Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Interaction of the electrophilic bis(pentafluorophenyl)iodonium cation $[(C_6F_5)_2I]^+$ with the ambident pseudohalogenide anions $[SCN]^-$ and $[CN]^-$

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ARTICLE INFO

Article history: Received 25 March 2014 Received in revised form 8 April 2014 Accepted 9 April 2014 Available online 23 April 2014

Keywords: Bis(pentafluorophenyl)iodonium salts Anion metathesis Ambident pseudohalides Molecular structure Ab initio computations

ABSTRACT

The iodonium pseudohalide compounds, $[(C_6F_5)_2I][X]$ (X = SCN and CN) were synthesized by means of fluoride substitution in $[(C_6F_5)_2I][F]$ with the Lewis acidic reagents $(CH_3)_3Si$ –NCS and $(CH_3)_3Si$ –CN. The isolated iodonium pseudohalides are intrinsically unstable solids. Decomposition resulted in equimolar amounts of C_6F_5I and C_6F_5SCN or C_6F_5I and C_6F_5CN , respectively. In case of $[(C_6F_5)_2I][SCN]$ single crystals could be grown from CH₂Cl₂. The crystal structure revealed a dimer with an eight membered ring formed by two ambident anions bridging the iodine atoms of two cations by N and S coordination. The favored dimerization of $[(C_6F_5)_2I][SCN]$ and $[(C_6F_5)_2I][CN]$ in the gas phase is supported by ab initio computations.

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1. Introduction

Non-fluorinated iodonium salts belong to the class of polyvalent iodine(III) compounds. First examples were very early synthesized by Viktor Meyer in 1894, namely phenyl(*p*-iodophenyl)iodonium salts with the anions Cl⁻, Br⁻, I⁻, and NO₃⁻ [1]. Generally, iodonium salts represent the most common type of iodine(III) compounds and have found numerous applications, e.g. as cationic photo initiators or as reagents in organic chemistry [2–6].

Non-fluorinated 1-alkynyl(phenyl)- and vinyl(phenyl)iodonium salts, with thiocyanate anions are mentioned in literature as intermediates for the synthesis of 1-alkynyl- and vinylthiocyanates, respectively [7,8]. Already in 1903 [3-CH₃C₆H₄(4-CH₃C₆H₄)I][CN] was reported as a first example of an iodonium salt with the cyanide anion and characterized by a m.p. of 104– 108 °C [9]. Salts with perfluoroorganyliodonium cations, [(R_F)₂I][X] have been known for ca. 50 years [10]. Generally, perfluorination of

http://dx.doi.org/10.1016/j.jfluchem.2014.04.006 0022-1139/© 2014 Published by Elsevier B.V. the organyl groups increases the electrophilicity of the iodonium cation. Thus, the bis(pentafluorophenyl)iodonium cation is characterized by a significantly higher electrophilicity in relation to the non-fluorinated diphenyliodonium cation, which is related to the higher partial positive charge on iodine(III). Consequently, the $[(C_6F_5)_21]^+$ cation shows remarkable cation—anion contacts even in combination with weakly coordinating anions such as $[BF_4]^-$ [11]. In combination with anions of high nucleophilicity, molecular species are accessible, e.g. in combination with F^- the oligomeric molecular compound $\{[(C_6F_5)_21][F]\}_n$ could be isolated. $\{[(C_6F_5)_2I][F]\}_n$ with a ψ -octahedral molecular geometry, contains two equivalent C_6F_5 groups and polar I–F bonds. In contrast, $(C_6F_5)_2I][F]\}_n$ by F/C_6F_5 substitution, is an example for a ψ -trigonal bipyramidal molecular geometry [12].

In the present contribution, we continue our investigations of bis(pentafluorophenyl)iodine compounds, which in the past covered the fields of alternative synthetic approaches [13], structural features [11], and electrochemical properties [14]. The ambident anions X^- (X = [SCN] and [CN]) possess one site with a remarkable nucleophilicity. We describe the interaction of these anions with the electrophilic $[(C_6F_5)_2I]^+$ cation as cation—anion contacts, $(C_6F_5)_2I]-X$, but present their formula in the simplified ionic way, $[(C_6F_5)_2I][X]$.





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$$\begin{array}{ccc} \Delta & & & & & & \\ \left[(C_6F_5)_2 I \right]^+ & \rightarrow & < \left[C_6F_5 \right]^+ > + C_6F_5 I & \longrightarrow & C_6F_5 - CN \end{array}$$

2. Results and discussion

2.1. Syntheses of bis(pentafluorophenyl)iodonium thiocyanate and cyanide

For the synthetic approach, $[(C_6F_5)_2I][Hal]$ (Hal = Cl, F) with a diaryliodonium fragment was chosen and a Hal/X substitution step (X = SCN or CN). The starting material $[(C_6F_5)_2I][F]$ was synthesized in a good yield from $C_6F_5IF_2$ and $Bi(C_6F_5)_3$ in CH_2Cl_2 (Eq. 1) and $[(C_6F_5)_2I][Cl]$ from the reaction of $[(C_6F_5)_2I][F]$ with $(CH_3)_3SiCl$ in CH_2Cl_2 (Eq. 2).

$$3C_6F_5IF_2 + Bi(C_6F_5)_3 \xrightarrow{CH_2Cl_2} 3[(C_6F_5)_2I][F] + BiF_3$$
(1)

$$[(C_6F_5)_2I][F] + (CH_3)_3SiCl \xrightarrow{CH_2Cl_2}[(C_6F_5)_2I][Cl] + (CH_3)_3SiF$$
(2)

For the synthesis of $[(C_6F_5)_2I][CN]$, two iodonium starting materials were investigated. No reaction proceeded when $[(C_6F_5)_2I][CI]$ was treated with $(CH_3)_3SiCN$ in CH_2Cl_2 at 20 °C (Eq. 3). The reaction of $[(C_6F_5)_2I][F]$ with trimethylsilyl cyanide was successful (Eq. 4a). Therefore, $[(C_6F_5)_2I][F]$ was also applied in the reaction with trimethylsilyl isothiocyanate (Eq. 4b).

$$[(C_6F_5)_2I][CI] + (CH_3)_3SiCN \twoheadrightarrow [(C_6F_5)_2I][CN] + (CH_3)_3SiCl$$
(3)

$$[(C_6F_5)_2I][F] + (CH_3)_3SiCN^{CH_2Cl_2}_{20\,^\circ C}[(C_6F_5)_2I][CN] + (CH_3)_3SiF \tag{4a}$$

$$[(C_6F_5)_2I][F] + (CH_3)_3Si - NCS_{20 \circ C}^{CH_2Cl_2}[(C_6F_5)_2I][SCN] + (CH_3)_3SiF \quad (4b)$$

The F/CN substitution with the moderate Lewis acidic reagents trimethylsilyl cyanide, $(CH_3)_3Si-CN$, and trimethylsilyl isothiocyanate, $(CH_3)_3Si-NCS$, can be described as an acid-assisted nucleophilic substitution at the iodine(III)–fluorine bond. After addition of the Lewis acidic reagent, the original suspension turned into a solution which subsequently changed back to a suspension. The driving force for these reactions is the high Si–F bond strength (e.g. the bond dissociation energy for F–SiF₃ is reported to 694 kJ/ mol) [15]) of the by-product, $(CH_3)_3SiF$. Both products, $[(C_6F_5)_2I][X]$, (X = CN and SCN) were isolated as white solids.

The thermal decomposition of the neat products can be described formally by two subsequent steps: elimination of $<[C_6F_5]^+>$ from the iodonium cation and addition of $<[C_6F_5]^+>$ to the soft nucleophilic terminus of the ambident anions (Scheme 1). More likely, the reaction route will be initiated by an electron transfer from the soft terminus of the anion to iodine(III) in the cation. After fragmentation of the radical $[(C_6F_5)_2I]^{\bullet}$ into C_6F_5I (a favored leaving group) and the $[C_6F_5]^{\bullet}$ radical, the latter can add to the pseudohalogen radical (Scheme 2).

The two products $[(C_6F_5)_21][X]$ (X = CN and SCN) are intrinsically unstable, even in the solid state, and decompose under formation of equimolar amounts of C_6F_5I and C_6F_5-CN or C_6F_5I and C_6F_5-SCN , respectively (Schemes 1 and 2).

The easy decomposition in solution represented a challenge to grow suitable single crystals. Fortunately, single crystals of $[(C_6F_5)_2I][SCN]$ were obtained from CH₂Cl₂ solutions at 10 °C. The attempt to get single crystals of $[(C_6F_5)_2I][CN]$ from CH₂Cl₂ or CH₃CN solutions at -10 to -20 °C failed.

The crystallographic data of $[(C_6F_5)_2I][SCN]$ are summarized in Table 1. The unit cell contains 18 molecules, which are arranged to 9 dimers. In the dimer (Fig. 1), each iodonium cation is coordinated by one N and S atom of the two bridging anions, which result in an eight membered ring with I^{III} –S–C–N– I^{III} and N– I^{III} –S subunits. The crystals of $[(C_6F_5)_2I][SCN]$ contain one symmetry independent molecule with a $[(C_6F_5)_2I]^*$ cation that features an almost right C– I–C angle (91.16(8)°). Each cation shows two contacts with I–N and I–S distances of 2.668(2) Å and 2.9361(6) Å, respectively. These distances are 24% and 22% shorter than the sum of van der Waals radii I–N (3.53 Å) and I–S (3.78 Å) [16] and 33% or 24% longer than estimated I–N and I–S single bonds. The angle under which the N- and S-terminus of the linear [SCN][–] anion coordinates to I^{III} differs significantly. The I–S–C angle was determined at 89.24(8)° whereas the I–N–C angle was 162.7(2)°.

The anion in the I–SCN–I bridge deviates only negligible from linearity (178.3(2)°). Comparison of the C–S distance (1.655(2) Å) and the C–N distance (1.154(3) Å) in the bridging SCN anion with typical C–S single (1.81 Å) or C=S double (1.61 Å) bonds and typical C=N double (1.22 Å) or triple C=N (1.11 Å) distances in combination with the coordination angle to $[(C_6F_5)_2I]^+$ lead to the valence bond representation $[S=C=N]^-$.

The coordination of N and S on iodine in the approximately square planar environment (ψ -octahedral molecular geometry) exerts influence on the opposite C–I bond. The distance C(8)–I (trans to I–S, coordination of soft sulfur) is elongated (2.118(2) Å)

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Table 1

Tuble I			
Crystallographic	and refinemen	t data for	[(C ₆ F ₅) ₂ I][SCN].

Compound	$[(C_6F_5)_2I][SCN]$
Empirical formula	C ₁₃ F ₁₀ INS
Crystal size (mm)	$0.37mm \times 0.12mm \times 0.10mm$
Crystal system	Trigonal
Space group	RĪ
Unit cell dimensions	$a = 29.0436(19)$ Å $\alpha = 90^{\circ}$
	$b = 29.0436(19) \text{ Å } \beta = 90^{\circ}$
	$c = 12.0175(8)$ Å $\gamma = 120^{\circ}$
Volume	8779.0(10)Å ³
Ζ	18
Density (calculated)	$1.767\mathrm{gcm^{-3}}$
Temperature	100(1)K
Radiation	MoK_{α} ($\lambda = 0.71073$ Å)
F(000)	4392
Theta range for data	1.40-30.55°
Final R indices	R1 = 0.0289, wR2 = 0.0637

relative to the C(2)–I distance (trans to I–N, coordination of hard nitrogen) of 2.100(4) Å. The elongation of the C–I bond in *trans*-position can be interpreted by a transfer of partial charge from S to I^{III} cf. the proposed ET reaction path in Scheme 2.

Iodonium compounds $[(C_6F_5)_2I][X]$ with a strong cation—anion interaction are soluble in coordinating and "non-coordinating" solvents and thus their ¹⁹F NMR data allow to conclude on the molecular dispersed species in solution (Table 2). In contrast, typical ionic iodonium salts, such as $[(C_6F_5)_2I][BF_4]$ with a weakly coordinating counter anion are insoluble in "non-coordinating" solvents such as CH₂Cl₂ (DN: 0 kJ/mol) [17]) but well soluble in coordinating CH₃CN (DN: 14.1 kJ/mol) [18]. In a CH₃CN solution of $[(C_6F_5)_2I][BF_4]$ a weakly by acetonitril coordinated $[(C_6F_5)_2I]^+$ cation is present indicated by the F^4 resonance at high frequency of -141.4 ppm. The F^4 resonance in $[(C_6F_5)_2I][SCN]$ in CH₃CN is significantly shifted to lower frequency indicative for a strong anion coordination. Comparable ¹⁹F NMR data are obtained for [(C₆F₅)₂I][SCN] in CH₂Cl₂ solutions. All three ¹⁹F NMR signals of the pentafluorophenyl groups appear in both solvents as well resolved signals, which contrasts to [(C₆F₅)₂I][CN], where all three signals of the C₆F₅ groups appear as broad singlets ($\Delta v_{1/2} \ge 63$ Hz). The absence of high resolved signals in combination with the low solubility of [(C₆F₅)₂I][CN] in both CH₂Cl₂ and CH₃CN solvents suggest an oligomeric structure in solution. The presence of one set of four ¹⁹F NMR resonances for both C₆F₅ groups is in agreement with a coordination number of 4 at iodine. Additionally, it is worth mentioning that in $[(C_6F_5)_2I][CN]$ the F^4 signal appears 6.4 ppm at lower frequency relative [(C₆F₅)₂I][BF₄]. In [(C₆F₅)₂I][CN] there is a stronger cation—anion contact than in $[(C_6F_5)_2I][SCN]$, comparable to that in $[(C_6F_5)_2I][F]$.



Fig. 1. X-ray crystal structure of $[(C_6F_5)_2I][SCN]$. Thermal ellipsoids are shown at the 50% probability level. Selected distances/Å and anglesj́: I(1)-C(2) 2.100(2), I(1)-C(8) 2.118(2), C(1)-S(1) 1.655(2), C(1)-N(1) 1.154(3), I(1)-S(1) 2.9361(6), I(1)-N(1A) 2.668(2), C(2)-I(1)-C(8) 91.16(8), I(1)-S(1)-C(1) 89.24(8), S(1)-C(1)-N(1) 178.3(2), I(1)-N(1A)-C(1A) 162.7(2).

The Raman bands in $[(C_6F_5)_2I][CN]$ at 197 cm⁻¹ and 2110 cm⁻¹ can be assigned to $\nu(C=I)$ and to $\nu(C\equiv N)$. The Raman bands at 191 cm⁻¹, 463 cm⁻¹, 747 cm⁻¹, and 2079 cm⁻¹ are characteristic for $[(C_6F_5)_2I][SCN]$. The band at 191 cm⁻¹ can be assigned to $\nu(C-I)$. Three fundamental vibrations exist for the linear NCS ligand (point group $C_{\infty V}$), namely the two stretching vibrations $\nu(CN)$ and $\nu(CS)$ and the twofold degenerated deformation mode $\delta(SCN)$ [19]. The vibration $\nu(CN)$ is expected at 2079 cm⁻¹, $\nu(CS)$ at 747 cm⁻¹, and $\delta(SCN)$ at 463 cm⁻¹.

 $[(C_6F_5)_2I][SCN]$ and $[(C_6F_5)_2I][CN]$ are intrinsically unstable, even in the solid state. $[(C_6F_5)_2I][SCN]$ shows a sharp decomposition point at 148 °C. Decomposition in a sealed glass capillary under dry Ar at 150 °C gave C_6F_5SCN [20] and C_6F_5I in a 1:1 molar ratio.

 $[(C_6F_5)_2l][CN]$ – like fluoroaryliodine dicyanides [21] – has no melting point and decomposes at 94 °C. Decomposition in a sealed glass capillary at 94 °C under dry Ar resulted in C_6F_5CN [22] and C_6F_5I in a 1:1 molar ratio.

Ab initio computations were performed on the RHF level using the LANL2DZ basis set to obtain bond distances and angles and natural population analysis charges for the monomeric gas phase molecules (C_6F_5)₂I–NCS (1), (C_6F_5)₂I–SCN (2), (C_6F_5)₂I–CN (3), and (C_6F_5)₂I–NC (4) (1–4: see Fig. A in Table 3) and for the dimeric gas phase molecules {(C_6F_5)₂I–NCS–(C_6F_5)₂I–SCN-} (5, see Fig. B in Table 3) and {(C_6F_5)₂I–CN–(C_6F_5)₂I–SCN-} (6, see Fig. B in Table 3). Important bond distances and angles and natural population analysis charges are compiled in Tables 3 and 4.

Та	ble	2
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⁹ F NMR shift values δ /ppm of [(C ₆ F ₅) ₂ I][SCN], [(C ₆ F ₅) ₂ I][CN], [(C ₆ F ₅) ₂ I][F], [(C ₆ F ₅) ₂ I][CI],	, and $[(C_6F_5)_2I][BF_4]$ in CH_2Cl_2 and CH_3CN .
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Compound	Solvent	Temp. (°C)	$F^{2,6}$ (ppm)	F^4 (ppm)	<i>F</i> ^{3,5} (ppm)				
$[(C_6F_5)_2I][SCN]$	CH_2Cl_2	0	-123.7	-144.7	-156.6				
	CH ₃ CN	0	-123.4	-145.3	-156.5				
[(C ₆ F ₅) ₂ I][CN]	$CH_2Cl_2^a$	-10	-125.5	-147.9	-158.5				
	CH ₃ CN ^a	-40	-125.5	-148.0	-157.5				
$[(C_6F_5)_2I][F]$	CH_2Cl_2	24	-124.4	-147.8	-158.3				
	CH_3CN	24	-124.4	-148.3	-158.1				
$[(C_6F_5)_2I][CI]$	CH_2Cl_2	24	-122.9	-144.6	-156.3				
	CH ₃ CN	24	-124.0	-146.2	-156.9				
$[(C_6F_5)_2I][BF_4][11]^b$	CH ₃ CN	24	-120.4	-141.4	-155.7				

^a Broad singlets ($\Delta v_{1/2} \ge$ 63 Hz).

^b This ionic compound is insoluble in CH₂Cl₂ at 24 °C.

Table 3

Calculated^a bond distances/Å, angles/ $^{\circ}$, and natural population analysis charges NC/e⁻ of [(C₆F₅)₂I]⁺ compounds with ambident anions X⁻.

$\{[(C_6F_5)_2I]X\}_n$	Figure	C ¹ –I	C ⁷ –I	$A(C^1-I-C^7)$	$A(C^2-C^1-C^6)$	$A(C^8-C^7-C^{12})$	$D(C^1-I-C^7-C^8)$	$D(C^7 - I - C^1 - C^2)$	NC(C ¹)	NC(Ar ¹)	$NC(C^7)$	NC(Ar ²)	NC(I)
X = NCS, n = 1	А	2.091 ^b	2.176 ^c	89.07	119.10	117.05	121.08	108.71	-0.405	-0.188	-0.497	-0.404	1.426
X = SCN, n = 1	Α	2.095 ^b	2.175 ^c	90.20	119.21	117.64	121.46	107.94	-0.424	-0.164	-0.464	-0.348	1.224
$X = SCN, n = 2^d$	В	2.108	2.112	92.04	118.16	118.41	113.52	108.68	-0.454	-0.269 ^d	-0.429	-0.250^{d}	1.365
X = CN, n = 1	Α	2.095 ^b	2.245 ^c	86.48	118.99	116.61	124.23	107.04	-0.412	-0.202	-0.507	-0.489	1.307
X = NC, n = 1	Α	2.092 ^b	2.210 ^c	87.43	118.96	116.69	122.54	108.52	-0.406	-0.207	-0.505	-0.459	1.434
$X = CN, n = 2^{e}$	В	2.098 ^e	2.130 ^e	92.07	118.44	117.76	116.36	113.19	-0.429	-0.243	-0.463	-0.318	1.408

^a RHF level, LANL2DZ basis set.

^b Aryl group in the equatorial position of the ψ-tbp moiety of iodine (Fig. A, idealized).

^c Aryl group in the axial position of the ψ -tbp moiety of iodine (Fig. A, idealized).

^d Two SCN anions bridge ambidently two iodonium cations: C^1 (Ar¹) is *trans* to the nitrogen contact, C^7 (Ar²) is *trans* to the sulfur contact.

^e Two CN anions bridge ambidently two iodonium cations: C¹ (Ar¹) is *trans* to the carbon contact, C⁷ (Ar²) is *trans* to the nitrogen contact.



Table 4

Calculated^a cation-anion contacts/Å, angles/°, and natural population analysis charges NC/e⁻ of [(C₆F₅)₂I]⁺ compounds with ambident anions X⁻.

$\{[(C_6F_5)_2I]X\}_n$	Figure	I–X	I—X′	$A(X-I-C^1)$	$A(X-I-C^7)$	$A(X'-I-C^1)$	$A(X'-I-C^7)$	A(X-I-X')	NC(X)	NC(X')
X = NCS, n = 1	А	2.267	-	79.59	168.58	-	-	-	-0.834 ^e	-
$X = SCN, n = 1^{f}$	А	2.963	-	84.13	174.24	-	-	-	-0.713 ^g	-
X = SCN, n = 2	В	2.649 ^h	3.219 ⁱ	169.5 ^j	77.7 ^k	79.2	170.6	111.2	-0.846^{1}	-0.846^{m}
X = CN, n = 1	А	2.299	-	81.78	168.20	-	-	-	-0.617 ⁿ	-
X = NC, n = 1	А	2.197	-	80.91	168.28	-	-	-	-0.768°	-
X = CN, n = 2	В	2.962 ^p	2.499 ^q	175.68	92.03	173.22	81.24	94.65	0.051	-0.899

^a RHF level, LANL2DZ basis set.

^e NC(N) = -0.908, NC(C) = 0.350, NC(S) = -0.276.

^f A(I-S-C) = 98.38.

^g NC(S) = -0.355, NC(C) = 0.123, NC(N) = -0.481.

^h I–N cation–anion contact; A(I–N–C)=157.5°.

ⁱ I–S cation–anion contact; A(I–S–C)=93.0°.

^j A(C¹–I–N).

^k $A(C^7-I-N)$.

¹ NC(N) = -0.718, NC(C) = 0.284, NC(S) = -0.412.

^m NC(S) = 0.412, NC(C) = 0.284, NC(N) = -0.718.

ⁿ NC(C) = -0.205, NC(N) = -0.412.

^q I–N cation–anion contact; $A(I-N-C)=145.5^{\circ}$.

The calculated bond distances and angles for **1–4** are discussed regarding their approximate ψ -tbp molecular geometry. The I–N distance in **1** (2.267 Å) is significantly longer than in **4** (2.197 Å) and the corresponding I–C⁷ bond in *trans*-position shorter, respectively. The triad C⁷–I–N behaves like an asymmetric hypervalent bond. The partial positive charge on iodine in **1** and **4** is higher than in their isomers **2** and **3** with I–S and I–C contacts. In agreement with the concept of hypervalency the partial charge as well of the aryl group, Ar², in *trans*-position of **1–4** as of the *ipso*-carbon atom, C⁷, is more negative than that of Ar¹ and C¹, respectively. I–S in **2** was determined at 2.963 Å. The distance I–CN (2.299 Å) in **3** is only slightly longer than I–C⁷ in *trans*-position (2.245 Å), but significantly longer than I–C¹ (2.095 Å).

The dimers **5** and **6** are discussed regarding their ψ -octahedral molecular geometry. In dimer **5**, the two bridging SCN ligands and the two iodine centers form a planar eight membered ring. In **5** the I–N distance (2.649 Å) is strongly elongated with respect to monomer **1** (2.267 Å). It fits satisfactorily with the value in the crystal structure (2.668(2) Å) whereas the I–S distance is overestimated. The different coordination modus of sulfur and nitrogen

of both bridging SCN ligands in the solid state structure is also found in the gas state, even though with slight deviations: A(I–S– C) 89.24(1)° vs. 93.0° and A(I–N–C) 162.7(2)° vs. 157.5. In **5** the value of the partial positive charge on iodine is situated between that of the monomeric isomers **1** and **2**. In agreement with a nearly ψ -octahedral molecular geometry of **5** the negative partial charge of the aryl groups Ar¹ and Ar² is of similar quantity.

Dimer **6** contains a central six membered nearly planar (D(I–C–N–I) = 1.5°) ring with two CN ligands and two iodine atoms. The coordination of N on I resembles a sp² hybridized C-atom, whereas the angle I–N–C was determined at 145.5°. The angles $A(C^1–I-C^7) = 92.1°$ and A(NC–I–N) = 94.7° fit well with the ψ -octahedral molecular geometry of **6**.

The total energy of monomer **1** with the more polar I–N contact (partial charges: I = 1.426 e⁻, N = -0.908 e⁻) compared to monomer **2** with I–S (partial charges: I = 1.224 e⁻, S = -0.355 e⁻) is 19.8 kJ/mol lower. Dimerization of **1** or **2** is accompanied by a win of energy of 125.1 or 164.8 kJ/mol, respectively, and explains the dimerization of **5** in the solid state. Furthermore, the thermal decomposition in the solid state under formation of equimolar amounts of C₆F₅SCN and C₆F₅I becomes plausible when an electron

^o NC(N) = -1.081, NC(C) = 0.313.

^p I–C cation–anion contact; $A(I–C-N)=119.8^{\circ}$.

transfer proceeded from (soft and easy oxidizable) S to $I^{\rm III}$ in the dimer ${\bf 5}.$

A qualitatively similar but quantitatively less distinct trend is found for **3**, **4**, and **6**. Monomer **4** with a I–N contact is favored over **3** with a I–C contact by only 13.3 kJ/mol. Dimerization of **3** and **4** to **6** is accompanied by a win of total energy of 91.6 kJ/mol and 65.0 kJ/mol, respectively.

3. Conclusions

Iodonium salts with the strongly oxidizing cation $[(C_6F_5)_2I]^+$ form in combination with the ambident pseudohalide anions [SCN]⁻or [CN]⁻ in solution and in the gas phase oligomeric species with a ψ -octahedral molecular geometry. In case of $[(C_6F_5)_2I][SCN]$, a dimer was verified in the solid state by its single crystal structure. In the gas phase, the dimers are energetically favored over the monomeric isomers with ψ -trigonalbipyramidal molecular geometry. The monomers with the more polar I-N contact show a lower total energy than those with I-S or I-C contacts. Dimerization in the gas phase comes along with a remarkable win of energy and explains the high tendency to dimeric or oligomeric arrangements in solid state and in solution. The clear reaction path in the thermal decomposition of the neat iodonium compounds under formation of equimolar amounts of C₆F₅I and C₆F₅SCN or C₆F₅CN, respectively, becomes plausible for the dimeric structure, which enables an electron transfer from the soft terminus of the ambident anion to I^{III} . Fragmentation of the $[(C_6F_5)_2I]^{\bullet}$ radical into C_6F_5I and the $[C_6F_5]^{\bullet}$ radical is followed by combination of the $[C_6F_5]^{\bullet}$ and $[X]^{\bullet}$ radical in neighborhood or in the solvent cage.

4. Experimental part

4.1. General

Moisture sensitive compounds were handled under an atmosphere of dry argon. Reactions which were not corrosive for SiO₂ surfaces were carried out in standard glass equipment. Fluoro compounds which can undergo hydrolysis were handled in traps made from FEP tubes (outer/inner diameters: o.d. = 4.1 mm, i.d. = 3.5 mm, o.d. = 9.0 mm, i.d. = 8.0 mm, or o.d. = 25 mm, i.d. = 23 mm). CH₃CN (KMF) was purified by reflux and distillation in sequence over KMnO₄ and P₄O₁₀, respectively. CH₂Cl₂ (KMF) was washed in sequence with conc. H₂SO₄, aq solutions of Na₂CO₃, and H₂O. Finally, it was refluxed and distilled from P₄O₁₀, (CH₃)₃SiCl (Janssen Chimica, >97%) was distilled under dry Ar before use. (CH₃)₃SiCN was synthesized by literature procedure [23]. Trimethylsilyl isothiocyanate, (CH₃)₃SiNCS (ACROS ORGAN-ICS), was used as delivered.

NMR spectra were recorded on a Bruker spectrometer AVANCE 300 (¹⁹F at 282.40 MHz). The chemical shifts were referenced to CCl₃F (¹⁹F) (C₆F₆ as a secondary reference, $\delta = -162.9$ ppm). Raman spectra were recorded on the Bruker FT-Raman spectrometer RFS 100/S using the 1064 nm line of a Nd/YAG laser. The back-scattered (180°) radiation was sampled and analyzed (Stoke range: 50–4000 cm⁻¹). The samples were placed in glass capillaries.

X-ray diffraction data were collected at 100 ± 1 K using a Bruker D8 KAPPA series II diffractometer equipped with an APEX II area detector system. Crystal structure solution by Direct Methods and refinement on *F*2 were performed using the Bruker AXS SHELXTL software suite Version 2008/4/ \odot 2008 after data reduction and empirical absorption correction was performed using the Bruker AXS APEX 2 program Version 3/2009. For crystallographic and refinement details see Table 1.

The refinement was performed with 'solvent-free reflection data' following PLATON/SQUEEZE run. A refinement of the untreated reflection data set produces several peaks with $2.5-4.3 \text{ e}/\text{A}^3$

corresponding to highly disordered dichloromethane and acetonitrile molecules. The peaks attributed to chlorine and three to carbon atoms result in R1 = 0.0562.

The SQUEEZE refinement revealed voids with volumes of 800 Å³ at the positions 0,0,0; 1/3, 2/3, 0.58; and 2/3, 1/3, 0.25 corresponding to 337 electrons each [24].

Crystal structure data have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Enquiries for data can be directed to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K., CB2 1EZ or (e-mail) deposit@ccdc.cam.ac.uk or (fax) +44 (0) 1223 336033. Any requests sent to the Cambridge Crystallographic Data Centre for this material should quote the full literature citation and the reference number CCDC 989837.

DSC analyses were performed on a Netzsch 204 Phoenix instrument equipped with a CC220 controller; a TASC414/3A microprocessor system, and a personal computer. The solid samples (ca. 5 mg) were weighed in aluminum pans and closed by a pierced aluminum lid inside a glove box. The temperature difference between the sample and the empty reference pan with a pierced lid was measured choosing a temperature program of 10 K/ min. The raw data were processed using the Netzsch Proteus Software Version 4.2.

4.2. Synthesis of $[(C_6F_5)_2I][F]$

A solution of $C_6F_5IF_2$ (1.294 g, 3.898 mmol) in CH_2Cl_2 (3 mL) was added to an intensively stirred solution of $Bi(C_6F_5)_3$ (0.927 g, 1.307 mmol) in CH_2Cl_2 (20 mL) in an FEP trap ($d_i = 23$ mm). After 1 h, a solution of NaF (0.42 g, 10 mmol) in H₂O (10 mL) was added to the colorless solution. The stoppered trap was shaken intensively. At first, two "liquid" phases resulted, a turbid, colorless upper and a yellow-greenish lower which contained a white solid. Thereafter, the system changed into a three phase one with a colorless aqueous upper phase, a jellylike middle, and a colorless organic lower phase. At first, ca. 90% of the lower phase were carefully separated. Further, the remaining phases were 3-times extracted with CH₂Cl₂ (each 10 mL). The combined organic phases were washed with $H_2O(8 \text{ mL})$ and cooled to $-78 \degree C$. A white solid precipitated which was isolated and washed in sequence with CH_2Cl_2 and *n*-pentane (each 10 mL) at -60 °C. Afterwards crystallization from CH₂Cl₂ (each 3 mL, from 20 °C to -80 °C) was performed twice. Finally, the crystals were washed with npentane (2 mL) and dried in vacuum (0.05 hPa, 20 °C, 3 h; 100 °C, 1 h; 100-135 °C, 40 min).

Yield 91% (1.703 g, 3.458 mmol). Dec. 203 °C (vis.); 212 °C (DSC, exothermic, *T*_{Onset}). ¹⁹F NMR (CH₂Cl₂, 24 °C) δ −12.5 (s, Δν_{1/2} = 11 Hz, 1F, IF), −124.4 (m, 4F, *F*^{2.6}, C₆F₅), −147.8 (t, ³*J*(*F*⁴,*F*^{3.5}) = 20 Hz, 2F, *F*⁴, C₆F₅), −158.3 (m, 4F, *F*^{3.5}, C₆F₅). ¹⁹F NMR (CH₃CN, 24 °C) δ −10.3 (s, Δν_{1/2} = 24 Hz, 1F, IF), −124.4 (m, 4F, *F*^{2.6}, C₆F₅), −148.3 (t, ³*J*(*F*⁴,*F*^{3.5}) = 21 Hz, 2F, *F*⁴, C₆F₅), −158.1 (m, 4F, *F*^{3.5}, C₆F₅). Raman (20 °C) cm⁻¹ 72 (13), 84 (14), 114 (7), 125 (14), 159 (5), 176 (7), 196 (34), 230 (4), 255 (5), 280 (12), 352 (23), 386 (40), 441 (32), 492 (100), 586 (39), 615 (4), 720 (2), 772 (2), 797 (9), 803 (11), 1089 (8), 1144 (4), 1516 (3), 1635 (9).

A small quantity of $[(C_6F_5)_2I][F]$ was decomposed in a sealed glass capillary under dry Ar when heated up to 220 °C. After cooling to 20 °C, the content of the capillary was dissolved in CH₂Cl₂. The products C_6F_5I and C_6F_6 and the molar ratio 1:1 were proven by ¹⁹F NMR spectroscopy.

4.3. Synthesis of $[(C_6F_5)_2I][CI]$

 $(CH_3)_3SiCl$ (50 µL, 0.39 mmol) dissolved in CH_2Cl_2 (2 mL) was added to a suspension of $[(C_6F_5)_2I][F]$ (0.130 g, 0.271 mmol) in CH_2Cl_2 (4 mL) at 20 °C. A solution was formed. After 10 min, a white solid precipitated and the supernatant was separated. The

white solid was washed with *n*-pentane (4 mL) and dried in vacuum (0.05 hPa, 20 °C, 1 h).

Yield 91% (0.122 g, 0.246 mmol). Dec. (vis.) 231 °C. ¹⁹F NMR (CH₂Cl₂, 24 °C) δ –122.9 (m, 4F, $F^{2,6}$, C₆F₅), –144.6 (t, ³*J*(F^4 , $F^{3.5}$) = 20 Hz, 2F, F^4 , C₆F₅), –156.3 (m, 4F, $F^{3.5}$, C₆F₅); ¹⁹F NMR (CH₃CN, 24 °C) δ –124.0 (m, 4F, $F^{2.6}$, C₆F₅), –146.2 (tt, ³*J*(F^4 , $F^{3.5}$) = 20 Hz, ⁴*J*(F^4 , $F^{2.6}$) = 3 Hz, 2F, F^4 , C₆F₅), –156.9 (m, 4F, $F^{3.5}$, C₆F₅). Raman (20 °C) cm⁻¹ 73 (35), 83 (38), 101 (49), 118 (24), 176 (33), 194 (96), 234 (8), 280 (17), 351 (49), 385 (39), 440 (15), 491 (100), 584 (21), 618 (8), 715 (3), 790 (33), 1086 (20), 1286 (7), 1394 (7), 1634 (5).

A small amount of $[(C_6F_5)_2I][CI]$ was decomposed in a sealed glass capillary under dry Ar by heating up to 235 °C. After cooling to 20 °C, the product was dissolved in CH₂Cl₂ and C₆F₅I and C₆F₅Cl (molar ratio 1:1) were determined by ¹⁹F NMR spectroscopy.

4.4. Synthesis of $[(C_6F_5)_2I][CN]$

 $(CH_3)_3$ Si–CN (55 µL, 0.412 mmol) dissolved in CH_2Cl_2 (0.8 mL) was added to a suspension of $[(C_6F_5)_2I][F]$ (0.114 g, 0.237 mmol) in CH₂Cl₂ (2 mL) at 20 °C. A solution occurred immediately. After 2 min, a white solid precipitated. After 20 min, the supernatant became pale yellow and was separated. The white solid was washed with *n*-pentane (2 mL) and dried in vacuum (0.05 hPa, 20 °C, 20 min).

Yield 88% (0.102 g, 0.209 mmol). Dec. 94 °C (DSC, exothermic, T_{Onset}). ¹⁹F NMR (CH₂Cl₂, -10 °C) δ -125.5 (br, $\Delta \nu_{1/2}$ = 63 Hz, 4F, $F^{2.6}$, C₆F₅), -147.9 (br, $\Delta \nu_{1/2}$ = 70 Hz, 2F, F^4 , C₆F₅), -158.5 (br, $\Delta \nu_{1/2}$ = 69 Hz, 4F, $F^{3.5}$, C₆F₅). ¹⁹F NMR (CH₃CN, -40 °C) δ -125.5 (br, $\Delta \nu_{1/2}$ = 106 Hz, 4F, $F^{2.6}$, C₆F₅), -148.0 (br, 2F, F^4 , C₆F₅), -157.5 (br, $\Delta \nu_{1/2}$ = 111 Hz, 4F, $F^{3.5}$, C₆F₅). Raman (20 °C) cm⁻¹ 84 (70), 118 (22), 137 (53), 168 (69), 177 (63), 197 (100) ν (C-I), 212 (23), 231 (10), 279 (18), 348 (31), 354 (36), 388 (43), 442 (32), 490 (91), 534 (4), 586 (29), 611 (5), 779 (23), 805 (15), 1080 (9), 1093 (12), 1277 (11), 1386 (8), 1635 (9), 2110 (97) ν (CN).

A small sample of $[(C_6F_5)_2I][CN]$ was decomposed under dry Ar in a sealed glass capillary by heating up to 94 °C. After cooling to 20 °C the content of the capillary was dissolved in CH₂Cl₂. The products C_6F_5CN [22] and C_6F_5I were formed in a 1:1 molar ratio (¹⁹F NMR).

4.5. Synthesis of $[(C_6F_5)_2I][SCN]$

 $(CH_3)_3Si-NCS (20 \ \mu L, 0.142 \ mmol)$ dissolved in $CH_2Cl_2 (0.5 \ mL)$ was added to a suspension of $[(C_6F_5)_2I][F] (0.050 \ g, 0.104 \ mmol)$ in $CH_2Cl_2 (0.4 \ mL)$ at 20 °C. Spontaneously, a yellow solution was formed. After 5 min a white solid precipitated. After 1 h, the supernatant was separated. The white solid was washed with *n*-pentane (1.2 mL) and dried in vacuum (0.05 hPa, 20 °C, 30 min).

Yield 50% (0.027 g, 0.052 mmol). Dec. 148 °C (DSC, exothermic, $T_{\rm Onset}$). ¹⁹F NMR (CH₂Cl₂, 0 °C) δ –123.7 (m, 4F, $F^{2.6}$, C₆F₅), –144.7

(tt, ${}^{3}J(F^{4},F^{3,5}) = 21 \text{ Hz}, {}^{4}J(F^{4},F^{2,6}) = 5 \text{ Hz}, 2F, F^{4}, C_{6}F_{5}), -156.6 (m, 4F, F^{3,5}, C_{6}F_{5}), {}^{-19}F \text{ NMR} (CH_{3}CN, 0 °C) \delta -123.4 (m, 4F, F^{2,6}, C_{6}F_{5}), -145.3 (t, {}^{3}J(F^{4},F^{3,5}) = 20 \text{ Hz}, 2F, F^{4}, C_{6}F_{5}), -156.5 (m, 4F, F^{3,5}, C_{6}F_{5}), Ra (20 °C) cm^{-1} 85 (27), 103 (32), 156 (18), 191 (100) \nu(C-I), 237 (6), 278 (12), 349 (31), 387 (13), 440 (5), 463 (4), 490 (49), 584 (8), 609(3), 716 (2), 747 (3), 788 (38), 802 (7), 1086 (15), 1286 (7), 1394 (18), 1408 (7), 1513 (2), 1634 (3), 2079 (46) \nu(CN).$

A small amount of $[(C_6F_5)_2I][SCN]$ was decomposed in a sealed glass capillary under dry Ar when heated up to 150 °C. After cooling to 20 °C, the content in the capillary was dissolved in CH₂Cl₂. The products C_6F_5SCN [20] and C_6F_5I were determined by ¹⁹F NMR spectroscopy. They were present in a 1:1 molar ratio.

Acknowledgement

We gratefully acknowledge financial support by the Fonds der Chemischen Industrie.

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