Configurations of 1,3-bis(aryl)-1,3-diaza-2-thiaallenes in the crystal state

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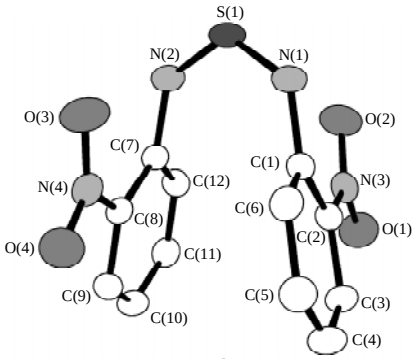
The σ,π-mixing responsible for the *Z,Z* configuration of the title compounds is indifferent to both withdrawing (NO_2) and releasing (OMe) π-electron character of *ortho*-substituents, and the arrangement of aromatic rings in the *Z,E* configuration orthogonally to the NSN plane is a universal way to overcome steric hindrances due to bulky (Bu^t, Br) *ortho*-substituents.

Azathienes $(RN=)_2S$, which are widely used as reagents and ligands in organoelement, heteroatom and coordination chemistry, prefer *Z,E* and *Z,Z* configurations in all states of aggregation (Scheme 1).[1] The *E,E* configuration was found only in the crystal state of some metal complexes[2,3] rather than in non-coordinated molecules.

With R = Ar, the relative importance of the *Z,E*[4–7] and *Z,Z*[6–9] configurations is determined by a complex stereoelectronic balance.[7,8] In particular, as shown by the PM3 calculations,[7,8] the *Z,Z* isomers of $(ArN=)_2S$ are stabilised by the σ,π-mixing of 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). In the case of polyfluorinated $(ArN=)_2S$, fluorine 2*p* AOs do not participate in the contributing MOs providing only an inductive influence upon them.[8] We can suppose the above interaction to be indifferent to both withdrawing and releasing π-electron character of other heteroatom substituents.



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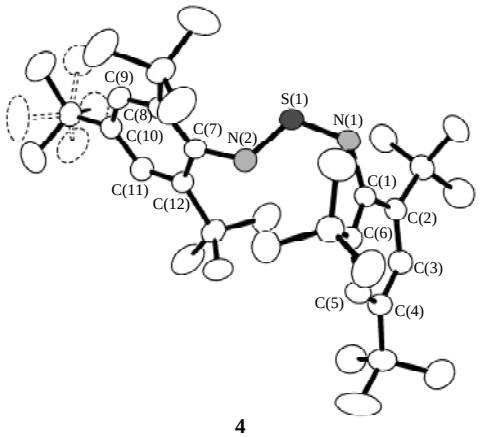

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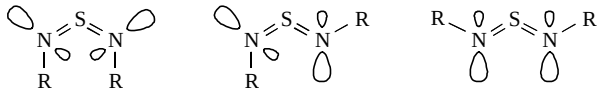
Figure 1 Molecular structure of **2** and **4**.§ For **2**, selected bond lengths (Å): S(1)–N(1) 1.515(3), S(1)–N(2) 1.514(3), N(1)–C(1) 1.410(4), N(2)–C(7) 1.416(4); selected bond angles (°): N(1)–S(1)–N(2) 123.44(15), S(1)–N(1)–C(1) 130.0(2), S(1)–N(2)–C(7) 129.4(2). For **4**, selected bond lengths (Å): S(1)–N(1) 1.528(2), S(1)–N(2) 1.527(2), N(1)–C(1) 1.433(3), N(2)–C(7) 1.425(3); selected bond angles (°): N(1)–S(1)–N(2) 117.0(1), S(1)–N(1)–C(1) 125.9(2), S(1)–N(2)–C(7) 122.3(2); selected torsional angles (°): S(1)–N(1)–C(1)–C(6) 72.4(3), S(1)–N(2)–C(7)–C(8) –60.6(3), N(2)–S(1)–N(1)–C(1) 16.3(2), N(1)–S(1)–N(2)–C(7) –165.3(2).



Z,Z **2,3** *Z,E* **1,4,5** *E,E*

1 R = 4-MeC_6H_4
2 R = 2-$NO_2C_6H_4$
3 R = 2-$MeOC_6H_4$
4 R = 2,4,6-$Bu^t_3C_6H_2$
5 R = 2,4,6-$Br_3C_6H_2$

Scheme 1

Indeed, as shown by X-ray structure analysis, compound **2**† (Figure 1)‡ possesses the same *Z,Z* configuration in the crystal as compound **3**.[6] The only difference is that *ortho*-MeO groups in **3** are oriented in the same direction, whereas *ortho*-NO_2 groups in **2** are arranged in opposite directions.

It was believed that a universal way to overcome steric hindrances induced by bulky *ortho*-substituents in $(ArN=)_2S$ is the arrangement of Ar rings in the *Z,E* configuration orthogonally to the NSN plane.[7] As shown by X-ray structure analysis, sterically hindered compound **4**† (Figure 1)‡,§ really exists in the crystal as the *Z,E* configuration in which the Ar rings are virtually perpendicular to the NSN plane. As parent

† Compound **2** was synthesised as transparent orange prisms, mp 141–142 °C (from benzene–hexane) as described earlier.[10]

Compound **4** (94%) was prepared from corresponding $ArNH_2$ and SF_4 according to a general method[11] as transparent orange crystals, mp 208–209 °C (from toluene). MS, *m/z* experimental (calculated): 550.4299 (550.4321), [M$^+$]. UV [heptane, λ_{max}/nm (lg ε)]: 420 (3.66). ^{1}H NMR (CS_2, 20 °C) δ: 7.14 (s, 2H), 1.31 (s, 18H), 1.26 (s, 9H). ^{13}C NMR, δ: 143.3, 139.1, 122.2, 120.1, 33.8, 32.2, 30.1, 29.3. ^{15}N NMR, δ: 334. A single crystal for X-ray diffraction analysis was prepared by slow evaporation of a solution of **4** in 4′-pentyl-4-biphenylcarbonitrile (Aldrich).

‡ *X-ray crystal data*. Compound **2**: $C_{12}H_8N_4O_4S$, *M* = 304.28, monoclinic, *a* = 8.159(3) Å, *b* = 12.444(4) Å, *c* = 12.867(4) Å, β = 94.56(3)°, *V* = = 1302.3(8) Å^3, space group $P2_1/n$, *Z* = 4, d_c = 1.552 g cm^{-3}, μ(CuKα) = = 2.446 mm^{-1}, *F*(000) = 624.

Compound **4**: $C_{36}H_{58}N_2S$, *M* = 550.90, triclinic, *a* = 9.979(3) Å, *b* = = 10.089(3) Å, *c* = 20.648(4) Å, α = 91.39(3)°, β = 101.91(3)°, γ = = 119.26(3)°, *V* = 1755.4(8) Å^3, space group $P\bar{1}$, *Z* = 2, d_c = 1.042 g cm^{-3}, μ(CuKα) = 0.979 mm^{-1}, *F*(000) = 608.

Data were measured on a Syntex $P2_1$ diffractometer with graphite monochromated CuKα radiation using θ/2θ scans. A correction for absorption was made for **2** according to the crystal faces (transmission: 0.25–0.58), and for **4** by the azimuthal scan method (transmission: 0.73–0.93). The structure of **2** was solved by the direct method and that of **4**, by the heavy atom method using the SHELXS-86 program. The structures were refined in the full-matrix anisotropic (isotropic for H atoms) approximation by the SHELXL-97 program. *R*, *S*, the number of independently observed reflections [$|F_0| > 4\sigma|F_0|$], 2θ < (°): **2**, 0.0533, 1.038, 1544, 140; **4**, 0.0447, 1.053, 3847, 114.

The parameters of the hydrogen atoms were given geometrically. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, 1999, issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/50.

compound **1** (taken as a 4,4′-dimethyl derivative) exists in the crystal as a nearly planar *Z,E* isomer,[4] we can conclude that bulky *ortho*-substituents such as Bu^t (Figure 1) and Br (compound **5**)[7] induce only conformational, not configurational, reorganization.

Thus, this work gives new important evidence in favour of our earlier conclusions.[7,8]

This work was supported by the Russian Foundation for Basic Research (grant nos. 96-03-33276 and 96-07-89181).

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§ The equality of S=N bond lengths found for **4** is not typical of all other (*Z,E*)-(ArN=)$_2$S with known real geometry in which the *E*-bond is slightly longer [by 0.009(2)–0.065(16) Å][6–8] than the *Z*-bond. Another feature is that N=S=N bonds are twisted (for torsional angles, see Figure 1). The aromatic rings adopt a boat-like conformation typical of 1-*R*-2,4,6-(Bu^t)$_3$C$_6$H$_2$ compounds[12] with the *E*-ring being less distorted than the *Z*-ring (*cf*. the X-ray data on structurally related phosphorus heterocumulenes).[13,14]

Received: 24th March 1999; Com. 99/1467