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

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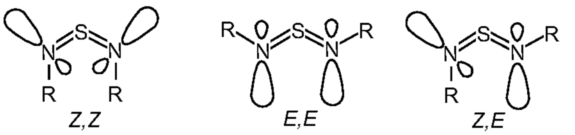
It has been shown by X-ray structure analysis, ^{1}H NMR spectroscopy (including NOE) and PM3 calculations that symmetric isomers of the title compounds in the crystal and in solution have a *Z,Z* configuration stabilized by n_N,π interaction, but not the *E,E* configuration suggested earlier.

Three geometrical isomers are possible for the azathienes $(RN=)_2S$ (Scheme 1) widely used in organoelement, heteroatom and coordination chemistry. With R = Ar in the absence of bulky *ortho*-substituents an almost planar *Z,E* isomer is realized in the crystal,[1,2] whereas an equilibrium mixture of major unsymmetric (*Z,E*) and minor symmetric (*E,E*, as supposed) isomers is formed in solution.[3,4] With bulky *ortho*-substituents, such as Me, the major isomer in solution was supposed to be the symmetric *E,E* one.[3,4]



Ar–N=S=N–Ar^1

1–5

	Ar	Ar^1
1	2,4,6-$Br_3C_6H_2$	2,4,6-$Br_3C_6H_2$
2	2,6-$Me_2C_6H_3$	2,6-$Me_2C_6H_3$
3	2,4,6-$Br_3C_6H_2$	2,6-$Me_2C_6H_3$
4	2,4,6-$Br_3C_6H_2$	2,3,5,6-Me_4C_6H
5	Ph	Ph

Scheme 1

However, H_f^0 values (PM3 with full geometry optimization) of **1–5** with (**1–4**)[†] or without (**5**) *ortho*-Br and/or Me show that the *E,E* isomer is the most unstable in all cases (by ~3–6 kcal mol^{-1}), probably, due to n_N repulsion (Scheme 1). The difference between the *Z,E* and *Z,Z* isomers is small (~0.5–3 kcal mol^{-1}); nevertheless, the former is the most stable for **5**, and the latter for **1–4**.

As shown by the X-ray structure analysis,[‡] **1** exists in the crystal as the *Z,E* isomer in which the rings are virtually perpendicular to the NSN plane, whereas **2** and **3** exist as *Z,Z* isomers in which the stacked rings are practically parallel to each other and almost perpendicular to the NSN plane (Fig. 1), reminiscent of molecular tweezers.[7]

As shown by ^{1}H NMR spectroscopy[§] including NOE[8] data for **4**, major isomers of **2–4** in solution possess the *Z,Z* configuration as well. At –110 °C the spectra of **2–4** show signals of the minor *Z,E* isomer. For **1** only one isomer is observed throughout the temperature range studied, which probably possesses the *Z,E* configuration as in the crystal.

Thus, $(ArN=)_2S$ overcomes steric strains induced by bulky *ortho*-substituents in two ways: (1) by the arrangement of rings in the *Z,E* isomer orthogonally to the NSN plane, and (2) by the change of configuration from *Z,E* to *Z,Z*. The first way seems to be a universal solution to the steric problem. The second way, paradoxically, leads to a sterically most hindered, in a general case, isomer (Scheme 1), indicating a complex stereoelectronic balance.

The *Z,Z* isomer of $(RN=)_2S$ was earlier found in the gas phase at R = H (along with the *Z,E* isomer),[9] at R = Me_3Si[10] and in the crystal state at R = R^{1}S.[11–13] The reason for the *Z,Z* configuration stability is the σ,σ interaction of $n_N^{\mp}$ with σ_{SiC} (R = Me_3Si)[14] or $n_{S(II)}$ (R = R^{1}S).[15]

As shown by the PM3 data, the *Z,Z* isomer of **2** is stabilized by the similar 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). The latter combinations also involve n_S.

The interaction above is known to be sensitive to the energies of the contributing MOs.[14] For $(RN=)_2S$ it essentially decreases, for example, from R = Me_3Si to R = Me; owing to this, the most stable isomer of $(MeN=)_2S$ is the *Z,E* isomer observed in the gas phase.[14,16] As evident from the PM3 results, Br and Me of **1–4** affect differently the energies of the ring π-orbitals interacting with $n_N^{\mp}$, which is in accordance with UPS data for 1,3,5-$Br_3C_6H_3$ and 1,3-$Me_2C_6H_4$.[17,18] Probably, due to this the *Z,E* isomer is preferable for **1**, and the *Z,Z* isomer for **2–4**.

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[†] Synthesized by a general procedure: **1**,[5] **2**,[3] **3**, **4**.[6] Transparent orange crystals (from hexane). Yield (%), m.p. (°C), M$^+$ (*m/z*) measured (calculated): **1**, 62, 135–136, 681.5207 (681.5199, ^{79}Br); **2**, 86, 63–64, 270.1192 (270.1191); **3**, 85, 92–93, 475.8200 (475.8195, ^{79}Br); **4**, 70, 113–115, 503.8521 (503.8505, ^{79}Br).

[‡] *X-ray structure data for* **1–3**: **1**, $C_{12}H_4Br_6N_2S$, M = 687.66, triclinic, $a = 8.688(1)$, $b = 8.966(1)$, $c = 12.349(2)$ A, $\alpha = 80.37(1)$, $\beta = 82.78(1)$, $\gamma = 65.07(1)°$, $U = 858.4(2)$ A , space group $P1$, $Z = 2$, $D_c = 2.661$ g cm^{-1}, μ(Cu-K$_\alpha$) = 182.1 cm^{-1}, $F(000) = 632$. **2**, $C_{16}H_{18}N_2S$, M = 270.39, monoclinic, $a = 19.864(4)$, $b = 7.573(1)$, $c = 11.753(6)$ A, $\beta = 124.25(1)°$, $U = 1461.4(4)$ A , space group $C2/c$, $Z = 4$, $D_c = 1.229$ g cm^{-1}, μ(Cu-K$_\alpha$) = 18.1 cm^{-1}, $F(000) = 576$. **3**, $C_{14}H_{11}Br_3N_2S$, M = 479.03, triclinic, $a = 10.578(2)$, $b = 11.596(2)$, $c = 14.174(3)$ A, $\alpha = 106.83(1)$, $\beta = 99.07(1)$, $\gamma = 98.53(1)°$, $U = 1608.4(5)$ A , space group $P1$, $Z = 4$, $D_c = 1.978$ g cm^{-1}, μ(Cu-K$_\alpha$) = 105.4 cm^{-1}, $F(000) = 920$. Data were measured on a Syntex P2$_1$ diffractometer with graphite monochromated Cu-K$_\alpha$ radiation using θ-2θ scans. An analytical correction for absorption was used. The structures were solved by direct methods and refined in the anisotropic approximation. R is the number of independently observed reflections [$|F_0| > 4\sigma|F_0|$], 2θ < (°): **1**, 0.056, 2639, 140; **2**, 0.047, 1042, 130; **3**, 0.055, 3536, 120. The parameters of the hydrogen atoms were given geometrically and were not refined except for **2**. Atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre; see Notice to Authors, *Mendeleev Commun.*, 1994, issue 1.

[§] *^{1}H NMR data for* **1–4**, δ (CS_2) 20 °C: **1**, 7.51 (s); **2**, 6.70 (m 3H), 2.03, (s 6H); **3**, 7.46 (s 2H), 6.85 (m 3H), 2.19 (s 6H); **4**, 7.37 (s 2H), 6.62 (s 1H), 2.09 (s 6H), 2.02 (s 6H). –110 °C: **1**, 7.45; *Z,Z* isomer and *Z* ring of *Z,E* isomer: **2**, 6.58, 1.93; **3**, 7.38, 6.81, 2.20; **4**, 7.19, 6.53, 1.98, 1.89; *E* ring of *Z,E* isomer: **2**, 6.92, 2.21; **3**, 7.70, 7.15, 2.41; **4**, 7.58, 6.80, 2.24, 2.13. The *Z,E* isomer content is 12%, 16% and 15%, respectively.

NOE data for **4**: NOEDIFF.AUR, Bruker AM-400, 400.13 MHz, 30 °C, ~ 0.2 M degassed solution in 4:1 $CS_2/CDCl_3$. Acquisition parameters: 32 K data points; spectral width 3012 Hz; digital resolution 0.1 Hz point^{-1}; pulse width 11 μs (90°); relaxation delay 48 s; irradiation time 12 s; irradiation power 40 dB below 0.2 W; number of scans 272. Irradiation Me^{3,5} resonance (δ 2.09 s) produces a 19% increase in the H^4 signal intensity (δ 6.62 s) and a 2% increase in the H$^{3',5'}$ signal intensity (δ 7.37 s), indicating a proximity of rings which is only possible in the *Z,Z* isomer.

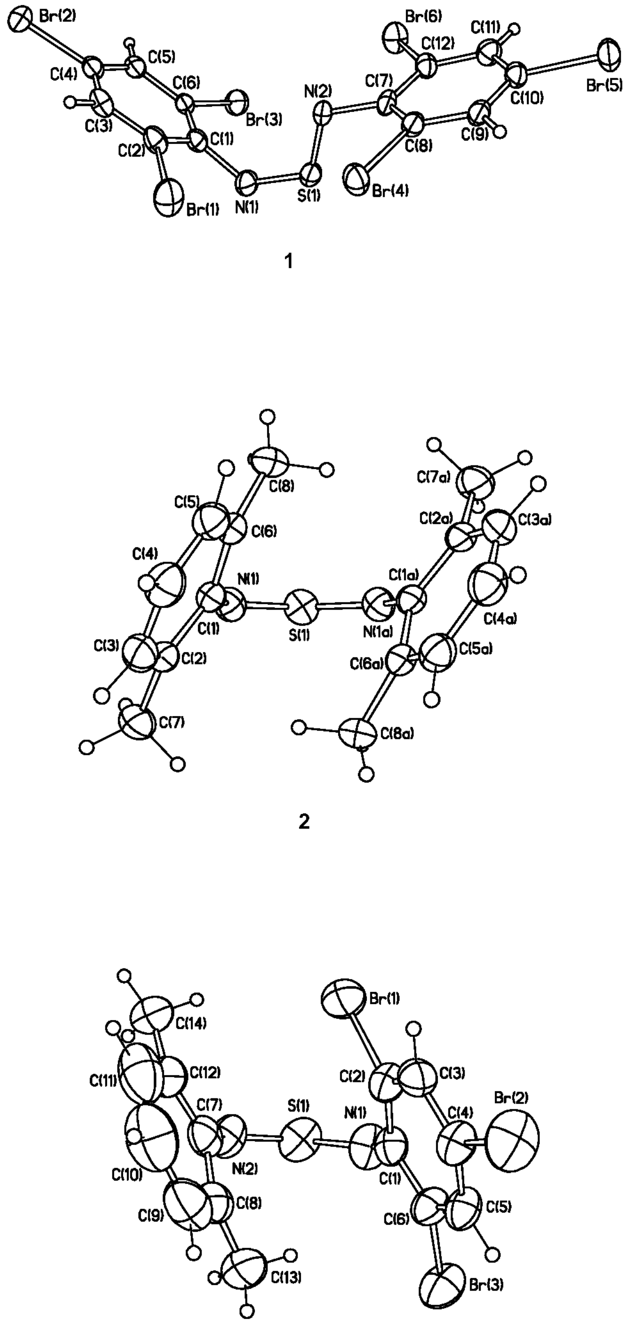

Fig. 1 Structure of molecules **1**–**3**. Selected bond lengths (A), valence and torsion angles (°). **1**: S(1)–N(1) 1.510(7), S(1)–N(2) 1.523(7), N(1)–C(1) 1.43(1), N(2)–C(7) 1.423(9), av. C–Br 1.896, av. C–C 1.380; N(1)–S(1)–N(2) 115.8(4), S(1)–N(1)–C(1) 125.3(6), S(1)–N(2)–C(7) 116.0(5), S(1)–N(1)–C(1)–C(2) -86(1), S(1)–N(2)–C(7)–C(8) -86.0(8). **2**: [N(1a)–C(8a) obtained from basic atoms by $1-x$, y, $3/2-z$ transformation]: S(1)–N(1) 1.526(2), N(1)–C(1) 1.423(3), av. C–Me 1.501, av. C_{ar}–C_{ar} 1.386; N(1)–S(1)–N(1a) 127.2(2), S(1)–N(1)–C(1) 131.8(2), S(1)–N(1)–C(1)–C(6) 62.8(5). **3** (two independent molecules): S(1)–N(1) 1.527(8), 1.518(9); S(1)–N(2) 1.547(8), 1.504(8); N(1)–C(1) 1.42(1), 1.41(1); N(2)–C(7) 1.40(1), 1.44(1); av. C–Br 1.89; av. C–Me 1.51, av. C_{ar}–C_{ar} 1.38; N(1)–S(1)–N(2) 126.1(4), 126.5(5); S(1)–N(1)–C(1) 132.5(6), 133.7(6); S(1)–N(2)–C(7) 130.1(7), 131.4(7); S(1)–N(1)–C(1)–C(2) −67(1), 71(1); S(1)–N(2)–C(7)–C(8) −69(1), 69.1.

References

1 G. Leandri, V. Busetti, G. Valle and M. Mammi, *J. Chem. Soc., Chem. Commun.*, 1970, 413.
2 V. Busetti, *Acta Crystallogr., Sect. B*, 1982, **38**, 665.
3 J. Kuyper and K. Vrieze, *J. Organomet. Chem.*, 1975, **86**, 127.
4 W. Sicinska, L. Stefaniak, M. Witanowski and G. A. Webb, *J. Mol. Struct.*, 1987, **158**, 57.
5 A. V. Zibarev, A. O. Miller, Yu. V. Gatilov and G. G. Furin, *Heteroatom Chem.*, 1990, **1**, 443.
6 E. S. Levchenko and Z. I. Shokol, *Zh. Org. Khim.*, 1969, **5**, 472 [*J. Org. Chem. USSR (Engl. Transl.)*, 1969, 459].
7 S. C. Zimmerman, *Bioorg. Chem. Front.*, 1991, **2**, 33.
8 D. Neuhaus and W. Williamson, *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, Weinheim: VCH, 1989.
9 R. D. Suenram, F. J. Lovas and W. J. Stevens, *J. Mol. Spectrosc.*, 1985, **112**, 482.
10 D. G. Anderson, H. E. Robertson, D. W. H. Rankin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1989, 859.
11 J. Leitch, S. C. Nyburg, D. A. Armitage and M. J. Clark, *J. Cryst. Mol. Struct.*, 1973, **3**, 337.
12 F. P. Olsen and J. C. Barrick, *Inorg. Chem.*, 1973, **12**, 1353.
13 E. M. Holt, S. L. Holt and K. J. Watson, *J. Chem. Soc., Dalton Trans.*, 1974, 1357.
14 H. S. Rzepa and J. D. Woolins, *J. Chem. Soc., Dalton Trans.*, 1988, 3051.
15 R. M. Bannister and H. S. Rzepa, *J. Chem. Soc., Dalton Trans.*, 1989, 1609.
16 J. Kuyper, P. H. Isselmann, F. C. Mijlhoff, A. Spelbos and G. Renes, *J. Mol. Struct.*, 1975, **29**, 247.
17 C. N. R. Rao, P. K. Basu and M. S. Hegde, *Appl. Spectrosc. Rev.*, 1979, **15**, 1.
18 K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, Halsted Press, New York, 1981.

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