Reactions of Arylthiazylamides with Internal and External Fluoro Electrophiles − Formation of Products with Unusual Structures

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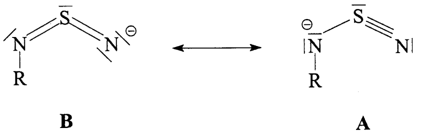
The heteroatom reactivity of the title anions [as $(Me_2N)_3S^+$ and Cs^+ salts] toward both internal and external fluoro electrophiles has been investigated. The intramolecular nucleophilic cyclization of $[ArNSN]^-$ (as the cesium salts) bearing at least one *ortho* fluorine afforded 2,1,3-benzothiadiazoles (e.g. **2a**,**b**), whereas intermolecular condensation with polyfluorinated pyridine and naphthalene afforded Ar–N=S=N–R with R = 4-Py_F (**4**) and R = 2-Np_F (**8**). Further interaction of $[ArNSN]^-$ with **4** or **8** proceeded with the transfer of NSN units resulting in $(ArN{=})_2S$ (**5**) and $[RNSN]^-$, followed by decomposition (R = 4-Py_F) to 4-Py_FNH_2 (**6**) or intramolecular cyclization (R = 2-Np_F) to the polyfluorinated thiadiazole **9**. The compounds of types **4**, **5**, **8**, and **9** have been characterized by single-crystal X-ray diffraction as having both *Z,E* and *Z,Z* configurations [**8** and **9** as molecular complexes with $C_{10}F_8$ and $(Ph–N{=})_2S$ (**5e**), respectively, featuring π-stacking interactions of the arene–polyfluoroarene type]. Besides normal aryl–polyfluoroaryl interactions, the **8**·$C_{10}F_8$ complex also displays unusual polyfluoroaryl–polyfluoroaryl π-stacking.

Introduction

We recently reported the preparation, isolation, and X-ray structural characterization of $(Me_2N)_3S^+$ (TAS^+) salts of $[RNSN]^-$ anions (R = Me_3C, Me_3Si,[1] various aryl substituents[2,3]). It emerged from the X-ray data that due to the unexpectedly short terminal SN bond, these anions should be regarded as thiazylamide (**A**) rather than as sulfurdiimide (**B**) anions (Scheme 1),[1−3] in accordance with calculations at the MP2/6−31G* and B3LYP/6−311+G* levels of theory. Thus, the $[RNSN]^-$ anions belong to the rare class of compounds featuring sulfur−nitrogen triple bonds and therefore they deserve more detailed investigation.



Scheme 1

Previously, some $[RNSN]^-$ anions (R = Ar_F−X−; X = −, S) generated in situ in the form of Cs^+ salts have been shown to be involved in intramolecular nucleophilic *ortho* cyclizations, which resulted in the previously unknown and otherwise inaccessible polyfluorinated 2,1,3-benzothiadiazoles (X = −, Ar_F = 4-RC_6F_4),[4] naphtho[1,2-*c*]- and naphtho[2,3-*c*][1,2,5]thiadiazoles (X = −; Ar_F = 2-$C_{10}F_7$),[5] or 1,3,2,4-benzodithiadiazines (X = S; Ar_F = C_6F_5), depending on Ar_F and X.[6] With Ar_F = 4-Py_F and X = −; S (4-Py_F = 2,3,5,6-tetrafluoro-4-pyridinyl), however, no heterocycles could be prepared, and polyfluorinated 4-aminopyridine was the major product instead.[7] It follows from the available data[4−7] that the reactivity of these intermediate anions toward internal electrophiles (*ortho* cyclization), as well as their stability,[1−3] depends strongly on the substituents at the NSN^- moiety {whilst TAS^+ $[RNSN]^-$ salts (R = Me_3C, Me_3Si) are moderately stable at room temperature,[1] their R = Ar analogues decompose rapidly at temperatures above −20 °C[2,3]}.

The present paper provides detailed experimental information on the reactivity of $[RNSN]^-$ anions (as the TAS^+ and Cs^+ salts; R = Ar) towards both internal and external fluoro electrophiles, as well as a description of nontrivial structural features of the synthesized compounds.

Results and Discussion

Reactivity of Arylthiazylamides $[ArNSN]^-$ Towards Internal Fluoro Electrophiles

The starting point for our considerations was the isolation of salts with fluorinated anions $[Ar_FNSN]^-$,[2,3] which are probable intermediates in the CsF-induced intramolecular *ortho* cyclization of polyfluorinated sulfurdiimides $Ar_FNSNSiMe_3$ to give polyfluorinated benzo- and naphthothiadiazoles.[4,5] This approach might be extended to low-fluorinated derivatives (e.g. **1a**,**b**). When treated with CsF in boiling CH_3CN, cyclization to the well-known 2,1,3-benzothiadiazole **2a**[8] and its previously unreported 4-fluoro derivative **2b** was observed (the 5-F isomer of **2b** was prepared some time ago[9]). Our approach represents a use-

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ful extension of the established methods for the preparation of carbocyclic-substituted derivatives of **2a**.[8]

Comparison of the ^{15}N NMR spectra of **2a** [δ^{15}N = 329.9 (t, J = 0.5 Hz)] and **2b** [δ^{15}N = 330.1 (s), 325.1 (d, J = 2.9 Hz)] allows assignment of the low-field signal of **2b** to N^1 and the high-field signal to N^3. This assignment is also consistent with the known tendency[10] for enhanced shielding of those nitrogen nuclei that are *ortho* to F in fluorinated (hetero)aromatics.

The method seems to be restricted to fluoride as a leaving group; no heterocyclic products could be obtained under the same conditions from the corresponding *ortho*-Cl- or *ortho*-O_2N-containing precursors $ArNSNSiMe_3$ **1c**,**d** [Ar = 2,6-$Cl_2C_6H_3$ (**1c**), 2-$O_2N-C_6H_4$ (**1d**)]. Only the corresponding amines $ArNH_2$ were isolated. This cyclization (Scheme 2) would require a conversion of CsF into CsCl and $CsNO_2$, respectively, which is thermodynamically unattractive and thus responsible for the lack of cyclization.

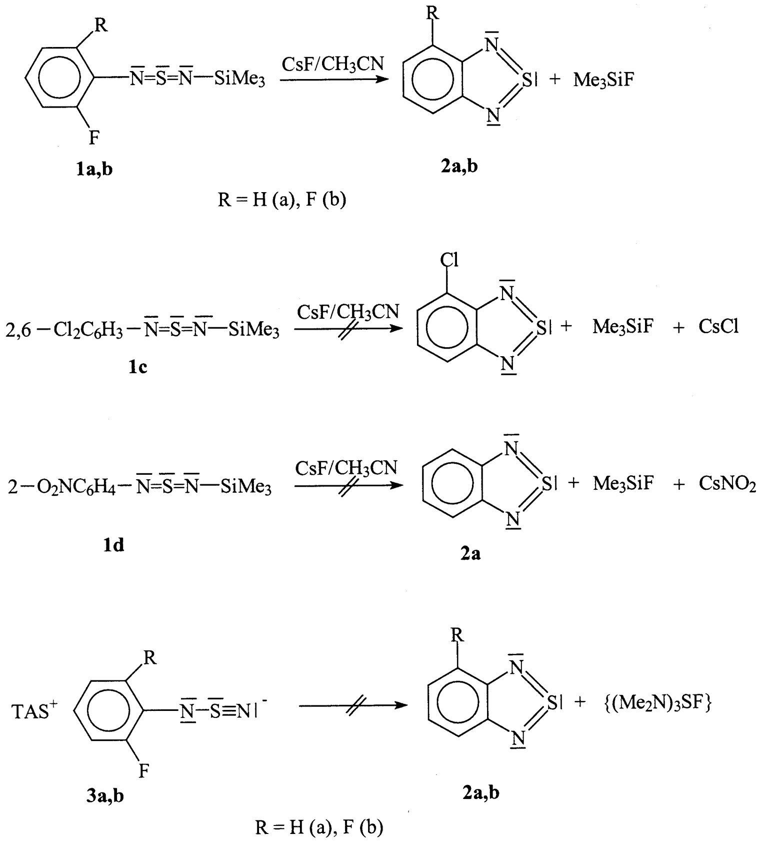
Although attempts to isolate polyfluorinated $[Ar_FNSN]^-$ anions have proved unsuccessful,[2,3] $[2\text{-}FC_6H_4NSN]^-$ (**3a**) and $[2,6\text{-}F_2C_6H_3NSN]^-$ (**3b**), the likely intermediates en route to benzothiadiazole formation (Scheme 2), have been isolated and structurally characterized in the form of TAS^+ salts.[2] Thermal decomposition of salts **3a**,**b** (Scheme 2) gave only tarry products and none of the expected thiadiazoles **2a**,**b**. This failure to isolate the expected cyclization products from the thermal decomposition of **3a**,**b** is not at variance with the formation of arylthiazylamide anions as intermediates. In the decomposition reactions of the TAS^+ salts, fluoride is an unfavorable leaving group, thus the activation barrier for this intramolecular fluoride exchange seems to exceed the stability[2,3] of the arylthiazylamide anions.

Trapping of Arylthiazylamides $[ArNSN]^-$ by External Fluoro Electrophiles

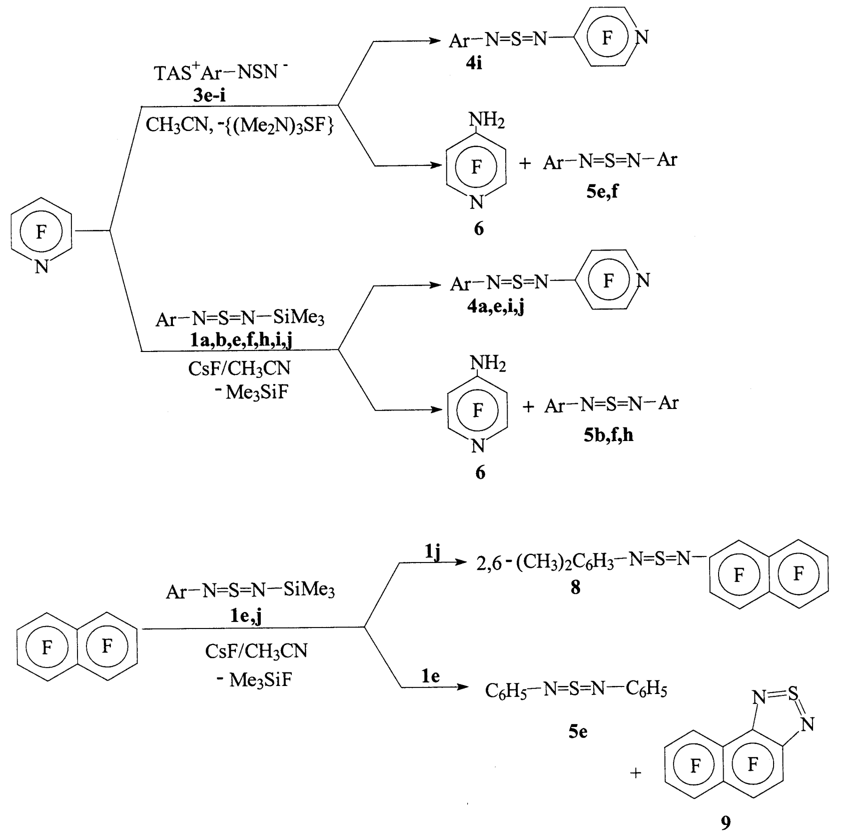
In view of the unsuccessful attempts to obtain benzothiadiazoles by intramolecular fluoride elimination from TAS^+ $[Ar_FNSN]^-$, it was expected that trapping and stabilization of the $ArNSN^-$ moiety should only be possible, if at all, with highly reactive fluoro electrophiles. Highly reactive electrophiles of this type are pentafluoropyridine and octafluoronaphthalene.[11]

It has been found that reactions of arylthiazylamide anions as their TAS^+ and Cs^+ salts with these external electrophiles afford two types of products. In the case of pentafluoropyridine, the products are the expected *N*-aryl-*N′*-(2,3,5,6-tetrafluoro-4-pyridinyl)sulfurdiimides (**4**) and the rather unexpected symmetric *N,N′*-bis(aryl)sulfurdiimides (**5**), as well as 4-amino-2,3,5,6-tetrafluoropyridine (**6**), depending on the Ar group and the cation (Scheme 3).

With TAS^+ salts in CH_3CN at −40 °C, it was found that the expected trapping product **4i** could only be obtained with an anion bearing a strongly electron-releasing *para*-substituent (e.g. CH_3O) on the aromatic ring. In all other such experiments, only **6** and the symmetric compounds **5**



Scheme 2



Scheme 3

were produced, except in the case of anions bearing strongly electron-withdrawing *para*-substituents (e.g. CF_3), where no products could be identified in the resulting dark tar (Scheme 3).

With Cs^+ salts in CH_3CN, the expected trapping products **4a**,**e**,**i**,**j** were obtained from the parent anion $[PhNSN]^-$ and its 2-fluoro-, 4-methoxy-, and 2,6-dimethyl-substituted derivatives, whereas amine **6** and symmetric sulfurdiimides **5b**,**f**,**h** were isolated from the reaction mixtures in all other cases (Scheme 3). With starting material **1h** (Ar = 4-$CF_3C_6H_4$), bearing a strong acceptor substituent, the latter were obtained in only trace amounts.

In the reaction of $C_{10}F_8$ with Cs^+ $[2,6\text{-XyNSN}]^-$ (2,6-Xy = 2,6-dimethylphenyl), typical octafluoronaphthalene β-substitution[11] proceeded to afford the expected *N*-(2,6-Xy)-*N′*-(2-Np_F) sulfurdiimide **8** (2-Np_F = 1,3,4,5,6,7,8-heptafluoronaphth-2-yl) (Scheme 3), which was isolated from the reaction mixture as a molecular complex **8**·$C_{10}F_8$. Complexes of this type have not been reported previously. In contrast, reaction of $C_{10}F_8$ with Cs^+ $[PhNSN]^-$ unexpectedly yielded the polyfluorinated naphtho[1,2-*c*][1,2,5]thiadiazole (**9**) and the symmetric sulfurdiimide $(PhN{=})_2S$ (**5e**) (Scheme 3), which was again isolated from the reaction mixture as a molecular complex **5e**·**9** and was of a previously unknown type.

The dichotomous reactivity of $[ArNSN]^-$ anions toward external fluoro electrophiles cannot be attributed solely to the influence of the aryl substituents since the alkylthiazylamides $[AlkNSN]^-$ [Alk = *t*Bu, adamant-1-yl (1-Ad)] show similar behaviour. Thus, the expected nonsymmetric sulfurdiimide 1-Ad−N=S=N−Py_F-4 was obtained from Cs^+ $[1\text{-AdNSN}]^-$ and pentafluoropyridine, whereas reaction of Cs^+ $[AlkNSN]^-$ (Alk = *t*Bu,1-Ad) with octafluoronaphthalene resulted in the heterocycle **9**.[12]

Thus, although the described anions have the thiazylamide structure,[2,3] they rearrange to a sulfurdiimide form in the final reaction products. In this context, it is interesting to note that the carbon analogues of the title anions, $[RNCN]^-$ (R = Me_3Si), have similar $R{-}\underline{N}{-}C{\equiv}\overline{N}^-$ structures[13a] according to X-ray crystallographic data. They form $R'_2C{=}\overline{N}{-}C{\equiv}\overline{N}$ derivatives upon reaction with $R'_2C{=}O$.[14] By analogy, the initial products of the reactions of the title anions with fluoro electrophiles R_FF can be envisaged as $R_F(Ar)\overline{N}{-}\overline{S}{\equiv}\overline{N}$ undergoing intramolecular rearrangement to the more stable $R_F\overline{N}{=}\overline{S}{=}\overline{N}{-}Ar$ compounds due to the known general instability of these $R\overline{S}{\equiv}\overline{N}$ derivatives.[3] When such a rearrangement of the initial reaction products is not possible, as in the case of $R'_2C{=}\overline{N}{-}\overline{S}{\equiv}\overline{N}$ obtained from the reaction of $Cs^+Me_3Si{-}\overline{\underline{N}}{-}\overline{\underline{N}}{-}CR'_2$ with $R'_2C{=}O$, they are stabilized in a different manner, namely as $R'_2C{=}\overline{N}{-}\overline{N}{=}CR'_2$ compounds (R′ = various aryls).[13b]

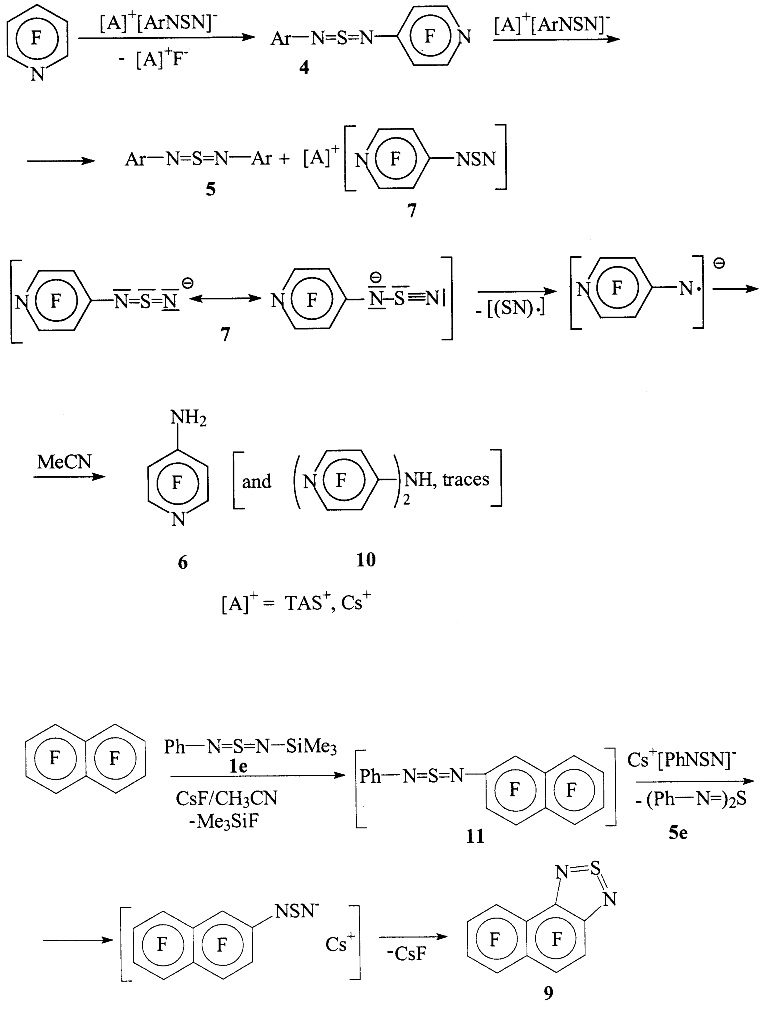
It is quite likely that the expected trapping products **4** are formed in all cases, but that in some cases this reaction is very slow, and in the presence of an effective excess of the starting salt further interaction of the trapping product and the salt is possible to give the symmetric $(ArN{=})_2S$ (**5**) and the $[4\text{-Py}_F\text{NSN}]^-$ anion **7**. It is known that **7** does not undergo nucleophilic ring-closure even in boiling CH_3CN; it only decomposes to give the corresponding amine **6**[7] (Scheme 4). The identification of traces of $(4\text{-Py}_F)_2NH$ (**10**) in some experiments implies the participation of $[4\text{-Py}_F\text{N}^{\cdot-}]$ intermediates.

In the case of octafluoronaphthalene, further interaction of type **11** trapping products with the starting salt leads to the $[2\text{-Np}_F\text{NSN}]^-$ anion (Scheme 4), which, in contrast to **7**, is known to undergo highly regioselective intramolecular cyclization resulting in **9** as the major product.[5]

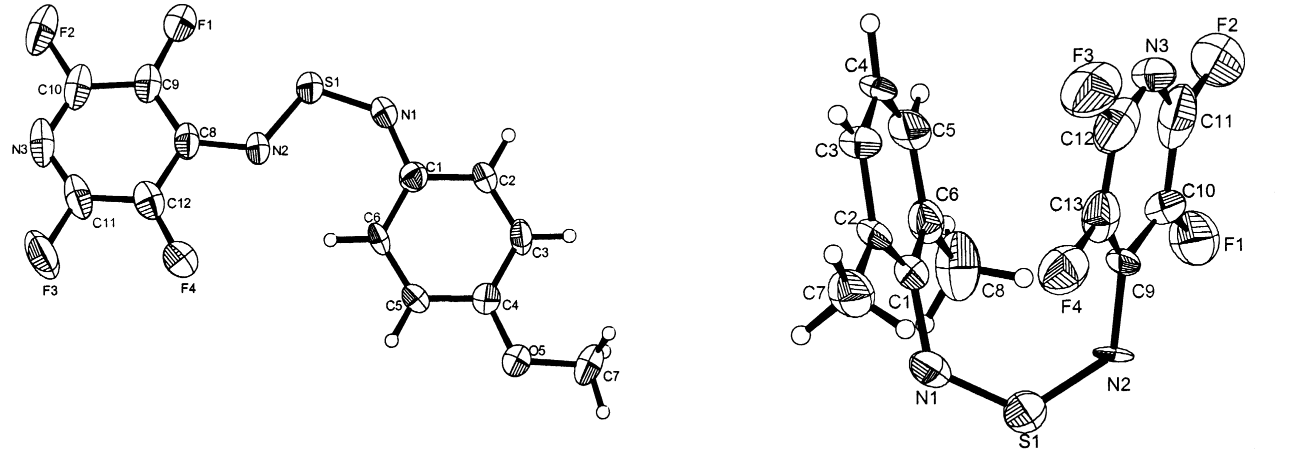
To the best of our knowledge, transfer of the NSN^- moiety from aromatics to polyfluoroaromatics, as depicted in Scheme 4, has not previously been observed. The driving force behind this substituent exchange is probably the well-known high electron affinity of polyfluoroaromatics.

The structures of the expected **4i,j** and **8·C₁₀F₈** and the unexpected **5f** and **5e·9** trapping products were confirmed by X-ray crystallographic analysis (see below). The structure of **5b**[15] had been determined previously.

Some of the synthesized compounds were also characterized by $^{14/15}N$ NMR spectroscopy. Three signals in the ^{15}N NMR spectrum of **4i** ($\delta^{15}N$ = 292.5, 278.7, and 217.8) could be assigned to Ar−N=, 4-Py_F−N=, and 4-Py_F, respectively, by comparison with the spectra of **5e** ($\delta^{14}N$ = 294),[16] **5b** (see below), other $(Ar{-}N{=})_2S$ compounds,[17] and **6** [$\delta^{15}N$ = 212.1 (t, J = 50.0 Hz), 50.2 (t, J = 91.3 Hz)]. This assignment is also consistent with the known tendency[10] for enhanced shielding of those nitrogens that are *ortho* to F in fluorinated functional aromatics [*cf.* also **5e**[16] and **5b** ($\delta^{15}N$ = 272.1)]. The ^{15}N NMR spectrum of **8**·$C_{10}F_8$ features two resonances ($\delta^{15}N$ = 312.8, 266.4), which could be assigned on the basis of similar arguments as above to 2,6-Xy−N= and 2-Np_F−N=, respectively. The ^{14}N NMR spectrum of **5e·9** shows a broad resonance ($\Delta\nu_{1/2} \approx$ 2000 Hz) with two well-defined maxima [$\delta^{14}N$ = 332 (**9**) and 301 (**5e**)], which are in very good

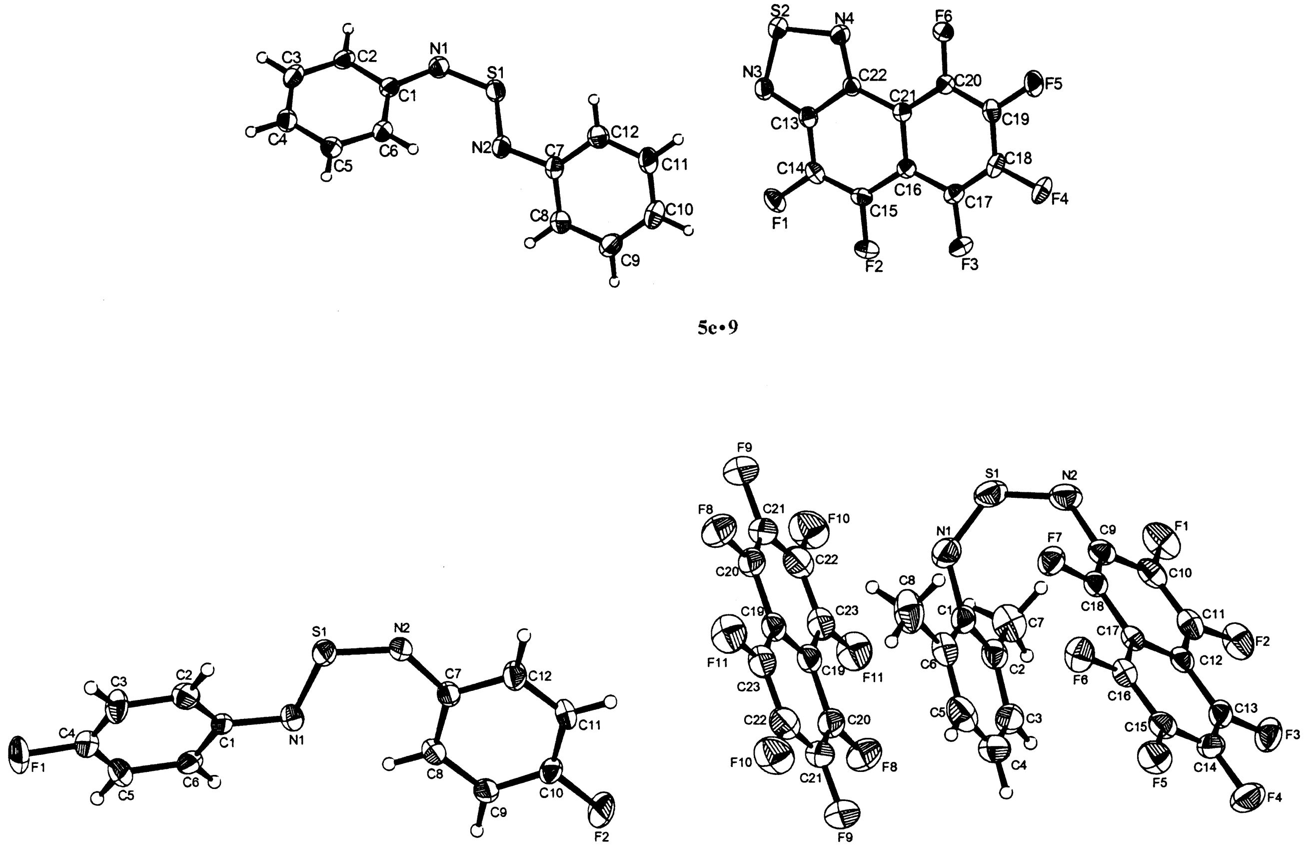


Scheme 4



4i **4j**

Figure 1. X-ray structures of the sulfurdiimides (Z,E)-4-$CH_3O-C_6H_4-NSN-C_5F_4N$-4 (**4i**) and (Z,Z)-2,6-$(CH_3)_2C_6H_3-NSN-C_5F_4N$-4 (**4j**), selected bond lengths (pm) and angles (°): **4i:** C1−N1 138.7(6), N1−S1 153.2(4), S1−N2 156.9(4), N2−C8 138.9(6); C1−N1−S1 132.7(3), N1−S1−N2 112.3(2), S1−N2−C8 124.2(4); τ RC_6H_4/NSN 2.8(3), NSN/C_5F_4N 6.8(2); **4j:** (two independent molecules) C1−N1 142.9(5), 143.2(5); N1−S1 152.7(3), 152.9(3); S1−N2 154.3(3), 154.4(3); N2−C9 140.2(4), 139.9(5); C1−N1−S1 125.6(2), 127.0(3); N1−S1−N2 122.96(17), 123.05(17); S1−N2−C9 127.9(3), 126.5(3); τC_8H_9/NSN 68.62, 65.60; τNSN/C_5F_4N 63.46, 61.83



5e•9

5f **8 • $C_{10}F_8$**

Figure 2. X-ray structures of $(C_6H_5N)_2S$ (**5e**)·$C_{10}F_6N_2S$ (**9**), $(4-FC_6H_4N)_2S$ (**5f**), and 2,6-$(CH_3)_2C_6H_3NSNC_{10}F_7$ (**8**)·1/2$C_{10}F_8$, selected bond lengths (pm) and angles(°): **5e·9:** C1−N1 140.5(3), N1−S1 153.5(2), S1−N2 155.3(2), N2−C7 142.5(2); C1−N1−S1 131.4(1), N1−S1−N2 116.7(1), S1−N2−C7 115.8(1), τ_1 13.1(1), τ_2 41.9(2); C13−N3 133.4(3), N3−S2 162.3(2), S2−N4 163.1(2), N4−C22 133.4(2), C22−C13 142.5(3); C13−N3−S2 105.5(1), N3−S2−N4 100.8(1), S2−N4−C22 105.9(1), N4−C22−C13 113.4(2), C22−C13−N3 114.5(2); **5f:** C1−N1 142.5(7), N1−S1 155.5(5), S1−N2 153.9(6), N2−C7 140.3(8); C1−N1−S1 116.7(4); N1−S1−N2 116.3(3), S1−N2−C7 131.8(4); τ_1 31.4(3); τ_2 7.6(4); **8**·1/2$C_{10}F_8$: C1−N1 142.5(3), N1−S1 152.2(2), S1−N2 154.4(2), N2−C9 140.4(3); C1−N1−S1 128.7(1), N1−S1−N2 123.7(1), S1−N2−C9 126.0(1); τ_1 68.2(1), τ_2 60.9(1)

agreement with the data for free **9** [$\delta^{15}N = 338.3$ (d, $J = 15.0$ Hz)[5] and 325.0 (d, $J = 7.0$ Hz; this work)] and **5e** (see above).[16]

Structures of the Synthesized Sulfurdiimides RNSNR′

The trapping products of types **4** and **8** might be particularly interesting as ligands for coordination compounds as they possess two very different electron lone-pairs on the NSN fragments, along with a lone-pair from the tetrafluoropyridyl moiety in the case of **4**. According to X-ray crystallographic data (Figures 1 and 2, Tables 1 and 2), they adopt *Z*,*E* and *Z*,*Z* configurations in the solid state, typical of bis(aryl)sulfurdiimides.[3,15,18−23] Thus, in the crystal, compound **4i** exists as the perfectly planar *Z*,*E* isomer, whereas **4j** and **8** (in the complex with $C_{10}F_8$) exist as *Z*,*Z* isomers with the rings being essentially parallel to one another and perpendicular to the NSN plane. The bis(aryl)sulfurdiimide parent compound **5e** (liquid in the pure state)[24] adopts the nonplanar *Z*,*E* configuration in the complex with **9**, whereas compound **5f** has an almost planar *Z*,*E* configuration. Compound **5b** (*Z*,*Z* isomer in the crystal)[15] has been structurally characterized previously.

Table 3 lists the data obtained in this work along with selected representative conformational data for previously reported bis(aryl)sulfurdiimides.[3,15,18−23] Sterically unhindered bis(aryl)sulfurdiimides adopt the *Z*,*E* configuration with the less electron-withdrawing substituent in the *Z*-position. Steric strain in this position is released by adopting a wide CNS angle (≈130°), which is 10−15° wider than that for the *E*-substituents. A further reason for the small angle in the *E*-position is the rotation of the aryl ring out of the NSN plane by 30−40°. For strongly electron-withdrawing groups (C_6F_5, C_5F_4N), this torsion angle is very small (7°), leading to an appreciable opening of the CNS angle (124−125°).

In *Z*,*E*-($2,4,6\text{-}Br_3C_6H_2N{=})_2S$, steric strain is released through the adoption of an almost perpendicular orientation of the aryl groups relative to the NSN plane. As pointed out previously, substitution of H by F, Br, or Me in the *o*,*o*-positions, although sterically less favoured, leads to the *Z*,*Z*-configuration.[21,22] Steric strain in these cases is released by a parallel rotation of both groups out of the NSN plane by 55−70°. In spite of this, the NSN angle in the *Z*,*Z*-configuration is 10° larger than that in the *Z*,*E* derivatives.

Notably, with planar molecular geometry in the *Z*,*E* configuration (*cf.* **4i**), the synthesized compounds satisfy the primary requirements for materials with nonlinear optical properties in that they contain donor (Ar) and acceptor (4-Py_F) fragments connected by an −N=S=N− bridge capable of π-conjugation.[25]

Table 1. Crystal and refinement data of **4i**,**j**

	4i	**4j**[a]
Empirical formula	$C_{12}H_7F_4N_3OS$	$C_{13}H_9F_4N_3S$
Molecular weight	317.27	315.29
Temperature	173(2) K	173(2) K
Wavelength	71.073 pm	71.073 pm
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/a$
Unit cell dimensions	$a = 1777.1(6)$ pm $b = 837.2(2)$ pm $c = 1710.5(4)$ pm $\beta = 94.53(3)°$	$a = 1447.0(4)$ pm $b = 2675.6(6)$ pm $c = 1390.8(4)$ pm $\beta = 90.0°$
Volume	2.537(1) nm^3	5.39(1) nm^3
Z	8	16
Density (calculated)	1.661 Mg/m^3	1.556 Mg/m^3
Absorption coefficient	0.306 mm^{-1}	0.283 mm^{-1}
$F(000)$	1280	2560
Crystal size/mm^3	0.6 × 0.4 × 0.2 mm^3	0.70 × 0.50 × 0.20 mm^3
θ range for data collection	2.69 to 22.50°	2.68 to 27.51°
Index ranges	$-1 \le h \le 19$ $-1 \le k \le 9$ $-18 \le l \le 18$	$-16 \le h \le 16$ $-34 \le k \le 34$ $-15 \le l \le 17$
Reflections collected	2080	11990
Independent reflections	1568 ($R_{int} = 0.0537$)	5859 ($R_{int} = 0.0401$)
Max. and min. transmission		0.9456 and 0.8266
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	1568/0/194	5859/0/387
Goodness of fit on F^2	1.002	1.014
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0520$, $wR2 = 0.1294$	$R1 = 0.0527$, $wR2 = 0.1152$
R indices (all data)	$R1 = 0.0904$, $wR2 = 0.1522$	$R1 = 0.0900$, $wR2 = 0.1329$
Absolute structure parameter	−	−
Extinction coefficient	0.0003(2)	0.00011(6)
Largest diff. peak and hole	377 and −307 e·nm^{-3}	234 and −407 e·nm^{-3}

[a] Due to the twinning by reticular merohedry, an orthorhombic intensity-weighted reciprocal lattice was chosen (with doubled cell volume) to describe the monoclinic structure.

Table 2. Crystal and refinement data for **5e·9**, **5f**, and **8**·$1/2C_{10}F_8$

	5e·9	**5f**	**8**·$1/2C_{10}F_8$
Empirical formula	$C_{12}H_{10}N_2SC_{10}F_6N_2S$	$C_{12}H_8F_2N_2S$	$C_{18}H_9F_8N_2S1/2C_{10}F_8$
Molecular weight	508.46	250.26	554.38
Temperature	173(2) K	173(2) K	173(2) K
Wavelength	71.073 pm	71.073 pm	71.073 pm
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1$	$Pca2/_1$	$P\bar{1}$
Unit cell dimensions	a = 612.4(1) pm b = 750.5(1) pm c = 2174.2(2) pm β = 90.83(1)°	a = 1200.8(3) pm b = 1287.8(4) pm c = 706.1(5) pm	a = 766.7(1) pm b = 1087.0(1) pm c = 1298.3(1) pm α = 83.15(1)° β = 87.35(1)° γ = 78.12(1)°
Volume	0.9992(2) nm^3	1.0919(9) nm^3	1.0510(2) nm^3
Z	2	4	2
Density (calculated)	1.690 Mg/m^3	1.522 Mg/m^3	1.752 Mg/m^3
Absorption coefficient	0.342 mm^{-1}	0.299 mm^{-1}	0.268 mm^{-1}
F(000)	512	512	552
Crystal size/mm^3	0.80 × 0.60 × 0.30 mm^3	1.2 × 0.2 × 0.1 m^3	0.80 × 0.50 × 0.50 mm^3
θ range for data collection	2.81 to 27.50°	3.16 to 27.48°	2.63 to 27.50°
Index ranges	$-7 \leq h \leq 7$ $-9 \leq k \leq 9$ $-28 \leq l \leq 28$	$-1 \leq h \leq 15$ $-1 \leq k \leq 16$ $-1 \leq l \leq 9$	$-9 \leq h \leq 1$ $-10 \leq k \leq 14$ $-16 \leq l \leq 16$
Reflections collected	8750	1546	5406
Independent reflections	4581 (R_{int} = 0.0392)	1299 (R_{int} = 0.0363)	4433 (R_{int} = 0.0277)
Max. and min. transmission	0.9042 and 0.7713		0.8777 and 0.8142
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	4581/1/309	1299/1/156	4433/0/339
Goodness of fit on F^2	1.066	1.006	1.018
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0326, $wR2$ = 0.0843	$R1$ = 0.0557, $wR2$ = 0.1269	$R1$ = 0.0418, $wR2$ = 0.1098
R indices (all data)	$R1$ = 0.0353, $wR2$ = 0.0858	$R1$ = 0.1024, $wR2$ = 0.1497	$R1$ = 0.0528, $wR2$ = 0.1176
Absolute structure parameter	−0.07(6)	0.2(3)	
Extinction coefficient	0.0052(12)	0.008(3)	0.007(14)
Largest diff. peak and hole	255 and 384 $e \cdot nm^{-3}$	385 and −314 $e \cdot nm^{-3}$	224 and 323 $e \cdot nm^{-3}$

Table 3. Bis(aryl)sulfurdiimides $Ar-N=S=N-Ar^1$

Ar	Ar^1		Conf. exp. Ar Ar^1	Conf. calcd.[a] Ar Ar^1	$C_{Ar}NS$	$\tau_{Ar/NSN}$	$C_{Ar1}NS$	$\tau_{Ar^1/NSN}$	NSN	ref.
C_6H_5	C_6H_5	**5e**	*Z,E*	*Z,E*[18]	131.4	13.1	115.8	41.9	116.7	
p-C_6H_4F	p-C_6H_4F	**5f**	*Z,E*		131.8	8.7	116.7	31.4	116.3	
C_6H_5	C_6F_5		*Z,E*	*Z,E*	133.2	1.9	124.6	1.8	113.6	[22]
2,4,6-$Br_3C_6H_2$	2,4,6-Br_3CH_2		*Z,E*	*Z,E*	125.3	83.0	116.0	82.3	115.8	[21]
p-$MeOC_6H_4$	4-NC_5F_4	**4i**	*Z,E*		132.7	2.8	124.2	7.2	112.3	
2,6-$Me_2C_6H_3$	2,6-$Me_2C_6H_3$		*Z,Z*	*Z,Z*	127.2	32.0	131.8	37.5	127.2	[21]
2,6-$Me_2C_6H_3$	2,4,6-$Br_3C_6H_3$		*Z,Z*	*Z,Z*	132.5	64.2	130.1	67.0	126.1	[21]
					133.7	65.5	131.4	69.7	126.5	
2,6-$Me_2C_6H_3$	2-$C_{10}F_7$	**9**	*Z,Z*		128.7	68.2	126.0	60.9	123.7	
2,6-$Me_2C_6H_3$	4-NC_5F_4	**4j**	*Z,Z*		125.6	68.6	127.9	63.5	123.0	
					127.0	65.6	126.5	61.8	123.1	
2,6-$Me_2C_6H_3$	C_6F_5		*Z,Z*	*Z,Z*	129.5	63.0	128.0	67.1	123.8	[22]
C_6F_5	C_6F_5		*Z,Z*	*Z,E*	126.7	59.5	128.4	60.9	123.9	[22]
					127.7	59.2	127.4	59.7	123.2	
2,6-$F_2C_6H_3$	2,6-$F_2C_6H_3$	**5b**	*Z,Z*		128.5	56.5	128.5	56.4	125.2	[15]

[a] At the PM3 level of theory.[21,22]

Even more interesting than the stereochemistry of the bis(aryl)sulfurdiimides is the interaction of one of the phenyl rings of $(C_6H_5N=)_2S$ (**5e**) with the heteropolyfluoroaromatic system **9** in the solid state, as well as the interaction of 2,6-$Me_2C_6H_3N=S=NC_{10}F_7$ (**8**) with $1/2C_{10}F_8$ (Figures 3 and 4).

It should be noted that noncovalent interactions between aromatic and polyfluoroaromatic groups[26−28] (a special

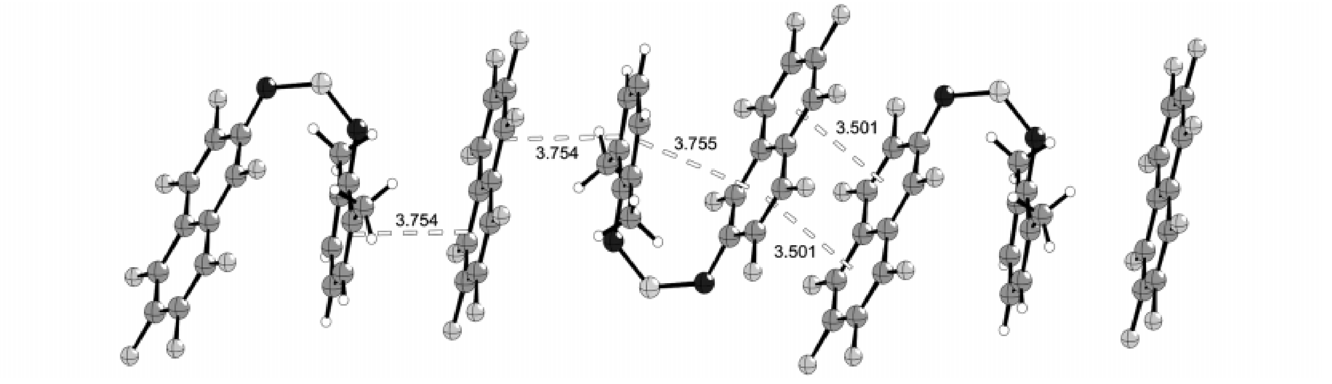


Figure 3. π-Stacking of the arene−polyfluoroarene and polyfluoroaryl−polyfluoroaryl types in the crystal of **8**·$C_{10}F_8$

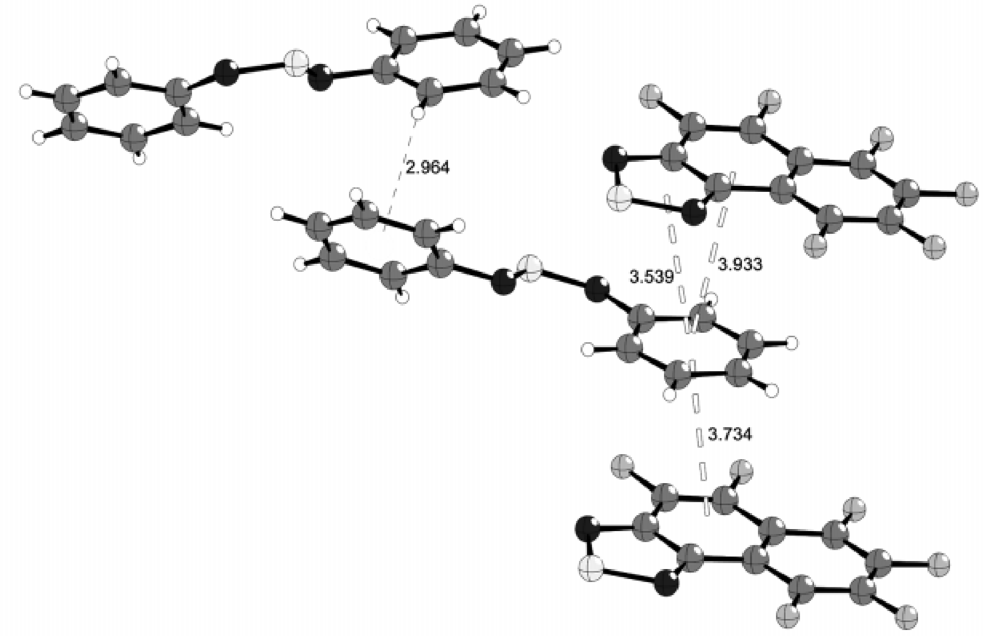


Figure 4. π-Stacking of the arene−polyfluoroarene type in the crystal of **5e·9**

case of noncovalent interactions between aromatic units that is known to play a significant role in determining the structures and properties of molecular assemblies in biology, supramolecular chemistry, and materials science)[29,30] have been extensively studied in recent years, leading to important new possibilities in crystal engineering for the design of advanced functional materials.[31−36] Co-crystals of benzene/hexafluorobenzene,[37,38] their (poly)substituted derivatives,[31,32,34,37,39] biphenyl/decafluorobiphenyl,[40] naphthalene/octafluoronaphthalene[41] and larger aromatic hydrocarbon/fluorocarbon,[42,43] and of decamethylferrocene/perfluorophenanthrene[44] have been produced and have been found to involve alternating 1:1 π-stacking. This face-to-face stacking arrangement is thought to be dominated by electrostatic forces,[45] in particular by large but opposite-in-sign quadrupole moments of the C_6H_6 and C_6F_6 components.[27] The electrostatic potential map of benzene reveals concentrations of negative potential above and below the molecular plane, and a ring of positive potential in the plane centred on the hydrogens; hexafluorobenzene possesses the opposite charge distribution[46] (see also ref.[31]).

Significantly, neither heterocycles (**5e·9**) nor markedly bent (tweezer-like) molecules (**8**·$C_{10}F_8$) have previously been found to be involved in noncovalent arene−polyfluoroarene interactions, with one probable exception in the latter case being a complex of 1,4-diiodotetrafluorobenzene with a cone-shaped 1,3-bis(pyridylmethyl)calix[4]arene.[47]

Both complexes **5e·9** and **8**·$C_{10}F_8$ feature face-to-face π-stacking of the arene−polyfluorene type.[26−28] Additionally, **8**·$C_{10}F_8$ shows another structural motif, namely an unprecedented π-stacking of the heptafluoronaphth-2-yl moieties with an interplanar separation of 350.1 pm (Figure 3), thus representing a new type of arene−polyfluoroarene complex. (It is noteworthy that the crystal packing of octafluoronaphthalene does not, of course, reveal any π-stacking interactions, but rather a face-to-edge orientation of neighbouring molecules[48]). The peculiarity mentioned above is in sharp contrast to the purely electrostatic interpretation of the interactions under consideration and clearly requires further investigation, both experimentally and especially theoretically. It seems that the dispersion forces[27] (responsible, for example, for the solid-state structure of octafluoronaphthalene[48]) should also be taken into account.

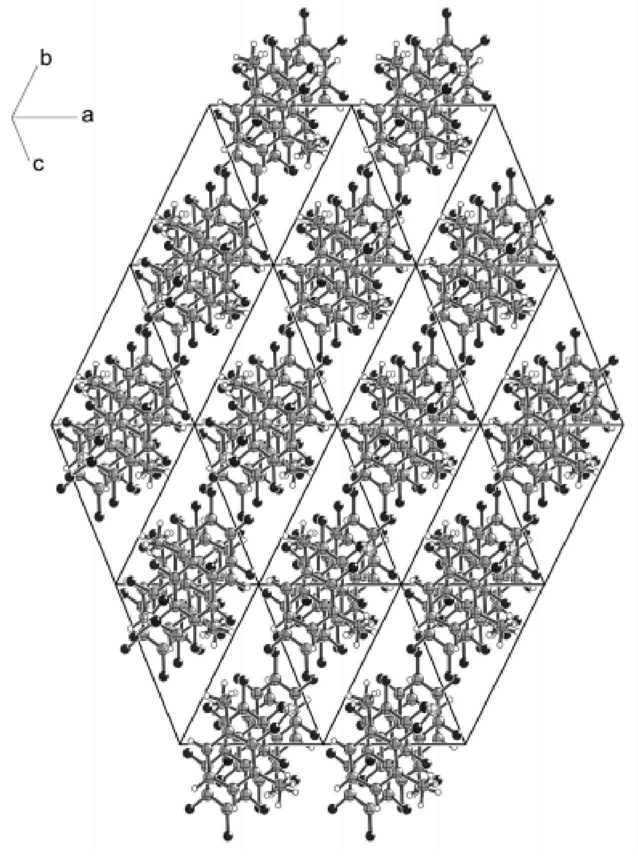


Figure 5. Crystal packing of **8**·$C_{10}F_8$

On the other hand, a 2,6-dimethylphenyl−2,6-dimethylphenyl interaction is not seen.

Within the stacks, the arene−polyfluoroarene separation is 353.9−393.3 pm for **5e·9** and 350.1−375.5 pm for **8**·$C_{10}F_8$, as compared to 377 pm for the lowest-temperature phase of the benzene/hexafluorobenzene co-crystals[38] and 368.6−377.1 pm for the naphthalene/octafluoronaphthalene co-crystals.[41]

The crystal packing of **8**·$C_{10}F_8$ and **5e·9** is depicted in Figures 5 and 6.

The alternating stacked aryl−polyfluoroaryl arrangement is concluded to be a general supramolecular motif of significant importance with regard to new developments in crystal engineering.[32] In view of the fact that **5e·9** and **8**·$C_{10}F_8$ combine π-stacked structures with the potential ability to coordinate transition metals through NSN bridges, the findings of this work can be envisaged as offering new prospects in this field.

Conclusions

The intramolecular nucleophilic cyclization of arylthiazylamides bearing at least one *ortho* fluorine offers a novel synthetic approach to 2,1,3-benzothiadiazoles. Despite some complications, the interaction of arylthiazylamides with fluoro electrophiles such as pentafluoropyridine and octafluoronaphthalene makes it possible to synthesize *N*-aryl-*N'*-(tetrafluoro-4-pyridinyl)sulfurdiimides (**4**) and *N*-aryl-*N'*-(heptafluoronaphth-2-yl)sulfurdiimides (**8**), which are not readily accessible by other means. Thus, the intramolecular nucleophilic cyclization of arylthiazylamide anions has now been expanded to intermolecular condensation. Compounds **4** and **8** represent promising ligands for coordination chemistry. With planar molecular geometries in the *Z,E* configuration (*cf.* **4i**), these compounds also satisfy

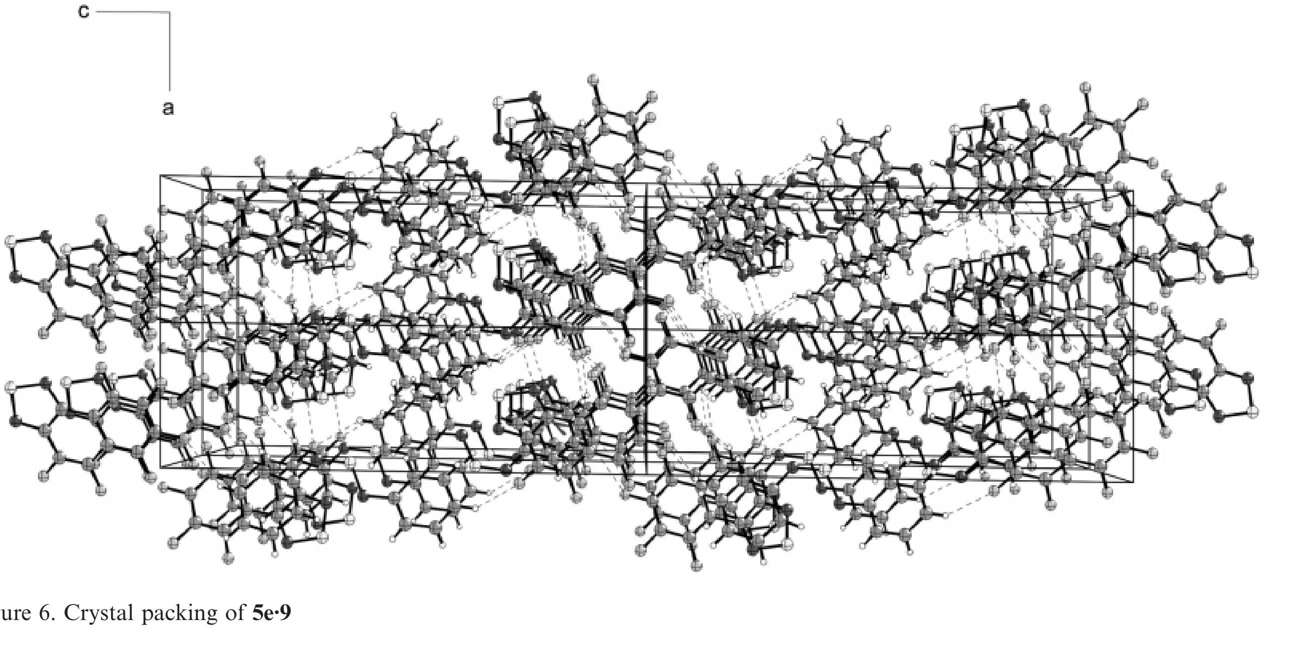


Figure 6. Crystal packing of **5e·9**

the primary requirements for materials with nonlinear optical properties as they contain donor (Ar) and acceptor (4-Py_F) fragments connected by an −N=S=N− bridge capable of π-conjugation. Complexes **5e·9** and **8**·$C_{10}F_8$ are the first examples of a heterocycle (**9**) and an essentially nonplanar tweezer-like molecule (*Z,Z*-**8**) to feature arene−polyfluoroarene π-stacking interactions. Besides typical aryl−polyfluoroaryl stacking, the crystal packing of **8**·$C_{10}F_8$ also reveals an unprecedented supramolecular motif, namely polyfluoroaryl−polyfluoroaryl π-stacking, thus making this a new type of arene−polyfluoroarene complex.

Experimental Section

General Remarks: ^1H and ^{19}F NMR spectra were recorded on a Bruker DPX-200 spectrometer, and ^{13}C NMR spectra on a Bruker DRX-500 spectrometer, at frequencies of 200.13, 188.28, and 125.76 MHz, respectively, with samples in $CDCl_3$ solution; chemical shifts are given with respect to TMS (^1H, ^{13}C) or $CFCl_3$ (^{19}F) Nitrogen NMR spectra were measured on a Bruker DRX-500 spectrometer at frequencies of 67.80 MHz (^{15}N) and 36.14 MHz (^{14}N) with samples in $CDCl_3$ solution; chemical shifts are given relative to NH_3 (liq.). − High-resolution mass spectra (EI, 70 eV) were measured with a Finnigan MAT MS 8200 mass spectrometer. − UV/Vis spectra were recorded on a Specord UV/Vis instrument with samples in heptane solution.

Crystallographic Analysis: The single-crystal X-ray structure determinations (Tables 1 and 2) were carried out on a Siemens P4 diffractometer using graphite-monochromated Mo-K_α (0.71073 Å) radiation. Refinement based on F^2; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. Programs used: SHELX-97[49] and DIAMOND.[50]

The transparent crystals were mounted on a thin glass fibre using KEL-F oil. The structures were solved by direct methods (SHELXS[49]). Subsequent least-squares refinements (SHELXL-97−2[49]) located the positions of the remaining atoms in the electron density maps. All non H-atoms were refined anisotropically.[51]

Syntheses: TASF was prepared by established methods;[52] 1-aryl-3-(trimethylsilyl)sulfurdiimides Ar−N=S=N−$SiMe_3$ (**1a**,**b**,**e**−**j**) were obtained by known procedures.[3] Tris(dimethylamino)sulfonium arylthiazylamides TAS^+ $[ArNSN]^-$ were synthesized as described previously.[2,3] Cesium fluoride was calcinated immediately prior to use. The syntheses described below were performed in dry solvents with stirring under an argon atmosphere. The reagents were added dropwise and the solvents were distilled off under reduced pressure. The compounds **2a**,[8] **6**,[53] and **5b**,**f**[54] have been reported previously. Table 4 lists the physical and analytical data for the synthesized compounds.

1-Aryl-3-(trimethylsilyl)sulfurdiimides (1c,d): A solution of the appropriate ArNSO[55] (60 mmol) in hexane (25 mL) was added to a suspension of $LiN(SiMe_3)_2$ (10.0 g, 60 mmol) in hexane (50 mL) at −30 °C. The temperature was raised to 20 °C over a period of 2 h, and then a solution of Me_3SiCl (6.6 g, 60 mmol) in hexane (10 mL) was added. The precipitate formed was filtered off, the solvent was distilled, and the residue was distilled in vacuo. Compounds **1c**,**d** were obtained as orange oils.

2,1,3-Benzothiadiazole (2a) and 4-Fluoro-2,1,3-benzothiadiazole (2b): A solution of the appropriate Ar−N=S=N−$SiMe_3$ (**1a**,**b**) (20 mmol) in CH_3CN (25 mL) was added to a boiling suspension of CsF (3.04 g, 20 mmol) in CH_3CN (75 mL) over a period of 30 min. After a further 30 min, the reaction mixture was allowed

Table 4. Characterization of the synthesized compounds

Compound	Yield [%]	m.p. [°C]	b.p. [°C/mm]	^1H NMR, δ [ppm]	^{19}F NMR, δ [ppm]	Molecular formula [MS: M^+ [*m*/*z*], measured (calculated)]
1c	50	–	80−81/0.01	7.29 (2 H), 6.94 (1 H), 0.02 (9 H)	–	$C_9H_{12}Cl_2N_2SSi$: 277.9864 (277.9868, ^{35}Cl)
1d	60	–	88−90/0.01	7.91 (1 H), 7.55 (1 H), 7.36 (1 H), 7.23 (1 H), 0.16 (9 H)	–	$C_9H_{13}N_3O_2SSi$: 255.0494 (255.0498)
2a	23	45−46	–	7.99 (2 H), 7.55 (2 H)	–	$C_6H_4N_2S$ 136.0097 (136.0095)
2b	55	29−30	–	7.51 (d, 1 H), 7.28 (ddd, 1 H), 6.97 (dd, 1 H)	−121.1 (dd)	$C_6H_3FN_2S$: 54.0006 (154.0001)
4a	48	85−86	–	7.48 (1 H), 7.17−7.12 (2 H), 6.95 (1 H)	−92.2 (2 F), −118.0 (1 F), −148.5 (2 F)	$C_{11}H_4F_5N_3S$: 305.0073 (305.0046)
4e	55	102−103	–	7.62 (2 H), 7.34 (3 H)	−92.1 (2 F), −149.6 (2 F)	$C_{11}H_5F_4N_3S$: 287.0140 (287.0140)
4i	60[a][b]	122−123	–	8.06 (2 H), 6.88 (2 H), 3.82 (3 H)	−92.1 (2 F), −150.4 (2 F)	$C_{12}H_7F_4N_3OS$: 317.0243 (317.0246)
4j	73	74−75	–	6.86 (3 H), 2.16 (6 H)	−92.8 (2 F), −149.3 (2 F)	$C_{13}H_9F_4N_3S$: 315.0450 (315.0453)
5b	40	108−109	–	6.89 (1 H), 6.62 (2 H)	−118.0	$C_{12}H_6F_4N_2S$: 286 (286)
5f	44[a] 37[b]	94−95	–	7.43 (2 H), 7.07 (2 H)	−114.9	$C_{12}H_8F_2N_2S$: 250.0371 (250.0376)
6	40−45[a] 23−25[b]	87−88	–	4.66	−94.6 (2 F), −165.5 (2 F)	$C_5H_2F_4N_2$: 166 (166)
8·$C_{10}F_8$	48	109−110	–	7.16 (2 H), 6.97 (1 H), 2.14 (6 H)	−126.3 (1 F), −142.5 (1 F), −146.8 (1 F), −147.5 (1 F), −150.3 (1 F), −155.9 (1 F), −156.6 (1 F), −146.3 (2 F), −154.8 (2 F)	$C_{18}H_9F_7N_2S$ (**8**): 418.0369 (418.0375)
5e·9	25	83−84	–	7.35−7.17	−138.1 (1 F), −143.4 (1 F), −143.9 (1 F), −147.9 (1 F), −151.5 (1 F), −153.0 (1 F)	$C_{10}F_6N_2S$ (**9**): 293.9678 (293.9686)

[a] From the Cs^+ salt. − [b] From the TAS^+ salt.

to cool to 20 °C, filtered, and the solvent was distilled off. The residue (a mixture of the target heterocycle and the corresponding $ArNH_2$, according to ^1H NMR and MS data) was redissolved in Et_2O (50 mL) and treated with 6 N hydrochloric acid (20 mL). The organic layer was separated, dried with $CaCl_2$, and the solvent was distilled off. The residue was sublimed in vacuo and then recrystallized from hexane. Compounds **2a** and **2b** were obtained as long colorless needles.

2b: ^{13}C NMR: δ = 156.0 (C^{7a}), 152.4 (C^4), 145.2 (C^{3a}), 128.7 (C^6), 116.8 (C^7), 112.0 (C^5). − UV/Vis: λ_{max} (log ε) = 307 nm (3.83) [*cf.* **2a:** 311 nm (4.15)].[56]

Under the same conditions, only the parent $ArNH_2$ compounds were obtained from **1c**,**d** (yields 50% and 65%, respectively).

Interaction of $[TAS]^+$ $[ArNSN]^-$ Salts (3e−i) with Pentafluoropyridine: *N*-(4-Methoxyphenyl)-*N′*-(2,3,5,6-tetrafluoro-4-pyridinyl)sulfurdiimide (4i), *N,N′*-Bis(aryl)sulfurdiimides (5e−f), and 4-Amino-2,3,5,6-tetrafluoropyridine (6): C_5F_5N (0.85 g, 5 mmol) was condensed onto a solution of $[TAS]^+$ $[ArNSN]^-$ (**3e**−**i**; 5 mmol) in CH_3CN (20 mL) at −196 °C by means of a vacuum line. After 16 h at −40 °C, the solvent was distilled off at the same temperature, and the residue was sublimed in vacuo and recrystallized from hexane. Compound **4i** was obtained as ruby-red crystals (single crystals suitable for X-ray structure analysis were obtained by a further recrystallization from $CHCl_3$). Compounds **5** and **6** were separated by fractional sublimation in vacuo followed by recrystallization from hexane. In the case of **3e**, compound **5e** was identified in the reaction mixture spectroscopically (^1H NMR and MS). In the case of **3g**,**h**, no products were identified.

CsF-Induced Interaction of Ar−N=S=N−SiMe$_3$ (1a,b,e,f,h−j) with Pentafluoropyridine: *N*-Aryl-*N′*-(2,3,5,6-tetrafluoro-4-pyridinyl)sulfurdiimides (4a,e,i,j), *N,N′*-Bis(aryl)sulfurdiimides (5b,f,h), 4-Amino-2,3,5,6-tetrafluoropyridine (6), and Bis(2,3,5,6-tetrafluoro-4-pyridinyl)amine (10): Solutions of the appropriate Ar−N=S=N−SiMe$_3$ (**1a**,**b**,**e**,**f**,**h**−**j**; 5 mmol) and C_5F_5N (0.85 g, 5 mmol) in CH_3CN (5 mL aliquots) were added to a suspension of CsF in CH_3CN (25 mL) at 20 °C. After 1 h, the reaction mixture was filtered, the solvent was distilled off, and the residue was sublimed in vacuo and then recrystallized from hexane. Compounds **4a**,**e**,**i**,**j** were obtained as orange-red crystalline solids. Compounds **5b**,**f** and **6** were separated by fractional sublimation followed by recrystallization (**5b**,**f**: orange crystals; **6**: long colorless needles). In the case of **1h**, traces of **5h** and **6** were identified in the reaction residue by spectroscopic means (^1H and ^{19}F NMR, MS).

4e: UV/Vis: λ_{max} (log ε) = 412 nm (3.93) [*cf.* $(Ar-N=)_2S$].[54]

In some experiments, small amounts of compound **10** were identified alongside **6**; this could be isolated at a trace level by vacuum sublimation followed by recrystallization from hexane. **10**: Colorless crystals; m.p. 152−153 °C; ^1H NMR: δ = 8.30. − ^{19}F NMR: δ = −92.0, −153.6; these correspond to the published data.[57]

CsF-Induced Interaction of Ar−N=S=N−SiMe$_3$ (1e,j) with Octafluoronaphthalene: 4,5,6,7,8,9-Hexafluoronaphtho[1,2-*c*][1,2,5]thiadiazole (9; complex with 5e) and *N*-(2,6-Dimethylphenyl)-*N′*-(1,3,4,5,6,7,8-heptafluoronaphth-2-yl)sulfurdiimide (8; complex with $C_{10}F_8$): A solution of the appropriate Ar−N=S=N−SiMe$_3$ (**1e**,**j**) (5 mmol) and $C_{10}F_8$ (1.36 g, 5 mmol) in CH_3CN (25 mL) was added to a boiling suspension of CsF (0.76 g, 5 mmol) in MeCN (50 mL) over a period of 30 min. After a further 30 min, the reaction mixture was allowed to cool to 20 °C, the solvent was distilled off, and the residue was sublimed in vacuo and recrystallized from hexane. Compound **9** (as a complex with **5e**) was obtained as shiny orange crystals, while compound **8** (as a complex with $C_{10}F_8$) was obtained as transparent orange-red scales. Single crystals of **8**·$C_{10}F_8$ suitable for X-ray structure analysis (red prisms) were obtained by a further crystallization from $CHCl_3$.

8·$C_{10}F_8$: ^{13}C NMR: δ (2,6-Xy) = 144.2, 127.1, 125.4, 119.4, 18.2.

9·5e: ^{13}C NMR: δ (**5e**) = 145.3, 128.7, 126.7, 123.1.

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