Arylsulfurdiimides: a new class of sulfur–nitrogen anion

Andrey V. Zibarev,[a] **Enno Lork**[b] **and Rüdiger Mews***[b]†

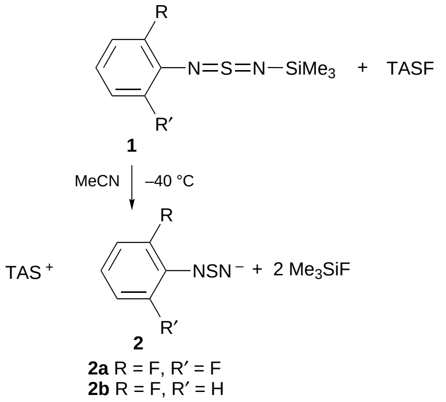
[a] *Institute of Organic Chemistry, Russian Academy of Sciences, Siberian Division, 630090 Novosibirsk, Russia*
[b] *Institut für Anorganische und Physikalische Chemie der Universität Bremen, Leobener Straße NW2, Postfach 330440, D-28334 Bremen, Germany*

***N*-Aryl-*N*′-trimethylsulfurdiimides (aryl = 2,6-$F_2C_6H_3$, 2-FC_6H_4) react with TASF to give quantitatively the corresponding TAS salts with the $ArNSN^-$ anions (2a, 2b), isoelectronic with arylthionylimides 3; because of the short terminal SN bond the anions should be regarded as thiazylamide rather than sulfurdiimide anions.**

Sulfurdiimide salts K^+RNSN^- [R = Me_3C,[1] Me_3Si,[1] $(Me_3C)_2P$,[2] $(Me_3C)_2As$,[2] $PhSO_2$[3]] have been prepared from the appropriate silyl derivatives $RNSNSiMe_3$ and KNH_2 or $KOCMe_3$ while $Li^+Me_3NSN^-$ was obtained from $Me_3SnNSNSnMe_3$ and LiMe.[4] The reaction of $Me_3SiNSNSiMe_3$ and $KOCMe_3$ under more drastic conditions leads to the cleavage of the second Si–N bond with formation of K_2N_2S,[5] which has been used, particularly by the research groups of Herberhold and Chivers as reagents in the chemistries of groups 14 and 15.[6] Protonation with CF_3CO_2H leads to unstable RNSNH (R = Me_3C, Me_3Si) and HNSNH, respectively.[7] Titanosulfurdiimides are obtained from $K^+Me_3CNSN^-$ and Cp_2TiCl_2.[8] Strong covalent metal–nitrogen interaction is expected for these complexes as Woollins and coworkers have shown for *cis*-$[Pt(NSNSiMe_3)_2(PPh_3)_2]$[9] and $[Pt(NSNSC_6H_4NO_2\text{-}4)_2(Ph_2PCH_2CH_2PPh_2)]$.[10]

Arylsulfurdiimide anions are unknown, fluoroarylsulfur diimide anions are likely intermediates in the CsF promoted cyclisation of *N*-fluoroaryl-*N*′-silylsulfurdiimides $Ar_FNSNSiMe_3$ under elimination of Me_3SiF to give benzothiadiazoles.[11,12] Even spectroscopic evidence for these intermediates is lacking.

Upon cleavage of the SiN bond in $Ar_FNSNSiMe_3$ with TASF $\{[(Me_2N)_3S]^+[Me_3SiF_2]^-\}$[13] the sulfurdiimide salts **2** are readily available (Scheme 1).



Scheme 1

After removal of all volatiles at −30 to −20 °C, salts **2** are isolated in quantitative yield as orange–yellow solids.‡ On warming to room temperature these highly reactive salts decompose immediately to give brown tars. With MeI they react even at −35 °C to give Ar_FNSNMe.

Single crystals of salts **2** were obtained from MeCN–diethyl ether solutions at −40 °C and X-ray data were collected at −110 °C. Figs. 1 and 2 show the anions of salts **2a** and **2b**; for comparison the structure of 2,6-difluorophenylthionylimide $C_6H_3F_2NSO$ **3a** (Fig. 3), isoelectronic with **2a**, was also determined.§ All three compounds adopt the *Z*-conformation and the torsion angle between the aryl plane and the NSA group

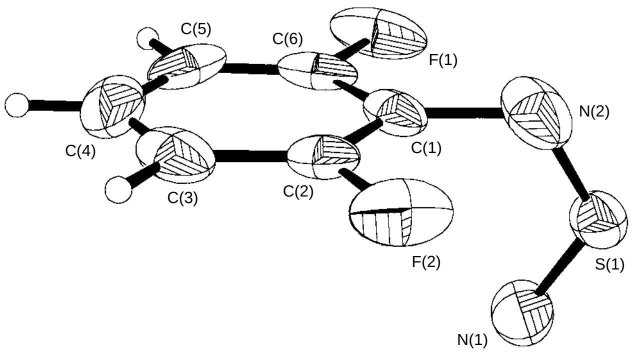


Fig. 1 Structure of the anion of **2a** with selected bond distances (pm) and angles (°) (average of three independent anions): S(1)–N(1) 144.2, S(1)–N(2) 158.9, N(2)–C(1) 140.7; N(1)–S(1)–N(2) 122.3, S(1)–N(2)–C(1) 119.0; τ = 77.7

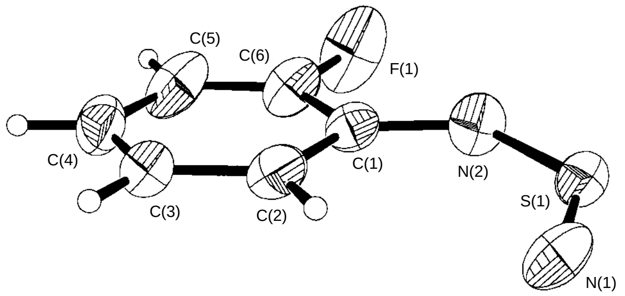


Fig. 2 Structure of the anion of **2b** with selected bond distances (pm) and angles (°): S(1)–N(1) 145.8(4), S(1)–N(2) 159.9(4), N(2)–C(1) 139.0(6), N(1)–S(1)–N(2) 124.8(2), C(1)–N(2)–S(1) 126.5(3); τ = 6.8(5)

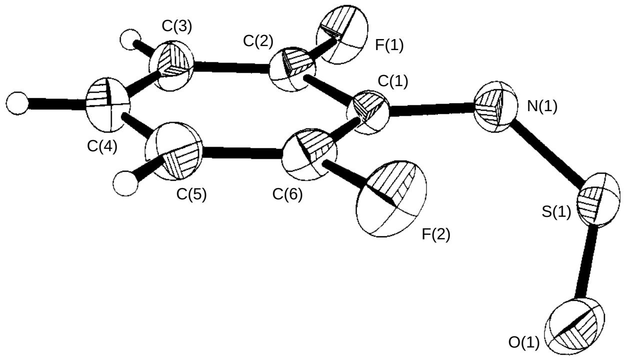
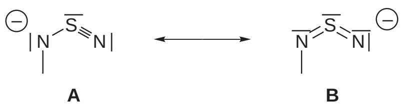


Fig. 3 Structure of **3a** with selected bond distances (pm) and angles (°): S–O 144.8(1), S–N 151.5(1), N–C 140.4(2), N–S–O 120.7(1), C–N–S 130.1(1); τ = 43.6(1)

(A = O,N) seems to be determined by the electronic repulsion between the *ortho* substituents and these groups. In the thionylimide **3a** this angle is 43.6°, in the corresponding negatively charged sulfurdiimide anions these angles are between 75.6 and 79.0° (three independent molecules). In **2b** this repulsion forces the NSN group almost into the aryl plane (τ = 6.8°).

According to the bond lengths in the –NSN– fragment the anions of salts **2** should be regarded as thiazylamides **A** rather than sulfurdiimides **B** (Scheme 2).



Scheme 2

The terminal SN bond distances in **2a** (144.2 pm) and **2b** (145.8 pm) correspond to the $S^{IV}\equiv N$ triple bond in thiazylhalides (NSF 144.6 pm,[14] NSCl 145.0 pm[15]) and $(CF_3)_2NO(SN)$ (142.3 pm)[16] and also agree well with the SO bond in the isoelectronic thionylimide $2,6\text{-}C_6H_3F_2NSO$ **3a** (144.8 pm). In thiazyl derivatives the XSN angle is 117–119°, in **3a** 120.7° and in the anions of **2** 122–125°. For the bridging SN bonds of **2** the distances 158.9 pm for **2a** and 159.9 pm for **2b** are between double and single bond lengths.

A. Z. is grateful to Deutsche Forschungsgemeinschaft and to Russian Foundation for Basic Research (project 96-03-33276) for financial support.

Notes and References

† E-mail: mews@chemie.uni-bremen.de

‡ *Preparation of* ***2***: TASF[13] (1.37 g, 5 mmol) was placed into one side of a two-armed lambda-shaped glass vessel fitted with a Teflon valve, 5 mmol of the corresponding $ArNSNSiMe_3$ **1**[17] was placed into the other side. In a vacuum line 20 ml of MeCN was distilled onto TASF, this solution was mixed with **1** at −40 °C and stirred at this temperature for 2 h. Then 30 ml of Et_2O was condensed onto the reaction mixture at −196 °C, the λ-tube was placed into a cryostat at −40 °C for crystal growth and **2a** and **2b** were obtained as orange–yellow crystalline solids after removal of the solvents. Because of their thermal instability the compounds were characterised only by low temperature X-ray crystallography.

§ *Crystal data*: $C_{12}H_{21}F_2N_5S_2$ **2a**, monoclinic, space group $P2_1/c$, a = 1666.7(6), b = 1159.4(4), c = 2549.0(11) pm; β = 92.42(3)°, U = 4.921(3) nm^3, Z = 12, D_c = 1.366 g cm^{-3}, μ = 0.345 mm^{-1}, $F(000)$ 2136, crystal dimensions 1.1 × 0.4 × 0.2 mm, 12 180 reflections collected with 2.64 < θ < 27.52°, 9824 used in structural analysis. The data for **2a**, **2b** and **3a** were collected on a Siemens P4 diffractometer using Mo-Kα radiation (λ = 71.073 pm) at 173 K. The structures were solved by direct methods.[18] All non-hydrogen atoms were refined anisotropically. The refinement (597 parameters) converged with wR_2 = 0.2521 (R_1 = 0.0867) and final difference electron density maxima and minima of 1510 and −840 e nm^{-3}.

$C_{12}H_{22}FN_5S_2$ **2b**: monoclinic, space group $C2/c$, a = 2685.2(6), b = 898.8(2), c = 1505.1(5) pm, β = 115.54(2)°, U = 3.278(2) nm^3, Z = 8, D_c = 1.295 g cm^{-3}, μ = 0.333 mm^{-1}, $F(000)$ 1360, crystal dimensions 0.5 × 0.4 × 0.1 mm. 4477 reflections collected with 2.65 < θ < 22.50°, 2147 used in structural analysis. The refinement (189 parameters) converged with wR_2 = 0.1381 (R_1 = 0.0555) and final difference electron maxima and minima of 493 and −383 e nm^{-3}.

$C_6H_3F_2NOS$ **3a**: monoclinic, space group $C2_1/c$, a = 374.37(4), b = 2106.4(3), c = 873.7(2) pm, β = 100.95(1)°, U = 0.6765(2) nm^3, Z = 4, D_c = 1.720 g cm^{-3}, μ = 0.448 mm^{-1}, $F(000)$ 352, crystal dimensions 0.8×0.6×0.5 mm. 2041 reflections collected with 2.56 < θ < 27.49°, 1402 used in structural analysis. The refinement (102 parameters) converged with wR_2 = 0.0809 (R_1 = 0.0297) and final difference electron maxima and minima of 337 and −229 e nm^{-3}. CCDC 182/817.

1 D. Hänssgen and B. Ross, *Z. Anorg. Allg. Chem.*, 1981, **473**, 80.
2 M. Herberhold, W. Ehrenreich, W. Bühlmeyer and K. Guldner, *Chem. Ber.*, 1986, **119,** 1424.
3 H. W. Roesky, W. Schmieder and W. S. Sheldrick, *Chem. Commun.*, 1981, 1013; H. W. Roesky, W. Schmieder, W. Isenberg, W. S. Sheldrick and G. M. Sheldrick, *Chem. Ber.*, 1982, **115**, 2714.
4 D. Hänssgen and R. Steffens, *J. Organomet. Chem.*, 1982, **236**, 53.
5 M. Herberhold and W. Ehrenreich, *Angew. Chem., Int. Ed. Engl.*, 1986, **21**, 633.
6 *Gmelin Handbook of Inorganic and Organometallic Chemistry, Sulfur Nitrogen Compounds*, Part 7, Springer, Berlin, 1991, p.10 ff.
7 M. Herberhold, W. Jellen, W. Bühlmeyer, W. Ehrenreich and J. Reiner, *Z. Naturforsch., Teil B*, 1985, **40**, 1229.
8 M. Herberhold, F. Neumann, G. Süss-Fink and U. Thewalt, *Inorg. Chem.*, 1987, **26**, 3612.
9 N. P. C. Walker, M. B. Hursthouse, C. P. Warrens and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1985, 227.
10 R. Jones, D. J. Williams, P. T. Wood and J. D. Woollins, *Polyhedron*, 1989, **8**, 91.
11 A. V. Zibarev and A. O. Miller, *J. Fluorine Chem.*, 1990, **50**, 359.
12 I. Yu. Bagryanskaya, Yu. V. Gatilov, A. O. Miller, M. M. Shakirov and A. V. Zibarev, *Heteroatom Chem.*, 1994, **5**, 561.
13 W. J. Middleton, *Org. Synth.*, 1985, **64**, 221.
14 R. L. Cook and W. H. Kirchhoff, *J. Chem. Phys.*, 1967, **47**, 4521.
15 T. Beppo, E. Hirota and Y. Morino, *J. Mol. Spectrosc.*, 1970, **36**, 386; W. C. Emken and K. Hedberg, *J. Chem. Phys.*, 1973, **58**, 2195.
16 G. Hartmann, R. Mews, G. M. Sheldrick, R. Anderskewitz, M. Niemeyer and H. J. Emeleus, *J. Fluorine Chem.*, 1986, **34**, 46.
17 A. V. Zibarev and R. Mews, unpublished work.
18 Structure solution and graphics, Siemens SHELXTL-Plus: G. M. Sheldrick, Release 4.0 for Siemens R3 Crystallographic Research Systems, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1989; Structure refinement, SHELXL-93, G. M. Sheldrick, University of Göttingen.

Received in Cambridge, UK, 13th February 1998; 8/01262H