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The first *N*-alkyl-*N'*-polyfluorohetaryl sulfur diimide

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Dedicated to Prof. em. Dr. mult Dr. h.c. Alois Haas on the occasion of his 70th birthday.

Abstract

The first Alk–N=S=N–Het_F sulfur diimide **6** (Alk = adamant-1-yl, Het_F = 2,3,5,6-tetrafluoropyrid-4-yl) was prepared by trapping of the corresponding alkylthiazylamide $[\text{AlkNSN}]^-$ **3** with pentafluoropyridine, followed by X-ray structural characterization. For **6**, the *Z,E* configuration was found. From the reaction of **3** with octafluoronaphthalene, hexafluorinated naphthothiadiazole **7** was isolated along with the parent AlkNH_2. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alkylthiazylamide; Fluoroelectrophiles; Sulfur diimides; Polyfluorinated; X-ray structure determination

1. Introduction

The chemistry of R–N=S=N–R sulfur diimides, the aza-analogs of sulfur dioxide, is an important part of contemporary main group chemistry [1–3]. Polyfluorinated ($\text{R}=\text{R}_\text{F}$) sulfur diimides, especially non-symmetric, belong however, to relatively little studied systems.

Recently, we described the first preparation and X-ray structural characterization of arylthiazylamides $[\text{ArNSN}]^-$ (as salts of the tris(dimethylamino)sulfonium, TAS^+, cation) [4]. Their reactions (as both TAS^+ and Cs^+ salts) with external fluoro electrophiles afforded, in particular, the previously unknown Ar–N=S=N–R_F sulfur diimides (R_F = 2,3,5,6-tetrafluoropyrid-4-yl, 1,3,4,5,6,7,8-heptafluoronaphth-2-yl) [5]. The latter possess two very different electron lone-pairs on the nitrogens of the NSN fragment, along with the lone pair at the sulfur and a lone-pair from the tetrafluoropyridyl moiety. Thus, they are promising ligands for coordination chemistry [2] with possible applications in the field of molecular electronics [6]. Donor abilities of the tetrafluoropyridyl fragment are obviously weak, nevertheless coordination compounds of pentafluoropyridine have been reported [7,8].

The present article deals with an expansion of the approach presented above for alkylthiazylamides [9] as a method for the preparation of previously undescribed Alk–N=S=N–R_F sulfur diimides. For the sake of obtaining solid derivatives suitable for X-ray crystallography Alk = adamant-1-yl (1-Ad) was chosen. The special stereoelectronic demand of this bridgehead substituent [10] was also taken into account.

2. Results and discussion

The $[\text{1-AdNSN}]^-$ anion **3** was prepared in three steps from 1-AdNH_2 (Scheme 1) and unambiguously characterized in solution as the TAS^+ salt **4** by multinuclear (^{1}H, ^{13}C and ^{14}N) NMR spectroscopy. Because of microtwinning, the X-ray crystal structure of **4** was not solved. However, on the basis of ^{14}N NMR data the 1-Ad group of **3** is in the stereoelectronically favoured *Z*-position, i.e. the same as for the *t*-Bu group in the related $[t\text{-BuNSN}]^-$ anion (cf. δ ^{14}N of **3** with those of structurally defined $[t\text{-BuNSN}]^-$) [9].

It was found that **3** readily reacts in the form of the in situ generated Cs^+ salt **5** with pentafluoropyridine under mild conditions to give the target compound **6** in high yield (Scheme 2).

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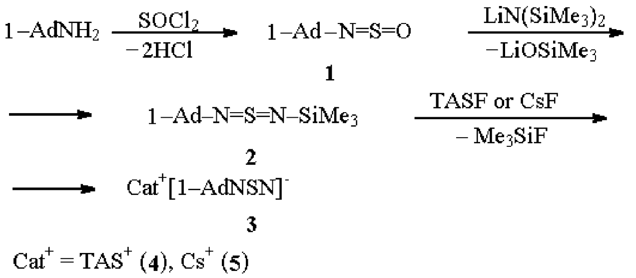
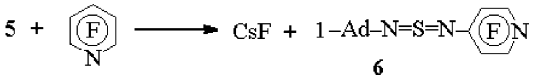


Scheme 1.



Scheme 2.

Table 1
Crystal data and structure refinement for **6**

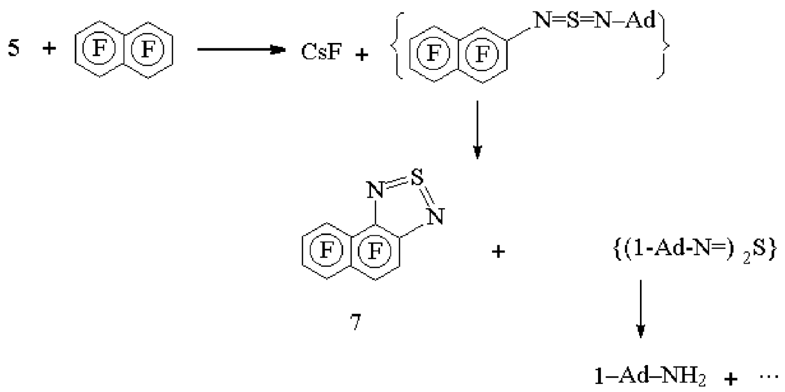
Empirical formula	$C_{15}H_{15}F_4N_3S$
Formula weight	345.36
Temperature	173(2)
Wavelength	71.073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (pm)	946.0(3)
b (pm)	1836.6(5)
c (pm)	905.8(2)
β (°)	112.59(2)
Volume (nm^3)	1.4530(7)
Z	4
Density[a] (Mg/m^3)	1.579
Absorption coefficient (mm^{-1})	0.269
F(0 0 0)	712
Crystal size (mm^3)	$0.60 \times 0.50 \times 0.25$
θ range for data	2.22–27.48°
Index ranges	$-11 \le h \le 12$, $-23 \le k \le 1$, $-11 \le l \le 1$
Reflections collected	4209
Independent reflections	3303 [R(int) = 0.0515]
Completeness to $\theta = 27.48°$	99.2%
Maximum and minimum transmission	0.9357 and 0.8551
Data/restraints/parameters	3303/0/210
Goodness-of-fit on F^2	1.020
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0568$, $wR_2 = 0.1381$
R indices (all data)	$R_1 = 0.0908$, $wR_2 = 0.1587$
Largest diffraction peak and hole (e Å^{-3})	0.386 and −0.631

[a] Calculated.

From the reaction of salt **5** with octafluoronaphthalene however, the hexafluorinated naphthothiadiazole **7** (Scheme 3) was isolated along with 1-$AdNH_2$. This type of reactivity of the $[RNSN]^-$ anion, the transfer of an $[NSN]^-$ unit from R onto polyfluoroaromatics, has recently been observed [5] for the reaction of $[PhNSN]^-$ with $C_{10}F_8$. This reaction resulted in the formation of **7** and $(Ph–N=)_2S$. In this case the only difference is that 1-$AdNH_2$ was obtained as reaction by-product instead of $(1\text{-}Ad–N=)_2S$. It is clear, that in contrast even to its closest analogue $(t\text{-}Bu–N=)_2S$ [11], the $(1\text{-}Ad–N=)_2S$ molecule is sterically overstrained (due to the fact that *t*-Bu is flexible whilst 1-Ad is rigid [10]) in all possible (*Z*,*E*, *Z*,*Z* and *E*,*E*) configurations and therefore unstable. One possible intermediate in the decomposition might be the $[1\text{-}AdN]^-$ radical anion, similar to the formation of 4-Pyr_FNH_2 (and $(ArN=)_2S$) from the reaction of Pentafluoropyridine and $A^+[ArNSN]^-$ [5].

According to the X-ray diffraction data (Table 1), compound **6** exists in the crystal in the *Z*,*E* configuration (Fig. 1). It is also consistent with the *Z*-orientation of the 1-Ad substituent in the parent anion **3.** The orientation of the tetrafluoropyridyl group in **6** corresponds to the known general trend of *Z*,*E* sulfur diimides [5] to have the more electron-withdrawing substituent in the *E*-position.

Similar to *Z*-(4-$MeOC_6H_4$)–NSN–(C_5F_4N-4)-*E* [5], the C(1)N(2)S(1)N(1)C(11) framework is almost planar; C(1) deviates from the NSN plane by −6.8°, C(11) by 3.9°. The dihedral angle between the sulfur–nitrogen– and the heterocyclic fragment of **6** is equal to 47°. In the –N=S=N– moiety the two sulfur nitrogen bonds are not equal, with N(2)–S(1) being significantly shorter than N(1)–S(1) (Fig. 1). Compared to the aryl derivative, the increased +*I*-effect of the adamantyl group leads to a decrease of the N(2)–S(1) dis-



Scheme 3.

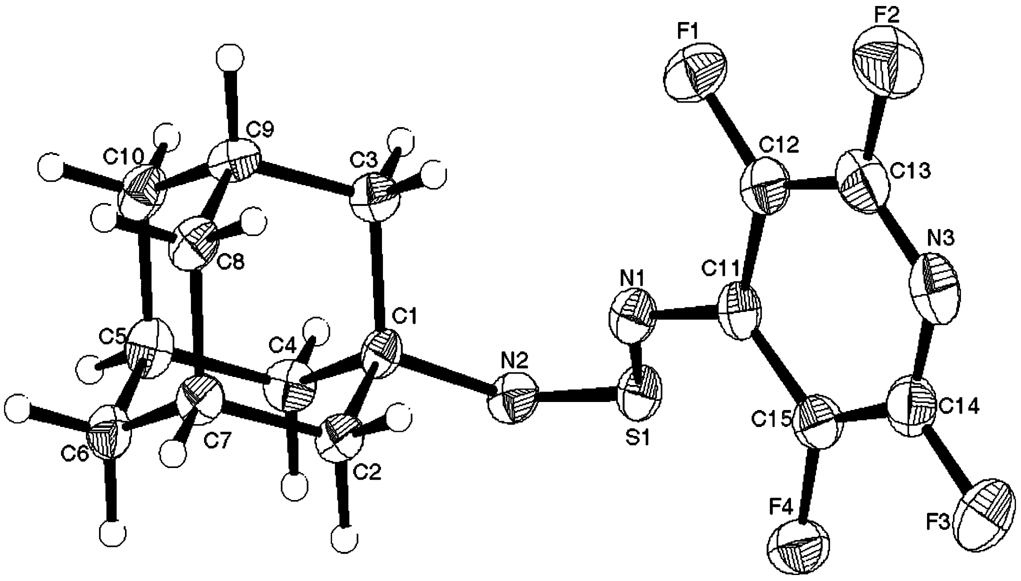


Fig. 1. The X-ray structure of molecule **6**, showing 50% probability ellipsoids. Selected bond lengths (pm) and bond angles (°): C(1)N(2) 148.5(3), N(2)S(1) 151.0(3), S(1)N(1) 156.2(2), N(1)C(11) 138.9(4); C(1)N(2)S(1) 129.39(19), N(2)S(1)N(1) 115.22(13), S(1)N(1)C(11) 121.4(2).

tance due to the increasing anomeric effect. This interaction widens the NSN angle in **6** to 115.22(13)° (compared to 112.3° in the aryl derivative), while the angles C(1)N(2)S(1) and S(1)N(1)C(11) decrease by approximately 3°.

3. Conclusion

Thus, the condensation of $[ArNSN]^-$ anions with external fluoro electrophiles is now expanded to $[AlkNSN]^-$ anions, and the first derivative **6** of previously unknown Alk–N=S=N–Het_F sulfur diimides is prepared and structurally defined.

4. Experimental

The ^1H and ^{19}F NMR spectra were recorded on a Bruker DPX-200 spectrometer, ^{13}C, ^{14}N and ^{15}N NMR spectra on a Bruker DRX-500 spectrometer, at 200.13, 188.28, 125.76, 36.14 and 67.80 MHz, respectively; chemical shifts are given with respect to TMS (^1H, ^{13}C), $CFCl_3$ (^{19}F) or CH_3NO_2 ($^{14,15}N$).

High-resolution mass spectra (EI, 70 eV) were measured with a Finnigan MAT MS 8200 mass spectrometer.

4.1. Crystallographic analysis

The single crystal X-ray structure determinations (Table 1) were carried out on a Siemens P4 diffractometer using Mo Kα (0.71073 Å) radiation with a graphite monochromator. Refinement based on F^2; $R_1 = \Sigma||F_o| - |F_c||$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{1/2}$. Programs used: SHELX-97 [12] and DIAMOND [13]. The structures were solved by direct methods (SHELXS) [12]. Subsequent least squares refinement (SHELXL 97-2) [12] located the positions of the remaining atoms in the electron density maps. All non-H atoms were refined anisotropically.[2]

The crystals were mounted using KEL-F oil on a thin glass fiber.

N-Sulfinyladamant-1-ylamine **1** (yellow oil, boiling point 58–60 °C/0.01 mm) was prepared in 85% yield by the standard procedure [14] from 1-$AdNH_2$ (Aldrich) and $SOCl_2$ in benzene. MS, *m/z* 197.0868 (M^+; calculated for $C_{10}H_{15}NOS$ 197.0874). NMR δ ($CDCl_3$): ^1H: 2.18-2.14 (9H), 1.71 (6H).

N-(Adamant-1-yl)-N′-trimethylsilyl sulfur diimide **2** (orange oil, boiling point 72–73 °C/0.01 mm, which solidifies upon standing to yellow crystals, melting point 24–25 °C) was prepared in 95% yield by the general method [4,15] from **1** and $LiN(SiMe_3)_2$ in hexane at −30 °C under argon. MS, *m/z* 268.1432 (M^+; calculated for $C_{13}H_{24}N_2SSi$ 268.1429). NMR δ ($CDCl_3$): ^1H: 2.19 (9H), 1.78 (6H), 0.31 (9H).

Tris(dimethylamino)sulfonium adamant-1-ylthiazylamide **4**: 1.37 g (0.005 mol) of tris(dimethylamino)sulfonium trimethyldifluorosilicate (TASF) [16] was placed into one side of a two-armed λ-shaped glass vessel fitted with a Teflon valve, 1.34 g (0.005 mol) of **2** was placed into the other side, under argon. In a vacuum line 20 ml of MeCN and 30 ml of THF were distilled onto the TASF at −196 °C, this solution was mixed with **2** at −40 °C. After 2 h at this temperature, 30 ml of Et_2O was condensed onto the reaction mixture at

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[2] Crystallographic data (excluding structure factors) for the structure of **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 174422. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

−196 °C, and the λ-tube was placed into a cryostat at −40 °C for crystal growth. The air-sensitive salt **4** was obtained as transparent orange-yellow crystals (1.71 g; 95%) after removal of the solvents, melting point (sealed capillary) 125–126 °C (decomposition). NMR δ (CD_3CN): ^1H: 2.85 (18H, TAS^+), 2.11 (6H), 1.91 (3H), 1.61 (6H); ^{13}C: 38.28 (TAS^+), 57.33, 44.66, 37.47, 30.73, ^{14}N: 105, −70, −321 (TAS^+).

N-(Adamant-1-yl)-N′-(2,3,5,6-tetrafluoropyrid-4-yl) sulfur diimide **6**: A solution of 1.34 g (0.005 mol) of **2** and 0.85 g (0.005 mol) of C_5F_5N in 5 ml of MeCN was added dropwise to a stirred suspension of 0.76 g (0.005 mol) of freshly calcinated CsF in 20 ml of MeCN under an argon atmosphere at 20 °C. The reaction mixture was stirred overnight, filtered, the solvent was distilled off under reduced pressure, and the residue was sublimed in vacuo and recrystallized from hexane. Compound **6** was obtained as orange-yellow crystals, melting point 59–60 °C, yield 1.47 g (85%). MS, *m/z* 345.0920 (M^+; calculated for $C_{15}H_{15}F_4N_3S$ 345.0923). NMR δ ($CDCl_3$): ^1H: 2.15 (3H), 2.02 (6H), 1.70 (6H); ^{19}F: −92.8 (2F), −148.0 (2F); ^{13}C: 143.6 (dt), 135.9 (t), 134.7 (dd), 65.6, 44.0, 35.7, 29.6; ^{15}N: −3.2 (s), −146.7 (t, $J = \sim 15$ Hz), −156.6 (t, $J = \sim 50$ Hz).

4,5,6,7,8,9-Hexafluoronaphtho[1,2-c][1,2,5]thiadiazole **7**: A solution of 1.34 g (0.005 mol) of **2** and 1.36 g (0.005 mol) of $C_{10}F_8$ in 10 ml of MeCN was added dropwise to a stirred suspension of 0.76 g (0.005 mol) of freshly calcinated CsF in 10 ml of MeCN under an argon atmosphere at 20 °C. The mixture was stirred for 1 h, refluxed for 30 min, cooled to 20 °C, and filtered. The solvent was distilled off under reduced pressure, and the residue was gradually sublimed in vacuo to separate unreacted $C_{10}F_8$ and **7** (at 20 °C for $C_{10}F_8$, and at 120 °C for 7). Compound **7** was obtained as bright-yellow needles after recrystallization from hexane/$CHCl_3$ 1:1, yield 0.59 g (80%). The melting point (133–134 °C) and ^{19}F NMR spectrum (δ ^{19}F: −138.1, −143.4, −143.9, −147.9, −151.5, −153.0) correspond to previously reported values [17]. Unreacted $C_{10}F_8$ was recovered in 0.58 g (85%) yield.

The reaction precipitate (consisted of CsF and 1-$AdNH_2$) was extracted with boiling toluene, filtered hot, and the filtrate was evaporated under reduced pressure. The white crystalline residue was identified as 1-$AdNH_2$ (0.57 g, 75%) by comparison of its melting point and ^1H NMR spectrum with those of an authentic sample.

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