

The first stable R–N=S=N–H sulfur diimide

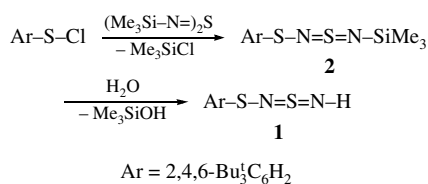
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The title sulfur diimide R–N=S=N–H with R = 2,4,6-Bu₃C₆H₂S was synthesised and structurally characterised; in the *Z,E* configuration, the SNSN plane orthogonal to the aromatic ring plane.

1,3-Disubstituted sulfur diimides R–N=S=N–R (R = Alk, Ar, etc.) are well-known reagents and ligands. However, the parent compound H–N=S=N–H is only spectroscopically detected^{1,2} under special conditions due to its enormous instability. Seemingly for the same reason, monosubstituted R–N=S=N–H derivatives have neither been isolated nor unambiguously characterised.^{2,3} This work deals with the synthesis and X-ray structural characterization of first stable R–N=S=N–H sulfur diimide **1** (R = 2,4,6-Bu₃C₆H₂S).



Scheme 1

In an one-pot two-step preparation procedure (Scheme 1),[†] the key step is the heterogeneous hydrolysis of precursor **2** by atmospheric moisture to substitute a hydrogen atom for the Me₃Si group. The kinetically unfavourable reaction conditions, as well as bulky *ortho* substituents in the aryl moiety, prevent compound **1** from further hydrolysis, and this target product is stable in air for at least several months.

According to X-ray crystallography data (Figure 1),[‡] crystalline compound **1** exists as the *Z,E* configuration. The sulfur–nitrogen fragment is planar to within ±0.012 Å and perpendicular to the mean plane of the aromatic ring [the dihedral angles are 89.1(1) and 89.9(1)° for two crystallographically independent molecules]. The aromatic ring reveals a minor boat-like distortion typical of 1-R-2,4,6-Bu₃C₆H₂ compounds.^{4,5}

In the N=S=N moiety of **1** the bond lengths are not identical. The terminal double bond (S=N–H) is slightly shorter than the internal one (Figure 1) but definitely longer than the bond distance of 1.517 Å observed by microwave spectroscopy in the *Z,E* isomer of H–N=S=N–H in a gas phase.¹ The N=S=N bond angle in **1** (Figure 1) also markedly differs from that found for the *Z,E* configuration of H–N=S=N–H (115.7°).¹ Note that the

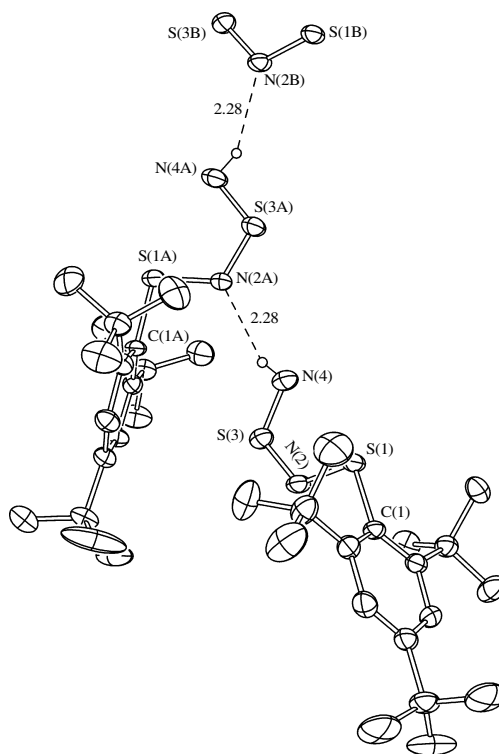


Figure 1 The molecular structure of compound **1**. Selected bond lengths (Å) for two crystallographically independent molecules: C(1)–S(1) 1.795(4), 1.798(4); S(1)–N(2) 1.672(4), 1.678(4); N(2)–S(3) 1.554(4), 1.557(3); S(3)–N(4) 1.546(4), 1.536(4); N(4)–H 0.78(4), 0.81(4); selected bond angles (°) C(1)–S(1)–N(2) 99.6(2), 99.5(2); S(1)–N(2)–S(3) 117.3(2), 117.8(2); N(2)–S(3)–N(4) 109.3(2), 110.2(2).

discussed geometrical parameters are different for the *Z,E* and *Z,Z* isomers of **1** detected in a gas phase.¹

In a crystal, the molecules of **1** form a hydrogen-bonded 1D network along the crystallographic axis *a* (Figure 1) featured a shortened⁶ N–H...N contact of 2.28 Å. Weak non-covalent interactions are of considerable interest because of their implication

[†] Synthesis and spectral properties of 4-[2,4,6-tri(tert-butyl)phenyl]-1,3-diaza-2,4-dithiabuta-1,2-diene **1** and 1-trimethylsilyl-4-[2,4,6-tri(tert-butyl)phenyl]-1,3-diaza-2,4-dithiabuta-1,2-diene **2**. In an argon atmosphere, to a stirred solution of 0.84 g (0.004 mol) of (Me₃SiN=)₂S¹⁴ in 10 ml of CH₂Cl₂ was added dropwise a solution of 1.25 g (0.004 mol) of 2,4,6-Bu₃C₆H₂SCl¹⁵ in 15 ml of the same solvent at 20 °C. After 2 h, the solvent was distilled off under a reduced pressure and the residual yellow oil (compound **2**) was exposed to air until solidification ceased (~2 weeks). The solid product was sublimed in a vacuum and recrystallised from hexane. Compound **1** was obtained in 80% yield (1.08 g) as transparent yellow needles, mp 117–118 °C. ¹H NMR (CDCl₃) δ: 9.33 (1H), 7.51 (2H), 1.50 (18H), 1.32 (9H). ¹³C NMR (CDCl₃) δ: 155.7, 153.3, 129.0, 123.3, 38.3, 35.2, 32.9, 31.1. ¹⁵N NMR [NH₃ (liq.)] δ: 310, 260. UV [heptane, λ_{max}/nm (log ε)]: 351 (3.93). MS, *m/z*: 338.1859 (M⁺; calc. for C₁₈H₃₀N₂S₂ 338.1850).

Compound **2**: yellow oil, non-distillable in a vacuum of 0.01 Torr, 1.60 g (~100%). ¹H NMR (CDCl₃) δ: 7.55 (2H), 1.55 (18H), 1.37 (9H), 0.11 (9H). MS, *m/z*: 410 (M⁺; calc. for C₂₁H₃₈N₂S₂Si 410).

Variable-temperature ¹H NMR spectra of compound **1** were measured for a solution in [D₈]toluene at 295–173 K.

[‡] X-ray crystal data. Compound **1**: C₁₈H₃₀N₂S₂, *M* = 338.56, triclinic, *a* = 10.3461(16), *b* = 12.148(2) and *c* = 16.403(3) Å, α = 81.494(13)°, *b* = 88.645(11)°, γ = 88.979(12)°, *V* = 2038.2(6) Å³, space group *P*1̄, *Z* = 4, *d*_{calc} = 1.103 g cm^{−3}, μ(MoKα) = 0.261 mm^{−1}, *F*(000) = 736.

A single crystal for X-ray crystallography was prepared by the slow evaporation of a solution of compound **1** in toluene. The data were measured on a Bruker P4 diffractometer with graphite monochromated MoKα radiation using θ/2θ scans (2θ < 50°). The structure was solved by the direct methods using the SHELXS-86 program and refined in the full-matrix anisotropic (isotropic for H atoms) approximation by the SHELXL-97 program. Measured independent reflections 7166, observed reflections [|*F*_o| > 4σ(*F*_o)] 3013, *R*_{obs} = 0.0651, *wR*₂ (all data) = 0.1672, *S* = 0.849.

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.*, Issue 1, 2002. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/115.

in regulating the arrangement of organic molecules in crystalline solids. In particular, the hydrogen bonds are known to be a general supramolecular motif of significant importance with regard to new developments in crystal engineering.^{6,7}

In the solid state, the closest structural analogues of compound **1** with a known real geometry, *i.e.*, the compounds $n\text{-O}_2\text{NC}_6\text{H}_4\text{-S-N=S=N-SiMe}_3$ ($n = 4,^8 2^9$), $6\text{-HC}_6\text{F}_4\text{-S-N=S=N-SiMe}_3$ ¹⁰ and $4\text{-RC}_6\text{H}_4\text{-S-N=S=N-C}_6\text{H}_4\text{R}'\text{-4}$ ($\text{R} = \text{R}' = \text{H};$ ¹¹ $\text{R} = \text{NO}_2$, $\text{R}' = \text{OMe}$ ¹²), all possess the same *Z,E* configuration (with the ArS group in the *Z* position) featured a planar sulfur–nitrogen fragment. In contrast to **1**, however, the molecular conformations are planar or nearly planar with the only exception for the methoxy derivative¹² where the dihedral angle between $4\text{-MeOC}_6\text{H}_4$ and $\text{NSNSC}_6\text{H}_4\text{NO}_2\text{-4}$ planes is $\sim 40^\circ$.

In the ^1H NMR spectra of compound **1**, the signal of the N–H group is solvent sensitive and shifted downfield on going from toluene ($\delta^1\text{H}$ 9.07) to chloroform ($\delta^1\text{H}$ 9.33). Variable-temperature ^1H NMR spectra of compound **1** display fast isomeric equilibrium in solution inherent in sulfur diimides.^{5,13} Thus, the singlets at 9.07 (N–H), 7.51 (aromatic C–H) and 1.50 ppm ($2,6\text{-Bu}_2$) are sharp at 22°C but definitely broadened at -20°C . At -90°C , the signal of the N–H group is resolved into two peaks with $\delta^1\text{H}$ 9.57 and 9.38 (the intensity ratio is $\sim 4:1$), whilst the other above broadened signals are not resolved even at -100°C . The signal at 1.32 ppm (4-Bu^1) is independent of temperature.

Thus, sterically hindered (kinetically stabilised) compound **1** was prepared and structurally characterised as the first stable R-N=S=N-H sulfur diimide.

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References

- 1 R. D. Suenram, F. J. Lovas and W. J. Stevens, *J. Mol. Spectrosc.*, 1985, **112**, 482.
- 2 A. Haas, U. Fleischer, M. Maetschke and V. Staemmler, *Z. Anorg. Allg. Chem.*, 1999, **625**, 684.
- 3 M. Herberhold, W. Jellen, W. Buehlmeier, W. Ehrenreich and J. Reiner, *Z. Naturforsch., B*, 1985, **40**, 1229.
- 4 F. H. Allen and O. Kennard, *Chemical Automation Design News*, 1993, **8**, 31.
- 5 I. Yu. Bagryanskaya, Yu. V. Gatilov and A. V. Zibarev, *Mendelev Commun.*, 1999, 157.
- 6 L. N. Kuleshova and M. Yu. Antipin, *Usp. Khim.*, 1999, **68**, 3 (*Russ. Chem. Rev.*, 1999, **68**, 3).
- 7 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
- 8 R. Jones, D. J. Williams, R. T. Wood and J. D. Woollins, *Polyhedron*, 1989, **8**, 91.
- 9 A. V. Zibarev, Yu. V. Gatilov, I. Yu. Bagryanskaya and S. N. Konchenko, *Polyhedron*, 1992, **11**, 2787.
- 10 A. Yu. Makarov, I. Yu. Bagryanskaya, F. Blockhuys, C. van Alsenoy, Yu. V. Gatilov, V. V. Knyazev, A. M. Maksimov, T. V. Mikhulina, V. E. Platonov, M. M. Shakirov and A. V. Zibarev, *Eur. J. Inorg. Chem.*, in press.
- 11 I. Yu. Bagryanskaya, Yu. V. Gatilov, M. M. Shakirov and A. V. Zibarev, *Zh. Strukt. Khim.*, 1996, **37**, 363 [*J. Struct. Chem. (Engl. Transl.)*, 1996, **37**, 318].
- 12 K. Bestari, R. T. Oakley and A. W. Cordes, *Can. J. Chem.*, 1991, **69**, 94.
- 13 (a) I. Yu. Bagryanskaya, Yu. V. Gatilov, M. M. Shakirov and A. V. Zibarev, *Mendelev Commun.*, 1994, 167; (b) I. Yu. Bagryanskaya, Yu. V. Gatilov, M. M. Shakirov and A. V. Zibarev, *Mendelev Commun.*, 1994, 136.
- 14 I. Yu. Bagryanskaya, Yu. V. Gatilov, A. O. Miller, M. M. Shakirov and A. V. Zibarev, *Heteroatom Chem.*, 1994, **5**, 561.
- 15 R. Mayer, D. Decker, S. Bleisch and G. Domschke, *J. Prakt. Chem.*, 1987, **329**, 81.

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