

Second-Nearest-Neighbor Effects upon N NMR Shieldings in Models for Solid Si_3N_4 and C_3N_4

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NMR shifts are generally determined mainly by the nearest-neighbor environment of an atom, with fairly small changes in the shift arising from differences in the second-nearest-neighbor environment. Previous calculations on the $(\text{SiH}_3)_3\text{N}$ molecule used as a model for the local environment of N in crystalline α - and β - Si_3N_4 gave N NMR shieldings much larger than those measured in the solids and gave the wrong order for the shifts of the inequivalent N sites (e.g., N1 and N2 in β - Si_3N_4). We have now calculated the N NMR shieldings in larger molecular models for the N2 site of β - Si_3N_4 and have found that the N2 shielding is greatly reduced when additional N1 atoms (second-nearest-neighbors to the central N2) are included. The calculated N2 shieldings (using the GIAO method with the 6-31G* basis set and 6-31G* SCF optimized geometries) are 288.1, 244.7, and 206.0 ppm for the molecules $(\text{SiH}_3)_3\text{N}$, $\text{Si}_6\text{N}_5\text{H}_{15}$, and $\text{Si}_9\text{N}_9\text{H}_{21}$ (central N2), respectively, while the experimental shielding of N2 in β - Si_3N_4 is about 155 ppm. Second-nearest-neighbor effects of only slightly smaller magnitude are calculated for the analog C molecules. At the same time, the effects of molecule size upon Si NMR shieldings and N electric field gradients are small. The local geometries at the N2-like Ns in $\text{C}_6\text{N}_5\text{H}_{15}$ and $\text{C}_9\text{N}_9\text{H}_{21}$ are calculated to be planar, consistent with the planar local geometry recently calculated for N in crystalline C_3N_4 using density functional theory. © 1997 Academic Press

INTRODUCTION

For electropositive atoms such as Si and Al, solid-state NMR spectroscopy has proven to be an extremely valuable technique for characterizing the nearest-neighbor and second-nearest-neighbor environment (1). For a material such as Si_3N_4 one would therefore expect that by studying both the Si and the N NMR one could characterize a range of coordination shells about each of the atoms and thereby completely define the midrange order within the material, whether it was crystalline or amorphous. N NMR shieldings in solids have been much less studied than Si shieldings, but it does appear possible to delineate shielding ranges for local structural types, just as in Si NMR, although the shielding ranges within a local type are considerably larger (2). Studies on the α and β crystalline forms of Si_3N_4 identified a number of magnetically distinct N environments (3).

For the higher symmetry β form, the N2 site, with threefold rotational symmetry, showed a chemical shift of 68.9 ppm, relative to the ammonium resonance of solid NH_4NO_3 , while the N1 site, without threefold symmetry, showed a shift around 51 ppm. Earlier calculations on simple $(\text{SiH}_3)_3\text{N}$ models for Si_3N_4 with geometries appropriate to the N1 and N2 sites gave an incorrect order for the shieldings of the two sites, as well as absolute values of the shielding which were too high by about 100 ppm (4). Assuming that the NH_4^+ resonance in aqueous NH_4NO_3 solution and in solid NH_4NO_3 is the same, the N absolute shielding scale (5) gives shielding values of 170 and 153 for the N1 and N2 sites of β - Si_3N_4 , while the values calculated for the $(\text{SiH}_3)_3\text{N}$ molecules were around 255–285 ppm (depending upon whether one chose an optimized or experimental geometry). The reported shift for the gas-phase $(\text{SiH}_3)_3\text{N}$ molecule (6) translates into a value of 281 for the absolute shielding, in reasonable accord with the calculated value at the equilibrium geometry. Studies on somewhat larger molecules (with both a central N and a second-neighbor N) showed large conformation-dependent effects upon the shielding of the central nitrogen (4), but adding up these long range effects for the inequivalent sites in Si_3N_4 became quite complicated, and it was not clear whether the effects of different second-nearest-neighbors would actually be additive or would saturate, with the effect of additional second-nearest neighbors much smaller than that of the first such neighbor.

Recently interest in Si_3N_4 has increased due to the prediction by Liu and Cohen (7) that a β - Si_3N_4 structural form of C_3N_4 would be harder than diamond. Guo and Goddard (8) questioned Liu and Cohen's assumptions about the locally planar C geometry in C_3N_4 based on their calculations for a hexamethylenetetramine, $\text{N}_4\text{C}_6\text{H}_{12}$, model with nonplanar NC_3 groups, but Teter and Hemley (9) found exactly such a planar structure using density functional band theoretical methods, without the symmetry constraints of Liu and Cohen. It has proven extremely difficult to produce a solid with the C_3N_4 composition, with most of the materials prepared being much richer in C (10). Characterization of amorphous compounds of C_3N_4 or similar composition could be aided by

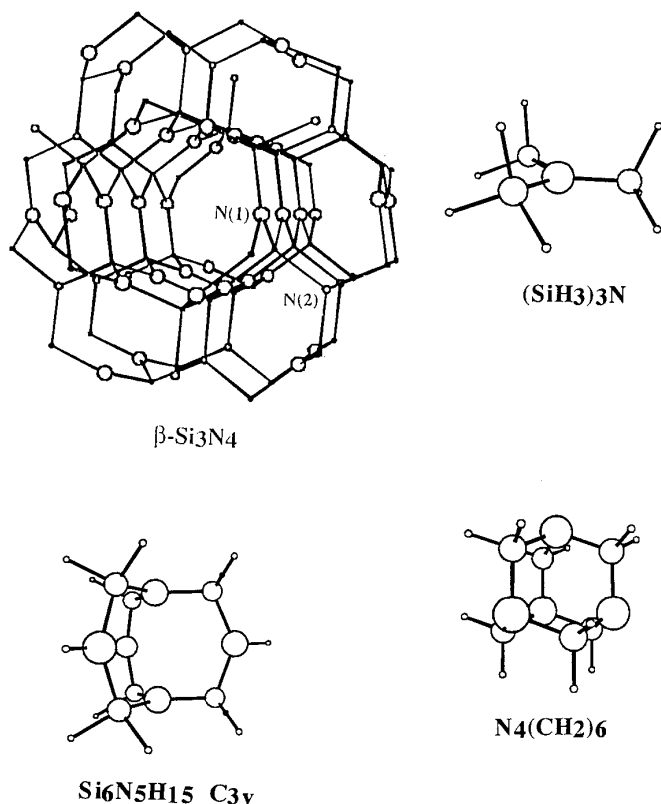


FIG. 1. The crystal structure of $\beta\text{-Si}_3\text{N}_4$ and some model molecules used to describe it and its C analog (N atoms are shown as the larger atoms, H as the smaller). The N2 sites are labeled in the crystal structure model and lie along the C_3 axes in the molecules.

measurement and interpretation of their solid-state N NMR spectra. It may therefore be valuable to study nonlocal effects upon the N NMR shielding for both Si_3N_4 and C_3N_4 . Recently Hughbanks and Tian (10) analyzed the stability of the $\beta\text{-C}_3\text{N}_4$ structure (shown in Fig. 1) in terms of N–N repulsions, using a $\text{C}_6\text{N}_5\text{H}_{15}$ model for a fragment of the structure containing two N2-type atoms whose NC_3 planes lay perpendicular to the c axis (shown in Fig. 1; note the mislabeling of N1 and N2 in Hughbanks and Tian). This molecule is considerably different than hexamethylenetetramine (also shown in Fig. 1), used by Guo and Goddard as a model for C_3N_4 .

To address questions concerning N NMR shieldings as well as energetics and other properties we carried out Hartree–Fock SCF calculations on $(\text{SiH}_3)_3\text{N}$, $\text{Si}_6\text{N}_5\text{H}_{15}$, and $\text{Si}_9\text{N}_9\text{H}_{21}$ and a number of related molecules, as well as their C analogs, using 6-31G* (12) or better basis sets and using the capabilities of the software packages GAMESS (13) and GAUSSIAN94 (14) to evaluate structures, energies, NMR shieldings, and electric field gradients at N. The nuclear quadrupole coupling constant at N was then calculated using the Hartree–Fock value for the quadrupole moment of ^{15}N (15). The NMR shieldings are calculated with GAUSSIAN94 using the GIAO method (16).

RESULTS

Geometries have been optimized for $(\text{SiH}_3)_3\text{N}$, $\text{Si}_6\text{N}_5\text{H}_{15}$, and $\text{Si}_9\text{N}_9\text{H}_{21}$ and their C analogs and for $(\text{SiH}_3)_2\text{N}(\text{SiH}_2\text{NH}_2)$, $(\text{SiH}_2\text{NH}_2)_3\text{N}$, and other molecules, within various symmetry constraints as specified in the tables. The geometries of some of these molecules are shown in Fig. 2. The N2 site in $\beta\text{-Si}_3\text{N}_4$ has only C_3 symmetry. Lowering the symmetry from C_{3v} to C_3 in the $\text{Si}_6\text{N}_5\text{H}_{15}$ molecule reduces the energy by 8.1 kcal/mol, although the local geometry of the NSi_3 groups is almost unchanged. Rather the NSi_2H groups distort, adopting a geometry more like that in $\beta\text{-Si}_3\text{N}_4$.

N NMR shieldings evaluated using the GIAO method and 6-31G* basis sets for the various compounds are given in Table 1. For comparison, the same method applied to the NH_3 and NH_4^+ free molecules gives shieldings of 267.3 and 254.3 ppm, respectively. Electric field gradients and quadrupole coupling constants at the N nucleus evaluated at the 6-31G* SCF level are given in Table 2.

While the N shielding calculated for $(\text{SiH}_3)_3\text{N}$ is in reasonable accord with experiment (288 ppm calc. vs 281 ppm exp.), it is much larger than the N shieldings observed for solid Si_3N_4 . As the model molecule is enlarged, the shielding

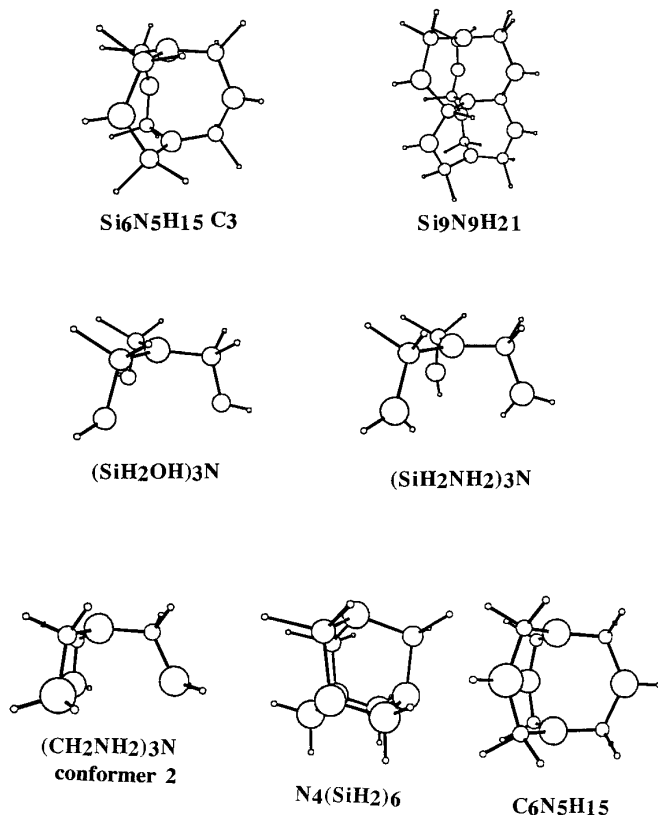


FIG. 2. Optimized geometries for other molecules whose N NMR shieldings are given in Table 1 (N atoms are shown as the larger atoms, H as the smaller). The N2 sites lie along the C_3 axes.

TABLE 1

N NMR Shieldings Evaluated at the GIAO SCF Level Using 6-31G* Basis Sets and 6-31G* Geometries for Si Compounds (6-31G(2d) Geometries for C Compounds)

Molecule	Symmetry	σ_N (ppm)
(SiH ₃) ₃ N	C _{3v}	288.1
(SiH ₃) ₂ N(SiH ₂ NH ₂)	C ₁	256.8
(SiH ₂ NH ₂) ₃ N	C _{3v}	247.7
Si ₆ N ₅ H ₁₅	C _{3v}	244.7
	C ₃	230.1
Si ₉ N ₉ H ₂₁	D _{3h}	206.1 (inner)
		237.1 (outer)
(CH ₃) ₃ N		
Nonplanar	C ₃	263.2
Planar	C _{3h}	307.2
C ₆ N ₅ H ₁₅	C _{3v}	259.3
C ₉ N ₉ H ₂₁	D _{3h}	235.9 (inner)
		248.7 (outer)
(SiH ₂ OH) ₃ N	C _{3v}	221.6
(SiH ₂ CH ₃) ₃ N	C _{3v}	260.8

of the most central N2-type N drops, from 288.1 in (SiH₃)₃N to 244.7 or 230.1 ppm in Si₆N₅H₁₅ (depending upon whether we optimize in C_{3v} or C₃ geometry) and then to 206.0 ppm for the central N2 in Si₉N₉H₂₁ (optimized only in D_{3h} symmetry because of its size). The outer N2 in Si₉N₉H₂₁ has a slightly lower shielding (237.1 ppm) than the N2 in (C_{3v} symmetry) Si₆N₅H₁₅ (244.7 ppm). Based on these results we see that the shielding of a central N2 is decreased about 43–58 ppm by the inclusion of the shell with three N1 and a second N2, is decreased a slightly smaller amount by the next such shell but is decreased only about 8 ppm by a third shell. It is important to note that the change in N shielding produced by exchanging C for Si in the first coordination shell (i.e., (CH₃)₃N vs (SiH₃)₃N) is only around 25 ppm—thus the *second-nearest-neighbor N1-type atoms actually change the shielding more strongly than do the nearest-neighbor Si or C atoms*.

The calculated shielding of the N2-like nitrogen is similar for Si₆N₅H₁₅ and for (SiH₂NH₂)₃N (244.7 vs 247.7 ppm), a molecule which is similar but lacks the bottom NSi₃ group. This indicates that it is mainly the three N1-type atoms which influence the shielding of the top N2, not the other N2 on the bottom. In our previous calculations (4) we found that when one of the SiH₃ groups in (SiH₃)₃N was replaced by a SiH₂NH₂ group the shielding of the central N was reduced by an amount strongly dependent upon the conformation of the molecule. The geometry of the N1-type atom in Si₆N₅H₁₅ corresponds closely to case e in Fig. 4 of Ref. (4), which is deshielded by about 16 ppm compared to that in (SiH₃)₃N. Naively multiplying this effect by three would project a 48-ppm deshielding for (SiH₂NH₂)₃N vs (SiH₃)₃N, compared to the 40 ppm actually obtained in the present calculations.

Of course the calculation schemes used were somewhat different—the RPA LORG (17) method in the earlier work and the GIAO method in the present—but the results seem quite comparable. The calculated difference in shielding between (SiH₃)₃N and the optimized geometry of (SiH₃)₂N-(SiH₂NH₂) is very close to 30 ppm in both the present results and the earlier RPA LORG results.

In the earlier calculations we considered only one geometry (the calculated equilibrium value) for the molecule with one -SiH₃ group replaced by a -SiH(NH₂)₂ group. The equilibrium conformation of the two exterior N lone pairs with respect to the central N was such that the shielding of this molecule was about the same as that for the equilibrium geometry of (SiH₃)₂N(SiH₂NH₂), with only one N1 atom. Thus we could not previously determine whether the second-neighbor effects on the N shielding would *saturate* with just one N second-nearest-neighbor. The present results indicate that they *do not*—that *n neighbors of a given type produce approximately n times the shielding effect of a single such neighbor*. Of course the effects do still fall off with distance, with fourth-neighbor effects much smaller than the second-neighbor effect. However, the deshielding effect is not limited to other N atoms. A calculation on (SiH₂OH)₃N, in which the -NH₂ groups connected to Si are replaced by -OH groups, gives a shielding at the N2-type N of 227.1 ppm, even more deshielded than that in (SiH₂NH₂)₃N. Thus, such effects should also appear in SIALON-type ceramics (2). When the -NH₂ groups are replaced by -CH₃ groups, as in (SiH₂CH₃)₃N, the deshielding effect is much less (only about 27 ppm compared to that in (SiH₃)₃N). However, since some deshielding still occurs even for the -CH₃ case, it is not simply the interaction of lone-pair orbitals which produces the deshielding.

Although the N2-like sites show a large change in shielding in the different molecules, the shieldings of the

TABLE 2

Electric Field Gradients at ¹⁵N (in Atomic Units) Evaluated for the Molecules of Table 1 at the 6-31G* SCF Level (NQCC Obtained Using Hartree-Fock Values for the ¹⁵N Quadrupole Moment)

Molecule	<i>eq</i> (AU)	NQCC (MHz)
(SiH ₃) ₃ N	0.550	2.00
(SiH ₂ NH ₂) ₃ N	0.468	1.70
Si ₆ N ₅ H ₁₅	0.491	1.79
Si ₉ N ₉ H ₂₁	0.488 (inner)	1.78
	0.513 (outer)	1.87
(CH ₃) ₃ N	1.319 (nonplanar C ₃)	4.80
	1.592 (planar C _{3h})	5.79
C ₆ N ₅ H ₁₅	1.423	5.18
C ₉ N ₉ H ₂₁	1.507 (inner)	5.49
	1.434 (outer)	5.22

N1-like sites and the Si sites are much less affected by molecular size. The N1-like NSi_2H groups in $\text{Si}_6\text{N}_5\text{H}_{15}$ and $\text{Si}_9\text{N}_9\text{H}_{21}$ show shieldings of 247.5 and 245.5 respectively, while the Si atoms in SiH_2N_2 environments in these two molecules have almost the same shielding, 467.5 ppm. Of course, neither the N1-like sites nor the Si sites have the right set of nearest neighbors to accurately model the N1 or Si sites of Si_3N_4 . Any reliable model for the shielding of the N1 site would essentially have to be N1 centered, with at least the correct first- (i.e., three Si's) and second-nearest neighbors about N1. Also, in $\text{Si}_6\text{N}_5\text{H}_{15}$ the N1-like site already has a full complement of second-nearest-neighbor N2 atoms and going to the larger molecule $\text{Si}_9\text{N}_9\text{H}_{21}$ introduces only second-nearest-neighbor N1s and fourth-nearest-neighbor N2s.

By contrast to the NMR shielding of N2, the electric field gradient (EFG) at the N2 nucleus seems to be affected much less by changes in the molecular size, with the EFG changing by only about 10% between $(\text{SiH}_3)_3\text{N}$ and $\text{Si}_9\text{N}_9\text{H}_{21}$. The calculated NQCC for the largest model is about 1.78 MHz, reasonably consistent with the value of 2.1 MHz obtained by Olivieri and Hatfield (18). This is clearly associated with delocalization of N2p electron density onto the silyl groups, although such delocalization is better interpreted as involving the Si-C σ^* orbitals rather than Si3d orbitals (19). There seems to be little correlation between the calculated N EFGs and NMR shielding constants, indicating that the delocalization of N2p electron density which reduces the EFG is not the main source of the change in NMR shielding.

Calculated trends in shieldings are similar for the analog C compounds, although the second-neighbor effect seems to be saturating more quickly. Increasing the molecular size certainly reduces the N shielding, so long as we compare it with a $(\text{CH}_3)_3\text{N}$ molecule with a local planar geometry (i.e., constrained to C_{3v}). Unconstrained $(\text{CH}_3)_3\text{N}$ is nonplanar C_{3v} and has a smaller N NMR shielding. The nonplanarity at the N in $(\text{CH}_3)_3\text{N}$ can of course be rationalized using simple molecular orbital arguments (20). It is important to note that $\text{C}_6\text{N}_5\text{H}_{15}$, $\text{C}_9\text{N}_9\text{H}_{21}$, and $(\text{CH}_2\text{NH}_2)_3\text{N}$ were all optimized in C_{3v} symmetry to allow a nonplanar local NC_3 geometry but in each case *the local geometry about N was essentially planar*. By contrast the same method (6-31G* SCF) with the same C_{3v} symmetry constraint gives a large departure from planarity at N for the hexamethylenetetramine, $\text{N}_4(\text{CH}_2)_6$, molecule used by Guo and Goddard as a model for solid C_3N_4 and a significant nonplanarity for a different conformer of $(\text{CH}_2\text{NH})_3\text{N}$, still with C_{3v} symmetry but with the N lone pair in the N-C-N plane rather than perpendicular to it. Equilibrium C-N-C angles calculated at the 6-31(2d) SCF level are given in Table 3 for a number of molecules. Clearly the planarity of the NC_3 group depends rather strongly upon other interactions within the molecule. In fact, geometries in the NSi_3 groups show the same effects as those in the C compounds. The optimized geometry of

TABLE 3
Equilibrium C-N-C Angles Evaluated at the 6-31 (2d) SCF Level for Various Molecules (All Optimizations in C_{3v} Symmetry, Except for D_{3h} Symmetry in $\text{C}_9\text{N}_9\text{H}_{21}$)

Molecule	$\langle\text{C-N-C}\rangle$
$(\text{CH}_3)_3\text{N}$	111.8
$\text{N}_4\text{C}_6\text{H}_{12}$	108.1
$(\text{CH}_2\text{NH}_2)_3\text{N}$	
Conformer 1	119.9
Conformer 2	117.9
$\text{C}_6\text{N}_5\text{H}_{15}$	119.7
$\text{C}_9\text{N}_9\text{H}_{21}$	118.0

$\text{N}_4(\text{SiH}_2)_6$ shows a decidedly nonplanar NSi_3 group. We examined the energies of the molecular orbitals for planar and pyramidal geometries of $\text{C}_6\text{N}_5\text{H}_{15}$ but were unable to obtain any simple explanation for why this molecule shows a planar geometry at N2.

DISCUSSION

While it is clear that the NMR shielding of N2-like Ns is reduced by the presence of second-nearest-neighbor N1-like atoms, an orbital interpretation is not necessarily straightforward. In the RPA LORG method the shielding can be decomposed into contributions from localized MOs (LMOs), the most important of which are those centered on the magnetic nucleus. Comparing $(\text{SiH}_3)_3\text{N}$ and $(\text{SiH}_3)_2\text{N}(\text{SiH}_2\text{NH}_2)$ using this approach we find that 24 ppm of the total shielding difference of 30 ppm can be attributed to changes in contributions from the four valence LMOs on N. The contributions from the N2p lone-pair-like LMO and the sigma LMO bonding from the N to the $-\text{SiH}_2\text{NH}_2$ group both become more negative by about 9 ppm as we replace one H by a $-\text{NH}_2$ group. But since the changes in ground state properties such as the N EFGs do not closely parallel the changes in the N NMR shielding it seems that the NMR results cannot be interpreted in terms of the ground state electron distribution alone. Rather changes in the virtual orbital space are the main cause of changes in the LMO contributions to the shielding.

In the conventional formulation, contributions to the paramagnetic part of the NMR shielding involve matrix elements of both the angular momentum and the angular momentum divided by the cube of the electron's distance from the origin, and it is this second matrix element which is responsible for the localized character of the paramagnetic shielding. We can simulate such localization to some extent by examining the virtual orbitals in an equivalent ionic core state, which also provides a semiquantitative description of the X-ray absorption spectrum for that nucleus (21). For example, in $(\text{SiH}_3)_2\text{N}(\text{SiH}_2\text{NH}_2)$ we can convert the central N nucleus

to O, creating a positive ion, and then examine the empty orbitals of that ion. The basic electronic structure in the valence region of Si_3N_4 has been studied by X-ray emission and X-ray absorption spectroscopy. The top of the valence region was found to be essentially $\text{N}2p$ in character while the bottom of the conduction band has primarily $\text{Si}3p$ character (22). We find for the core-ion state of $(\text{SiH}_3)_2\text{N}$ (SiH_2NH_2) that some of the low-lying empty orbitals have $\text{N}2p$ character from the $\text{N}1$ -type atoms mixed into $\text{N}2$ - Si σ^* character, consistent with the general idea that $\text{N}2$ - $\text{N}1$ interactions are responsible for the deshielding. Unfortunately, the orbital eigenvalue spectrum and orbital compositions are so complicated that we cannot identify a particular orbital interaction as responsible for the deshielding as we did in the case of SiH_3Cl (21b).

It is important to realize that although we have established that second-nearest and further neighbors have substantial effects upon the absolute shieldings of the $\text{N}2$ -type atoms in β - Si_3N_4 we still have only a semi-quantitative value for that shielding. We also have not yet reproduced the difference in shielding between the $\text{N}1$ and $\text{N}2$ sites. To do so we would have to construct another model which was $\text{N}1$ centered and which extended at least through fourth-nearest neighbors. It is not even clear that models of the same size (e.g., having approximately the same total number of N atoms) would give comparable results for the $\text{N}1$ and $\text{N}2$ sites, since the two sites might differ in their susceptibility to long range effects.

It also seems clear that identifying the presence of planar three-coordinate N in Si_3N_4 -like sites in C_xN_y solids using N NMR will be difficult—second-nearest and more distant neighbors will strongly influence the shielding. It may well be easier to recognize such species by focusing on X-ray absorption/inner shell electron energy loss spectra (23) or vibrational spectra (24). For example, the most intense features in the IR spectra of $(\text{SiH}_3)_3\text{N}$ and $(\text{CH}_3)_3\text{N}$ are calculated to occur at scaled $6\text{-}31\text{G}^*$ SCF values of 904 and 1023 cm^{-1} , respectively. The calculated value for $(\text{SiH}_3)_3\text{N}$ is consistent with the 885- cm^{-1} value seen in silicon nitride films (24).

Our results bear some resemblance to recent theoretical studies of conformational (25a, b, c) and solvent (25d) effects on NMR shieldings. However, the conformational and solvent effects on N (and C) shieldings described in these papers are considerably smaller in magnitude than the effects described here. In studies such as those in Ref. (25) the shielding is still essentially determined by the nearest-neighbor atoms, with more distant atoms causing only fairly small changes in shielding.

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