$$CF_3OO\cdot + PF_3 \rightarrow CF_3O\cdot + OPF_3 \qquad (17)$$

$$CF_3O\cdot + O_2 \rightarrow CF_3OOO\cdot \qquad (7)$$

$$CF_3OOO\cdot + PF_3 \rightarrow CF_3OO\cdot + OPF_3 \qquad (18)$$

Registry No. $(CF_3)_3P$, 432-04-2; $(CF_3)_3PO$, 423-01-8; $(CF_3)_2P(O)F$, 34005-83-9; $CF_3P(O)F_2$, 19162-94-8; CF_3PF_2, 1112-04-5; $(CF_3)_2PF$, 1426-40-0; $(CF_3O)_3PO$, 68423-90-5.

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Trimethylamine, Trisilylamine, and Trigermylamine: A Comparative Study of Ionization Energies, Charge Distribution, and Bonding

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Received March 30, 1978

Calculations of the electronic structures of $(CH_3)_3N$, $(SiH_3)_3N$, and $(GeH_3)_3N$ by the Xα scattered-wave self-consistent-field method give a good account of the measured ionization energies and allow a detailed assessment of the various bond types. Interactions involving d orbitals are most important in the silicon compound, in which the highest occupied ("lone pair") orbital is stabilized most; significant pπ–pπ bonding is found in deeper orbitals. Other features of the bonding are the appreciable interaction between nitrogen and the M–H bonds and the high polarities of the M–H and M–N bonds. The planarity of $(SiH_3)_3N$ is ascribed principally to electrostatic rather than to d-orbital interactions.

Introduction

The substitution of a silyl group for a methyl group has well-defined effects on the properties of a neighboring oxygen or nitrogen atom; the ionization energy is increased, donor properties are weakened, and the interbond angle is increased. The planarity of the skeletal conformations of trisilylamine[1] and trigermylamine,[2] as contrasted with the pyramidal structures of trimethylamine,[3] trisilylphosphine,[4] and trisilylarsine,[5] has frequently been attributed to pπ–dπ bonding, especially in trisilylamine. Such interactions provide at least a plausible explanation for the other properties of the Si–N and Si–O bonds and account for some features of the photoelectron spectra of halosilanes.[6] The evidence for π bonding has been critically reviewed[7] for many types of silicon compounds.

While there seems no doubt that pπ–dπ interactions occur in trisilylamine, they are not the only important factor,[8] and may not, in themselves, induce planarity. A theoretical investigation[9] of the (hypothetical) molecule SiH_3NH_2 confirms the occurrence of weak pπ–dπ conjugation in the highest (N lone pair) molecular orbital, but it has only a small effect on the difference in energy between the planar and pyramidal forms, the latter being favored slightly, as found experimentally for *N*-silyldimethylamine.[10] The tendency toward planarity in related compounds is ascribed principally to electrostatic repulsion arising from inductive release from silicon to nitrogen[9] and also to nonbonded interactions.[11] The inversion barrier at three-coordinated nitrogen in fact depends on many factors,[12] and all pairwise interactions contribute significantly,[13] though their relative importance varies. It is therefore important to carry out accurate calculations on certain key molecules, especially those whose properties are known in detail.

Few such investigations have been reported. The bond energies in Me_3NH^+ and $Me_3N\cdot BH_3$ have been calculated in a Hartree–Fock framework with a 4-31G basis set,[14] but it is difficult to extend calculations of this type to molecules with several heavy atoms, particularly when d orbitals are included. The orbital ordering and symmetry species of the methyl amines have been studied by CNDO/2 and MINDO/2 methods,[15] principally in relation to their photoelectron spectra, and, in another (exploratory) calculation,[16] orbital compositions and ionization energies of the N lone-pair orbitals were obtained for two conformations of $(CH_3)_3N$ and $(SiH_3)_3N$. In view of the results referred to above, it is important to determine the lower levels also and to carry the comparison as far as $(GeH_3)_3N$. We have therefore made a comparative study of the electronic structures of the three molecules $(CH_3)_3N$, $(SiH_3)_3N$, and $(GeH_3)_3N$. We have used the Xα method to obtain good accuracy (as judged by a comparison of calculated and experimentally determined ionization energies) with reasonable economy in computer time. The results are used to assess the chemical bonding in these molecules.

Calculation Procedure

The calculations were made by the overlapping-spheres version of the all-electron self-consistent-field Xα scattered-wave method[17]

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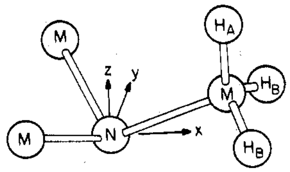

Figure 1. Coordinate axes for $(MH_3)_3N$. Symmetry C_{3v} is assumed, N, M, and H_A being coplanar with xz. Each MH_3 group has threefold symmetry about the N–M bond.

Table I. Geometrical Details of Molecules $(MH_3)_3N^a$

	bond lengths, Å		bond angles, deg	
M	M-N	M-H^b	H-M-H	M-N-M
C^{c,f}	1.451	1.102	108.1	(i) 110.9, (ii) 120
Si^{d,g}	1.734	1.485	110.8	(i) 110.9, (ii) 120
Ge^{e,h}	1.836	1.531	106.4	120

[a] See Figure 1. [b] Mean values. [c] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, 51, 1580 (1969). Equilibrium pyramidal conformation. [d] B. Beagley and A. R. Conrad, *Trans. Faraday Soc.*, **66**, 2740 (1970). Equilibrium planar conformation. [e] C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, **6**, 231 (1970). Ge-H distance and H-Ge-H angle assumed to be the same as in $(GeH_3)_2O$ (C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley, and S. Cradock, *J. Chem. Soc., A*, 315 (1970)). [f] Sphere radii (a_0): N, 1.617; H, 1.200; C, 1.675; outer, 5.282. [g] Sphere radii (a_0): N, 1.714; H, 1.486; Si, 2.220; outer, 6.423. [h] Sphere radii (a_0): N, 1.796; H, 1.501; Ge, 2.369; outer, 6.800.

(Xα–SW). The ratios of the radii of the atomic spheres were determined by Norman's method,[18] and their absolute values (Table I) were taken, as in previous work,[19,20] to be 20% greater than those required for mutual tangency. The calculations used standard values[21] of the exchange correlation parameter α and a basis set of spherical harmonics: $l = 0, 1$ on N; $l = 0, 1, 2$ on C, Si, Ge; $l = 0$ on H. Ionization energies were obtained by Slater's transition-state method,[22] which allows for relaxation. Calculations were performed for $(CH_3)_3N$ and $(SiH_3)_3N$ in both planar and pyramidal conformations and for planar $(GeH_3)_3N$. Figure 1 shows the coordinate system; structural and calculational parameters are given in Table I.

Results and Discussion

A comparison of the calculated and experimental ionization energies of the three molecules in their equilibrium conformations is presented in Table II. The calculations give a good account of the measured energies, trisilylamine being correctly calculated to have the highest N lone-pair ionization energy. The greatest discrepancy in the upper occupied levels is the overestimate (by 0.66 eV) of the first ionization energy of $(CH_3)_3N$, which reverses the positions of the first two members of the experimental sequence $(CH_3)_3N < (GeH_3)_3N < (SiH_3)_3N$. Comparison with other methods is possible for trimethylamine. Both the CNDO/2 and MINDO/2 calculations[15] reverse the 2e and $3a_1$ assignments, the latter being the better numerically. If the (unsatisfactory) MINDO/2 results for the two lowest levels are omitted, the mean absolute error of the MINDO/2 calculations is 1.13 eV, compared with 0.84 for the Xα–SW method.

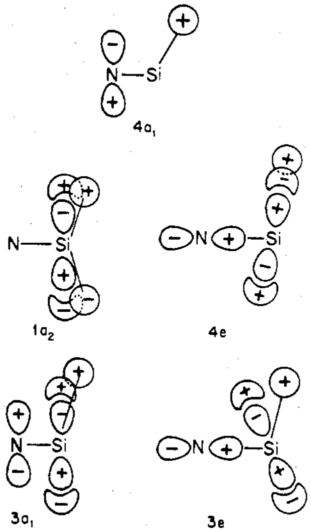

Figure 2. Schematic overlap diagrams of N(2p), Si(3p), and H(1s) orbitals in planar $(SiH_3)_3N$. All in xz plane, except $1a_2$ (xy plane).

The individual atomic contributions to the molecular orbitals can be assessed in various ways. Partial wave analyses of the individual MO's, normalized to the total number of electrons in the MO, for each of the five cases examined are given in Table III, and analyses of the total valence charge, in Table IV. The one-electron energies specified in Table III represent differential orbital electronegativities in the Xα theory[17] and are not the theoretical ionization energies of Table II. The lowest orbitals (1a, 1e, $2a_1$, 2e) are strongly σ bonding and need no further qualitative discussion. The higher occupied orbitals ($3a_1$, 3e, 4e, $1a_2$, $4a_1$) show significant features which are discussed below. They are shown schematically in Figure 2 for $(SiH_3)_3N$. The highest occupied orbital, $4a_1$, is composed mostly of a nitrogen lone-pair $2p_z$ orbital with some delocalization onto the neighboring MH_3 groups (M = C, Si, Ge). The next lower orbitals, $1a_2$ and 4e, are M–H bonding orbitals, the first by symmetry and the second to an extent depending on the pyramidal angle; in the planar conformation, the M–H bond is largely isolated from the nitrogen atom. These two orbitals together have a high electron density on hydrogen when M = Si or Ge.

Orbitals $3a_1$ and 3e are of special interest, the first having

Table II. Theoretical and Experimental Ionization Energies (eV) of $(CH_3)_3N$, $(SiH_3)_3N$, and $(GeH_3)_3N$

	$(CH_3)_3N$		$(SiH_3)_3N$		$(GeH_3)_3$	
level^c	theory	expt^a	theory	expt^b	theory	expt^b
$4a_1$	9.11	8.44	9.61	9.7	8.91	9.2
4e	12.17	12.3, 12.74	11.24		10.67	
$1a_2$	12.69	13.1	11.39	10.8–13.0	10.68	
3e	13.03	13.67	11.76		10.91	
$3a_1$	14.50	15.68	12.47		11.57	
2e	14.68	16.0	13.08	13.7	12.28	
$2a_1$	18.18	19.46	15.24	16.6	15.21	
1e	20.66	22.5	16.85	18.2	16.58	
$1a_1$	26.56	28.3	25.44		23.88	

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Table III. Partial Wave Decompositions

			population[a]					
level	energy, Ry	atom	s	p	d	total	intersphere charge	outer-sphere charge
			Trimethylamine: Pyramidal					
$4a_1$	−0.416	N	0.0424	0.9797	0	1.0221	0.4376	0.0645
		C	0.0067	0.0394	0.0220	0.0681		
		H_A	0.0720	0	0	0.0302		
		H_B	0.0093	0	0			
4e	−0.665	N	0	0.8295	0	0.8295	0.1559	0.1446
		C	0.0101	0.4834	0.0428	0.5363		
		H_A	0.0191	0	0	0.1401		
		H_B	0.2006	0	0			
$1a_2$	−0.703	N	0	0	0	0	0.0060	0.0685
		C	0	0.2798	0.0173	0.2971		
		H_A	0	0.0029	0	0.1146		
		H_B	0.1704	0	0			
3e	−0.732	N	0	0.0454	0	0.0454	0.2410	0.1495
		C	0.0003	0.5368	0.0264	0.5635		
		H_A	0.3933	0	0	0.2081		
		H_B	0.1155	0	0			
$3a_1$	−0.846	N	0.0035	0.1895	0	0.1930	0.3248	0.0540
		C	0.0004	0.2311	0.0072	0.2387		
		H_A	0.1338	0	0	0.0791		
		H_B	0.0518	0	0			
2e	−0.848	N	0	0.7767	0	0.7767	0.3283	0.0996
		C	0.0094	0.5143	0.0201	0.5440		
		H_A	0.0847	0	0	0.1293		
		H_B	0.1516	0	0			
$2a_1$	−1.107	N	0.3108	0.0007	0	0.3115	0.0828	0.0626
		C	0.1507	0.1177	0.0113	0.2797		
		H_A	0.0872	0	0	0.0782		
		H_B	0.0737	0	0			
1e	−1.288	N	0	0.3678	0	0.3678	0.2289	0.0673
		C	0.6979	0.0113	0.0007	0.7099		
		H_A	0.1162	0	0	0.1341		
		H_B	0.1430	0	0			
$1a_1$	−1.678	N	0.9992	0.0212	0	1.0204	0.1815	0.0033
		C	0.1759	0.0461	0.0077	0.2297		
		H_A	0.0120	0	0	0.0117		
		H_B	0.0116	0	0			
			Trimethylamine: Planar					
$4a_1$	−0.312	N	0	1.0901	0	1.0901	0.4018	0.0641
		C	0	0.0158	0.0285	0.0443		
		H_A	0.0697	0	0	0.0346		
		H_B	0.0171	0	0			
4e	−0.673	N	0	0.7375	0	0.7375	0.1908	0.1553
		C	0.0084	0.4969	0.0377	0.5430		
		H_A	0.0095	0	0	0.1430		
		H_B	0.1798	0	0			
$1a_2$	−0.691	N	0	0	0	0	0.0291	0.0729
		C	0	0.2797	0.0153	0.2950		
		H_A	0	0.0035	0	0.1122		
		H_B	0.1665	0	0			
3e	−0.723	N	0	0.0557	0	0.0557	0.2593	0.1467
		C	0.0002	0.5283	0.0285	0.5570		
		H_A	0.3576	0	0	0.2073		
		H_B	0.1322	0	0			
$3a_1$	−0.821	N	0.0001	0.2012	0	0.2013	0.3336	0.0544
		C	0.0001	0.2308	0.0064	0.2373		
		H_A	0.1599	0	0	0.0775		
		H_B	0.0363	0	0			
2e	−0.837	N	0	0.7982	0	0.7982	0.3387	0.1017
		C	0.0094	0.5142	0.0207	0.5443		
		H_A	0.0550	0	0	0.1253		
		H_B	0.1605	0	0			
$2a_1$	−1.085	N	0.2992	0	0	0.2992	0.0724	0.0647
		C	0.1511	0.1216	0.0112	0.2839		
		H_A	0.0723	0	0	0.0791		
		H_B	0.0825	0	0			
1e	−1.285	N	0	0.4027	0	0.4027	0.2458	0.0658
		C	0.6993	0.0079	0.0007	0.7079		
		H_A	0.1266	0	0	0.1291		
		H_B	0.1303	0	0			

Table III (*Continued*)

		population[a]						
level	energy, Ry	atom	s	p	d	total	intersphere charge	outer-sphere charge
$1a_1$	−1.646	N	1.0219	0	0	1.0219	0.2049	0.0035
		C	0.1716	0.0423	0.0069	0.2208		
		H_A	0.0115	0	0	0.0119		
		H_B	0.0121	0	0			
			Trisilylamine:	Pyramidal				
$4a_1$	−0.543	N	0.0257	1.0096	0	1.0353	0.4045	0.0373
		Si	0.0038	0.0189	0.0498	0.0725		
		H_A	0.0859	0	0	0.0339		
		H_B	0.0079	0	0			
$1a_2$	−0.648	N	0	0	0	0	0.1468	0.0812
		Si	0	0.1629	0.0347	0.1976		
		H_A	0	0.0006	0	0.1310		
		H_B	0.1962	0	0			
4e	−0.665	N	0	0.5503	0	0.5503	0.3616	0.1556
		Si	0.0034	0.2759	0.0911	0.3704		
		H_A	0.0270	0	0	0.2024		
		H_B	0.2901	0	0			
3e	−0.678	N	0	0.0021	0	0.0021	0.3850	0.1659
		Si	0.0018	0.3424	0.0543	0.3985		
		H_A	0.4039	0	0	0.2504		
		H_B	0.1737	0	0			
$3a_1$	−0.762	N	0.0010	0.1825	0	0.1835	0.3846	0.0578
		Si	0.0024	0.1643	0.0156	0.1823		
		H_A	0.1385	0	0	0.0919		
		H_B	0.0686	0	0			
2e	−0.767	N	0	1.1217	0	1.1217	0.3380	0.0969
		Si	0.0226	0.3587	0.0633	0.4446		
		H_A	0.1700	0	0	0.1234		
		H_B	0.1001	0	0			
$2a_1$	−0.959	N	0.1181	0.0105	0	0.1286	0.2555	0.0560
		Si	0.2102	0.0457	0.0159	0.2718		
		H_A	0.1131	0.	0	0.0828		
		H_B	0.0676	0	0			
1e	−1.041	N	0	0.6151	0	0.6151	0.4345	0.0546
		Si	0.6354	0.0191	0.0058	0.6603		
		H_A	0.0994	0	0	0.1017		
		H_B	0.1029	0	0			
$1a_1$	−1.616	N	1.3192	0.0160	0	1.3352	0.0825	0.0003
		Si	0.0933	0.0676	0.0294	0.1903		
		H_A	0.0015	0	0	0.0013		
		H_B	0.0012	0	0			
			Trisilylamine:	Planar				
$4a_1$	−0.488	N	0	1.0108	0	1.0108	0.4043	0.0447
		Si	0.0001	0.0032	0.0563	0.0595		
		H_A	0.0820	0	0	0.0401		
		H_B	0.0192	0	0			
$1a_2$	−0.634	N	0	0	0	0	0.1408	0.0876
		Si	0	0.1655	0.0325	0.1980		
		H_A	0	0.0008	0	0.1309		
		H_B	0.1959	0	0			
4e	−0.650	N	0	0.1287	0	0.1287	0.4031	0.1738
		Si	0.0022	0.3196	0.0627	0.3845		
		H_A	0.3745	0	0	0.2380		
		H_B	0.1697	0	0			
3e	−0.676	N	0	0.3217	0	0.3217	0.4583	0.1618
		Si	0.0023	0.2915	0.0740	0.3678		
		H_A	0.1089	0	0	0.2172		
		H_B	0.2714	0	0			
$3a_1$	−0.728	N	0.0002	0.2353	0	0.2355	0.4315	0.0577
		Si	0.0005	0.1594	0.0120	0.1719		
		H_A	0.1776	0	0	0.0845		
		H_B	0.0379	0	0			
2e	−0.757	N	0	1.1328	0	1.1328	0.3228	0.1014
		Si	0.0307	0.3550	0.0666	0.4523		
		H_A	0.0999	0	0	0.1207		
		H_B	0.1311	0	0			
$2a_1$	−0.930	N	0.1009	0.0001	0	0.1010	0.2490	0.0619
		Si	0.2101	0.0479	0.0164	0.2744		
		H_A	0.0724	0	0	0.0850		
		H_B	0.0913	0	0			

Table III (*Continued*)

			population[a]					
level	energy, Ry	atom	s	p	d	total	intersphere charge	outer-sphere charge
1e	−1.036	N	0	0.7112	0	0.7112	0.4308	0.0512
		Si	0.6263	0.0232	0.0072	0.6567		
		H_A	0.0890	0	0	0.0930		
		H_B	0.0950	0	0			
$1a_1$	−1.596	N	1.3505	0	0	1.3505	0.1054	0.0003
		Si	0.0868	0.0633	0.0276	0.1777		
		H_A	0.0011	0	0	0.0012		
		H_B	0.0012	0	0			
				Trigermylamine:	Planar			
$4a_1$	−0.443	N	0	1.1097	0	1.1097	0.3880	0.0382
		Ge	0	0.0033	0.0461	0.0494		
		H_A	0.0710	0	0	0.0351		
		H_B	0.0172					
$1a_2$	−0.606	N	0	0	0	0	0.1352	0.0840
		Ge	0	0.1781	0.0319	0.2100		
		H_A	0	0.0011	0	0.1278		
		H_B	0.1911	0	0			
4e	−0.612	N	0	0.3389	0	0.3389	0.3427	0.1625
		Ge	0.0036	0.3357	0.0685	0.4078		
		H_A	0.2518	0	0	0.2147		
		H_B	0.1961	0	0			
3e	−0.629	N	0	0.2222	0	0.2222	0.4237	0.1525
		Ge	0.0017	0.3375	0.0645	0.4037		
		H_A	0.2343	0	0	0.2211		
		H_B	0.2145	0	0			
$3a_1$	−0.676	N	0.0001	0.2108	0	0.2109	0.3819	0.0581
		Ge	0.0002	0.1745	0.0124	0.1871		
		H_A	0.1792	0	0	0.0875		
		H_B	0.0417	0	0			
2e	−0.710	N	0	1.2201	0	1.2201	0.3211	0.0882
		Ge	0.0056	0.4030	0.0485	0.4571		
		H_A	0.0667	0	0	0.1110		
		H_B	0.1332	0	0			
$2a_1$	−0.939	N	0.1320	0	0	0.1320	0.1628	0.0507
		Ge	0.2394	0.0585	0.0132	0.3111		
		H_A	0.0740	0	0	0.0801		
		H_B	0.0832	0	0			
1e	−1.035	N	0	0.4415	0	0.4415	0.3214	0.0522
		Ge	0.7300	0.0061	0.0027	0.7388		
		H_A	0.1051	0	0	0.1076		
		H_B	0.1088	0	0			
$1a_1$	−1.505	N	1.3169	0	0	1.3169	0.0976	0.0003
		Ge	0.0989	0.0552	0.0352	0.1893		
		H_A	0.0019	0	0	0.0020		
		H_B	0.0020	0	0			

[a] For a single atom of each type. For hydrogen, the "total" is the weighted mean $(H_A + 2H_B)/3$.

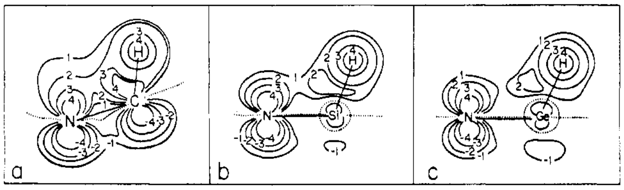

Figure 3. Contour plots of the $3a_1$ orbital of (a) $(CH_3)_3N$, (b) $(SiH_3)_3N$, and (c) $(GeH_3)_3N$. Contour specification: 1 = 0.05, 2 = 0.07, 3 = 0.10, 4 = 0.13 in units of (probability)$^{1/2}$ a_0^{-3}. The dotted lines represent nodal surfaces.

an appreciable Npπ–Mpπ component and, as a previously unrecognized feature, a significant hyperconjugative N–H interaction through the p_z orbital at M. Contour plots of the $3a_1$ orbital for each molecule are shown in Figure 3. The relative strengths of the hyperconjugative interactions exhibited by $3a_1$ are $(CH_3)_3N > (SiH_3)_3N > (GeH_3)_3N$, as shown by the contour plots and the ionization energies of the three molecules. In the related 3e orbital, a weaker hyperconjugative N–H interaction is again mediated by a p orbital combination at M.

The contribution of d orbitals to the bonding depends on M and on the orbital. The total d population increases in the order $(CH_3)_3N$ (0.47 e) < $(GeH_3)_3N$ (0.93 e) < $(SiH_3)_3N$ (1.08 e). The greater part of this density, 68% for planar $(SiH_3)_3N$, lies in the highest five occupied levels ($3a_1$–$4a_1$), but d orbitals make some contributions to all the molecular orbitals (Table IV). The fraction of d-orbital character is greatest in a given molecule in the $4a_1$ orbital, in which the dominant lone-pair character is modified by weak pπ–dπ interactions. The d character of $3a_1$, the principal π-bonding orbital, is much less. The concentration of d electrons is greater in the two levels 3e and 4e, which between them include

Table IV. Atomic Populations and Charge Distributions in $(CH_3)_3N$, $(SiH_3)_3N$, and $(GeH_3)_3N^a$

molecule	atomic sphere populations	intersphere charges[b]	outer-sphere charges[b]	net atomic charges
$(CH_3)_3N$	N: 2s, 1.36; 2p, 3.21 C: 2s, 1.05; 2p, 2.26; 3d, 0.16 H (av): 1s, 0.92	1.99	0.71	N: 0.05+ C: 0.23+ H: 0.08–
$(SiH_3)_3N^c$	N: 2s, 1.45; 2p, 3.54 Si: 3s, 0.96; 3p, 1.43; 3d, 0.36 H (av): 1s, 1.01	2.94	0.74	N: 0.56– Si: 0.80+ H: 0.21–
$(SiH_3)_3N^d$	N: 2s, 1.45; 2p, 3.52 Si: 3s, 0.99; 3p, 1.50; 3d, 0.38 H (av): 1s, 0.99; 2p, 0.06	2.34	0.71	N: 0.43– Si: 0.77+ H: 0.21–
$(GeH_3)_3N$	N: 2s, 1.45; 2p, 3.54 Ge: 4s, 1.08; 4p, 1.55; 4d, 0.32 H (av): 1s, 0.99	2.58	0.69	N: 0.49– Ge: 0.65+ H: 0.16–

[a] Equilibrium geometries. [b] Intersphere charge allocated to N, M (C, Si, Ge), and H in the ratios 5:4:1. Outer-sphere charge allocated equally to all H. [c] $l = 0$ on H. [d] $l = 0, 1$ on H.

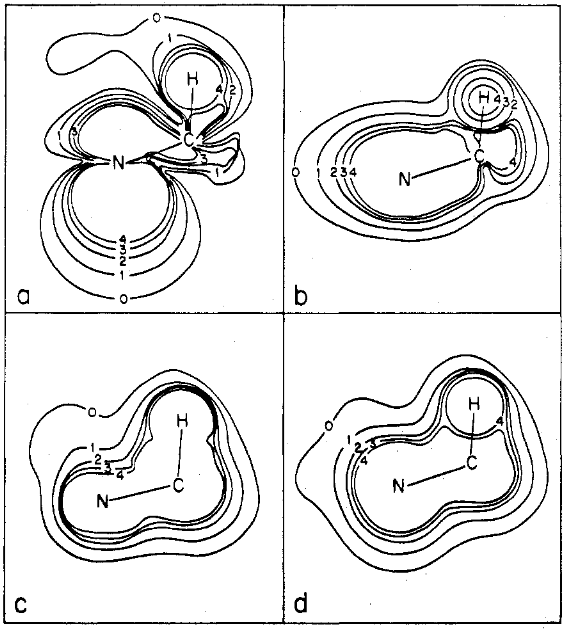

Figure 4. Electron density in xz plane of $(CH_3)_3N$ (pyramidal): (a) $4a_1$, (b) $1a_1 + 2e$, (c) $2a_1 + 3a_1 + 1e + 3e + 4e + a_2$, (d) sum of all occupied valence orbitals. Contour specifications: 0, 0.0002; 1, 0.0006; 2, 0.0014; 3, 0.0022; 4, 0.0032 [e a_0^{-3} times the factors (a) 2, (b) 4, (c) 12, and (d) 18].

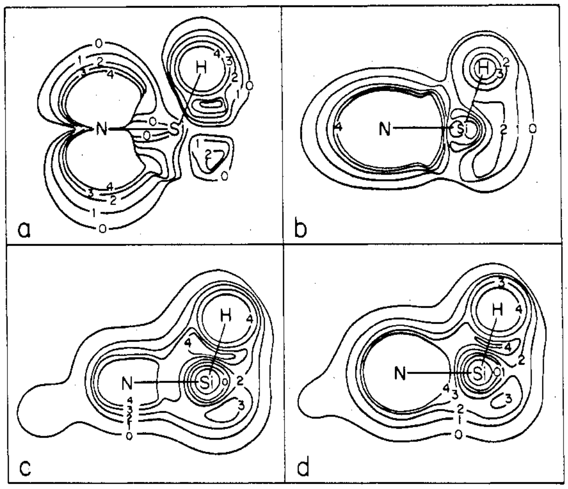

Figure 5. Electron density in xz plane of $(SiH_3)_3N$ (planar). Details as in Figure 4.

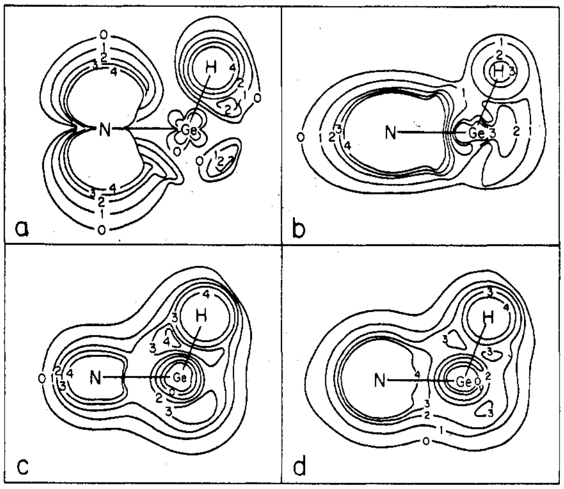

Figure 6. Electron density in xz plane of $(GeH_3)_3N$ (planar). Details as in Figure 4.

about 40% of the total d-electron population of $(SiH_3)_3N$.

A valuable qualitative insight into the bonding is obtained by plotting charge distributions over selected sets of molecular orbitals. Although any selection must be arbitrary, division into the following groups seems realistic and is better for $(SiH_3)_3N$ and $(GeH_3)_3N$ than for $(CH_3)_3N$: (a) $4a_1$, $N2p_z$ lone pair; (b) $1a_1 + 2e$, N–M σ bonds; (c) $2a_1 + 3a_1 + 1e + 3e + 4e + 1a_2$, M–H σ bonds. The charge distributions in the xz plane for each of these groups, and (d) the total valence charge, are plotted in Figures 4–6 (a–d). Figures 5a and 6a show clearly the d-orbital contribution to the $4a_1$ orbital and otherwise illustrate the different charge distributions of Table IV. With respect to the total charge density (Figures 4d, 5d, and 6d), the C–N bond is much less polar than the Si–N and Ge–N bonds; there is substantial migration of charge from silicon (or germanium) to nitrogen and to hydrogen. The charges on the elements indicate that the order of electronegativity of the heavy elements is N > C ≫ Ge > Si. The bond polarity $C^+–H^-$ is clearly established and is interesting in the light of Fliszar's view that such a polarity is essential to the understanding of the ^{13}C NMR shifts in alkyl groups, inductive effects, and the stability of carbonium ions.[23] Polarities in the opposite sense are often obtained from Mulliken population analyses, probably[23] because of the arbitrary (half and half) allocation of overlap population. In the present work, the charge is partitioned directly in various spatial regions, and especially since the ratios of the sphere atomic radii are taken to be in the same ratio as those of the neutral atoms, the allocation of charge seems realistic. The hydridic nature of the silyl group is of course well established experimentally.

The description of the molecular orbitals given above, although it modifies the current qualitative views on bonding

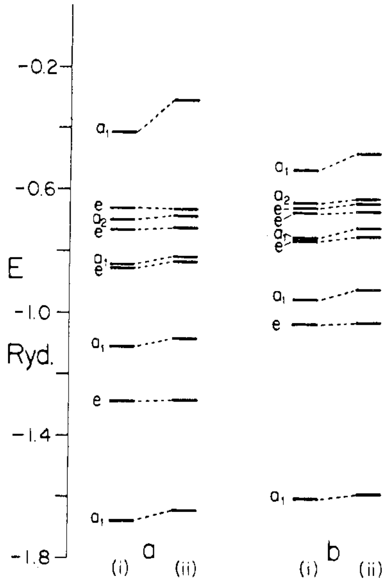

Figure 7. One-electron energies (Ry) of (a) $(CH_3)_3N$ and (b) $(SiH_3)_3N$ in two conformations: (i) pyramidal; (ii) planar.

in this type of molecule, suggests no obvious cause for the planarity of $(SiH_3)_3N$. The N p_z population in the planar conformations of both $(CH_3)_3N$ and $(SiH_3)_3N$ exceeds that in the pyramidal form, but any consequent difference in π bonding is outweighed by the stronger σ bonds in the pyramidal form. This is demonstrated by a comparison of the one-electron energies for the two conformations of the two molecules (Figure 7). The one-electron levels of both molecules are stabilized in going from the planar to the pyramidal structure. For the highest occupied MO, stabilization occurs chiefly by interaction with a low-lying lowest unoccupied MO and is expected to decrease with increasing σ donation from the outer groups to nitrogen,[24] as we have found (Figure 7; stabilization energy of $(SiH_3)_3N < (CH_3)_3N$). Such arguments have been used to rationalize the trends in bond angles and inversion barriers but are incomplete for highly polar molecules,[25] such as (linear) Li_2O. The repulsion of the polar groups may then be decisive, and we believe that the skeletal planarity of $(SiH_3)_3N$ and $(GeH_3)_3N$ is caused chiefly by Si–Si, Ge–Ge, and H–H electrostatic repulsion. The lower N–C bond polarity implies weaker C–C repulsion, and the pyramidal conformation remains stable. The present work agrees with the conclusions reached earlier[9,11,12] either in a qualitative manner or from calculations carried out on a different basis and with Bock's conjecture[26] that the widening of the central angle in $(SiH_3)_2O$ may be as much a mechanism to relieve Coulombic repulsions as it is a manifestation of $p\pi$–$d\pi$ interaction. The pyramidal structures of trisilylphosphine[4] and trisilylarsine[5] are consistent with this view, since in both cases the Pauling electronegativities would indicate a smaller positive charge on silicon than in $(SiH_3)_3N$. The electrostatic barrier to a nonplanar conformation in $(SiH_3)_3N$ would also reduce its base strength.

Conclusions

In all three compounds, $(CH_3)_3N$, $(SiH_3)_3N$, and $(GeH_3)_3N$, the main strength of the molecule resides in the σ bonds. The Si–N and Ge–N bonds are highly polar, and electrostatic repulsion between SiH_3 or GeH_3 groups is probably responsible for the planarity of $(SiH_3)_3N$ and $(GeH_3)_3N$. Of the higher orbitals, the N lone pair displays a small but significant amount of π bonding to the neighboring groups; the d-orbital contribution to π bonding for this orbital and for the whole molecule decreases, in the order $(SiH_3)_3N > (GeH_3)_3N > (CH_3)_3N$. The $3a_1$ and 3e orbitals show significant $p\pi$–$p\pi$ bonding and a hyperconjugative N–H interaction. The $1a_2$ and 4e orbitals are M–H bonding; 4e also displays N–M bonding which varies with bond angle, reaching a minimum in the planar form.

Acknowledgment. We are grateful to the National Research Council of Canada for financial support, to the University of British Columbia for a Killam Fellowship (to L.N.), and to N. P. C. Westwood for helpful comments.

Registry No. $(CH_3)_3N$, 75-50-3; $(SiH_3)_3N$, 13862-16-3; $(GeH_3)_3N$, 22856-27-5.

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