radius would imply higher multiplicity for all bonds, but the conclusions about the similarity of the bonding in CrO_2F_2 and CrO_2Cl_2 would remain.

According to VSEPR theory, the amount of space in the coordination sphere of an atom occupied by single, double, and triple bonds to that atom increases with increasing bond multiplicity. Application of this and a few other simple postulates of the theory has led to successful predictions of the relative magnitudes of bond angles in a wide variety of substances among which are the sulfuryl and selenyl halides whose structures are summarized in Table V. As is seen from the table, however, the theory fails for the chromyl halides, where the angle between the bonds to the oxygen atoms is found to be slightly smaller than that between the halogen bonds. This angle relationship is also found in several other pairs of similar molecules that differ in having a main-group vs. a transition-metal atom at the central position.

The angle differences just mentioned, though puzzling, are no more so than some other structural features of the group 6 molecules revealed in Table V. For example, the OMX angles are remarkably similar in all five cases. Also, the O·O distances for the sulfur and chromium compounds differ by at most about 0.12 Å, despite the large differences in the M=O bond lengths and OMO bond angles. We see no simple model of the bonding which successfully rationalizes all features of the structures in Table V. In respect to the difference between the FMF angles in SO_2F_2 and CrO_2F_2, however, both GMD[5] and BMO[6] have noted that Coulomb repulsion between the fluorine atoms should be greater in the latter than in the former because their atomic charges are larger in the latter. BMO have also pointed out that the FCrF angle bending constant is smaller than the FSF constant and that the observed relative values for ∠FMF in the two compounds are consistent with a balancing of these repulsions and angle strains.

Our values for the symmetrized force constants for CrO_2F_2 are similar to those found in CrO_2Cl_2[2,14] for all modes except those comprising primarily Cr—X bond stretches. For these modes the Cr—F constants, while still in the single-bond range, are nearly twice the magnitude of the corresponding Cr—Cl ones, a difference similar to that observed for fluorine and chlorine bonded to other atoms. The consistency of the force fields for these two molecules supports the conclusion obtained from comparison of the bond lengths that the bonding in them is similar. Finally, we note that BMO[6] have obtained values for the internal stretching and stretch-stretch interaction constants that differ only very slightly from those derived from our symmetry force field. The values in aJ/Å^2 (BMO in parentheses) are f(CrO) = 7.470 (7.429), f(CrF) = 4.746 (4.774), f(CrO,CrO) = 0.341 (0.382), f(CrF,CrF) = 0.187 (0.384), and f(CrO,CrF) = 0.284 (0.390). The differences may be attributed to the different structures used in the normal-coordinate analyses.

Acknowledgment. This work was supported by the National Science Foundation under Grants CHE78-04258 and CHE81-10541 and by a grant from the Oregon State University Computer Center.

Registry No. CrO_2F_2, 7788-96-7.

Supplementary Material Available: Tables of vibrational wavenumbers and isotopic shifts, the force constant correlation matrix, total scattered intensities, calculated backgrounds, and average molecular intensities from the three camera distances (14 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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Photoelectron Spectroscopic and Theoretical Study of Tris(trimethylsilyl)amine and Related Silylamines. Real and Hypothetical Planar Tertiary Amines

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The lowest ionization potential (IP), corresponding to ionization of a nitrogen 2p "lone-pair" orbital, was studied experimentally via photoelectron spectroscopy (PES) and theoretically by using semiempirical (MNDO) and ab initio methods, in the three series $(CH_3)_{3-n}N(SiH_3)_n$, $(CH_3)_{3-n}N(Si(CH_3)_3)_n$, and $(CH_3CH_2CH_2)_{3-n}N(Si(CH_3)_3)_n$, n = 0-3. The ab initio calculations on $(CH_3)_2NSiH_3$ predict a very flat potential surface around nitrogen, suggesting a balance of forces tending toward pyramidal and planar geometries. The results do not wholly support a previous interpretation of electron diffraction data for this molecule. The question of d-orbital participation in the Si-N bond is discussed in terms of an effect on the geometry of the silylamines and an effect on the IP's of the silylamines. A method of extrapolating measured IP's to arrive at the vertical IP of a (hypothetical) planar tertiary amine has been presented. For planar trimethylamine a vertical IP of 7.7-7.9 eV is predicted. For planar tri-*n*-propylamine the vertical IP is predicted to be 7.4 eV. MNDO calculations on tri-*tert*-butylamine suggest that the reason for its nonexistence is entirely steric, not electronic.

Introduction

Tris(trimethylsilyl)amine is an intriguing compound for at least two reasons. First, it is quite remarkable that three extremely bulky trimethylsilyl groups can "fit" around one nitrogen while three *tert*-butyl groups cannot, or, at least, have not yet been made to fit.[1] Second, tris(trimethylsilyl)amine is fascinating because it is an aliphatic amine that is planar, whereas other amines are pyramidal.

We have undertaken a photoelectron spectroscopic (PES) and theoretical study of tris(trimethylsilyl)amine and related silylamines, the results of which we report herein.

Experimental Section

Except for *N*,*N*-bis(trimethylsilyl)propylamine and *N*-(trimethylsilyl)di-*n*-propylamine, all compounds were commercial samples (Petrarch Systems, Inc.) whose purity was checked by H NMR. The two compounds mentioned above were synthesized by literature

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(1) Methyldi-*tert*-butylamine has recently been synthesized: Audeh, C. A.; Fuller, S. E.; Hutchinson, R. J.; Lindsay-Smith, J. R. *J. Chem. Res., Miniprint* **1979**, 2984.

0020-1669/83/1322-0895$01.50/0

Table I. First Ionization Potentials (eV)

	$n = 0$	$n = 1$	$n = 2$	$n = 3$
$(CH_3)_{3-n}N(SiH_3)_n$	$8.5,^a$ $8.44,^b$	8.5^a	9.2^a	9.7^a
$(CH_3)_{3-n}N(Si(CH_3)_3)_n$	8.53^c	8.03	8.21	8.58,
$(CH_3CH_2CH_2)_{3-n}N(Si(CH_3)_3)_n$	7.92^c	7.83	8.18	8.60^d

[a] Reference 4. [b] Reference 24. [c] Reference 23. [d] Starzewski, K. A. O.; Dieck, H. T.; Bock, H. *J. Organomet. Chem.* 1974, *65*, 311.

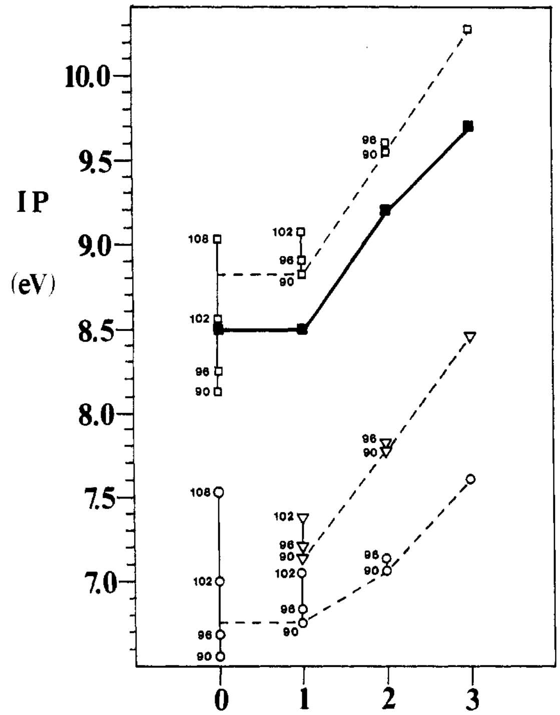


Figure 1. Lowest IP of $(CH_3)_{3-n}N(SiH_3)_n$: experimental (■) and calculated by ab initio methods STO-3G (○), STO-3G* (▽), and 6-21G (□). At n = 0–2, calculations were performed at several values of θ shown in this figure and in Table II.

methods[2,3] and purified by distillation.

Photoelectron spectra were obtained on a Perkin-Elmer Model PS-18 spectrometer. Xenon and argon were used as calibrants in all runs, and all data quoted herein represent an average of several spectra.

Results

Photoelectron spectra for the series $(CH_3)_{3-n}N(SiH_3)_n$, n = 0–3, have been obtained previously,[4] and the first ionization potential (IP) of each member of the series is given in Table I and plotted in Figure 1. Shown also in Table I and plotted in Figure 2 are the measured first IP's in the series $(CH_3)_{3-n}N(Si(CH_3)_3)_n$, n = 0–3, and $(CH_3CH_2CH_2)_{3-n}N(Si(CH_3)_3)_n$, n = 0–3, which were determined here.

Calculations were carried out at two levels of sophistication, namely MNDO[5] and ab initio.[6] In the semiempirical calculations, the geometry was optimized with respect to energy. At the ab initio level, several standard basis sets were employed—STO-3G, STO-3G* (which includes d orbitals on silicon), and 6-21G. In addition, the standard STO-3G* basis was augmented by adding d orbitals to nitrogen (d-orbital exponent = 0.8). The geometries employed in these calculations are recorded in Table II, and the results are shown in Table III. The parameter θ is defined as follows, with trimethylamine as an example:

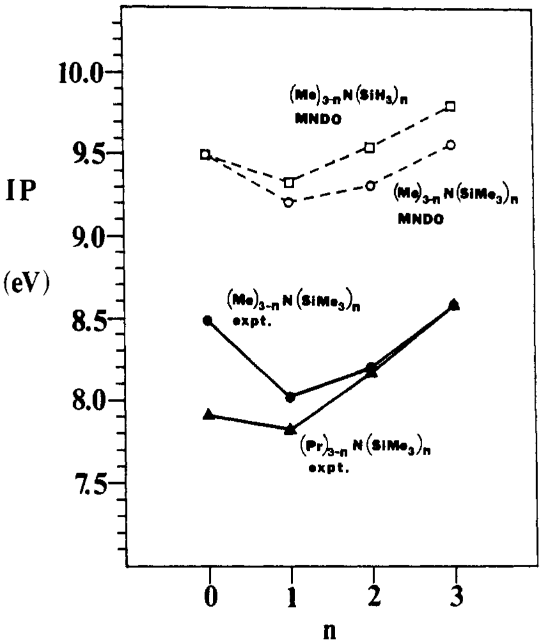
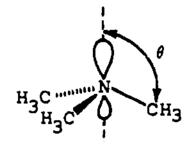


Figure 2. Experimental lowest IP of $(CH_3)_{3-n}N(Si(CH_3)_3)_n$ (●) and $(CH_3CH_2CH_2)_{3-n}N(Si(CH_3)_3)_n$ (▲) and lowest IP calculated by MNDO for $(CH_3)_{3-n}N(Si(CH_3)_3)_n$ (○) and $(CH_3)_{3-n}N(SiH_3)_n$ (□).



In order to keep these ab initio calculations manageable, the R–N–R′ and R–N–R angles in R_2NR' were set equal to each other even when R ≠ R′. This seems to be an allowable procedure when R and R′ are CH_3 and SiH_3; certainly it would be unsatisfactory for CH_3 and $SiMe_3$. When R and R′ are CH_3 and SiH_3, variation of θ is expected to be the major geometric effect, and keeping R–N–R′ and R–N–R angles equal constitutes a minor perturbation.

Discussion

Ab Initio Results. (i) Planarity of $(CH_3)_2NSiH_3$. A critical factor in the calculations reported here was the geometry about nitrogen. Electron diffraction studies have been carried out on $(CH_3)_{3-n}N(SiH_3)_n$, n = 1–3. The conclusion for trisilylamine[7] and methyldisilylamine[8] was that nitrogen was planar. In the case of dimethylsilylamine, the published geometry had the heavy atoms slightly nonplanar.[9] However, the author has indicated that the diffraction data do not strictly rule out a planar geometry.[10]

The reason for our concern about geometry is apparent when one examines the behavior of trimethylamine. At the STO-3G level, an energy minimum is reached at θ = 101.2° (by using a three-point parabolic fit): experimentally, θ = 108°.[11] At

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(10) Personal communication from D. W. H. Rankin to M.L.M.

(11) Wollrab, J. E.; Laurie, V. W. *J. Chem. Phys.* **1969**, *51*, 1580.

Table II. Geometries Used in Calculations^{a}

		C-N	Si-N	C-H	Si-H	H-C-N	H-Si-N	planarity^{b}
$(CH_3)_3N$	ab initio^{c}	1.46		1.10		109.471		varied
	MNDO	1.462		1.115		111.34		sum = 350
	exptl	1.451 ± 0.003^{d}		1.095 ± 0.008^{d}		110.6 ± 0.5^{d}		sum = 333^{d}
		1.454 ± 0.045^{e}		1.111 ± 0.081^{e}		109.8 ± 1.3^{e}		sum = 332^{e}
$(CH_3)_2NSiH_3$	ab initio	1.44	1.77	1.10	1.44	109.471	112.00	varied
	MNDO	1.441	1.771	1.117	1.442	111.676	108.847	sum = 360
	exptl^{f}	1.462 ± 0.004	1.715 ± 0.004	1.084 ± 0.008	1.485^{g}	109.5^{g}	109.5^{g}	Si-N-C = 120.0 ± 0.4
								C-N-C = 111.1 ± 1.2
$CH_3N(SiH_3)_2$	ab initio	1.43	1.76	1.10	1.44	109.471	112.00	varied
	MNDO	1.430	1.763	1.119	1.443	111.84	109.16	sum = 360
	exptl^{h}	1.465 ± 0.005	1.726 ± 0.003	1.05 ± 0.004	1.486 ± 0.008			sum = 360
$N(SiH_3)_3$	ab initio		1.76		1.44		112.00	sum = 360
	MNDO		1.758		1.443		109.38	sum = 359
	exptl^{i}		1.734 ± 0.002		1.485^{g}		108.1 ± 0.6	sum = 359
$(CH_3)_2NSi(CH_3)_3$	MNDO	1.442	1.791	1.117 (*N*-CH_3)	1.859 (Si-C)	111.844	109.647 (C-Si-N)	sum = 360
				1.105 (*Si*-CH_3)		111.313 (H-C-Si)		
$CH_3N(Si(CH_3)_3)_2$	MNDO	1.435	1.790	1.116 (*N*-CH_3)	1.861 (Si-C)	112.403	110.424 (C-Si-N)	sum = 360
				1.105 (*Si*-CH_3)		111.368 (H-C-Si)		
$N(Si(CH_3)_3)_3$	MNDO		1.800	1.104	1.865 (Si-C)	111.663 (H-C-Si)	112.690 (C-Si-N)	sum = 360
	exptl^{j}		1.759					sum = 360
$(CH_3)_2NC(CH_3)_3$	MNDO	1.458 (*N*-*t*-Bu)		1.116 (CH_3)		111.86		Me-N-Bu = 122.6
		1.480 (*N*-Me)		1.109 (*t*-Bu)		110.75 (C-C-N)		Me-N-Me = 114.8
				1.565 (C-C; *t*-Bu)		111.86 (H-C-C)		sum = 360
$CH_3N(C(CH_3)_3)_2$	MNDO	1.494 (*N*-*t*-Bu)		1.115 (CH_3)		112.67		*t*-Bu-N-*t*-Bu = 131.6
		1.469 (*N*-Me)		1.108 (*t*-Bu)		112.47 (C-C-N)		*t*-Bu-N-Me = 114.2
				1.568 (C-C; *t*-Bu)		112.20 (H-C-C)		sum = 360
$N(C(CH_3)_3)_3$	MNDO	1.516		1.108		112.76 (H-C-C)		sum = 360
				1.576 (C-C; *t*-Bu)		114.53 (C-C-N)		

[a] MNDO entries refer to geometries optimized by calculation; bond lengths in angstroms, bond angles in degrees. [b] Heavy atoms about central nitrogen; sum refers to sum of angles about N. [c] All basis sets used identical geometries. [d] Reference 11. [e] Beagley B.; Hewitt, T. G. *Trans. Faraday Soc.* 1968, *64*, 2561. [f] Reference 9. [g] Assumed. [h] Reference 8. [i] Reference 7. [j] Reference 20.

Table III. Results of ab Initio Calculations[a]

basis	$(CH_3)_3N$			$(CH_3)_2NSiH_3$			$CH_3N(SiH_3)_2$			$N(SiH_3)_3$		
	θ	IP	E	θ	IP	E	θ	IP	E	θ	IP	E
STO-3G	90	6.55	−171.171 65	90	6.76	−419.394 83	90	7.06	−667.620 30	90	7.62	−915.036 95
	96	6.68	−0.000 88	96	6.84	+0.001 38	96	7.13	+0.000 80			
	102	7.00	−0.002 92	102	7.05	+0.004 51						
	108	7.53	+0.000 68									
STO-3G*				90	7.13	−419.475 59	90	7.77	−667.784 99	90	8.45	−916.105 42
				96	7.20	+0.001 61	96	7.82	+0.005 76			
				102	7.37	+0.005 41						
STO-3G* + d on N	90	6.40	−171.187 78	90	7.02	−419.497 86						
	96	6.55	−0.002 31	96	7.10	+0.000 53						
	102	6.94	−0.008 05									
	108	7.55	−0.009 74									
6-21G	90	8.13	−173.042 66	90	8.82	−424.105 58	90	9.55	−675.172 14	90	10.28	−926.247 7
	96	8.25	−0.000 04	96	8.90	+0.002 42	96	9.60	+0.002 52			
	102	8.56	+0.000 88	102	9.07	+0.006 26						
	108	9.03	+0.002 36									
6-21G*				90	8.83	−424.156 29	90	9.53	−675.200 75			

[a] IP refers to the negative of the energy of highest occupied MO (eV). Energy (au) is listed in full for $\theta = 90°$ and subsequent entries are relative to $\theta = 90°$.

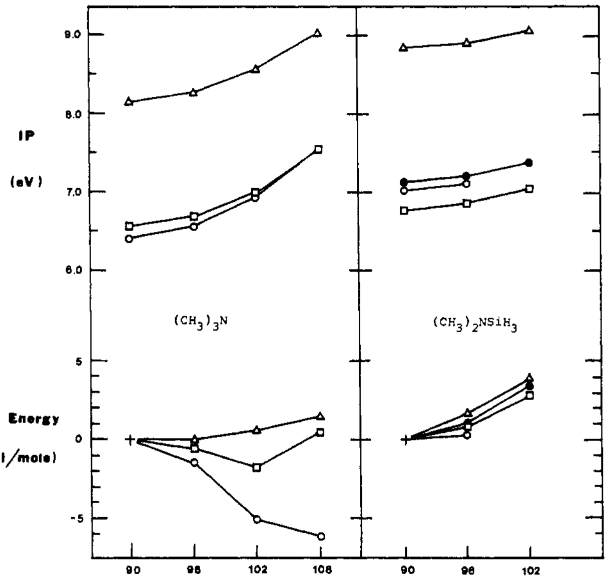

Figure 3. Total energy and lowest IP calculated for $(CH_3)_3N$ and $(CH_3)_2NSiH_3$ as a function of θ. These are ab initio calculations: STO-3G (□), STO-3G* (●), 6-21G (△), STO-3G* + d orbitals on N (○). Energies are given relative to $\theta = 90°$.

the 6-21G level the E vs. θ curve is quite flat (Figure 3), the extrema differing by only 1.5 kcal/mol. Only when d orbitals are included on nitrogen does the calculation approach reality, reaching a minimum at $\theta = 107.5°$. Significantly, the effect of such modest changes in θ on the lone-pair IP is quite dramatic. For example, although total energy at the 6-21G level spanned a range of only 1.5 kcal/mol, the lone-pair IP (which by Koopmans' theorem can be taken to be minus the energy of the HOMO) varied over a wide range of 0.90 eV (21 kcal/mol). This is reasonable; the lone-pair orbital is essentially pure p when the system is planar, and it mixes in s character as the system becomes more pyramidal. Therefore, the question of planarity or nonplanarity of $(CH_3)_2NSiH_3$ must be treated with great care in order to do a credible calculation of the lone-pair IP for this molecule. As can be seen from Table III, every basis set yields the result that the planar form of $(CH_3)_2NSiH_3$ is more stable than the pyramidal form. Here it is most reasonable to compare $\theta = 90°$ to $\theta = 96°$, since larger values of θ are probably not realistic in this case. When we make this comparison, the energy difference between these two values of θ is 0.87 kcal/mol for STO-3G, 1.52 kcal/mol for 6-21G, 1.01 kcal/mol for STO-3G*, but only 0.33 kcal/mol at the most sophisticated level—STO-3G* + d orbitals on nitrogen. In the case of $CH_3N(SiH_3)_2$, which is certainly planar, the differences in energy between $\theta = 90°$ and $\theta = 96°$ are generally larger: 0.50 kcal/mol for STO-3G, 1.58 kcal/mol for 6-21G, and 3.62 kcal/mol for STO-3G* (planar more stable in each case). Here the trend is toward a larger energy difference as the basis set becomes more sophisticated—just the reverse of the $(CH_3)_2NSiH_3$ case in which the energy difference between planar and pyramidal tends to decrease at higher level of theory. In the $(CH_3)_2NSiH_3$ case, a fair generalization is that all of the energy differences are exceedingly small. The significance we attach to them is that the problem of planarity in $(CH_3)_2NSiH_3$ cannot be unambiguously resolved solely by calculations at the level at which they have been carried out. A saving feature, however, is that the range of IP's spanned by the realistic range θ = 90–96° in this system (about 0.08 eV) is somewhat smaller than the range of IP's spanned by the similarly realistic range θ = 102–108° in trimethylamine (an average 0.54 eV). Thus, a slight ambiguity in geometry in the case of $(CH_3)_2NSiH_3$ produces less of an effect on the predicted IP than a slight ambiguity in geometry in the case of $(CH_3)_3N$. Another avenue along which to attack this problem is to compare the experimental IP's with the calculated IP's in the series $(CH_3)_{3-n}N(SiH_3)_n$, n = 1–3. From Figure 1 one sees that the experimental IP's increase fairly linearly from n = 1 to n = 3. To best reproduce this linearity, at the 6-21G, STO-3G*, or STO-3G level, one must use the θ = 90° value for $(CH_3)_2NSiH_3$. This argues in favor of planarity for this compound but does not provide conclusive evidence, of course.

(ii) Importance of d Orbitals. The importance of silicon d orbitals in the description of Si–N compounds is a question that has been discussed.[12-19] Baybutt, Guest, and Hillier[16] used a crude basis set and argued that the pyramidal geometry of trimethylamine could be predicted without the inclusion of d orbitals, but the planar geometry of trisilylamine could only

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(15) Nagy, J.; Hencsei, P. *J. Organomet. Chem.* **1972**, *38*, 261.
(16) Baybutt, P.; Guest, M. F.; Hillier, I. H. *Proc. Roy. Soc. London, Ser. A* **1973**, *333*, 225.
(17) Shea, K. J.; Gobeille, R.; Bramblett, J.; Thompson, E. *J. Am. Chem. Soc.* **1978**, *100*, 1611.
(18) Thuraisingham, R. A. *Indian J. Chem., Sect A* **1979**, *18A*, 509.
(19) Noodleman, L.; Paddock, N. L. *Inorg. Chem.* **1979**, *18*, 354.

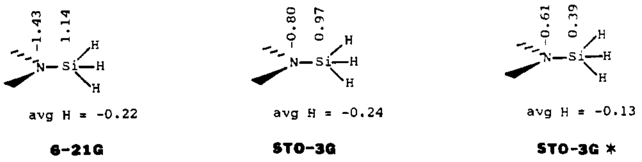
be obtained when d orbitals were included. They found a total d-orbital population of 1.41 e, which is quite high. Their total energy for trisilylamine was −892.49 au, which should be compared with the energies listed in Table III. These authors characterized their calculations as being of "an exploratory nature". These same calculations were repeated by Thuraisingham[18] using a better basis set, with more or less the same results. That is, trisilylamine became planar only when d orbitals were used. Total energy was −922.47, and d-orbital population was 0.93 e. Noodleman and Paddock[19] have done Xα–SCF calculations on $(CH_3)_3N$, $(SiH_3)_3N$, and $(GeH_3)_3N$ and found d-orbital participation highest in the case of trisilyamine (1.08 e). They found the bulk of d-orbital contribution to be in the high-lying occupied MO's, as one might expect.

The discussion of the importance of d orbitals may be divided into two parts: the importance of d orbitals in accounting for the observed IP's and the importance of d orbitals in explaining the planarity of the silylamines.

We find that the trends in lone-pair IP's for the Si–N compounds investigated can be described quite well without recourse to the inclusion of d orbitals, as can be seen from the curves in Figure 1. This indicates that the contribution of d orbitals must be fairly constant throughout the series. This is indeed the case; total d-orbital population per silicon in $(CH_3)_{3-n}N(SiH_3)_n$ is 0.328 e for $n = 1$, 0.333 e for $n = 2$, and 0.341 e for $n = 3$. The absolute magnitudes of the calculated IP's are, however, a sensitive function of whether or not d orbitals are used in the calculation. This is reasonable since, qualitatively, the high-lying d orbitals would be expected to mix most strongly with occupied orbitals highest in energy, namely the 2p lone pair on nitrogen. Thus, the calculated IP for $N(SiH_3)_3$ is 7.62 eV at the STO-3G level and 8.45 at the STO-3G* level.

The question of geometry as a function of d-orbital participation is quite ticklish, since the energy differences involved are very small, as previous investigators have noted. In the case of $CH_3N(SiH_3)_2$, the STO-3G basis yields the planar form more stable than the $\theta = 96°$ form by only 0.50 kcal/mol. This is qualitatively correct but quantitatively dubious. At the STO-3G* level, the planar form is more stable by 3.62 kcal/mol, a more reasonable number. The population per silicon (planar form) is 0.33 e.

Noodleman and Paddock[19] explain the geometry of $N(SiH_3)_3$ by positing that the N–Si bond is quite polar and Si–Si and H–H electrostatic repulsions force the system to be planar. We suggest that planarity results from the operation of both the electrostatic effect of Noodleman and Paddock and the existence of p–d π bonding. Examination of the total atomic charges for $N(SiH_3)_3$ reveals a highly polar Si–N bond when d orbitals are omitted:



6-21G **STO-3G** **STO-3G ***

Total Atomic Charges for $N(SiH_3)_3$

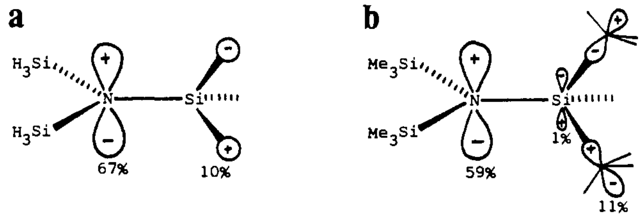
However, at the STO-3G* level this polarity has been greatly decreased, indicating that the net effect of the presence of d orbitals is to render silicon a better electron acceptor. It may be argued that the inclusion of d orbitals obviously makes p–d π bonding more important, which would favor planarity, but at the same time makes the Si–N and Si–H bonds less polar, which would tend not to favor planarity. It seems the two effects are connected.

Semiempirical Results. The MNDO method (Table IV) fares poorly in reproducing the "slope" of IP's in the series $(CH_3)_{3-n}N(SiH_3)_n$, $n = 1$–3. One success however is the fairly constant Si–N bond length throughout this series (1.771 Å for $n = 1$, 1.763 Å for $n = 2$, and 1.758 Å for $n = 3$) predicted by MNDO in agreement with experiment (1.715 Å for $n = 1$,[9] 1.726 Å for $n = 2$,[8] and 1.734 Å for $n = 3$[7]). For $CH_3N(SiH_3)_2$ MNDO yields a Si–N–Si angle of 123.2°, which should be compared with the angle of 127.7 ± 0.1° found experimentally.[8] This widening of the Si–N–Si angle by MNDO cannot be an artifact of p–d π bonding since there are no d orbitals in the basis; probably the dipolar repulsion noted by Noodleman and Paddock[19] is responsible here.

The real strength of MNDO is its ability to handle systems with a large number of atoms in reasonable lengths of computing time, with credible results. Therefore it was possible to do calculations for the trimethylsilylamines $(CH_3)_{3-n}N(Si(CH_3)_3)_n$, $n = 1$–3; the results are shown in Figure 2. As can be seen, the fit is very good, the theoretical points being displaced upward from the experimental points by a roughly constant 1.1 eV.

One may now compare the silylamines to the trimethylsilylamines. Experimentally, on going from $(CH_3)_2NSiH_3$ to $(CH_3)_2NSi(CH_3)_3$, the IP is lowered by 0.47 eV. On making two silyl replacements, viz. $CH_3N(SiH_3)_2$ to $CH_3N(Si(CH_3)_3)_2$, one would expect an effect twice as large and indeed this is found—the drop is 0.99 eV. However making three replacements—$N(SiH_3)_3$ to $N(Si(CH_3)_3)_3$—does not result in an effect 3 times larger. The change is 1.12 eV. This phenomenon is reproduced by the MNDO calculations. The reductions in calculated IP on making one, two, and three silyl to trimethylsilyl alterations are 0.12, 0.23, and 0.24 eV, respectively. One many speculate that the reason for the odd behavior of the tris(trimethylsilyl)amine is the Si–N bond is longer than the Si–N bond in either the mono- or bis(trimethylsilyl)amine. To the best of our knowledge, the structural parameters of the latter two compounds have not been reported. The Si–N bond length in tris(trimethylsilyl)amine is 1.759 Å,[20] and it will be of interest to see whether this will be found to be appreciably longer than the Si–N bond length in the mono- and bis(trimethylsilyl) cases. The Si–N bond length calculated by MNDO, is, however, roughly constant throughout the trimethylsilyl series (see Table II).

Regardless of the magnitude of the drop in IP on going from $-SiH_3$ to $-SiMe_3$, how can one rationalize a drop at all? To explain the IP's, one must focus on the HOMO's. In the case of $-SiH_3$ substituents, the HOMO is (of course) mainly nitrogen $2p_z$, but with substantial contribution from two of the three hydrogens on each silicon as shown here schematically (diagram a):



HOMO of (a) $N(SiH_3)_3$ and (b) $N(Si(CH_3)_3)_3$

From the sums of the squares of coefficients, the contribution of the AO's to the MO are given above. Silicon contributes negligibly; 97% of the orbital is accounted for by nitrogen and hydrogen. In the trimethylsilyl case (b, above) the HOMO is the same except carbon hybrids replace the H 1s orbitals. We propose a qualitative picture that explains the drop in IP effected by replacing SiH_3 by $SiMe_3$:

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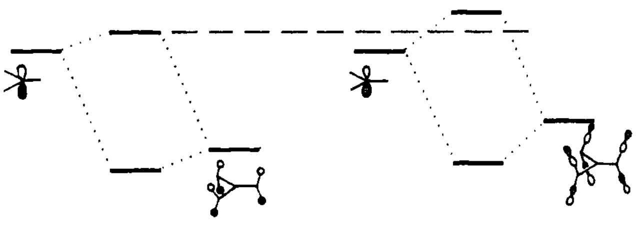
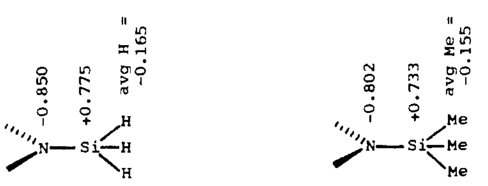
[20] Gundersen, G.; Rankin, D. W. H. paper presented at the Ninth Austin Symposium on Molecular Structure, University of Texas, Austin, TX, March 1–3, 1982.



(a) $N(SiH_3)_3$ (b) $N(Si(CH_3)_3)_3$

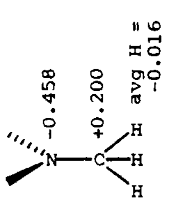
The widening of the Si–N–Si angle in $CH_3N(Si(CH_3)_3)_2$ is again in evidence. This angle is calculated to be 130.6°. The question of the planarity of $(CH_3)_2NSi(CH_3)_3$ cannot be attacked as rigorously as was done for $(CH_3)_2NSiH_3$. The MNDO method is known to render amines more planar than they should be,[21] so the fact that MNDO's minimum-energy geometry for $(CH_3)_2NSi(CH_3)_3$ was planar is not especially convincing. However, if one believes that $(CH_3)_2NSiH_3$ is planar (vide supra), then it is reasonable that the trimethylsilyl analogue will be also.

It is interesting to examine the total atomic charges for the case of trisilylamine vs. tris(trimethylsilyl)amine. As can be seen here



Total Atomic Charges for (a) $N(SiH_3)_3$ and (b) $N(Si(CH_3)_3)_3$

methyl is slightly electron-donating relative to hydrogen, but the presence of methyl groups does not increase electron density on nitrogen. Charge separation in these silylamines is much greater than, for example, that in trimethylamine:



Total Atomic Charges for $N(CH_3)_3$

This lends support to the notion of dipole–dipole repulsion as a large factor determining the geometries of these silylamines, as propounded by Noodleman and Paddock.[19]

It is probably not the lack of such electrostatic repulsions, however, that plagues tri-*tert*-butylamine. By MNDO, tri-*tert*-butylamine has a ΔH_f 295 kcal/mol above that of tris(trimethylsilyl)amine. It would be erroneous to draw any quantitative conclusions about the stability of tri-*tert*-butylamine on this basis, but such a difference is consistent with the fact that tri-*tert*-butylamine has never been synthesized. (The MNDO procedure has some trouble with *tert*-butyl groups;[21] viz., *tert*-butylamine is calculated to be 13.8 kcal/mol less stable than found experimentally, while this error is 4.7 kcal/mol in the case of NH_3. The difference, 9.1 kcal/mol per *tert*-butyl group, can be applied as a correction, but the new ΔH_f for tri-*tert*-butylamine, +40.0 kcal/mol, is still 268 kcal/mol above that of tris(trimethylsilyl)amine. One may calculate ΔH for the processes

$$6(CH_3)_3CH + N_2 \rightarrow 2N(C(CH_3)_3)_3 + 3H_2 \quad (1)$$

$$6(CH_3)_3SiH + N_2 \rightarrow 2N(Si(CH_3)_3)_3 + 3H_2 \quad (2)$$

using MNDO-derived ΔH_f's.[22] One finds ΔH_1 = +289.5 kcal/mol and ΔH_2 = −63.5 kcal/mol. This indicates again the thermodynamic instability of tri-*tert*-butylamine relative to tris(trimethylsilyl)amine.

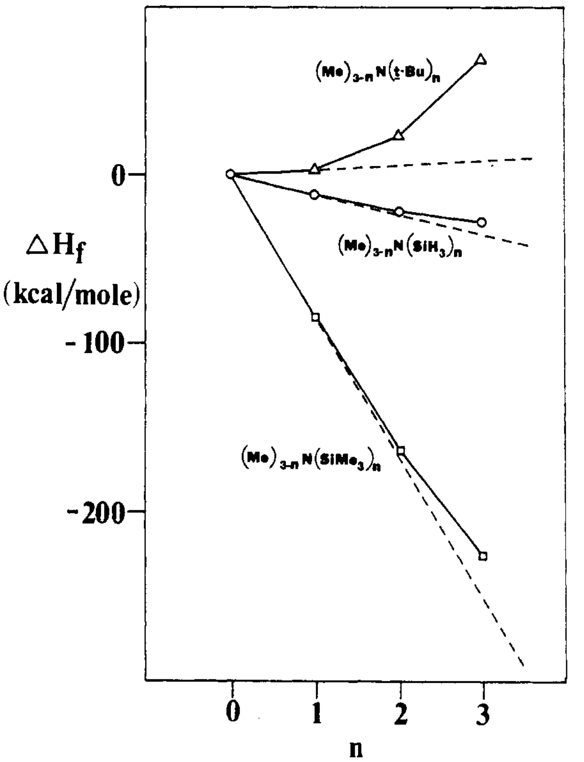
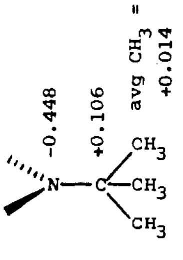


Figure 4. Heats of formation calculated by MNDO for $(CH_3)_{3-n}N(t\text{-}Bu)_n$ (△), $(CH_3)_{3-n}N(SiH_3)_n$ (○), and $(CH_3)_{3-n}N(SiMe_3)_n$ (□). Dashed lines are extrapolations of the slopes from $n = 0$ to $n = 1$.

The MNDO-derived geometry of tri-*tert*-butylamine is interesting. The C–N bonds, in typical amines about 1.45 Å (cf. Me_3N), are here 1.516 Å—a lengthening of about 5%. The C–C bonds, typically about 1.54 Å, are 1.576 Å—a lengthening of 2%. One should realize that a major change in bond length (e.g., C═C to C—C) is something on the order of 15%. Therefore a 5% lengthening, not involving a change in hybridization at either terminus, is quite substantial. It is fair to say tri-*tert*-butylamine is abnormally stretched. The compound is essentially planar even in the absence of the polar bonds and electrostatic repulsions of Noodleman and Paddock.[19]



Total Atomic Charges for $N(C(CH_3)_3)_3$

In tris(trimethylsilyl)amine there are six nonbonded H–H distances of 1.98 Å (H's on different carbons). In tri-*tert*-butylamine, there are nine such close H–H contacts—six are 1.99–2.00 Å, and three are 1.85–1.86 Å. Thus, tri-*tert*-butylamine has greater steric distress than its silyl analogue.

This point can be made in another way. The difference in ΔH_f between $(CH_3)_3N$ and $(CH_3)_2NR$, where R = SiH_3, $SiMe_3$, or CMe_3, is in most part due to the electronic nature

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(21) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

(22) McKee, M. L., unpublished results.

Table IV. Results of MNDO Calculations

	ΔH_f, kcal/mol	IP, eV
$(CH_3)_3N$	−2.37	9.49
$(CH_3)_2NSiH_3$	−14.08	9.33
$CH_3N(SiH_3)_2$	−24.73	9.54
$N(SiH_3)_3$	−31.13	9.79
$(CH_3)_2NSi(CH_3)_3$	−87.29	9.21
$CH_3N(Si(CH_3)_3)_2$	−166.38	9.31
$N(Si(CH_3)_3)_3$	−227.70	9.55
$(CH_3)_2NC(CH_3)_3$	+1.57	9.13
$CH_3N(C(CH_3)_3)_2$	+20.72	9.07
$N(C(CH_3)_3)_3$	+67.32	9.11

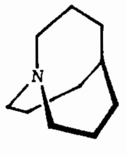
of the substituent and not to CH_3--R steric repulsion. One may extrapolate this effect to determine the ΔH_f for CH_3NR_2 and NR_3. The difference between the extrapolated ΔH_f and the ΔH_f actually calculated gives an indication of the contribution of steric repulsions as distinct from electronic effects. This is done in Figure 4. For the case of R = SiH_3 there seems to be little if any steric strain associated with $N(SiH_3)_3$. For $N(SiMe_3)_3$, one sees a fair difference between the extrapolation and the actual calculation. It is known that MNDO underestimates the stability of sterically crowded molecules, for example molecules with *tert*-butyl groups, as noted above. The following data[21,22] allow a correction to be made for this idiosyncrasy of MNDO:

	calcd ΔH_f, kcal/mol	obsd ΔH_f, kcal/mol	calcd ΔH_f − obsd ΔH_f, kcal/mol
$(CH_3)_3C\text{-}CH_3$	−24.6	−40.3	+15.7
$(CH_3)_3Si\text{-}CH_3$	−89.9	−52.6	−37.3
$H\text{-}CH_3$	−11.9	−17.9	+6.0

Thus we may apply a correction of −9.7 kcal/mol per *tert*-butyl group and +43.3 kcal/mol per trimethylsilyl group. When this is done, tris(trimethylsilyl)amine lies 25 kcal/mol above the extrapolated line while tri-*tert*-butylamine lies 55 kcal/mol above the extrapolated line. This suggests that there is 30 kcal/mol worth of steric hindrance in tri-*tert*-butylamine not present in tris(trimethylsilyl)amine.

Planar Amines. Returning now to the measured IP's, one may derive an interesting quantity. From Figure 1, one notes that from $n = 1$ to $n = 3$ the experimental points increase approximately linearly. Further, if one believes that $(CH_3)_2NSiH_3$ is planar, then all three points refer to planar silylamines. Therefore extrapolating the IP's to $n = 0$ would yield the IP of planar trimethylamine. This number turns out to be 7.9 eV. As a check, the trimethylsilyl series (Figure 2, filled circles) should also give the IP of planar trimethylamine at $n = 0$. This series gives 7.7 eV. Therefore we find, experimentally, the vertical IP corresponding to a nitrogen 2p orbital in planar trimethylamine is 7.7–7.9 eV.

The only bona fide planar aliphatic amine we are aware of is manxine:



Manxine
(1-azabicyclo[3.3.3]undecane)

The photoelectron spectrum of this molecule is fascinating;[23] since the neutral molecule and radical cation are both rigidly planar about nitrogen, the adiabatic and vertical processes are coincident and occur at 7.04 eV. Our value of 7.7–7.9 eV for planar trimethylamine is not suitable for comparison since the lone-pair IP for a tertiary amine depends on the nature of the alkyl groups. For example, Me_3N has an IP of 8.5[4] or 8.44 eV,[24] while $(n\text{-}Pr)_3N$ has an IP of 7.92 eV.[25] Therefore we measured the IP's in the series $(n\text{-}Pr)_{3-n}N(SiMe_3)_n$, $n = 1$–3 (Figure 2), which can be extrapolated to $n = 0$ to yield the IP for planar $(n\text{-}Pr)_3N$. This turns out to be 7.4 eV, which is a vertical IP. Since tri-*n*-propylamine is not rigid, unlike manxine, vertical and adiabatic IP's would not be expected to be coincident. The difference between 7.4 eV and 7.04 eV must represent reorganization in the *n*-propyl groups and/or C–N bond rotation. That is, for tri-*n*-propylamine, roughly half the difference between adiabatic (7.04 eV) and vertical (7.92 eV) IP is due to planarization about N, and half is due to C–N rotation or conformational changes in the *n*-propyl groups.

A final observation can be made concerning the trends in IP's. For tertiary alkylamines, the nitrogen lone-pair IP depends on the alkyl groups, as we have mentioned. From the difference in IP between Me_3N and $n\text{-}Pr_3N$, the effect of one methyl to *n*-propyl transformation is −0.19 eV. However, from the difference in IP between Me_2NSiMe_3 and $(n\text{-}Pr)_2NSiMe_3$, one methyl to *n*-propyl transformation is worth only −0.10 eV in this case. When two trimethylsilyl groups are present, $MeN(SiMe_3)_2$ vs. $n\text{-}PrN(SiMe_3)_2$, a methyl to *n*-propyl transformation is worth only −0.03 eV. Clearly, when one or more trimethylsilyl groups are present, the nature of remaining alkyl group(s) is of minor importance in determining IP.

Conclusions

We have concerned ourselves here with the question of planarity at nitrogen. We find in trimethylamine that polarization functions on nitrogen are essential in reproducing the observed pyramidal geometry of the molecule. However, this level of theory predicts a planar structure for $(CH_3)_2NSiH_3$. In this case the energy difference between planar and pyramidal is so small as to render the prediction merely a suggestion. A planar structure is not strictly inconsistent with the electron diffraction data.

We have shown the relation between the electrostatic effect of Noodleman and Paddock and p–d π-bonding arguments in explaining the planarity of $N(SiH_3)_3$.

In consideration of the as yet unsynthesized tri-*tert*-butylamine, both p–d π bonding and highly polar C–N and C–C bonds are absent. The predicted planarity is strictly the result of steric effects. Tri-*tert*-butylamine is estimated to be roughly 30 kcal/mol less stable sterically than tris(trimethylsilyl)amine.

The measured IP's allow extrapolation to give the vertical IP of *planar* trialkylamine. For planar trimethylamine IP = 7.7–7.9 eV, and for planar tri-*n*-propylamine IP = 7.4 eV.

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Registry No. $(CH_3)_3N$, 75-50-3; $(CH_3)_2N(SiH_3)$, 2875-98-1; $(CH_3)N(SiH_3)_2$, 4459-06-7; $N(SiH_3)_3$, 13862-16-3; $(CH_3)_2N(Si(CH_3)_3)$, 2083-91-2; $(CH_3)N(Si(CH_3)_3)_2$, 920-68-3; $N(Si(CH_3)_3)_3$, 1586-73-8; $(CH_3CH_2CH_2)_3N$, 102-69-2; $(CH_3CH_2CH_2)_2N(Si(CH_3)_3)$, 4006-63-7; $(CH_3CH_2CH_2)N(Si(CH_3)_3)_2$, 7331-84-2.

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[23] Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4136.

[24] Kimura, K.; Osafune, K. *Mol. Phys.* **1975**, *29*, 1073.

[25] Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311.