Three-Membered Ring Formation by Si···N Interactions in Aminosulfenylsilanes

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The reaction of dimethylaminosulfenylchloride Me_2NSCl with trichlorosilane $HSiCl_3$ and triethylamine gives elemental sulphur and Me_2NSiCl_3. The aminosulfenylsilane $Me_2NSSiCl_3$ is postulated to be an intermediate of this reaction. *Ab initio* calculations (MP2/6–311G(d,p)) on Me_2N-S-SiH_3, Me_2N-S-SiH_2Cl, Me_2N-S-SiH_2F, and Me_2N-S-$SiCl_3$ have been carried out, demonstrating the occurrence of acute valence angles at sulphur and short Si···N distances, which are indicative of NSSi three-membered rings. The strength of the Si···N interactions depends on the electronegativity of the substituent at silicon in *anti*-position to the nitrogen atom and is strongest in the *anti* conformer of Me_2N-S-SiH_2F (< NSSi 68°, Si···N 2.208 Å). The coordination spheres of the nitrogen atoms in the Me_2N-S-SiR_3 molecules are steeply pyramidal, which is in contrast to the planarised N atoms in other $SNMe_2$ compounds, such as Me_2NSCl. The crystal structure of this compound has been determined, as well as that of the product of the above reaction, Me_2NSiCl_3. Both have planar coordination geometries at the nitrogen atoms.

Key words: Sulfur, Silicon, Crystal Structure