# Density Functional Studies on Amino-Substituted Methane and Silane

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In all-electron density functional calculations on mono- and tetraaminosubstituted methane and silane the coordination around the nitrogen center is found, in complete agreement with experiment, to be less pyramidal in the silicon compounds. The calculated barrier to inversion at nitrogen is only 0.6 kcal/mol in silylamine, while in methylamine it is 5.5 kcal/mol. The larger flexibility is attributed to the greater ionic character of the Si−N bond compared to that of the C−N bond. In tetra(amino)methane, inversion of one amino group leads to a local minimum (calculated inversion barrier: 6.4 kcal/mol), while a corresponding structure (or barrier) does not exist for the silicon compound. Due to the steric influence of the amino groups, the barrier to rotation around the C−N bond is larger in the tetrasubstituted compound (6.4 kcal/mol compared to 2.3 kcal/mol in methylamine). While the average binding energy of the amino groups is similar in both tetra(amino)compounds, the binding energy of the fourth ligand is about 25% larger in the silicon compound for both homolytic and heterolytic bond cleavage. This difference arises from the relative stabilization of the tri(amino)methyl species, due to some π contribution to the C−N bond.

Replacing one hydrogen atom in methane by an amino group leads to methylamine, an experimentally and theoretically well-characterized compound. The silicon analogue of this compound, silylamine, has not yet been synthesized, but numerous theoretical studies have been devoted to it[1][2][3][4][5][6][7][8]. A comparison of the two molecules is interesting insofar as the geometry of the amino group differs: while the coordination of the nitrogen atom in methylamine is almost tetrahedral, most investigations concerning silylamine find the geometry of the amino group to be planar or almost planar[1][2][3][4][5]; nevertheless, a pyramidal structure has also been proposed[6][7]. There has been some controversy about whether an interaction of the nitrogen lone pair with the empty d-orbitals of silicon leads to planarity at nitrogen, but no evidence for this could be found[2][3][4][6][8]. The compounds formed by substitution of all four hydrogen atoms of methane and silane, tetra(amino)methane and tetra(amino)silane, are not known, but the dimethylamino derivatives could be synthesized[9][10]. Crystal structure data are only available for the carbon compound[10]. Systematic studies on $X(NR)_4$ ($X = C, Si$), for different substituents R, show that the geometry at the nitrogen center is strongly pyramidal for $X = C$, while the configuration for $X = Si$ depends on the group R[9][10]. These observations prompted us to investigate aminosubstituted methane and silane to answer the following questions: (i) What is the reason for the different degree of pyramidalization at nitrogen? (ii) Are the amino groups flexible in the sense that the energy difference between a pyramidal and a planar configuration, and possible barrier heights, are small?

We started our investigations with monosubstituted methane and silane since these compounds contain the relevant $XNH_2$ groups ($X = C, Si$) and then proceeded to the more complex tetrasubstituted compounds. To the best of our knowledge, no thorough theoretical investigation of the tetraamino compounds has been published so far. However, the bond dissociation energy for tetra(amino)silane has been calculated at the Hartree-Fock/MP4 level, however, no structural parameters were reported[7].

## Computational Details

All calculations have been performed with the Gaussian 94[11] package at the DF level using the 6-31G** basis set[12][13][14][15][16]. Density gradient corrected energy functionals (BLYP[17][18] or B3LYP[18][19][20]) were used throughout. Unless otherwise stated, the values given in the text refer to B3LYP calculations. All molecules were subjected to full geometry optimization. The partial optimization of structures which do not correspond to a stationary point of the potential energy surface have been carried out under the symmetry restrictions mentioned in the text. Transition states have been searched based on the algorithm proposed by Schlegel[21]. The atomic charges are derived from a Mulliken population analysis and from a Bader analysis ("atoms in molecules approach")[22][23][24]. In the Tables, the following generalized formulas are used: $XH_n(NH_2)_{4-n}$ where $X = C$ or Si, and $n = 0$ or 3.

### Methylamine $CH_3NH_2$ and Silylamine $SiH_3NH_2$

The calculated geometries of methylamine and silylamine are displayed in Figure 1[25] In Table 1 they are compared to experimental values for methylamine and *N*-silyldimethylamine (there are no experimental data available for silylamine)[26][27]. The geometrical parameters of methylamine obtained with the BLYP and B3LYP functionals compare well

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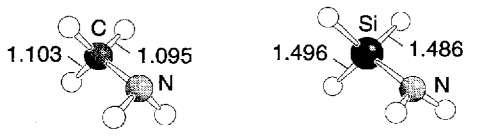
with experiment, BLYP yielding slightly longer bond lengths (up to 0.016 Å). Both molecules exhibit $C_s$ symmetry and a staggered equilibrium structure. The methyl and silyl groups are tilted away from the hydrogens of the amino group leading to two different N−X−H angles. Both molecules are non-planar at the nitrogen center. In the carbon compound the angle θ of the bisector of the amino group with the C−N bond (θ = 124.1°) is somewhat larger than the corresponding calculated angle in ammonia (θ = 116.7°). The tilt of the amino group is much less pronounced in the silicon compound, the angle θ (148.1°) is midway between the value in ammonia and a planar configuration. The different geometry around nitrogen in the two compounds may be rationalized with the help of the Valence Shell Electron Pair Repulsion Model (VSEPR)[28]. According to this model, a lone pair requires more space than a bonding electron pair since its charge density is closer to the central atom. Methylamine and silylamine may be viewed as an ammonia molecule in which one H atom is substituted by a $CH_3$ or $SiH_3$ group. The larger atomic radii of these moieties lead to a larger tilt angle θ in the substituted compounds as compared to ammonia. Since Si is less electronegative than C (Si: 1.8; C: 2.5[29]), the electronic charge density is displaced towards the nitrogen atom causing an increased repulsion, with the two hydrogen atoms bound to the nitrogen center. A larger degree of pyramidalization in the carbon compound is also in accordance with Bent's rule which states that atomic p character is concentrated in orbitals which are directed towards more electronegative substituents[30].

Table 1. Comparison of experimental and calculated bond lengths [Å] and bond angles [°] of methylamine and silylamine

| | $CH_3NH_2$ | | | $SiH_3NH_2$ | | |
|---|---|---|---|---|---|---|
| | exp.[a] | BLYP | B3LYP | exp.[b] | BLYP | B3LYP |
| d(X−N) | 1.471 | 1.479 | 1.464 | 1.715 | 1.752 | 1.736 |
| d(X−H) | 1.095 | 1.105[c] | 1.098[c] | 1.485 | 1.498[c] | 1.489[c] |
| d(N−H) | 1.019 | 1.027 | 1.017 | −[d] | 1.021 | 1.012 |
| ∠(H−X−H) | 108.1 | 107.4[c] | 107.4[c] | 109.5 | 108.1[c] | 108.1[c] |
| ∠(H−N−H) | 106.6 | 104.9 | 105.9 | 111.1[e] | 109.5 | 110.2 |
| ∠(X−N−H) | 110.3 | 108.9 | 109.7 | 120.0[f] | 117.8 | 119.1 |
| tilt angle θ | 125.5 | 122.1 | 124.1 | 152.2 | 143.9 | 148.1 |

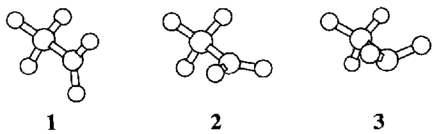
[a] Ref.[26]. − [b] Experimental structure of $SiH_3N(CH_3)_2$[27]. − [c] Average value; see Figure 1. − [d] $d(N-CH_3) = 1.462$. − [e] ∠($H_3C-N-CH_3$). − [f] ∠($Si-N-CH_3$).

Figure 1. SCHAKAL[25] plot of the optimized structures (B3LYP) of methylamine (left) and silylamine (right). Bond lengths in Å



The question arises, whether the different degree of pyramidalization at nitrogen is accompanied by a different flexibility of the amino groups in the two monoamines. A calculation on the y-coplanar structure **1**, in which the $NH_2$ group is planar, has been performed (Scheme 1).

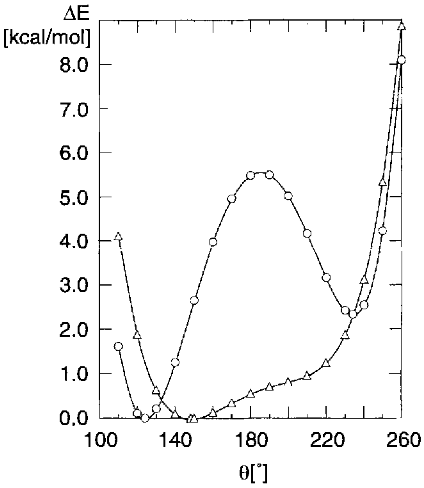
Scheme 1



For both molecules, **1** has one imaginary frequency of 698.4i $cm^{-1}$ for X = C and 274.4i $cm^{-1}$ for X = Si, and an analysis of the transition vector shows that **1** corresponds to the transition state for inversion at nitrogen. The calculated inversion barrier is 5.5 kcal/mol for methylamine (5.6 kcal/mol in experiment[26]), but only 0.6 kcal/mol for silylamine. For comparison, the value of the inversion barrier of ammonia has been calculated as 5.9 kcal/mol (experimental value: 5.9 kcal/mol[31]). The inversion at nitrogen is accompanied by a change of the N hybridization to $sp^2$ and a rotation of the $NH_2$ group around the X−N bond by 90°. As a calculation on the structure **2** shows, the energy of the latter movement is negligible, **2** being only 0.01 kcal/mol higher in energy than **1**. The calculated inversion barrier is thus a direct measure of the energy required for the rehybridization process. An NBO analysis[32] shows that the p contribution to the nitrogen lone pair amounts to 78.3% in the equilibrium geometry of the carbon compound and to 91.2% in the silicon analogue, in complete agreement with the differing degree of pyramidalization. In the transition state, the lone pair occupies a pure p orbital. During the inversion process, the energy of the NBO lone pair changes by 19.9 kcal/mol in silylamine, and by as much as 55.4 kcal/mol in methylamine. Thus, the difference in the inversion barriers of both compounds can be assigned to the large shift of the energy level of the lone pair in methylamine.

In order to characterize the rotation of the $NH_2$ group around the X−N bond, we calculated the eclipsed conformation **3**. For methylamine, **3** is a transition state (with one imaginary frequency of 332.0i $cm^{-1}$) which lies 2.3 kcal/mol above the minimum structure (experimental rotation barrier: 2.1 kcal/mol[26]). The rotation around the X−N bond invokes almost no change in the geometry at N, the tilt angle θ being only 1.8° larger in the transition state than in the minimum structure. Thus, the calculated rotation barrier represents the steric repulsion between the C−H and N−H bonds, which is only about 40% of the energy of the inversion. For silylamine, **3** is not a transition state. In Figure 2, the energy relative to the most stable structure is plotted for different values of the tilt angle θ. This movement connects the staggered structure (see Figure 1) with the eclipsed one (**3**). While for methylamine, a minimum at θ = (360° − 125.9°) = 234.1° exists, a monotone increase in energy is observed for silylamine. The different behavior of the two compounds can be rationalized by the relative heights of the inversion barriers. In methylamine, the barrier to inversion at nitrogen is higher than the barrier to rotation around the C−N bond. In silylamine, the energy required to rotate the amino group is higher than the inversion barrier so that an inversion at nitrogen occurs before an eclipsed conformation is reached. The energy of the eclipsed conformation of silylamine, with an angle θ corresponding to the one in the equilibrium geometry (211.9°), is about 1 kcal/mol (Figure 2) higher than that of the minimum structure. Thus, as expected, due to the larger X−N bond distance and the less pyramidal geometry at N in the silicon compound, the rotation around the Si−N bond is less hindered than the rotation around the C−N bond.

Figure 2. Energy change $\Delta E$ as function of the tilt angle θ. ○: $CH_3NH_2$, △: $SiH_3NH_2$



The calculations on the monoamines show that the DF method used yields both geometries and energetics that are in excellent agreement with experiment.

### Tetra(amino)methane $C(NH_2)_4$ and Tetra(amino)silane $Si(NH_2)_4$

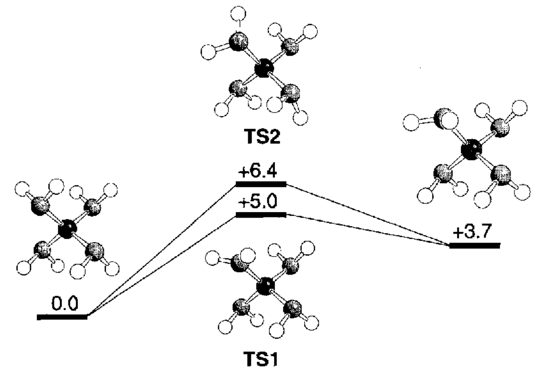
In Table 2 we compare salient structural features of tetra(amino)methane and tetra(amino)silane to experiment[10][33]. The optimized geometry of tetra(amino)methane is displayed on the left side of Figure 3. Both molecules have $D_{2d}$ symmetry. The four N atoms occupy the corners of a flattened tetrahedron; the distortion (N−X−N angle) is slightly larger in the silicon compound (see Table 2). Similar to the monoamines, the $NH_2$ groups are tilted away from the X−N bond in such a way that two amino groups connected by the larger N−C−N angle are facing each other. (This conformation is analogous to the staggered equilibrium structure in $XH_3-NH_2$.) Interestingly, the geometry of the $X-NH_2$ subunit is almost unchanged compared to the monoamines. Thus one may conclude that the amino groups do not influence each other much. Most calculated geometric parameters compare well to the experimental ones. The Si−N bond length is calculated 0.03−0.05 Å too long. For both the C and Si compounds, the calculated tilt angle θ is about 20° smaller than in experiment; given the much closer agreement between the other calculated and experimental values it seems that this difference is due to crystal packing effects.

Table 2. Comparison of bond lengths [Å] and bond angles [°] of tetra(amino)methane and tetra(amino)silane

| | $C(NH_2)_4$ | | | $Si(NH_2)_4$ | | |
|---|---|---|---|---|---|---|
| | Exp.[a] | BLYP | B3LYP | exp.[b] | BLYP | B3LYP |
| $d$(X−N) | 1.473 | 1.479 | 1.463 | 1.701 | 1.750 | 1.733 |
| ∠(N−X−N) | 105.8 | 104.6 | 104.9 | 103.9 | 102.3 | 102.6 |
| | 117.0 | 119.7 | 119.1 | 121.4 | 125.0 | 124.2 |
| ∠(H−N−H) | 109.6[c] | 108.2 | 108.9 | 110.1[d] | 110.3 | 111.1 |
| ∠(X−N−H) | 117.7[e] | 108.6 | 109.3 | 124.9[f] | 117.5 | 118.6 |
| tilt angle θ | 142.1 | 123.1 | 124.7 | 160.6 | 143.5 | 148.1 |

[a] Average values from $C(N(CH_3)_2)_4$[10]. − [b] Average values from $Si(NHCH_3)_4$[33]. − [c] ∠($H_3C-N-CH_3$). − [d] ∠($H-N-CH_3$). − [e] ∠($C-N-CH_3$). − [f] ∠($Si-N-CH_3$).

Figure 3. Energy difference (kcal/mol) relative to the equilibrium structure (left) of the transition states of inversion **TS1** and rotation **TS2** and the resulting local minimum (right)



As a measure of the "floppiness" of the amino groups, we calculated both compounds with a tilt angle θ of 180.0° (corresponding to a planar configuration at N) and 116.7° (configuration as in the ammonia molecule). As one would expect, the distortion to planarity costs less energy for the silicon compound, 0.8 kcal/mol per ligand, than for the carbon analogue, 6.3 kcal/mol per ligand, since the value of θ of the former is closer to planarity in the equilibrium structure. The distortion to a configuration at N corresponding to the one in ammonia leads to virtually no change in energy for the carbon compound (0.5 kcal/mol per ligand); a value of 2.8 kcal/mol per ligand is required for the silicon analogue. Thus the amino group in $Si(NH_2)_4$ is more flexible than in the carbon analogue.

In $C(NH_2)_4$, a second stable structure exists, in which one amino group is rotated by 180° around the C−N bond (Figure 3, right). Two different transition states connect the global minimum with this local minimum (Figure 3, middle), one via inversion (**TS1**, 584.8i $cm^{-1}$), the other one via rotation (**TS2**, 289.6i $cm^{-1}$) of the $NH_2$ group. The barrier to inversion is slightly lower than the barrier to rotation by 1.4 kcal/mol. A comparison with the energies of the corresponding transition states in methylamine reveals that while the barrier to inversion is of comparable size (5.5 kcal/mol and 5.0 kcal/mol, respectively), the rotation barrier is much higher in the tetra(amino) compound (6.4 kcal/mol as compared to 2.3 kcal/mol). The reason for the larger activation energy can be sought in the steric repulsion which is exerted on the rotating amino unit by the other three $NH_2$ groups. This steric influence leads to a slightly larger C−N bond length of the rotating group in the transition state of the tetra(amino) compound (1.480 Å) as compared to the one in methylamine (1.472 Å), while the C−N bond distance amounts to 1.463−1.464 Å in all stable minima. In contrast, the C−N bond length is similar in tetra(amino)methane and methylamine in the transition state of inversion (1.435 Å and 1.436 Å, respectively) and shorter than the equilibrium value due to the larger s character at nitrogen caused by the change of hybridization. In tetra(amino)silane, no comparable transition states could be identified as only one minimum structure could be found.

In order to characterize the bonding in the carbon- and siliconamines, we analyzed the charge distribution in the mono- and tetraamines in terms of the topological atoms method[22][23] at the BLYP level and compared the resulting atomic charges to the result of a Mulliken population analysis (Table 3). Although the magnitudes of the charges are quite different (as often, the absolute values are larger in the Bader analysis), both schemes predict the same trends with the exception of the C atom in methylamine which is found to be positive by the Bader analysis and slightly negative by the Mulliken scheme. As may be expected from electronegativity arguments (C: 2.5, Si: 1.8, N: 3.1[29]), the charge separation is larger for the compound containing the more electropositive silicon. These results correlate with the dipole moment along the X−N bond which is 0.327 Debye in methylamine, but 1.038 Debye in silylamine. While the negative charge on the amino group is roughly the same in the mono- as compared to the tetra-amino compound, the positive charge on the central atom increases upon substitution of the hydrogen atoms by $NH_2$ groups. This increase is less pronounced in the silicon compound, perhaps because in silylamine the silicon atom already bears a large positive charge. All these findings imply that the Si−N bond is more ionic. Such bonds have less directionality than strongly covalent ones. This situation brings to mind the decreasing value of the bending mode with decreasing electronegativity of X in X−NH species[26]. Also for the adsorption of small molecules on metal surfaces one finds that an ionic bond implies changes in the relative orientation of the adsorbate at low energetic cost[25].

Table 3. Partial charges [au] of C, Si, N, and $NH_2$ in mono- and tetra(amino)silanes from a Bader and Mulliken population analysis

| | X = C | | | X = Si | | |
|---|---|---|---|---|---|---|
| | C | N | $NH_2$ | Si | N | $NH_2$ |
| $XH_3NH_2$ | | | | | | |
| Bader | 0.369 | −0.939 | −0.300 | 2.793 | −1.474 | −0.740 |
| Mulliken | −0.163 | −0.553 | −0.112 | 0.467 | −0.671 | −0.184 |
| $X(NH_2)_4$ | | | | | | |
| Bader | 1.194 | −0.975 | −0.299 | 3.066 | −1.484 | −0.766 |
| Mulliken | 0.376 | −0.538 | −0.094 | 0.798 | 0.669 | −0.199 |

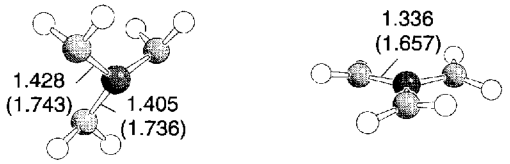
Finally, we discuss the strength of the X−N bonds in the various compounds under study[36][37]. To compare the X−N bond energies in the monoamines and tetraamines, we calculated the abstraction of one amino ligand via homolytic cleavage of the X−N bond (Table 4) which results in the moieties $^{\bullet}NH_2$ and $^{\bullet}XH_3$ or $^{\bullet}NH_2$ and $^{\bullet}X(NH_2)_3$ (Figure 4). Our results for the monoamines compare to within 5% with the experimental bond strengths, which proves the reliability of our method for the calculation of bond energies. MP4 calculations on the silicon compounds[7] yield up to 13% higher binding energies than the present DF calculations. The homolytic cleavage energy $E_R$ in tetra(amino)methane is slightly (2%) lower than in methylamine. In contrast, the Si−N bond strength is 11% higher in the tetracoordinated compound as compared to silylamine. Thus, while in methyl- and silylamine the bond strengths differ by about 10%, in the tetraamines the Si−N bond is 27% stronger than the C−N bond.

Table 4. Comparison of calculated and experimental binding energies (kcal/mol) of the amino group in $XH_3NH_2$ and $X(NH_2)_4$ (X = C, Si). $E_R$: homolytic, $E_I$: heterolytic bond cleavage

| | | $CH_3NH_2$ | $C(NH_2)_4$ | $SiH_3NH_2$ | $Si(NH_2)_4$ |
|---|---|---|---|---|---|
| $E_I$[a] | BLYP/B3LYP | | 191.5/194.9 | | 243.3/247.4 |
| $E_R$[b] | BLYP/B3LYP | 88.7/89.0 | 84.8/87.3 | 96.8/98.7 | 106.4/110.4 |
| | MP4[c] | | | 104.9 | 120.2 |
| | exp. | 84.9±1.1[d] | | 100[e] | |

[a] $E_I$: $X(NH_2)_4 \rightarrow X(NH_2)_3^+ + NH_2^-$. − [b] $E_R$: $X(NH_2)_4 \rightarrow {}^{\bullet}X(NH_2)_3 + {}^{\bullet}NH_2$. − [c] Ref.[7]. − [d] Ref.[36]. − [e] From $(CH_3)_3SiNHCH_3$[37].

Figure 4. Optimized geometries of the radical $^{\bullet}C(NH_2)_3$ (left) and of the guanidinium cation (right). Bond lengths in Å. The values of the analogous silicon compounds are given in parentheses



We also calculated the energy for heterolytic bond cleavage $E_I$. The guanidinium cation is stable in solution, while the silicon analogue has not yet been observed. Both cations have been shown to be nonplanar by calculations at the MP2 level[38][39]. The amino groups in the guanidinium cation are twisted out of the plane by 13.7° (14.9° with MP2[38]), for $Si(NH_2)_3^+$ a larger rotation is calculated (20.8°). We calculated $E_I$, and again we find the Si−N bond to be 27% stronger than the C−N bond.

Why is the X−N bond energy (homolytic or heterolytic) so significantly higher in the silicon tetraamine compound? In calculating the binding energy given in Table 4, the energy of the sum of $X(NH_2)_3^{n+}$ and $NH_2^{n-}$ ($n$ = 0 or 1) is added and compared to that of $X(NH_2)_4$. Frenking et al.[38][39] calculated the transition state for the rotation of one amino group in $X(NH_2)_3^+$ (X = C, Si) and observed an elongation of the C−N bond by 0.065 Å, while the Si−N bond distance remains essentially unchanged. They concluded that there is some more π contribution to the X−N bond in the guanidinium cation than in its silicon analogue. This means that for X = C the ion $X(NH_2)_3^+$ is comparatively more stable and thus the binding energy $E_I$ of the fourth ligand is smaller than for X = Si. Accordingly, tetra(amino)methane compounds are found to be strongly amidating agents in experiment, while tetra(amino)silanes are not[10].

A similar argument seems to hold for the radicals $^{\bullet}X(NH_2)_3$. A comparison of the calculated X−N bond lengths (Figure 4) to those of the mono- and tetraamino compounds (Table 1 and 2) reveals that while the Si–N bond lengths span the narrow range of 1.733 Å to 1.743 Å (and are close to the value of a Si–N single bond, 1.748 Å[40]), the C–N distance varies from 1.405 Å to 1.464 Å. The C–N bond in the triaminoradical is up to 0.05 Å shorter than in the mono- or tetraamino compound. Evidently, the $^{\bullet}C(NH_2)_3$ radical is also relatively stable which explains the low binding energy $E_R$ in $C(NH_2)_4$. One would expect that the average binding energy of all amino ligands [calculated as the fourth part of the energy difference of the reaction $X + 4\ NH_2 \rightarrow X(NH_2)_4$] differs less for the carbon and silicon compound than the binding energy of a single ligand. The calculated mean binding energy is 90.5 kcal/mol for $C(NH_2)_4$ and 89.3 kcal/mol for $Si(NH_2)_4$.

## Conclusions

Our calculations have shown that the geometry of the $XNH_2$ subunit is almost unchanged when the three H atoms bound to N of $XH_3NH_2$ (X = C, Si) are substituted by amino groups. The coordination around nitrogen is close to tetrahedral in the carbon compounds, while for X = Si the amino groups are less pyramidal. Although the Si–N bond in $XH_3NH_2$ is about 10% stronger than the C–N bond, the amino group is much more flexible in the silicon compound, which can be demonstrated by the very low inversion barrier of 0.6 kcal/mol in silylamine as compared to 5.5 kcal/mol in methylamine. This flexibility has been rationalized by considering the partially ionic character of the Si–N bond, which implies a less directional character than is found for the strongly covalent C–N bond. In methylamine, a barrier to rotation around the C–N bond is calculated to 2.3 kcal/mol. While the inversion at nitrogen corresponds to an electronic process (change in hybridization), the barrier to rotation is due to steric effects and amounts to only 40% of the energy needed for inversion. The rotation around the Si–N bond in silylamine is less hindered than the rotation around the C–N bond in methylamine. Nevertheless, a corresponding transition state does not exist in silylamine since the barrier to inversion is extremely low. In tetra(amino)methane, a second minimum exists, which is connected with the equilibrium structure either by a rotation or inversion of one amino group. The barrier to rotation is higher than in methylamine (6.4 kcal/mol) due to the steric repulsion of the other three $NH_2$ units. The C–N bond energy of the fourth amino ligand in the tetraamino compound is calculated to be approximately one quarter less than the corresponding Si–N bond. This difference has been ascribed to the stabilization of the $C(NH_2)_3$ species (radical or cation) due to some π character of the C–N bond which is absent in the silicon analogue. In contrast, the mean binding energy of the amino groups is very similar in both tetraamino compounds.

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