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Supramolecular Aggregation of Perfluoroorganyl Iodane Reagents in the Solid State and in Solution

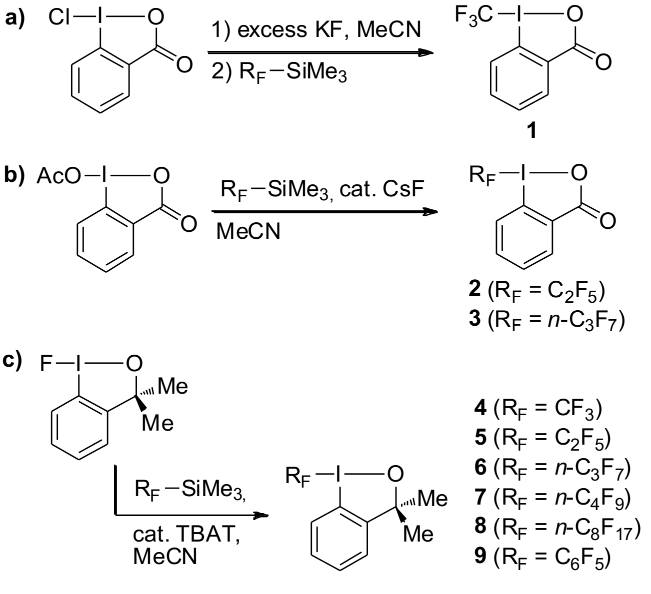
Phil Liebing,[a] Ewa Pietrasiak,[a] Elisabeth Otth,[a] Jorna Kalim,[a] Dustin Bornemann,[a] and Antonio Togni*[a]

Abstract: The crystal structures of different perfluoroorganyl iodanes are described, including four new benziodoxole derivatives with R_F = $^{n}C_3F_7$, $^{n}C_4F_9$, $^{n}C_8F_{17}$ and C_6F_5. In all compounds, the iodine atom shows significant Lewis acidity, and the fourth coordination site is readily filled by secondary bonding interactions, giving rise to a square-planar coordination. While the latter is a good model for benziodoxoles, benziodoxolone derivatives tend to further aggregation by additional weak I···O or I···Aryl contacts. The different interactions lead to the formation of various assemblies with different dimensions in the solid state. Protonation of the reagents results in formation of entirely different supramolecular structures, which are supported by hydrogen bonding. The structural features of the reagents in the solid state reflects well the behavior in solution, and the I-C(R_F) bond is influenced by coordination of Lewis-basic solvents to iodine and by hydrogen bonding with protic solvents. These solvent effects are more pronounced in reagents containing the trifluoromethyl fragment than in derivatives with longer R_F chains.

Introduction

Hypervalent iodine reagents for electrophilic perfluoroalkylation are readily accessible, bench-stable crystalline solids. The first developed and most popular members of this reagent class are 1-(trifluoromethyl)-1,2-benziodoxol-3(1*H*)-one ("acid reagent", as derived from *ortho*-iodobenzoic acid; **1**)[1,2] and trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole ("alcohol reagent", as derived from a tertiary alcohol; **4**).[2,3] The versatility of these reagents has been widely demonstrated in perfluoroalkylations of various organic substrates.[2] Very recently, we demonstrated that this class of reagents is also suitable for oxidative perfluoroalkylation of cobalt(II) complexes.[4] In the past five years, the library of iodane reagents has continuously been growing and now includes acid and alcohol reagents with functionalized CF_2CF_2X moieties (X = *e.g.* OAr, SAr, pyrazolyl).[5] Furthermore, we have shown that acid reagent analogs containing a hypervalent atom other than iodine are accessible, namely with tellurium. This reagent class is compatible with new fluorinated substituents, *e.g.* CHF_2 and C_6F_5.[6] However, knowledge regarding the preparation, molecular structures, and reactivity of iodane reagents with "simple" perfluoroalkyl chains is still very limited. Acid and alcohol reagents with the C_2F_5 group (**2**, **5**) have been briefly mentioned in the literature,[7, 8] as well as an acid reagent with the $^{n}C_3F_7$ group (**3**).[9] Reagents for the transfer of long perfluoroalkyl chains are interesting for potential applications in material sciences, *e.g.* for the development of coatings and organic electronics,[10] as well as liquid crystals.[11] Therefore, we decided to prepare derivatives with extended R_F groups and to study their structures and properties. Furthermore, we were interested in the question if corresponding reagents with perfluoroaryl groups are accessible using known synthetic strategies.

For the preparation of acid- and alcohol-type perfluoroalkyl iodane reagents, different protocols exist, all employing a silane as a perfluoroalkyl source. The trifluoromethyl acid reagent **1** is most conveniently prepared in a one-pot procedure, including chlorine-fluorine exchange from the corresponding chloroiodane with potassium fluoride, and reaction of the in situ formed fluoroiodane with Me_3SiCF_3 (Scheme 1a).[12] The C_2F_5 (**2**)[7] and *n*-C_3F_7 acid reagent (**3**)[9] have been prepared from the corresponding acetoxyiodane (Scheme 1b). A key precursor for the preparation of alcohol reagents with various perfluoroalkyl groups (**4–8**) is the corresponding fluoroiodane. As this compound is more stable than the acid analog, it can be isolated and used for further derivatization.[2,5,13] The fluorine atom is readily substituted by a perfluoroalkyl group upon reaction with the corresponding silane and an appropriate fluoride catalyst such as tetrabutylammonium difluorotriphenylsilicate (TBAT) in dry acetonitrile. We show here that this method is also well suited for the preparation of the pentafluorophenyl (C_6F_5) substituted derivative **9** (Scheme 1c).[2]



Scheme 1. Common synthetic routes to perfluoroorganyl iodanes of the acid reagent (a and b; **1–3**) and the alcohol reagent family (c; **4–9**).

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[a] P. Liebing, E. Pietrasiak, E: Otth, J. Kalim, D. Bornemann, A. Togni*
Department of Chemistry and Applied Biosciences
Swiss Federal Institute of Technology, ETH Zurich
Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland
E-mail: antonio.togni@inorg.chem.ethz.ch
Web: http://www.tognigroup.ethz.ch/

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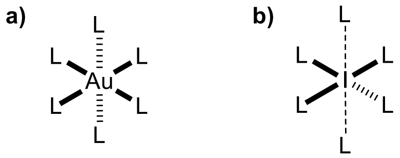
A characteristic structural feature of both acid and alcohol reagents is a T-shaped coordination of the iodine atom by the perfluoroalkyl group, an oxygen atom and an aryl substituent.[1–3,5,8] Typical for the iodane reagents is a significant Lewis acidity, which has been traced back to a σ-hole at the iodine atom.[14] This finding agrees well with the crystal structures of many oxygen containing compounds of trivalent iodine, where the fourth coordination site is occupied by short I···O contacts to adjacent molecules.[15–17] Thereby, a square-planar coordination of the iodine atom is highly favored, which suggests comparison with structurally related metal compounds such as gold(III) complexes. In the latter, the Au atom is well-known to display a square-planar coordination with four ligands, but additionally the fifth and the sixth coordination site are readily occupied in the crystalline state by secondary bonding interactions with free donor moieties (Scheme 2a).[18–20] For this reason, we wondered if similar additional bonding interactions are relevant for trivalent iodine, formally leading to penta- or hexa-coordination of the latter. Thus, it could be meaningful to distinguish between "secondary" bonding interactions (i.e. the occupancy of the fourth coordination site leading to square-planar coordination) and "tertiary" bonding interactions, i.e. the occupancy of further coordination sites by even weaker iodine-donor contacts (Scheme 2b).



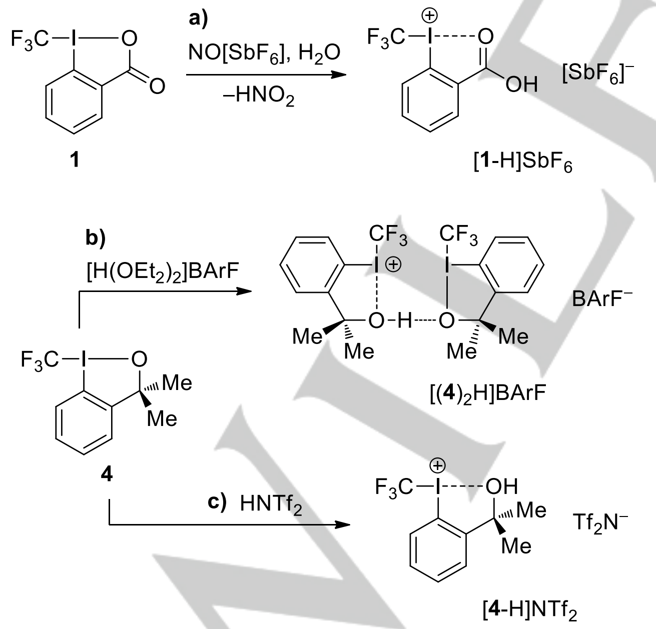
Scheme 2. Orders of bonding interactions in gold(III) complexes (a) and in compounds of trivalent iodine (b): primary bonds (bold continuous lines), secondary bonding interactions (bold dashed lines) and proposed tertiary bonding interaction (thin dashed lines; L = ligand/substituent).

The different bonding interactions might be relevant for reactions of the hypervalent iodine reagents with nucleophilic substrates, as a pre-organization of the reactants by adduct formation could take place. To gain a deeper understanding of the relationship between structures and reactivity of perfluoroorganyl iodane reagents, it is reasonable to investigate non-covalent bonding interactions of the compounds in the solid state and in solution. On the one hand, the coordinative unsaturation of the iodine atom can be expected to govern the solid state structures of the reagents, and analysis of intermolecular contacts can provide valuable information about possible modes of interaction. On the other hand, since chemical reactions of the iodanes occur usually in solution, we were interested in the interaction of these compounds with different solvents. The Lewis acidic nature of the reagents enables the formation of adducts with coordinating solvents, which can contribute to the solvent dependency of the reactivity. Adduct formation has been previously discussed for an alcohol reagent containing a functionalized CF_2CF_2-*o*-OC_6H_4Br group.[5] In this case, a sharp ^{19}F NMR signal has been obtained in $CDCl_3$, while in CD_3CN the signal is broadened due to dynamic exchange of coordinated solvent molecules. Moreover, it has been shown that acid reagent **1** can be activated by nucleophiles such as iodide[21] and tertiary amines.[22] In the latter contribution, the existence of a distinct Lewis acid-base adduct was supported by ^1H NMR titration, but the formation constant of such an adduct with *N*-methylmorphiline has been determined to be quite low at 3.83 l/mol.[22] In contrast, it has been found in our group that alcohol reagent **4** forms more stable adducts with Lewis acids, based on the oxygen atom as a nucleophilic functionality. For instance, the formation constant of an 1:1 adduct with $ZnBr_2$ has been determined to be 234(25) l/mol.[23] A similar behavior is reported for an acid reagent related to **1**, forming a crystalline 2:1 complex with $Zn(OTf)_2$ under coordination of the exposed carbonyl oxygen atom.[2,24,25] Moreover, several examples for a clean protonation of both acid and alcohol reagents with strong acids have been reported, revealing fairly stable iodonium salts.[2,25–29] For instance, **1** forms an adduct with one equiv. $H[SbF_6]$, [**1**-H]$[SbF_6]$,[26,27] while protonation of **4** with "Brookhart's acid" $[H(OEt)_2]$BArF (BArF = Tetrakis(3,5-bis-(trifluoromethyl)phenyl)borate)[30] furnishes the mixed-protonated salt [(**4**)$_2$H]BArF.[2,25] Both species have been briefly mentioned in previous review articles, and we now provide the full characterization thereof, together with the new triflimide salt [**4**-H]NTf_2.[27]

Since the crystal structures of literature-known iodane reagents have not been evaluated concerning non-covalent bonding interactions thus far, we hereby report a thorough study on supramolecular assemblies appearing in the crystal structures of different acid- and alcohol-type reagents, including four new alcohol reagents. We also include a detailed discussion of the crystal structures of the acid adducts [**1**-H]$[SbF_6]$, [**4**-H]NTf_2, and [(**4**)$_2$H]BArF, since we have been particularly interested in the influence of protonation on the supramolecular aggregation of the reagents. Moreover, to also expand on the knowledge about the species present in solution, we conducted a ^{19}F NMR study with different reagents in various donor and acceptor solvents. Similarities and differences between acid and alcohol reagents and between derivatives with different R_F groups, as well as possible influences on the reactivity of the compounds are discussed.

Results and Discussion

The new alcohol reagents **6–9** were prepared by reaction of the appropriate trimethylsilane R_F-$SiMe_3$ with the corresponding fluoroiodane in acetonitrile, following a previously described procedure (*cf.* Scheme 1c).[5] The synthesis of alcohol reagents **4**[13] and **5**,[8] as well as the synthesis of the acid reagents **1**–**3**[7,9,12] was reproduced from previously described procedures. All reagents are crystalline solids, which are stable at –20 °C for several months. The compounds are well soluble in acetonitrile, chloroform and methylene chloride. The new derivatives **6–9** have been characterized by ^1H, ^{13}C and ^{19}F NMR spectroscopy as well as elemental analysis (C, H) and high-resolution mass spectroscopy. The crystalline $H[SbF_6]$ adduct of acid reagent **1**, [**1**-H][SbF_6]·H_2O, was accidentally obtained by hydrolysis of NO[SbF_6] in a mixture with reagent **1** in CH_2Cl_2 (Scheme 3a).[27] However, the water turned out to be important for crystallization, and the very reactive compound seems to be stabilized by hydrogen bonding. X-ray structural analyses revealed that the acidic proton is unambiguously located at the exposed oxygen atom of the iodane molecule (see below). Nonetheless, attempts to isolate significant amounts of the product for full characterization have not been successful. Acid adducts of the alcohol reagent **4** are more easily prepared. Thus, the fairly stable, crystalline [(**4**)$_2$H]BArF has been obtained in almost quantitative yield by treatment of a CH_2Cl_2 solution of **4** with 0.5 equiv. [H(OEt)$_2$]BArF at r.t. (Scheme 3b). Attempts to prepare a corresponding 1:1 adduct, [**4**-H]BArF, led to a rather undefined amorphous material. The preference of the mixed-protonated adduct over a simple [**4**-H]BArF salt can most likely be explained by a more favorable crystal packing of the large [(**4**)$_2$H]$^+$ cation with the bulky BArF$^-$ counterion. Nevertheless, we also succeeded in preparing a fully protonated form of **4** by treatment with triflimide ($HNTf_2$) in CH_2Cl_2, revealing [**4**-H]NTf_2 in a straightforward manner (Scheme 3c). The latter compound is more reactive than [(**4**)$_2$H]BArF and tends to decomposition at ambient temperature. In both acid adducts of **4**, the acidic proton is unambiguously located at the iodane oxygen atom, as it has been verified by X-ray structural analysis (see below). Additionally, the two products could be fully characterized by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy. For [**4**-H]NTf_2, a sharp ^{1}H NMR signal of the acidic proton at 6.76 ppm in dry $CDCl_3$ was observed, while the same was not visible in the case of [(**4**)$_2$H]BArF. The latter compound displays only one set of ^{1}H, ^{19}F and ^{13}C NMR signals of the iodane, indicating that the acidic proton undergoes rapid dynamic exchange between the two iodane moieties. The ^{19}F NMR signal is drastically downfield-shifted as compared to **4** (–40.1 ppm), and for both compounds the shift is remarkably similar at –22.9 ppm ([**4**-H]NTf_2) and –22.6 ppm ([(**4**)$_2$H]BArF). The downfield shift is typical for trifluoromethyl iodanes with enhanced iodonium character, as it has been repeatedly reported.[2,23–28] Moreover, we noticed that the value of $|^1J_{C,F}|$ is strongly influenced by protonation as well, decreasing from 396 Hz for **4** in $CDCl_3$, to 371 Hz ([**4**-H]NTf_2) or 372 Hz ([(**4**)$_2$H]BArF), respectively.



Scheme 3. Protonation of the trifluoromethyl derivatives **1** and **4** with in situ generated $HSbF_6$ (a), with "Brookhart's acid" [H(OEt)$_2$]BArF (b; BArF = Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate), and with $HNTf_2$ (c).

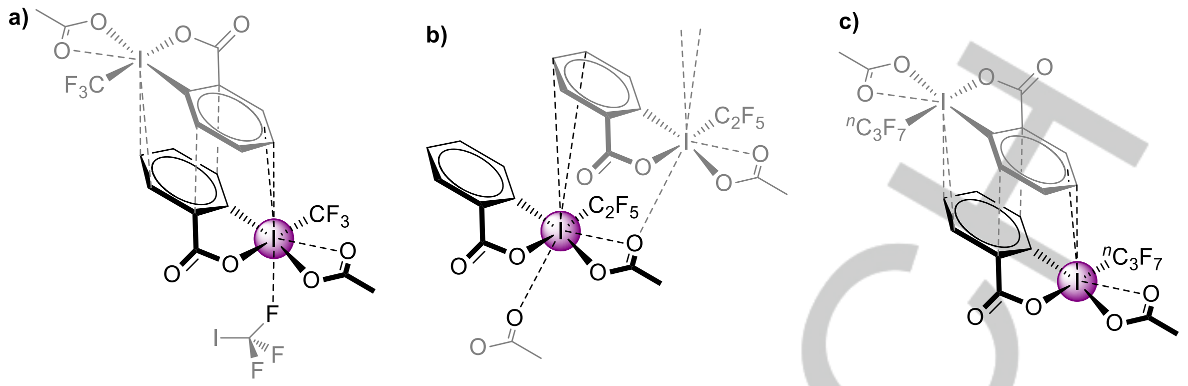
Crystal structures:

Single crystals of **2**, **3** and **7–9** suitable for X-ray structure analysis have been obtained directly from the reaction mixture or by recrystallization from an appropriate solvent (see Experimental section). The molecular structures are illustrated in Figures S1–S4 in the SI, while crystallographic details are given in Table S1 in the SI. Selected geometric parameters are summarized in Table 1. The crystals obtained of **6** were unsuitable for X-ray diffraction. The crystal structures of **1** (CSD[31] ref. code IXOKAH),[1] **4** (KEWNUW)[3] and **5** (AWEFUF)[8] have been reported previously and are included in the discussion of supramolecular aggregation. In all of these compounds, well-defined molecules with a typical T-shaped coordination of the iodine atom are present, where the O-I-C(R_F) fragment slightly deviates from linearity with a bond angle of 168.0(6)–173.63(6)°. The I-C(R_F) bond length is primarily determined by the nature of the oxygen donor group *trans* to the R_F substituent, as described previously.[2,3] Thus, in the alcohol reagents **4, 5, 7** and **8** comprising a strongly electron-donating alkoxy moiety, the I-C(R_F) bond is significantly elongated, while the I-O bond is strongly shortened as compared to the acid reagents **1–3**. Moreover, the I-C(R_F) bond length was found to depend also on the nature of the R_F group itself, being elongated on going from CF_3 to longer perfluoroalkyl chains.

Table 1. Selected interatomic distances (pm) and angles (deg.) in compounds **1–5**, **7** and **8**.

Compound	I-C(R_F)	I-O	O-I-R_F	I···O[a]
1[1]	221.9(4)	228.3(2)	170.5(1)	302.1(3)
2	224.1(2)	227.5(2)	172.81(8)	309.8(2)
3	223.9(2)	227.3(2)	168.93(7)	303.7(2)
4[3]	226.7(3)	211.8(2)	169.78(7)	299.8(1)
5[6]	229.9(2)	211.8(1)	173.53(6)	298.4(2)
7	230.8(2)	212.3(1)	173.63(6)	297.5(1)
8	230.2(2)	212.9(1)	172.36(6)	292.9(1)

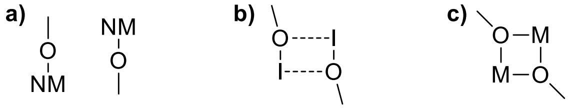
[a] Shortest intermolecular contact.



Scheme 4. Schematic representation of the environment of the iodine atom in the acid reagents **1** (a),[1] **2** (b), and **3** (c).

As foreshadowed above, the crystal structures of compounds **1–9** go beyond simple monomeric molecules, and intermolecular I···O contacts far below the sum of Van-der-Waals radii of I and O (which is 350 pm[17]) have been found in all compounds. In the acid reagents **1–3**, the iodine atom displays a pseudo-square-planar coordination resulting from chelating coordination of a carboxy moiety of an adjacent molecule, comprising a short (302.1(3)–309.8(2) pm) and a longer (310.1(2)–327.3(2) pm) I···O contact. It is worth mentioning that the carboxy moiety shows no tendency towards chelating coordination in some related acid reagents, namely with CSD[31] ref. code GUGZUF (I···O 276.4(4) pm)[32] and WACBOU (I···O 305.0(2) pm).[5] Chelating carboxylate coordination similar as in **1–3** has also been observed in other compounds of trivalent iodine, e.g. 1-Acetoxy-1,2-benziodoxol-3(1*H*)-one (CSD[31] ref. code ABZIOX)[33] and PhI(OOCCF$_3$)$_2$ (CSD[31] ref. code CEZBEO01).[34] Regardless of the different coordination mode of the COO group, the secondary I···O interactions lead to the formation of supramolecular polymeric chains in all acid-type iodane reagents (Figure 1a). In all **1–3**, the fifth coordination site at iodine seems to be occupied by a I···Aryl interaction with an adjacent molecule, which is best described as a η^2-coordination of the *ortho*-phenylene ring in each case (cf. Figures S5–S7 in the SI). Even though adducts of elemental iodine with π-donors are well-characterized by spectroscopic techniques,[35,36] crystal structure data on I···Aryl contacts are lacking. The shortest I···C contacts in **1–3** are 367.6(4)–384.8(2) pm, which is close to the sum of Van der Waals radii of I and C, 368 pm.[37] In **1** and **3**, these interactions lead to dimeric motifs (Scheme 4a, c), which may be further supported by π-π interactions between the phenylene rings. The closest C···C contacts are 365.9(5) pm (**1**) and 371.0(3) pm (**3**), respectively, which is in the range of weak attractive interaction.[38,39] In contrast, a chain-like arrangement is realized in **2** (Scheme 4b). This aggregation mode is most likely supported by another relevant I···O contact of 344.7(2) pm, which formally occupies the sixth coordination site at iodine. The significance of this "tertiary" I···O bond is corroborated by its influence on the other bonds around iodine. In particular, the secondary I···O bond in **2** is comparatively long at 309.8(2) pm, while the same is shorter in **1** (302.1(3) pm)[1] and **3** (303.7(2) pm). Both the tertiary I···O and I···Aryl interactions in **1–3** lead to the formation of puckered two-dimensional arrays in the crystal (Figure 1b, c). In **1**, the sixth coordination site may be regarded as occupied by a weak I···F contact to a CF$_3$ group to an adjacent layer (I···F 345.5(2) pm; cf. sum of Van der Waals radii of I and F 333 pm[37]), while it remains free in **3**.

Since no additional oxygen donor atom is present in the alcohol reagents **4–9**, coordinative saturation of the iodine center is realized by μ-bridging coordination of the alkoxide O atom. As a result, supramolecular dimers are formed in all perfluoroalkyl derivatives **4–8**, featuring a cyclic planar I$_2$O$_2$ core (Figure 2). The corresponding I···O contacts are comparatively short at 292.9(1)–299.8(1) pm, which is in agreement with the electron-rich nature of the alkoxy donor groups. Not surprisingly, similar dimers can be found upon analysis of previously published crystal structures of related compounds (e.g. CSD[31] entries OCIFIQ (I···O 304.0(2) pm),[1] HUQVEV (I···O 304.5(1) pm)[40] and HUQTAP (I···O 298.1(3) pm)[40]), as well as in the corresponding fluoroiodane (YAYDAF; I···O 294.7(4) and 304.6(4) pm)[41] and chloroiodane (HUQSES; I···O 291.8(3) pm).[40] As to the formation of supramolecular dimers, alkoxyiodanes such as **4–8** can formally be regarded as intermediates between non-metal derivatives of alcohols and metal alkoxide complexes. While classical non-metal compounds contain a distinct NM-O single bond without any tendency toward dimerization (NM = non-metal, *e.g.* C in ethers),[42] metal complexes with alkoxide ligands exist frequently as discrete dimers with two M-O bonds per M atom (M = metal).[43,44] (Scheme 5).



Scheme 5. Typical motifs in the molecular structure of alkoxides of different elements: non-metal (a), hypervalent iodine (b), metal (c).

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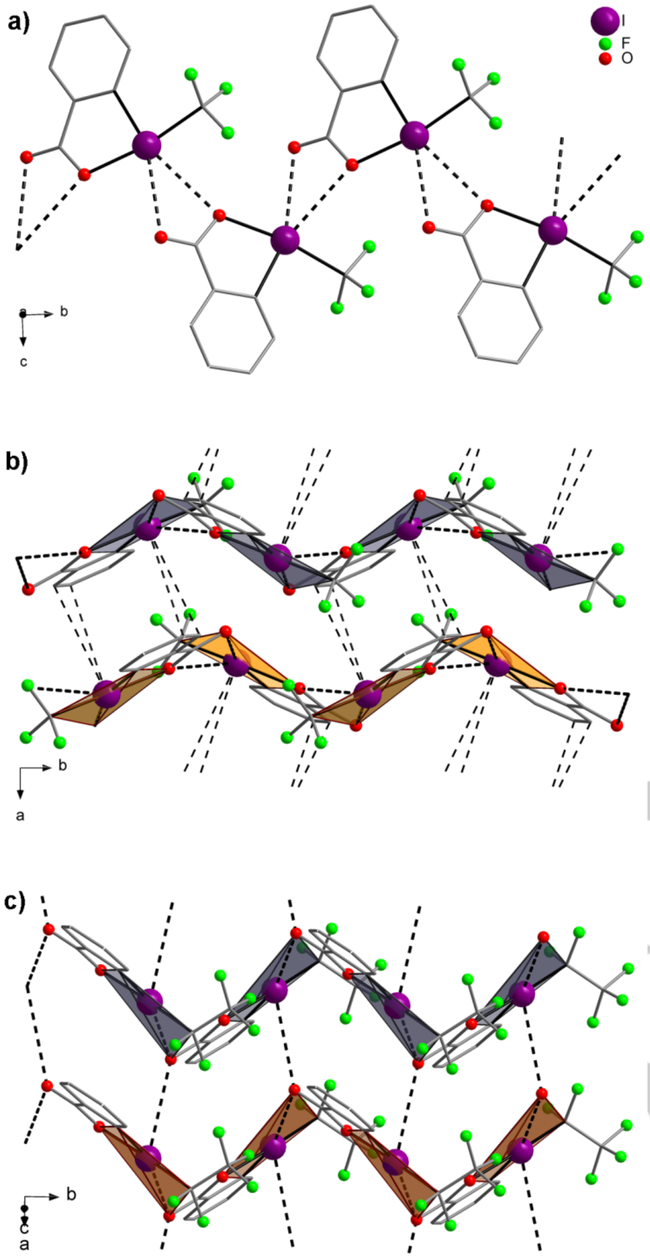


Figure 1. Supramolecular polymeric chains in acid reagents as exemplified by **1**[1] (a), two-dimensional arrays formed by further aggregation of these chains by I···Aryl contacts in **1** (b), and by additional I···O contacts in **2** (c; coordination squares around the I atoms of two adjacent chains highlighted in different colours).

In the alcohol reagents **4–8**, the square-planar coordination of the iodine atom seems to be a good approximation to reality, since no defined interactions of the fifth and sixth coordination site of the iodine atom can be assigned in most of the compounds (Scheme 6b). As compared to the acid-type reagents, this finding might be traced back to a lower Lewis acidity of the iodine center due to the strongly electron-donating alkoxy group, which leads to reduced tendency toward coordination numbers higher than four. Additionally, a more efficient shielding of the iodine center by the methyl groups in the alcohol reagents might also be of relevance. An exception is the trifluoromethyl derivative **4**, where a conspicuously short I···H-C contact to a perpendicularly oriented phenylene group exists (I···H 326.9(3) pm; Scheme 6a; cf. Figure S7 in the SI). This is very close to the upper limit of significant I···H bonds, which is defined in the literature to be 325 pm.[45] Therefore, the environment of the iodine atom in **4** can formally be described with a square-pyramidal [3+1+1] coordination with the weak I···H-C contact at the apex. This arrangement might be further supported by an O···H-C contact to the same phenylene group (O···H 282.3(3) pm).

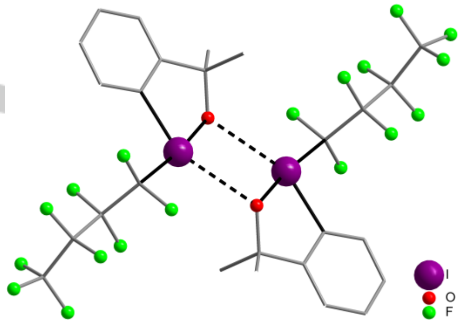
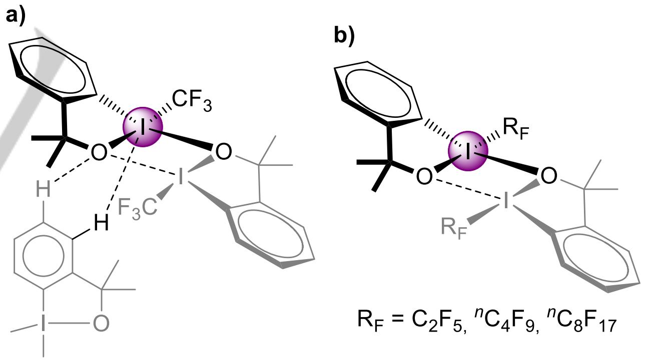


Figure 2. Supramolecular dimers in alcohol reagents as exemplified by the *n*-C_4F_9 derivative **7** (H atoms are omitted for clarity).



Scheme 6. Schematic representation of the environment of the iodine atom in the alcohol reagents **4** (a),[3] and **5–8** (b),[8]

The single crystals of the pentafluorophenyl alcohol reagent **9** did not allow for full structure refinement, but we decided to include this compound in the discussion since its supramolecular structure is surprisingly different than that of the perfluoroalkyl derivatives **4–8**. Namely, μ-bridging coordination of the oxygen donor results in the formation of polymeric chains rather than dimers (Figure 3). This arrangement seems not to be supported by π-interactions between the *ortho*-phenylene and C_6F_5 moieties by significant extent, as they are not properly oriented (*e.g.* angle between *ortho*-phenylene and C_6F_5 planes approx.

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60°). It has been discussed earlier that a slightly displaced parallel orientation between a hydrocarbon and a perfluorocarbon aryl ring is energetically most favored, while between two perfluoroarenes non-directed van-der-Waals interactions are of more importance.[46] The iodine atom in **9** displays no defined tertiary bond interactions with any donor moieties, which can most likely be addressed to efficient shielding of the iodine center by the bulky C$_6$F$_5$ group.

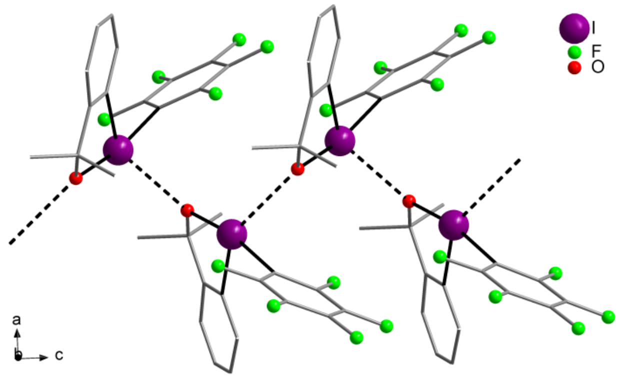


Figure 3. Supramolecular polymeric chains in the perfluorophenyl alcohol reagent **9** (H atoms omitted for clarity).

Crystallographic details on the acid adducts [**1**-H][SbF$_6$]·H$_2$O, [**4**-H]NTf$_2$, and [(**4**)$_2$H]BArF are summarized in Table S2 in the SI, and the molecular structures are illustrated in Figures S8–S11 in the SI. The hexafluoroantimonate salt of protonated acid reagent **1** crystallizes as a hydrate, [**1**-H][SbF$_6$]·H$_2$O. In this compound, the proton is located at the exposed O atom of the carboxyl moiety. As a result of protonation, the I-O bond is considerably elongated from 228.3(2) pm in **1**,[1] to 245.2(3) pm. In contrast, the I-CF$_3$ bond length remains virtually unchanged at 220.8(3) pm. The supramolecular structure of [**1**-H][SbF$_6$]·H$_2$O is entirely different from that in **1**. It is best described as a dimer of contact ion pairs, featuring a centrosymmetric I$_2$O$_2$ ring as a central structural motif (Figure 4; cf. Figure S12 in the SI). The fourth coordination site of the iodine atom is occupied by a close contact to the [SbF$_6$]$^-$ counterion (I···F 299.9(3) pm), which is comparable in length to that observed in previously reported BF$_4^-$ salts of related iodonium species, e.g. CSD[31] entries FAKNUD (I···F 292.4(3) pm),[28] and HUQTIX (I···F 302.8(3) pm).[40] However, the I···F bond in [**1**-H][SbF$_6$]·H$_2$O is displaced from the iodane's coordination plane with an angle of approx. 65°. This can be traced back to two additional relevant bonding interactions of the iodine atom, namely coordination of an H$_2$O molecule (I···OH$_2$ 327.7(3) pm), and a weak I···O(carbonyl) contact to the adjacent iodane molecule (I···O 341.9(3) pm). The dimeric supramolecular structure of [**1**-H][SbF$_6$]·H$_2$O might be further supported by another weak I···F contact of 356.4(3) pm. Consequently, the bonding of the iodine atom can be described as a rather irregular [3+1+3] coordination. The H$_2$O ligand is additionally fixed by an $R_2^2(12)$-type[47] O-H···O bond to the protonated carboxyl group, which is comparatively strong (O···O 255.3(3) pm, O···H approx. 158 pm) relative to literature data.[45,48] The two hydrogen bond donor moieties of the H$_2$O ligand are involved in O-H···F bonding with [SbF$_6$]$^-$ counterions (O···F 272.8(4) and 288.4(4) pm; H···F approx. 190 and 203 pm).

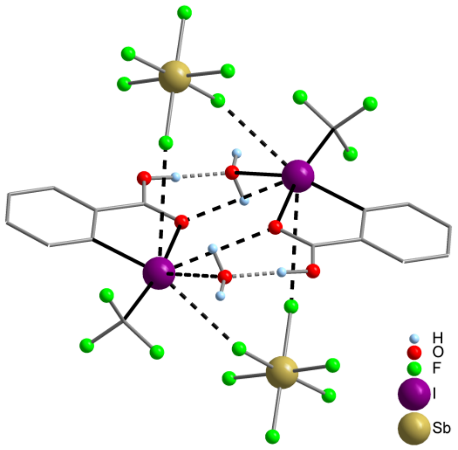


Figure 4. Supramolecular dimer of contact ion pairs of [**1**-H][SbF$_6$]·H$_2$O in the crystal (H atoms attached to C atoms omitted for clarity).

In [**4**-H]NTf$_2$, protonation of the alkoxy moiety results in drastic elongation of the I-O bond from 211.8(2) pm in **4**,[3] to 249.5(1) pm. Different from the protonated acid reagent [**1**-H][SbF$_6$]·H$_2$O, the I-CF$_3$ bond in [**4**-H]NTf$_2$ is significantly shortened to 219.9(2) pm, as compared to free **4**.[3] The iodine atom displays an irregular hexa-coordination by a chelating Tf$_2$N$^-$ anion (I···O 322.7(1) and 324.1(1) pm), and a weaker contact to another Tf$_2$N$^-$ anion (I···O 346.2(1) pm; cf. Figure S13 in the SI). The latter counterion is additionally fixed by an O-H···N bond (O···N 282.1(2) pm; H···N approx. 203 pm), which is comparable in strength with O-H···N bonds in classical organic molecules such as amides.[48] This connectivity pattern leads to a polymeric zigzag chain architecture (Figure 5).

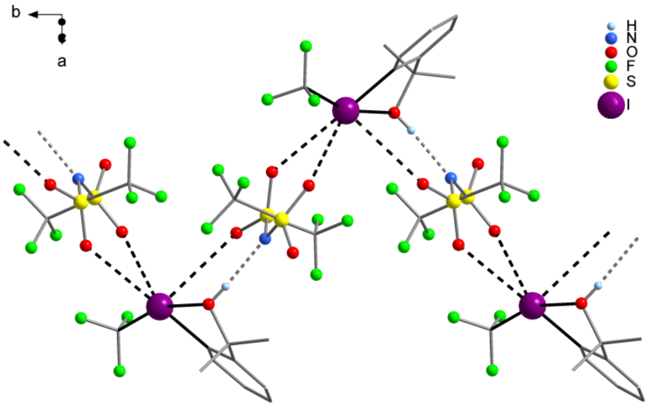


Figure 5. Supramolecular "zigzag" chains of [**4**-H]NTf$_2$ in the crystal (H atoms attached to C atoms omitted for clarity).

The molecular structure of $[(\mathbf{4})_2H]BArF$ is more complex than that of $[\mathbf{4}\text{-}H]NTf_2$, as comprising a protonated and a non-protonated molecule of **4** (Figure 6). These two units are linked by an asymmetric O-H···O bond, i.e. the proton is clearly located at one of the molecules. This hydrogen bond can be regarded as moderately strong with an O···O separation of 258.4(4) pm (H···O approx. 160 pm).[45,48] The asymmetric nature of the hydrogen bond is corroborated by the I-O bond lengths, which are very different in the two molecules. The I-O bond in the protonated molecule is 244.0(3) pm and therefore similar as in $[\mathbf{4}\text{-}H]NTf_2$, while the non-protonated part of the $[(\mathbf{4})_2H]^+$ cation contains a considerably shorter I-O bond of 225.7(2) pm. Nonetheless, both values are much larger than in free reagent **4**.[3] The I-CF_3 bond length within the protonated iodane moiety is similar to that in $[\mathbf{4}\text{-}H]NTf_2$, at 221.4(6) pm. However, the I-CF_3 bond in the non-protonated iodane moiety is also slightly shortened as compared to free **4**, to 223.4(5) pm. The assembly of the two iodane molecules within the $[(\mathbf{4})_2H]^+$ cation seems to be promoted not exclusively by the mentioned O-H···O bond, but also by mutual weak I···Aryl interactions between the two parts of the aggregate. For both iodine atoms, this interaction is best described as a η^2-coordination, with the closest I···C separations being 370.7(4) pm for the exposed and 381.1(4) pm for the inner iodine atom. These values are in the same range as in **1–3**. The mixed protonation of the two iodane molecules results in different contribution to further supramolecular aggregation (cf. Figure S14 in the SI). The non-protonated part of the $[(\mathbf{4})_2H]^+$ cation undergoes typical dimerization via µ-bridging coordination of the alkoxy moiety, leading to a centrosymmetric I_2O_2 ring just as in free **4**. The same does not take place in the protonated iodane moiety, since protonation of the alkoxy moiety disables µ-bridging coordination. Instead, the fourth coordination site of the specific iodine atom is occupied by a close contact to a CF_3 group of the $BArF^-$ counterion. Consequently, the supramolecular structure of $[(\mathbf{4})_2H]BArF$ can be, similarly as in the case of $[\mathbf{1}\text{-}H][SbF_6]\cdot H_2O$, described as a dimer of contact ion pairs. The shortest I···F contact is relatively long at 317.1(2) pm, which can be explained by the weak donor ability of the CF_3 group as compared to SbF_6^- and BF_4^-.[28,40] The fifth coordination site of both iodine atoms is efficiently blocked by the above-mentioned I···Aryl contacts. For the exposed iodine atom, the sixth coordination site may be filled by a weak I···F contact to another $BArF^-$ anion (I···F 351.3(3) pm), while in the case of the inner iodine atom spacial proximity to methyl groups prevents an additional contact to any donor moiety.

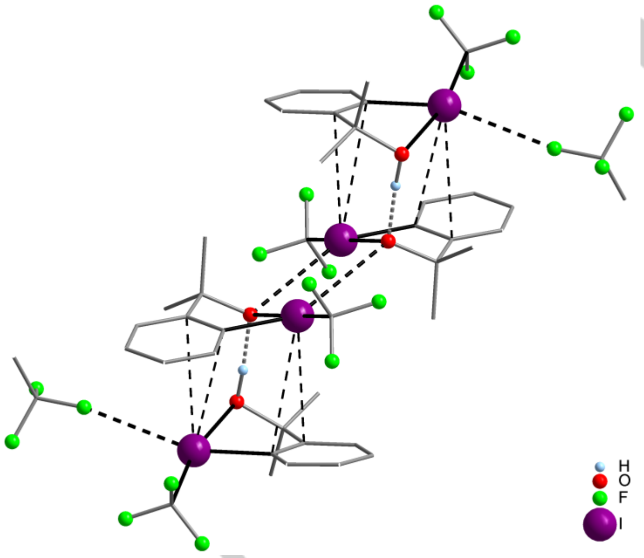


Figure 6. Supramolecular dimer of contact ion pairs of $[(\mathbf{4})_2H]BArF$ in the crystal (H atoms attached to C atoms omitted for clarity; $BArF^-$ anions reduced to CF_3 groups with contact to iodine).

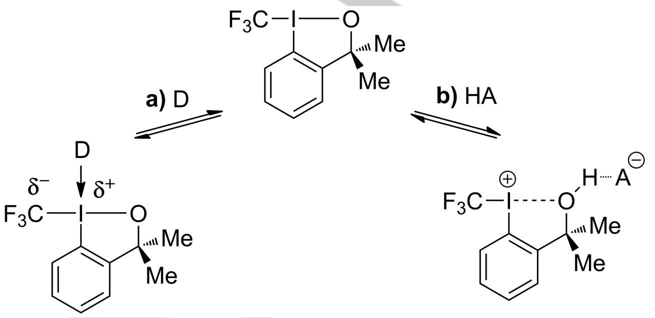
Solution NMR studies:
Since compounds **1–3** and **9** are well soluble in organic solvents, it can be expected that the polymeric supramolecular aggregates present in the solid state are readily broken down to small molecular entities in solution. However, the dimers existent in **4–8** might be of relevance in solutions of low polarity solvents. Aside from monomer-dimer equilibria for the latter compounds, we were interested in the interaction with different donor and acceptor solvents. Regarding the solid state structures of reagents **1–9** and the protonated reagents $[\mathbf{1}\text{-}H][SbF_6]\cdot H_2O$, $[\mathbf{4}\text{-}H]NTf_2$ and $[(\mathbf{4})_2H]BArF$, the bonding and reactivity can be expected to be influenced both by hydrogen bonding and by coordination of donor solvents to the iodine atom. The $^1J_{C,F}$ coupling constant of the CF_3 or CF_2 moiety directly attached to iodine turned out to be a useful measure for these reagent-solvent interactions. Chemical shifts are less suited, since they are more strongly influenced by non-bonding solute/solvent interactions and are therefore usually difficult to interpret (with the exception of protonation, which leads to strong downfield-shift of the ^{19}F NMR signal in the CF_3 derivatives **1** and **4**[2,23–28]; cf. Figures S47–S49 in the SI). To compare acid- and alcohol-type reagents on the one hand, and CF_3 and longer R_F groups on the other hand, the values of $|^1J_{C,F}|$ (which are readily available from the ^{19}F NMR spectra, cf. Figure S50 in the SI) have been determined for solutions of compounds **1**, **2**, and **4** and **5** in a variety of solvents with different donor and acceptor properties (Table 2). In CH_2Cl_2 which is both a poor donor and a poor acceptor, the value of $|^1J_{C,F}|$ is 381 Hz for the CF_3 acid reagent **1**, and 398 Hz for the corresponding alcohol reagent **4**. This difference reflects the more electron-rich nature of the alkoxy moiety as compared to the carboxy moiety, which results in a higher electron-density at the CF_3 fragment. High $|^1J_{C,F}|$ values have generally been observed in compounds with a high negative charge density at the C atom (*e.g.* in trifluoromethyl silicates[49] or metal complexes with CF_3 ligands[4,50]), while considerably smaller values are reported for CF_3 compounds having an electronegative group attached to the C atom.[51] However, the $|^1J_{C,F}|$ values of the α-CF_2 group of the acid- and alcohol-type C_2F_5 derivatives are virtually equal at 334 Hz (**2**) and 335 Hz (**5**). Consequently, $|^1J_{C,F}|$ is not exclusively determined by the I-C(R_F) bond length, as the latter is significantly different in **2** and **5** (*cf.* Table 1). For the CF_3 derivatives **1** and **4**, the value of $|^1J_{C,F}|$ is slightly but significantly

increased (assuming an error of ±1 Hz for the measured values) in coordinating solvents with respect to the values for CH_2Cl_2 as a reference, *e.g.* in DMSO to 383 Hz (**1**) and 402 Hz (**4**), respectively. This finding can be regarded as evidence for the presence of solvent adducts according to Scheme 7a. The increase of $|^1J_{C,F}|$ by solvent coordination can be interpreted taking into account electron donation of the newly added ligand, which also results in an increased electron density at the CF_3 group (as it stabilizes the positive formal charge at the iodine center). Slightly increased $|^1J_{C,F}|$ values for **1** and **4** have also been obtained in benzene and toluene, which are typical π-donating solvents. These examples suggest (in agreement with the proposed I···Aryl interactions in the crystal structures of **1–4**) that the above-described effect is not limited to classical σ-donating solvents, and that the iodane reagents seem to be able to form π-complexes with arenes. Plotting the observed $|^1J_{C,F}|$ values against Gutmann's donor numbers[52] of the corresponding solvents, no clear correlation can be inferred (Figure 7). For instance, high coupling constants for **4** have been found in pyridine and DMSO featuring high donicity, but the extremely strong donor solvent NEt_3 gave an unexpectedly small $|^1J_{C,F}|$ value. Nonetheless, it is to be assumed that a strong interaction with high donicity solvents exists, as the acid reagents **1** and **2** turned out to readily undergo undefined decomposition in NEt_3 (and all tested reagents **1**, **2**, **4** and **5** in hexamethylphosphoric amide, HMPA, too). Generally, a major disadvantage of Gutmann's model for the quantification of solvent donor strength is its simplicity, e.g. not differentiating between hard and soft donors.[53]

Table 2. $^1J_{F,C}$ values (Hz) for selected perfluoroalkyl iodane reagents (**1**, **2**, **4**, **5**) in various solvents (rounded to integers; for C_2F_5 derivatives **4** and **5**: values for the CF_2 moiety).

Solvent	1	2	4	5
CH_2Cl_2	381	334	398	335
$CHCl_3$	380	336	396	334
Benzene	384	336	400	335
Toluene	384	335	400	334
Et_2O	383	– [a]	398	334
MeCN	380	333	399	335
$P(OMe)_3$	383	332	399	334
THF	384	332	400	334
DMSO	383	334	402	336
Py	384	334	401	335
NEt_3	– [d]	– [d]	399	335
EtOH	380	334	394	334
H_2O[b]	377	334	393	334
HOAc	377	335	385	334
TFA	368	– [c]	367	– [c]

[a] ^{13}C satellites not resolved due to low solubility. [b] with ca. 30 vol.-% MeCN to improve solubility. [c] α-CF_2 signal overlapped by solvent signal. [d] fast decomposition.



Scheme 7. Proposed influence of a) donor (D) and b) protic acceptor (HA) solvents on the electron distribution within reagent **4**.

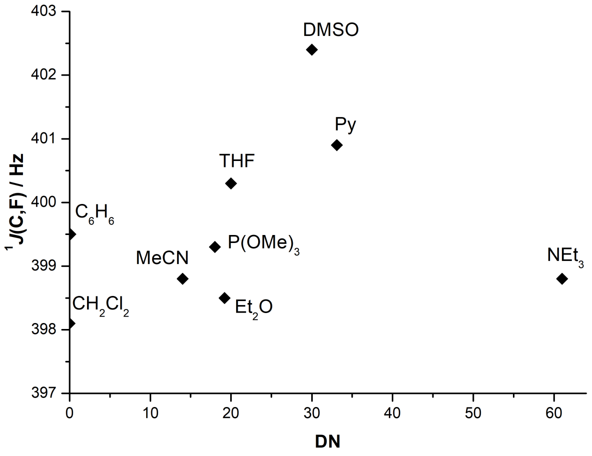


Figure 7. Plot of selected $|^1J_{C,F}|$ values observed for **4** against solvent donor numbers (DN; values taken from [52]).

In contrast, protic solvents such as EtOH, H_2O and HOAc turned out to exert the opposite effect on the C-F coupling, thus resulting in a decrease of $|^1J_{C,F}|$ as compared to the respective value for CH_2Cl_2. Less surprising, this effect is particularly pronounced in the strongly acidic solvent trifluoroacetic acid (TFA), where drastically decreased $|^1J_{C,F}|$ values of 368 Hz (**1**) and 367 Hz (**4**) indicate full protonation of the reagent. The value for **4** in TFA is similar to the values observed for the isolated acid adducts [**4**-H]NTf_2 and [(**4**)$_2$H]BArF. Generally, decrease of $|^1J_{C,F}|$ in protic solvents can be attributed to an electron-withdrawing effect by formation of a hydrogen bond including the iodane's O atom, formally enhancing iodonium cation character of the iodane (Scheme 7b). Plotting $|^1J_{C,F}|$ against Gutmann's solvent acceptor numbers,[53] a clear correlation can only be distinguished for protic solvents exhibiting high acceptor numbers, showing decreasing $|^1J_{C,F}|$ with increasing acceptor number (Figure 8). The poor correlation for the other solvents may be again due to missing differentiation between hard and soft Lewis acids,[53] and to the opposing effect of donating solvents on the coupling constant (*e.g.* MeCN is both a donor and acceptor solvent). For the most acidic solvents $CHCl_3$, EtOH, H_2O, HOAc and TFA, the $|^1J_{C,F}|$ values correlate much better with the solvents' pK_A values.[54] (Figure 9). This correlation is best described with a typical exponential growth function, running toward a limit value of 397 Hz for high pK_A values. This agrees well with the value of 398 Hz for CH_2Cl_2, which is a very poor acceptor.[52] Experiments with **4** in different CH_2Cl_2/EtOH, CH_2Cl_2/HOAc and CH_2Cl_2/TFA mixtures revealed a strong impact on $|^1J_{C,F}|$ even at low percentages of the protic component, which is in agreement with the previous finding that 1:1 adducts as shown in Scheme 7b are readily formed (cf. Figure S54 in the SI).[25,27] In contrast, the effect of donor solvents on $|^1J_{C,F}|$ only becomes significant at a large excess of the donor, as experiments with different CH_2Cl_2/toluene, CH_2Cl_2/pyridine and CH_2Cl_2/DMSO mixtures have shown (cf. Figure S53 in the SI). Consequently, the interaction of the reagents with donor solvents can be assumed to be weaker than with acceptor solvents, being in agreement with the small adduct formation constant reported for **1** with *N*-methylmorpholine.[22] In the C_2F_5 derivatives **2** and **5**, the discussed solvent effects seem to be generally much less pronounced than in the CF_3 derivatives **1** and **4**, as $|^1J_{C,F}|$ values have been obtained in a very narrow range of 334±2 Hz (**2**) or 335±1 Hz (**5**), respectively.

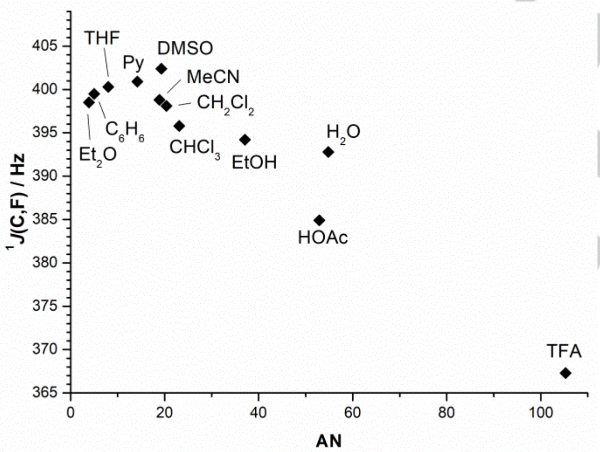


Figure 8. Plot of selected $|^1J_{C,F}|$ values observed for **4** against solvent acceptor numbers (AN; values taken from [52]).

In spite of the above discussed evidence for interactions of **1–9** with different solvents, attempts to detect well-defined dissolved species by ^{19}F NMR spectroscopy failed. Thus, for each compound and solvent only one sharp signal has been obtained. For **4** (whose high solubility allowed for low temperature experiments), a single sharp resonance was observed even at –90 °C in CD_2Cl_2, and 1:1 mixtures thereof with various donor and acceptor solvents (*e.g.* MeCN, NEt_3, EtOH; cf. Figures S51 and S52 in the SI). Consequently, we assume that the dynamic exchange of solvent molecules is too fast to be resolved by NMR techniques. The energies of aggregation as well as the molecular structures of defined solvated species could be the subject of computational studies in future research.

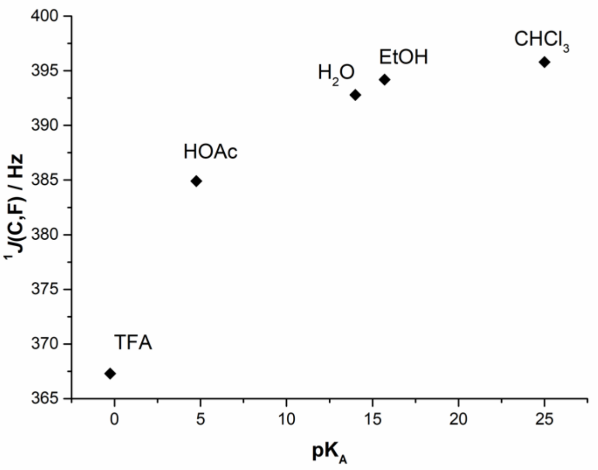


Figure 9. Plot of $|^1J_{C,F}|$ values observed for **4** in protic solvents against solvent pK_A values (taken from [54]).

Conclusions

Notwithstanding the simple molecular structure of perfluoroalkyl and perfluoroaryl iodane reagents, these compounds show a rich supramolecular structural chemistry. In summarizing the results reported here, we have shown that the iodine atom can be formally regarded as coordinatively unsaturated, which is the reason for the pronounced tendency toward supramolecular aggregation in the solid state. Thereby, a square-planar coordination of the iodine atom is strongly favored and realized by a secondary I···O or I···F bond. While this model seems to be well suited for the alcohol reagents **4–9**, we have demonstrated that coordination numbers higher than four are also feasible. In the case of the acid reagents **1–3**, introduction of the term "tertiary bonding interactions" with regard to the fifth and sixth coordination site of the iodine atom seems legitimate. This includes not only weak I···O or I···F contacts, but also I···Aryl interactions. Nevertheless, there is a fine line between secondary and tertiary bonding interactions, and particularly in the case of the iodonium salts [**1**-H][SbF_6]·H_2O and [**4**-H]NTf_2 the two categories cannot be clearly distinguished. The crystal structure analyses of the acid adducts of **1** and **4** also demonstrate impressively that protonation exert considerable influence on the molecular and supramolecular structures of the reagents.

The solution NMR studies presented in this work agree well with our findings from the crystal structure analyses, indicating that similar intermolecular interactions are relevant in solution. This includes coordination of donor solvents to iodine on the one hand, and hydrogen bonding with protic solvents on the other hand. Both types of interactions can be assumed to exert a significant impact on the reactivity of the dissolved reagent. As discussed earlier, perfluoroalkyl iodane reagents can serve formally as a R_F^+ source when activated with a Lewis acid, while they feature a pronounced radical chemistry under other conditions (transition metal catalysis, one-electron reduction, etc.).[2,55] Exploiting the different solvent effects can help enhance or suppress a particular reaction pathway. While clean electrophilic R_F^+ reactivity can be expected to be prominent in acceptor solvents, reactions including R_F radicals seem to be more pronounced in donor solvents.[22] The different aggregation modes in solution also give insight into possible pre-organization of the reagent and a substrate in solution by σ-donation, π-donation, or hydrogen bonding. Knowledge regarding these interactions is valuable in predicting and understanding the reactivity of known and new acid- and alcohol-type reagents in future research.

Experimental Section

General: Preparation of the compounds was carried out with the exclusion of moisture under an inert argon atmosphere using standard Schlenk techniques. Solvents were obtained from common suppliers, distilled and dried over molecular sieves (4 Å). Fluoro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole ("Fluoroiodane"),[13] the silanes (n-C_4F_9)$SiMe_3$[56] and (n-C_8F_{17})$SiMe_3$[56], as well as the known perfluoroalkyl iodanes **1**,[12] **2**,[7] **3**,[9] and **4**[13] were prepared according to published procedures. All other starting materials were obtained from commercial sourced and used without further purification. Automated flash column chromatography was performed on a CombiFlash Rf200 System from Teledyne ISCO with built-in UV-detector and fraction collector. Teledyne ISCO RediSep Rf flash columns used have a 0.035–0.070 mm particle size and 230–400 mesh. NMR spectra were recorded on a Bruker Avance III HD Nanobay 300 (300 MHz), Bruker DPX-400 (400 MHz), or a Bruker DPX-500 (500 MHz) spectrometer, in Chloroform-*D* at ambient temperature (298(2) K). ^{1}H NMR shifts are referenced to the residual ^{1}H signal of the deuterated solvent ($CHCl_3$: δ_H = 7.260 ppm), ^{13}C NMR shifts to the deuterated solvent itself ($CDCl_3$: δ_C = 77.16 ppm). ^{19}F NMR shifts are referenced to neat $CFCl_3$ (δ_F = 0.00 ppm). ^{13}C chemical shifts of CF_2 and CF_3 groups have been determined from ^{19}F/^{13}C HMBC spectra. Elemental analyses (C, H) were performed with a LECO TruSpec Micro apparatus. High-resolution mass spectra (HRMS) were measured on a Bruker Daltonics maXis ESI-QTOF or a Bruker UltraFlex II MALDI-TOF mass spectrometer.

Single crystal X-ray diffraction: Single crystals of the literature-known acid reagents suitable for X-ray structural analysis have been obtained from a saturated CH_2Cl_2/Et_2O (v:v approx. 1:1) solution at –18 °C (**2**) or by slow evaporation of a CH_2Cl_2 solution at 5 °C (**3**). Single-crystals of the new compounds **7–9**, [**1**-H][SbF_6]·H_2O, [**4**-H]NTf_2, and [(**4**)$_2$]BArF have been obtained as described below. X-ray intensity data have been collected on a Bruker Apex II diffractometer equipped with a Apex II CCD area detector, using graphite-monochromated Mo-K$_\alpha$ radiation, at T = 100(2) K. The structures were solved by intrinsic phasing methods (SHELXT-2014/5[57]) and refined by full matrix least-squares methods on F^2 (SHELXL-2014/7[58]), using Olex 1.2.[59] For compound **2**, the absolute configuration was determined using $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ quotients.[60] For [**1**-H][SbF_6]·H_2O, [**4**-H]NTf_2, and [(**4**)$_2$]BArF, the position of the acidic proton was located in the difference Fourier map and refined freely. Even though this approach is somewhat arguable for crystal structures containing iodine as a heavy atom, it led to meaningful results due to the high quality of the dataset in each case. Further experimental data and details on structure refinement are summarized in Tables S1 and S2 in the SI. Crystallographic data including structure factors have been deposited at the CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers **875434** and **1825241–1825246** (cf. Tables S1 and S2 in the SI), or the publication DOI (http://www.ccdc.cam.ac.uk).

Synthesis of Trimethyl(perfluorophenyl)silane: The compound was prepared following a modified literature procedure.[61–63] A solution of pentafluorobenzene (1.3 ml, 11.9 mmol, 1.0 equiv.) in diethyl ether (10 ml) was added dropwise to a mixture of ^{n}BuLi (8.9 ml, 1.6 mol/l in hexanes, 14.3 mmol, 1.2 equiv.) and diethyl ether (60 ml) at –78 °C. The resulting pale yellow solution was stirred for 1 h at –78 °C, and subsequently Me_3SiCl (3.0 ml, 23.8 mmol, 2.0 equiv.) was added dropwise. Stirring was continued overnight, allowing the mixture to warm to room temperature. A white, water-soluble precipitate (presumably LiCl) was formed during this time. The mixture was poured into ice water (100 ml) and the reaction vessel rinsed with ice water and *tert*-butyl methyl ether. The organic phase was separated and the aqueous phase extracted with *tert*-butyl methyl ether (2 × 90 ml). The combined organic extracts were dried over $MgSO_4$ and filtered over a pad of Celite. The solvent was removed on a rotary evaporator (35 °C, 500 mbar), and the residue distilled under reduced pressure at a bath temp. of 85 °C, revealing the product as colourless oil (b.p. 57–60 °C at 2 mbar). Yield: 1.36 g (48%). The identity of the compound was established by comparison of the NMR data with reference data.[64]

General procedure for preparation of reagents 5–9: To a suspension of Fluoroiodane (475 mg, 1.7 mmol, 1.3 equiv.*) in acetonitrile (5 ml), TBAT (7 mg, 0.01 mmol, 1 mol-%) was added at –20 °C. The corresponding (perfluoroorganyl)trimethylsilane (1.3 mmol, 1.0 equiv.) was subsequently added dropwise within 20 min. The yellow to brownish mixture was stirred for 1 h at –20 °C and for 30 min at r.t. For compounds **6** and **9**, the reaction mixture was evaporated to dryness and the product isolated by automated flash column chromatography. For compounds **5**, **7** and **8**, the reaction solution was cooled to –50 °C to ensure complete precipitation of the product. The precipitate was filtered off in the cold, washed with –50 °C cold acetonitrile (2×3 ml) and carefully dried *in vacuo*, revealing a colourless crystalline solid (Caution: prolonged drying in high vacuum can lead to sublimation of the product).

3,3-Dimethyl-1-(perfluoro-*n*-propyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]-iodoxole ("*n*-C_3F_7 alcohol reagent"; 6): Yield: 480 mg (86%). M.p. 50 °C, Anal. calcd. for $C_{12}H_{10}F_7IO$ (M = 430.10 g/mol): C 33.51, H 2.34 %; Found: C 33.89, H 2.41 %. **HRMS:** *m/z* calcd. for $[M+H]^+$, $C_{12}H_{11}F_7IO$: 430.9737; Found: 430.9743. **^{1}H NMR:** δ 1.49 (s, 6H; CH_3), 7.35–7.42 (2×m, 2H; C*H*), 7.49 (2×m, 2H; C*H*) ppm. **^{19}F NMR:** δ –79.8 (t, $^3J_{F,F}$ = 8.4 Hz, 3F; CF_3), –96.3 (m, 2F; α-CF_2), –121.7 (s, 2F; β-CF_2) ppm. **^{13}C NMR:** δ 30.6 (s; CH_3), 77.2 (s; *C*Me$_2$), 109.6 (m; β-CF_2), 111.4 (s; *C*-I), 112.5 (m; α-CF_2), 117.2 (m; CF_3), 127.4 (s; *C*H), 128.6 (m; *C*H), 129.7 (s; *C*H), 130.5 (s; *C*H), 149.7 (s; *C*-CMe$_2$) ppm.

3,3-Dimethyl-1-(perfluoro-*n*-butyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]-iodoxole ("*n*-C_4F_9 alcohol reagent"; 7): R$_f$ = 0.31 (*n*-hexane/ethyl acetate 80/20). Yield: 318 mg (51%). The m.p. of the low-melting solid could not be determined reliably. Anal. calcd. for $C_{13}H_{10}F_9IO$ (M = 480.11 g/mol): C 32.52, H 2.10 %; Found: C 32.43, H 2.17 %. **HRMS:** *m/z* calcd. for $[M+H]^+$, $C_{13}H_{11}F_9IO$: 480.9705; Found: 480.9702. **^{1}H NMR:** δ 1.50 (s, 6H; CH_3), 7.35–7.44 (2×m, 2H; C*H*), 7.49–7.57 (2×m, 2H; C*H*) ppm. **^{19}F NMR:** δ –80.9 (tt, $^3J_{F,F}$ = 9.6 Hz, $^4J_{F,F}$ = 2.7 Hz, 3F; CF_3), –95.5 (t, $^3J_{F,F}$ = 12.4 Hz, 2F; α-CF_2), –118.0 (m, 2F; CF_2), –125.8 (m, 2F; CF_2) ppm. **^{13}C**

NMR: δ 30.6 (s; C*H*$_3$), 77.3 (s; *C*Me$_2$), 108.5 (m; *C*F$_2$), 111.2 (m; *C*F$_2$), 111.5 (s; *C*-I), 117.7 (m; *C*F$_3$), 127.5 (s; *C*H), 128.6 (s; *C*H), 129.8 (s; *C*H), 130.6 (s; *C*H), 150.1 (s; *C*-CMe$_2$) ppm; α-*C*F$_2$ not observed. Single crystals of **7** suitable for X-ray structural analysis were obtained directly from the reaction solution.

3,3-Dimethyl-1-(perfluoro-*n*-octyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]-iodoxole ("*n*-C$_8$F$_{17}$ alcohol reagent"; 8): R$_f$ = 0.21 (*n*-hexane/ethyl acetate 85/15). Yield: 565 mg (64%). M.p. 82 °C. Anal. calcd. for $C_{17}H_{10}F_{17}IO$ (*M* = 680.14 g/mol): C 30.02, H 1.48 %; Found: C 30.17, H 1.54 %. **HRMS:** *m/z* calcd. for [M+H]$^+$, $C_{17}H_{11}F_{17}IO$: 680.9578; Found: 680.9575. **^{1}H NMR:** δ 1.50 (s, 6H; C*H*$_3$), 7.35–7.44 (2×m, 2H; C*H*), 7.49–7.58 (2×m, 2H; C*H*) ppm. **^{19}F NMR:** δ –80.7 (t, $^3J_{F,F}$ = 9.9 Hz, 3F; C*F*$_3$), –95.2 (m br, 2F; α-C*F*$_2$), –116.9 (s br, 2F; C*F*$_2$), –121.4 (s br, 2F; C*F*$_2$), –121.8 (s br, 4F; 2×C*F*$_2$), –122.6 (s br, 2F; C*F*$_2$), –126.0 (s br, 2F; C*F*$_2$) ppm. **^{13}C NMR:** δ 30.6 (s; *C*H$_3$), 77.2 (s; *C*Me$_2$), 108.4 (m; *C*F$_2$), 110.2 (m; *C*F$_2$), 111.3–110.3 (m; 3×*C*F$_2$), 111.3 (m; *C*F$_2$), 111.4 (s; *C*-I), 117.2 (m; *C*F$_3$), 127.6 (s; *C*H), 128.7 (s br; *C*H), 129.8 (s; *C*H), 130.6 (s; *C*H), 150.0 (s; *C*-CMe$_2$) ppm; α-*C*F$_2$ not observed. Single crystals of **8** suitable for X-ray structural analysis were obtained directly from the reaction solution.

3,3-Dimethyl-1-(perfluorophenyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]-iodoxole ("C$_6$F$_5$ alcohol reagent"; 9): *A larger excess of Fluoroiodane (910 mg, 2.3 equiv.) was used for preparation. R$_f$ = 0.19 (*n*-hexane/ethyl acetate 50/50). Yield: 455 mg (82%). M.p. 83–86 °C. Anal. calcd. for $C_{15}H_{10}F_5IO$ (*M* = 428.14 g/mol): C 42.08, H 2.35 %; Found: C 41.82, H 2.56 %. **HRMS:** *m/z* calcd. for [M+H]$^+$, $C_{15}H_{11}F_5IO$: 428.9769; Found: 428.9773. **^{1}H NMR:** δ 1.54 (s, 6H; C*H*$_3$), 6.72 (m, 1H; C*H*), 7.26 (m, 1H; C*H*), 7.40 (m, 1H; C*H*), 7.50 (m, 1H; C*H*) ppm. **^{19}F NMR:** δ –157.4 (m, 2F; *m*-C*F*), –148.8 (m, 1F; *p*-C*F*), –123.5 (m, 2F; *o*-C*F*) ppm. **^{13}C NMR:** δ 31.0 (s; *C*H$_3$), 76.5 (s; *C*Me$_2$), 101.1 (m; *i-C* C$_6$F$_5$), 111.6 (s; *C*-I of *ortho*-phenylene), 126.0 (s; *C*H), 127.2 (s; *C*H), 129.6 (s; *C*H), 130.6 (s; *C*H), 137.1 (m; *o*-*C*F), 143.7 (m; *p*-*C*F), 146.5 (m; *m*-*C*F), 149.0 (s; *C*-CMe$_2$) ppm. Single crystals of **9** suitable for X-ray structural analysis were obtained by slow evaporation of a CH_2Cl_2 solution at r.t.

[1-H][SbF$_6$]·H$_2$O: To a solution of **1** (316 mg, 1.0 mmol) in dichloromethane (10 ml), a solution of NO[SbF$_6$]* (266 mg, 1.0 mmol) in dichloromethane (2 ml) was added at r.t. while stirring. Immediate cooling to –78 °C led to the formation of colourless crystals, which were suitable for X-ray structural analysis. Attempts to isolate the product for full characterization failed due to the low stability of the compound. *The water required for hydrolysis of NO$^+$ and for crystallization was provided by handling the NO[SbF$_6$] in air, so it became moist. When **1** was reacted with dry NO[SbF$_6$], no defined product was observed.

[4-H]NTf$_2$: To a solution of **4** (1.00 g, 3.0 mmol) in dichloromethane (2 ml), a solution of HNTf$_2$ (0.85 g, 3.0 mmol) in dichloromethane (5 ml) was added at r.t. while stirring. Immediate cooling to –78 °C yielded colourless crystals, which were separated by filtration, washed with *n*-pentane (3×5 ml), and dried in vacuo. Yield: 1.70 g (92%). Anal. calcd. for $C_{12}H_{11}F_9INO_5S_2$ (*M* = 611.24 g/mol): C 23.58, H 1.81, N 2.29 %; Found: C 23.38, H 1.93, N 2.43 %. **^{1}H NMR**: δ 1.73 (s, 6H; C*H*$_3$), 6.76 (s, 1H; O*H*), 7.60–7.75 (4×m, 4H; C*H*) ppm. **^{19}F NMR**: δ –78.6 (s, 6F; S-C*F*$_3$ NTf$_2$), –22.8 (s, 3F; I-C*F*$_3$) ppm. **^{13}C NMR**: δ 29.5 (s; *C*H$_3$), 76.7 (s; *C*Me$_2$), 102.3 (q, $|^1J_{C,F}|$ = 371 Hz; I-*C*F$_3$), 107.2 (s; *C*-I), 119.5 (q, $|^1J_{C,F}|$ = 321 Hz, *C*F$_3$ NTf$_2$), 129.8 (s; *C*H), 129.9 (s; *C*H), 132.6 (s; *C*H), 132.9 (s; *C*H), 145.8 (s; *C*-CMe$_2$) ppm.

[(4)$_2$H]BArF: NaBArF (65 mg, 0.073 mmol) was dissolved in diethyl ether (2 ml) and a solution of hydrogen chloride in diethyl ether (37 µl, 2.0 mol/l, 0.073 mmol) was added at r.t. After 10 min of stirring, the solution was evaporated to dryness. The solid residue was extracted with dichloromethane (2 ml), the insoluble matter (NaCl) removed by filtration and rinsed with further dichloromethane (0.5 ml). The so-obtained [H(OEt)$_2$]BArF^{30} solution was added dropwise to a stirred solution of **4** (48 mg, 0.147 mmol) in dichloromethane (1 ml) at r.t., and stirring was continued for 10 min. The solution was subsequently reduced to 0.5 ml, and then stored at –20 °C until colourless crystals have formed (ca. 4 h). *n*-Pentane (1 ml) was added to the cold solution to ensure complete crystallization of the product. The crystals were isolated by filtration, washed with *n*-pentane (2 ml), and dried in vacuo. Yield: 105 mg (95 %). Anal. calcd. for $C_{52}H_{33}BF_{30}I_2O_2$ (*M* = 1524.39 g/mol): C 40.97, H 2.18 %; Found: C 41.02, H 2.22 %. **^{1}H NMR**: δ 1.68 (s, 6H; C*H*$_3$), 7.23 (s br, 2H; C*H*), 7.44–7.70 (5×m, 18H; C*H*) ppm; O*H* not observed. **^{19}F NMR**: δ –62.4 (s, 24F; Ar-C*F*$_3$ BArF), –22.6 (s, 6F; I-C*F*$_3$) ppm. **^{13}C NMR**: δ 30.0 (s; *C*H$_3$), 109.7 (s; *C*-I), 124.7 (q, $|^1J_{C,F}|$ = 272 Hz; *C*F$_3$ BArF), 128.5–133.2 (unresolved signals of iodane and BArF), 134.9 (s; 2,6-CH BArF), 146.4 (s; *C*-CMe$_2$) ppm. **^{11}B NMR**: δ –6.6 (s) ppm.

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Keywords: Perfluoroalkyl • Perfluoroaryl • Hypervalent Iodine • Crystal Structure • Supramolecular • Secondary Bonding Interactions • Iodonium • ^{19}F NMR

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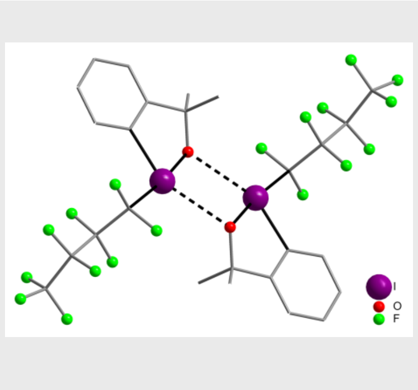
FULL PAPER

The solid state structures of perfluoroorganyl iodane reagents are governed by secondary I···O bonds, giving rise to square-planar coordination of the iodine atom in a first approximation. In solution, the I-C(R_F) bond is influenced by coordination of Lewis-basic solvents to iodine, and by hydrogen bonding with protic solvents.



Hypervalent Iodine Reagents

*Phil Liebing, Ewa Pietrasiak, Elisabeth Otth, Jorna Kalim, Dustin Bornemann, and Antonio Togni**

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Supramolecular Aggregation of Perfluoroorganyl Iodane Reagents in the Solid State and in Solution