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**First Isolation and Structural Characterization of N-base
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Abstract.

The adducts of aryliodinedifluorides Ar_fIF_2 , ($\text{Ar}_f = \text{C}_6\text{F}_5$; $x\text{-FC}_6\text{H}_4$, $x = 2, 3, 4$) and aryliodinedicyanide $4\text{-FC}_6\text{H}_4\text{I}(\text{CN})_2$ 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 (λ^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 Ψ -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, RIX_2 , are hitherto unknown in literature. We have investigated the coordination of mono- and bidentate N-bases on Ar_fIX_2 molecules ($X = F, CN$).

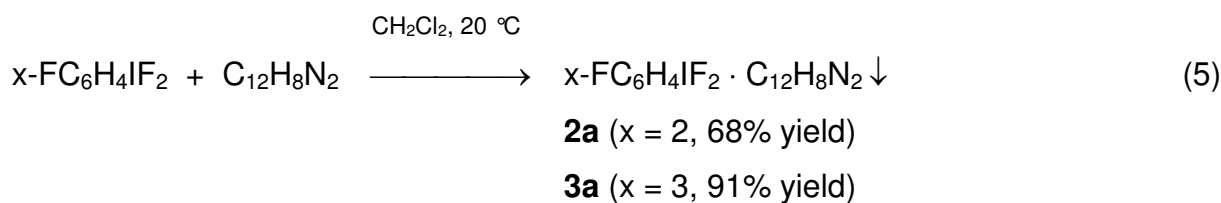
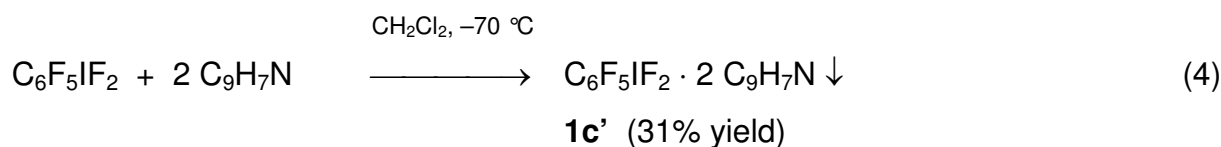
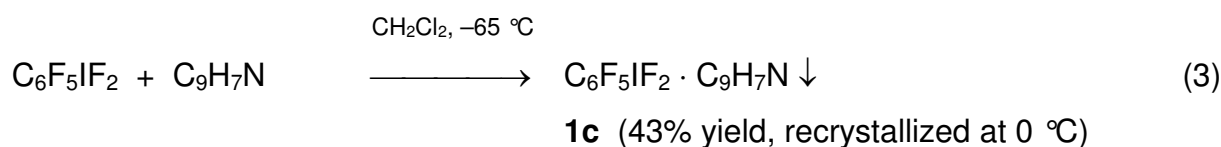
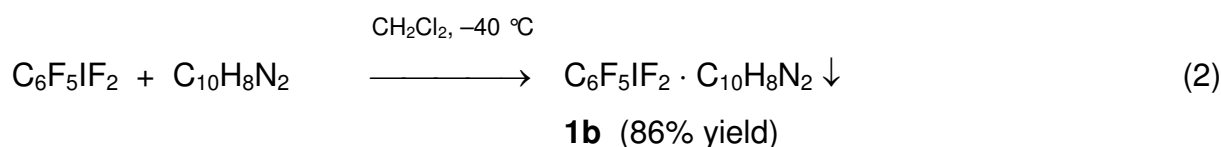
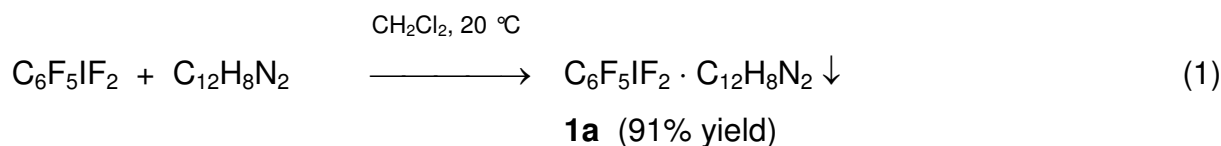
N-base coordination on the parent compound, IF_3 , was discussed controversially. In an early communication, the adduct formation of IF_3 with quinoline, pyridine, acetonitrile, trimethylamine, dimethylformamide, 2,2'-bipyridine, and pyrazine was reported [6] without structural data. In a later paper 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 CH₂Cl₂ 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 CH₂Cl₂ 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-FC₆H₄I(CN)₂ · C₁₂H₈N₂ (**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.



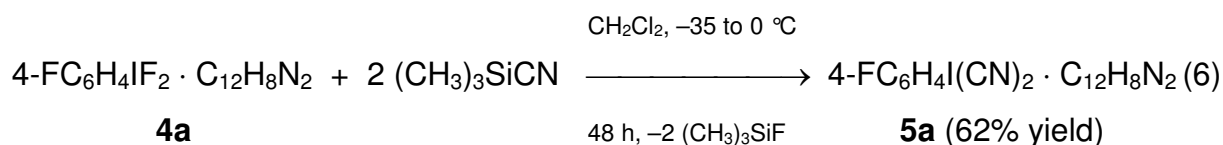
4a (x = 4, 93% yield)

The molar ratio C₆F₅IF₂ (**1**) to C₉H₇N (**c**) in the two quinoline adducts **1c** and **1c'** was determined by ¹H and ¹⁹F NMR spectroscopy using the internal quantitative standard 1,3,5-F₃C₆H₃ to relate the integrals of the donor and acceptor.

The thermal behaviour and stability of the adducts and of the I^{III} 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^{III} molecules. The 2,2'-bipyridine and the phenanthroline adduct of C₆F₅IF₂, 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-FC₆H₄IF₂ · 1,10-phenanthroline adduct (**4a**):
isolation of the 4-FC₆H₄I(CN)₂ · 1,10-phenanthroline adduct (**5a**)*

To show the influence of the N-base coordination in the adduct on the reactivity of the hypervalent IF₂ triad, we investigated the fluorine/cyano substitution with the acidic reagent (CH₃)₃SiCN (eq. (6)).



(CH₃)₃SiCN was able to substitute the two I^{III}-bonded fluorine atoms in **4a** by cyano groups. Neither the acidic reagent (CH₃)₃SiCN nor the acidic by-product (CH₃)₃SiF 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 (CH₃)₃SiF. 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 C₆F₅ group is a sensitive probe for detecting characteristic changes at the I^{III} atom of C₆F₅IX₂ compounds in solution by ¹⁹F NMR spectroscopy. Steric influences and the number of ligands at I^{III} 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^{III} on the π-system of the C₆F₅ 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 CH₂Cl₂ give rise to a low frequent shift of all four resonances of **1**, most pronounced for the *p*-F atom and the IF₂ group (see Table 2). Coordination of the first N-base proceeds *trans* to the C₆F₅ group in a mode comparable to an asymmetric hypervalent C-I--base bond. Thus, the partial charge on the N atoms and on the C₆F₅ 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 λ³-iodane molecule. The increase of charge in the R_fIF₂ subunit of the adduct explains the shielding of the fluorine atoms, as well of the C₆F₅ group as of the IF₂ 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 IF₂ 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 IF₂ group is also observed in case of *x*-FC₆H₄IF₂ (**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 C₆F₅ group in **1** after coordination (Table 2). Principally, the analogue ¹⁹F shift tendency was also described for the aliphatic compound CF₃IF₂ when the coordinating ligand CH₃CN (solvent) was changed for pyridine. [11] The assignment of the ¹H NMR resonances of the *x*-FC₆H₄IF₂ and 4-FC₆H₄I(CN)₂ adducts with N-bases suffered from contradictions in the assignment of the monovalent 2- and 3-FC₆H₄I [12, 13] and the related trivalent 2- and 3-FC₆H₄I^{III} iodine compounds [14]. Therefore, we had to clarify the situation by ¹H-¹³C

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3 correlated spectra. We compile all ^1H NMR data in Table 4. All ^1H resonances of
4 phenanthroline in **1a**, **3a**, **4a**, and **5a** appeared deshielded after coordination. In the
5 phenanthroline adducts of Ar_fIF_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}C NMR spectroscopic data of **1a** and **1b** are less informative than their ^{19}F
11 NMR data. The 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 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 IF_2 vibration frequencies which
26 proceeded along with coordination on the Ar_fIF_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 cm^{-1}) relative to non-coordinated R_fIF_2 ,
32 whereas in case of $x\text{-FC}_6\text{H}_4\text{IF}_2$ a small increase (3 to 14 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 cm^{-1} , respectively, whereas base **c** caused lowering of only 36 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 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 CH_3CN , CH_2Cl_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^{III} is comparable with that in IF₃ 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 [(C₆H₅)₂I · C₁₂H₈N₂][BF₄] · 0.5
15 CH₂Cl₂ [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 [BF₄]⁻ anion.
18

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 C²-C^{2'} bond in
21 **b**, the adduct **1b** shows a small deviation from the pentagonal plane in the
22 coordination sphere of I^{III}. As a consequence of the free rotation of the C²-C^{2'} 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^{6,6'} 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 C₆F₅IF₂ molecules is weakly coordinated by one quinoline
30 base (Figure 3a). The second C₆F₅IF₂ molecule is part of a dimer with a
31 rhombohedral I₂F₂ 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^{III}-C₆F₅ bond.
35

36 In 4-FC₆H₄I(CN)₂ · C₁₂H₈N₂ (**5a**) (Figure 4), the two N-atoms of the rigid bidentate
37 base 1,10-phenanthroline, the *ipso*-C atom of the C₆F₅ 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-FC₆H₄
5 group and of fluorine (IF₂), the partial positive charge on I^{III} is smaller in **5** than in **1**
6 (**Table 3**). Parallel, the Ar_f-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^{III}--F or I^{III}--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^{III} 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 C₆F₅ group are less stable than with weakly electron-withdrawing x-FC₆H₄ groups
21 with respect to uncoordinated Ar_fIF₂. The energy of adduct formation of C₆F₅IF₂ with
22 N-bases in the gas phase (ΔHF) decreases in the order: phenanthroline > 2,2'-
23 bipyridine > 2 pyridine > 2 CH₃CN > picoline(2) > pyridine > lutidine(2,6) > CH₃CN.
24 Adduct formation of 4-FC₆H₄IF₂ with phenanthroline is more exothermic than that of
25 4-FC₆H₄I(CN)₂. Significant changes in the NMR spectra, especially in ¹⁹F NMR, can
26 be deduced on changes in the partial charges in the iodine(III) environment by
27 coordination: the Ar_f 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). CH₃CN (KMF) was refluxed and distilled
50 from KMnO₄ and repeatedly refluxed and distilled from P₄O₁₀. CH₂Cl₂ (KMF) was
51 treated in sequence with conc. H₂SO₄, Na₂CO_{3(aq)}, H₂O and finally refluxed and
52 distilled from P₄O₁₀. The solvents *n*-pentane and *n*-hexane were distilled and stored
53 over sodium. C₆F₅IF₂ was prepared by a modified fluorination of C₆F₅I [1, 20], 2-, 3-,
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3 and 4-FC₆H₄IF₂ from the corresponding x-FC₆H₄I(OAc)₂ compounds and HF_{aq} [21],
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5 3- and 4-FC₆H₄I(OAc)₂ using protocol [22]. (CH₃)₃SiCN was synthesized by a
6
7 literature procedure [23]. 1,10-phenanthroline and 2,2'-bipyridine (Merck KGaA) were
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9 used as delivered. Quinoline (Merck KGaA) was stored over molecular sieve (3 Å).
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11 NMR spectra were recorded on a Bruker spectrometer AVANCE 300 (¹³C at 75.47
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13 MHz, ¹⁹F at 282.40 MHz, and ¹H at 300.13 MHz). The chemical shifts were
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15 referenced to TMS (¹³C), CCl₃F (¹⁹F) (C₆F₆ as a secondary reference, δ = -162.9
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17 ppm), and TMS (¹H). The Raman spectra were recorded on a Bruker FT-Raman
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19 spectrometer RFS 100/S using the 1064 nm line of a Nd:YAG laser. The
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21 backscattered (180°) radiation was sampled and analysed (Stoke range: 50 to 4000
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23 cm⁻¹). 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⁻¹) using a
26
27 laser power of ≤ 250 mW. For X-ray diffraction see (Table 6).

28 ***N*-base adducts of C₆F₅IF₂ and x-FC₆H₄IF₂ (x = 2, 3, 4)**

29 *Synthesis of C₆F₅IF₂ · C₁₂H₈N₂ (1a)*

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31 A solution of phenanthroline (0.272 g, 1.509 mmol) in CH₂Cl₂ (1.3 mL) was added to
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33 a stirred solution of C₆F₅IF₂ (0.497 g, 1.497 mmol) in CH₂Cl₂ (1.2 mL) in a 8 mm i.d.
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35 FEP reaction trap. Spontaneously, a white solid adduct precipitated from the reaction
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37 mixture. After 20 min the supernatant was separated. The solid residue was washed
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39 with CH₂Cl₂ (0.5 mL) and dried in vacuum (0.05 hPa, 20 °C, 60 min). C₆F₅IF₂ ·
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41 C₁₂H₈N₂ was obtained in 91% yield (0.701 g, 1.367 mmol).

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43 DSC measurements on C₆F₅IF₂ · C₁₂H₈N₂ showed decomposition at 198 °C (T_{onset},
44
45 exothermic effect). The solubility of C₆F₅IF₂ · C₁₂H₈N₂ was determined to 31 g/L in
46
47 CH₂Cl₂ at 24 °C.

48
49 Single crystals of C₆F₅IF₂ · C₁₂H₈N₂ were grown from a saturated (60 °C) CH₂Cl₂
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51 solution at 20 °C.

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

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

25
26 Ra ($20\text{ }^{\circ}\text{C}$) $\bar{\nu}$ (cm^{-1}): 93 [100], 128 [32], 164 [49], 185 [16], 205 [23], 222 [24], 238
27 [15], 279 [10], 351 [22], 385 [26], 441 [24], 471 [22], 494 [41], 512 [86], 520 [55], 585
28 [21], 761 [67], 804 [9], 1015 [7], 1038 [20], 1150 [8], 1316 [7], 1370 [93], 1395 [11],
29 1433 [31], 1502 [5], 1572 [20], 1620 [7], 3065 [28].
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32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

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

A solution of quinoline (310 μL , 2.616 mmol) in CH_2Cl_2 (0.7 mL) was added to a
stirred solution of $\text{C}_6\text{F}_5\text{IF}_2$ (0.431 g, 1.299 mmol) in CH_2Cl_2 (0.5 mL) in a 8 mm i.d.
FEP reaction trap. A purple solution resulted. After 1 h the solution was cooled to
 $-70\text{ }^{\circ}\text{C}$ and a solid product precipitated. The supernatant was separated and the
solid residue was washed with *n*-pentane (1 mL) and dried in vacuum (0.05 hPa, 20
 $^{\circ}\text{C}$, 1 h). The pale purple solid was extracted repeatedly with *n*-hexane. The *n*-
hexane extracts (20 mL) were combined and cooled to $-80\text{ }^{\circ}\text{C}$. A white solid formed
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

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

22 A solution of phenanthroline ($x = 2$: 0.346 g, 1.920 mmol; $x = 3$: 0.345 g, 1,914 mmol;
23 $x = 4$: 0.362 g, 2.009 mmol) in CH_2Cl_2 (1 mL) was added to a stirred solution of x -
24 $FC_6H_4IF_2$ ($x = 2$: 0.507 g, 1.950 mmol; $x = 3$: 0.500 g, 1,923 mmol; $x = 4$: 0.517 g,
25 1.988 mmol) in CH_2Cl_2 (2 mL) in a 8 mm i.d. FEP reaction trap and formed a
26 colourless mixture.
27
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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].
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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-FC₆H₄IF₂ · C₁₂H₈N₂ showed a melting point at 146 °C
4 (T_{onset}, endothermic effect) and decomposition at 147 °C (T_{onset}, exothermic effect).
5
6 The solubility of 3-FC₆H₄IF₂ · C₁₂H₈N₂ was determined to 12 g/L in CH₃CN at 24 °C.
7
8 Ra (20 °C) $\bar{\nu}$ (cm⁻¹): 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],
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12 1041 [27], 1052 [4], 1097 [6], 1163 [10], 1201 [5], 1266 [5], 1295 [40], 1341 [20],
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14 1406 [68], 1423 [8], 1447 [24], 1470 [3], 1505 [14], 1563 [4], 1588 [19], 1603 [10],
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16 1621 [9], 3061 [30], 3073 [43], 3091 [13].
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18 4-FC₆H₄IF₂ · C₁₂H₈N₂ was obtained in 93% yield (0.814, 1.849 mmol).
19

20 DSC measurements on 4-FC₆H₄IF₂ · C₁₂H₈N₂ showed a melting point at 147 °C
21 (T_{onset}, endothermic effect) and decomposition at 149 °C (T_{onset}, exothermic effect).
22
23 Ra (20 °C) $\bar{\nu}$ (cm⁻¹): 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],
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26 856 [2], 886 [2], 1008 [2], 1041 [24], 1094 [7], 1140 [4], 1154 [10], 1200 [4], 1220 [2],
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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].
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34 *Synthesis of 4-FC₆H₄I(CN)₂ · C₁₂H₈N₂ (5a)*

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36 A solution of (CH₃)₃SiCN (40 μL, 0.300 mmol) in CH₂Cl₂ (0.3 mL) was added to the
37
38 stirred cold (−35 °C) suspension of 4-FC₆H₄IF₂ · C₁₂H₈N₂ (0.047 g, 0.107 mmol) in
39
40 CH₂Cl₂ (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-FC₆H₄I(CN)₂ · C₁₂H₈N₂ was obtained in 62%
49
50 yield (0.030 g, 0.066 mmol).

51 Ra (20 °C) $\bar{\nu}$ (cm⁻¹): 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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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
$\text{C}_6\text{F}_5\text{IF}_2^{\text{a)}$	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	-
$2\text{-FC}_6\text{H}_4\text{IF}_2^{\text{a)}$	61 [8]	
$3\text{-FC}_6\text{H}_4\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	146	147
$3\text{-FC}_6\text{H}_4\text{IF}_2^{\text{a)}$	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
$4\text{-FC}_6\text{H}_4\text{IF}_2^{\text{a)}$	103 [8]	
$\text{IF}_3^{\text{a)}$	no	-28 [9]

^{a)} For comparison

Table 2 ^{19}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 Ar_fIX_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 ₂ , $\tau_{1/2}/\text{Hz}$
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	CH_2Cl_2	24	-125.3	-149.8	20 Hz	4 Hz	-159.2	-154.0, 13
	CH_3CN	24	-124.9	-148.1	20 Hz	5 Hz	-158.1	-153.4, 13
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$	CH_2Cl_2	24	-124.7	-148.3	20 Hz	4 Hz	-158.9	-156.3, 12
	CH_3CN	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
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_9\text{H}_7\text{N}^{\text{b)}$	CH_2Cl_2	24	-123.1	-145.3	20 Hz	5 Hz	-157.8	-160.7, 12
$\text{C}_6\text{F}_5\text{IF}_2 \cdot 2 \text{C}_9\text{H}_7\text{N}^{\text{b)}$	CH_2Cl_2	24	-123.3	-145.7	20 Hz	5 Hz	-157.9	-161.3, 11
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_5\text{H}_5\text{N}^{\text{b)}$	CH_2Cl_2	24	-122.9	-145.1	20 Hz	5 Hz	-157.6	-159.4, 13
$\text{C}_6\text{F}_5\text{IF}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}^{\text{b)}$	CH_2Cl_2	24	-123.1	-145.5	20 Hz	-	-157.8	-161.2, 17
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_6\text{H}_7\text{N}^{\text{b)}$	CH_2Cl_2	24	-122.8	-145.0	21 Hz	5 Hz	-157.6	-161.1, 12
$\text{C}_6\text{F}_5\text{IF}_2 \cdot 2 \text{C}_6\text{H}_7\text{N}^{\text{b)}$	CH_2Cl_2	24	-123.2	-145.6	20 Hz	5 Hz	-157.8	-162.3, 11
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_7\text{H}_9\text{N}^{\text{b)}$	CH_2Cl_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
	CH_3CN	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
	CH_2Cl_2	24	-99.1	-	-	-	-	-163.6, 54
$2\text{-FC}_6\text{H}_4\text{IF}_2^{\text{a)}$	CH_3CN	24	-98.6	-	-	-	-	-162.5, 10
	CH_2Cl_2	24	-97.8	-	-	-	-	-165.3, 7
$3\text{-FC}_6\text{H}_4\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	CH_3CN	24	-97.6	-	-	-	-	-163.8, 13
	CH_2Cl_2	24	-	-	-	-	-109.1	-175.1, 5

1		CH ₃ CN	24	-	-	-	-	-108.6	-172.7,	6
2										
3	3-FC ₆ H ₄ IF ₂ ^{a)}	CH ₂ Cl ₂	24	-	-	-	-	-108.4	-175.0,	9
4										
5		CH ₃ CN	24	-	-	-	-	-108.1	-173.0,	10
6										
7	4-FC ₆ H ₄ IF ₂ · C ₁₂ H ₈ N ₂	CH ₂ Cl ₂	24	-	-109.2	-	-	-	-174.6,	7
8										
9		CH ₃ CN	24	-	-108.0	-	-	-	-171.2,	12
10										
11	4-FC ₆ H ₄ IF ₂ ^{a)}	CH ₂ Cl ₂	24	-	-109.1	-	-	-	-174.6,	7
12										
13		CH ₃ CN	24	-	-107.8	-	-	-	-171.1,	9
14										
15	4-FC ₆ H ₄ I(CN) ₂ · C ₁₂ H ₈ N ₂	CH ₂ Cl ₂	24	-	-106.8	-	-	-	-	
16										
17		CH ₃ CN	24	-	-105.3	-	-	-	-	
18										
19	4-FC ₆ H ₄ I(CN) ₂	CH ₂ Cl ₂	24	-	-104.8	-	-	-	-	

19 a) For comparison

21 b) Reaction mixture

Table 3 Calculated geometrical parameters and natural atomic charges, NBO, (RHF, LANL2DZ [10]) of Ar_fI_X₂ · N-base adducts

Compound	Distances and angles					NBO analysis (I ^{III} environment)				
	C ¹ -I/Å	I-X/Å	I--N/Å	∠ X-I-X/°	∠ C ¹ -I--N/°	C ¹ Ar _f	I	X	N N-base	ΔHF(Coord.) ^{a)}
1a	2.104	2.033	2.883	160.1	151.2	-0.434	1.777	-0.744	-0.593 ^{b)}	-103.7
					151.2	-0.335			0.046	
1b	2.103	2.031	2.901	160.1	151.7	-0.434	1.776	-0.743	-0.598 ^{c)}	-94.6 ^{d)}
					151.7	-0.332			0.042	
1c	2.088	2.015	2.970	166.0	159.2	-0.440	1.734	-0.730	-0.621 ^{e)}	-46.9
		2.021				-0.281		-0.735	0.019	
1 · C₅H₅N	2.089	2.014	2.951	164.9	156.2	-0.437	1.734	-0.729	-0.623 ^{f)}	-48.7
		2.021				-0.288		-0.735	0.019	
1 · 2 C₅H₅N	2.094	2.024	3.077	160.1	143.8	-0.430	1.764	-0.738	-0.604 ^{f)}	-76.8
		2.025	3.082		143.6	-0.311		-0.738	0.023 ^{g)}	
1 · 2-(CH₃)C₅H₄N	2.089	2.014	2.955	165.4	158.3	-0.439	1.734	-0.729	-0.650 ^{h)}	-49.4
		2.022				-0.290		-0.736	0.021	
1 · 2,6-(CH₃)₂C₅H₄N	2.087	2.017	3.089	165.6	180.00	-0.440	1.732	-0.731	-0.667 ⁱ⁾	-43.7
						-0.286			0.016	
1 · CH₃CN	2.082	2.012	3.092	165.0	180.00	-0.437	1.730	-0.728	-0.493 ^{j)}	-36.9
						-0.281			0.006	
1 · 2 CH₃CN	2.084	2.006	3.015	164.8	167.9	-0.441	1.746	-0.721	-0.532 ^{j, k)}	-73.7
		2.028	5.518		125.9	-0.284		-0.745	0.003 ^{l)}	

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

^{a)} $\Delta\text{HF}(\text{Coord.}) = \text{HF}(\text{Ar}_f\text{IX}_2 \cdot \text{N-base}) - (\text{HF}(\text{Ar}_f\text{IX}_2) + \text{HF}(\text{N-base}))$. ^{b)} NBO(N atom) of the uncoordinated N-base -0.493. ^{c)} NBO(N atom) of the uncoordinated N-base (*cis*-conformation, local minimum) -0.514. ^{d)} 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. ^{e)} NBO(N atom) of the uncoordinated N-base -0.530. ^{f)} NBO(N atom) of the uncoordinated N-base -0.537. ^{g)} Sum of NBO values for both CH₃CN, individual NBO values: 0.011 for both coordinated py. ^{h)} NBO(N atom) of the uncoordinated N-base -0.567. ⁱ⁾ NBO(N atom) of the uncoordinated N-base -0.597. ^{j)} NBO(N atom) of the uncoordinated N-base -0.406. ^{k)} NBO(N atom) of very weakly coordinated CH₃CN -0.483. ^{l)} Sum of NBO values for both CH₃CN, individual NBO values: 0.007 (strongly coordinated CH₃CN), -0.004 (weakly coordinated CH₃CN).

Table 4 ^1H 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 δ/ppm of $x\text{-FC}_6\text{H}_4\text{I}$ groups	Shift values δ/ppm of phenanthroline base
1a	CH_2Cl_2	24	-	9.22 ($\text{H}^{2,9}\text{a}$), 8.37 ($\text{H}^{4,7}\text{b}$), 7.89 ($\text{H}^{5,6}\text{c}$), 7.69 ($\text{H}^{3,8}\text{d}$)
	CH_3CN	24	-	9.20 ($\text{H}^{2,9}$), 8.52 ($\text{H}^{4,7}$), 8.00 ($\text{H}^{5,6}$), 7.79 ($\text{H}^{3,8}$)
2a	CH_2Cl_2	24	8.29 (H^5), 7.61 (H^6), 7.41 (H^3) 7.31 (H^4)	9.19 ($\text{H}^{2,9}$), 8.25 ($\text{H}^{4,7}$), 7.77 ($\text{H}^{5,6}$), 7.61 ($\text{H}^{3,8}$)
	CH_3CN	24	8.35 (H^5), 7.68 (H^6), 7.50 (H^3), 7.38 (H^4)	9.12 ($\text{H}^{2,9}$), 8.35 ($\text{H}^{4,7}$), 7.85 ($\text{H}^{5,6}$), 7.68 ($\text{H}^{3,8}$)
3a	CH_2Cl_2	24	7.76 ($\text{H}^{2,6}$), 7.56 (H^5), 7.23 (H^4)	9.16 ($\text{H}^{2,9}$), 8.27 ($\text{H}^{4,7}$), 7.81 ($\text{H}^{5,6}$), 7.64 ($\text{H}^{3,8}$)
	CH_3CN	24	7.82 ($\text{H}^{2,6}$), 7.64 (H^5), 7.33 (H^4)	9.12 ($\text{H}^{2,9}$), 8.37 ($\text{H}^{4,7}$), 7.89 ($\text{H}^{5,6}$), 7.70 ($\text{H}^{3,8}$)
4a	CH_2Cl_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 ($\text{H}^{3,8}$)
	CH_3CN	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 ($\text{H}^{3,8}$)
5a	CH_2Cl_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 ($\text{H}^{3,8}$)
	CH_3CN	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- $\text{FC}_6\text{H}_4\text{I}$	CDCl_3	24	7.74 (H^5), 7.30 (H^6), 7.05 (H^3) 6.88 (H^4)	
	CH_3CN	24	7.72 (H^5), 7.32 (H^6), 7.07 (H^3) 6.90 (H^4)	
2- $\text{FC}_6\text{H}_4\text{IF}_2$	CH_2Cl_2	24	8.24 (H^5), 7.66 (H^6), 7.43 (H^3) 7.33 (H^4)	
	CH_3CN	24	8.30 (H^5), 7.69 (H^6), 7.48 (H^3) 7.35 (H^4)	
3- $\text{FC}_6\text{H}_4\text{I}$	CDCl_3	24	7.46 (H^6), 7.43 (H^2), 7.05 (H^5) 7.03 (H^4)	
	CH_3CN	24	7.45 ($\text{H}^{2,6}$), 7.07 ($\text{H}^{4,5}$)	
3- $\text{FC}_6\text{H}_4\text{IF}_2$	CH_2Cl_2	24	7.72 ($\text{H}^{2,6}$), 7.58 (H^5), 7.24 (H^4)	
	CH_3CN	24	7.73 ($\text{H}^{2,6}$), 7.59 (H^5), 7.28 (H^4)	
4- $\text{FC}_6\text{H}_4\text{I}$	CDCl_3	24	7.61 ($\text{H}^{2,6}$), 6.82 ($\text{H}^{3,5}$)	
	CH_3CN	24	7.62 ($\text{H}^{2,6}$), 6.86 ($\text{H}^{3,5}$)	
4- $\text{FC}_6\text{H}_4\text{IF}_2$	CH_2Cl_2	24	7.95 ($\text{H}^{2,6}$), 7.30 ($\text{H}^{3,5}$)	
	CH_3CN	24	8.01 ($\text{H}^{2,6}$), 7.32 ($\text{H}^{3,5}$)	

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

8 a) (dd, ³J(H^{2,9},H^{3,8}) = 4.6 Hz, ⁴J(H^{2,9},H^{4,7}) = 1.7 Hz). b) (dd, ³J(H^{4,7},H^{3,8}) = 8.1 Hz, ⁴J(H^{4,7},H^{2,9}) = 1.7 Hz). c) (s, τ_{1/2} = 1,2 Hz). d) (dd,
9 ³J(H^{3,8},H^{4,7}) = 8.1 Hz, ³J(H^{3,8},H^{2,9}) = 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}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 ¹	C ^{2,6}	$^1J(\text{C}^{2,6}, \text{F}^{2,6})$	C ^{3,5}	$^1J(\text{C}^{3,5}, \text{F}^{3,5})$	C ⁴	$^1J(\text{C}^4, \text{F}^4)$
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2^{\text{a)}$	CH_2Cl_2	24	109.9	144.4	249 Hz	137.0	255 Hz	143.7	257 Hz
$\text{C}_6\text{F}_5\text{IF}_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2^{\text{b)}$	CH_2Cl_2	24	107.4	144.3	251 Hz	136.9	256 Hz	144.0	246 Hz
$\text{C}_6\text{F}_5\text{IF}_2^{\text{c)}$	CH_2Cl_2	24	103.0	145.4	263 Hz	137.1	257 Hz	144.5	256 Hz

^{a)} $\text{C}_{12}\text{H}_8\text{N}_2$ 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)). ^{b)} $\text{C}_{10}\text{H}_8\text{N}_2$ 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')). ^{c)} For comparison.

Table 6 Influence of N-base coordination on selected vibrations in the Raman spectra of Ar_fIX₂ compounds

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

a) For comparison

b) -20 °C

c) $\bar{\nu}(\text{CN})$ of I(CN)₂

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

Compound	C ₆ F ₅ IF ₂ ·C ₁₂ H ₈ N ₂ (1a)	C ₆ F ₅ IF ₂ ·C ₁₀ H ₈ N ₂ (1b)	C ₆ F ₅ IF ₂ ·C ₉ H ₇ N (1c)	4-FC ₆ H ₄ I(CN) ₂ ·C ₁₂ H ₈ N ₂ (5a)
Empirical formula	C ₁₈ H ₈ F ₇ IN ₂	C ₁₆ H ₈ F ₇ IN ₂	C ₁₅ H ₇ F ₇ IN	C ₂₀ H ₁₂ FIN ₄
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 ⁻³	2.042 g cm ⁻³	2.059 g cm ⁻³	1.696 g cm ⁻³
Absorption coefficient	1.997 mm ⁻¹	2.096 mm ⁻¹	2.228 mm ⁻¹	1.821 mm ⁻¹
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 _α (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 ≤ h ≤ 29, -29 ≤ k ≤ 28, -38 ≤ l ≤ 38	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -17 ≤ l ≤ 16	-9 ≤ h ≤ 9, -18 ≤ k ≤ 18, -18 ≤ l ≤ 19	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	63471	6764	13120	35079
Independent reflections	16224 [<i>R</i> _{int}] = 0.0324]	3603 [<i>R</i> _{int}] = 0.0217]	7032 [<i>R</i> _{int}] = 0.0243]	4295 [<i>R</i> _{int}] = 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 ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	16224 / 0 / 1009	3603 / 0 / 235	7032 / 0 / 433	4163 / 0 / 236
Final R indices	<i>R</i> ₁ = 0.0301, <i>wR</i> ₂ = 0.0672	<i>R</i> ₁ = 0.0276, <i>wR</i> ₂ = 0.0667	<i>R</i> ₁ = 0.0322, <i>wR</i> ₂ = 0.0704	<i>R</i> ₁ = 0.0176, <i>wR</i> ₂ = 0.0468
Min./max. height in ΔF-map	0.63 and -0.56 eÅ ⁻³	0.95/-0.72 eÅ ⁻³	0.89/-0.51 eÅ ⁻³	0.70/-0.65 eÅ ⁻³
Programmes used [16, 17]		SMART, SAINT, SADABS, SHELXTL		Bruker AXS APEX 2 Vers. 2.0-2 2006

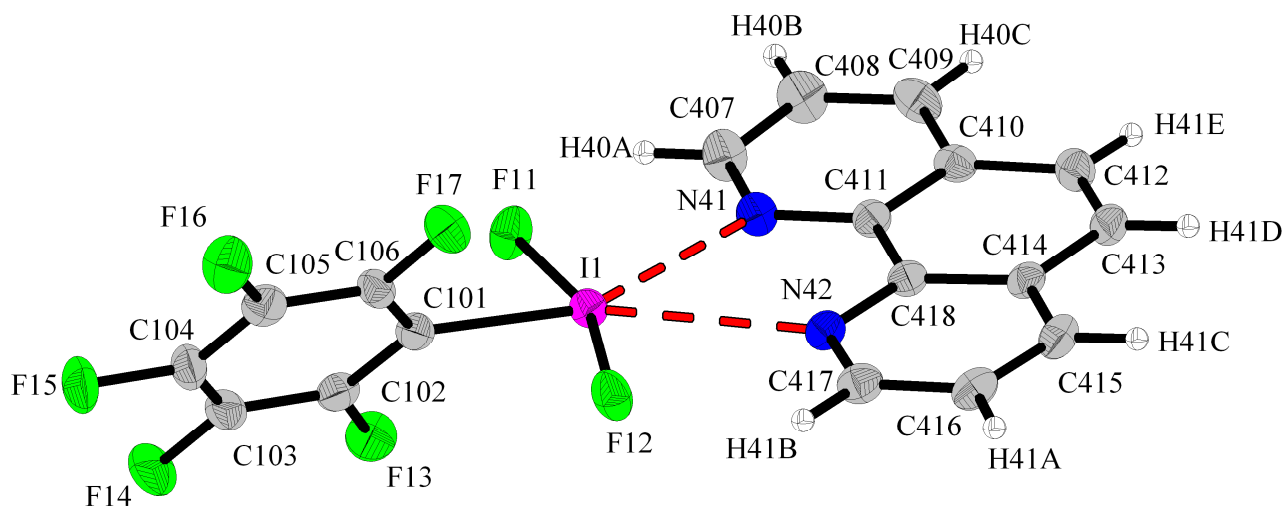


Figure 1 Molecular structure, numbering scheme, and intermolecular contacts of $C_6F_5IF_2 \cdot C_{12}H_8N_2$ (**1a**).

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).

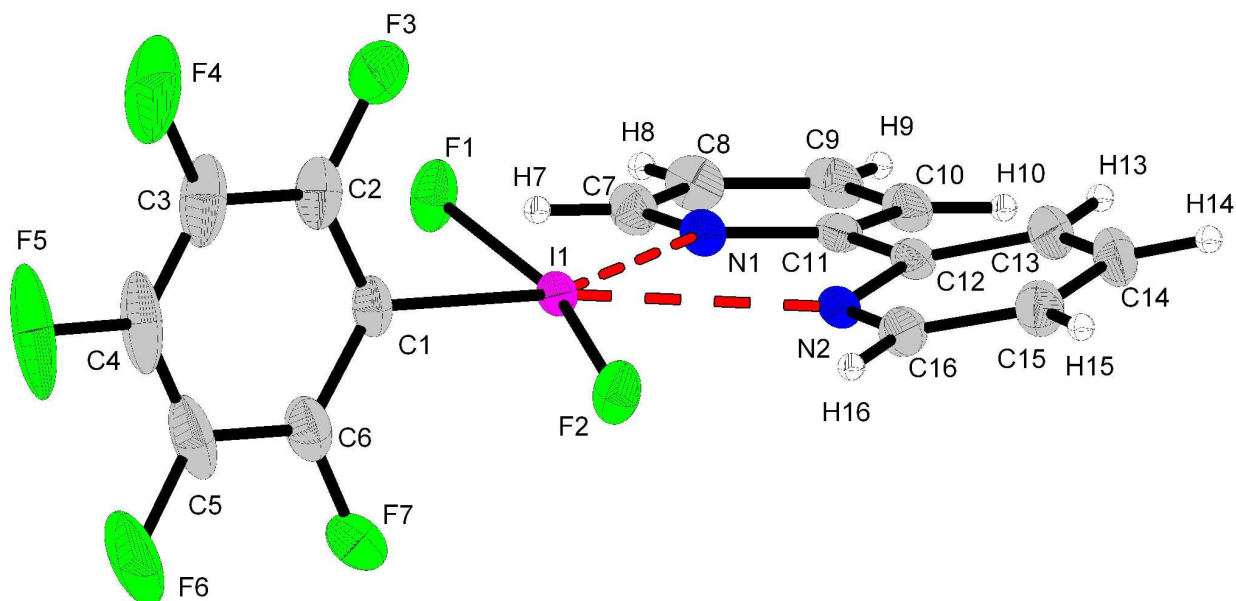


Figure 2 Molecular structure, numbering scheme, and intermolecular contacts of $C_6F_5IF_2 \cdot C_{10}H_8N_2$ (**1b**).

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).

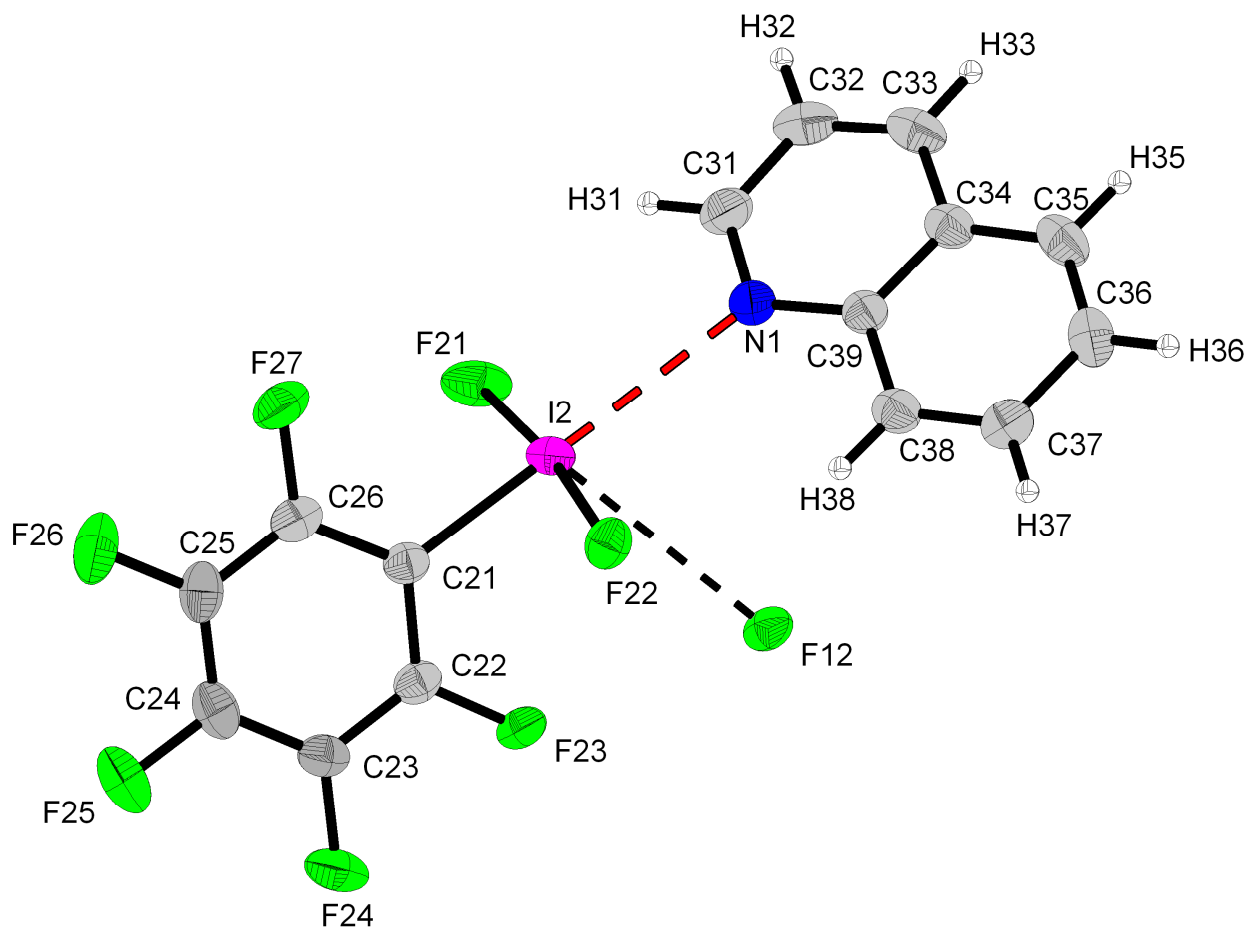


Figure 3a Molecular structure, numbering scheme, and intermolecular contacts of $C_6F_5IF_2 \cdot C_9H_7N$ (**1c**).

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).

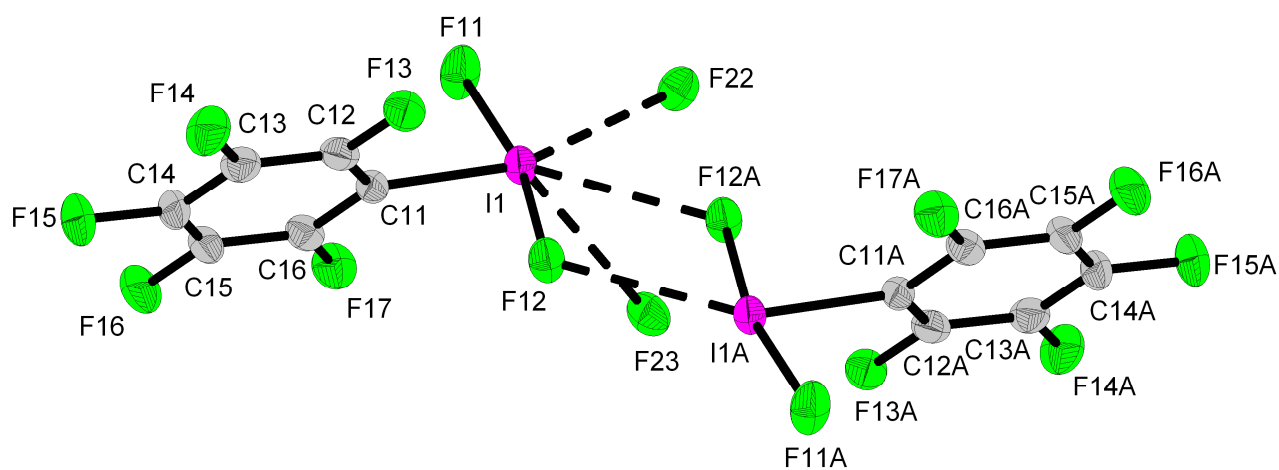


Figure 3b Molecular structure, numbering scheme, and intermolecular contacts of $C_6F_5IF_2 \cdot C_9H_7N$ (**1c**).

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).

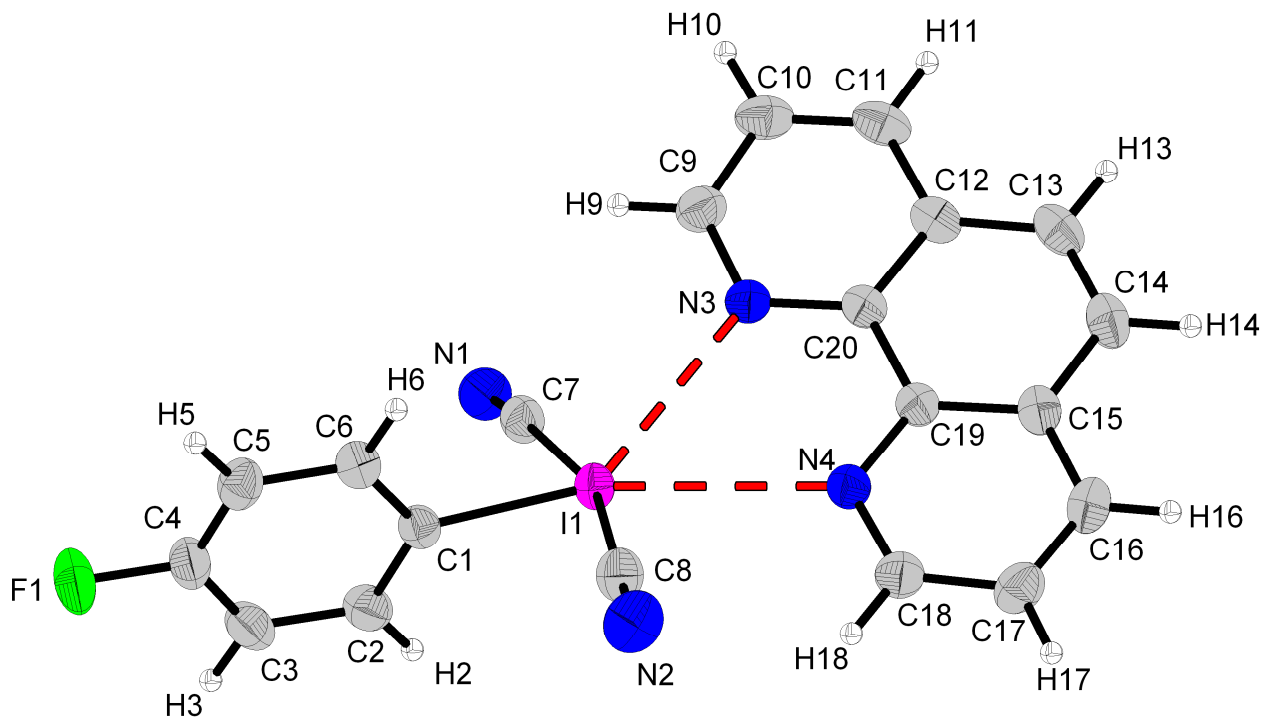


Figure 4 Molecular structure, numbering scheme, and intermolecular contacts of 4-FC₆H₄I(CN)₂ · C₁₂H₈N₂ (**5a**).

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).