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## First Isolation and Structural Characterization of N-base Adducts of Mono- and Perfluoroaryliodine(III) Compounds, ArfIX<sub>2</sub> (X = F, CN)

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Hermann-Josef Frohn, Markus E. Hirschberg, Ulrich Westphal, Roland Boese, Ulrich Floerke, et al.. First Isolation and Structural Characterization of N-base Adducts of Mono- and Perfluoroaryliodine(III) Compounds, ArfIX<sub>2</sub> (X = F, CN). *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2009, 635 (13-14), pp.2249. 10.1002/zaac.200900169 . hal-00484138

**HAL Id: hal-00484138**

**<https://hal.science/hal-00484138>**

Submitted on 18 May 2010

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**First Isolation and Structural Characterization of N-base  
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Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.200900169
Wiley - Manuscript type:	Article
Date Submitted by the Author:	25-Mar-2009
Complete List of Authors:	Frohn, Hermann-Josef; University of Duisburg-Essen, Inorganic Chemistry Hirschberg, Markus E.; University of Duisburg-Essen, Inorganic Chemistry Westphal, Ulrich; University of Duisburg-Essen, Inorganic Chemistry Boese, Roland; University of Duisburg-Essen, Inorganic Chemistry Floerke, Ulrich; University of Paderborn, , Inorganic and Analytical Chemistry Bläser, Dieter; University of Duisburg-Essen, Inorganic Chemistry
Keywords:	Iodine(III), Polyvalent iodine compounds, Multi-nuclear magnetic resonance, N-base adducts



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3 **First Isolation and Structural Characterization of N-base Adducts of**  
4 **Mono- and Perfluoroaryliodine(III) Compounds, Ar<sub>f</sub>I<sub>3</sub> (X = F, CN)**  
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25 Received Dec.     th, 2008.  
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**Abstract.**

The adducts of aryliodinedifluorides  $Ar_fIF_2$ , ( $Ar_f = C_6F_5$ ;  $x-FC_6H_4$ ,  $x = 2, 3, 4$ ) and aryliodinedicyanide  $4-FC_6H_4I(CN)_2$  with N-bases (phenanthroline, 2,2'-bipyridine, and quinoline) were isolated and characterized by their single crystal structure, Raman spectra, and their multi nuclear magnetic resonance spectra in solution. Their properties and their thermal decomposition are discussed with respect to the non-coordinated analogues.

Keywords: Iodine(III); Polyvalent iodine compounds; Fluoroaryliodine(III) compounds; 10-I-3 molecules ( $\lambda^3$ -iodanes); Multi-nuclear magnetic resonance; Molecular structures; N-base adducts.

## Introduction

Fluoroaryliodine(III) compounds,  $Ar_fIX_2$ , with electron-withdrawing ligands  $X = F, CN$  possess remarkable partial positive charge on iodine(III) and free coordination sites in the  $\Psi$ -trigonal bipyramidal environment of  $I^{III}$ . Thus,  $C_6F_5IF_2$  and  $C_6F_5I(CN)_2$  are characterized in the solid state by close intermolecular  $I^{III}\cdots F$  and  $I^{III}\cdots N$  contacts of av. 2.79 and 2.93 Å, respectively [1, 2]. Such electrostatic intermolecular interactions, which are often observed in case of hypervalent molecules, encouraged us to investigate the adduct formation of  $Ar_fIX_2$  with neutral N-bases and thereby to suppress the above mentioned intermolecular interactions. To our knowledge only three crystal structures of aryliodine(III) N-base adducts are known up to now. They concern exclusively iodonium(III) cations, (8-I-2) species [3], namely  $[(C_6H_5)_2I \cdot Py][BF_4]$ ,  $[(C_6H_5)_2I \cdot C_{12}H_8N_2][BF_4]$ , and  $[C_6H_5(t-Bu-CC)I \cdot C_{12}H_8N_2][BF_4]$ . [4, 5] Molecular structures of N-base adducts with (10-I-3) organyliodine(III) molecules,  $RfIX_2$ , are hitherto unknown in literature. We have investigated the coordination of mono- and bidentate N-bases on  $Ar_fIX_2$  molecules ( $X = F, CN$ ).

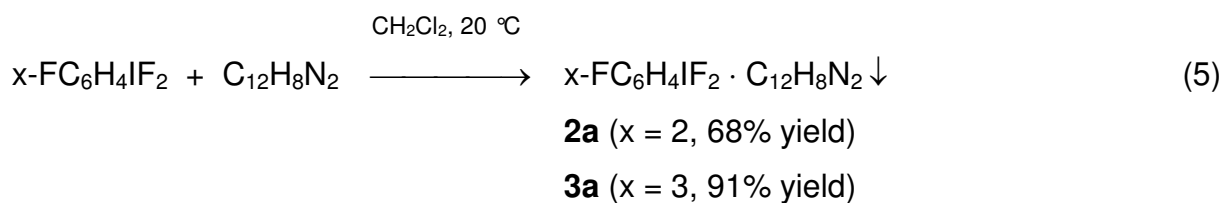
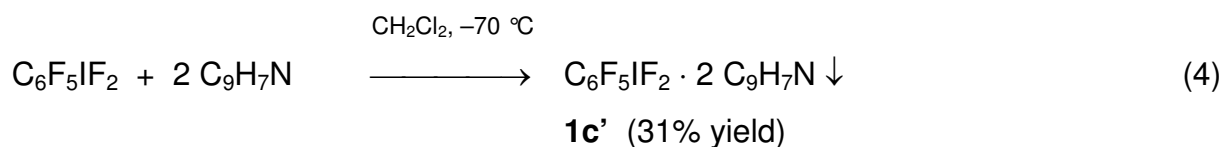
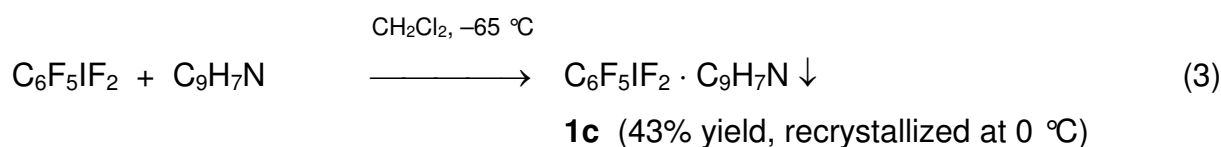
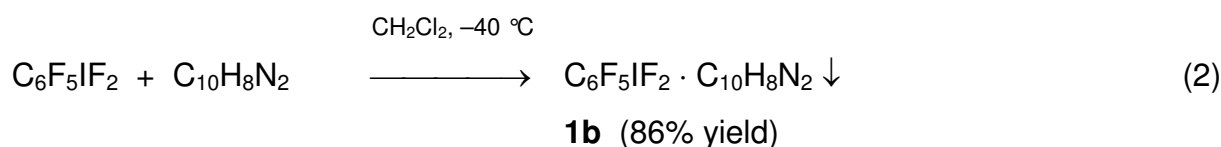
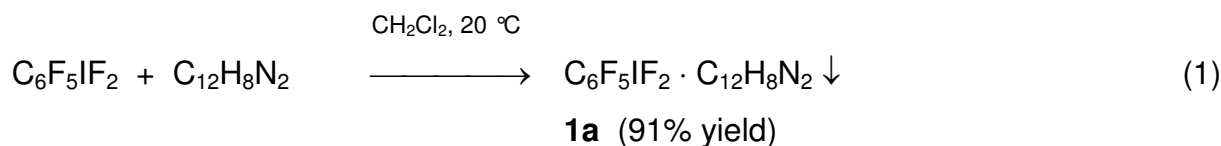
N-base coordination on the parent compound,  $IF_3$ , was discussed controversially. In an early communication, the adduct formation of  $IF_3$  with quinoline, pyridine, acetonitrile, trimethylamine, dimethylformamide, 2,2'-bipyridine, and pyrazine was reported [6] without structural data. In a later paper the principal instability of  $IF_3$  in the presence of the N-base  $CH_3CN$  was claimed under decomposition, even at temperatures below  $-28\text{ }^\circ\text{C}$ , the disproportionation temperature of  $IF_3$  itself [7].

## Results and Discussion

### *N-base adduct formation of $C_6F_5IF_2$ and $x-FC_6H_4IF_2$ ( $x = 2, 3, 4$ )*

Solutions of  $C_6F_5IF_2$  (**1**) and  $x-FC_6H_4IF_2$  ( $x = 2$  (**2**), 3 (**3**), 4 (**4**)) in the weakly coordinating solvent  $CH_2Cl_2$  were reacted with equimolar amounts or a slight excess of the bidentate N-bases 1,10-phenanthroline (**a**) and 2,2'-bipyridine (**b**). The colourless 1:1 adducts **1a** (eq. (1)), **3a**, and **4a** (eq. (5)) precipitated spontaneously at ambient temperature from their colourless reaction mixtures.  $C_6F_5IF_2$  and base **b** formed an orange reaction mixture of adduct **1b** (eq. (2)) which had to be cooled to  $-40\text{ }^\circ\text{C}$  in order to get precipitation allowing isolation of the colourless adduct in a

high yield. In order to obtain adduct **2a** as a solid, the solvent CH<sub>2</sub>Cl<sub>2</sub> had to be removed from the reaction mixture. The colourless adduct was isolated after washing with *n*-pentane. When equimolar amounts of the monodentate N-base quinoline (**c**) were added to the CH<sub>2</sub>Cl<sub>2</sub> solution of **1** at ambient temperature, the solution turned orange-brown and at -65 °C the crude 1:1 product was separated. After extraction with *n*-hexane and subsequent low-temperature crystallization, the colourless solid product **1c** was isolated (eq. (3)). In an independent 1:2 molar reaction of **1** and **c** a purple crude solid precipitated at -70 °C. Extraction of the solid with *n*-hexane and low-temperature crystallization led to the colourless product **1c'** with 1:2 stoichiometry (eq. (4)). In case of **1a**, **1b**, **1c**, and 4-FC<sub>6</sub>H<sub>4</sub>I(CN)<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> (**5a**) (preparation will be discussed in the next chapter) re-crystallization of the 1:1 adduct delivered single-crystals suitable for X-ray structural determination.



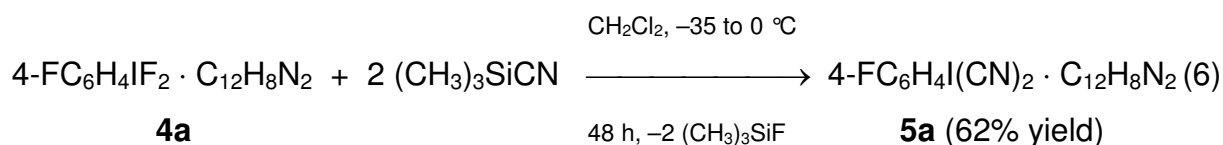
**4a** (x = 4, 93% yield)

The molar ratio C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> (**1**) to C<sub>9</sub>H<sub>7</sub>N (**c**) in the two quinoline adducts **1c** and **1c'** was determined by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy using the internal quantitative standard 1,3,5-F<sub>3</sub>C<sub>6</sub>H<sub>3</sub> to relate the integrals of the donor and acceptor.

The thermal behaviour and stability of the adducts and of the I<sup>III</sup> parent compounds (**Table 1**) differ significantly. We have found two series. All N-base adducts of the strong oxidizer **1** decompose at lower temperature than non-coordinated **1**, whereas the adducts of weaker oxidizers **2** to **4** are more stable than the uncoordinated I<sup>III</sup> molecules. The 2,2'-bipyridine and the phenanthroline adduct of C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub>, both decompose at 198 °C, the latter without an upstream melting whereas all other adducts decompose during or after melting. The low thermal stability of the 1:1- and 1:2-adduct of **1** with monodentate quinoline is indicative of a relatively weak I--N coordination due to the absence of stabilization by chelate formation.

*Fluorine/cyano substitution in the 4-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> · 1,10-phenanthroline adduct (**4a**): isolation of the 4-FC<sub>6</sub>H<sub>4</sub>I(CN)<sub>2</sub> · 1,10-phenanthroline adduct (**5a**)*

To show the influence of the N-base coordination in the adduct on the reactivity of the hypervalent IF<sub>2</sub> triad, we investigated the fluorine/cyano substitution with the acidic reagent (CH<sub>3</sub>)<sub>3</sub>SiCN (eq. (6)).



(CH<sub>3</sub>)<sub>3</sub>SiCN was able to substitute the two I<sup>III</sup>-bonded fluorine atoms in **4a** by cyano groups. Neither the acidic reagent (CH<sub>3</sub>)<sub>3</sub>SiCN nor the acidic by-product (CH<sub>3</sub>)<sub>3</sub>SiF coordinated on the basic N-atoms of **a**. Driving force of the fluorine/cyano substitution is the strong Si-F bond in the co-product (CH<sub>3</sub>)<sub>3</sub>SiF. It should be mentioned that the substitution described in eq. (6) proceeded remarkably slower (48 h at 0 °C) than in the non-coordinated molecule **4** (1 h at 20 °C) [2].

## Spectroscopic characteristics of Fluoroaryliodine(III) N-base adducts

### Multi-NMR spectroscopy

The C<sub>6</sub>F<sub>5</sub> group is a sensitive probe for detecting characteristic changes at the I<sup>III</sup> atom of C<sub>6</sub>F<sub>5</sub>IX<sub>2</sub> compounds in solution by <sup>19</sup>F NMR spectroscopy. Steric influences and the number of ligands at I<sup>III</sup> influence the *o*-fluorine shift values. Changes in the inductive effect of the ligands impact the *m*-fluorine resonance. Finally, changes of the polarising influence of I<sup>III</sup> on the π-system of the C<sub>6</sub>F<sub>5</sub> group affect the *p*-fluorine signal. We have found that addition of one equivalent of monodentate N-base (pyridine, 2-picoline, 2,6-lutidine, and quinoline) to a solution of **1** in CH<sub>2</sub>Cl<sub>2</sub> give rise to a low frequent shift of all four resonances of **1**, most pronounced for the *p*-F atom and the IF<sub>2</sub> group (see Table 2). Coordination of the first N-base proceeds *trans* to the C<sub>6</sub>F<sub>5</sub> group in a mode comparable to an asymmetric hypervalent C-I--base bond. Thus, the partial charge on the N atoms and on the C<sub>6</sub>F<sub>5</sub> group becomes more negative after coordination (Table 3). Overall, N-base coordination is accompanied by a small transfer of charge from the N-base to the λ<sup>3</sup>-iodane molecule. The increase of charge in the R<sub>f</sub>IF<sub>2</sub> subunit of the adduct explains the shielding of the fluorine atoms, as well of the C<sub>6</sub>F<sub>5</sub> group as of the IF<sub>2</sub> group. In agreement with this interpretation is the experimental observation that the addition of a second equivalent of monodentate N-base increases the described shift behaviour. But going from two equivalents of monodentate pyridines to one equivalent of bidentate 1,10-phenanthroline (**a**) or 2,2'-bipyridine (**b**) shows an unexpected deshielding of the IF<sub>2</sub> resonance, which exceeded that in uncoordinated **1**. This deshielding is associated with the presence of intramolecular I-F--H contacts. A similar deshielding of the IF<sub>2</sub> group is also observed in case of *x*-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> (**2**, **3**, and **4**) coordinated by the bidentate base **a**. The C-bonded F atoms in **2a**, **3a**, **4a**, and **5a** show shielding similar to the C<sub>6</sub>F<sub>5</sub> group in **1** after coordination (Table 2). Principally, the analogue <sup>19</sup>F shift tendency was also described for the aliphatic compound CF<sub>3</sub>IF<sub>2</sub> when the coordinating ligand CH<sub>3</sub>CN (solvent) was changed for pyridine. [11] The assignment of the <sup>1</sup>H NMR resonances of the *x*-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> and 4-FC<sub>6</sub>H<sub>4</sub>I(CN)<sub>2</sub> adducts with N-bases suffered from contradictions in the assignment of the monovalent 2- and 3-FC<sub>6</sub>H<sub>4</sub>I [12, 13] and the related trivalent 2- and 3-FC<sub>6</sub>H<sub>4</sub>I<sup>III</sup> iodine compounds [14]. Therefore, we had to clarify the situation by <sup>1</sup>H-<sup>13</sup>C



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3 correlated spectra. We compile all  $^1\text{H}$  NMR data in [Table 4](#). All  $^1\text{H}$  resonances of  
4 phenanthroline in **1a**, **3a**, **4a**, and **5a** appeared deshielded after coordination. In the  
5 phenanthroline adducts of  $\text{Ar}_f\text{IF}_2$ , the shielding of  $\text{H}^{2,9}$  depends on the partial positive  
6 charge on iodine and is strongest in case of **1a**. The stronger shielding of  $\text{H}^{2,9}$  in **5a**  
7 relative to **4a** proposes an influence additional to the charge on iodine in  $\text{Ar}_f\text{I}(\text{CN})_2$   
8 base adducts.  
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10 The  $^{13}\text{C}$  NMR spectroscopic data of **1a** and **1b** are less informative than their  $^{19}\text{F}$   
11 NMR data. The  $\text{C}^1$  resonance of **1a** and **1b** appear deshielded relative to **1** by 6.9  
12 and 4.4 ppm, respectively. Parallel to this, the  $\text{C}^4$  resonances of the adducts are  
13 slightly shielded with respect to **1** ([Table 5](#)).  
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### 23 *Raman spectroscopy*

24 Raman spectra of the neat solid adducts were measured in closed capillaries. The  
25 discussion will be focused on changes of the C-I and  $\text{IF}_2$  vibration frequencies which  
26 proceeded along with coordination on the  $\text{Ar}_f\text{IF}_2$  molecules ([Table 6](#)).  
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29 In the 1:1 adducts with the bidentate N-bases **a** and **b** as well as in 1:1 and 1:2  
30 adducts with the monodentate base **c**, the symmetric F-I-F vibration of  $\text{C}_6\text{F}_5\text{IF}_2$   
31 appears at a lower wave number ( $39$  to  $43\text{ cm}^{-1}$ ) relative to non-coordinated  $\text{R}_f\text{IF}_2$ ,  
32 whereas in case of  $x\text{-FC}_6\text{H}_4\text{IF}_2$  a small increase ( $3$  to  $14\text{ cm}^{-1}$ ) was found. By  
33 coordination, the I-C vibrations of  $\text{C}_6\text{F}_5\text{IF}_2$  and  $x\text{-FC}_6\text{H}_4\text{IF}_2$  were moved to lower  
34 energies. Coordination of base **a** and **b** lowered the C-I wave number in **1a** and **1b**  
35 by  $57$  and  $61\text{ cm}^{-1}$ , respectively, whereas base **c** caused lowering of only  $36\text{ cm}^{-1}$  for  
36 the 1:1 as well as for the 1:2 adduct. In case of the adducts **2a**, **3a**, and **4a** adduct  
37 formation was accompanied by an increase of the C-I wave number of  $24$  to  $31\text{ cm}^{-1}$ .  
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### 48 *Molecular structure and packing of Fluoroaryliodine(III) N-base adducts*

49 Single crystals of  $\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$  (**1a**),  $\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$  (**1b**),  $\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_9\text{H}_7\text{N}$   
50 (**1c**), and  $4\text{-FC}_6\text{H}_4\text{I}(\text{CN})_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$  (**5a**) were grown from  $\text{CH}_3\text{CN}$ ,  $\text{CH}_2\text{Cl}_2$ , or from *n*-  
51 pentane. The crystallographic data of **1a**, **1b**, **1c**, and **5a** are summarized in [Table 7](#).  
52 In **1a** the two N-atoms of the rigid planar bidentate base 1,10-phenanthroline, the two  
53 hypervalently bonded F-atoms and the *ipso*-C-atom form a planar environment  
54 around I(III) with coordination number 5. The distorted pentagonal planar  
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3 coordination of I<sup>III</sup> is comparable with that in IF<sub>3</sub> reported by Seppelt [18] which  
4 showed two significant I--F contacts to two adjacent molecules. The crystals of **1a**  
5 contain four symmetry independent molecules. **1a** presents four features worth  
6 mentioning (a) a longer C-I distance (av. 2.11 Å) than in **1** (av. 2.07 Å), (b) slightly  
7 longer I-F distances (av. 2.01 Å) than in **1** (av. 1.99 Å), (c) short I--N contacts (av.  
8 2.83 Å), and (d) very small N-I-N bite angles (av. 58°). These data agree well with  
9 calculated values of the adduct in the gas phase. Even the experimentally  
10 determined F-I-F angle (av. 161°) fits well with the calculated one (160.1°) and is  
11 compressed compared to **1** (171°, calc. 166°) (Table 3).  
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14 Comparison of the I--N contacts in **1a** with those in [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>][BF<sub>4</sub>] · 0.5  
15 CH<sub>2</sub>Cl<sub>2</sub> [5] which are 2.925(4) and 3.164(4) Å revealed unexpected long contacts in  
16 the I(III) cation-base adduct in comparison with the molecule-base adduct **1a** due to  
17 an additional I--F contact of the cation to the [BF<sub>4</sub>]<sup>-</sup> anion.  
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19 2,2'-bipyridine (**b**) allows shorter I--N contacts to **1** (av. 2.79 Å) and slightly larger bite  
20 angles N-I-N' (58.16(7)°) (Figure 2) than **a**. Because of the rotatable C<sup>2</sup>-C<sup>2'</sup> bond in  
21 **b**, the adduct **1b** shows a small deviation from the pentagonal plane in the  
22 coordination sphere of I<sup>III</sup>. As a consequence of the free rotation of the C<sup>2</sup>-C<sup>2'</sup> bond,  
23 the two pyridine planes form an interplanar angle of 13.4(1)°. The changes of  
24 structural parameters by N-base coordination in **1b** are similar to that in **1a**: C-I  
25 (2.115(3) Å) and I-F (av. 2.00 Å). The shorter I--N contacts in **1b** relative to **1a** cause  
26 a more compressed F-I-F angle (158.63(8)°). Significant F--H<sup>6,6'</sup> contacts of av. 2.35  
27 Å compared to the sum of van der Waals radii H-F of 2.67 [19] are worth mentioning.  
28 In the 1:1 product with quinoline (**1c**), four symmetry independent molecules are  
29 present. One of the two C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> molecules is weakly coordinated by one quinoline  
30 base (Figure 3a). The second C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> molecule is part of a dimer with a  
31 rhombohedral I<sub>2</sub>F<sub>2</sub> ring (Figure 3b). Consequently, the second quinoline molecule is  
32 co-crystallized without any I--N contact (< 5 Å). The 1:1 adduct shows the longest I--  
33 N contact in the series reported here (2.9370(27) Å). Strongly simplified, the I--N  
34 contact is *trans* orientated to the I<sup>III</sup>-C<sub>6</sub>F<sub>5</sub> bond.  
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36 In 4-FC<sub>6</sub>H<sub>4</sub>I(CN)<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> (**5a**) (Figure 4), the two N-atoms of the rigid bidentate  
37 base 1,10-phenanthroline, the *ipso*-C atom of the C<sub>6</sub>F<sub>5</sub> group, and each C atom of  
38 the two cyano groups form a pentagonal planar environment of I(III). It is expedient  
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3 to compare the related adduct **1a** and **5a** concerning their main molecular  
4 parameters. Caused by the lower electron-withdrawing property of the 4-FC<sub>6</sub>H<sub>4</sub>  
5 group and of fluorine (IF<sub>2</sub>), the partial positive charge on I<sup>III</sup> is smaller in **5** than in **1**  
6 (**Table 3**). Parallel, the Ar<sub>f</sub>-I distance (2.1112(16) Å) and the I--N distances in **5a** (av.  
7 2.99 Å) are longer in **5a** than in **1a**.  
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### 13 **Conclusions**

14 Fluoroaryliodine difluorides as well as fluoroaryliodine dicyanide show remarkable  
15 intermolecular contact (I<sup>III</sup>--F or I<sup>III</sup>--N) in the solid state. Coordination of these types  
16 of molecules by bidentate N-bases have in common (a) that a pentagonal  
17 coordination on I<sup>III</sup> results and (b) that no interaction of the F-I-F or NC-I-CN triads  
18 with adjacent iodine(III) is observed. The thermal stability of the isolated solid  
19 adducts exhibits a clear tendency: adducts with the strongly electron-withdrawing  
20 C<sub>6</sub>F<sub>5</sub> group are less stable than with weakly electron-withdrawing x-FC<sub>6</sub>H<sub>4</sub> groups  
21 with respect to uncoordinated Ar<sub>f</sub>IF<sub>2</sub>. The energy of adduct formation of C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> with  
22 N-bases in the gas phase (ΔHF) decreases in the order: phenanthroline > 2,2'-  
23 bipyridine > 2 pyridine > 2 CH<sub>3</sub>CN > picoline(2) > pyridine > lutidine(2,6) > CH<sub>3</sub>CN.  
24 Adduct formation of 4-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> with phenanthroline is more exothermic than that of  
25 4-FC<sub>6</sub>H<sub>4</sub>I(CN)<sub>2</sub>. Significant changes in the NMR spectra, especially in <sup>19</sup>F NMR, can  
26 be deduced on changes in the partial charges in the iodine(III) environment by  
27 coordination: the Ar<sub>f</sub> group as well as the iodine-bonded fluorine atoms increase their  
28 partial negative charge by N-base coordination.  
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### 46 **Experimental Section**

47 All moisture sensitive compounds were handled under an atmosphere of dry argon.  
48 Reactions were carried out in traps constructed from FEP tubes (o.d. = 4.1 mm, i.d.  
49 = 3.5 mm or o.d. = 9.0 mm, i.d = 8.0 mm). CH<sub>3</sub>CN (KMF) was refluxed and distilled  
50 from KMnO<sub>4</sub> and repeatedly refluxed and distilled from P<sub>4</sub>O<sub>10</sub>. CH<sub>2</sub>Cl<sub>2</sub> (KMF) was  
51 treated in sequence with conc. H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3(aq)</sub>, H<sub>2</sub>O and finally refluxed and  
52 distilled from P<sub>4</sub>O<sub>10</sub>. The solvents *n*-pentane and *n*-hexane were distilled and stored  
53 over sodium. C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> was prepared by a modified fluorination of C<sub>6</sub>F<sub>5</sub>I [1, 20], 2-, 3-,  
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3 and 4-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> from the corresponding x-FC<sub>6</sub>H<sub>4</sub>I(OAc)<sub>2</sub> compounds and HF<sub>aq</sub> [21],  
4  
5 3- and 4-FC<sub>6</sub>H<sub>4</sub>I(OAc)<sub>2</sub> using protocol [22]. (CH<sub>3</sub>)<sub>3</sub>SiCN was synthesized by a  
6  
7 literature procedure [23]. 1,10-phenanthroline and 2,2'-bipyridine (Merck KGaA) were  
8  
9 used as delivered. Quinoline (Merck KGaA) was stored over molecular sieve (3 Å).  
10  
11 NMR spectra were recorded on a Bruker spectrometer AVANCE 300 (<sup>13</sup>C at 75.47  
12  
13 MHz, <sup>19</sup>F at 282.40 MHz, and <sup>1</sup>H at 300.13 MHz). The chemical shifts were  
14  
15 referenced to TMS (<sup>13</sup>C), CCl<sub>3</sub>F (<sup>19</sup>F) (C<sub>6</sub>F<sub>6</sub> as a secondary reference, δ = -162.9  
16  
17 ppm), and TMS (<sup>1</sup>H). The Raman spectra were recorded on a Bruker FT-Raman  
18  
19 spectrometer RFS 100/S using the 1064 nm line of a Nd:YAG laser. The  
20  
21 backscattered (180°) radiation was sampled and analysed (Stoke range: 50 to 4000  
22  
23 cm<sup>-1</sup>). The powdered samples were measured in melting point capillaries or FEP  
24  
25 tubes (typical operation parameters: 512 scans and a resolution of 2 cm<sup>-1</sup>) using a  
26  
27 laser power of ≤ 250 mW. For X-ray diffraction see (Table 6).

### 28 ***N*-base adducts of C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> and x-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> (x = 2, 3, 4)**

#### 29 *Synthesis of C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> (1a)*

30  
31 A solution of phenanthroline (0.272 g, 1.509 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.3 mL) was added to  
32  
33 a stirred solution of C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> (0.497 g, 1.497 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL) in a 8 mm i.d.  
34  
35 FEP reaction trap. Spontaneously, a white solid adduct precipitated from the reaction  
36  
37 mixture. After 20 min the supernatant was separated. The solid residue was washed  
38  
39 with CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) and dried in vacuum (0.05 hPa, 20 °C, 60 min). C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> ·  
40  
41 C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> was obtained in 91% yield (0.701 g, 1.367 mmol).

42  
43 DSC measurements on C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> showed decomposition at 198 °C (T<sub>onset</sub>,  
44  
45 exothermic effect). The solubility of C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> was determined to 31 g/L in  
46  
47 CH<sub>2</sub>Cl<sub>2</sub> at 24 °C.

48  
49 Single crystals of C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> were grown from a saturated (60 °C) CH<sub>2</sub>Cl<sub>2</sub>  
50  
51 solution at 20 °C.

52  
53  
54 Ra (20 °C)  $\bar{\nu}$  (cm<sup>-1</sup>): 93 [38], 117 [20], 154 [13], 184 [100], 251 [12], 268 [15], 279  
55  
56 [8], 352 [22], 388 [10], 412 [30], 434 [24], 443 [4], 462 [9], 474 [3], 490 [86], 513 [3],  
57  
58 551 [17], 585 [8], 713 [61], 769 [2], 799 [16], 858 [5], 888 [3], 963 [1], 1044 [33], 1075  
59  
60

[4], 1083 [7], 1095 [8], 1139 [5], 1190 [3], 1205 [5], 1219 [2], 1254 [5], 1270 [7], 1279 [6], 1297 [55], 1314 [3], 1344 [18], 1408 [91], 1427 [10], 1446 [35], 1469 [2], 1506 [11], 1565 [7], 1589 [24], 1600 [18], 1621 [5], 1635 [2], 3075 [33].

### *Synthesis of $C_6F_5IF_2 \cdot C_{10}H_8N_2$ (**1b**)*

A solution of 2,2'-bipyridine (0.179 g, 1.145 mmol) in  $CH_2Cl_2$  (0.7 mL) was added to a stirred solution of  $C_6F_5IF_2$  (0.361 g, 1.088 mmol) in  $CH_2Cl_2$  (1.2 mL) in a 8 mm i.d. FEP reaction trap. An orange solution resulted. After 2 h the solution was cooled to  $-40$  °C and the white solid adduct precipitated. The supernatant was separated and the solid residue was washed with *n*-hexane (3 mL) and dried in vacuum (0.05 hPa, 20 °C, 2h).  $C_6F_5IF_2 \cdot C_{10}H_8N_2$  was obtained in 86% yield (0.456 g, 1.367 mmol). DSC measurements on  $C_6F_5IF_2 \cdot C_{12}H_8N_2$  showed a melting point at 111 °C ( $T_{onset}$ , endothermic effect) and decomposition at 198 °C ( $T_{onset}$ , exothermic effect). Single crystals of  $C_6F_5IF_2 \cdot C_{10}H_8N_2$  were grown from a saturated (20 °C)  $CH_3CN$  solution at  $-30$  °C.

$^{13}C$  NMR ( $CH_3CN$ , 24 °C):  $\delta$  155.7 (m, C(2,2'),  $C_{10}H_8N_2$ ), 150.0 (ddd,  $^1J(C^{6,6'},H) = 180$  Hz,  $^2J(C^{6,6'},H^{5,5'}) = 7$  Hz,  $^3J(C^{6,6'},H^{4,4'}) = 4$  Hz, C(6,6'),  $C_{10}H_8N_2$ ), 145.8 (dm,  $^1J(C^4,F^4) = 259$  Hz, C(4),  $C_6F_5IF_2$ ), 145.4 (dm,  $^1J(C^{2,6},F^{2,6}) = 250$  Hz, C(2,6),  $C_6F_5IF_2$ ), 138.2 (dm,  $^1J(C^{4,4'},H^{4,4'}) = 163$  Hz, C(4,4'),  $C_{10}H_8N_2$ ), 138.2 (dm,  $^1J(C^{3,5},F^{3,5}) = 251$  Hz, C(3,5),  $C_6F_5IF_2$ ), 124.8 (dm,  $^1J(C^{5,5'},H^{5,5'}) = 165$  Hz, C(5,5'),  $C_{10}H_8N_2$ ), 121.7 (dd,  $^1J(C^{3,3'},H^{3,3'}) = 165$  Hz,  $^2J(C^{3,3'},H^{4,4'}) = 7$  Hz, C(3,3'),  $C_{10}H_8N_2$ ), 105.9 (m, C(1),  $C_6F_5IF_2$ ).

Ra (20 °C)  $\bar{\nu}$  ( $cm^{-1}$ ): 90 [58], 142 [21], 180 [100], 238 [18], 282 [17], 341 [17], 352 [29], 384 [20], 442 [16], 487 [81], 492 [81], 555 [5], 584 [15], 618 [7], 636 [4], 650 [4], 732 [6], 766 [34], 801 [17], 1001 [74], 1041 [6], 1061 [36], 1087 [8], 1151 [13], 1254 [9], 1276 [17], 1307 [61], 1397 [9], 1425 [8], 1483 [28], 1570 [31], 1589 [82], 1636 [5], 3063 [20], 3083 [30].

### *Synthesis of $C_6F_5IF_2 \cdot C_9H_7N$ (**1c**)*

A solution of quinoline (170  $\mu$ L, 1.435 mmol) in  $CH_2Cl_2$  (0.7 mL) was added to a stirred solution of  $C_6F_5IF_2$  (0.427 g, 1.286 mmol) in  $CH_2Cl_2$  (0.5 mL) in a 8 mm i.d.

1  
2  
3 FEP reaction trap. An orange-brown solution resulted. After 2 h the solution was  
4 cooled to  $-65\text{ }^{\circ}\text{C}$  and a solid product precipitated. The supernatant was separated  
5 and the solid residue was washed with *n*-pentane (1 mL) and dried in vacuum (0.05  
6 hPa,  $20\text{ }^{\circ}\text{C}$ , 1 h). The pale brown solid was extracted repeatedly with *n*-hexane and  
7 the *n*-hexane extracts were combined (20 mL) and finally cooled to  $-65\text{ }^{\circ}\text{C}$ . A white  
8 solid precipitated, which was separated and dried in vacuum (0.05 hPa,  $20\text{ }^{\circ}\text{C}$ , 1h).  
9  $\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_9\text{H}_7\text{N}$  was obtained in 43% yield (0.256 g, 0.555 mmol) and showed  
10 decomposition at  $80\text{ }^{\circ}\text{C}$  (heating in a closed capillary). The solubility of  $\text{C}_6\text{F}_5\text{IF}_2 \cdot$   
11  $\text{C}_9\text{H}_7\text{N}$  was determined to 9 g/L in *n*-hexane at  $24\text{ }^{\circ}\text{C}$ . The molar ratio  $\text{C}_6\text{F}_5\text{IF}_2$  to  
12  $\text{C}_9\text{H}_7\text{N}$  in the adduct was confirmed by  $^1\text{H}$  and  $^{19}\text{F}$  NMR using the internal standard  
13 1,3,5- $\text{F}_3\text{C}_6\text{H}_3$ .  
14  
15

16 Single crystals of  $\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_9\text{H}_7\text{N}$  were grown from a saturated ( $20\text{ }^{\circ}\text{C}$ ) *n*-pentane  
17 solution at  $0\text{ }^{\circ}\text{C}$ .  
18

19  $^1\text{H}$  NMR (*n*-hexane,  $24\text{ }^{\circ}\text{C}$ ):  $\delta$  8.83 (dd,  $^3J(\text{H}^2, \text{H}^3) = 4\text{ Hz}$ ,  $^4J(\text{H}^2, \text{H}^4) = 2\text{ Hz}$ , 1H,  $\text{H}^2$ ),  
20 8.13 (d,  $^3J(\text{H}^8, \text{H}^7) = 9\text{ Hz}$ , 1H,  $\text{H}^8$ ), 7.99 (d,  $^3J(\text{H}^4, \text{H}^3) = 8\text{ Hz}$ , 1H,  $\text{H}^4$ ), 7.68 (d,  
21  $^3J(\text{H}^5, \text{H}^6) = 8\text{ Hz}$ , 1H,  $\text{H}^5$ ), 7.59 (m, 1H,  $\text{H}^7$ ), 7.42 (m, 1H,  $\text{H}^6$ ), 7.23 (dd,  $^2J(\text{H}^3, \text{H}^4) = 8$   
22 Hz,  $^3J(\text{H}^3, \text{H}^2) = 4\text{ Hz}$ , 1H,  $\text{H}^3$ ).  
23

24 Ra ( $20\text{ }^{\circ}\text{C}$ )  $\bar{\nu}$  ( $\text{cm}^{-1}$ ): 93 [100], 128 [32], 164 [49], 185 [16], 205 [23], 222 [24], 238  
25 [15], 279 [10], 351 [22], 385 [26], 441 [24], 471 [22], 494 [41], 512 [86], 520 [55], 585  
26 [21], 761 [67], 804 [9], 1015 [7], 1038 [20], 1150 [8], 1316 [7], 1370 [93], 1395 [11],  
27 1433 [31], 1502 [5], 1572 [20], 1620 [7], 3065 [28].  
28  
29

### 30 *Synthesis of $\text{C}_6\text{F}_5\text{IF}_2 \cdot 2\text{ C}_9\text{H}_7\text{N}$ (**1c'**)*

31 A solution of quinoline (310  $\mu\text{L}$ , 2.616 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.7 mL) was added to a  
32 stirred solution of  $\text{C}_6\text{F}_5\text{IF}_2$  (0.431 g, 1.299 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL) in a 8 mm i.d.  
33 FEP reaction trap. A purple solution resulted. After 1 h the solution was cooled to  
34  $-70\text{ }^{\circ}\text{C}$  and a solid product precipitated. The supernatant was separated and the  
35 solid residue was washed with *n*-pentane (1 mL) and dried in vacuum (0.05 hPa,  $20$   
36  $^{\circ}\text{C}$ , 1 h). The pale purple solid was extracted repeatedly with *n*-hexane. The *n*-  
37 hexane extracts (20 mL) were combined and cooled to  $-80\text{ }^{\circ}\text{C}$ . A white solid formed  
38 which was separated and dried in vacuum (0.05 hPa,  $20\text{ }^{\circ}\text{C}$ , 1h).  $\text{C}_6\text{F}_5\text{IF}_2 \cdot 2\text{ C}_9\text{H}_7\text{N}$   
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3 was obtained as a white solid in 31% yield (0.256 g, 0.434 mmol).  $C_6F_5IF_2 \cdot 2 C_9H_7N$   
4 showed decomposition at 80 °C (heating in a closed capillary). The solubility of  
5  $C_6F_5IF_2 \cdot 2 C_9H_7N$  was determined to 16 g/L in *n*-hexane at 24 °C. The molar ratio  
6  $C_6F_5IF_2$  to  $C_9H_7N$  in the adduct was proved by  $^1H$  und  $^{19}F$  NMR using the internal  
7 standard 1,3,5- $F_3C_6H_3$ .  
8

9  
10  
11  
12 Ra (20 °C)  $\bar{\nu}$  ( $cm^{-1}$ ): 84 [100], 164 [31], 204 [39], 221 [14], 278 [8], 351 [19], 385  
13 [13], 441 [28], 493 [34], 512 [42], 519 [44], 585 [16], 762 [44], 803 [7], 1015 [6], 1038  
14 [14], 1087 [5], 1143 [6], 1371 [60], 1396 [8], 1434 [19], 1503 [4], 1574 [13], 1620 [6],  
15 3067 [22].  
16  
17  
18  
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### 20 21 22 *Syntheses of $x-FC_6H_4IF_2 \cdot C_{12}H_8N_2$ ( $x = 2$ (**2a**), 3 (**3a**), and 4 (**4a**))*

23  
24 A solution of phenanthroline ( $x = 2$ : 0.346 g, 1.920 mmol;  $x = 3$ : 0.345 g, 1,914 mmol;  
25  $x = 4$ : 0.362 g, 2.009 mmol) in  $CH_2Cl_2$  (1 mL) was added to a stirred solution of  $x$ -  
26  $FC_6H_4IF_2$  ( $x = 2$ : 0.507 g, 1.950 mmol;  $x = 3$ : 0.500 g, 1,923 mmol;  $x = 4$ : 0.517 g,  
27 1.988 mmol) in  $CH_2Cl_2$  (2 mL) in a 8 mm i.d. FEP reaction trap and formed a  
28 colourless mixture.  
29

30  
31  
32  $x = 2$ : The solvent was removed from the reaction solution in vacuum (0.05 hPa, -30  
33 to -20 °C, 1h). The solid was washed with *n*-pentane (24 mL) and dried in vacuum  
34 (0.05 hPa, 20 °C, 1h).  
35

36  
37 2- $FC_6H_4IF_2 \cdot C_{12}H_8N_2$  was obtained in 68% yield (0.584, 1.327 mmol) and showed a  
38 melting point at 129 °C (heating in a closed glass capillary).  
39

40  
41 Ra (20 °C)  $\bar{\nu}$  ( $cm^{-1}$ ): 74 [25], 90 [25], 108 [65], 152 [21], 165 [5], 206 [12], 222 [4],  
42 240 [4], 248 [3], 260 [57], 305 [3], 403 [5], 411 [24], 431 [3], 450 [2], 459 [9], 471 [22],  
43 482 [73], 514 [2], 538 [14], 551 [12], 646 [23], 710 [62], 769 [2], 818 [5], 855 [4], 885  
44 [2], 949 [3], 1020 [12], 1042 [27], 1099 [7], 1142 [2], 1162 [4], 1187 [3], 1231 [4],  
45 1265 [9], 1291 [45], 1309 [4], 1341 [20], 1404 [100], 1421 [15], 1446 [27], 1471 [3],  
46 1506 [20], 1562 [8], 1588 [18], 1602 [8], 1620 [9], 3037 [7], 3059 [8], 3070 [17], 3081  
47 [4].  
48  
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54  $x = 3$  and 4: White solids precipitated at 20 °C and were separated after 1 h and  
55 washed with *n*-pentane (24 mL) and dried in vacuum (0.05 hPa, 20 °C, 1h). 3-  
56  $FC_6H_4IF_2 \cdot C_{12}H_8N_2$  was obtained in 91% yield (0.771, 1.751 mmol).  
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3 DSC measurements on 3-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> showed a melting point at 146 °C  
4 (T<sub>onset</sub>, endothermic effect) and decomposition at 147 °C (T<sub>onset</sub>, exothermic effect).  
5  
6 The solubility of 3-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> was determined to 12 g/L in CH<sub>3</sub>CN at 24 °C.  
7  
8 Ra (20 °C)  $\bar{\nu}$  (cm<sup>-1</sup>): 68 [52], 85 [100], 139 [9], 158 [13], 185 [8], 230 [17], 267 [57],  
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10 411 [28], 472 [11], 485 [65], 552 [18], 653 [19], 711 [68], 806 [4], 847 [4], 1000 [37],  
11  
12 1041 [27], 1052 [4], 1097 [6], 1163 [10], 1201 [5], 1266 [5], 1295 [40], 1341 [20],  
13  
14 1406 [68], 1423 [8], 1447 [24], 1470 [3], 1505 [14], 1563 [4], 1588 [19], 1603 [10],  
15  
16 1621 [9], 3061 [30], 3073 [43], 3091 [13].  
17

18 4-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> was obtained in 93% yield (0.814, 1.849 mmol).  
19

20 DSC measurements on 4-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> showed a melting point at 147 °C  
21 (T<sub>onset</sub>, endothermic effect) and decomposition at 149 °C (T<sub>onset</sub>, exothermic effect).  
22  
23 Ra (20 °C)  $\bar{\nu}$  (cm<sup>-1</sup>): 79 [100], 118 [16], 144 [13], 220 [12], 238 [29], 256 [23], 410  
24 [22], 430 [2], 457 [10], 489 [28], 514 [2], 551 [14], 580 [4], 628 [4], 710 [50], 804 [20],  
25  
26 856 [2], 886 [2], 1008 [2], 1041 [24], 1094 [7], 1140 [4], 1154 [10], 1200 [4], 1220 [2],  
27  
28 1267 [4], 1293 [34], 1342 [13], 1360 [1], 1406 [62], 1421 [8], 1447 [21], 1507 [12],  
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30 1562 [5], 1592 [12], 1620 [6], 3067 [56].  
31  
32

### 33 34 *Synthesis of 4-FC<sub>6</sub>H<sub>4</sub>I(CN)<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> (5a)*

35  
36 A solution of (CH<sub>3</sub>)<sub>3</sub>SiCN (40 μL, 0.300 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 mL) was added to the  
37  
38 stirred cold (−35 °C) suspension of 4-FC<sub>6</sub>H<sub>4</sub>IF<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> (0.047 g, 0.107 mmol) in  
39  
40 CH<sub>2</sub>Cl<sub>2</sub> (0.3 mL). The suspension was stored at 0 °C. After 24 h the supernatant was  
41  
42 separated and the crystals were washed with *n*-pentane and dried in vacuum (0.05  
43  
44 hPa, −10 °C, 15 min). When the supernatant was stored for further 24 h at 0 °C,  
45  
46 crystals precipitated, which were separated and washed with *n*-pentane and dried in  
47  
48 vacuum (0.05 hPa, −10 °C, 15 min). 4-FC<sub>6</sub>H<sub>4</sub>I(CN)<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> was obtained in 62%  
49  
50 yield (0.030 g, 0.066 mmol).

51 Ra (20 °C)  $\bar{\nu}$  (cm<sup>-1</sup>): 85 [100], 108 [74], 150 [27], 204 [11], 232 [85], 317 [32], 340  
52 [28], 357 [27], 412 [23], 551 [13], 577 [16], 623 [9], 709 [33], 806 [27], 1007 [6], 1045  
53 [15], 1100 [10], 1150 [5], 1168 [9], 1267 [5], 1294 [22], 1343 [11], 1405 [46], 1420  
54 [11], 1451 [12], 1566 [6], 1594 [15], 1622 [6], 2139 [43], 3063 [38].  
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3 *Acknowledgements.* We gratefully acknowledge financial support by the Fonds der  
4 Chemischen Industrie and the donation of chemicals by Solvay Fluor and Derivate  
5 GmbH.  
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**Table 1** Thermal stabilities of selected  $\text{Ar}_r\text{IF}_2 \cdot \text{N-base}$  adducts and related  $\text{I}^{\text{III}}\text{-F}$  compounds.

Compound	mp.[°C]	dec [°C]
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	no	198
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$	111	198
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_9\text{H}_7\text{N}$	50	80
$\text{C}_6\text{F}_5\text{IF}_2 \cdot 2 \text{C}_9\text{H}_7\text{N}$	50	80
$\text{C}_6\text{F}_5\text{IF}_2$ <sup>a)</sup>	46–47 [1]	307 [1]
$2\text{-FC}_6\text{H}_4\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	129	-
$2\text{-FC}_6\text{H}_4\text{IF}_2$ <sup>a)</sup>	61 [8]	
$3\text{-FC}_6\text{H}_4\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	146	147
$3\text{-FC}_6\text{H}_4\text{IF}_2$ <sup>a)</sup>	75–76 [8]	
$4\text{-FC}_6\text{H}_4\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	147	149
$4\text{-FC}_6\text{H}_4\text{IF}_2$ <sup>a)</sup>	103 [8]	
$\text{IF}_3$ <sup>a)</sup>	no	-28 [9]

<sup>a)</sup> For comparison

**Table 2**  $^{19}\text{F}$  NMR data of  $\text{C}_6\text{F}_5\text{IF}_2$  and  $x\text{-FC}_6\text{H}_4\text{IF}_2$  N-base adducts ( $x = 2, 3, 4$ ) and the  $4\text{-FC}_6\text{H}_4\text{I}(\text{CN})_2$  phenanthroline adduct and the related uncoordinated  $\text{Ar}_f\text{IX}_2$  compounds

Compound	Solvent	Temp./ $^{\circ}\text{C}$	<i>o</i> -F	<i>p</i> -F	$^3J(\text{F}^4, \text{F}^{3,5})$	$^4J(\text{F}^4, \text{F}^{2,6})$	<i>m</i> -F	<i>l</i> -F <sub>2</sub> , $\tau_{1/2}/\text{Hz}$
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	$\text{CH}_2\text{Cl}_2$	24	-125.3	-149.8	20 Hz	4 Hz	-159.2	-154.0, 13
	$\text{CH}_3\text{CN}$	24	-124.9	-148.1	20 Hz	5 Hz	-158.1	-153.4, 13
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$	$\text{CH}_2\text{Cl}_2$	24	-124.7	-148.3	20 Hz	4 Hz	-158.9	-156.3, 12
	$\text{CH}_3\text{CN}$	24	-124.0	-146.3	20 Hz	-	-157.7	-157.8, 43
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_9\text{H}_7\text{N}$	<i>n</i> -hexane	24	-122.9	-146.3	20 Hz	6 Hz	-158.4	-155.6, 13
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_9\text{H}_7\text{N}^{\text{b)}$	$\text{CH}_2\text{Cl}_2$	24	-123.1	-145.3	20 Hz	5 Hz	-157.8	-160.7, 12
$\text{C}_6\text{F}_5\text{IF}_2 \cdot 2 \text{C}_9\text{H}_7\text{N}^{\text{b)}$	$\text{CH}_2\text{Cl}_2$	24	-123.3	-145.7	20 Hz	5 Hz	-157.9	-161.3, 11
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_5\text{H}_5\text{N}^{\text{b)}$	$\text{CH}_2\text{Cl}_2$	24	-122.9	-145.1	20 Hz	5 Hz	-157.6	-159.4, 13
$\text{C}_6\text{F}_5\text{IF}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}^{\text{b)}$	$\text{CH}_2\text{Cl}_2$	24	-123.1	-145.5	20 Hz	-	-157.8	-161.2, 17
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_6\text{H}_7\text{N}^{\text{b)}$	$\text{CH}_2\text{Cl}_2$	24	-122.8	-145.0	21 Hz	5 Hz	-157.6	-161.1, 12
$\text{C}_6\text{F}_5\text{IF}_2 \cdot 2 \text{C}_6\text{H}_7\text{N}^{\text{b)}$	$\text{CH}_2\text{Cl}_2$	24	-123.2	-145.6	20 Hz	5 Hz	-157.8	-162.3, 11
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_7\text{H}_9\text{N}^{\text{b)}$	$\text{CH}_2\text{Cl}_2$	24	-122.6	-144.5	21 Hz	5 Hz	-157.3	-160.0, 14
	$\text{CH}_2\text{Cl}_2^{\text{a)}$	24	-122.1	-143.6	23 Hz	5 Hz	-156.9	-158.7, 13
	$\text{CH}_3\text{CN}$	24	-122.9	-144.5	20 Hz	5 Hz	-157.0	-160.6, 14
$2\text{-FC}_6\text{H}_4\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	<i>n</i> -hexane	24	-122.6	-145.3	20 Hz	5 Hz	-157.9	-153.1, 13
	$\text{CH}_2\text{Cl}_2$	24	-99.1	-	-	-	-	-163.6, 54
$2\text{-FC}_6\text{H}_4\text{IF}_2^{\text{a)}$	$\text{CH}_3\text{CN}$	24	-98.6	-	-	-	-	-162.5, 10
	$\text{CH}_2\text{Cl}_2$	24	-97.8	-	-	-	-	-165.3, 7
$3\text{-FC}_6\text{H}_4\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	$\text{CH}_3\text{CN}$	24	-97.6	-	-	-	-	-163.8, 13
	$\text{CH}_2\text{Cl}_2$	24	-	-	-	-	-109.1	-175.1, 5

1		CH <sub>3</sub> CN	24	-	-	-	-	-108.6	-172.7,	6
2	3-FC <sub>6</sub> H <sub>4</sub> IF <sub>2</sub> <sup>a)</sup>	CH <sub>2</sub> Cl <sub>2</sub>	24	-	-	-	-	-108.4	-175.0,	9
3		CH <sub>3</sub> CN	24	-	-	-	-	-108.1	-173.0,	10
4	4-FC <sub>6</sub> H <sub>4</sub> IF <sub>2</sub> · C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	24	-	-109.2	-	-	-	-174.6,	7
5		CH <sub>3</sub> CN	24	-	-108.0	-	-	-	-171.2,	12
6	4-FC <sub>6</sub> H <sub>4</sub> IF <sub>2</sub> <sup>a)</sup>	CH <sub>2</sub> Cl <sub>2</sub>	24	-	-109.1	-	-	-	-174.6,	7
7		CH <sub>3</sub> CN	24	-	-107.8	-	-	-	-171.1,	9
8	4-FC <sub>6</sub> H <sub>4</sub> I(CN) <sub>2</sub> · C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	24	-	-106.8	-	-	-	-	
9		CH <sub>3</sub> CN	24	-	-105.3	-	-	-	-	
10	4-FC <sub>6</sub> H <sub>4</sub> I(CN) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	24	-	-104.8	-	-	-	-	

19 a) For comparison

20 b) Reaction mixture

**Table 3** Calculated geometrical parameters and natural atomic charges, NBO, (RHF, LANL2DZ [10]) of Ar<sub>f</sub>I<sub>X</sub><sub>2</sub> · N-base adducts

Compound	Distances and angles					NBO analysis (I <sup>III</sup> environment)				
	C <sup>1</sup> -I/Å	I-X/Å	I--N/Å	∠ X-I-X/°	∠ C <sup>1</sup> -I--N/°	C <sup>1</sup> Ar <sub>f</sub>	I	X	N N-base	ΔHF(Coord.) <sup>a)</sup>
<b>1a</b>	2.104	2.033	2.883	160.1	151.2	-0.434	1.777	-0.744	-0.593 <sup>b)</sup>	-103.7
					151.2	-0.335			0.046	
<b>1b</b>	2.103	2.031	2.901	160.1	151.7	-0.434	1.776	-0.743	-0.598 <sup>c)</sup>	-94.6 <sup>d)</sup>
					151.7	-0.332			0.042	
<b>1c</b>	2.088	2.015	2.970	166.0	159.2	-0.440	1.734	-0.730	-0.621 <sup>e)</sup>	-46.9
		2.021				-0.281		-0.735	0.019	
<b>1 · C<sub>5</sub>H<sub>5</sub>N</b>	2.089	2.014	2.951	164.9	156.2	-0.437	1.734	-0.729	-0.623 <sup>f)</sup>	-48.7
		2.021				-0.288		-0.735	0.019	
<b>1 · 2 C<sub>5</sub>H<sub>5</sub>N</b>	2.094	2.024	3.077	160.1	143.8	-0.430	1.764	-0.738	-0.604 <sup>f)</sup>	-76.8
		2.025	3.082		143.6	-0.311		-0.738	0.023 <sup>g)</sup>	
<b>1 · 2-(CH<sub>3</sub>)C<sub>5</sub>H<sub>4</sub>N</b>	2.089	2.014	2.955	165.4	158.3	-0.439	1.734	-0.729	-0.650 <sup>h)</sup>	-49.4
		2.022				-0.290		-0.736	0.021	
<b>1 · 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N</b>	2.087	2.017	3.089	165.6	180.00	-0.440	1.732	-0.731	-0.667 <sup>i)</sup>	-43.7
						-0.286			0.016	
<b>1 · CH<sub>3</sub>CN</b>	2.082	2.012	3.092	165.0	180.00	-0.437	1.730	-0.728	-0.493 <sup>j)</sup>	-36.9
						-0.281			0.006	
<b>1 · 2 CH<sub>3</sub>CN</b>	2.084	2.006	3.015	164.8	167.9	-0.441	1.746	-0.721	-0.532 <sup>j, k)</sup>	-73.7
		2.028	5.518		125.9	-0.284		-0.745	0.003 <sup>l)</sup>	

1											
2											
3	<b>1</b>	2.079	2.003	-	166.4	-	-0.428	1.673	-0.719	-	-
4							-0.235				
5	<b>4a</b>										
6		2.152	2.034	3.089	167.7	153.3	-0.342	1.666	-0.751	-0.562 <sup>b</sup>	-65.9
7							-0.178			0.014	
8											
9	<b>4</b>	2.149	2.014	-	171.2	-	-0.303	1.550	-0.736	-	
10											
11	<b>5a</b>	2.137	2.254	3.290	166.5	154.7	-0.289	1.289	-0.601	-0.558 <sup>b)</sup>	-58.1
12											
13	<b>5</b>	2.155	2.239	-	171.7	-	-0.248	1.178	-0.585	-	-

<sup>a)</sup>  $\Delta\text{HF}(\text{Coord.}) = \text{HF}(\text{Ar}_f\text{IX}_2 \cdot \text{N-base}) - (\text{HF}(\text{Ar}_f\text{IX}_2) + \text{HF}(\text{N-base}))$ . <sup>b)</sup> NBO(N atom) of the uncoordinated N-base -0.493. <sup>c)</sup> NBO(N atom) of the uncoordinated N-base (*cis*-conformation, local minimum) -0.514. <sup>d)</sup> calculated from 2,2'-bipy with *cis*-conformation (local minimum); with 2,2'-bipy in the ground state (*trans*-conformation)  $\Delta\text{HF}(\text{Coord.}) = -58.6$  kJ/mol. <sup>e)</sup> NBO(N atom) of the uncoordinated N-base -0.530. <sup>f)</sup> NBO(N atom) of the uncoordinated N-base -0.537. <sup>g)</sup> Sum of NBO values for both CH<sub>3</sub>CN, individual NBO values: 0.011 for both coordinated py. <sup>h)</sup> NBO(N atom) of the uncoordinated N-base -0.567. <sup>i)</sup> NBO(N atom) of the uncoordinated N-base -0.597. <sup>j)</sup> NBO(N atom) of the uncoordinated N-base -0.406. <sup>k)</sup> NBO(N atom) of very weakly coordinated CH<sub>3</sub>CN -0.483. <sup>l)</sup> Sum of NBO values for both CH<sub>3</sub>CN, individual NBO values: 0.007 (strongly coordinated CH<sub>3</sub>CN), -0.004 (weakly coordinated CH<sub>3</sub>CN).

**Table 4**  $^1\text{H}$  NMR data of  $\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{phenanthroline}$  and  $x\text{-FC}_6\text{H}_4\text{IF}_2 \cdot \text{phenanthroline}$  ( $x = 2, 3, 4$ ) and related iodo compounds

Compound	Solvent	T/°C	Shift values $\delta/\text{ppm}$ of $x\text{-FC}_6\text{H}_4\text{I}$ groups	Shift values $\delta/\text{ppm}$ of phenanthroline base
<b>1a</b>	$\text{CH}_2\text{Cl}_2$	24	-	9.22 ( $\text{H}^{2,9}$ ) <sup>a</sup> , 8.37 ( $\text{H}^{4,7}$ ) <sup>b</sup> , 7.89 ( $\text{H}^{5,6}$ ) <sup>c</sup> , 7.69 ( $\text{H}^{3,8}$ ) <sup>d</sup>
	$\text{CH}_3\text{CN}$	24	-	9.20 ( $\text{H}^{2,9}$ ), 8.52 ( $\text{H}^{4,7}$ ), 8.00 ( $\text{H}^{5,6}$ ), 7.79 ( $\text{H}^{3,8}$ )
<b>2a</b>	$\text{CH}_2\text{Cl}_2$	24	8.29 ( $\text{H}^5$ ), 7.61 ( $\text{H}^6$ ), 7.41 ( $\text{H}^3$ ) 7.31 ( $\text{H}^4$ )	9.19 ( $\text{H}^{2,9}$ ), 8.25 ( $\text{H}^{4,7}$ ), 7.77 ( $\text{H}^{5,6}$ ), 7.61 ( $\text{H}^{3,8}$ )
	$\text{CH}_3\text{CN}$	24	8.35 ( $\text{H}^5$ ), 7.68 ( $\text{H}^6$ ), 7.50 ( $\text{H}^3$ ), 7.38 ( $\text{H}^4$ )	9.12 ( $\text{H}^{2,9}$ ), 8.35 ( $\text{H}^{4,7}$ ), 7.85 ( $\text{H}^{5,6}$ ), 7.68 ( $\text{H}^{3,8}$ )
<b>3a</b>	$\text{CH}_2\text{Cl}_2$	24	7.76 ( $\text{H}^{2,6}$ ), 7.56 ( $\text{H}^5$ ), 7.23 ( $\text{H}^4$ )	9.16 ( $\text{H}^{2,9}$ ), 8.27 ( $\text{H}^{4,7}$ ), 7.81 ( $\text{H}^{5,6}$ ), 7.64 ( $\text{H}^{3,8}$ )
	$\text{CH}_3\text{CN}$	24	7.82 ( $\text{H}^{2,6}$ ), 7.64 ( $\text{H}^5$ ), 7.33 ( $\text{H}^4$ )	9.12 ( $\text{H}^{2,9}$ ), 8.37 ( $\text{H}^{4,7}$ ), 7.89 ( $\text{H}^{5,6}$ ), 7.70 ( $\text{H}^{3,8}$ )
<b>4a</b>	$\text{CH}_2\text{Cl}_2$	24	7.96 ( $\text{H}^{2,6}$ ), 7.31 ( $\text{H}^{3,5}$ )	9.13 ( $\text{H}^{2,9}$ ), 8.28 ( $\text{H}^{4,7}$ ), 7.82 ( $\text{H}^{5,6}$ ), 7.64 ( $\text{H}^{3,8}$ )
	$\text{CH}_3\text{CN}$	24	8.07 ( $\text{H}^{2,6}$ ), 7.37 ( $\text{H}^{3,5}$ )	9.12 ( $\text{H}^{2,9}$ ), 8.38 ( $\text{H}^{4,7}$ ), 7.90 ( $\text{H}^{5,6}$ ), 7.70 ( $\text{H}^{3,8}$ )
<b>5a</b>	$\text{CH}_2\text{Cl}_2$	0	8.24 ( $\text{H}^{2,6}$ ), 7.29 ( $\text{H}^{3,5}$ )	9.23 ( $\text{H}^{2,9}$ ), 8.32 ( $\text{H}^{4,7}$ ), 7.85 ( $\text{H}^{5,6}$ ), 7.68 ( $\text{H}^{3,8}$ )
	$\text{CH}_3\text{CN}$	0	8.30 ( $\text{H}^{2,6}$ ), 7.37 ( $\text{H}^{3,5}$ )	9.12 ( $\text{H}^{2,9}$ ), 8.39 ( $\text{H}^{4,7}$ ), 7.92 ( $\text{H}^{5,6}$ ), 7.71 ( $\text{H}^{3,8}$ )
2- $\text{FC}_6\text{H}_4\text{I}$	$\text{CDCl}_3$	24	7.74 ( $\text{H}^5$ ), 7.30 ( $\text{H}^6$ ), 7.05 ( $\text{H}^3$ ) 6.88 ( $\text{H}^4$ )	
	$\text{CH}_3\text{CN}$	24	7.72 ( $\text{H}^5$ ), 7.32 ( $\text{H}^6$ ), 7.07 ( $\text{H}^3$ ) 6.90 ( $\text{H}^4$ )	
2- $\text{FC}_6\text{H}_4\text{IF}_2$	$\text{CH}_2\text{Cl}_2$	24	8.24 ( $\text{H}^5$ ), 7.66 ( $\text{H}^6$ ), 7.43 ( $\text{H}^3$ ) 7.33 ( $\text{H}^4$ )	
	$\text{CH}_3\text{CN}$	24	8.30 ( $\text{H}^5$ ), 7.69 ( $\text{H}^6$ ), 7.48 ( $\text{H}^3$ ) 7.35 ( $\text{H}^4$ )	
3- $\text{FC}_6\text{H}_4\text{I}$	$\text{CDCl}_3$	24	7.46 ( $\text{H}^6$ ), 7.43 ( $\text{H}^2$ ), 7.05 ( $\text{H}^5$ ) 7.03 ( $\text{H}^4$ )	
	$\text{CH}_3\text{CN}$	24	7.45 ( $\text{H}^{2,6}$ ), 7.07 ( $\text{H}^{4,5}$ )	
3- $\text{FC}_6\text{H}_4\text{IF}_2$	$\text{CH}_2\text{Cl}_2$	24	7.72 ( $\text{H}^{2,6}$ ), 7.58 ( $\text{H}^5$ ), 7.24 ( $\text{H}^4$ )	
	$\text{CH}_3\text{CN}$	24	7.73 ( $\text{H}^{2,6}$ ), 7.59 ( $\text{H}^5$ ), 7.28 ( $\text{H}^4$ )	
4- $\text{FC}_6\text{H}_4\text{I}$	$\text{CDCl}_3$	24	7.61 ( $\text{H}^{2,6}$ ), 6.82 ( $\text{H}^{3,5}$ )	
	$\text{CH}_3\text{CN}$	24	7.62 ( $\text{H}^{2,6}$ ), 6.86 ( $\text{H}^{3,5}$ )	
4- $\text{FC}_6\text{H}_4\text{IF}_2$	$\text{CH}_2\text{Cl}_2$	24	7.95 ( $\text{H}^{2,6}$ ), 7.30 ( $\text{H}^{3,5}$ )	
	$\text{CH}_3\text{CN}$	24	8.01 ( $\text{H}^{2,6}$ ), 7.32 ( $\text{H}^{3,5}$ )	



1	2-FC <sub>6</sub> H <sub>4</sub> I(CN) <sub>2</sub> <sup>e)</sup>	CH <sub>2</sub> Cl <sub>2</sub>	-10	8.25 (H <sup>5</sup> ), 7.78 (H <sup>6</sup> ), 7.54 (H <sup>3</sup> ) 7.40 (H <sup>4</sup> )
2	3-FC <sub>6</sub> H <sub>4</sub> I(CN) <sub>2</sub> <sup>e)</sup>	CH <sub>2</sub> Cl <sub>2</sub>	-10	8.04-8.05 (H <sup>2,6</sup> ), 7.64 (H <sup>5</sup> ), 7.47 (H <sup>4</sup> )
3				
4	4-FC <sub>6</sub> H <sub>4</sub> I(CN) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-10	8.21 (H <sup>2,6</sup> ), 7.31 (H <sup>3,5</sup> )
5				
6	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	24	9.10 (H <sup>2,9</sup> ), 8.25 (H <sup>4,7</sup> ), 7.79 (H <sup>5,6</sup> ), 7.61 (H <sup>3,8</sup> )
7				

8 a) (dd, <sup>3</sup>J(H<sup>2,9</sup>,H<sup>3,8</sup>) = 4.6 Hz, <sup>4</sup>J(H<sup>2,9</sup>,H<sup>4,7</sup>) = 1.7 Hz). b) (dd, <sup>3</sup>J(H<sup>4,7</sup>,H<sup>3,8</sup>) = 8.1 Hz, <sup>4</sup>J(H<sup>4,7</sup>,H<sup>2,9</sup>) = 1.7 Hz). c) (s, τ<sub>1/2</sub> = 1,2 Hz). d) (dd,  
9 <sup>3</sup>J(H<sup>3,8</sup>,H<sup>4,7</sup>) = 8.1 Hz, <sup>3</sup>J(H<sup>3,8</sup>,H<sup>2,9</sup>) = 4.6 Hz). e) The assignments proposed in [2] which were based on [12, 13, 14] are now  
10 corrected.  
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**Table 5**  $^{13}\text{C}$  NMR data of the  $\text{C}_6\text{F}_5\text{IF}_2$  group in  $\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$  and  $\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$  adducts

Compound	Solvent	T/°C	C <sup>1</sup>	C <sup>2,6</sup>	$^1J(\text{C}^{2,6}, \text{F}^{2,6})$	C <sup>3,5</sup>	$^1J(\text{C}^{3,5}, \text{F}^{3,5})$	C <sup>4</sup>	$^1J(\text{C}^4, \text{F}^4)$
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2^{\text{a)}$	$\text{CH}_2\text{Cl}_2$	24	109.9	144.4	249 Hz	137.0	255 Hz	143.7	257 Hz
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2^{\text{b)}$	$\text{CH}_2\text{Cl}_2$	24	107.4	144.3	251 Hz	136.9	256 Hz	144.0	246 Hz
$\text{C}_6\text{F}_5\text{IF}_2^{\text{c)}$	$\text{CH}_2\text{Cl}_2$	24	103.0	145.4	263 Hz	137.1	257 Hz	144.5	256 Hz

<sup>a)</sup>  $\text{C}_{12}\text{H}_8\text{N}_2$  base: 123.6 (dm,  $^1J(\text{C}^{3,8}, \text{H}^{3,8}) = 166$  Hz, C(3,8)), 126.5 (dm,  $^1J(\text{C}^{5,6}, \text{H}^{5,6}) = 163$  Hz, C(5,6)), 129.0 (m, C(4a,6a)), 136.9 (dm,  $^1J(\text{C}^{4,7}, \text{H}^{4,7}) = 163$  Hz, C(4,7)), 144.8 (m, C(10a,10b)), 150.4 (dm,  $^1J(\text{C}^{2,9}, \text{H}^{2,9}) = 183$  Hz, C(2,9)). <sup>b)</sup>  $\text{C}_{10}\text{H}_8\text{N}_2$  base: 121.1 (dm,  $^1J(\text{C}^{3,3'}, \text{H}^{3,3'}) = 167$  Hz, C(3,3')), 123.9 (dm,  $^1J(\text{C}^{5,5'}, \text{H}^{5,5'}) = 165$  Hz, C(5,5')), 137.3 (dm,  $^1J(\text{C}^{4,4'}, \text{H}^{4,4'}) = 164$  Hz, C(4,4')), 149.6 (ddd,  $^1J(\text{C}^{6,6'}, \text{H}^{6,6'}) = 181$  Hz,  $^2J(\text{C}^{6,6'}, \text{H}^{5,5'}) = 7$  Hz,  $^3J(\text{C}^{6,6'}, \text{H}^{4,4'}) = 4$  Hz, C(6,6')), 154.5 (m, C(2,2')). <sup>c)</sup> For comparison.

**Table 6** Influence of N-base coordination on selected vibrations in the Raman spectra of Ar<sub>f</sub>IX<sub>2</sub> compounds

Compound	$\bar{\nu}(\text{C-I})$	$\bar{\nu}(\text{IF}_2)$
C <sub>6</sub> F <sub>5</sub> I <sup>a)</sup>	204	-
C <sub>6</sub> F <sub>5</sub> IF <sub>2</sub> <sup>a)</sup>	241	533
IF <sub>3</sub>	-	488 [15]
C <sub>6</sub> F <sub>5</sub> IF <sub>2</sub> · C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	184	490
C <sub>6</sub> F <sub>5</sub> IF <sub>2</sub> · C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	180	492
C <sub>6</sub> F <sub>5</sub> IF <sub>2</sub> · C <sub>9</sub> H <sub>7</sub> N	205	493
C <sub>6</sub> F <sub>5</sub> IF <sub>2</sub> · 2C <sub>9</sub> H <sub>7</sub> N	205	494
2-FC <sub>6</sub> H <sub>4</sub> I <sup>a)</sup>	252	-
2-FC <sub>6</sub> H <sub>4</sub> IF <sub>2</sub> <sup>a)</sup>	236	479
2-FC <sub>6</sub> H <sub>4</sub> IF <sub>2</sub> · C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	260	482
3-FC <sub>6</sub> H <sub>4</sub> I <sup>a)</sup>	259	-
3-FC <sub>6</sub> H <sub>4</sub> IF <sub>2</sub> <sup>a)</sup>	236	480
3-FC <sub>6</sub> H <sub>4</sub> IF <sub>2</sub> · C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	267	485
4-FC <sub>6</sub> H <sub>4</sub> I <sup>a)</sup>	245	-
4-FC <sub>6</sub> H <sub>4</sub> IF <sub>2</sub> <sup>a)</sup>	230	475
4-FC <sub>6</sub> H <sub>4</sub> IF <sub>2</sub> · C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	256	489
4-FC <sub>6</sub> H <sub>4</sub> I(CN) <sub>2</sub> <sup>a,b)</sup>	236	2134 / 2153 <sup>c)</sup>
4-FC <sub>6</sub> H <sub>4</sub> I(CN) <sub>2</sub> · C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	232	2139 <sup>c)</sup>

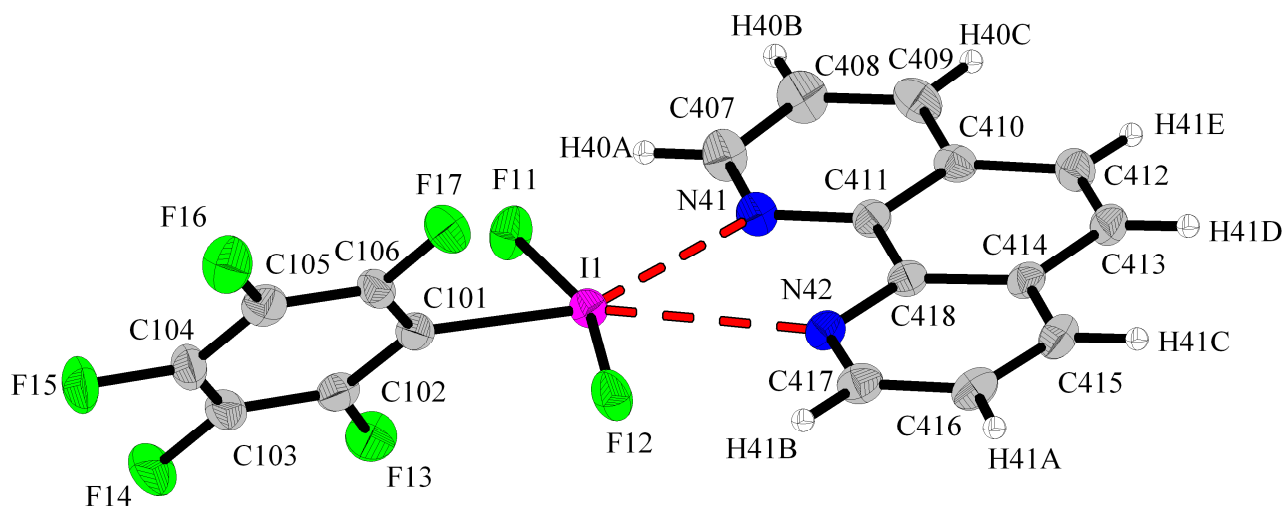
a) For comparison

b) -20 °C

c)  $\bar{\nu}(\text{CN})$  of I(CN)<sub>2</sub>

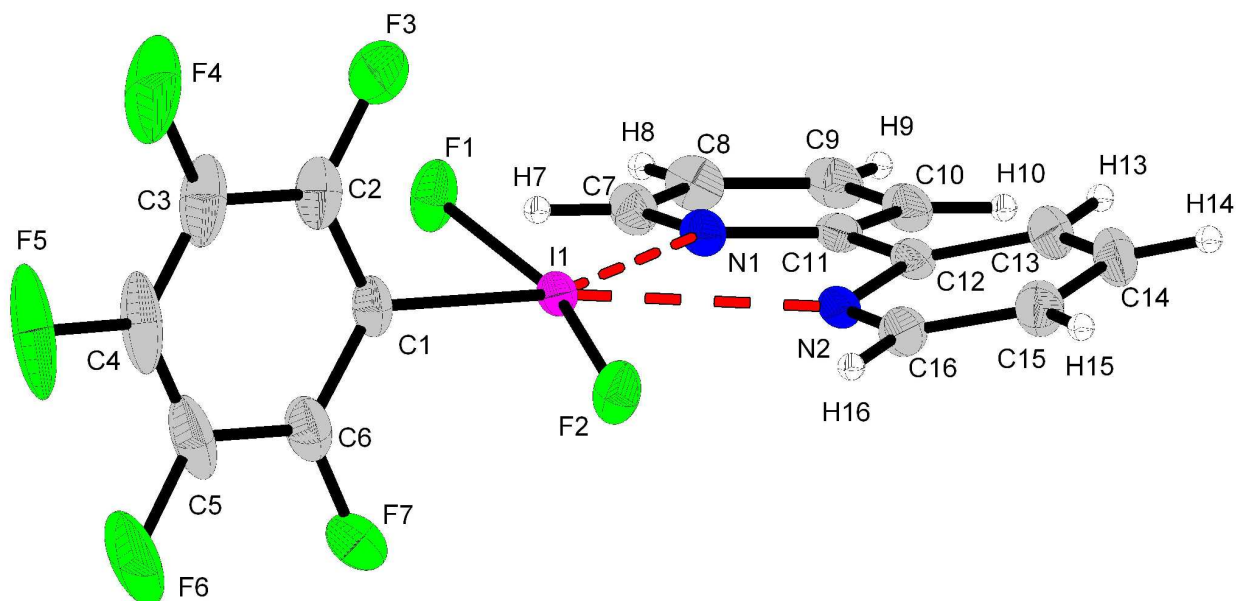
**Table 7** Crystallographic and refinement data for **1a**, **1b**, **1c**, and **5a**

Compound	C <sub>6</sub> F <sub>5</sub> IF <sub>2</sub> ·C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> ( <b>1a</b> )	C <sub>6</sub> F <sub>5</sub> IF <sub>2</sub> ·C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> ( <b>1b</b> )	C <sub>6</sub> F <sub>5</sub> IF <sub>2</sub> ·C <sub>9</sub> H <sub>7</sub> N ( <b>1c</b> )	4-FC <sub>6</sub> H <sub>4</sub> I(CN) <sub>2</sub> ·C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> ( <b>5a</b> )
Empirical formula	C <sub>18</sub> H <sub>8</sub> F <sub>7</sub> IN <sub>2</sub>	C <sub>16</sub> H <sub>8</sub> F <sub>7</sub> IN <sub>2</sub>	C <sub>15</sub> H <sub>7</sub> F <sub>7</sub> IN	C <sub>20</sub> H <sub>12</sub> FIN <sub>4</sub>
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>C2/c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 22.0333(8) Å <i>b</i> = 21.9268(8) Å <i>β</i> = 108.588(1)° <i>c</i> = 29.1927(11) Å	<i>a</i> = 7.2338(6) Å <i>α</i> = 109.159(1)° <i>b</i> = 9.0312(7) Å <i>β</i> = 102.962(2)° <i>c</i> = 13.3352(10) Å <i>γ</i> = 93.238(1)°	<i>a</i> = 7.3199(11) Å <i>α</i> = 83.097(3)° <i>b</i> = 14.236(2) Å <i>β</i> = 77.322(3)° <i>c</i> = 14.743(2) Å <i>γ</i> = 89.980(3)°	<i>a</i> = 7.5076(13) Å <i>α</i> = 84.468(6)° <i>b</i> = 10.2585(18) Å <i>β</i> = 82.378(6)° <i>c</i> = 11.836(2) Å <i>γ</i> = 80.908(6)°
Temperature	120(2) K	120(2) K	120(2) K	193(2) K
Z	32	2	4	2
Density (calculated)	2.036 g cm <sup>-3</sup>	2.042 g cm <sup>-3</sup>	2.059 g cm <sup>-3</sup>	1.696 g cm <sup>-3</sup>
Absorption coefficient	1.997 mm <sup>-1</sup>	2.096 mm <sup>-1</sup>	2.228 mm <sup>-1</sup>	1.821 mm <sup>-1</sup>
F(000)	7872	468	880	444
Crystal size	0.39 x 0.27 x 0.18 mm	0.44 x 0.30 x 0.25 mm	0.48 x 0.18 x 0.17 mm	0.28 x 0.15 x 0.12 mm
Diffractometer	Bruker AXS SMART APEX with APEX II area detector system	Bruker AXS SMART APEX with APEX II area detector system	Bruker AXS SMART APEX with APEX II area detector system	Siemens SMART three axis goniometer with APEX II area detector system
Radiation		MoK <sub>α</sub> (λ = 0.71073 Å)		
Theta range for data collection	1.35° to 28.08°	1.67° to 27.48°	1.43° to 27.88°	1.74° to 28.21°
Index ranges	-27 ≤ <i>h</i> ≤ 29, -29 ≤ <i>k</i> ≤ 28, -38 ≤ <i>l</i> ≤ 38	-9 ≤ <i>h</i> ≤ 9, -11 ≤ <i>k</i> ≤ 11, -17 ≤ <i>l</i> ≤ 16	-9 ≤ <i>h</i> ≤ 9, -18 ≤ <i>k</i> ≤ 18, -18 ≤ <i>l</i> ≤ 19	-9 ≤ <i>h</i> ≤ 9, -13 ≤ <i>k</i> ≤ 13, -15 ≤ <i>l</i> ≤ 15
Reflections collected	63471	6764	13120	35079
Independent reflections	16224 [ <i>R</i> <sub>(int)</sub> = 0.0324]	3603 [ <i>R</i> <sub>(int)</sub> = 0.0217]	7032 [ <i>R</i> <sub>(int)</sub> = 0.0243]	4295 [ <i>R</i> <sub>(int)</sub> = 0.0352]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	16224 / 0 / 1009	3603 / 0 / 235	7032 / 0 / 433	4163 / 0 / 236
Final R indices	<i>R</i> <sub>1</sub> = 0.0301, <i>wR</i> <sub>2</sub> = 0.0672	<i>R</i> <sub>1</sub> = 0.0276, <i>wR</i> <sub>2</sub> = 0.0667	<i>R</i> <sub>1</sub> = 0.0322, <i>wR</i> <sub>2</sub> = 0.0704	<i>R</i> <sub>1</sub> = 0.0176, <i>wR</i> <sub>2</sub> = 0.0468
Min./max. height in ΔF-map	0.63 and -0.56 eÅ <sup>-3</sup>	0.95/-0.72 eÅ <sup>-3</sup>	0.89/-0.51 eÅ <sup>-3</sup>	0.70/-0.65 eÅ <sup>-3</sup>
Programmes used [16, 17]		SMART, SAINT, SADABS, SHELXTL		Bruker AXS APEX 2 Vers. 2.0-2 2006



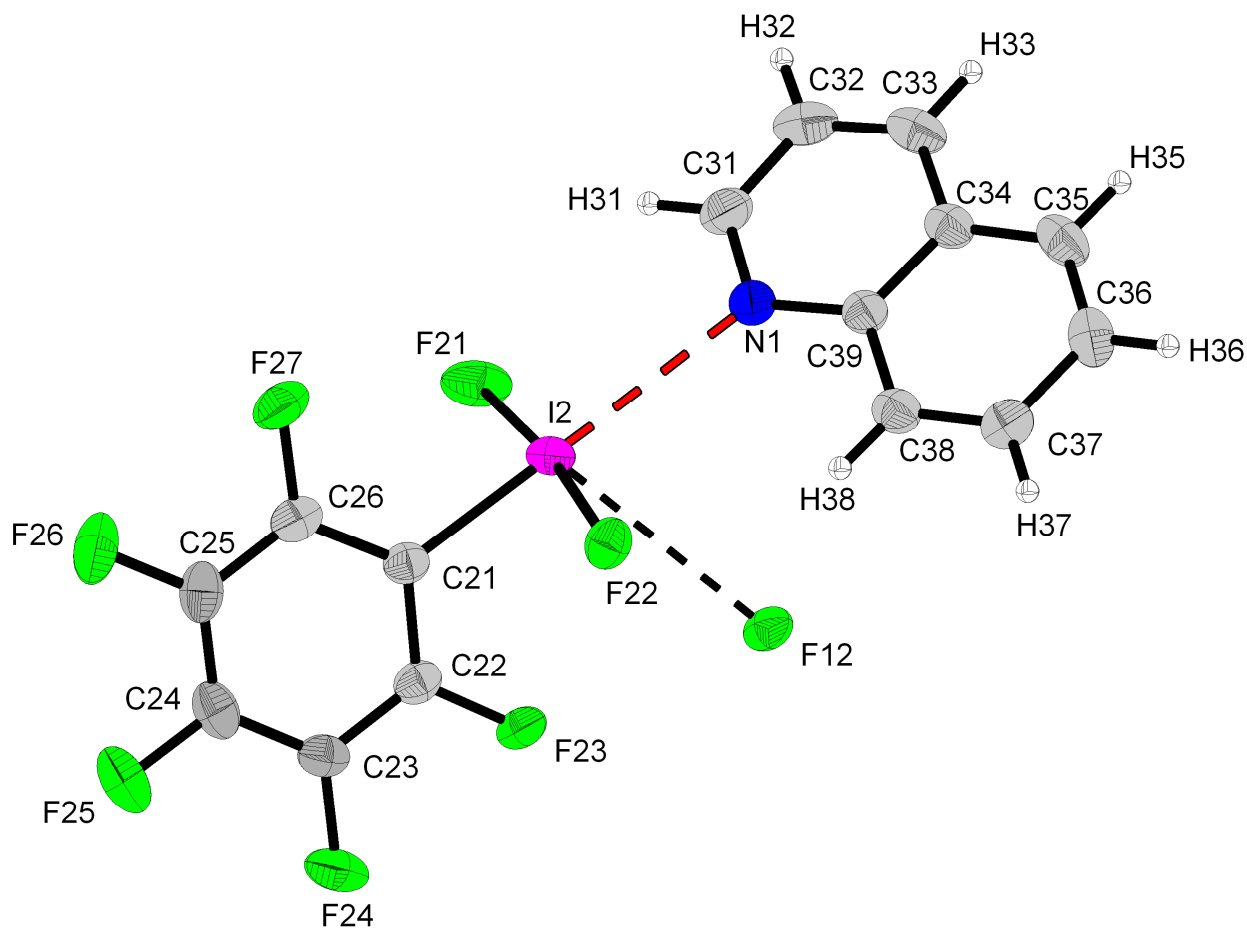
**Figure 1** Molecular structure, numbering scheme, and intermolecular contacts of  $C_6F_5IF_2 \cdot C_{12}H_8N_2$  (**1a**).

Selected distances/Å and angles/°: C(101)-I(1) 2.105(3), F(11)-I(1) 2.0047(15), F(12)-I(1) 2.0065(15), I(1)-N(41) 2.8248(26), I(1)-N(42) 2.8085(21), F(11)-H(40A) 2.3154(19), F(12)-H(41B) 2.2848(17), C(101)-I(1)-F(11) 80.93(8), C(101)-I(1)-F(12) 80.22(8), F(11)-I(1)-F(12) 161.07(7), N(41)-I(1)-N(42) 58.27(6).



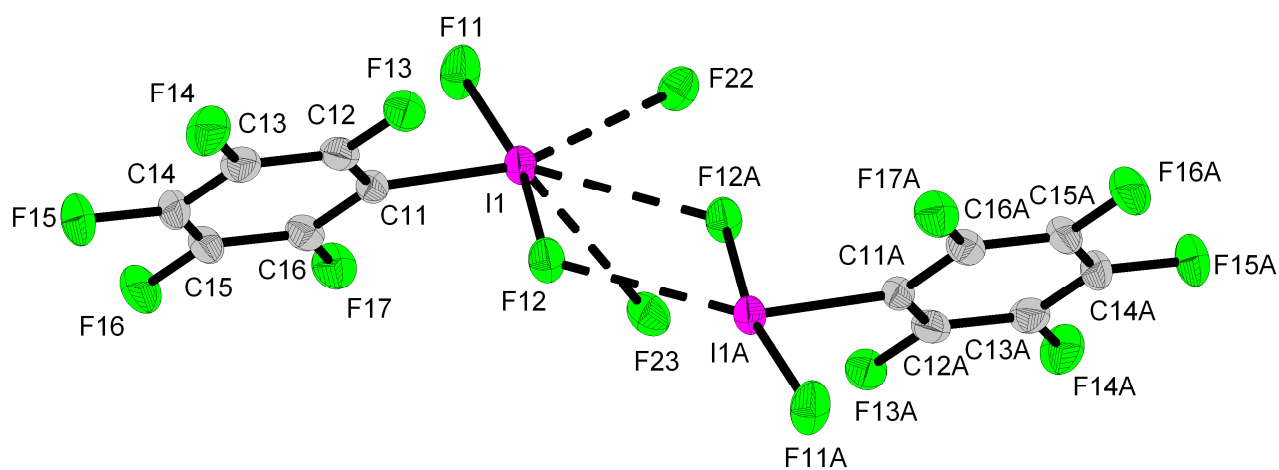
**Figure 2** Molecular structure, numbering scheme, and intermolecular contacts of  $C_6F_5IF_2 \cdot C_{10}H_8N_2$  (**1b**).

Selected distances/Å and angles/°: C(1)-I(1) 2.115(3), F(1)-I(1) 2.0031(18), F(2)-I(1) 2.0073(17), I(1)-N(1) 2.7863(22), I(1)-N(2) 2.7968(21), F(1)-H(7) 2.3640(17), F(2)-H(16) 2.3414(18), C(1)-I(1)-F(1) 79.46(9), C(1)-I(1)-F(2) 79.22(9), F(1)-I(1)-F(2) 158.63(8), N(1)-I(1)-N(2) 58.16(7).



**Figure 3a** Molecular structure, numbering scheme, and intermolecular contacts of  $C_6F_5IF_2 \cdot C_9H_7N$  (**1c**).

Selected distances/Å and angles/°: C(21)-I(2) 2.078(3), F(21)-I(2) 1.976(2), F(22)-I(2) 2.0132(19), I(2)-N(1) 2.9370(27), F(12)-I(2) 3.2123(20), C(21)-I(2)-F(21) 87.13(11), C(21)-I(2)-F(22) 85.46(10), F(21)-I(2)-F(22) 172.59(8).



**Figure 3b** Molecular structure, numbering scheme, and intermolecular contacts of  $C_6F_5IF_2 \cdot C_9H_7N$  (**1c**).

Selected distances/Å and angles/°: C(11)-I(1) 2.075(3), F(11)-I(1) 1.981(2), F(12)-I(1) 2.0022(18), I(1)-F(12A) 2.8405(19), I(1)-F(22) 2.881(2), I(1)-F(23) 3.395(2), C(11)-I(1)-F(11) 83.58(10), C(11)-I(1)-F(12) 82.33(10), F(11)-I(1)-F(12) 165.86(8).



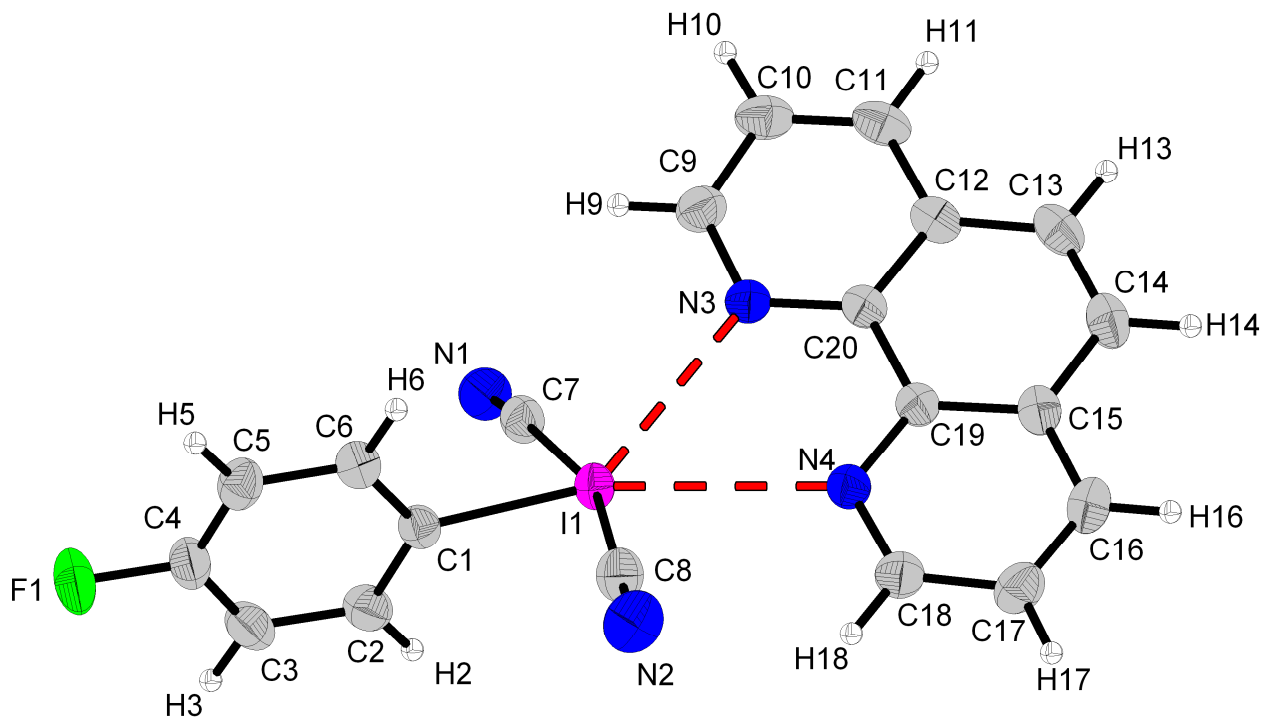


Figure 4 Molecular structure, numbering scheme, and intermolecular contacts of 4-FC<sub>6</sub>H<sub>4</sub>I(CN)<sub>2</sub> · C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> (**5a**).

Selected distances/Å and angles/°: C(1)-I(1) 2.1112(16), I(1)-C(7) 2.2622(18), I(1)-C(8) 2.2674(19), I(1)--N(3) 3.0227(15), I(1)--N(4) 2.9565(15), C(1)-I(1)-C(7) 80.91(6), C(1)-I(1)-C(8) 84.12(6), C(7)-I(1)-C(8) 164.70(7), N(3)--I(1)--N(4) 54.94(4).