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Halide anions driven self-assembly of haloperfluoroarenes: Formation of one-dimensional non-covalent copolymers

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ABSTRACT

The supramolecular organization in six solid assemblies involving iodo- and bromoperfluoroarene derivatives is described. Single crystal X-ray analyses show that the formation of the supramolecular architectures is controlled by $\mathrm{I^-\cdots Br{-}Ar_F}$, $\mathrm{I^-\cdots I{-}Ar_F}$, $\mathrm{Br^-\cdots I{-}Ar_F}$, and $\mathrm{Cl^-\cdots I{-}Ar_F}$ halogen bondings thus proving the $\mathrm{X^-\cdots X'{-}Ar_F}$ supramolecular synthon, where X can be the same as or different from X′, is particularly robust. In five of the described architectures halide anions form two halogen bondings and form infinite chains wherein dihaloperfluoroarenes, which function as bidentate electron acceptors, and halide anions, which function as bidentate electron donors, alternate. This behaviour shows halide anions have a fair tendency to work as bidentate halogen bonding acceptors.

1. Introduction

The electron density around halogen atom in organic halides is anisotropically distributed. A region of positive electrostatic potential is present along the extension of the C–X bond axis (X = Cl, Br, I) and this electropositive crown, also named σ-hole, is surrounded by an electroneutral ring and, further out, an electronegative belt [1]. Halogen atoms can thus work as electron donors in directions perpendicular to the C–X bond (at the electronegative belt) and as electron acceptors on the extension of the C–X bond (at the electropositive crown). The extent of this electropositive crown increases with the polarizability of the halogen and its magnitude also depend on the electron withdrawing power of the neighbouring groups on the carbon skeleton [2]. For instance, chlorine in CH_3Cl does not present any positive electrostatic potential, but it appears in CH_2FCl, and becomes even greater in CF_3Cl; similarly, in iodomethane derivatives the positive charge on iodine atom increases with the fluorination degree, being 0.009 in CH_3I and 0.165 in CF_3I [3]. In general, iodoperfluorocarbons, and iodine substituted heteroaromatic cations, typically present particularly remarkable σ-holes on the iodine atom.

The term halogen bonding (XB) has been introduced to designate any non-covalent interaction D···X–Y in which X is an electrophilic halogen atom (Lewis acid, XB-donor), D is a donor of electron density (Lewis base, XB-acceptor), and Y is carbon, nitrogen, halogen, etc. [4] The presence of a σ-hole accounts for the formation of XBs, as this electropositive region can interact attractively with any electron rich sites. In the last decade a renewed interest in XB proved the effectiveness of the interaction in driving self-assembly processes and the XB rapidly became a new paradigm in supramolecular chemistry [5]. The use of neutral electron donors (most frequently pyridine, amine, carbonyl, and ether moieties) is now well established. It allows for the self-assembly of a variety of supramolecular architectures in the solid and the obtainment of useful functional properties [6]. The use of anionic electron donors in XB directed processes has received far less attention [7] and in this paper we will describe the formation of halogen bonded (X-bonded) supramolecular structures when iodo- and bromoperfluorocarbon derivatives interact with iodide, bromide, or chloride anions.

In general, the number of XBs formed by a given anion can vary from one aggregate to another as a function of the composition of

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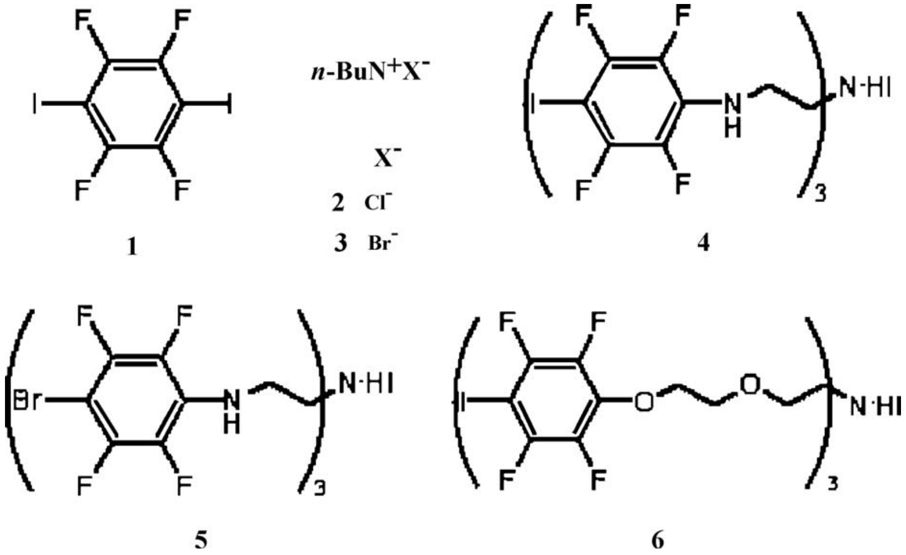
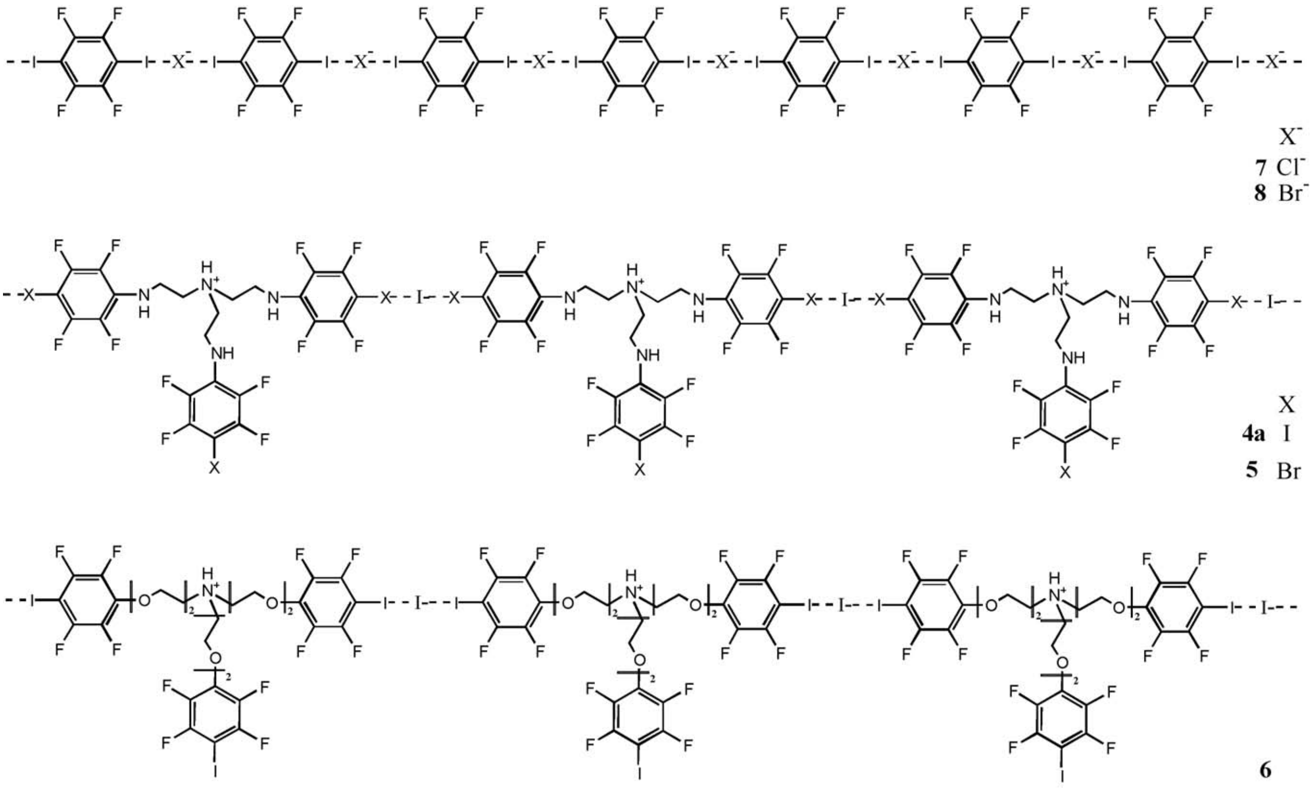


Scheme 1. XB donors and acceptors.

the system, the molecular structure of the interacting partners, and the overall geometric and electronic requirements in the crystal packing. For instance, bromide and iodide anions most frequently give rise to two or three XBs [8], but the formation of one [9], four [10], or even five [11], six or eight [10a,11,12] XBs has been reported. Here we describe how on evaporation of solutions of 2,3,5,6-tetrafluoro-1,4-diiodobenzene (**1**) and tetra-*n*-butylammonium chloride or bromide, (**2** and **3**, respectively, Scheme 1), the 1:1 crystalline adducts **7** and **8** are formed wherein **1** and chloride or bromide anions work as bidentate XB donors and acceptors, respectively, and alternate along the formed supramolecular anionic infinite chains (Scheme 2).

In order to check if also iodide anions have a possible tendency to form two XBs, we studied the interactions' pattern in tris-(2,3,5,6-tetrafluoro-4-iodophenyl)ammonium iodides **4** and **6** and the structurally related tris-(2,3,5,6-tetrafluoro-4-bromophenyl)ammonium iodide **5** (Scheme 1). The chemical structure of modules **4**–**6** makes three XB donor sites available to any iodide anions so that iodide anions could work as mono-, bi-, or tridentate XB acceptors and afford, for instance, discrete dimeric adducts, infinite chains, or honeycomb nets, respectively. Actually, in crystalline **4**–**6** too, the presence of X-bonded infinite chains is observed, wherein iodide anions are bidentate XB acceptors and bridge the iodo- or bromotetrafluorobenzene rings of two different



Scheme 2. X-bonded infinite chains wherein iodide anions are bidentate XB acceptors.

Table 1
Selected crystallographic and data collection parameters for X-bonded adducts **4–8**.

	7	**8**	**4a**	**4b**	**5**	**6**
Formula	$C_{22}H_{36}\ ClF_4I_2N$	$C_{24}H_{16}\ Br_3F_4I_2N$	$C_{24}H_{16}F_{12}I_4N_4$	$C_{24}H_{16}F_{12}I_4N_4$	$C_{24}H_{16}\ Br_3F_{12}IN_4$	$C_{30}H_{25}F_{12}I_4NO_6$
M	679.77	724.23	1096.01	1096.01	955.04	1231.11
Crystal color	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless
Dimension [mm^3]	0.17 × 0.28 × 0.30	0.28 × 0.32 × 0.36	0.04 × 0.05 × 0.24	0.04 × 0.08 × 0.32	0.11 × 0.19 × 0.32	0.10 × 0.12 × 0.27
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	9.1025(12)	49.295(6)	7.9773(12)	7.775(2)	8.1986(12)	7.8994(12)
b [Å]	13.951(2)	8.6878(10)	13.853(2)	21.702(6)	13.793(2)	27.005(4)
c [Å]	21.671(3)	13.944(2)	26.390(3)	18.075(5)	26.977(3)	17.766(3)
β [°]	94.89(2)	102.86(2)	93.33(2)	94.94(2)	94.06(2)	94.99(2)
V [Å^3]	2742.0(7)	5821.9(13)	2911.4(7)	3038.5(14)	3043.0(7)	3775.5(10)
Z	4	8	4	4	4	4
T [K]	90	297	297	297	297	90
ρ_{calc} [g cm^{-1}]	1.647	1.653	2.500	2.396	2.085	2.166
μ(Mo-Kα) [mm^{-1}]	2.427	3.567	4.383	4.200	5.089	3.402
$2\theta_{max}$ [°]	31.56	25.36	27.50	27.54	27.52	25.00
Data collected	54256	28887	58392	56837	60426	75872
Unique data	0.0259	0.0344	6594	6942	6996	11885
R_{int}	8776	5328	0.0510	0.0506	0.0346	0.0298
No. of obs. data $I_o > 2\sigma(I_o)$]	8048	3675	3035	4815	5648	9785
No. of parameters	415	344	400	406	461	526
No. of restraints	0	226	547	22	85	366
R_{all}	0.0200	0.0586	0.1491	0.1109	0.0494	0.0502
R_{obs}	0.0171	0.0324	0.0844	0.0819	0.0383	0.0377
wR_{all}	0.0405	0.0781	0.2539	0.2410	0.1105	0.0994
wR_{obs}	0.0394	0.0690	0.2299	0.2187	0.1044	0.0994
Goodness-of-fit	1.034	1.018	0.898	1.055	1.053	1.074
$\Delta\rho_{min,max}$ [e Å^{-3}]	−0.35, 0.69	−0.46, 0.44	−1.30, 1.88	−1.51, 2.90	−1.14, 0.96	−2.16, 1.61
CCDC	731756	731757	731752	731753	731754	731755

ammonium cations, the third halotetrafluorobenzene remaining uninvolved in any XB formation (Scheme 2).

2. Results and discussion

It is common that the number of ligands which surround anions, and form their coordination sphere, largely exceeds the requirements of the neutrality principle both in the solid and in solution [13]. In most cases these ligands are hydrogen bonding (HB) donors, as in organic materials strong (e.g. –OH, $-NH_2$, etc.) and weak (e.g. –CH) hydrogen bonding donor sites are ubiquitous. An iodoperfluorocarbon forming a X-bonded anionic adduct can thus be interpreted as the iodoperfluorocarbon substituting for a HB donor in the coordination sphere of the anion. Such a substitution may occur at one, or some, or all of the sites in the coordination sphere of the anion. This accounts for the variability in the number of XBs formed by a given anion.

The X-bonded architectures formed by anions can be divided into two groups, the *heteromeric three component systems* and the *heteromeric two component systems* [14]. These two groups can be identified as they present some specific features in relation to the effect that the composition of the system and the molecular structure of the interacting partners have on the number of XBs formed by a given anion. The identification of these two groups thus helps in identifying the key factors determining the number of XBs formed by an anion.

2.1. Co-crystals 7 and 8

The X-bonded co-crystals **7** and **8** have been obtained by mixing equimolar amounts of 1,4-diiodotetrafluorobenzene (**1**) and tetra-*n*-butylammonium chloride (**2**) or bromide (**3**) and by using the slow evaporation technique. Adducts **7** and **8** are two cases of heteromeric three component systems which, in general, are formed when an XB-donor (diiodotetrafluorobenzene **1** in our cases) self-assembles with a salt (the ammonium chloride and bromides **2** and **3**, in our case). The anion is the XB acceptor, the cation plays no active role, as far as XB formation is concerned, and the XB donor is a third neutral halogenated component present in the co-crystal.

Melting point analysis, beside the usual advantages of simple and fast measurements, gives a reliable proof that **7** and **8** are well-defined chemical species rather than a mechanical mixture of starting modules. When a solid is a mixture of two non-interacting compounds, it commonly has a melting point broad and lower than the pure components. Indeed, melting points of both **7** and **8** are sharp (474–477 K and 453–457 K, respectively,) and much higher than those of pure starting modules (**1**, 381–383 K; **2**, 356–359 K; **3**, 374–478 K). Although the numerous parameters affecting the crystal packing prevents from quantitatively predicting the strength of the intermolecular interactions moving from the observed melting points, the dramatic melting points' increase in **7** and **8**, compared to starting materials, indicates the interactions driving the assembly of starting modules are quite strong in both adducts. The FT-IR, ^{1}H, and ^{19}F NMR spectra of **7** and **8** correspond approximately to the sum of the spectra of the starting modules, the minor changes being consistent with XBs presence. ^{1}H and ^{19}F NMR spectra in the presence of 2,2,2-trifluoroethyl ether as

Table 2
XB distances (Å), angles (°), and R_i ratios for X-bonded adducts **4–8**. $R_i = XB_i/(rvdW1 + rvdW2)$ were the rwdW1 is the van der Waals radius of the halogen (1.98 and 1.85 Å for I and Br, respectively) and rvdW2 is the radius of the halide anion (2.16, 195, 1.81 Å for I$^-$, Br$^-$, and Cl$^-$, respectively, Ref. [16]).

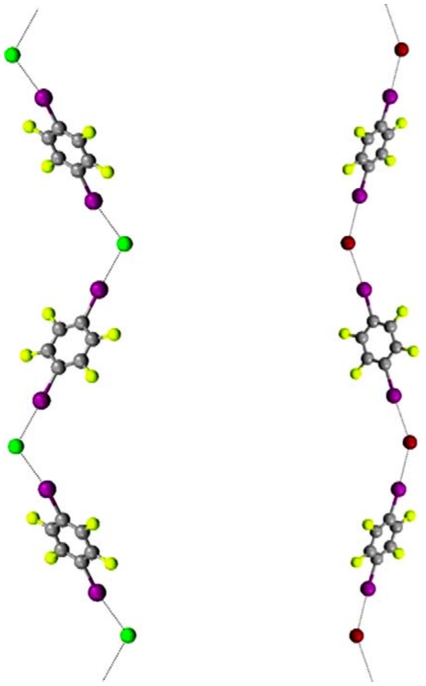
Structure	XB	$X^-\cdots X_1$ (Å)	R_1	$X^-\cdots X_2$	R_2	$X\cdots X^-\cdots X$ (°)
7[a]	$Cl^-\cdots I$	2.9758(7)	0.79	3.0906(6)	0.82	108.03(1)
8	$Br^-\cdots I$	3.1721(7)	0.81	3.2216(7)	0.82	138.38(2)
4a	$I^-\cdots I$	3.548(2)	0.87	3.652(2)	0.88	64.77(3)
4b	$I^-\cdots I$	3.720(2)	0.91			
5	$I^-\cdots Br$	3.6206(7)	0.99	3.7600(7)	0.94	63.38(2)
6[a]	$I^-\cdots I$	3.4920(5)	0.84	3.5010(5)	0.85	128.88(1)

[a] Data at 90 K.

internal standard for signal integration [15], revealed the **1**:**2** and **1**:**3** ratio were 1:1.

Single crystal X-ray diffraction analysis of **7** and **8** (Table 1) has given details about the supramolecular organisation of these co-crystals, confirming that the $Cl^{-}\cdots I$ and $Br^{-}\cdots I$ XBs are responsible for the self-assembly of the iodofluorocarbon **1** with the ammonium salts **2** and **3**. From the compositional point of view, the two co-crystals differ only for the halide anion (Cl^{-} in **7** and Br^{-} in **8**), but despite this apparently minor difference, the two crystals are not isostructural; the space groups of **7** and **8** are $P2_1/c$ and $C2/c$, respectively, and non-minor packing differences exist between the two co-crystals. All the geometric parameters (Table 2) are completely consistent with X-bonded systems, $X^{-}\cdots I$ XBs being as short as 0.80 times the sum of van der Waals radius of iodine and the corresponding halide ionic radius [16].

Both the heteromeric three component systems are characterised by the presence of infinite, one-dimensional, and X-bonded chains where the diiodotetrafluorobenzene and the halide anions alternate and behave as ditopic XB donors and acceptors, respectively (Fig. 1). The coordination spheres of two halides are completed by one HB with an acidic N-CH_2 hydrogen atom. Both infinite chains adopt a zig-zag arrangement and the $I\cdots X^{-}\cdots I$ angle is much larger in **7** than in **8**. Moreover, in **7** all the benzene rings are almost perpendicular to the plane containing halide anions, while in **8** they are alternatively parallel and perpendicular to the same plane (the perpendicular ring is rotationally disordered and both the refined models are nearly perpendicular to the halide plane).



Q1 **Fig. 1.** Mercury *ball and stick* plots of supramolecular anions of cocrystals **7** and **8**. Colour code: C, gray; F, green; I, violet; Cl, green; Br, brown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

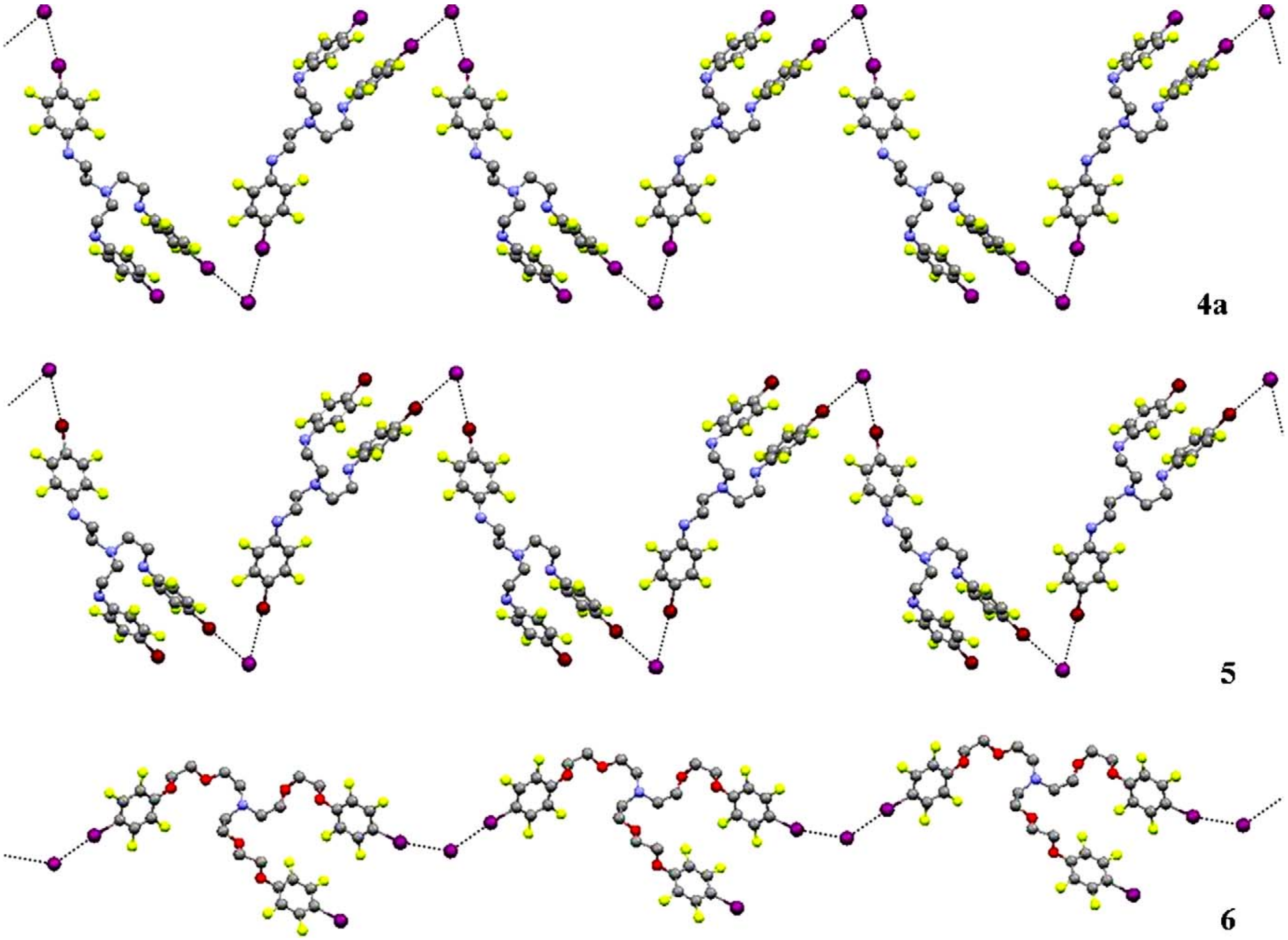


Fig. 2. Mercury projections of **4a**, **5** and **6** infinite chains in *ball and stick* style. Colour code: C, gray; F, green; I, violet; N, blue; O, red; H not shown for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2.2. *Crystals* **4**–**6**

Ammonium iodides **4**–**6** are heteromeric two-component systems, namely they are salts wherein the halogen substituted cation functions as the XB donor and the anion functions as the XB acceptor. In heteromeric two-component systems the requirements of charge balance heavily affects the number of XBs formed by the anion as the number of C–X groups in the halocarbon cation determines the maximum number of XBs the anion can form. This is the case, among others, in monohalopyridinium halides and monohaloanilinium halides where the monodentate cation forces the potentially polydentate anion to form a single XB and gives rise to discrete adducts [17]. When in the same systems the cation bears two or three halogen atoms, its ability to function as a di- or tridentate XB donor frequently can elicits the di- or tridentate potential of halide anions and infinite chains [18] or (6,3) nets [19] can be formed, respectively.

Crystals of ammonium iodides **4**–**6** suitable for X-ray structure determination were obtained on crystallization from acetone and by using the isotherm diffusion technique with chloroform as the external solvent. The iodotetrafluorophenyl salt **4** afforded two polymorphs **4a** and **4b** while the bromotetrafluorophenyl salt **5** and the iodotetrafluorophenyl salt **6** both gave a single polymorph (Table 1). In the last two compounds and in **4a**, iodide anions function as bidentate XB acceptors and interact with two halotetrafluorophenyl groups of two different ammonium cations. One of the two remaining halotetrafluorophenyl groups of ammonium cations also works as XB donors towards iodide anions and X-bonded infinite chains are formed where cations and anions alternate (Fig. 2).

Differently, in **4b** both cations and anions are monodentate and X-bonded discrete ion pairs are formed (Fig. 3). In all these structures, the overall crystal packing requirements clearly prevent the XB donor potential of the cation, and of the anion, from being saturated. In fact, one or two halotetrafluorophenyl groups (in **4a**, **5**, and **6** or **4b**, respectively) form no XB. It is interesting to observe that all $I^- \cdots I$ interactions in **4a**, **b** and **6** are much shorter than the sum of the van der Waals radius of iodine and the iodide anion radius (Table 2) while $I^- \cdots Br$ distances in **5** are quite close to the corresponding sum of the van der Waals radius of bromine and the iodide anion radius. When neutral electron donors are used, bromoperfluorocarbons are weaker XB donors than iodoperfluorocarbon analogues and the above-discussed differences between **4**, **6** and **5** shows this is also the case when anionic electron donors are used.

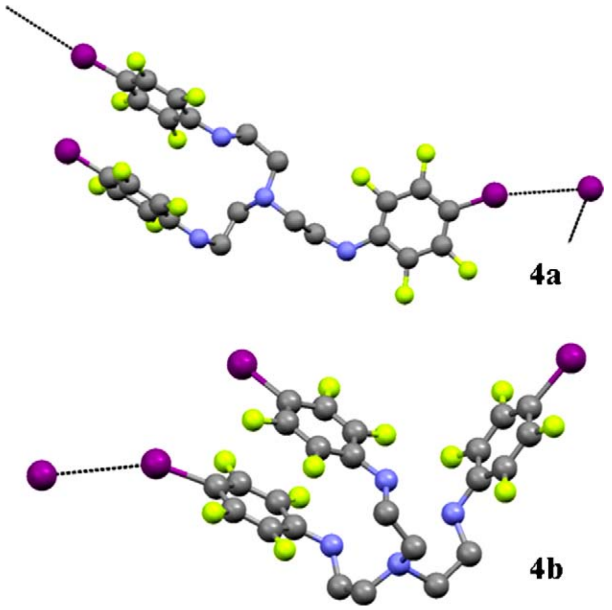


Fig. 3. Mercury *ball and stick* structures of **4a** and **4b** showing the different XB patterns and cation conformations. Colour code: C, gray; F, yellow; I, violet; N, blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

As discussed in the Introduction, halide anions frequently have a complex coordination sphere where XB and HB may coexist. This is the case for **4a** where several short $I^- \cdots H$ contacts are present. As expected, $I^- \cdots H\text{–}N$ distances are shorter than $I^- \cdots H\text{–}C$ distances and the shortest HB involves the inner $(N\text{–}H)^+$ group ($I^- \cdots N$ distance 3.316 Å). Also in **5** and **6**, the shortest HB involves the inner $(N\text{–}H)^+$ group ($I^- \cdots N$ distances are 3.492 and 3.570 Å in **5** and **6**, respectively) while in **4b** the only of $I^- \cdots N$ contacts is as long as 3.709 Å.

3. Conclusions

A quite large number of solid supramolecular assemblies have been obtained on interaction of iodo- and bromoperfluoroarenes with neutral XB acceptors [20] while few examples are reported where anionic XB acceptors are used [21]. In this paper we have described six solid assemblies where the supramolecular architectures formation is controlled by $I^- \cdots Br\text{–}Ar_F$, $I^- \cdots I\text{–}Ar_F$, $Br^- \cdots I\text{–}Ar_F$, and $Cl^- \cdots I\text{–}Ar_F$ halogen bondings. Clearly, the supramolecular organization of haloperfluoroarene derivatives can be effectively driven by halide anions and the $X^- \cdots X'\text{–}Ar_F$ supramolecular synthon (X being the same as or different from X′) seems to be particularly robust.

In five of the described assemblies halide anions form two XBs and this behaviour is consistent with generalizations from the Cambridge Structure Database according to which halide anions seem to have a bias towards the formation of two or three XBs [14]. In heteromeric three component systems, anions can, in principle, give any number of XBs, if the stoichiometry in the formed adducts varies conveniently. In our cases, when ammonium chloride **2** and bromide **3** self-assemble with diiodotetrafluorobenzene **1**, three, four, or even more XBs can be formed if the halide anion:diiodotetrafluorobenzene ratio in the resulting co-crystal is not 1:1 (as in **7** and **8**) but becomes 1:1.5 or 1:2 etc. The number of XBs given by the anion is not pre-established also in heteromeric three component systems, the chemical nature of these systems simply fixing the maximum number of XBs the anion can give rise too. Indeed, iodide anions in **4**–**6** can form one, two, or three XBs if two, one, or zero halotetrafluorobenzene residues remain uninvolved in XB formation. The preferential dicoordinate behaviour of halide anions observed in the structure here described probably derives from a balance between the inherent coordination profile of halide anions, the molecular structure of the interacting partners, and general entropic reasons. If working as tri- or tetra-coordinating sites, halide anions would probably form two- or three-dimensional networks [8–12], but these processes are much less likely to occur than the observed formation of infinite chains (one-dimensional nets).

4. Experimental

4.1. *General*

Commercial HPLC-grade solvents were used without further purification. Starting materials were purchased from Sigma–Aldrich, Acros Organics, and Apollo Scientific. Reactions were carried out in oven-dried glassware under a nitrogen atmosphere. Melting points were determined with a Reichert instrument by observing the melting and crystallising process through an optical microscope. Thermal analyses were recorded with a Linkam

DSC600 Stage (temperature range: −196–600 °C) coupled with the LN94 cooling system. ^{1}H NMR and ^{19}F NMR spectra were recorded at ambient temperature with a Bruker AV 500 spectrometer. Unless otherwise stated, $CDCl_3$ or CD_3CN were used as both solvent and internal standard in ^{1}H NMR spectra (δ_{CHCl3} = 7.26, δ_{CHD2CN} = 1.94). For ^{19}F NMR spectra, $CDCl_3$ or CD_3CN were used as solvent and $CFCl_3$ as internal standard. All chemical shift values were given in ppm. IR spectra were obtained in KBr pellets in a PerkinElmer 2000 FT-IR spectrometer. The values were given in wave numbers and were rounded to 1 cm^{-1} upon automatic assignment. The mass spectra were recorded with a Finnigan Mod TSQ-70 instrument in FAB mode from a m-NBA matrix. The X-ray crystal structures were determined using a Bruker Smart Apex diffractometer.

4.1.1. *Co-crystal* **7** *and* **8**

The slow evaporation technique was used. Equimolar amounts 1,4-diiodotetrafluorobenzene (**1**) and of the tetra-*n*-butylammonium chloride (**2**) or bromide (**3**) are separately dissolved in acetonitrile at room temperature, only as much solvent as necessary is used for complete dissolution. The saturated solutions are mixed in an open clear borosilicate glass vial and placed in a closed cylindrical wide-mouth bottle containing vaseline oil. Solvents are allowed to slowly evaporate at room temperature and to be absorbed by vaseline oil until the white crystals of **7** and **8** are formed. The crystals are filtered off the mother liquor (from which one to two further crystal fractions could be obtained in the same manner), washed with *n*-pentane and rapidly dried in air at room temperature. **7**: mp 474–477 K; IR. ν_{max} (selected bands) 2959, 2873, 1452, 937, 755 cm^{-1}. **8**: mp 453–457 K; IR. ν_{max} (selected bands) 2957, 2875, 1453, 937, 756 cm^{-1}.

4.2. *Tris-(2-(2,3,5,6-tetrafluoro-4-iodophenyl)-aminoethyl)ammonium iodide (***4***)*

A mixture of tris(2-aminoethyl)amine (1.0 mmol, 150 mg), pentafluoroiodobenzene (5.0 mmol, 0.67 mL) and K_2CO_3 (3.5 mmol, 483 mg) are stirred in 1 mL of refluxing THF for 48 h. The reaction is monitored by TLC on silica gel plates with CH_2Cl_2 as eluent. The solution is filtered and the solvent is evaporated. Flash chromatography (230–400 mesh) of the dry crude mixture with petroleum ether: CH_2Cl_2 3:2 (R_f = 0.56) affords a clean product, which is further purified by crystallisation from dichloromethane to yield a yellow solid (0.48 g, 50%). m.p. 351 K; ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.3 (3H, br, NH), 3.5 (6H, q, *J* = 6 Hz, NH-C$\underline{H}_2$), 2.8 (6H, t, *J* = 6 Hz, N-CH_2); ^{19}F NMR (235 MHz, $CDCl_3$): δ −158.1 (2F, d, *J* = 19.4 Hz, CF-CN), −123.5 (2F, d, *J* = 19.4 Hz, CF-CI). IR: ν_{max} (selected bands) 3345, 2846, 1638, 1484, 1459, 1153, 1073, 958, 803 cm^{-1}.

1.0 mL of 57% aqueous HI solution is mixed with 2.0 mL of MeOH and water is removed by adding sufficient amount of anhydrous Na_2SO_4. The solution is filtered and added to a solution of tris-(2-(2,3,5,6-tetrafluoro-4-iodophenyl)-aminoethyl)amine in toluene under vigorous stirring. The precipitate **4** is filtered after 30 min at room temperature. Two different thermal events can be detected (by visual inspection and by DSC analyses) at 327 K (minor) and 468 K (major); ^{1}H NMR (250 MHz, CD_3CN): δ 5.1 (br, NH), 3.8 (6H, brq, NH-C$\underline{H}_2$), 3.6 (6H, brt, N-CH_2); ^{19}F NMR (235 MHz, CD_3CN): δ −158.1 (2F, d, CF-CN), −126.4 (2F, d, CF-CI). IR: ν_{max} (selected bands) 3247, 2889, 1638, 1460, 1364, 1115, 969, 956 cm^{-1}.

4.3. *Tris-(2-(2,3,5,6-tetrafluoro-4-bromophenyl)-aminoethyl)ammonium iodide (***5***)*

Tris-(2-(2,3,5,6-tetrafluoro-4-bromophenyl)-aminoethyl)amine was prepared in 65% isolated yield from tris(2-aminoethyl)amine and pentafluorobromobenzene through a procedure strictly similar to that described above for the iodo analogue. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.3 (3H, br, NH), 3.5 (6H, t, *J* = 6 Hz, NH-C$\underline{H}_2$), 2.8 (6H, t, *J* = 6 Hz, N-CH_2), ^{19}F NMR (235 MHz, $CDCl_3$): δ −159.2 (2F, d, *J* = 18.3 Hz, CF-CN), −136.3 (2F, d, *J* = 18.3 Hz, CF-CBr). IR: ν_{max} (selected bands) 3396, 2841, 1641, 1493, 1260, 1155, 1076, 956, 827 cm^{-1}.

1.0 mL of 57% aqueous HI solution is mixed with 2.0 mL of MeOH and anhydrous Na_2SO_4 is added in sufficient amount to remove water. The solution is filtered and added to a solution of tris-(2-(2,3,5,6-tetrafluoro-4-bromophenyl)-aminoethyl)amine in toluene under vigorous stirring. After 30 min at room temperature the formed precipitate is filtered. m.p. 465–467 K; ^{1}H NMR (250 MHz, CD_3CN): δ 5.1 (br, NH), 3.8 (6H, q, NH-C$\underline{H}_2$), 3.6 (6H, t, N-CH_2); ^{19}F NMR (235 MHz, CD_3CN): δ −159.2 (2F, d, CF-CN), −139.4 (2F, d, CF-CBr). IR: ν_{max} (selected bands) 3277, 2955, 1642, 1492, 1162, 957, 829 cm^{-1}.

4.4. *Tris((2-(2,3,5,6-tetrefluoro-4-iodophenoxy)ethoxy)-ethyl)ammonium iodide (***6***)*

In the first reaction step tris(2-hydroxyethoxyethyl)amine was synthesized. Na_2CO_3 (3.0 equiv., 5.46 mmol, 579 mg) is added to a solution of 2-(2-aminoethoxy)ethanol (1.0 equiv., 1.82 mmol, 192 mg) in 1.5 mL of *p*-xylene. The resulting heterogeneous mixture is heated to 120 °C and 2-(2-chloroethoxy)ethanol is added (2.2 equiv., 4.02 mmol, 500 mg). After stirring overnight the reaction mixture is filtered, the yellowish solid taken up with EtOH, filtered again, and the solvent removed. The residue is subjected to column chromatography (SiO_2, MeOH/EtOAc 1:1) to give a pale yellow oil (412 mg, 81%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.35 (brs, 6H), 3.60–3.55 (m, 12H), 2.65 (t, 6H, *J* = 5.0 Hz). ESI-MS, positive-ion mode: *m*/*z* 282 [M$^+$+H], 304 [M+Na$^+$]. IR: ν_{max} 3282, 2918, 2860, 2820, 1481, 1447, 1360, 1353, 1312, 1286, 1253, 1120, 1105, 1078, 1063, 1044, 1025, 927, 914, 887, 827 cm^{-1}. In the second step tris(2-hydroxyethoxyethyl)amine (1.0 equiv., 0.370 mmol, 104 mg), iodopentafluorobenzene (9 equiv., 3.33 mmol, 980 mg) and Cs_2CO_3 (3 equiv., 1.11 mmol, 384 mg) are heated to 80 °C under vigorous stirring for 18 h. The product is purified by flash chromatography (230–400 mesh), increasing the solvent polarity from pure *n*-hexane to *n*-hexane: EtOAc 1:1. Tris((2-(2,3,5,6-tetrefluoro-4-iodophenoxy)ethoxy)-ethyl)amine is obtained as slightly yellowish oil (229 mg, 50% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.35 (t, 6H, *J* = 4.5 Hz), 3.76 (t, 6H, *J* = 4.5 Hz), 3.56 (t, 6H, *J* = 5.8 Hz), 2.74 (t, 6H, *J* = 5.8 Hz). ^{19}F NMR (235.3 MHz, $CDCl_3$): δ −121.99 (d, 6F), −154.58 (d, 6F); ESI-MS, positive-ion mode: *m*/*z* 1103 [M+H$^+$], 1126 [M+Na$^+$]. IR: ν_{max} (selected bands) 2929, 2869, 1630, 1477, 1357, 1271, 1092, 970, 865, 797 cm^{-1}. 1.0 mL of 57% aqueous HI solution is mixed with 2.0 mL of MeOH and anhydrous Na_2SO_4 is added in sufficient amount to remove water. The solution is filtered and added to a solution of tris((2-(2,3,5,6-tetrefluoro-4-iodophenoxy)ethoxy)-ethyl)amine in toluene under vigorous stirring. After 30 min at room temperature the precipitate is filtered.

4.4.1. *Crystal* **4a**, *b*, **5** *and* **6**

Crystals suitable for X-ray analyses of **4a**,**b**, **5** *and* **6** have been obtained adopting the diffusion technique. The compounds are dissolved in acetone in an opened vial which is placed in a closed cylindrical wide-mouth bottle containing chloroform. Solvents are allowed to mix by slow diffusion in gas and liquid phase at room temperature until crystals were formed. The crystals are filtered off the mother liquor (from which one to two further crystal fractions could be obtained in the same manner), washed with *n*-pentane and rapidly dried in air at room temperature.

4.4.2. X-ray structures determination

Table 1 reports the crystallographic data. All crystal data were obtained using a Bruker diffractometer with CCD area-detector and Mo-Kα radiation (λ = 0.71073 Å). Structures were solved by *SIR2002* [22] and refined by *SHELX-97* [23]. A first data collection of **6** was carried on at room temperature; data were very poor due to the high librational disorder involving all the three iodotetrafluorobenzenes; we report data of a second data collection at low temperate. Also data of **7** were collected at low temperature; data of this structure were very good, in contrast of all the other that are more or less disordered. Crystals of **4a** and **4b** were always mixed together, grown epitaxially; they were always very small and any attempt to grow separately the two polymorphs failed; data of both the two structures are then quite poor. With exclusion of **7**, all the structures were refined using restraints and constraints on the disordered parts.

Copies of the **4a**, **4b**, **5**, **6**, **7**, and **8** data can be obtained, free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

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