences of 1,2-dihalotetrafluoroethane in different solvents, the literature reported that the order in which the R_f–X···El [R_f = per(poly)fluorper(poly)fluoroalkyl] interaction became weaker was N > S ≥ O.[11b,c] But, we find that the melting point of supramolecular complex **8** of **1b** with 1,4-dioxane (**7**) is 51–52 °C,[14] while a mixture of **1b** and 1,4-oxathiane is still liquid even at −20 °C. At the same time, 1,4-dithiane and **1b** also failed to give a complex at room temperature (Scheme 5).

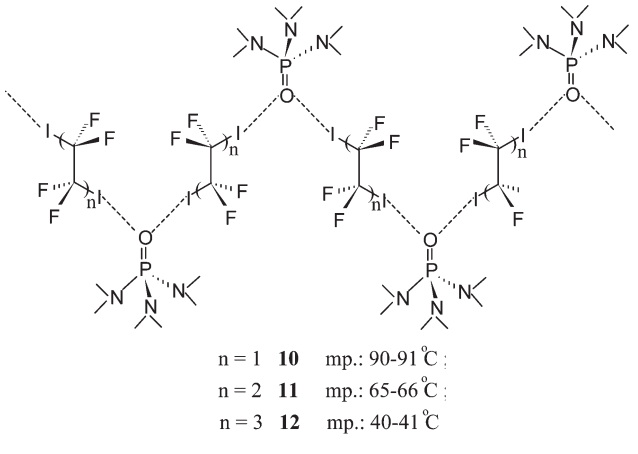
Furthermore, from an equimolar mixture of 1,2-diiodotetrafluoroethane (**1b**) and 2-methylbenzothiazole (**13**) in chloroform, the complex **14** (Scheme 6) was isolated as a yellowish crystal. S···I–R_f interactions are not present in the complex. The distances between S and I are 3.894(1) and 4.123(1) Å, clearly longer than 3.78 Å, the sum of the corresponding van der Waals radii of I (1.98 Å)[19] and S (1.80 Å).[19] The crystal packing map of complex **14** is shown in Fig. 5. An equimolar complex of **1b** and **13** was not formed even as we increased the molar ratio of **1b** in the reaction.

On the basis of these experimental results, the S atom should be ranked last in ability to form co-crystals with R_f–I. This might be partly because of the existence of an S–S interaction in these systems. This is a particular case of soft-hard theory.[20] Our explanation is that the powerful electron-withdrawing ability of the R_f group pulls and holds much of the electron cloud from the I atom, making it less soft when it interacts with a base.

Thus, though studying chemical shifts of the –CF2– groups geminal to the halogen atom in ^{19}F NMR spectra is helpful to understand halogen bonding,[14] it can be fallible to use them to predict the stability of the obtained solid state complexes.[13b] The success of getting stable complexes based on the N···Br–R_f interaction and the above stability ordering of HMPA···I$(CF_2CF_2)_n$I (n = 1–3), whose –CF2– chemical shifts have been reported in our previous work,[14] also support this conclusion.

To investigate how different kinds of substituent groups effect the donor-acceptor interaction we reacted 1,2-diiodotetrafluoroethane (**1b**) with pyrazine, 2-methylpyrazine, ethylpyrazine (**15**) and pyrazinecarbonitrile (**16**). Complexes **17**, **18** and **19**, which are based on sp^2N···I interactions, were formed (see Schemes 7 and 8).

There are two main effects on the formation of the complexes when we introduce different substituent groups on

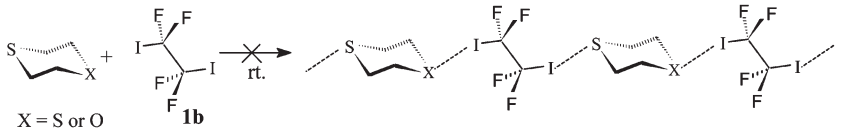


Scheme 4

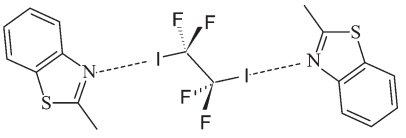
Table 1 Donor-acceptor interaction and its geometrical parameters in the studied complexes

Complex	Interaction	X···B/Å	R_f–X···B/°	P^c	Q^d
3[a]	C4–Br1···N1(sp^3)	2.864(3)	168.0(3)	0.842	1.554
	C5–Br1···N1(sp^3)		165.5(3)		
4[a]	C4–I1···N1(sp^3)	2.818(3)	170.2(2)	0.798	1.380
	C5–I1···N1(sp^3)		167.1(2)		
5[12a]	C1–Br1···N1(sp^2)	3.025(9)	172.2(9)	0.890	1.643
6	C1–I1···N(sp^3)	2.817(3)	176.8(1)	0.798	1.380
	C2–I2···O(sp^3)	2.862(3)	172.2(1)	0.817	1.335
8[14]	C1–I1···O(sp^3)	2.814(12)	163.3(3)	0.804	1.313
10	C7–I1···O(sp^2)	2.808(5)	175.7(2)	0.802	1.310
	C8–I2···O(sp^2)	2.824(5)	177.0(2)	0.807	1.317
11[14]	C7–I1···O(sp^2)	2.835(11)	170.6(9)	0.810	1.322
	C10–I2···O(sp^2)	2.864(11)	177.0(8)	0.818	1.336
14	C1–I···N(sp^2)	2.864(2)	176.0(1)	0.842	1.403
	C1–I···S1	3.893(1)	113.1(1)	1.030	1.481
	C1–I···S2	4.123(1)	125.5(1)	1.091	1.568
17	C1–I1···N1(sp^2)	2.928(5)	170.8(2)	0.829	1.434
18[b]	C1–I1···N1(sp^2)	2.913(7)	177.1(3)	0.825	1.427

[a] In complexes **3** and **4**, the C_f atom has two positions, C4 and C5, with equal occupancies. [b] In complex **18**, the methyl group randomly appears on the two positions of the pyridine ring. [c] *P* = distance/sum of van der Waals radii,[16] which are: N 1.55 Å, O 1.52 Å, S 1.80 Å, Br 1.85 Å, I 1.98 Å. [d] *Q* = distance/covalent bond length,[15] which are: N–Br 1.843 Å, N–I 2.042 Å, O–I 2.144 Å, S–I 2.629 Å.



Scheme 5



Scheme 6

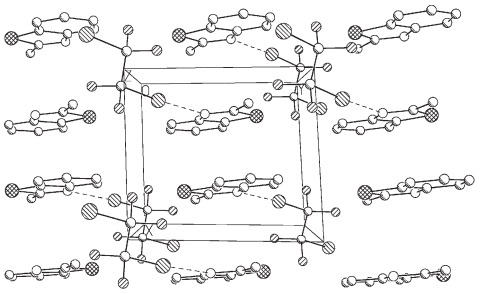


Fig. 5 Crystal packing of **14** viewed down the *c* axis. Two kinds of molecules are distinctly joined by N···I–R_f interactions (dotted lines).

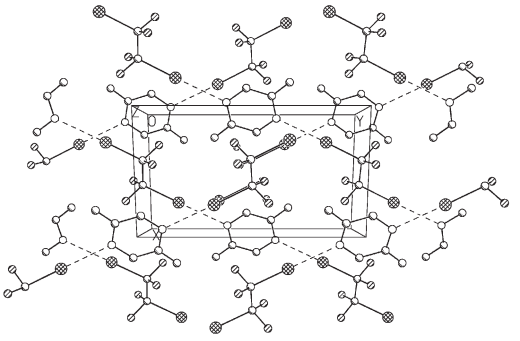


Fig. 6 Crystal packing of **18** viewed down the *c* axis. Two kinds of molecules are distinctly joined by N···I–R_f interactions (dotted lines).

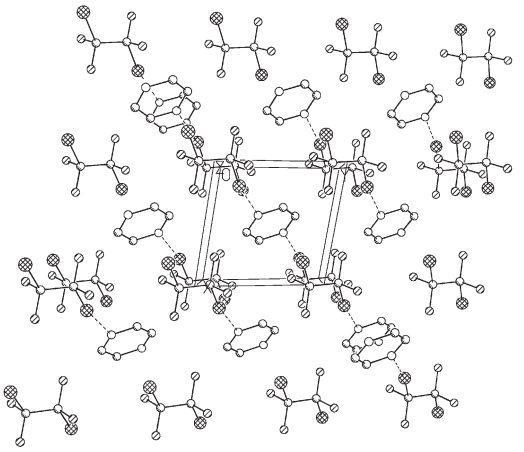
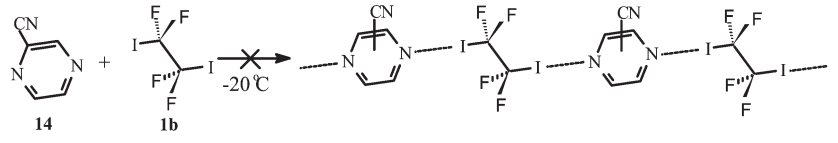


Fig. 7 Crystal packing of **17** viewed down the *c* axis. Two kinds of molecules are distinctly joined by N···I–R_f interactions (dotted lines).

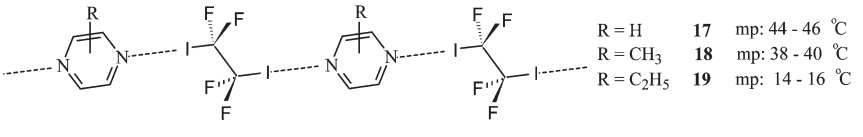
pyrazine. One is the steric effect. Introducing a substituent into a complex will affect the packing of the co-crystal, which is relevant to the stability of the complex. The other effect is the electronic effect. Generally speaking, adding an electron-donating group to the pyrazine ring increases the electron density on the N atoms, thus stabilizing the complex. In contrast, electron-withdrawing groups reduce the stability of a complex. In complex **18** we successfully introduced a methyl group into the complex (Fig. 6). We find that the distance between the $sp^2N\cdots I–R_f$ is slightly shorter than that in complex **17** (Fig. 7), showing that the electron-releasing effect of the methyl group will help this type of interaction. If an ethyl group, which is larger than the methyl group but has a similar inductive effect, is added to the pyrazine ring, the melting point of the complex decreases noticeably. As an example of a negative inductive effect, the mixture of **16** and **1b** is a liquid even when the temperature is reduced to −20 °C.

As for sp^2O, we also find that if we replace three $–N(CH_3)_2$ groups in HMPA by $–OCH_3$, $–OC_2H_5$[14] or $–C_6H_5$ groups there are no complexes formed at room temperature. Thus, we know that sp^2O and sp^2N are sensitive to the different kinds of substituents that connect to them though double bonds.

In Table 1, some important results of the X-ray analysis of all these complexes are summarized. This list includes



Scheme 7



Scheme 8

$sp^3N\cdots Br–R_f$, $sp^2N\cdots Br–R_f$,[12a] $sp^3N\cdots I–R_f$, $sp^2N\cdots I–R_f$, $sp^3O\cdots I–R_f$; $sp^2O\cdots I–R_f$ interactions, as well as interactions of $sp^2N\cdots I–R_f$ with different substituents. There is some disorder in the crystal structures of complexes **3**, **4** and **18**. In complexes **3** and **4**, the C_f atom has two positions, C4 and C5, with equal occupancy and each fluorine atom also occupies two positions with equal occupancy. In complex **18** the methyl group randomly appears on the two positions of the pyridine ring. However, all results of the complexes reported in the paper have errors of less than 0.008 Å and 0.4°, which are precise enough to show the nature of this interaction. All the *P* (distance/sum of van der Waals radii) and *Q* (distance/covalent bond length) values of these complexes are listed in Table 1 for comparison.

Conclusions

Base on the experimental results in this paper and some previous work in this field,[11–14] we draw the following conclusions for these kinds of interactions. (1) For electron-acceptor atoms, the tendency to form interactions is in the order $R_f–I > R_f–Br > R_f–Cl$. This agrees with the order of their polarizabilities but is opposite to the sequence of their electronegativities. (2) For electron-donor atoms the following is observed. (a) For a given donor atom, the higher the electron density on the atom, the stronger is its electron-donor ability; for instance, $O^-\cdots I–R_f$[13a] > $sp^2O\cdots I–R_f$ (in **12**) > $sp^3O\cdots I–R_f$ (in **6**). (b) Generally speaking, N > O > S. However, for relatively weak interactions a selective supramolecular synthesis could be realized as a consequence of the electron charge distribution and the molecular structure of the Lewis bases and acids. (3) The directions of these interactions are along the extended C–X bond axis.

A substantial amount of recent research has converged to the view that an understanding of weak intermolecular interactions is a most important priority in both chemical and biological sciences today. Thanks to our reported experimental method (see below) to grow and collect X-ray data of co-crystal complexes that are easily disordered, we successfully collected precise X-ray crystallographic data on relatively weak interactions. These results are not only important to understanding the nature of intermolecular interactions but also valuable to researchers who eagerly search for different kinds of useful interactions, which could be applied in host-guest chemistry,[21] biomimetic reactions,[22] nanotechnology[23] and many other prospective fields.[24–29]

Experimental

Co-crystallization

The general process is that 1,2-dihalogentetrafluoroalkane and Lewis base are mixed in equimolar amounts in chloroform and the solvent is slowly evaporated. Crystals then are collected for recrystallization. Melting points were measured on a Temp-Melt Apparatus and are uncorrected. Compounds like 1,4-oxathiane, pyrazine, 2-methylpyrazine, ethylpyrazine and pyrazinecarbonitrile, were bought from Aldrich. Solvents were not purified and dried before use.

Recrystallization

Because of the low quality of this type of crystals, before data collection all co-crystals have been recrystallized by using the sublimation method in a sealed glass tube kept at −20 °C for 2–6 months (60–200 days). A suitable size co-crystal on the inside wall of this tube was selected for data collection. Otherwise, using non-recrystallised crystals, we got more disordered results.

X-Ray data collection

Most crystals of this type are easily sublimed and many reported structures are very disordered; thus, we must use a low temperature technique to collect X-ray data, but as this type of crystals have very low packing density most crystals will be cracked. We decreased the temperature step by step, at a cooling rate of 10 °C per ten minutes, from 253 to 180 K. Single-crystal X-ray data of all complexes were collected on a NONIUS Kappa-CCD Diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) below

Table 2 X-Ray crystallographic data of donor-acceptor complexes

	3	**4**	**6**	**10**	**14**	**17**	**18**
CCDC number	214914	214915	214916	214917	214918	214919	214920
Empirical formula	$C_8H_{14}N_2F_4Br_2$	$C_8H_{14}N_2F_4I_2$	$C_7H_{11}NOF_4I_2$	$C_8H_{18}N_3OF_4PI_2$	$C_{18}H_{14}N_2F_4S_2I_2$	$C_6H_4N_2F_4I_2$	$C_7H_6N_2F_4I_2$
Formula weight	374.03	468.01	454.97	533.02	652.23	433.91	447.94
Melting point/K	303	400	316	363	310	318	312
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*P*-1	$P2_1/c$	*P*-1	*P*-1	$P2_1/c$
a/Å	15.2502(3)	15.8483(3)	6.8922(2)	7.280(1)	6.9160(5)	6.2536(5)	6.9365(5)
b/Å	10.4520(4)	10.4889(3)	6.8945(3)	16.461(3)	7.7021(5)	6.4403(7)	11.5354(10)
c/Å	10.5597(3)	10.7354(3)	14.5254(7)	14.947(3)	10.6364(7)	7.5067(7)	8.1604(4)
α/°	90	90	77.793(3)	90	80.528(4)	106.843(5)	90
β/°	127.509(2)	128.488(1)	81.707(3)	101.89(3)	78.781(4)	107.535(6)	110.487(4)
γ/°	90	90	77.341(3)	90	85.991(4)	93.925(6)	90
U/Å^3	1334.96(7)	1396.98(6)	654.75(5)	1692.1(6)	547.75(6)	271.87(4)	611.66(8)
Z	4	4	2	4	1	1	2
Abs. coeff./mm^{-1}	6.096	4.526	4.828	3.846	3.101	5.803	5.163
T/K	175	170	175	170	170	165	175
Total reflect.	11 598	13 549	11 699	26 205	10 511	4840	7820
Unique reflect.	1796	2011	3690	4806	3047	1214	1391
Number of reflect.	1329	1566	3571	4095	2646	1172	1124
R_{int}	0.0565	0.0836	0.0431	0.0541	0.0549	0.0461	0.0590
R_1 [$I > 2\sigma(I)$]	0.0374	0.0343	0.0340	0.0584	0.0348	0.0320	0.0416
wR_2 [$I > 2\sigma(I)$]	0.0734	0.0820	0.0849	0.1818	0.0777	0.0848	0.0925
R_1 (all data)	0.0593	0.0508	0.0414	0.0676	0.0444	0.0332	0.0542
wR_2 (all data)	0.0815	0.0887	0.0896	0.1886	0.0819	0.0856	0.1007

180 K. Absorption correction was based on the Multi-Scan method.[30] The structures were solved and refined on F^2 by SHELXS-97.[31] Details of the data collection and refinement are reported in Table 2.‡

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