Nitrogen Inversion Barrier and Nature of the Si–N Bond in Silylamine: an *ab initio* SCF-LCAO-MO Study

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Summary The electronic structure (nature of the N–Si bond, *d*-orbital participation) and the energy barrier to nitrogen inversion in silylamine have been studied using extended Hartree–Fock SCF-LCAO-MO calculations.

The electronic structure and the molecular properties of compounds containing bonds between first- and second-row elements have been subject to many experimental and theoretical investigations, one of the main concerns being the effect of the *d*-orbitals of the second-row element.[1] Trico-ordinated nitrogen sites bearing directly linked silicon,[†][2] phosphorus,[3,4] or sulphur[4,5] atoms are either planar or present low barriers to pyramidal inversion.

Within the framework of our theoretical studies of structural effects on inversion barriers[6,7] we report here some results of extended Hartree–Fock calculations of silylamine, SiH_3–NH_2. Calculations have been performed with the general program IBMOL[8] using a basis set of Gaussian functions: (12 . 9/5) for the SiH_3 group[9] and (10 . 6/5) for the NH_2 group[10][‡] (Sub-case SC 1); to these orbitals, a set of *d*-functions on N (exponent d_N 1·0) and a set of *p*-functions on H of the NH_2 group (exponent p_H 0·50) have been added (Sub-case SC 2); further additions comprise two sets of *d*-functions on Si (exponents d_1 0·75 and d_2 0·15) (Sub-case SC 3).[§] This basis set: SiH_3 (12 . 9 . 2/5), NH_2 (10 . 6 . 1/5 . 1) has then been contracted into: SiH_3 (6 . 4 . 2/2), NH_2 (4 . 2 . 1/2 . 1). The molecular geometry has been adapted from $(SiH_3)_2NH$.[2] Calculations have been performed for four values of the pyramidality angle ϕ: 0, 15, 35, and 60° without further geometry optimization. The variations of total energy as a function of ϕ are shown in the Figure for SC 1, SC 2, and SC 3.

We describe here the results concerning the nitrogen inversion barrier and the nature of the Si–N bond.

(i) In SC 3, silylamine is found to be non-planar with an energy minimum of $-346{\cdot}28821$ a.u. at $\phi = 30° 45'$. The total energy for $\phi = 0°$ amounts to $-346{\cdot}28717$, giving a barrier to nitrogen inversion

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[†] *N*-Silylaziridine derivatives display very low inversion barriers (probably below 6 kcal mole^{-1}) (ref. 3).

[‡] Basis set composition is given using the following convention: (number of *s*-functions . number of *p*-functions . number of *d*-functions on heavy atom/number of *s*-functions . number of *p*-functions on hydrogen atom): (*s* . *p* . *d*/*s* . *p*).

[§] Because of the length of the computations and the need of computing several geometries at the NH_2 site, no *p*-functions have been added to H in the SiH_3 group. This unbalances the basis set and locally affects the population analysis in the SiH_3 group. It should however leave the Si–N bond and even more so the NH_2 site nearly unaffected. A calculation including p_H-functions for the SiH_3 group will be described in the final report.

of 0·65 kcal mol^{-1}. This low barrier (the inversion barrier of NH_3 amounts to 5·8 kcal mol^{-1}) is in agreement with the planar structure of $(SiH_3)_2NH$[2] and with the low inversion barriers ($\leqslant$ 6 kcal mol^{-1}) in *N*-silylaziridines.[3] Analysis of the energy components shows that the barrier is of the attractive type.[11]

(ii) Silylamine is found to be planar when no *d*-functions on nitrogen are included in the basis set (SC 1). Thus the presence of *d* polarization functions on the inverting site has a marked effect on inversion barriers.¶ In addition, it is seen (Figure) that d_N and p_H-functions on the NH_2 group (SC 2) flatten the energy curve.

(iii) In the absence of *d*-functions on Si (SC 2), the energy minimum (−346·22776) is at $\phi = 32° 5'$, and the inversion barrier amounts to 0·8 kcal mol^{-1}. Thus, the presence or the absence of *d*-orbitals on Si leaves the inversion barrier and the geometry at the nitrogen site nearly unaffected. In terms of empirical effects, the barrier decrease from NH_3 to SiH_3–NH_2 may be ascribed to inductive release of electron density from Si to N** but not to $(d$–$p)\pi$-conjugation.

(iv) The inclusion of *d*-functions on Si increases the total Si–N overlap population from 0·6 (SC 1) to 0·85 (SC 3) electron and leads to a 0·25 electron population transfer from N to Si [*ca.* 0·1 electron transfer from $N(p_z)$ in the highest occupied MO (HOMO)]. π-Type contributions to the Si–N bond arise from $Si(d_{xz^2})$–$N(p_z)$ overlap [0·13 overlap population due almost entirely to the HOMO (nitrogen lone pair MO)] and from $Si(p_z)$–$N(p_z)$ overlap (0·1). Because of negative overlap populations, the total *d* gross atomic population on Si is zero; the largest individual gross population is found to be $Si(d_{xz}) = 0·14$ arising almost entirely from d_2 in the HOMO. It should also be noted that the addition of d_1 and d_2 to SC 1 leads only to a very small decrease in total energy (0·015 a.u.). (These results are all for the form $\phi = 35°$). It is difficult to decide whether these results should be interpreted as $(d$–$p)\pi$-bonding in the usual chemical sense or as a polarization[15] effect of the *d*-functions on Si. These functions participate only weakly in molecular bonding. However, the HOMO is clearly a π-type MO containing mainly $Si(d_{xz})$ (0·14 e) and $N(p_z)$ (1·22 e) and corresponds quite closely to the usual picture of (weak) $(d$–$p)\pi$-conjugation between the nitrogen lone pair and the silicon *d*-orbitals (see also semi-empirical calculations on trisilylamine[16]).

(v) As inversion proceeds, electron density is transferred into the nitrogen $2p_z$ orbital (+ 0·1) and the Si–N overlap population increases very slightly (+0·04). The $(d_{xz}$–$p_z)$ Si–N π-type overlap is the same in the transition state ($\phi = 0°$) (only +0·02 increase) as in the ground state ($\phi = 35°$). In the transition state the HOMO contains 70% $N(2p_z)$, 7% $Si(d_{xz})$, and 12% $H_1(s)$.

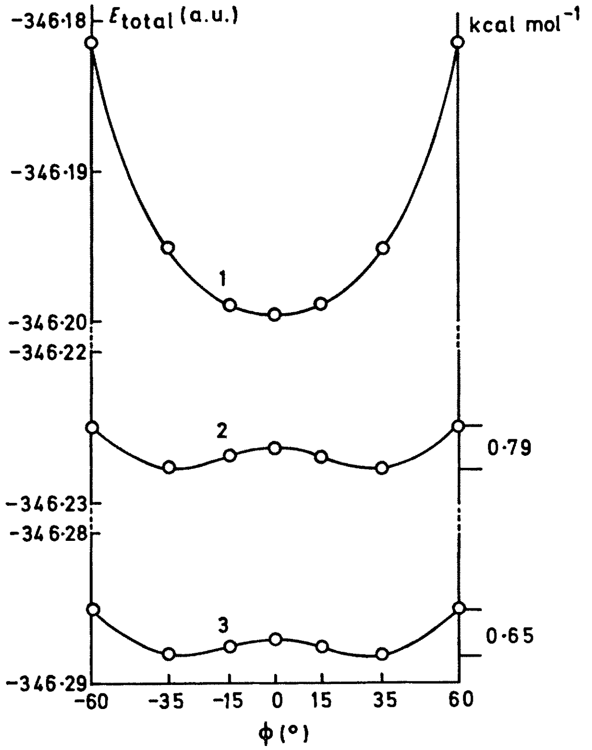
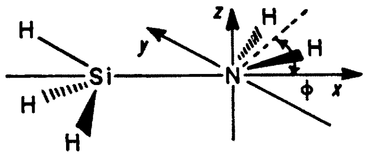


FIGURE. *Variation of the total energy of the* SiH_3–NH_2 *molecule during nitrogen inversion in the three cases* SC1, SC2, *and* SC3 (*see text*).



In conclusion, Si–N$(d$–$p)\pi$-overlap contributes only weakly to the molecular stability in the electronic ground state of silylamine, but a specific participation to the HOMO is found.††

Silicon *d*-orbital effects are very similar in the ground and transition states of the nitrogen inversion process and it is

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¶ The importance of *d*-functions on N in the computation of nitrogen inversion barriers has also been demonstrated for ammonia (ref. 12), fluoramine (ref. 13), and cyanamide (ref. 13).

** Electron-attracting substituents are known to raise the barrier (see references in ref. 14).

†† To assess the importance (and the relevance) of the $(d$–$p)\pi$-bonding problem it would be very instructive: first, to compare the Si–N bond of silylamine to the C–N bond of methylamine (with *d*-functions on C and N); second, to compare the amount of π-type character in the Si–N bond of silylamine to that in the N(1)–C bond of cyanamide (ref. 13) $H_2N(1)$–CN, where the presence of lone-pair conjugation [$(p$–$p)\pi$-type] is generally accepted. These points will be discussed in the final account of this work.

not necessary to invoke increased (*d–p*) π-conjugation in the transition state to explain the low nitrogen inversion barriers and the flattened or planar nitrogen sites found in silylamines.

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