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Phenyliodine(V) fluorides

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Abstract

The known compound phenyltetrafluoroiodine(V) is shown by X-ray diffraction to have a tetragonal pyramidal structure with an apical phenyl group. This structure is compared to that of $IF(OTeF_5)_4$, where the apical position is occupied by the fluorine atom. $C_6H_5IF_4$ adds F^-, forming $C_6H_5IF_5^-$, which has a pentagonal pyramidal structure with an apical phenyl group. Fluoride abstraction from $C_6H_5IF_4$ by SbF_5 results in the formation of the cation $C_6H_5IF_3^+$, which has a pseudotrigonal bipyramidal structure with the phenyl group occupying an equatorial position. Isoelectronic $C_6H_5IOF_2$ has a similar structure, with the phenyl group and oxygen atom both occupying equatorial positions.
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1. Introduction

The compound $C_6H_5IF_4$ has been known since 1968 [1]. Aryl iodine tetrafluorides can be prepared by three different methods: (1) fluorination of ArI [2]; (2) arylation of IF_5 [3]; and (3) conversion of $ArIO_2$ into $ArIF_4$ with SF_4 [1]. It has always been assumed that the aryl group in these compounds is positioned at the apex of a tetragonal pyramid, with the four fluorine atom occupying basal positions. The key evidence for this particular geometric isomer comes from ^{19}F NMR spectra, which in all cases and under all conditions shows only a single line, and by analogy with the known structures of $C_6F_5IF_4$ and CF_3IF_4 [4,5]. This structure is predicted by a simple bonding model: the longer 3-center-4-electron basal bonds in a square pyramid can better accommodate the more electronegative fluorine atoms relative to the shorter apical 2-center-2-electron apical bond.

A precise structure of the parent compound $C_6H_5IF_4$ is presented in this paper. Little is known about the chemical reactions of these compounds, so we have also studied two of their simplest possible reactions, the addition and loss of a fluoride ion. The formation of both IF_6^- and IF_4^+ from IF_5 is known since long [6–9]. The question was whether $C_6H_5IF_4$ can also act as fluoride ion acceptor and/or donor, and what the resulting structures would be. Finally, $C_6H_5IOF_2$, known since 1901 [10], can be considered as the first hydrolysis product of $C_6H_5IF_4$, (although it is more conveniently prepared from $C_6H_5IO_2$). Its precise structure had not been determined, so it is also reported in this paper.

2. Results and discussions

2.1. $C_6H_5IF_4$

The reaction of $C_6H_5IO_2$ with SF_4 is the method of choice for the preparation of $C_6H_5IF_4$ [1]. The reaction is nearly quantitative, and the gaseous byproducts can be removed easily. $C_6H_5IF_4$ is a crystalline material with surprising thermal stability to about 300 °C. However, it hydrolyses quickly. The ^{19}F NMR spectrum shows the same single line regardless of the method of preparation, so there is no indication of geometric isomerism. The chemical shift is somewhat solvent dependent, indicating varying strengths of interaction with various solvents. Crystal structure determinations of iodine(V)fluorides are rare, although the square-pyramidal structure of IF_5, with a very complex set of intermolecular interactions, has long been known [11]. More recently, the crystal structures of $C_6F_5IF_4$ and CF_3IF_4 have appeared [4,5]. In these two molecular structures the expected square pyramidal geometry with the organic substituent in the apical position was confirmed.

Single crystals of $C_6H_5IF_4$ were readily obtained from a diethylether solution at -50 °C. The resulting crystal

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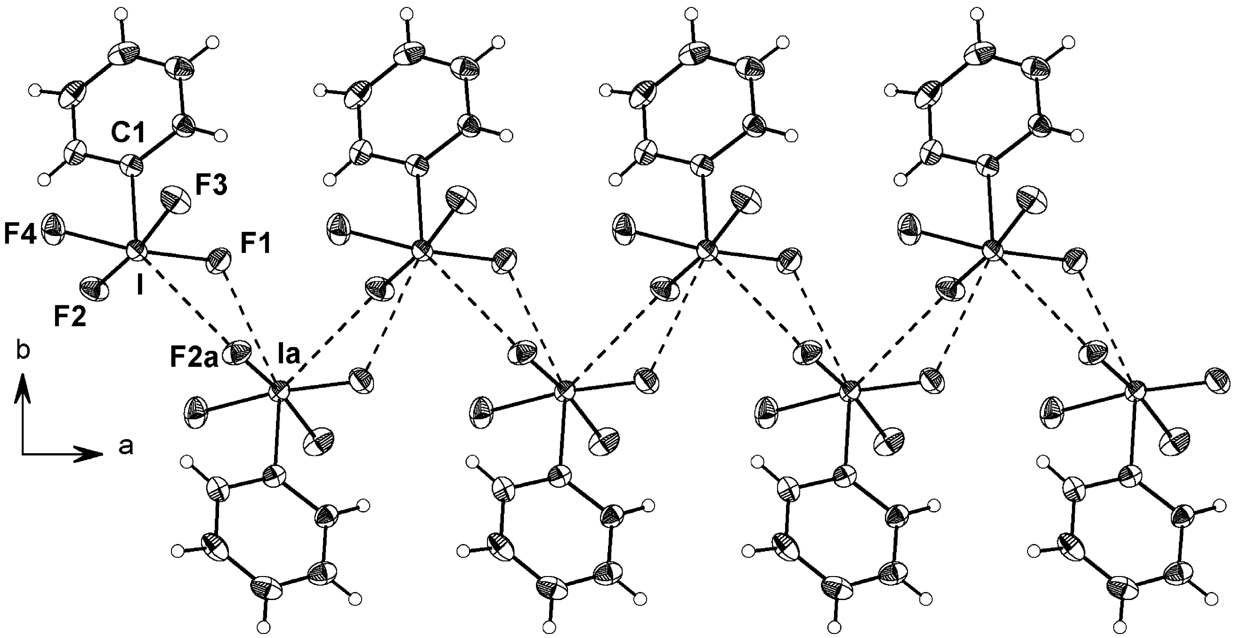

Fig. 1. Structure of $C_6H_5IF_4$ in the crystal, ortep representation, 50% probability ellipsoids.

structure is shown in Fig. 1, and interatomic distances and angles are listed in Table 1. While the same basic structure of CF_3IF_4 and $C_6H_5IF_4$ is clearly evident, the intermolecular interactions are noteworthy. Basal fluorine atoms make contacts to neighboring iodine atoms, resulting in a zigzag chain. The I–F bond lengths (average 194 pm) are longer than in IF_5 (average 187 pm), CF_3IF_4 (average 192 pm), or $C_6F_5IF_4$ (average 191 pm). This is certainly a consequence of the weaker electron withdrawing power of a C_6H_5 group compared to F, CF_3, or C_6F_5 substituents. The I–C bond length of 207.7 pm is nearly the same as in $C_6F_5IF_4$ (208 pm) and much shorter than in CF_3IF_4 (222 pm). The average C–I–F angle of 85.35° is slightly larger than the average C–I–F angles in other iodine(V) compounds such as IF_5 (81.9°), CF_3IF_4 (82.1°), and $C_6F_5IF_4$ (84.3°).

2.2. *IF(OTeF$_5$)$_4$*

Although belonging to a different class of compounds, we wanted to compare the molecular structure of $C_6H_5IF_4$ with $IF(OTeF_5)_4$. This compound was first described as the final reaction product of IF_5 and $B(OTeF_5)_3$, and this is still the method of choice for its preparation [12,13]. Note that the fifth fluorine atom is not substituted in this reaction. But the compound $I(OTeF_5)_5$ can be made by the reaction of $I(OTeF_5)_3$ with $Xe(OTeF_5)_2$ [12,13].

Analysis of the ^{19}F NMR spectrum of $IF(OTeF_5)_4$ led to the conclusion that the fluorine atom occupies the axial position and the four $OTeF_5$ groups occupy the four equivalent basal positions of a square pyramid. This assignment is confirmed by the single crystal X-ray structure determination. Interatomic distances and angles are listed in Table 2. The structure, shown in Fig. 2, consists of square pyramidal $IF(OTeF_5)_4$ molecules with only weak intermolecular interactions (similar to the weak interactions typically observed in most $OTeF_5$ compounds). There is the same umbrella-type structure observed for $C_6H_5IF_4$. The F–I–O angles are 85.50 and 80.23°. The noteworthy difference is the apical fluorine atom. This finding once has led to the unlikely conclusion that the $OTeF_5$ group may be more electronegative than fluorine [12,13]. However, the preference of substituents for apical versus basal positions seems to be governed by other,

Table 1
Important bond distances (pm) and angles (°) of $C_6H_5IF_4$

I–F1	195.7 (3)	F1–I–C1	84.2 (2)
I–F2	194.8 (3)	F2–I–C1	85.7 (1)
I–F3	192.1 (3)	F3–I–C1	85.5 (1)
I–F4	193.6 (3)	F4–I–C1	86.0 (2)
I–C1	207.7 (4)		
C–C	137.7 (4)–140.0 (4)		
C–H	87 (3)–96 (4)		
I···F1	307.4 (3)	C1–I···F1	146.5 (2)
I···F2	323.4 (3)	C1–I···F2	142.2 (2)

Table 2
Important bond distances (pm) and angles (°) of $FI(OTeF_5)_4$

I–F1	182.7(4)	F1–I–O1	85.5 (1)
I–O1	193.9(3)	F1–I–O2	80.2 (1)
I–O2	200.6(3)	O1–I–O1′	171.0 (2)
Te1–O1	188.3(3)	O2–I–O2′	160.5 (2)
Te2–O2	186.0(3)	O1–I–O2	87.7 (7)
Te–F	181.5(3)–184.0(3)	F–Te–F	87.0 (1)–91.3 (2), 176.1 (1)–178.5 (1)
		F–Te–O	88.4 (1)–92.8 (2), 177.5 (1), 178.4 (1)

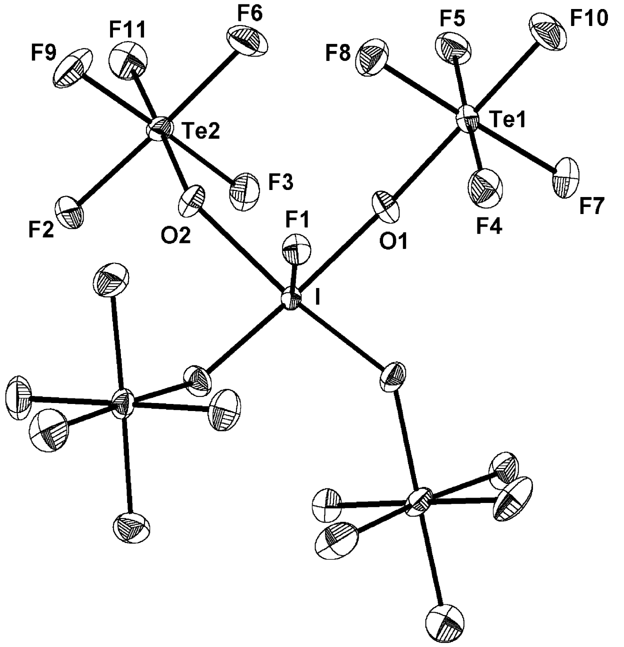

Fig. 2. Structure of $FI(OTeF_5)_4$ in the crystal, ortep representation, 50% probability ellipsoids.

more subtle effects than in addition to substituent electronegativity. Nevertheless, it should be kept in mind that $OTeF_5$ containing compounds are often quite similar to the corresponding fluorides.

2.3. $C_6H_5IF_5^-$

The intermolecular I···F contacts in $C_6H_5IF_4$ indicate that the iodine atom might act as a fluoride ion acceptor and the fluorine atoms as donor ligands. The chemical realization in the first case would be the reaction of $C_6H_5IF_4$ with F^-. We have chosen 1,1,3,3,5,5-hexamethylpiperidinium fluoride (pip^+F^-) as a source of F^- [14]. This salt contains a large quaternary ammonium cation and can thus be considered a source of nearly "naked" fluoride ions. Its F^- donor ability is better than those of the more commonly used reagents CsF and $(CH_3)_4N^+F^-$ [15]. Furthermore, the irregular shape of the cation does not promote crystallographic disorder as does the symmetric geometry of the $(CH_3)_4N^+$ cation. The multistep preparation of pip^+F^- is the price one must pay to accrue these advantages [14].

The compound $C_6H_5IF_4$ reacted with pip^+F^- in acetonitrile at −30 °C, forming colorless, hydrolytically sensitive $pip^+C_6H_5IF_5^-$. The compound was characterized by Raman and NMR spectroscopy and by its single crystal structure determination. The ^{19}F NMR spectrum shows only one line, indicating either static or dynamic equivalence of all five fluorine atoms. The crystal structure, shown in Fig. 3, revealed the composition $pip^+\ C_6H_5IF_5^-\cdot CH_3CN$. Interatomic distances and angles are listed in Table 3. The acetonitrile molecules act as spacers between the cation/anion layers and do not seem to have much influence on the coordination geometry of the iodine atom.

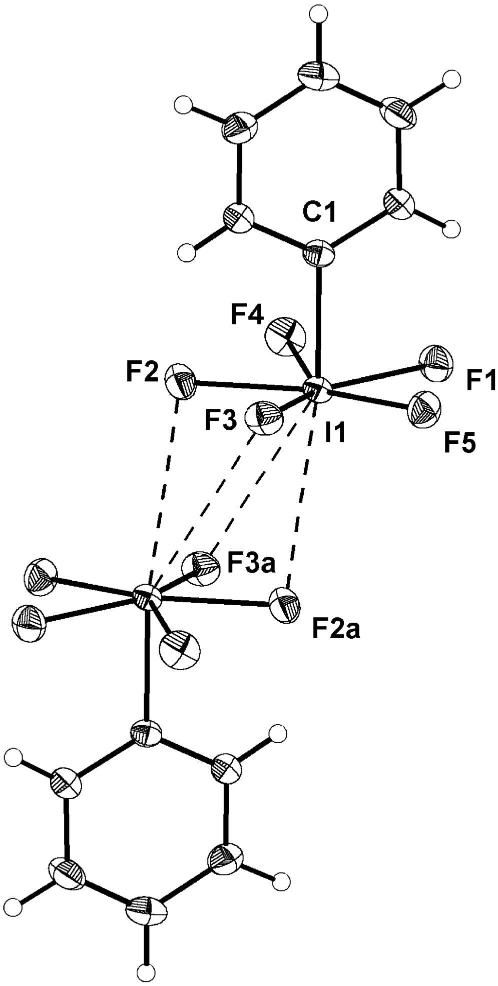

Fig. 3. Structure of $C_6H_5IF_5^-$ in $pip^+C_6H_5IF_5^-\ CH_3CN$. Shown is the weakly associated dimeric anion. For an overview of the entire structure see deposited data.

There are weak interactions between the fluorine atoms and the methyl protons of the pip^+ cation. Interestingly, the anions come in pairs due to four weak I···F interactions of 324.5(1) and 339.2(1) pm length. Each $C_6H_5IF_5^-$ anion has the shape of a regular pentagonal IF_5 unit with an apical phenyl group. Compared with $C_6H_5IF_4$, the I–F bonds are elongated to 202 pm (average) and the I–C bond is elongated to 209.4(1) pm. The C–I–F angles are below 90° (84.76(5)–88.73(5)°). Such pentagonal molecular geometries are rare, but not without precedent. Two relevant example are XeF_5^- [16] and IF_5^{2-} [17]. Even more relevant are the chemically similar anions $XeOF_5^-$ [18,19] and IOF_5^{2-} [20] that have the same pentagonal-pyramidal structure. The first examples of pentagonal-pyramidal coordination was observed in isoelectronic Te(IV) dithiocarbamates [21].

It would have been difficult to predict the correct structure for $C_6H_5IF_5^-$. Although the aforementioned anions all contain the pentagonal AF_5 unit, the related species IF_6^-

Table 3
Important bond distances (pm) and angles (°) of $C_6H_5IF_5^-$ in $pip^+C_6H_5IF_5^- \cdot CH_3CN$

I–F1	203.4 (1)
I–F2	202.1 (1)
I–F3	201.2 (1)
I–F4	200.6 (1)
I–F5	202.7 (1)
I–C1	209.4 (2)
C–C	138.4 (2)–139.1 (2)
C–H	92 (2)–96 (2)
I···F2	339.2 (1)
I···F3	324.9 (1)
F–I–F	71.21 (4)–72.57 (4) 142.34 (4)–144.33 (4)
F1–I–C1	88.64 (5)
F2–I–C1	84.76 (5)
F3–I–C1	88.34 (5)
F4–I–C1	85.73 (5)
F5–I–C1	85.97 (5)

and XeF_6 are best described as C_{3v}-monocapped ψ-octahedra (for a short review on the structure of XeF_6 in the gaseous state [9,22,23]). The reason for this structural ambiguity is clearly the number of seven electron pairs at iodine. It is well known that the three possible geometries for an AF_7 species (pentagonal bipyramid and C_{3v}- and C_{2v}-monocapped octahedra) are very close in energy. To complicate matters further, some AB_6E species (E: nonbonding electron pair), such as BrF_6^- and ClF_6^-, have regular octahedral geometries [14,24–27]. Octahedral symmetry seems to prevail when the central atom is small or the ligand atoms are large (TeI_6^{2-}) [28].

The strong band at 503 cm^{-1} in the Raman spectrum of $pip^+C_6H_5IF_5^-$ has been tentatively assigned to $\nu_s(IF_5)$ (assuming local C_{5v} symmetry) by analogy with the assignments for $XeOF_5^-$ and IOF_5^{2-}, where the corresponding bands are found at 451 and 485 cm^{-1}.

2.4. $C_6H_5IF_3^+$ SbF_6^-

The reaction of $C_6H_5IF_4$ with SbF_5 in anhydrous HF afforded $C_6H_5IF_3^+SbF_6^-$ as colorless platelets. The compound is stable only below −20 °C. The crystal structure, shown in Fig. 4, revealed that the cation and anion are interconnected by Sb–F···I bridges, resulting in a chain-like arrangement. Interatomic distances and angles are listed in Table 4. The angles within the SbF_6^- anions are close to 90 and 180°. The Sb–F distances involving the bridging F atoms are only slightly elongated. If the cations are viewed as isolated species, they exhibit the expected SF_4-type structure, with a relatively linear F–I–F fragment (163.0(2)°) with I–F bond length of 189.4(3) and 189.9(3) pm. The third fluorine atom (I−F = 182.1(3) pm) and the ipso carbon atom (I−C = 208.4(5) pm) occupy equatorial positions in the pseudo-trigonal-bipyramidal structure. The cations ClF_4^+, BrF_4^+, and IF_4^+ all have similar structures [29]. The two Sb–F···I contacts to neighbouring SbF_6^- units in $C_6H_5IF_3^+SbF_6^-$ complete the *pseudo*-pentagonal-bipyramidal structure with two axial fluorine atoms. The chain-like arrangement of cations and anions is very similar to the crystal structures of $ClF_4^+SbF_6^-$ and $BrF_4^+SbF_6^-$. In $IF_4^+SbF_6^-$, however, the cation-anion interactions result in a nine-coordinate environment around the iodine atom. In summary, the five equatorial positions in $C_6H_5IF_3^+SbF_6^-$ are occupied by the

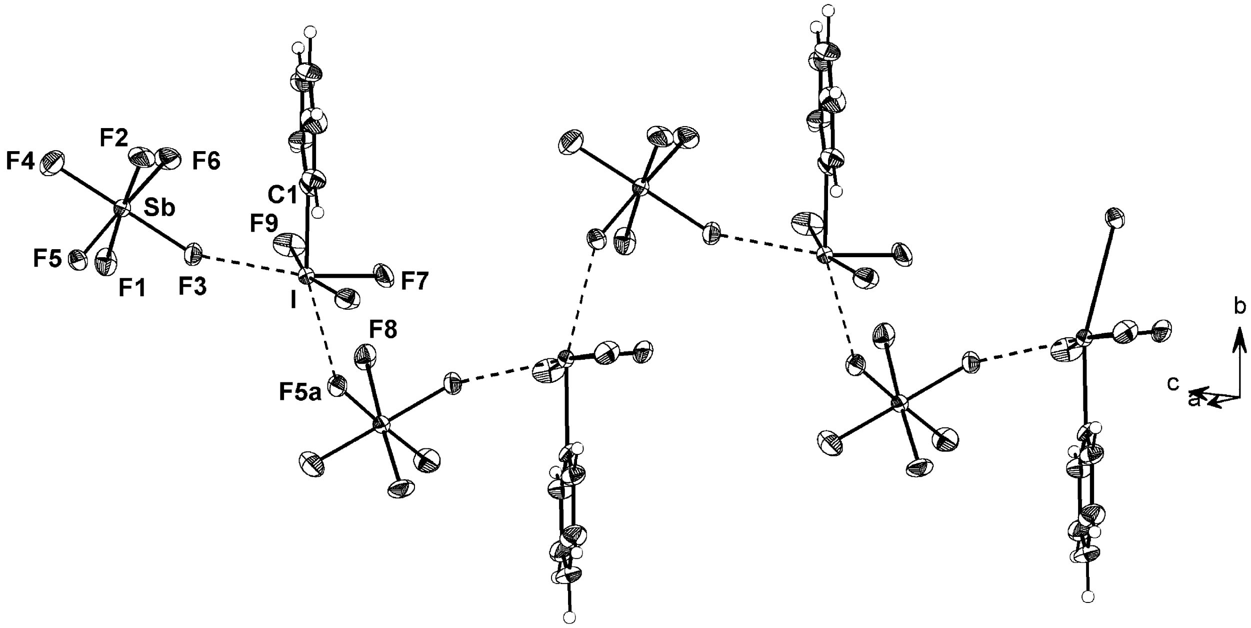

Fig. 4. Structure of $C_6H_5IF_3^+SbF_6^-$, ortep representation, 50% probability ellipsoids. Shown is the bridged cation-anion chain.

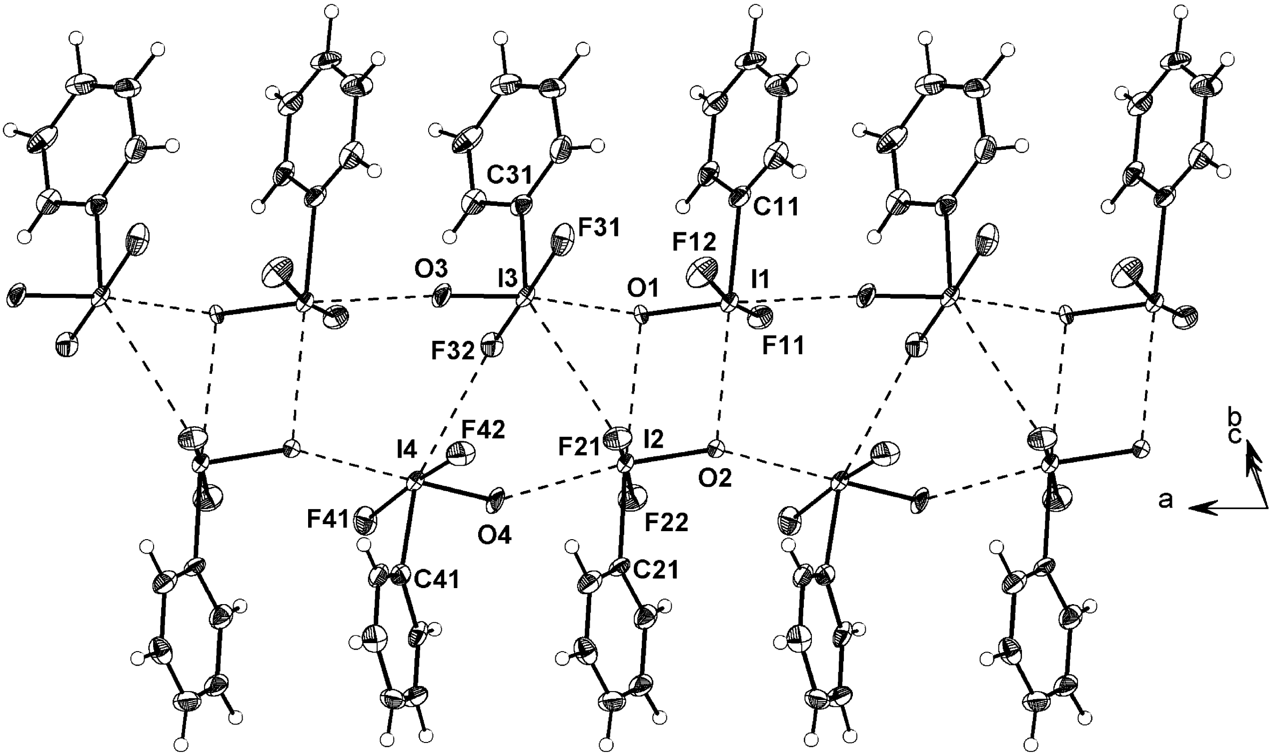

Fig. 5. Structure of $C_6H_5IOF_2$ the four crystallographic different molecules, ortep representation, 50% probability ellipsoids.

phenyl-group carbon atom, one strongly bonded fluorine atom, two bridging fluorine atoms from SbF_6^- anions, and the non-bonding electron pair. A similar pentagonal environment but with three strongly bonded fluorine atoms in a T shape and two longer contacts to fluorine atoms from neighboring molecules was found in crystalline IF_3 [30].

Table 4
Important bond distances (pm) and angles (°) of $C_6H_5IF_3^+SbF_6^-$

I–F7	182.7 (3)
I–F8	189.9 (3)
I–F9	189.4 (3)
I–C1	208.4 (5)
C–C	136.8 (9)–139.6 (10)
C–H	85 (5)–95 (6)
Sb–F1	187.9 (3)
Sb–F2	186.6 (3)
Sb–F3	191.5 (3)
Sb–F4	186.3 (3)
Sb–F5	187.7 (3)
Sb–F6	186.2 (3)
I···F3	255.9 (3)
I···F5	279.9 (3)
F7–I–F8	82.0 (2)
F7–I–F9	81.8 (2)
F8–I–F9	163.0 (2)
C1–I–F7	96.5 (2)
C1–I–F8	87.4 (2)
C1–I–F9	89.2 (2)
F3···I···F5	117.2 (2)
F–Sb–F	88.4 (2)–91.6 (2), 176.9 (2)–179.6 (2)

2.5. $C_6H_5IOF_2$

The original preparation of $C_6H_5IOF_2$ is easily reproduced [10]. It is a colorless crystalline solid that is stable up to 216°, at which temperature it decomposes with a mild explosion. The two fluorine atoms are equivalent by ^{19}F NMR spectroscopy. In the Raman spectrum the I=O and IF stretching frequencies can be assigned. A pseudo trigonal bipyramidale structure is established by a single crystal structure determination. There are four crystallographically distinct molecules in the asymmetric unit as shown in Fig. 5 and Table 5. The average I–F bond distance of 195.5(3) is only a little longer

Table 5
Important bond distances (pm) and angles (°) of $C_6H_5IOF_2$, four crystallographic different molecules in the unit, $n = 1–4$

I(n)–O(n)	179.0 (4), 178.1 (4), 177.9 (4), 178.6 (4)
I(n)–F(n1)	194.9 (3), 196.2 (3), 195.3 (3), 193.9 (3)
I(n)–F(n2)	196.9 (3), 195.0 (3), 196.3 (3), 196.8 (3)
I(n)–C(n1)	210.1 (6), 210.7 (5), 209.7 (5), 209.1 (5)
C–C	135.3 (9)–139.7 (8)
C–H	78 (5)–101 (5)
I···O	266.9 (4), 271.1 (4), 272.6 (4), 288.5 (4), 290.2 (4), 291.2 (4)
I···F	303.8 (3), 329.2 (3)
O(n)–I(n)–F(n1)	90.9 (2), 90.1 (2), 91.6 (2), 90.0 (2)
O(n)–I(n)–F(n2)	91.6 (2), 91.1 (2), 92.0 (2), 93.2 (2)
O(n)–I(n)–C(n1)	99.4 (2), 101.2 (2), 100.0 (2), 98.7 (2)
F(n1)–I(n)–F(n2)	171.3 (1), 174.0 (2), 173.2 (2), 170.7 (3)
F(n1)–I(n)–C(n1)	85.8 (2), 86.4 (2), 86.5 (2), 87.4 (2)
F(n2)–I(n)–C(n1)	85.6 (2), 87.6 (2), 87.2 (2), 83.5 (2)

than in the isoelectronic species $C_6H_5IF_3^+$. The average I–O bond length of 178.4(4) pm is typical for an I=O double bond. The solid-state packing is dominated by I=O···I bridges of 266.9(4), 271.1(4), and 272.6(4) pm, resulting in infinite molecular chains. The chains are interconnected by longer I=O···I contacts (288.2(4), 290.2(4), and 291.2(4) pm) and I–F···I contacts (>300 pm), resulting in the formation of infinite double chains.

3. Experimental details

3.1. General techniques

All reactions were performed in dried glass or PFA (Polyperfluoroethene perfluorovinylether) tubes under an argon atmosphere or under vacuum. Solvents were dried using conventional procedures. Water- and oxygen-sensitive compounds were handled in an argon-filled dry box (UB 150 B/G) with residual H_2O/O_2 contents of less than 1 ppm.

NMR spectra were recorded on a 400 MHz multinuclear JEOL Lambda 400 spectrometer. Chemical shifts are relative to tetramethylsilane (^1H, ^{13}C) or $CFCl_3$ (^{19}F). Raman spectra were recorded in glass or PFA capillaries with a Bruker model RFS 100 FT-Raman spectrometer using 1064 nm Nd-YAG laser excitation and an energy of 5–550 mW.

Single crystal structures were determined using an Enraf-Nonius CAD 4 four circle diffractometer or on a Bruker Smart-CCD-1000 M diffractometer. Both instruments are equipped with a Mo Kα, ($\lambda = 0.71073$ pm) X-ray source and a graphite monochromator. Crystals were cut, when necessary, and mounted under cooled nitrogen using a special device of local design [31]. Absorption correction: CAD4: ψ scan method, CCD: equilibration of symmetry related reflections (SADABS procedure). Solution and refinement of the structures were done using the SHELXL programs version 1993 and 1997 [32]. All atoms except hydrogen are refined anisotropically. Hydrogen atoms are refined with one (isotropic) displacement factor for all hydrogen atoms.

3.2. Starting materials

$C_6H_5IO_2$ [33], $B(OTeF_5)_3$ [34], 1,1,3,3,5,5 hexamethylpiperidiumfluoride [14] are prepared following literature procedures. SF_4, IF_5, and SbF_5 are available from laboratory stock and are vacuum distilled prior to use. IF_5 is treated with a small pressure of elemental fluorine prior to the distillation to remove traces of elemental iodine. Anhydrous HF is obtained by several distillations in metal vacuum lines from commercial HF (~99%).

3.3. Synthesis of C_6H_5–IF_4

A 50 ml stainless steel autoclave is filled with 4.72 (20 mmol) $C_6H_5IO_2$, and 13 ml $CHCl_3$ is added [1]. At −196 °C 6.5 g (60 mmol) SF_4 is condensed in. The autoclave is heated 2 h at 70, 100, and 130°, and finally 3 h at 150 °C. At room temperature all volatile material is pumped into a −196° cold trap and disregarded. $C_6H_5IF_4$ is obtained essentially quantitative as a slightly yellow, hydrolytically sensitive crystalline solid. $^{19}F(Et_2O)$ $\delta = -25.63$ ppm. Suitable crystals are obtained from a Et_2O solution that is cooled slowly to −50 °C. Experimental details of the crystal structures and results are laid down in Tables 1 and 6.

3.4. Synthesis of 1,1,3,3,5,5 hexamethyl piperidinium phenyl pentafluoro iodate pip$^+$ $C_6H_5IF_5^-$

In the drybox 140 mg (0.5 mmol) $C_6H_5IF_4$ and 150 mg (0.8 mol) pip$^+$F$^-$ are weighed into a 12 mm inner diameter

Table 6
Experimental detail for the crystal structure determinations

Compound	$C_6H_5IF_4$	$FI(OTeF_5)_4$	pip$^+C_6H_5IF_5^-$ CH_3CN	$C_6H_5IF_3^-$ SbF_6^-	$C_6H_5IOF_2$
Formula	$C_6H_5F_4I$	$F_{21}IO_4Te_4$	$C_{18}H_3$ F_5IN_2	$C_6H_5F_9ISb$	$C_6H_5F_2IO$
a (pm)	597.8 (1)	1912.5 (3)	1173.0 (2)	556.4 (1)	833.37 (2)
b (pm)	1058.5 (1)	992.5 (1)	1756.5 (2)	2401.7 (6)	1201.49 (4)
c (pm)	1181.8 (1)	985.6 (1)	1059.7 (2)	867.3 (2)	1603.48 (5)
α (pm)	90.0	90.0	90.0	90.0	69.183 (2)
β (pm)	90.0	96.39 (1)	92.65 (1)	105.90 (1)	81.145 (2)
γ (pm)	90.0	90.0	90.0	90.0	70.602 (2)
V ($10^6 pm^3$)	748	1859 (4)	2181 (5)	1114.6 (4)	1141.4 (1)
I (°C)	−128	−100	−120	−80	−80
Space group	$P2_1cn$(No33)	C2/c	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z reflections	4	4	4	4	8
Measured	2954	8822	27349	13260	11731
Independent	2758	2342	6656	3320	8372
Parameters	121	133	342	171	422
Instrument	CAD4	CCD	CCD	CCD	CCD
R_1	0.019	0.026	0.031	0.035	0.031
wR_2	0.048	0.061	0.054	0.058	0.059

PFA reaction vessel. With help of a glass vacuum line 5 ml acetonitril are condensed in at −196 °C. The mixture is warmed under stirring to −30 °C, and both solids dissolve. After a short period a colorless precipitation occurs. Further stirring for 1 h at −30 °C completes the reaction. The supernatant solvent is removed, the crystalline solid is washed with little CH_3CN at −30 °C, followed by drying in high vacuum at −30 °C. The colorless product is very sensitive against moisture, and stays undecomposed at room temperature only for minutes, due to loss of acetonitril from the lattice.

^{19}F NMR (CD_3CN, −25 °C). $\delta = 10$ ppm, broad. Raman spectrum (crystalline −40 °C, cm^{-1}): 3091 (vw), 3074 (vw), 3039 (vw), 2960 (w), 2931 (w), 2910 (vw), 2873 (vw), 2254 (w), 2110 (w), 1582 (vw), 1567 (vw), 1470 (w), 1427 (vw), 1370 (vw), 1263 (w), 1176 (vw), 1135 (w), 1096 (vw), 1045 (w), 1033 (vw), 1016 (w), 1004 (vw), 995 (w), 970 (w), 941 (w), 916 (vw), 904 (w), 830 (w), 818 (w), 784 (w), 660 (w), 609 (w), 570 (w), 552 (w), 503 ($\nu_s IF_5$) (s), 474 (w), 425 (w), 372 (m), 351 (w), 340 (w), 317 (w), 298 (w), 270 (w), 251 (m), 226 (w), 174 (w), 155 (w), 106 (vs).

Single crystals are obtained from a CH_3CN solution by slow cooling from 10 to −35 °C. Results see Tables 3 and 6.

3.5. Synthesis of $C_6H_5IF_3^+SbF_6^-$

In the dry box 140 mg (0.5 mol) $C_6H_5IF_4$ are weighed into a PFA reaction vessel of 6.5 mm inner diameter. 3 ml anhydrous HF and 200 mg (0.9 mmol) SbF_5 are condensed into the vessel with help of a metal vacuum line at −196 °C. The vessel is sealed and warmed to −30 °C under shaking. Slow cooling to −80 °C affords colorless platelets of $C_6H_5IF_3^+SbF_6^-$. Experimental details and results of the single crystal structure determination are laid down in Tables 4 and 6. Above −20 °C the compound turns blue, finally black under decomposition.

^{19}F NMR (SO_2, −60 °C): $\delta = -39.9$ (I–F), −111.4 (SbF, broad). ^1H NMR (SO_2, −60 °C): $\delta = 7.116.83$ ppm. Raman (crystalline −100 °C cm^{-1}): 2973 (w), 2927 (w), 2877 (w), 1454 (w), 1095 (w), 1052 (w), 882 (m), 807 (w), 732 (s), 577 (s), 203 (w).

3.6. Synthesis of $C_6H_5IOF_2$

3.5 mg (14.8 mol) $C_6H_5IO_2$ are weighted into a 200 ml PFA vessel [10]. 40% HF in H_2O is added until the $C_6H_5IO_2$ is completely dissolved at room temperature. The solution is heated for 30 min to 60 °C, then cooled to room temperature, then to 0 °C. Colorless needles are crystallizing out. The supernatant solution is decanted, and the product is dried in vacuum at 25 °C. The yield is essentially quantitative. $C_6H_5IOF_2$ is moisture sensitive, and decomposes at 224 °C under mild explosion. It is little (CH_3CN) or not soluble in organic solvents such as CH_2Cl_2, $CFCl_3$.

^{19}F NMR (CD_3CN): $\delta = -29.7$ ppm. Raman (crystalline 25 °C, cm^{-1}): 3070 (w), 1581 (vw), 1564 (vw), 1185 (vw), 1167 (vw), 1013 (m) (νIO), 992 (w), 821 (w), 787 (ν_sIF) (s), 730 (w), 657 (w), 653 (w), 605 (vw), 527 (w), 509 (w), 384 (vw), 330 (w), 319 (w), 299 (w), 264 (m), 254 (m), 216 (w), 140 (m).

Experimental details and results of the single crystal structure determination see Tables 5 and 6.

3.7. Synthesis of $FI(OTeF_5)_4$

In the dry box 2 g (2.7 mmol) $B(OTeF_5)_3$ are weighed in a PFA reaction vessel of 12 mm inner diameter, equipped with a magnetic stirring bar. At the metal vacuum line 5 ml $CFCl_3$ and 0.44 g (2 mmol) IF_5 are condensed into the vessel at −196 °C. The mixture is warmed under stirring to −20 °C, gas evolution (BF_3) sets in. The gas is occasionally pumped off. After termination of the gassing all volatile materials are pumped away between −40 and −20 °C. The colorless product is crystallized from n–C_4F_9–SO_2F. $FTe(OTeF_5)_4$ is moisture sensitive and decomposes slowly at room temperature.

^{19}F NMR (SO_2ClF, −20 °C): ab_4x spectrum, $\delta_a = -46.5$, $\delta_b = -35.5$, $\delta_x = 99.5$ ppm, $J_{ab} = 180$ Hz, $J^{125}Te–F_b = 3696\,Hz$. Raman spectrum (crystalline −50 °C, cm^{-1}): 1439 (w), 1218 (m), 1209 (w), 952 (w), 923 (w), 824 (w), 709 (s), 672 (vs), 663 (s), 627 (m), 502 (m), 477 (m), 428 (vs), 323 (m), 307 (m), 261 (m), 251 (m), 235 (m), 202 (w), 164 (m), 129 (vs), 107 (m).

Suitable single crystals for the crystal structure determination are obtained from a solution in SO_2ClF by cooling from −20 to −78 °C. Experimental details and results of the crystal structure determination see Tables 2 and 6.

Crystallographic data (excluding structure factors) for the structures of the phenyliodine compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 216480 ($C_6H_5IF_4$), CCDC 214290 ($pip^+C_6H_5IF_5^-$), CCDC 214289 (C_6H_5-$IF_3^+SbF_6^-$), and CCDC 214291 ($C_6H_5IOF_2$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: (+44)1223-336033 or E-mail: deposit@ccdc.com.ac.uk.) The crystallographic data of $FI(OTeF_5)_4$ can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Fax: (+49)7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), by quoting the depository number CSD 413244.

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