On the Nature of the Si=N Double Bond and the Ease of Bending at Nitrogen

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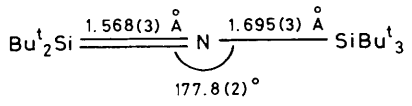
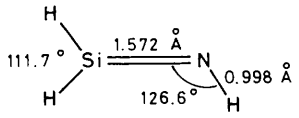
Ab initio calculations (6–31G* basis set) indicate $H_2Si{=}NH$ to be bent (∠SiNH = 126.6°), but to have a low linearization barrier (6.0 kcal/mol at MP4/6–31G*) so that, in accord with experimental results, an electropositive SiH_3 substituent at nitrogen results in a nearly linear structure (∠SiNSi = 175.6°); the Si=N double bond is 54.1 kcal/mol weaker than two Si–N single bonds whereas the corresponding difference is only 1.6 kcal/mol for C=N *vs.* two C–N bonds. (1 cal = 4.184 J.)

Compounds with double bonds to second row elements, once thought to be practically non-existent, are now being synthesized with increasing frequency.[1,2] Room temperature stability can often be achieved by the use of bulky substituents, which prevent further reactions. In this manner, Wiberg *et al.*[2] were able to prepare (**1**), the first silylimine derivative. *X*-Ray analysis showed characteristic bond lengths, Si=N 1.568(3), Si–N 1.695(3) Å, and a nearly linear Si–N–Si angle of 177.8(2)°. This widening was attributed either to steric repulsions between the bulky substituents or to electrical effects of the $SiBu^t_3$ group.

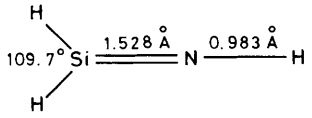
Such experimental successes notwithstanding, theoretical calculations contribute detailed information concerning the bonding, electronic structures, and energies of such systems, and have the advantage that the parent compounds, devoid of possible substituent effects, can be studied. Indeed, $H_2Si{=}NH$ structures (**2**) and (**3**) were included in our recent survey of silicon compounds with multiple bonds.[1] The calculated SiNH bond angle differed significantly at the two theoretical levels employed, 132.8° at 3–21G (a small split valence basis set), but 180.0° at 3–21G(*) (3-21G augmented with d functions but only on silicon). However, both of these basis sets, are likely to be deficient for such applications; d-type polarization functions are known to be necessary for the adequate description of valence angles in ammonia and for the estimation of its inversion barrier.[3a,b] The same may apply to imino nitrogen. In view of Wiberg's experimental results, we have repeated our calculation at a higher level of theory



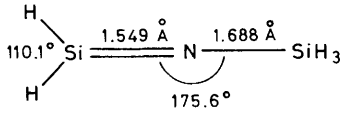
(1)



(2), C_s



(3), C_{2v}



(4), C_s

(6–31G*, with d-functions on both N and Si),[4] which one can employ with confidence for such problems.[3a] The 6–31G* geometry of (**4**) is in good agreement with the *X*-ray results on (**1**). The SiNSi angle is 175.6°, the N–Si single bond length is 1.688 Å, and the Si=N length is 1.549 Å, only slightly shorter than that found by experiment. This difference may well be due to substituent effects in (**4**). However, it seems clear that electronic rather than steric effects are responsible for the nearly linear SiNSi arrangement in (**1**) and (**4**).

The 6–31G* SiNH angle in (**2**) is 126.6°, substantially smaller than that found in (**1**) and in (**4**). However, as suspected by Wiberg,[2] the bending potential energy surfaces are quite flat. The barrier to linearization of (**2**) is 3.3 kcal/mol† at 6–31G* and only somewhat higher, 6.0 kcal/mol, when electron correlation corrections are taken into account (MP4/6–31G*//6–31G*).

$$H_2C{=}NH + SiH_2(^1A_1) \rightarrow \underset{(2)}{H_2Si{=}NH} + CH_2(^3B_1) + 49.2\ \text{kcal/mol} \quad (1)$$

$$H_2Si{=}NH + SiH_4 + NH_3 \rightarrow 2H_3Si{-}NH_2 - 54.1\ \text{kcal/mol} \quad (2)$$

(**2**)

Based on equation (1) and MP4/6–31G*//3–21G(*) data corrected for zero point energy (ZPE) differences, we estimated the bond dissociation energy of the double bond in $H_2Si{=}NH$ to be 55.1 kcal/mol smaller than that of the double bond in $H_2C{=}NH$.[1] (Refined at MP4/6–31G*//6–31G* + ZPE, this value becomes 49.2 kcal/mol.) However, bond energies are often defined differently.[3a] For example, equation (2), evaluated at MP4/6–31G*//6–31G* + ZPE, indicates the Si=N double bond in (**2**) to be 54.1 kcal/mol weaker than two Si–N single bonds. Each of the latter have been estimated to have a bond strength of 98.7 kcal/mol.[1] On this basis, the total strength of the Si=N double bond is 143.3 kcal/mol, or only 44.6 kcal/mol higher than that of a Si–N single bond.

† 1 cal = 4.184 J.

By comparison, the C=N double bond is only 1.6 kcal/mol weaker than two C–N single bonds, equation (3). Since the dissociation energy [D°_{298} ($MeNH_2$)] is 84.9 ± 1.1 kcal/mol,[5] the total C=N bond energy is 168.2 kcal/mol or 83.2 kcal/mol higher than that of a C–N bond. While, on this basis, the *total* energy of the Si=N double bond is only 24.9 kcal/mol weaker than its C=N counterpart, the difference in π-bond contributions is larger, 38.6 kcal/mol.

$$H_2C{=}NH + CH_4 + NH_3 \rightarrow 2H_3C{-}NH_2 - 1.6\ \text{kcal/mol} \quad (3)$$

The nature of the bonding in these compounds is revealed by natural population analysis using natural localized molecular orbitals.[6] This method is superior to Mulliken analysis, *e.g.*, in being largely basis set independent. Both the Si–N σ- and π-bonding orbitals in (**2**)—(**4**) are all strongly polarized, with 74—82% of the electron density centered on the more electronegative nitrogen. The nitrogen charges increase from (**2**) (−1.38), to (**3**) (−1.46), to (**4**) (−1.72); the Si charges change correspondingly in the positive direction. The Si=N bond length, 1.573 Å in (**2**), becomes substantially shorter (1.528 Å) on linearization (**3**). This strengthening of the Si=N double bond on linearization, due to the increase in the s contribution to nitrogen hybridization [from $sp^{1.4}$ in (**2**) to $sp^{0.7}$ in (**3**)], compensates for the angle distortion at nitrogen. The net result is a considerably lower linearization barrier than that calculated for $H_2C{=}NH$ at the same level, 32.7 kcal/mol.[1] This difference is due mainly to the larger electronegativity difference between silicon and nitrogen than between carbon and nitrogen.[7] In (**2**)—(**4**), the nitrogen lone pair is delocalized only to a small (3—5%) extent into empty silicon orbitals. Since these orbitals are comprised of 5 to 6 times more p- than d-character, valence shell expansion ['$(d–p)_\pi$ bonding'] is insignificant. Similarly, the large SiNSi bond angles in (**1**) and (**4**) are due largely to electronegativity effects.[7]

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