

# A Simple Electrostatic Model for Trisilylamine: Theoretical Examinations of the $n \rightarrow \sigma^*$ Negative Hyperconjugation, $p_\pi \rightarrow d_\pi$ Bonding, and Stereoelectronic Interaction

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**Abstract:** A block-localized wave function method was used to examine the stereoelectronic effects on the origin of the structural difference between trisilylamine and trimethylamine. The pyramidal geometry of trimethylamine along with its high basicity is consistent with the traditional VSEPR (valence shell electron-pair repulsion) model for  $\sigma$  bonding. On the other hand, in trisilylamine, the silicon d orbitals make modest contribution to the electronic delocalization, although the key factor in charge delocalization is still  $n_N \rightarrow \sigma_{SiH}^*$  negative hyperconjugation. Interestingly, the gain in  $p_\pi \rightarrow d_\pi$  bonding stabilization is offset by a weaker negative hyperconjugation effect in trisilylamine, resulting in an overall smaller delocalization energy ( $-18.5$  kcal/mol) than that in trimethylamine ( $-23.9$  kcal/mol), which contains little  $p_\pi \rightarrow d_\pi$  bonding character. Significantly, because of the relatively low electronegativity of silicon, the N–Si bond is much more polar than the N–C bond. Weinhold's natural population analyses of the BLW and HF wave functions for these compounds reveal that the origin of the planar geometry of trisilylamine is due to the polar  $\sigma$ -effect that yields significant long-range electrostatic repulsion between the silyl groups. In addition, it was found that only the most electronegative substituents such as F and OH can result in a pyramidal geometry at the nitrogen center for silylamines. This is in good accord with the recent X-ray structure of a pyramidal silylamine,  $N(CH_3)(OCH_3)(SiH_3)$ .

## Introduction

The notion that  $p_\pi \rightarrow d_\pi$  donation is responsible for the unusually short bond distances of second-row elements of main groups is ubiquitous in the literature and textbooks.<sup>1–10</sup> For

example, the short sulfur–oxygen bond distance in  $SO_4^{2-}$  is attributed to the donation of the lone-pair electrons of oxygen to the vacant 3d atomic orbitals of the sulfur atom. Similar explanations can be found to illuminate the structures of  $PO_4^{3-}$ ,  $SiO_4^{4-}$ , and  $ClO_4^-$ . However, recent theoretical analyses cast serious doubt on the d-orbital hypothesis of main group elements.<sup>5–9</sup> Kutzelnigg<sup>5</sup> showed that the X–O bond in  $H_3PO$ ,  $H_2P(O)F$ ,  $H_2SO$ , etc. can be described with the traditional valence s- and p-type orbitals by allowing these atomic orbitals to deform, whereas Reed and Weinhold's natural population analyses revealed that the occupancy of the sulfur d function is very small.<sup>6</sup> Reed and Schleyer<sup>7</sup> further demonstrated that  $n \rightarrow \sigma^*$  negative hyperconjugation<sup>11</sup> is important in controlling hypervalency, and that the d orbitals on the central atom play only a secondary role in  $\pi$ -bonding. By optimizing the d-function exponents in various molecules of first- and second-row elements systematically, Magnusson<sup>8a</sup> was able to show that d functions of second-row atoms are polarization functions in nature. These functions do not take a valence role, a conclusion

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also reached by Cruickshank and Eistenstein<sup>9</sup> based on analyses of the deformation density map.

Although these theoretical studies provide compelling evidence for a minor role of d orbitals in the bonding of second-row main group elements, there is still controversy over other main group compounds, including silylamine, another prototypical example demonstrating the existence of dative  $p_{\pi}$ - $d_{\pi}$  bonding in textbooks.<sup>1</sup> Trisilylamine,  $N(\text{SiH}_3)_3$ , has a planar  $\text{Si}_3\text{N}$  skeleton, which is essentially not basic,<sup>12</sup> suggesting that the unshared pair of electrons is delocalized into the empty 3d orbitals of silicon atoms. In addition, Rhodes<sup>13</sup> suggests that there is EPR evidence to support the concept of Si-N  $p_{\pi}$ - $d_{\pi}$  bonding in silylamines. In contrast, the valence isoelectronic system  $N(\text{CH}_3)_3$  is a strong base and has a pyramidal structure.<sup>14</sup> This has been attributed to pure  $\sigma$ -bonding interaction and a lack of  $p_{\pi}$ - $d_{\pi}$  interaction.

To corroborate recent theoretical findings that d orbitals play a minor role in bonding for main group elements,<sup>15</sup> Schleyer and co-workers<sup>7</sup> proposed that the  $n \rightarrow \sigma_{\text{XH}}^*$  negative hyperconjugation effect may be responsible for the difference between the physical and structural properties of first- and second-row elements. In other studies, it has been suggested<sup>1c,16</sup> that the planarity may be caused by the electrostatic repulsion among the silyl groups since the Si-N bond is more polar than the C-N bond. So far, there is no clear criterion to quantify the relative contributions from various factors to the bonding properties of main group compounds, including the dative  $p_{\pi} \rightarrow d_{\pi}$  bonding,  $n \rightarrow \sigma_{\text{SiH}}^*$  negative hyperconjugation, and steric and electrostatic repulsion. Although various population analysis schemes and other techniques based on electron-density distribution have been widely used to discuss electron-flow and bonding features, they can only provide an indirect assessment. It would be highly desirable to derive an energy decomposition scheme that can dissect individual contributions to the bonding of main group elements.

In this paper, we employ a block-localized wave function (BLW) method<sup>17</sup> to estimate the stabilization energy due to electronic delocalization of the lone-pair electrons from nitrogen to the vicinal substituent groups and to rationalize the geometry difference between  $N(\text{CH}_3)_3$  (tetrahedral) and  $N(\text{SiH}_3)_3$  (planar) observed experimentally. For  $N(\text{CH}_3)_3$ ,  $n$  electron delocalization is entirely due to  $n_{\text{N}} \rightarrow \sigma_{\text{CH}}^*$  negative hyperconjugation,<sup>11</sup> whereas for  $N(\text{SiH}_3)_3$ , both  $n_{\text{N}} \rightarrow \sigma_{\text{SiH}}^*$  negative hyperconjugation and  $p_{\pi} \rightarrow d_{\pi}$  interaction can make significant contributions. Attempts will be made to distinguish between these two mechanisms. Furthermore, the extent of electron flow will be assessed by means of the natural population analysis.<sup>6,10,18</sup> The present study demonstrates that it is the polar  $\sigma$ -effect, rather than the  $\pi$ -type  $p_{\pi} \rightarrow d_{\pi}$  donation and negative hyperconjugation interaction, that makes the predominant contribution in determining the observed planar geometry in trisilylamine. There is strong evidence supporting this simple electrostatic picture, which revises the traditional view of the significant role of d-orbital participation in bonding of main group elements.<sup>1,2</sup> In

what follows, we present computational procedures, followed by results and discussion.

## 2. Methodology

The primary aim of this study is to provide a quantitative assessment of the magnitude of the electronic delocalization in  $N(\text{CH}_3)_3$  and  $N(\text{SiH}_3)_3$  and factors that determine the planarity of the  $N(\text{SiH}_3)_3$  geometry. To accomplish this goal, we construct a diabatic state using a strictly block-localized wave function (BLW) method developed recently,<sup>17</sup> where the lone nitrogen pair is strictly localized on the central nitrogen atom. Such a diabatic state provides a reference point for computation of delocalization energies, analogous to the resonance energy of benzene relative to 1,3,5-cyclohexatriene,<sup>19a</sup> as defined by Pauling and Wheland.<sup>20</sup> Of course, the localized diabatic state which we define can also be modeled by means of ab initio valence bond (VB) approaches.<sup>19</sup> Unfortunately, computational difficulties in the VB method prohibit us from applying this approach to large molecular systems such as those considered here.

The block-localized wave function  $\Psi(\text{BLW})$  is defined to circumvent the delocalized nature of molecular orbitals in Hartree-Fock (HF) theory, which is not directly adequate for the present analysis.<sup>17</sup> In contrast to standard localization procedures via unitary transformation, which yield localized bond orbitals containing a mixture of orthogonalization and delocalization tails, we partition all electrons and basis orbitals of a system into  $k$  subgroups. Each molecular orbital (MO) in a subgroup is written as a linear combination of the primitive basis functions in that subspace. The Slater determinant wave function is then constructed with use of these occupied MOs of the molecular system:

$$\Psi(\text{BLW}) = \hat{A}(\Phi_1 \Phi_2 \dots \Phi_k) \quad (1)$$

where  $\Phi_i$  is a successive product of the occupied MOs in the  $i$ th subgroup, and  $\hat{A}$  is an antisymmetrizing operator. While the above wave function is subject to the restriction that the MOs in the same subgroup must be orthogonal (similar to the normal HF method), the MOs between different subgroups are allowed to overlap (a feature of the VB approach), and are thus nonorthogonal. Clearly, restriction on the length of each MO expansion corresponds to the hypothesis that each electron is confined to a physical region (a piece of the whole target system). The way that the BLW is defined implies that both orthogonalization and delocalization tails are avoided in the very beginning. Consequently, the BLW method can be used to estimate the conventional conjugation and hyperconjugation effect as well as charge-transfer effect between groups and molecules. Although in many cases a block-localized wave function describes a specific (not necessarily the most stable) resonance structure, the BLW configuration is far more general than the VB resonance structure. Note that once we remove the restriction on the length of expansion of the MOs in eq 1, the BLW method returns to the familiar HF-SCF theory.

With the construction of a block-localized wave function, the delocalization energy (DE) can be conveniently defined as follows:

$$\text{DE} = E[\Psi(\text{HF})] - E[\Psi(\text{BLW})] \quad (2)$$

The diabatic state for the planar structure of  $N(\text{CH}_3)_3$  and  $N(\text{SiH}_3)_3$  is defined by a BLW where the lone nitrogen pair occupies an orbital expanded with the primitive basis functions of  $\pi$  symmetry centered on the nitrogen atom ( $p_{\pi}$ ). All other electrons occupy MOs expanded with the remaining primitive basis functions. While the latter MOs in the second block are constrained to be mutually orthogonal, the  $p_{\pi}$  orbital in the first block has nonzero overlap with these MOs. Thus, such a diabatic state does not contain electronic delocalization from

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the lone nitrogen pair to the adjacent CH<sub>3</sub> or SiH<sub>3</sub> groups. Therefore, we can quantitatively estimate the stabilization energy brought about by delocalization of the nitrogen lone pair to the methyl or silyl group(s). This treatment is analogous to recent works on the role of conjugation on the acidity of formic acid and the rotational barrier in formamide by Hiberty and co-workers<sup>21</sup> and by us.<sup>22</sup>

To shed light on the relationship between the number of substituent groups and the electronic delocalization, methylamine (H<sub>2</sub>NCH<sub>3</sub>) and silylamine (H<sub>2</sub>NSiH<sub>3</sub>) are also investigated. In all systems, the central nitrogen atom has an sp<sup>2</sup> hybridization mode with the lone-pair electrons occupying a single p<sub>π</sub> orbital.

There are two types of electronic delocalization in N(SiH<sub>3</sub>)<sub>3</sub>, namely the n<sub>N</sub>→σ<sub>SiH</sub>\* negative hyperconjugation and the dative p<sub>π</sub>→d<sub>π</sub> bonding. Consequently, the DE of eq 2 may be expressed as the sum of these two contributions.

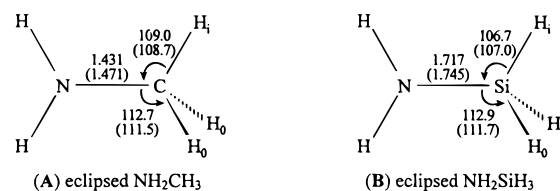
$$DE = DE(n_{\text{N}} \rightarrow \sigma_{\text{SiH}}^*) + DE(p_{\pi} \rightarrow d_{\pi}) \quad (3)$$

Difficulties exist, however, to decompose DE into DE(n<sub>N</sub>→σ<sub>SiH</sub>\*) and DE(p<sub>π</sub>→d<sub>π</sub>) exactly because the d orbitals on the silicon atom not only act as the receptor for the p<sub>π</sub>→d<sub>π</sub> interaction, but also are involved in the σ-bonding with the connecting nitrogen and hydrogen atoms, e.g., in σ<sub>SiH</sub>\*. Reed and Schleyer pointed out that the d orbitals serve to polarize the σ<sub>AX</sub>\* orbitals.<sup>7a</sup> As a "rough" estimate, the DE(n<sub>N</sub>→σ<sub>SiH</sub>\*) term in eq 3 may be obtained by performing HF-SCF and BLW-SCF calculations without the d functions. Then, DE(p<sub>π</sub>→d<sub>π</sub>) can be computed by the difference between DE, which includes d orbitals on non-hydrogen atoms, and DE(n<sub>N</sub>→σ<sub>SiH</sub>\*), which does not include d basis functions. In the present study, BLW calculations are performed by using a program developed by us, in which the primitive integrals are read from the output file of GAUSSIAN-94.<sup>23</sup> Gradient-based optimization techniques have not been implemented for BLW geometry optimizations. Since only one or two critical bonds and angles are optimized in the BLW calculation, a grid-search approach is used by successively varying each geometrical variable until the lowest energy is obtained. All other routine MO calculations are carried out with GAUSSIAN-94.<sup>23</sup>

### 3. Results and Discussions

The planar structure of N(XH<sub>3</sub>)<sub>3</sub> (C<sub>3h</sub> symmetry) together with the eclipsed NH<sub>2</sub>XH<sub>3</sub> (C<sub>s</sub> symmetry), where X is either a carbon or a silicon atom, are optimized at the HF and MP2 level with the 6-31G(d) and 6-311G(pd) basis set.<sup>23</sup> Except for N(SiH<sub>3</sub>)<sub>3</sub>, the planar structures are transition states, corresponding to the inversion of the two pyramidal configurations. The transition structures are predicted to be 8.9 (11.5) kcal/mol higher in energy than the minimum structure for N(CH<sub>3</sub>)<sub>3</sub>, 6.0 (6.7) kcal/mol for NH<sub>2</sub>CH<sub>3</sub>, and 0.4 (0.5) kcal/mol for NH<sub>2</sub>SiH<sub>3</sub>, at the HF/6-31G(d) and MP2/6-311G(pd) level (in parentheses). Since our focus is on the origin of the planarity of N(SiH<sub>3</sub>)<sub>3</sub>, the planar structures are more relevant and are used as references in the present analysis of stereoelectronic effects.<sup>24</sup>

Basis set and electron correlation effects have been found to have minimal influence on the optimized geometries at the



**Figure 1.** Optimized structures at the HF/6-31G(d) and BLW/6-31G(d) levels. Bond distances are given in angstroms and bond angles in degrees. BLW/6-31G(d) values are listed in parentheses.

**Table 1.** Total Energies and Delocalization Energies Estimated with the 6-31G(d) Basis Set

	<i>E</i> (au)			energy (kcal/mol)	
	HF	BLW <sup>a</sup>	BLW <sup>b</sup>	VDE	TDE
NH <sub>2</sub> CH <sub>3</sub>	-95.20031	-95.18711	-95.18827	-8.3	-7.6
N(CH <sub>3</sub> ) <sub>3</sub>	-173.25513	-173.21699	-173.21983	-23.9	-22.2
NH <sub>2</sub> SiH <sub>3</sub>	-346.28338	-346.26818	-346.26862	-9.5	-9.3
N(SiH <sub>3</sub> ) <sub>3</sub>	-926.48982	-926.46033	-926.46044	-18.5	-18.4

<sup>a</sup> Computed using the HF/6-31G(d) optimized geometries. <sup>b</sup> Computed using the BLW/6-31G(d) optimized geometries.

Hartree-Fock and MP2 levels (Supporting Information). Consequently, the 6-31G(d) basis set is adopted in the analysis.

**NH<sub>2</sub>CH<sub>3</sub> and NH<sub>2</sub>SiH<sub>3</sub>.** To quantify the electronic delocalization effect on the geometry and energy in NH<sub>2</sub>XH<sub>3</sub> (X = C and Si), structures are optimized by using both the *localized* BLW and *delocalized* HF methods with the 6-31G(d) basis set (Figure 1). Total energies and computed delocalization energies (DE) are given in Table 1, where the vertical delocalization energy (VDE) is the energy difference between the delocalized state (HF) and the localized, diabatic state (BLW) at the same (HF) geometry. The theoretical delocalization energy (TDE) is defined as the energy difference between the optimized structures of the delocalized state and the diabatic state. Note that the definition of VDE and TDE is a generalization of vertical resonance energy (VRE) and theoretical resonance energy (TRE) for the conjugated system.<sup>19</sup>

Electronic delocalization from the lone nitrogen pair to the antibonding orbital of the methyl (silyl) group shall result in shortening of the central N-C (N-Si) bond and deformation of the methyl (silyl) group. In the diabatic state for NH<sub>2</sub>XH<sub>3</sub>, the N-X bond is a pure N(sp<sup>2</sup>)-X(sp<sup>3</sup>) single bond since the lone-pair electrons of nitrogen are strictly localized in the BLW calculation. The electronic delocalization effect reduces the N-C bond length by 0.040 Å in NH<sub>2</sub>CH<sub>3</sub> on going from the BLW to the HF structure. Concomitantly, the system is stabilized by -8.3 kcal/mol in DE. This may be compared with a change of 0.028 Å in bond distance and a DE of -9.5 kcal/mol for NH<sub>2</sub>-SiH<sub>3</sub>. Deformation of the substituent group, due to the n<sub>N</sub>→σ<sub>SiH</sub>\* negative hyperconjugation, is known to be opposite to the conventional (positive) hyperconjugation in, e.g., carbocations.<sup>25</sup> In the latter case, electrons delocalize from the substituent group into the vacant p<sub>π</sub> orbital, resulting in a decrease in bond angle.<sup>7a</sup> In the present case, however, the charge density delocalizes from the nitrogen lone pair to the out-of-plane σ\* orbital of XH<sub>3</sub>. The weakening of the bond order in the participating σ bond is reflected by an increase in bond angle. Quantitatively, both the

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**Table 2.** Computed Energy Contributions to the Total VDE from  $n_N \rightarrow \sigma_{\text{SiH}}^*$  Negative Hyperconjugation and  $p_\pi \rightarrow d_\pi$  Bonding Interactions (kcal/mol)

	<i>E</i> (au)		VDE (kcal/mol)	
	HF/6-31G <sup>a</sup>	BLW/6-31G <sup>a</sup>	$n_N \rightarrow \sigma_{\text{SiH}}^*$ <sup>b</sup>	$p_\pi \rightarrow d_\pi$ <sup>c</sup>
NH <sub>2</sub> CH <sub>3</sub>	-95.16911	-95.15846	-6.7	-1.6
N(CH <sub>3</sub> ) <sub>3</sub>	-173.18084	-173.14968	-19.6	-4.3
NH <sub>2</sub> SiH <sub>3</sub>	-346.21142	-346.20198	-5.9	-3.6
N(SiH <sub>3</sub> ) <sub>3</sub>	-926.30320	-926.28586	-10.9	-7.6

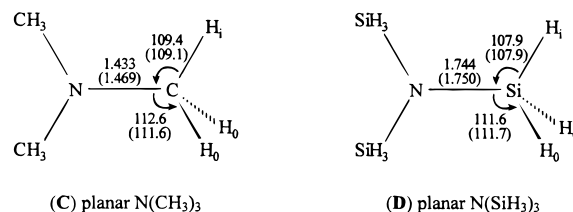
<sup>a</sup> HF/6-31G(d) geometries are used. <sup>b</sup>  $\text{VDE}(n_N \rightarrow \sigma_{\text{SiH}}^*) = E(\text{HF}/6-31\text{G}) - E(\text{BLW}/6-31\text{G})$ . <sup>c</sup>  $\text{VDE}(p_\pi \rightarrow d_\pi) = \text{VDE}(\text{total}) - \text{VDE}(n_N \rightarrow \sigma_{\text{SiH}}^*)$ .  $\text{VDE}(\text{total})$  is listed in Table 1.

$\theta(\text{NCH}_0)$  and  $\theta(\text{NSiH}_0)$  angle are found to increase by  $1.2^\circ$  due to charge delocalization from the lone nitrogen pair. There is no noticeable change for the in-plane  $\theta(\text{NXH}_i)$  angle since the  $\text{XH}_i$  bond is unable to participate in negative hyperconjugation. Energetically, the delocalization energy in NH<sub>2</sub>SiH<sub>3</sub> is predicted to be greater than that in NH<sub>2</sub>CH<sub>3</sub> ( $-9.5$  vs  $-8.3$  kcal/mol), suggesting that the electronic delocalization is enhanced when more diffused valence orbitals are involved. This finding is similar to the case of H<sub>2</sub>CXNH<sub>2</sub> ( $X = \text{O}, \text{S}, \text{and Se}$ ), which have been recently investigated with the same methodology.<sup>22</sup>

To estimate the contribution of d orbitals to the electronic delocalization in these compounds, results from HF-SCF and BLW-SCF calculations using the 6-31G and 6-31G(d) basis sets are compared in Table 2. Here, the HF/6-31G(d) geometries are used in all calculations. With the removal of d functions, the electronic delocalization effect can be uniquely attributed to the  $n_N \rightarrow \sigma_{\text{XH}}^*$  negative hyperconjugation. Thus, the difference between the vertical delocalization energies computed with and without d orbitals provides a reasonable quantification of the  $p_\pi \rightarrow d_\pi$  bonding energy (eq 3). For NH<sub>2</sub>CH<sub>3</sub>, the  $n_N \rightarrow \sigma_{\text{XH}}^*$  negative hyperconjugation contributes  $-6.7$  kcal/mol to the total DE, which gives a predicted  $\text{DE}(p_\pi \rightarrow d_\pi)$  of  $-1.6$  kcal/mol. However,  $p_\pi \rightarrow d_\pi$  interactions are expected to be small in NH<sub>2</sub>-CH<sub>3</sub> because of the large energy gap between 2p and 3d atomic orbitals. Thus, the computed  $\text{DE}(p_\pi \rightarrow d_\pi)$  perhaps is an artifact of the standard Gaussian basis set containing six Cartesian d orbitals. Assuming the same basis-set artifact in NH<sub>2</sub>CH<sub>3</sub> and NH<sub>2</sub>SiH<sub>3</sub>, the net  $p_\pi \rightarrow d_\pi$  interaction in NH<sub>2</sub>SiH<sub>3</sub> is estimated to be about  $-2.0$  kcal/mol. This is relatively a small contribution to the overall electronic delocalization energy ( $-9.5$  kcal/mol). Without this correction, the dative  $p_\pi \rightarrow d_\pi$  bonding would be 38% ( $-3.6$  kcal/mol) of the total DE in NH<sub>2</sub>SiH<sub>3</sub>. Clearly, the  $p_\pi \rightarrow d_\pi$  interaction makes an important contribution to bonding in second-row main group elements. Nevertheless,  $p_\pi \rightarrow d_\pi$  bonding is evidently less significant than the negative hyperconjugation effect in trisilylamine (Table 2).

Although the decomposition scheme of eq 3 is approximate,<sup>26</sup> the above analysis does provide valuable information on the relative contributions of the  $n_N \rightarrow \sigma^*$  negative hyperconjugation and the  $p_\pi \rightarrow d_\pi$  bonding for main group elements.<sup>7</sup> The present results are consistent with the finding that d orbitals only play a secondary role in bonding involving second-row main group elements, while the  $n_N \rightarrow \sigma^*$  negative hyperconjugation is the main mechanism for charge delocalization in silylamine.

**N(CH<sub>3</sub>)<sub>3</sub> and N(SiH<sub>3</sub>)<sub>3</sub>.** Depicted in Figure 2 are optimized structures of N(CH<sub>3</sub>)<sub>3</sub> and N(SiH<sub>3</sub>)<sub>3</sub> at the BLW/6-31G(d) and HF/6-31G(d) levels. As NH<sub>2</sub>CH<sub>3</sub> (A), electronic delocalization has significant effects on the planar structure of N(CH<sub>3</sub>)<sub>3</sub> (C). The N-C bond length decreases from 1.469 Å in the BLW structure to 1.433 Å in the HF structure (Figure 2). On the other hand, the difference between the BLW and HF structures for

**Figure 2.** Optimized structures for N(CH<sub>3</sub>)<sub>3</sub> and N(SiH<sub>3</sub>)<sub>3</sub> at the HF/6-31G(d) and BLW/6-31G(d) levels. Bond distances are given in angstroms and bond angles in degrees. BLW/6-31G(d) values are listed in parentheses.

N(SiH<sub>3</sub>)<sub>3</sub> is much smaller. There is virtually no change in bond angle, while the N-Si bond is slightly reduced by 0.006 Å.

Indeed, it is seen from Table 1 that the computed delocalization energy for N(CH<sub>3</sub>)<sub>3</sub> is additive with successive substitution of methyl groups, e.g., the VDE and TDE for N(CH<sub>3</sub>)<sub>3</sub> are roughly three times the corresponding values for NH<sub>2</sub>CH<sub>3</sub>. However, the VDE and TDE for N(SiH<sub>3</sub>)<sub>3</sub> are only twice of those for NH<sub>2</sub>SiH<sub>3</sub>. The predicted VDE (TDE) of  $-23.9$  ( $-22.2$ ) kcal/mol for N(CH<sub>3</sub>)<sub>3</sub> is greater than that of  $-18.5$  ( $-18.4$ ) kcal/mol for N(SiH<sub>3</sub>)<sub>3</sub>. Now that a much larger VDE in N(CH<sub>3</sub>)<sub>3</sub> is not sufficient to yield a planar structure as the ground state for trimethylamine, it is inconceivable that a smaller delocalization energy in N(SiH<sub>3</sub>)<sub>3</sub>, which contains both negative hyperconjugation and  $p_\pi \rightarrow d_\pi$  bonding effect, can be rationalized as the primary reason responsible for its planar geometry.

The computed VDE is again decomposed into  $\text{VDE}(n_N \rightarrow \sigma_{\text{XH}}^*)$  and  $\text{VDE}(p_\pi \rightarrow d_\pi)$ . The d-orbital effect is leveled off at  $-4.3$  kcal/mol for N(CH<sub>3</sub>)<sub>3</sub>, whereas the dative  $p_\pi \rightarrow d_\pi$  interaction in N(SiH<sub>3</sub>)<sub>3</sub> is estimated to be  $-7.6$  kcal/mol. This further demonstrates that d orbitals on a silicon atom play a secondary role in bonding compared to negative hyperconjugation ( $-10.9$  kcal/mol). Comparing with N(CH<sub>3</sub>)<sub>3</sub>, it is interesting to note that the slight increase in  $\text{VDE}(p_\pi \rightarrow d_\pi)$  in N(SiH<sub>3</sub>)<sub>3</sub> is more than offset by the decrease in its negative hyperconjugation energy.

Interestingly, there is strong evidence to suggest that stereo-electronic repulsion among the silyl groups is responsible for the planar geometry of N(SiH<sub>3</sub>)<sub>3</sub>. Two types of repulsion are possible thanks to the higher polarity of the N-Si bond than that of N-C: (1) steric repulsion associated with the Pauli exchange repulsion and (2) long-range Coulombic repulsion. It is difficult to uniquely separate the two contributions in electronic structural calculations. However, considering the fact that NH<sub>2</sub>SiH<sub>3</sub>, where there is little steric effect between H and SiH<sub>3</sub>, is already nearly planar at the nitrogen center,<sup>24</sup> it appears that long-range electrostatic repulsion would be more significant in stereoelectronic effect for N(SiH<sub>3</sub>)<sub>3</sub>. Additional support is provided by considering the HF/6-31G(d) optimized structures for the series of (SiH<sub>3</sub>)<sub>2</sub>NX, where X = H, CH<sub>3</sub>, and C(CH<sub>3</sub>)<sub>3</sub>. The planar structure is the global minimum for all three compounds. At the HF/6-31G(d) level, the  $\theta(\text{SiNX})$  angles are computed to be  $114.5^\circ$ ,  $116.6^\circ$ , and  $119.7^\circ$  for X = H, CH<sub>3</sub>, and C(CH<sub>3</sub>)<sub>3</sub>, respectively. Steric repulsion increases the Si-N-X bond angle considerably as X changes from H to C(CH<sub>3</sub>)<sub>3</sub>. However, even for the largest substituent, steric repulsion between the silyl and *tert*-butyl group ( $119.7^\circ$ ) is not enough to overcome the repulsion between two silyl groups ( $120.6^\circ$ ). Therefore, the difference in bond angle must be due to long-range, electrostatic effects (see below) rather than steric effects. Analogously, in the analysis of the bond angle widening about oxygen in silyl ethers compared to alkyl ethers, Shambayati et

**Table 3.** Computed Weinhold Natural Atomic Orbital Population ( $P$ ) and Partial Charges ( $q$ ) from the Delocalized State  $\Psi(\text{HF})$  and the Strictly Localized State  $\Psi(\text{BLW})$  (in electrons)

	$\Psi(\text{HF}-\text{SCF})$					$\Psi(\text{BLW}-\text{SCF})$				
	$q(\text{N})$	$q(\text{X})$	$q(\text{CH}_3)$	$P(\text{p}_\pi)$	$P(\text{d})$	$q(\text{N})$	$q(\text{X})$	$q(\text{CH}_3)$	$P(\text{p}_\pi)$	$P(\text{d})$
$\text{NH}_2\text{CH}_3$	-0.9666	-0.3919	0.1813	1.9646	0.0097	-0.9890	-0.3847	0.2027	1.9917	0.0089
$\text{N}(\text{CH}_3)_3$	-0.5963	-0.3832	0.1988	1.8980	0.0095	-0.6541	-0.3755	0.2180	1.9778	0.0088
$\text{NH}_2\text{SiH}_3$	-1.3884	1.3345	0.5594	1.9359	0.0538	-1.4233	1.3622	0.5995	1.9878	0.0490
$\text{N}(\text{SiH}_3)_3$	-1.8471	1.3375	0.6157	1.8845	0.0477	-1.8932	1.3567	0.6311	1.9652	0.0453

al. also ruled out steric effects and  $n \rightarrow d$  interactions on the basis of the Walsh diagram and an orbital interaction analysis.<sup>27</sup>

To provide support to the present electrostatic model, we performed natural population analysis on  $\Psi(\text{HF})$  and  $\Psi(\text{BLW})$ . The computed partial charges, along with the Weinhold natural population on the  $\text{p}_\pi$  orbital of nitrogen and the d functions on carbon and silicon, are presented in Table 3. Since the lone-pair electrons are strictly localized in the BLW calculation, the electron population on the nitrogen  $\text{p}_\pi$  orbital would be expected to be exactly 2. However, there is always some arbitrariness in charge population analysis, which may alter the natural orbital population slightly from the integer. Indeed, there is a small deviation as shown in Table 3. Consequently, the natural population derived from  $\Psi(\text{BLW})$  is adopted as a reference to analyze the charge flow due to delocalization. The  $n_{\text{N}} \rightarrow \sigma_{\text{XH}}^*$  negative hyperconjugation results in a decrease in the  $\text{p}_\pi$  population by 0.027 and 0.080 e in  $\text{H}_2\text{NCH}_3$  and  $\text{N}(\text{CH}_3)_3$ , respectively. Note that the amount of charge transfer in  $\text{N}(\text{CH}_3)_3$  is three times that of  $\text{H}_2\text{NCH}_3$ , consistent with the additive change in the predicted VDE (Table 1). In contrast, the dissipation of the  $\text{p}_\pi$  natural populations ( $P(\text{p}_\pi)$ ) is found to be 0.052 and 0.081 e for  $\text{H}_2\text{NSiH}_3$  and  $\text{N}(\text{SiH}_3)_3$ , respectively, which is far from additive. Interestingly, the charge transfer from  $\text{p}_\pi$  to the substituent group is more pronounced in  $\text{H}_2\text{NSiH}_3$  than  $\text{H}_2\text{NCH}_3$ , perhaps because there is also some  $\text{p}_\pi \rightarrow \text{d}_\pi$  delocalization in addition to  $n_{\text{N}} \rightarrow \sigma_{\text{XH}}^*$  negative hyperconjugation.

The role of d orbitals in bonding is verified by comparing the corresponding natural population from the  $\Psi(\text{HF})$  and  $\Psi(\text{BLW})$  wave functions (Table 3). In all cases, the increase in d charge population ( $P(\text{d})$ ) is negligible, with the exception of  $\text{H}_2\text{NSiH}_3$ , which has the largest charge exodus at 0.005 e.

The calculated charge distribution indicates that nitrogen is a strong  $\sigma$  acceptor with large partial negative charges. For both methylamine and trimethylamine, the carbon atom has a negative charge of about -0.39 e. However, due to the low electronegativity of silicon, the N-Si bond is strongly ionic with a partial charge of ca. +1.34 e on Si. This is echoed by an increase in the partial negative charge on N from -1.39 to -1.85 e in going from  $\text{H}_2\text{NSiH}_3$  to  $\text{N}(\text{SiH}_3)_3$ . In contrast, the negative charge on nitrogen decreases from -0.97 to -0.60 e in the methylamine series. The total partial charge for the silyl group is 0.56 and 0.62 e in  $\text{H}_2\text{NSiH}_3$  and  $\text{N}(\text{SiH}_3)_3$ , respectively, which may be compared with 0.18 and 0.20 e in  $\text{H}_2\text{NCH}_3$  and  $\text{N}(\text{CH}_3)_3$ . Since each silyl group carries about three times more positive charge than a methyl group, electrostatic repulsion is undoubtedly stronger between the silyl groups in trisilylamine than that between methyl groups in trimethylamine. Such an electronic repulsion would strongly favor a planar geometry, which has the largest separations between the silyl groups. Therefore, the origin for the planarity of  $\text{N}(\text{SiH}_3)_3$  is largely from the polar  $\sigma$ -effect, which gives rise to increased (long-range) electrostatic repulsion.

**Table 4.** Computed  $\theta_\tau$  (deg) and the NPA Partial Charges for Substituted Silylamines ( $\text{NHXSih}_3$ ) at the HF/6-31G(d) and MP2/6-311G(dp) Levels

X	HF/6-31G(d)		MP2/6-311G(dp)	
	$\theta_\tau$	$q(\text{X})^a$	$\theta_\tau$	$q(\text{X})^a$
$\text{SiH}_3$	360.0	0.5909	359.8	0.5749
$\text{PH}_2$	360.0	0.4630	360.0	0.4440
SH	359.8	0.3075	359.6	0.2893
$\text{NH}_2$	357.2	0.0242	352.5	0.0184
$\text{CH}_3$	355.7	0.2057	351.5	0.1981
H	352.2	0.4092	349.1	0.3784
Cl	345.7	0.1031	342.9	0.0948
OH	335.7	-0.1451	332.8	-0.1443
F	329.2	-0.3061	327.9	-0.3167

<sup>a</sup> Partial charges range from 0.39 to 0.43 e on the hydrogen attached to nitrogen and from 0.56 to 0.60 e on the silyl group for all compounds.

On the basis of this electrostatic picture for  $\text{N}(\text{SiH}_3)_3$ , it may be anticipated that a pyramidal structure for silylamine can be obtained if a substituent with strong electron-withdrawing power is attached to the nitrogen. Indeed, Mitzel and Oberhammer recently reported the X-ray crystal structure of  $\text{N}(\text{CH}_3)(\text{SiH}_3)(\text{OCH}_3)$ , which is nonplanar at the nitrogen center.<sup>15</sup> To further elaborate on our electrostatic model for  $\text{N}(\text{SiH}_3)_3$ , we carried out calculations on a series of substituted silylamines,  $\text{HXNSih}_3$  ( $\text{X} = \text{H}, \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}, \text{SiH}_3, \text{PH}_2, \text{SH}, \text{Cl}$ ), at the HF/6-31G(d) and MP2/6-311G(dp) levels. The sum of the three optimal angles,  $\theta_\tau = \theta(\text{HNX}) + \theta(\text{HNSi}) + \theta(\text{XNSi})$ , is used to characterize the deviation from planarity at the central nitrogen atom. With this definition, a perfect planar geometry has a  $\theta_\tau$  angle of  $360^\circ$ . The computed  $\theta_\tau$  values are listed in Table 4, along with the calculated partial charges of the substituent atoms or groups. There is a good correlation between the pyramidization angle and the computed NPA atom/group charge. For most systems, the substituent group is less electron withdrawing than nitrogen. Thus, the substituent group has a positive partial charge, giving rise to a net repulsion with the silyl group. This results in a roughly planar geometry ( $\text{sp}^2$  hybridization) at the nitrogen center. For the OH- and F-substituted compounds, both of which have higher electronegativity than nitrogen, the fluorine atom and the hydroxyl group have negative partial charges, resulting in an electrostatic attraction with the silyl group and net stabilization of the pyramidal geometry. The computed  $\theta_\tau$  angle of  $336^\circ$  for  $\text{HN}(\text{OH})\text{SiH}_3$  is in good accord with the experimental value of  $332.3^\circ$  for  $\text{N}(\text{CH}_3)(\text{SiH}_3)(\text{OCH}_3)$ .<sup>15</sup>

#### 4. Conclusion

A block-localized wave function method was used to examine the stereoelectronic effect on the structure and energetics of trisilylamine and trimethylamine. Quantum mechanical calculations on the delocalized and the strictly localized states reveal that the electronic delocalization stabilization in the planar

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$\text{N}(\text{SiH}_3)_3$  is smaller than that in the planar  $\text{N}(\text{CH}_3)_3$ . This demonstrates that the dative  $\text{p}_\pi \rightarrow \text{d}_\pi$  bonding theory and the  $\text{n}_\text{N} \rightarrow \sigma_{\text{SiH}}^*$  negative hyperconjugation picture cannot be directly responsible for the planarity of the  $\text{N}(\text{SiH}_3)_3$  structure. In trimethylamine the  $\pi$ -type negative hyperconjugation effect is not sufficient to overcome the repulsion of the  $\sigma$  bonds with the lone-pair electrons on nitrogen, consistent with the VSEPR (valence-shell electron-pair repulsion) model.<sup>28</sup> Thus, trimethylamine adopts a pyramidal geometry. In trisilylamine, the silicon d orbitals make noticeable contributions to the electronic delocalization, although the key factor in charge delocalization is still through  $\text{n}_\text{N} \rightarrow \sigma_{\text{SiH}}^*$  negative hyperconjugation. Interestingly, the gain in  $\text{p}_\pi \rightarrow \text{d}_\pi$  bonding stabilization is offset by a weaker negative hyperconjugation effect in trisilylamine, resulting in a smaller overall delocalization energy ( $-18.5$  kcal/mol) than that in trimethylamine ( $-23.9$  kcal/mol), which contains little  $\text{p}_\pi \rightarrow \text{d}_\pi$  bonding character. Significantly, because of the relatively low electronegativity of the silicon atom, the N–Si bond is much more polar than the N–C bond, producing a remarkable polar  $\sigma$ -effect. Using Weinhold's natural population analyses of the BLW and HF wave functions, we found that the partial charge is much larger on the silyl group in  $\text{N}(\text{SiH}_3)_3$  than that on the methyl group in  $\text{N}(\text{CH}_3)_3$ . Concomitantly, the nitrogen atom possesses a greater partial negative charge in  $\text{N}(\text{SiH}_3)_3$  than in  $\text{N}(\text{CH}_3)_3$ . All stereoelectronic factors considered, we attribute the origin of the planar geometry of trisilyl-

amine to the polar  $\sigma$ -effect that yields significant long-range electrostatic repulsion between the silyl groups.

Natural population analyses on a series of substituted silylamines provide additional support to the electrostatic model. It is found that only the most electronegative substituents such as F and OH can have electrostatic attraction with the silyl group, leading to noticeable pyramidal geometry at the nitrogen center. This is in accord with the recent X-ray structure of  $\text{N}(\text{CH}_3)(\text{OCH}_3)(\text{SiH}_3)$ , which has a nonplanar structure at the nitrogen center.<sup>16</sup>

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**Supporting Information Available:** Tables of optimized geometries for substituted amines at the HF and MP2 levels and distances between N and Si for  $\text{NH}_2\text{SiH}_3$  and  $\text{N}(\text{SiH}_3)_3$  and figures showing the isoelectrostatic potential contours for  $\text{N}(\text{CH}_3)_3$  and  $\text{N}(\text{SiH}_3)_3$  computed at the HF/6-31G(d) level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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