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Structures of Two Organosilyl Azides

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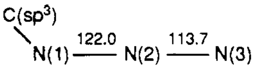
X-ray crystal structures were determined for trimesitylazidosilane (**3**) and 1,1-dimesityl-2,2-diphenyl-2-*tert*-butylazidodisilane (**4**). The N_1–N_2 and N_2–N_3 bond lengths (pm) in both compounds are nearly equal, being 115.8 and 117.0 for **3** and 117.0 and 114.7 for **4**, respectively. These silyl azides thus differ markedly from organic azides, in which N_2–N_3 is much shorter than N_1–N_2. Molecular orbital calculations predict N_2–N_3 to be 6 pm shorter than N_1–N_2 in H_3SiN_3 (**5**). The N–N–N angle is 173.7° for **3** and 174.9° for **4**, in good agreement with the calculated value for **5**.

The bonding in covalent azides is generally discussed in terms of two canonical forms, A and B,[1-3] with the

A B

relative importance of each form dependent upon the substituent R. Changes in the electronic properties of R are reflected in changes in the N–N bond distances, and in this regard X-ray crystallography provides a valuable tool in assessing substituent effects in covalent azides.

In 1983, Kaftory[3], summarized the results of several X-ray diffraction studies and determined the mean N–N bond lengths for azide groups attached to both sp^3- and sp^2-carbon atoms (**1** and **2**, bond distances in pm). On the



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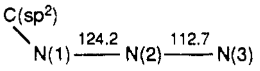

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basis of these numbers, canonical form B is the predominant contributor in each class of compounds. However, the difference between the N–N bonds is greater in **2** than in **1**, indicating that B is less important in alkyl azides than in aryl azides. Two models—one based on electronegativity effects and the other on resonance effects—can account for this observation.

Using the first model, the carbon atom in **1** is less electronegative than that in **2**. Therefore, the C–N bond is more polar in alkyl than the aryl azides and the N–N bond lengths in **1** should more closely resemble those found in ionic azides.[4]

The second model uses a resonance effect to explain the difference between **1** and **2**. Donation of electron density from the p orbital on N(1) to a π-system would enhance the contribution of canonical form B. According to this model, B contributes less to the bonding in alkyl azides because a π-interaction is not possible.

Table I. Selected Bonding Parameters for 3[a]

Bond Lengths, pm			
Si(1)–N(1)	181.4 (2)	Si(1)–C(1)	188.7 (3)
N(1)–N(2)	115.8 (4)	Si(1)–C(10)	189.2 (3)
N(2)–N(3)	117.0 (4)	Si(1)–C(19)	188.8 (3)
Bond Angles, deg			
Si(1)–N(1)–N(2)	125.8 (2)	C(19)–Si(1)–N(1)	106.2 (1)
N(1)–N(2)–N(3)	173.7 (3)	C(1)–Si(1)–C(10)	113.3 (1)
C(1)–Si(1)–N(1)	105.2 (1)	C(1)–Si(1)–C(19)	115.1 (1)
C(10)–Si(1)–N(1)	101.7 (1)	C(10)–Si(1)–C(19)	113.7 (1)
Torsion Angles, deg			
C(1)–Si(1)–N(1)–N(2)	107.4 (3)		
C(10)–Si(1)–N(1)–N(2)	−134.2 (3)		
C(19)–Si(1)–N(1)–N(2)	−15.0 (3)		
Si(1)–N(1)–N(2)–N(3)	−177.9 (3.0)		

[a] Estimated standard deviations in parentheses.

Organosilyl azides have been known since 1962,[5] but they have been the subject of very few structural studies. Early work showed that the NNN infrared antisymmetric stretch in triphenylazidosilane appears at a higher frequency than the corresponding band in alkyl azides, suggesting that resonance form B should be the most important contributor in silyl azides.

A B

If this were the case, one might expect the N(2)–N(3) bond to be shorter than the N(1)–N(2) bond. An early X-ray structural analysis of Ph_3SiN_3, based on a rather small data set, indicated just the opposite; the N(1)–N(2) and N(2)–N(3) bond distances were reported as 115 and 125 pm, respectively.[6] From these results, it was proposed that A is the major contributor to the electronic structure of organosilyl azides.

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(1) Treinin, A. In *Chemistry of the Azide Group*; Patai, S., Ed.; Interscience: London, 1971; pp 1–52.

(2) Golub, A. M.; Kohler, H.; Skopenko, V. V. In *Chemistry of Pseudohalides*; Elsevier: Amsterdam, 1986; pp 32–36.

(3) Kaftory, M. In *The Chemistry of Halides, Pseudohalides, and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; pp 1254–1258.

(4) In the azide ion the N–N distances are 116.6 pm. See: Choi, C. S. *Acta Crystallogr., Sect. B* **1969**, *25B*, 2638.

(5) West, R.; Thayer, J. *J. Am. Chem. Soc.* **1962**, *84*, 1763. Thayer, J.; West, R. *Inorg. Chem.* **1964**, *3*, 406–409. Thayer, J.; West, R. *Inorg. Chem.* **1964**, *3*, 889–893. Connolly, J. W.; Urry, G. *Inorg. Chem.* **1962**, *1*, 718. Wiberg, N.; Raschig, F.; Susfmann, R. *Angew. Chem.* **1962**, *74*, 388, 716. Sundermeyer, W. *Chem. Ber.* **1963**, *96*, 1293. Reichle, W. *Inorg. Chem.* **1964**, *3*, 402.

(6) Corey, E.; Cody, V.; Glick, M.; Radonovich, L. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1714. A preliminary electron-diffraction study of silyl azide (**5**) has also been published, but the N–N distances were not determined. See: Glidewell, C.; Robiette, A. G. *Chem. Phys. Lett.* **1974**, *28*, 290.

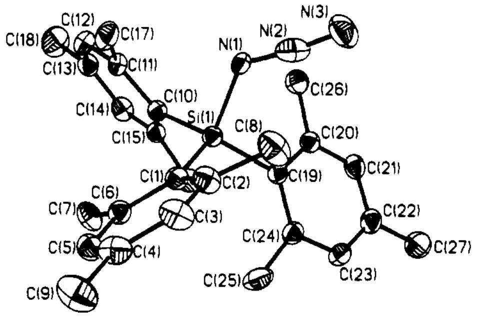


Figure 1. Thermal ellipsoid plot showing the numbering scheme in 3 (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

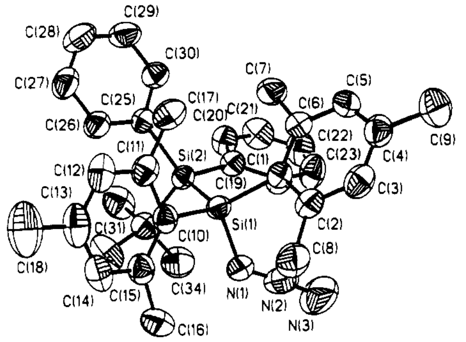
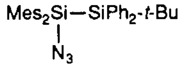


Figure 2. Thermal ellipsoid plot showing the numbering scheme in 4 (50% probability ellipsoids). Hydrogen atoms omitted for clarity.

In an effort to shed more light on this question,[7] we undertook the X-ray structural analysis of two organosilyl azides, tris(2,4,6-trimethylphenyl)azidosilane (3) and 1,1-bis(2,4,6-tri-methylphenyl)-2,2-diphenyl-2-*tert*-butylazidodisilane (4). In addition, molecular orbital calculations were carried out for the parent compound silyl azide (5).

Mes_3SiN_3

3



$$Mes_2\underset{\displaystyle N_3}{\underset{|}{Si}}-SiPh_2\text{-}t\text{-}Bu$$

4

H_3SiN_3

5

Mes = 2,4,6-trimethylphenyl

Results and Discussion

X-ray Crystallography. The numbering schemes for 3 and 4 are in Figures 1 and 2, respectively. Selected bonding parameters for each compound are shown in Tables I and II. Table III has been constructed in order to facilitate comparison of the molecular structures of 3 and 4 with that of triphenylazidosilane.[6,7] Final atomic coordinates are given in Tables IV and V.

Structure of Trimesitylazidosilane, 3. The N(1)-N(2) bond length in 3 is measured to be slightly shorter than the N(2)-N(3) bond, but the difference of 1.2 pm is within three standard deviations and so may not be real. Thus, the N-N bond distances in 3 are nearly equal, showing that within the context of the valence bond model, form A (Si—N═N═N) is a much more important contributor than B (Si—N—N≡N). The weighting of A in 3 is also decidedly greater than in the organic azides 1 or 2. The reasons for this are not clear, but the result can be rationalized in terms of the electronegativity effect discussed earlier. Since a Si-N_3 bond is more polar than a C-N_3 bond, silyl azides are expected to more closely resemble ionic azides. This view is supported by Mulliken population analysis for silyl and methyl azides (see below). The calculated charges on the N_3 group are −0.425 and −0.265, respectively for these compounds.

Table II. Selected Bonding Parameters for 4[a]

Bond Lengths, pm			
Si(1)-Si(2)	241.2 (2)	Si(1)-C(1)	190.0 (4)
Si(1)-N(1)	178.2 (4)	Si(1)-C(10)	190.6 (4)
N(1)-N(2)	117.0 (5)	Si(2)-C(19)	189.6 (4)
N(2)-N(3)	114.7 (6)	Si(2)-C(25)	188.6 (4)
		Si(2)-C(31)	192.9 (5)
Bond Angles, deg			
Si(1)-N(1)-N(2)	129.1 (4)	C(10)-Si(1)-Si(2)	122.5 (1)
N(1)-N(2)-N(3)	174.9 (5)	C(19)-Si(2)-Si(1)	110.7 (1)
Si(2)-Si(1)-N(1)	99.1 (1)	C(25)-Si(2)-Si(1)	109.1 (1)
C(1)-Si(1)-N(1)	109.1 (2)	C(31)-Si(2)-Si(1)	111.5 (1)
C(10)-Si(1)-N(1)	104.7 (2)	C(19)-Si(2)-C(25)	110.8 (2)
C(1)-Si(1)-C(10)	108.7 (2)	C(19)-Si(2)-C(31)	108.3 (2)
C(1)-Si(1)-Si(2)	111.5 (1)	C(25)-Si(2)-C(31)	106.4 (2)
Torsion Angles, deg			
Si(2)-Si(1)-N(1)-N(2)	−103.0 (3)		
C(1)-Si(1)-N(1)-N(2)	140.6 (3)		
C(10)-Si(1)-N(1)-N(2)	24.1 (4)		
Si(1)-N(1)-N(2)-N(3)	−179.8 (4.9)		

[a] Estimated standard deviations in parentheses.

Table III. Comparison of the Bonding Parameters for 3 and 4 with Those Published for Triphenylazidosilane[6]

	bond lengths, pm			
	N(1)-N(2)	N(2)-N(3)	Si-C(av)	Si-N
Ph_3SiN_3	115 (4)	125 (6)	186 (1)	174 (2)
Mes_3SiN_3 (3)	115.8 (0.4)	117.0 (0.4)	188.9 (0.3)	181.4 (0.2)
$Mes_2(N_3)Si$-$SiPh_2$-*t*-Bu (4)	117.0 (0.5)	114.7 (0.6)	190.3 (0.4)[a]	178.1 (0.4)

	bond angles, deg	
	Si-N-N	N-N-N
Ph_3SiN_3	120.5 (2)	176.6 (3.0)
Mes_3SiN_3 (3)	125.8 (0.2)	173.7 (0.3)
$Mes_2(N_3)SiSiPh_2$-*t*-Bu (4)	129.1 (0.4)	174.9 (0.5)

[a] Si(1)-C distances.

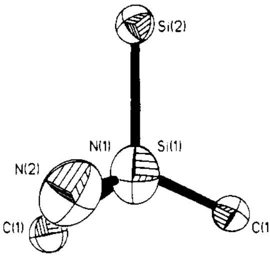


Figure 3. Newman projection down the Si(1)-N(1) bond axis in 4. The Si-Si-N-N torsion angle is 103°.

The Si-C bonds in 3, which average to 188.9 pm, are well within the range found in other hindered arylsilanes.[8] The Si-N bond is 181.4 pm and the Si-N-N bond angle is 125.8°, about 10° wider than the corresponding angle in carbon azides.[3] The nitrogen atoms in 3 are not quite colinear, as the N-N-N bond angle is 173.7°. Small de-

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(7) Several factors make the published[6] structure of Ph_3SiN_3 highly questionable. First, the errors in the bonding parameters are quite large (see Table III). Second, the *R* value (11%) is somewhat high. Third, the final model in this study was isotropic. At this level of refinement, the N-N distances in our azides were similar to those reported for Ph_3SiN_3. After converting to an anisotropic model, we obtained the bond distances in Tables I and II.

(8) The average Si-C bond distance in $(MeS_2SiH)_2$ is 187.3 pm[9] and that in Mes_2HSi-$SiH(t\text{-}Bu)_2$ is 190.2 pm.[10]

(9) Baxter, S.; Mislow, K.; Blount, J. *Tetrahedron* **1980**, *36*, 605.

(10) Weidenbruch, M.; Kramer, K.; Peters, K.; Schnering, H. *Z. Naturforsch., B* **1985**, *40*, 601.

Table IV. Final Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (pm^2 × 10^{-1}) for 3 with Standard Deviations in Parentheses

	x	*y*	*z*	U^a
Si(1)	-2010 (1)	-466 (1)	1663 (1)	22 (1)
N(1)	-2159 (2)	56 (2)	439 (2)	25 (1)
N(2)	-1961 (2)	783 (2)	282 (2)	39 (1)
N(3)	-1794 (3)	1502 (2)	31 (2)	50 (1)
C(1)	-3515 (2)	-636 (2)	1954 (2)	25 (1)
C(2)	-4353 (3)	20 (2)	1731 (2)	31 (1)
C(3)	-5462 (3)	-115 (2)	1931 (2)	36 (1)
C(4)	-5795 (3)	-878 (2)	2375 (2)	35 (1)
C(5)	-4965 (2)	-1515 (2)	2627 (2)	31 (1)
C(6)	-3845 (2)	-1416 (2)	2425 (2)	26 (1)
C(7)	-3038 (3)	-2152 (2)	2765 (3)	35 (1)
C(8)	-4103 (3)	913 (2)	1304 (3)	45 (1)
C(9)	-7005 (3)	-1012 (3)	2589 (3)	48 (1)
C(10)	-1260 (2)	-1524 (2)	1409 (2)	23 (1)
C(11)	-1641 (2)	-2007 (2)	532 (2)	28 (1)
C(12)	-1026 (3)	-2737 (2)	279 (2)	34 (1)
C(13)	-53 (3)	-3025 (2)	860 (2)	35 (1)
C(14)	280 (3)	-2580 (2)	1744 (2)	31 (1)
C(15)	-300 (2)	-1847 (2)	2037 (2)	25 (1)
C(16)	128 (3)	-1460 (2)	3047 (2)	30 (1)
C(17)	-2723 (3)	-1799 (2)	-148 (2)	39 (1)
C(18)	608 (4)	-3812 (2)	560 (3)	54 (1)
C(19)	-114 (2)	301 (2)	2543 (2)	24 (1)
C(20)	-79 (2)	624 (2)	2255 (2)	25 (1)
C(21)	596 (3)	1200 (2)	2884 (2)	32 (1)
C(22)	297 (3)	1477 (2)	3797 (2)	33 (1)
C(23)	-696 (3)	1140 (2)	4084 (2)	33 (1)
C(24)	-1399 (2)	559 (2)	3495 (2)	27 (1)
C(25)	-2431 (3)	223 (2)	3944 (2)	41 (1)
C(26)	394 (3)	361 (2)	1305 (2)	32 (1)
C(27)	1027 (3)	2115 (2)	4442 (3)	49 (1)
H(3)	-6020	335	1755	40
H(5)	-5172	-2042	2953	35
H(7A)	-2329	-1919	3086	40
H(7B)	-2902	-2491	2190	40
H(7C)	-3373	-2521	3229	40
H(8A)	-3374	1128	1602	49
H(8B)	-4692	1304	1463	49
H(8C)	-4116	883	589	49
H(9A)	-7095	-1576	2889	51
H(9B)	-7503	-973	1967	51
H(9C)	-7195	-559	3035	51
H(12)	-1292	-3051	-326	36
H(14)	938	-2785	2176	34
H(16A)	-501	-1290	3391	35
H(16B)	621	-964	3001	35
H(16C)	547	-1923	3411	35
H(17A)	-3310	-1636	250	40
H(17B)	-2955	-2313	-534	40
H(17C)	-2595	-1326	-592	40
H(18A)	1342	-3885	947	63
H(18B)	700	-3734	-135	63
H(18C)	151	-4324	632	63
H(21)	1293	1413	2675	34
H(23)	-911	1314	4721	38
H(25A)	-2444	-402	3852	44
H(25B)	-3131	470	3623	44
H(25C)	-2349	355	4649	44
H(26A)	89	-193	1056	35
H(26B)	1208	316	1457	35
H(26C)	207	805	805	35
H(27A)	522	2498	4745	57
H(27B)	1519	2458	4079	57
H(27C)	1478	1784	4956	57

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

viations of this sort have also been observed in carbon azides[3] and are not surprising since the energy required to bend the azide group is predicted to be very small.[11] While crystal packing forces and steric interactions could account for this nonlinearity, it may also be true that covalent azides are intrinsically bent at N(2).

Structures of Azidodisilane 4. The N-N bond lengths in **4** differ by 2.3 pm, with N(2)-N(3) shorter than N(1)-N(2). This difference is in the same direction as, but much smaller than, that in the organic azides **1** and **2**. Again using the valence bond model, form A is the dominant contributor in **4**, but apparently not to the same extent as in **3**.

The Si-N bond distance in **4** is 3.2 pm shorter than in **3**,[12] and the Si-Si bond length of 241.2 pm is slightly longer than that in other hindered disilanes.[13] In addition, as shown in the Newman projection of Figure 3, the Si-Si bond is almost perpendicular to the N(1)-N(2) bond, the Si-Si-N-N torsion angle being 103.0°. This geometry would permit (and could actually be due to) delocalization of π-electron density from the p orbital on N(1) to the Si-Si σ^* orbital. This delocalization may account in part for the longer Si-Si bond and shorter Si-N bond in **4**. However, steric interactions probably also play a major role in these variations.

Hyperconjugative electron delocalization from N(1) to the Si-Si bond also accounts nicely for the N-N bond lengths in **4**. Such back-donation would increase the relative weighting of B (Si—N—N≡N) in **4**, resulting in a longer N(1)-N(2) bond an a shorter N(2)-N(3) bond (as compared to **3**).

The average length found for the two Si(1)-C bonds in **4** is about 1.5 pm longer than in **3**, a fact that might be attributable to larger steric interactions in the former. Another piece of information indicative of this is the Si-N(1)-N(2) bond angle in **4**, which is more than 3° greater than that in **3**. As in **3**, the azide group in **4** is bent at the center nitrogen (the N-N-N bond angle being 174.9°) and the Si-N-N-N fragment is in a trans planar orientation (the torsion angle being within experimental error of 180°).

Molecular Orbital Calculations. Table VI summarizes the geometry predictions for silyl azide (**5**) at various levels of theory. The predicted bond angles are relatively insensitive to the level of theory and are in good agreement with the experimental values. The SiN bond length is shortened somewhat by the inclusion of d orbitals on Si and N and lengthened slightly when correlation corrections are included. Both of these trends are to be expected and leave the SiN distance slightly shorter than the experimental values at the highest level of theory [MP2/MC-311G(d)]. At the SCF level, theory predicts the N(2)-N(3) bond of silyl azide to be 12-13 pm shorter than the N(1)-N(2) bond. This contradicts the experimental results obtained for **3** and **4** discussed earlier. Addition of correlation corrections reduces the calculated difference between the two bond lengths to 5-6 pm, with the terminal bond still predicted to be shorter. The MP2/MC-311G(d) N(2)-N(3) bond length is in excellent agreement with that from the X-ray structure of **3** and slightly longer than that of **4**. The N(1)-N(2) bond lengths predicted for **5** are 7 and 5 pm longer than those in **3** and **4**, respectively.

It is useful to compare the foregoing results with those for methyl azide. The RHF/6-31G(d) N(2)-N(3) and N(1)-N(2) bond lengths in methyl azide are 110.2 and 122.8 pm, respectively, while the MP2/6-31G(d) values are 116.3 and 124.3 pm, respectively. The SCF bond length difference in methyl azide is therefore the same as in silyl

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(11) Roberts, J. *Chem. Ber.* **1961**, *94*, 273.

(12) The Si-N bond in both **3** and **4** is significantly longer than those found in disilazanes. See: Glidewell, C.; Holden, H. *Acta Crystallogr., Sect B* **1981**, *37*, 754 and references therein.

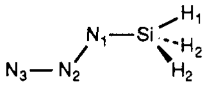
(13) The Si-Si bond distances in $(Mes_2HSi)_2$[9] and $Mes_2HSiSiH(t\text{-}Bu)_2$[10] are 235.6 and 239.8 pm, respectively.

Table V. Final Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($pm^2 \times 10^{-1}$) for 4 with Standard Deviations in Parentheses

	x	*y*	*z*	U^a		*x*	*y*	*z*	U^a
Si(2)	2328 (1)	8836 (1)	1573 (1)	43 (1)	H(5)	−416	4934	570	69
Si(1)	3410 (1)	7095 (1)	1351 (1)	43 (1)	H(7a)	1424	7378	619	72
N(1)	4613 (4)	6921 (3)	1864 (1)	60 (1)	H(7b)	348	6624	314	72
N(2)	5809 (4)	7090 (3)	1905 (2)	74 (2)	H(7c)	1942	6412	294	72
N(3)	6978 (4)	7241 (5)	1980 (2)	130 (3)	H(8a)	3030	5631	2312	81
C(1)	2133 (4)	5870 (3)	1320 (2)	44 (1)	H(8b)	3820	4741	2022	81
C(2)	2039 (4)	5012 (4)	1671 (2)	52 (2)	H(8c)	2655	4343	2340	81
C(3)	1072 (4)	4146 (4)	1589 (2)	60 (2)	H(9a)	−1343	3121	794	111
C(4)	155 (4)	4102 (4)	1190 (2)	65 (2)	H(9b)	−1560	3290	1337	111
C(5)	221 (4)	4945 (4)	852 (2)	58 (2)	H(9c)	−449	2426	1184	111
C(6)	1196 (4)	5811 (3)	912 (2)	49 (2)	H(12)	5385	8241	−164	68
C(7)	1234 (4)	6630 (4)	496 (2)	64 (2)	H(14)	6786	5277	391	73
C(8)	2942 (5)	4935 (4)	2135 (2)	70 (2)	H(16a)	4596	4901	1294	80
C(9)	−888 (5)	3142 (5)	1112 (3)	100 (3)	H(16b)	6141	5312	1362	80
C(10)	4509 (4)	6996 (3)	820 (2)	41 (1)	H(16c)	5701	4386	978	80
C(11)	4524 (4)	7809 (4)	448 (2)	45 (2)	H(17a)	2970	8802	650	77
C(12)	5390 (4)	7675 (4)	82 (2)	55 (2)	H(17b)	3156	8892	102	77
C(13)	6259 (4)	6749 (4)	60 (2)	60 (2)	H(17c)	4178	9533	473	77
C(14)	6210 (4)	5936 (4)	406 (2)	61 (2)	H(18a)	6876	7144	−582	99
C(15)	5350 (4)	6032 (3)	780 (2)	49 (2)	H(18b)	7334	5902	−449	99
C(16)	5412 (5)	5060 (4)	1133 (2)	71 (2)	H(18c)	8149	6929	−209	99
C(17)	3634 (4)	8859 (4)	416 (2)	64 (2)	H(20)	−371	7757	1423	67
C(18)	7251 (5)	6658 (6)	−329 (2)	94 (3)	H(21)	−2422	8006	947	80
C(19)	676 (4)	9104 (3)	1175 (2)	44 (1)	H(22)	−2637	9489	399	89
C(20)	−449 (4)	8377 (4)	1201 (2)	59 (2)	H(23)	−790	10736	339	84
C(21)	−1662 (4)	8518 (4)	919 (2)	69 (2)	H(24)	1289	10486	817	66
C(22)	−1790 (5)	9388 (5)	599 (2)	77 (2)	H(26)	2223	11341	1576	75
C(23)	−700 (5)	10120 (4)	563 (2)	70 (2)	H(27)	3821	12812	1562	91
C(24)	530 (4)	9974 (4)	848 (2)	55 (2)	H(28)	6155	12420	1497	95
C(25)	3594 (4)	10039 (3)	1529 (2)	47 (2)	H(29)	6919	10561	1469	86
C(26)	3185 (4)	11167 (4)	1553 (2)	61 (2)	H(30)	5328	9080	1478	73
C(27)	4128 (5)	12042 (4)	1544 (2)	79 (2)	H(32a)	244	7662	2179	88
C(28)	5504 (5)	11809 (4)	1508 (2)	82 (2)	H(32b)	1015	7709	2694	88
C(29)	5952 (4)	10721 (4)	1488 (2)	78 (2)	H(32c)	1682	7060	2283	88
C(30)	5004 (4)	9846 (4)	1496 (2)	65 (2)	H(33a)	48	9693	2129	91
C(31)	1870 (4)	8799 (4)	2229 (2)	56 (2)	H(33b)	1320	10507	2228	91
C(32)	1135 (6)	7704 (4)	2357 (2)	79 (2)	H(33c)	770	9810	2648	91
C(33)	918 (5)	9800 (4)	2314 (2)	82 (2)	H(34a)	3780	8288	2537	109
C(34)	3191 (5)	8934 (6)	2564 (2)	93 (3)	H(34b)	2888	8965	2881	109
H(3)	1047	3554	1822	71	H(34c)	3698	9611	2503	109

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VI. Geometries of H_3SiN_3 (5) from MO Calculations



	bond lengths, pm				
	N(1)–N(2)	N(2)–N(3)	N(1)–Si	Si–H(1)	Si–H(2)
RHF/3-21G	123.9	111.0	178.2	147.3	148.6
RHF/6-31G(d)	122.1	109.9	174.6	147.5	147.5
RHF/MC-311G(d)	121.7	109.2	174.5	146.8	147.9
MP2/6-31G(d)	122.9	117.3	176.1	147.5	147.5
MP2/MC-311G(d)	122.4	116.5	176.0	147.5	148.4

	bond angles, deg			
	NNN	NNSi	NSiH(1)	NSiH(2)
RHF/3-21G	174.0	127.5	105.1	111.5
RHF/6-31G(d)	175.8	123.7	105.5	110.9
RHF/MC-311G(d)	175.7	124.7	105.4	110.9
MP2/6-31G(d)	174.0	125.6	104.5	110.3
MP2/MC-311G(d)	173.9	124.9	104.7	110.2

azide, but the decrease in the gap is a bit smaller when correlation corrections are applied to the carbon compound. These predicted bond lengths may be compared with the gas-phase electron diffraction values[14] of 113.2 and 122.8 pm for methyl azide, so theory and experiment are in reasonable agreement here.

There are several possible reasons for the apparent disparity between the experimental and theoretical SiN and N(1)–N(2) bond lengths. It is certainly possible that higher levels of theory (either larger basis sets of more sophisticated wave functions) are needed, although extensive MCSCF calculations do not reveal significant configurational mixing. It is also likely that the substitution of mesityl groups for hydrogens has a strong steric and electronic effect.

Steric effects were simulated at the SCF/6-31G(d) level by forcing the silyl hydrogens to open to 120° angles. This, in fact, increases the SiN bond length from 174.6 to 184.2 pm, shortens the N(1)–N(2) bond by 2 pm, and slightly lengthens the N(2)–N(3) bond. All of these changes are in the direction of the experimental bond lengths. The electronic effects of the mesityl groups are more difficult to simulate; however, note that the 6-31G(d) SiN single bond length in silylamine is 172.5 pm,[15,16] nearly 1 pm shorter than that observed in the crystal structure.

Experimental Section

X-ray Crystallography. The syntheses of 3 and 4 are described elsewhere.[17] Crystals of each compound suitable for X-ray

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Table VII. Crystal Data and Crystallographic Details for 3 and 4

	3	4
empirical formula	$C_{27}H_{33}SiN_3$	$C_{34}H_{41}Si_2N_3$
fw, daltons	427	548
cryst dimens, mm	0.15 × 0.3 × 0.6	0.2 × 0.25 × 0.6
temp, K	165 (±5)	298
cell parameters		
a, Å	11.816 (4)	9.676 (2)
b, Å	15.235 (4)	11.810 (4)
c, Å	13.431 (5)	28.034 (5)
β, deg	97.30 (3)	94.84
V, Å^3	2398.2	3192.1
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
Z	4	4
D_{calcd}, g/cm^3	1.18	1.14
abs coeff μ, cm^{-1}	1.12	1.32
scan range, deg		
below $2\theta(K\alpha_1)$	0.75	0.75
above $2\theta(K\alpha_2)$	0.75	0.75
scan rate, deg/min	3.0–29.3	3.0–29.3
scan type	θ–2θ	$\theta/2\theta$
2θ limits, deg	3.5–54.9	3.5–50.66
$(\sin\theta)/\lambda_{max}$, Å^{-1}	0.649	0.602
unique data, theoretical	5496	5833
$F_o > 3\sigma(F_o)$	3444	3454
discrepancy indices		
R_1	0.058	0.078
R_2	0.059	0.065
P; weight = $1/(\sigma(F)^2 + p^2F^2)$	0.03	0.02
goodness of fit	1.33	1.58
data to variable ratio	11.2	9.1
largest shift/error in final cycle	0.21	0.25
ρ_{max} final map, e/Å^3	0.44	0.34

analysis were obtained from hexane by slow evaporation at room temperature. Data collection for **4** was performed on a Nicolet P3/F diffractometer and for **3** was performed on a Nicolet P-1 diffractometer equipped with a modified LT-1 low-temperature device. Both diffractometers were equipped with graphite-monochromated Mo ($\lambda(K\alpha)$ = 0.710 73 Å) x-radiation sources. Unit-cell parameters were obtained from least-squares refinements based on 25 reflections. During data collection, four standards were measured every 100 reflections to monitor the stability of the crystal. In the case of **4**, only small, random deviations in peak intensities were observed, whereas **3** showed approximately a 2% decrease in peak intensities during data collection (no correction was made). Empirical absorption corrections were applied to both data sets. Details of intensity measurements appear in Table VII.

The structures were solved by direct methods using the SHELXTL package of programs. The silicon atoms and most of the carbon atoms were located in the E maps; the remaining carbon atoms were revealed by subsequent difference electron density maps. The blocked-cascade least-squares refinements of the structures were based on F_o and used the relfections with $F_o > 3\sigma(F_o)$. Atomic form factors were taken from standard sources.[18] In the final refinement cycles, the non-hydrogen atoms were assumed to vibrate anisotropically, while the hydrogen atoms were included as idealized isotropic fixed contributors [CH bond length = 0.96 Å; U(hydrogen) = $1.2U$(attached carbon) methyl groups with idealized C_{3v} local symmetry with one rotational variable added per group to allow rotation about the C_3 axis]. The final values of the discrepancy indices $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ are in Table V. Final atomic parameters and anisotropic thermal parameters for each compound are available as supplementary material.

Computational Methods. Geometries were optimized by using the analytical gradient methods in GAUSSIAN82.[19] Three basis sets were used in this work. The smaller basis sets are the split valence 3-21G[20] and the split valence plus polarization 6-31G(d)[21] bases. A larger, triply split basis set combines the McLean–Chandler (MC) basis for silicon[22] and the 6-311G basis[23] for nitrogen and hydrogen. A set of 6d functions was added to the heavy atoms, yielding a final basis set denoted MC-311G(d). Geometries were optimized by using both self-consistent field (SCF) and second-order perturbation theory (MP2)[24,25] wave functions. All SCF structures were verified to be minima by analytically calculating and diagonalizing the matrices of energy second derivatives.

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Supplementary Material Available: Tables of anisotropic thermal parameters (2 pages); listings of structure factor amplitudes (46 pages). Ordering information is given on any current masthead page.

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