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Z,Z Isomers of Polyfluorinated 1,3-Bis(aryl)-1,3-diaza-2-thiaallenes, $(ArN=)_2S$, in the Crystal and in Solution

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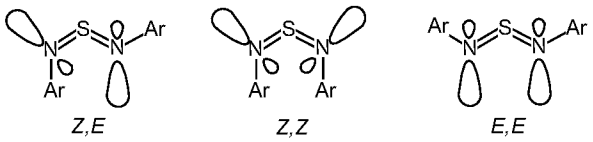
It has been shown by X-ray structure analysis, ^{19}F NMR spectroscopy and PM3 calculations that non-typical (it is assumed) *Z,Z* isomers of $(ArN=)_2S$, discovered only recently in the form of sterically hindered derivatives, are unexpectedly widespread being found for the title compounds as well.

Recently it has been shown[1] that $(ArN=)_2S$ widely used in organoelement, heteroatom and coordination chemistry overcomes the steric strains induced by bulky *ortho*-substituents in two ways: (1) by the arrangement of rings in a standard *Z,E* configuration orthogonal to the NSN plane, (2) by a change of configuration from *Z,E* to a previously unobserved *Z,Z* configuration. The first way seems to be a universal solution to the steric problem. The second way, paradoxically, leads to a sterically more hindered (in the general sense) isomer (Scheme 1), indicating a complex stereoelectronic balance in which electronic factors (n_N,π mixing) are more significant than steric factors.[1] It follows that unusual *Z,Z* configurations may be adopted not only by sterically hindered but by others $(ArN=)_2S$ as well. In this work polyfluorinated derivatives have been studied which are structurally uncharacterized as yet except for $TsN=S=NPh_F$ which possesses the *Z,E* configuration in the crystal.[2]



$Ar–N=S=N–Ar^1$

1–4

	Ar	Ar^1
1	C_6F_5	C_6H_5
2	$2,6\text{-}Me_2C_6H_3$	C_6F_5
3	C_6F_5	C_6F_5
4	C_6H_5	C_6H_5

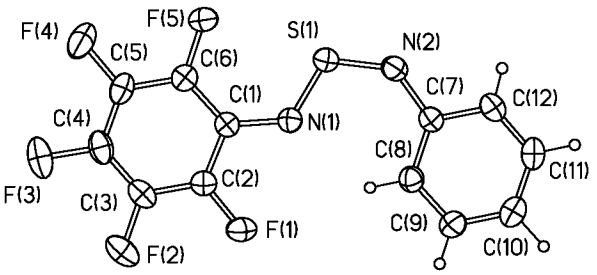
Scheme 1

H_f^0 values (PM3 with full geometry optimization) of **1–3**[†] show that the *E,E* isomer is the most unstable (by ~ 7.5–9 kcal mol^{-1}) of the three possible isomers (Scheme 1), as well as for the others $(RN=)_2S$.[1] The difference between the *Z,E* and *Z,Z* isomers is small (~ 0.5–1.5 kcal mol^{-1}); nevertheless, the former is the most stable for **1** and **3** (for compound **4** not containing fluorine as well)[1] and the latter for **2**.

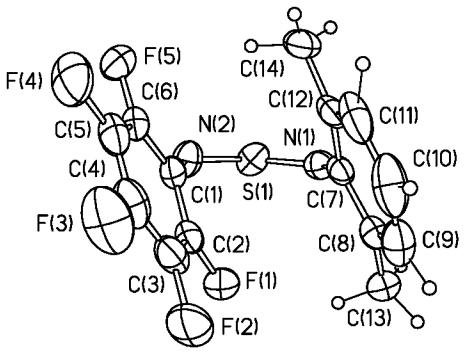
As shown by X-ray structure analysis,[‡] **1** exists in the crystal as a perfectly planar [extreme deviations are 0.076(2) and −0.067(2) A for F(3) and N(1), respectively] *Z,E* isomer, whereas **2** and **3** exist as *Z,Z* isomers (Fig. 1).

As confirmed by ^{1}H NMR data for the previously-studied $(ArN=)_2S$, the isomers observed in the crystal predominate in CS_2 solution[1] indicating crystal packing and/or solvation effects to be less significant for molecular configuration. For **1–3** low temperature spectral measurements in CS_2 were unsuccessful due to poor solubility. In a toluene solution of **1** or **2** only one isomer was observed by ^{1}H NMR in the range 20 to −90 °C. According to ^{19}F NMR data[§] **2** actually exists in this solution in the form of only one isomer, whereas **1** and **3** exist as an equilibrium mixture of three isomers each. Fig. 2 gives tentative isomer configurations as well as $G^{\neq}$ values for their interconversions obtained from exchange spectra calculations within a broadened singlet approximation using modified Bloch equations.[5] In the case of **3** the major isomer in solution possesses a *Z,E* configuration, as is evident from the form of the spectrum. Thus, **3** changes its configuration from *Z,Z* to *Z,E* on passing from the crystal to a toluene solution. This is probably due to the solvation of **3** by toluene *via* a typical, non-covalent π-stacking interaction between arenes and polyfluoroarenes.[5]

As shown by the PM3 data, the *Z,Z* isomers of **2** and **3** are stabilized by the same σ,π interaction as the *Z,Z* isomers of sterically hindered $(ArN=)_2S$:[1] n_N^- with π^- (where π correlates with the $1e_{1g}$S benzene MO) and n_N^+ with π^+ (where π correlates with the $1a_{2u}$ benzene MO); the latter combinations also involve n_S. Fluorine 2p AOs do not participate in these MOs.



1



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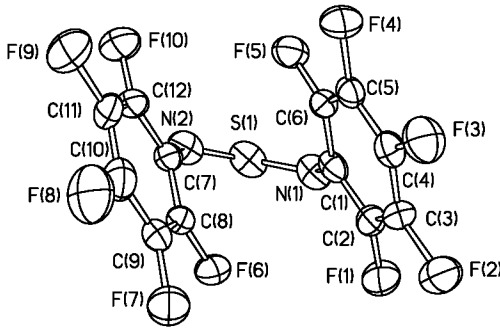

3

Fig. 1 Structure of molecules **1–3** in the crystal. Selected bond lengths (A), reduced contacts (A) and bond angles (°): **1**: S(1)–N(1) 1.551(3), S(1)–N(2) 1.525(3), N(1)–C(1) 1.392(4), N(2)–C(7) 1.397(4), C–F 1.347, C_{Ar}–C_{Ar} 1.382, C_{Ar_F}–C_{Ar_F} 1.379, S(1)···F(5) 2.823, N(1)–S(1)–N(2) 113.6(2), S(1)–N(1)–C(1) 124.6(2), S(1)–N(2)–C(7) 133.2(2), N(1)–C(1)–C(6) 128.1(3), N(2)–C(7)–C(8) 126.1(3). **2**: S(1)–N(1) 1.515(3), S(1)–N(2) 1.529(3), N(1)–C(7) 1.423(4), N(2)–C(1) 1.406(4), C–Me 1.505, C–F 1.338, C_{Ar}–C_{Ar} 1.385, C_{Ar_F}–C_{Ar_F} 1.371, S(1)···F(1) 3.178, S(1)···C(14) 3.359, N(1)–S(1)–N(2) 123.8(2), S(1)–N(1)–C(7) 129.5(2), S(1)–N(2)–C(1) 128.0(2). **3** (two independent molecules): S(1)–N(1) 1.533(8), 1.492(9); S(1)–N(2) 1.507(8), 1.522(8); N(1)–C(1) 1.42(1), 1.43(1); N(2)–C(7) 1.42(1), 1.411(9); C–F 1.342; C_{Ar_F}–C_{Ar_F} 1.366; S(1)···F(5) 3.070, 3.063; S(1)–F(6) 3.070, 3.067; N(1)–S(1)–N(2) 123.9(4), 123.2(3); S(1)–N(1)–C(1) 126.7(6), 127.7(6); S(1)–N(2)–C(7) 128.4(6), 127.4(6).

It is therefore clear that *Z,Z* isomers of $(ArN=)_2S$ are unexpectedly widespread.

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[†] **1** and **3** were synthesized as described earlier,[3] and **2** (85%) was obtained in a similar manner as transparent orange crystals (from hexane), m.p. 89–90 °C, M^+ (*m/z*) measured (calculated) 332.0405 (332.0406). UV (heptane) λ_{max}/nm (log ε): 425 (3.08).

[‡] *X-Ray structure data for* **1–3**: **1**, $C_{12}H_5F_5N_2S$, $M = 304.24$, monoclinic, $a = 9.570(1)$, $b = 5.847(1)$, $c = 21.249(3)$ A, $\beta = 96.35(1)°$, $U = 1181.7(3)$ A^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.710$ g cm^{-3}, μ(Cu-Kα) = 3.01 mm^{-1}, $F(000) = 608$. **2**, $C_{14}H_9F_5N_2S$, $M = 332.29$, monoclinic, $a = 9.921(2)$, $b = 12.796(3)$, $c = 11.245(2)$ A, $\beta = 94.90(3)°$, $U = 1422.3(5)$ A^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.552$ g cm^{-3}, μ(Cu-Kα) = 2.55 mm^{-1}, $F(000) = 672$. **3**, $C_{12}F_{10}N_2S$, $M = 394.20$, orthorhombic, $a = 8.631(3)$, $b = 9.731(3)$, $c = 31.920(10)$ A, $U = 2681(2)$A^3, space group $P2_12_12_1$, $Z = 8$, $D_c = 1.953$ g cm^{-3}, μ(Cu-Kα) = 3.39 mm^{-1}, $F(000) = 1536$. Data were measured on a Syntex $P2_1$ diffractometer with graphite monochromated Cu-Kα radiation using θ-2θ scans. An analytical correction for absorption was used. The structures were solved by direct methods and refined in the anisotropic-isotropic approximation. *R*, number of independent observed reflections [$|F_0| > 4\sigma|F_0|$], θ < (°): **1**, 0.0466, 1289, 57; **2**, 0.0772, 1995, 69; **3**, 0.0444, 1550, 57. The parameters of the hydrogen atoms were given geometrically and were not refined (**1**), or were obtained from difference Fourier synthesis (**2**). Atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre (see Notice to Authors, *Mendeleev Commun.*, 1994, issue 1).

[§] *^{19}F NMR data for* **1–3** ([$^2H_8$]toluene, internal C_6F_6) δ (AA′MM′X system standard for C_6F_5R [4]), 25 °C: **1**, 17.01 (2F, *o*-), 1.97 (1F, *p*-), −1.11 (2F, *m*-); **2**, 18.60 (2F), 4.00 (1F), 1.00 (2F); **3**, 20.01 (2F), 5.78 (1F), 0.02 (2F). −90 °C: **1**, three isomers with content in the mixture 70, 21 and 9%, respectively: 17.72, 2.24, −0.77; 17.06, 2.66, −1.43; 19.24, 3.80, −0.33; **2**, 18.70, 5.30, 1.60; **3**, two groups of signals with 6.6/6.7 intensity ratio (*Z,E* isomer, 92%): 22.00, 6.83, 0.32; 20.77, 6.08, 0.32; and an additional signal of 1.0 relative intensity at 17.36 (*Z,Z* isomer, 6%). Other signals of the *Z,Z* isomer of **3** overlap with the *Z,E* isomer signals. Besides, interconversion kinetics as well as small differences in the *Z* and *E* ring signal intensities of the *Z,E* isomer indicate the presence of one more isomer of **3** (*E,E*, ~ 2%).

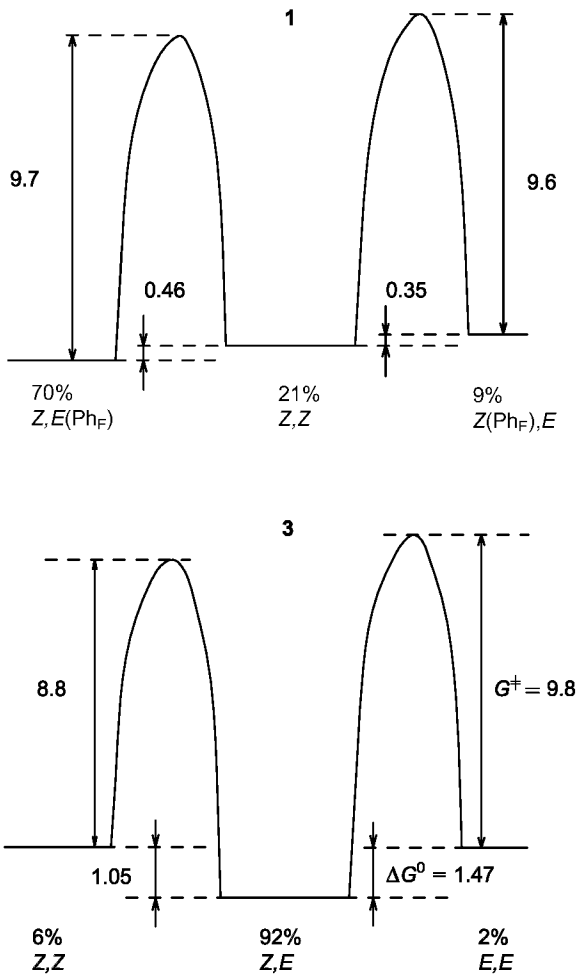

Fig. 2 Isomer mixture composition for **1** and **3** in toluene solution at −90 °C as well as $G^{\ddagger}$ and G^{0} values (±0.7 and 0.3, respectively; kcal mol^{-1}) for isomer interconversion according to ^{19}F NMR data. Compound **2** exists under these conditions in the form of only one isomer, most likely *Z,Z*.

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