The first stable R–N=S=N–H sulfur diimide
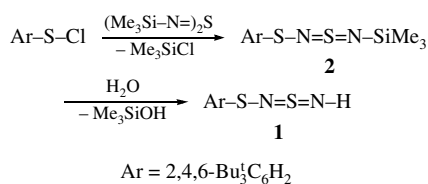
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The title sulfur diimide R–N=S=N–H with R = 2,4,6-Bu$_3^t$C$_6$H$_2$S was synthesised and structurally characterised; in the *Z,E* configuration, the SNSN plane orthogonal to the aromatic ring plane.

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-Bu$_3^t$C$_6$H$_2$S).

$$\text{Ar–S–Cl} \xrightarrow[\text{– Me}_3\text{SiCl}]{\text{(Me}_3\text{Si–N=)}_2\text{S}} \underset{\textbf{2}}{\text{Ar–S–N=S=N–SiMe}_3}$$

$$\xrightarrow[\text{– Me}_3\text{SiOH}]{\text{H}_2\text{O}} \underset{\textbf{1}}{\text{Ar–S–N=S=N–H}}$$

$$\text{Ar = 2,4,6-Bu}_3^t\text{C}_6\text{H}_2$$

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 Me$_3$Si 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-Bu$_3^t$C$_6$H$_2$ 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
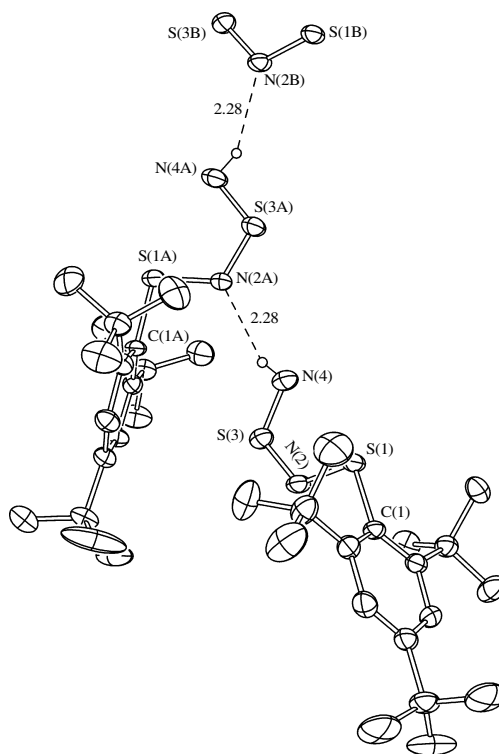

Figure 1 The molecular structure of compound **1**. Selected bond lengths (Å) for two crystallographically independent molecules: C(1)–S(1) 1.795(4), 1.798(4); S(1)–N(2) 1.672(4), 1.678(4); N(2)–S(3) 1.554(4), 1.557(3); S(3)–N(4) 1.546(4), 1.536(4); N(4)–H 0.78(4), 0.81(4); selected bond angles (°) C(1)–S(1)–N(2) 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 shortened[6] N–H···N contact of 2.28 Å. Weak non-covalent interactions are of considerable interest because of their implication

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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 $n\text{-}O_2NC_6H_4\text{-}S\text{-}N{=}S{=}N\text{-}SiMe_3$ ($n = 4$,[8] 2[9]), $6\text{-}HC_6F_4\text{-}S\text{-}N{=}S{=}N\text{-}SiMe_3$[10] and $4\text{-}RC_6H_4\text{-}S\text{-}N{=}S{=}N\text{-}C_6H_4R'\text{-}4$ ($R = R' = H$;[11] $R = NO_2$, $R' = OMe$[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 derivative[12] where the dihedral angle between $4\text{-}MeOC_6H_4$ and $NSNSC_6H_4NO_2\text{-}4$ planes is ~40°.

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 (δ^1H 9.07) to chloroform (δ^1H 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 ($2,6\text{-}Bu_2^t$) 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 δ^1H 9.57 and 9.38 (the intensity ratio is ~4:1), whilst the other above broadened signals are not resolved even at –100 °C. The signal at 1.32 ppm ($4\text{-}Bu^t$) 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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