2432 *Inorg. Chem.* **1988**, *27*, 2432-2436

Contribution from Ultrasystems Defense and Space Inc., 16775 Von Karman Avenue, Irvine, California 92714,
Office of Naval Research, 800 N. Quincy Street, Arlington, Virginia 22217,
and Crystalytics Company, P. O. Box 82286, Lincoln, Nebraska 68501

Boron–Nitrogen Polymers. 3. Nitrogen- and Oxygen-Bridged Compounds

K. J. L. Paciorek,*,[†] R. H. Kratzer,[†] P. F. Kimble,[†] J. H. Nakahara,[†] K. J. Wynne,[‡] and C. S. Day[§]

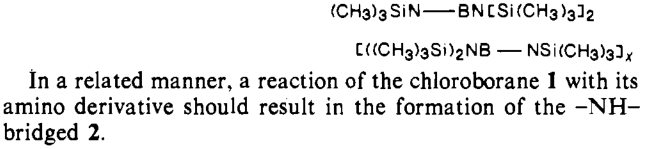
Received May 5, 1987

Iminobis{[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane} (**2**) and oxybis{[bis(trimethylsilyl)amino][(trimethylsilyl)-amino]borane} (**3**) were prepared by interaction of [bis(trimethylsilyl)amino][(trimethylsilyl)amino]chloroborane with amino-[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane and with wet triethylamine, respectively. **2** and **3** exhibited essentially identical infrared spectra; the DSC scans were also similar with two endotherms at temperatures lower than the melting points. Mass spectral breakdown patterns were closely corresponding, differing by one unit in the majority of the prominent peaks. From the metastables, the breakdown paths were established. **2** and **3** crystallize isomorphously in the monoclinic space group $P2_1/n$. For **2**, $a = 12.876$ (2) Å, $b = 14.828$ (3) Å, $c = 18.628$ (4) Å, $\beta = 97.07$ (2)°, $V = 3529$ (1) Å^3, $Z = 4$, $M_r = 533.8$, and the calculated density is 1.005 g/cm^3. Refinement led to $R_F = 4.1\%$ and $R_{wF} = 4.2\%$ for 5093 independent reflections. The structure of **2** confirms the presence of a central N_2BNBN_2 framework that is essentially planar with a B(1)–N(1)–B(2) angle of 135.9 (2)°. The shortest B–N bonds, B(2)–N(5) = 1.405 (3) Å and B(1)–N(3) = 1.423 (3) Å, are to nitrogens bonded to one silicon, while the longest B–N bonds, B(2)–N(4) = 1.485 (3) Å and B(1)–N(2) = 1.487 (3) Å, are to nitrogens bonded to two silicons. For **3**, $a = 12.826$ (3) Å, $b = 14.822$ (4) Å, $c = 18.557$ (4) Å, $\beta = 95.98$ (2)°, $V = 3509$ (1) Å^3, $Z = 4$, $M_r = 534.8$, and the calculated density is 1.012 g/cm^3. Refinement led to $R_F = 4.3\%$ and $R_{wF} = 4.0\%$ for 4458 independent reflections. Structure **3** differs from **2** only in the existence of a central B–O–B unit, wherein the boron-oxygen distances B(1)–O(1) = 1.380 (3) Å and B(2)–O(1) = 1.389 (3) Å are somewhat shorter than the corresponding B–N distances for **2**, B(1)–N(1) = 1.428 (3) Å and B(2)–N(1) = 1.446 (3) Å.

Introduction

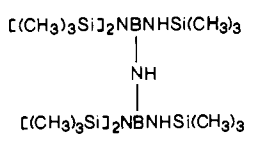
In contrast to the case for preceramic carbon polymers, where emphasis is on improved processing and elucidation of pyrolysis chemistry of known materials,[1] the synthesis of new materials plays a key role in non-carbon systems. Rather stringent requirements must be met for a useful preceramic polymer,[2] but the limitations of other methods of preparing and processing high-temperature BN ceramic materials (e.g., sintering, chemical vapor deposition) have focused increased attention on the preparation of processible precursors.

Boron–nitrogen chemistry has been intensively studied, but to date few tractable B–N polymers are known.[3] A Japanese patent[4] describes a resin derived from the thermolysis of 2,4,6-tri-amino-1,3,5-triphenylborazine, but these results have not proved reproducible.[5,6] We have therefore begun a systematic study of reactions that could lead to B–N macromolecules. In the course of investigation of processible preceramic precursors, it was found that having (trimethylsilyl)amino substituents leads to formation of pure boron nitride. This concept is exemplified by controlled pyrolysis of 2,4,6-triamino-1,3,5-tris(trimethylsilyl)borazine.[7,8] The presence of alkyl or aryl groups on nitrogen led invariably to carbon retention in the final product.[3-6] Unfortunately, however, the synthesis of the preceramic polymer precursor, namely 2,4,6-trichloro-1,3,5-tris(trimethylsilyl)borazine, is a low-yield multistep process. Work was thus initiated to identify suitable noncyclic monomers. Intramolecular or intermolecular dehydrohalogenation of [bis(trimethylsilyl)amino][(trimethylsilyl)-amino]chloroborane (**1**) would be expected to yield either a dimer or a polymeric system, i.e.



In a related manner, a reaction of the chloroborane **1** with its amino derivative should result in the formation of the –NH–bridged **2**.

In this paper, the synthesis, mass spectra, and crystallographic data for the above compound and its oxygen-bridged analogue **3** are discussed.



$$\begin{array}{c}\mathrm{[(CH_3)_3Si]_2NBNHSi(CH_3)_3}\\ |\\ \mathrm{NH}\\ |\\ \mathrm{[(CH_3)_3Si]_2NBNHSi(CH_3)_3}\end{array}$$

2

Experimental Section

General Considerations. Operations involving moisture- or air-sensitive materials were carried out either in an inert-atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen bypass, or in vacuo. Infrared spectra were recorded as double mulls (Kel-F oil No. 10 and Nujol) with a Perkin-Elmer infrared spectrophotometer, Model 1330. The mass spectrometric analyses were obtained by employing a Du Pont Model 21-491B spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph, equipped with a flame ionization detector. Gas chromatography was performed by employing a 10 ft × $^1/_8$ in. stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G and using a programming rate of 8 °C/min from 50 to 300 °C. NMR spectra were recorded on a JEOL FX900 broad-band spectrometer using C_6D_6 as solvent and TMS as external standard. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, and the crystal structure determinations by Crystalytics Co.

Preparation of Oxybis{[bis(trimethylsilyl)amino][(trimethylsilyl)-amino]borane} (3). At room temperature to stirred [bis(trimethylsilyl)-amino][(trimethylsilyl)amino]chloroborane (15.02 g, 50.94 mmol; prepared by the procedure of Wells and Collins[9,16]) was added triethylamine (116 g; refluxed over and distilled from potassium hydroxide). The

---

* To whom correspondence should be addressed.

[†] Ultrasystems Defense and Space Inc.

[‡] Office of Naval Research.

[§] Crystalytics Co.

(1) Jenkins, G. M.; Kawamura, K. *Polymer Carbons-Carbon Fibre, Glass and Char*; Cambridge University Press: London, 1976.

(2) Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *15*, 297.

(3) (a) Wagner, R. I.; Bradford, J. L. *Inorg. Chem.* **1962**, *1*, 99. (b) Shaw, S. Y.; Dubois, D. A.; Neilson, R. H. Presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987; Paper INORG 384. (c) Narula, C. K.; Janik, J. F.; Paine, R. T.; Schaeffer, R. Presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987; Paper INORG 386.

(4) Taniguchi, I.; Harada, K.; Maeda, T. Jpn. Patent 7653000, 1976; *Chem. Abstr.* **1976**, *85*, 96582v.

(5) Paciorek, K. J. L.; Kratzer, R. H.; Harris, D. H.; Smythe, M. E. *Polymer Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1984**, *25*, 15.

(6) Paciorek, K. J. L.; Harris, D. H.; Kratzer, R. H. *J. Polym. Sci.* **1986**, *24*, 173.

(7) Paciorek, K. J. L; Kratzer, R. H.; Harris, D. H.; Smythe, M. E.; Kimble, P. F. U.S. Patent 4581468, April 8, 1986.

(8) Paciorek, K. J. L.; Harris, D. H.; Krone-Schmidt, W.; Kratzer, R. H. Presented at the Third International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, San Diego, CA, Feb 23-27, 1987.

(9) Wells, R. L.; Collins, A. L. *Inorg. Chem.* **1968**, *7*, 419.

Table I. Experimental Data for the X-ray Diffraction Study of $\{[(CH_3)_3Si]_2NBNHSi(CH_3)_3\}_2NH$ (**2**) and $\{[(CH_3)_3Si]_2NBNHSi(CH_3)_3\}_2O$ (**3**)

	2	3
(A) Crystal Parameters		
temp, °C	20 ± 1	20 ± 1
cryst dimens, mm	0.50 × 0.55 × 0.70	irreg: min 0.45, max 0.80
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$[a]	$P2_1/n$[a]
a, Å	12.876 (2)	12.826 (3)
b, Å	14.828 (3)	14.822 (4)
c, Å	18.628 (4)	18.557 (4)
β, deg	97.07 (2)	95.98 (2)
V, Å^3	3529 (1)	3509 (1)
Z	4	4
mol wt	533.8	534.8
density (calcd), g/cm^3	1.005	1.012
(B) Measurement of Data		
radiation (graphite monochromated)	Mo K$\bar{\alpha}$ (λ = 0.71073 Å)	
orientation rflns: no.; range (2θ), deg	15; 25–30	
scan method; scan range, deg	ω, 1.00	
data collecn range, 2θ, deg; scan rate, deg/min	$3 < 2\theta < 43$, 6; $43 < 2\theta < 55$, 3	
no. of unique data	8120	8066
no. with $I > 3\sigma(I)$	5093	4458
check rflns, freq	6, 300	
no. of params refined	347	343
R_1	0.041	0.043
R_2	0.042	0.040
goodness-of-fit indicator	1.98	1.78

[a] An alternate setting of $P2_1/c$-C_{2h}^5 (No. 14).[10]

solution was refluxed for 6 h. After the mixture was cooled, triethylamine hydrochloride (3.64 g, 26.44 mmol) was filtered off and the starting materials and the byproducts were removed from the filtrate in vacuo at 49–87 °C (bath temperature). The residue (4.7 g, 34.9% yield), which crystallized partially on cooling, was purified by crystallization, initially under an inert atmosphere from Freon-113 and then in air from methanol, giving oxybis{[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane} (**3**): yield 3.35 g, 24.7%; mp 158–160 °C. Anal. Calcd for $C_{18}H_{56}N_4B_2Si_6O$: C, 40.43; H, 10.55; N, 10.48; B, 4.05; Si, 31.51. Found: C, 40.33; H, 10.38; N, 10.01; B, 4.02; Si, 31.70. ^{1}H NMR: 0.28 (s), 0.30 (s), and 3.17 ppm (s) in the ratio of 9:18:1.

Treatment of [Bis(trimethylsilyl)amino][(trimethylsilyl)amino]chloroborane with Water in the Presence of Triethylamine. To a vigorously stirred solution of the chloroborane (2.00 g, 6.78 mmol) in benzene (5 mL) was added a solution of triethylamine (1.37 g, 13.57 mmol) and water (61.0 mg, 3.39 mmol) in benzene (5 mL). Following 6-h reflux, triethylamine hydrochloride (yield 510 mg, 55%) was filtered off and the filtrate was evaporated in vacuo. The residual liquid (830 mg), as determined by GC, was composed of 12% hexamethyldisilazane, 11% amino[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane, 39% aminobis[bis(trimethylsilyl)amino]borane, and 15% (7.1% yield) oxybis{[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane}.

Preparation of Amino[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane. Ammonia (12 mL, ~520 mmol) was distilled, at −78 °C, in vacuo into a solution of [bis(trimethylsilyl)amino][(trimethylsilyl)amino]chloroborane (40.13 g, 136.10 mmol) in hexane (100 mL). A white precipitate formed immediately. Once the transfer was completed, the reaction mixture was stirred at −78 °C for 1 h. Subsequently, it was brought to atmospheric pressure under a nitrogen bypass and was allowed to warm slowly to room temperature. This was followed by a 1-h reflux. After removal of the precipitated ammonium chloride (8.07 g), distillation gave 29.44 g (78.5%) of the pure product: bp 64–65 °C (3.0 mmHg) (lit.[9] bp 70 °C (2 mmHg)). A 32% yield was reported in the literature[9] with use of gaseous ammonia.

Reaction of Amino[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane and [Bis(trimethylsilyl)amino][(trimethylsilyl)amino]chloroborane in the Presence of Triethylamine. To a stirred mixture of amino[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane (4.16 g, 15.10 mmol) and [bis(trimethylsilyl)amino][(trimethylsilyl)amino]chloroborane (4.60 g, 15.60 mmol) was added at room temperature, over a period of 5 min, triethylamine (3.32 g, 31.92 mmol; dried over $LiAlH_4$). Subsequently, the mixture was heated at 100 °C for 18 h, giving 1.17 g (54.4%) of triethylamine hydrochloride. The unreacted starting materials were removed from the filtrate in vacuo at a bath temperature of 60–110 °C. Crystallization of the solid residue (5.29 g) from Freon-113 gave 3.51 g (48.4%) of iminobis{[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane} (**2**). Final crystallization from methanol afforded the pure product, mp 169–171 °C. Anal. Calcd for $C_{18}H_{57}N_5B_2Si_6$: C, 40.50; H, 10.76; B, 3.92; N, 13.12; Si, 31.47. Found: C, 40.24; H, 10.72; B, 3.54; N, 12.92; Si, 31.36. ^{1}H NMR: 0.25 (s), 0.30 (s), 2.70 (s), and 3.39 ppm (s) in the ratio of 18:36:1:2. The IR spectrum is given in Figure 1.

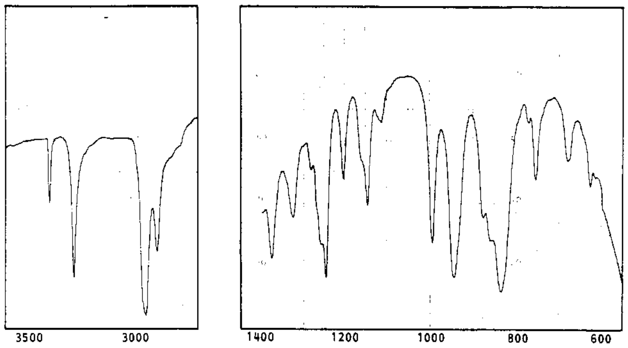


Figure 1. Infrared spectrum of iminobis{[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane} (**2**).

Table II. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $C_{18}H_{57}N_5Si_6B_2$[a]

atom type[b]	fractional coordinates			equiv isotropic thermal param, B, 10 Å^2[c]
	10^4x	10^4y	10^4z	
Si(1)	2049 (1)	782 (1)	1066 (1)	40 (1)
Si(2)	1622 (1)	2632 (1)	1722 (1)	45 (1)
Si(3)	4013 (1)	1325 (1)	3649 (1)	42 (1)
Si(4)	6411 (1)	3488 (1)	1938 (1)	45 (1)
Si(5)	6824 (1)	1639 (1)	1316 (1)	48 (1)
Si(6)	4356 (1)	2903 (1)	−116 (1)	41 (1)
B(1)	3369 (2)	1661 (2)	2128 (1)	31 (1)
B(2)	4843 (2)	2323 (2)	1389 (1)	29 (1)
N(1)	4388 (1)	1947 (1)	1995 (1)	33 (1)
N(2)	2445 (1)	1738 (1)	1568 (1)	32 (1)
N(3)	3236 (1)	1306 (1)	2821 (1)	39 (1)
N(4)	5986 (1)	2504 (1)	1486 (1)	32 (1)
N(5)	4204 (2)	2515 (1)	740 (1)	35 (1)
C(11)	3103 (2)	−69 (2)	1198 (2)	60 (1)
C(12)	1793 (3)	1016 (2)	83 (1)	69 (1)
C(13)	837 (2)	285 (2)	1349 (2)	79 (1)
C(21)	2435 (2)	3638 (2)	1978 (2)	65 (1)
C(22)	718 (2)	2897 (2)	898 (2)	68 (1)
C(23)	819 (2)	2410 (3)	2468 (2)	84 (1)
C(31)	3306 (2)	733 (2)	4318 (1)	67 (1)
C(32)	5276 (2)	748 (2)	3593 (2)	73 (1)
C(33)	4244 (3)	2512 (2)	3923 (2)	75 (1)
C(41)	5374 (2)	4361 (2)	1802 (2)	68 (1)
C(42)	6703 (3)	3333 (3)	2933 (2)	86 (1)
C(43)	7622 (2)	3932 (2)	1614 (2)	70 (1)
C(51)	7586 (2)	1888 (2)	549 (2)	75 (1)
C(52)	7788 (2)	1389 (3)	2120 (2)	89 (1)
C(53)	6063 (2)	602 (2)	1085 (2)	82 (1)
C(61)	5484 (2)	3671 (2)	−127 (2)	65 (1)
C(62)	4528 (3)	1951 (2)	−733 (2)	74 (1)
C(63)	3138 (2)	3517 (2)	−456 (2)	70 (1)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2. [c] This is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor.

X-ray Crystallographic Study. Compounds **2** and **3** crystallize isomorphously in the uniquely determined centrosymmetric monoclinic space group $P2_1/n$ (an alternate setting of $P2_1/c$-C_{2h}^5, No. 14).[10] Crystal data[11] are summarized in Table I. In Figures 2 and 3, molecular structures and numbering schemes are presented. Atomic coordinates for non-hydrogen atoms of **2** and **3** are listed with estimated standard

---

(10) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 99.

(11) See paragraph at end of paper regarding supplementary material.

Table III. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $C_{18}H_{56}N_4OSi_6B_2$[a]

atom type[b]	fractional coordinates 10^4x	10^4y	10^4z	equiv isotropic thermal param, B, 10 Å^2[c]
Si(1)	2031 (1)	835 (1)	1051 (1)	40 (1)
Si(2)	1602 (1)	2709 (1)	1678 (1)	45 (1)
Si(3)	4084 (1)	1427 (1)	3577 (1)	41 (1)
Si(4)	6424 (1)	3472 (1)	1956 (1)	44 (1)
Si(5)	6791 (1)	1615 (1)	1329 (1)	48 (1)
Si(6)	4419 (1)	2926 (1)	−123 (1)	41 (1)
B(1)	3347 (2)	1742 (2)	2087 (1)	31 (1)
B(2)	4826 (2)	2349 (2)	1395 (1)	28 (1)
O(1)	4346 (1)	2018 (1)	1978 (1)	33 (1)
N(2)	2429 (1)	1806 (1)	1534 (1)	32 (1)
N(3)	3231 (2)	1400 (2)	2785 (1)	39 (1)
N(4)	5969 (1)	2497 (1)	1507 (1)	32 (1)
N(5)	4228 (2)	2539 (2)	734 (1)	35 (1)
C(11)	3059 (2)	−36 (2)	1211 (2)	61 (1)
C(12)	1836 (3)	1047 (3)	55 (2)	69 (1)
C(13)	785 (3)	378 (3)	1330 (2)	82 (1)
C(21)	2426 (2)	3711 (2)	1928 (2)	65 (1)
C(22)	717 (2)	2967 (3)	849 (2)	68 (1)
C(23)	782 (3)	2498 (3)	2435 (2)	84 (1)
C(31)	3440 (3)	828 (2)	4290 (2)	64 (1)
C(32)	5328 (2)	865 (3)	3432 (2)	69 (1)
C(33)	4291 (3)	2617 (2)	3850 (2)	72 (1)
C(41)	5385 (2)	4344 (2)	1858 (2)	67 (1)
C(42)	6781 (3)	3306 (3)	2946 (2)	86 (1)
C(43)	7615 (2)	3916 (2)	1584 (2)	65 (1)
C(51)	7544 (3)	1839 (2)	536 (2)	68 (1)
C(52)	7782 (2)	1372 (3)	2115 (2)	83 (1)
C(53)	6006 (3)	579 (2)	1137 (2)	80 (1)
C(61)	5550 (2)	3696 (2)	−117 (2)	62 (1)
C(62)	4613 (3)	1970 (3)	−736 (2)	73 (1)
C(63)	3210 (2)	3546 (3)	−467 (2)	69 (1)

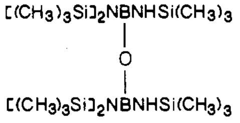
[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 3. [c] This is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor.

deviations in Tables II and III, respectively, whereas bond lengths are compared in Table IV and bond angles in Table V. X-ray diffraction intensity data for unique reflections of both compounds having $2\theta_{\mathrm{Mo}\,K\bar{\alpha}} < 55°$ were collected on a computer-controlled four-circle Nicolet autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation. The 31 non-hydrogen atoms of the asymmetric unit for **2** were located by using (SHELXTL) "direct methods" techniques, and these positions (with N(1) replaced by an oxygen atom) were used as a starting point for least-squares refinement of **3**. Counterweighted[12] cascade block-diagonal least-squares refinement of the structural parameters for the 31 anisotropic non-hydrogen and 57 (**2**) or 56 (**3**) isotropic hydrogen atoms from data with $2\theta_{\mathrm{Mo}\,K\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$ for each compound gave R_1[13] = 0.041 and R_2 = 0.042 for 5093 independent reflections of **2** and R_1 = 0.043 and R_2 = 0.040 for 4458 independent reflections of **3**. The 18 methyl groups of each compound were incorporated into the structural model as rigid rotors with sp^3-hybridized geometry and a C–H bond length of 0.96 Å. The isotropic thermal parameter of each methyl hydrogen was set at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded. The remaining hydrogen atoms were incorporated into the model as individual isotropic atoms.

All structure calculations employed recent tabulations of atomic form factors[14a] and anomalous dispersion corrections[14b] to the scattering factors of the Si atoms. The final refinement cycles employed a least-squares refinable extinction correction.[15] All calculations were performed on a Data General Eclipse S-200 or S-230 computer using the Nicolet EXTL and SHELXTL interactive crystallographic software packages as modified at Crystalytics Company, Lincoln, NE.

Results and Discussion

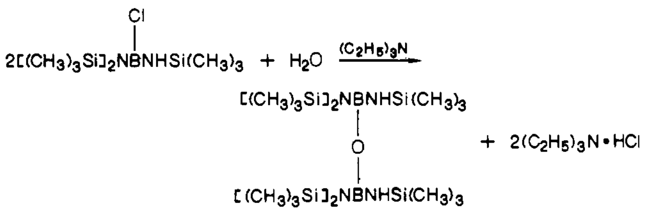
Compound **3** was obtained in 35% yield from [bis(trimethylsilyl)amino][(trimethylsilyl)amino]chloroborane on treatment with a 10–20-fold excess of triethylamine distilled from potassium hydroxide. Apparently, under these conditions, enough moisture is retained in triethylamine to allow the formation of the oxygen-bridged compound:



$$\begin{array}{c}[(CH_3)_3Si]_2NBNHSi(CH_3)_3\\ |\\ O\\ |\\ [(CH_3)_3Si]_2NBNHSi(CH_3)_3\end{array}$$

3

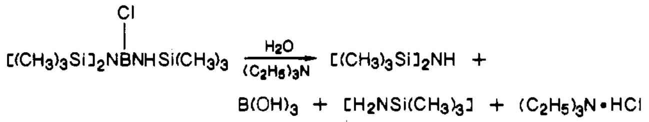
Conducting the reaction in benzene with use of the required quantity of water in the presence of triethylamine gave a 55% yield of triethylamine hydrochloride, but only a 7% yield of the oxygen-bridged product. On the basis of the other products formed, namely $[(CH_3)_3SiNH]_2BN[Si(CH_3)_3]_2$ or its isomer $\{[(CH_3)_3Si]_2N\}_2BNH_2$ (no differentiation could be made from the mass spectral fragmentation pattern), together with hexamethyldisilazane and amino[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane, $[(CH_3)_3Si]_2NB(NH_2)NHSi(CH_3)_3$ (or its isomer, $B[NHSi(CH_3)_3]_3$, it is clear that hydrogen chloride elimination followed by oxygen bridge formation



$$2\begin{array}{c}Cl\\ |\\ [(CH_3)_3Si]_2NBNHSi(CH_3)_3\end{array} + H_2O \xrightarrow{(C_2H_5)_3N} \begin{array}{c}[(CH_3)_3Si]_2NBNHSi(CH_3)_3\\ |\\ O\\ |\\ [(CH_3)_3Si]_2NBNHSi(CH_3)_3\end{array} + 2(C_2H_5)_3N\cdot HCl$$

3

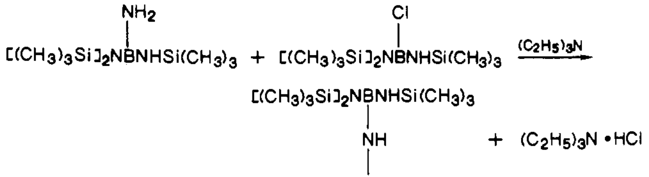
is not the only process occurring. A more extensive hydrolysis of the chloroborane must take place concurrently, i.e.



$$\begin{array}{c}Cl\\ |\\ [(CH_3)_3Si]_2NBNHSi(CH_3)_3\end{array} \xrightarrow[(C_2H_5)_3N]{H_2O} [(CH_3)_3Si]_2NH + B(OH)_3 + [H_2NSi(CH_3)_3] + (C_2H_5)_3N\cdot HCl$$

Inasmuch as (trimethylsilyl)amine is chemically unstable, it will redistribute into ammonia and hexamethyldisilazane. Their interaction with the chloroborane is most likely responsible for the formation of $[(CH_3)_3Si]_2NB(NH_2)NHSi(CH_3)_3$ and $[(CH_3)_3Si]_2NB[NHSi(CH_3)_3]_2$.

The nitrogen-bridged analogue $\{[(CH_3)_3Si]_2NBNHSi(CH_3)_3\}_2NH$ (**2**) was formed in 57% yield from the interaction of [bis(trimethylsilyl)amino][(trimethylsilyl)amino]chloroborane with amino[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane, i.e.



$$\begin{array}{c}NH_2\\ |\\ [(CH_3)_3Si]_2NBNHSi(CH_3)_3\end{array} + \begin{array}{c}Cl\\ |\\ [(CH_3)_3Si]_2NBNHSi(CH_3)_3\end{array} \xrightarrow{(C_2H_5)_3N} \begin{array}{c}[(CH_3)_3Si]_2NBNHSi(CH_3)_3\\ |\\ NH\\ |\\ [(CH_3)_3Si]_2NBNHSi(CH_3)_3\end{array} + (C_2H_5)_3N\cdot HCl$$

2

It exhibited physical and spectral characteristics very similar to those of the oxygen-bridged compound (**3**). This is illustrated by the close melting points (169–171 and 158–160 °C, respectively) and essentially identical IR spectra. The thermal behaviors of **2** and **3** are also similar as shown by DSC traces, where in the oxygen-bridged compound two strong endotherms were observed at 70 and 75 °C and in the nitrogen-bridged material at 85 and

---

(12) For counterweights: $\sigma_F = \{[\sigma(F_o)]^2 + (p|F_o|)^2\}^{1/2}$, where the "ignorance factor", p, has the value of 0.01 in this case.

(13) The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where w is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor.

(14) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–150.

(15) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

(16) Wells, R. L.; Collins, A. L. *Inorg. Chem.* **1966**, *5*, 1327.

Table IV. Comparison of Bond Lengths (Å) in Crystalline $\{[(CH_3)_3Si]_2NBNHSi(CH_3)_3\}_2Z$ for Z = NH (**2**) and Z = O (**3**)[a]

	values			values	
type[b]	**2** [X = N(1)]	**3** [X = O(1)]	type[b]	**2** [X = N(1)]	**3** [X = O(1)]
X-B(1)	1.428 (3)	1.380 (3)	B(1)-N(2)	1.487 (3)	1.483 (3)
X-B(2)	1.446 (3)	1.389 (3)	B(1)-N(3)	1.423 (3)	1.412 (4)
			B(2)-N(4)	1.485 (3)	1.476 (3)
Si(1)-N(1)	1.739 (2)	1.744 (2)	B(2)-N(5)	1.405 (3)	1.406 (3)
Si(2)-N(2)	1.743 (2)	1.746 (2)			
Si(3)-N(3)	1.732 (2)	1.739 (2)	Si(4)-N(4)	1.739 (2)	1.739 (2)
			Si(5)-N(4)	1.732 (2)	1.733 (2)
Si(1)-C(11)	1.848 (3)	1.847 (3)	Si(6)-N(5)	1.730 (2)	1.732 (2)
Si(1)-C(12)	1.853 (3)	1.865 (3)			
Si(1)-C(13)	1.859 (3)	1.858 (4)	Si(4)-C(41)	1.855 (3)	1.852 (3)
Si(2)-C(21)	1.850 (3)	1.854 (3)	Si(4)-C(42)	1.860 (3)	1.863 (3)
Si(2)-C(22)	1.851 (3)	1.853 (3)	Si(4)-C(43)	1.860 (3)	1.861 (3)
Si(2)-C(23)	1.861 (4)	1.867 (4)	Si(5)-C(51)	1.866 (4)	1.872 (4)
Si(3)-C(31)	1.851 (3)	1.857 (3)	Si(5)-C(52)	1.862 (3)	1.868 (4)
Si(3)-C(32)	1.852 (3)	1.844 (3)	Si(5)-C(53)	1.845 (3)	1.850 (3)
Si(3)-C(33)	1.848 (3)	1.847 (3)	Si(6)-C(61)	1.848 (3)	1.845 (3)
			Si(6)-C(62)	1.850 (3)	1.851 (4)
X-H(1)	0.77 (2)	...	Si(6)-C(63)	1.856 (3)	1.857 (3)
N(3)-H(3)	0.71 (2)	0.74 (2)			
N(5)-H(5)	0.71 (2)	0.78 (2)			

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figures 2 and 3.

Table V. Comparison of Bond Angles (deg) in Crystalline $\{[(CH_3)_3Si]_2NBNHSi(CH_3)_3\}_2Z$ for Z = NH (**2**) and Z = O (**3**)[a]

	values			values	
type[b]	**2** [X = N(1)]	**3** [X = O(1)]	type[b]	**2** [X = N(1)]	**3** [X = O(1)]
B(1)-X-B(2)	135.9 (2)	135.5 (2)	B(1)-X-H(1)	112 (2)	...
			B(2)-X-H(1)	112 (2)	...
Si(1)-N(2)-Si(2)	124.4 (1)	124.1 (1)			
Si(1)-N(2)-B(1)	118.1 (1)	118.2 (2)	Si(3)-N(3)-H(3)	114 (1)	114 (2)
Si(2)-N(2)-B(1)	113.1 (1)	113.3 (2)	B(1)-N(3)-H(3)	113 (1)	115 (2)
Si(3)-N(3)-B(1)	132.9 (1)	130.5 (2)			
Si(4)-N(4)-Si(5)	123.0 (1)	122.6 (1)	Si(6)-N(5)-H(5)	109 (2)	110 (1)
Si(4)-N(4)-B(2)	117.3 (1)	118.0 (2)	B(2)-N(5)-H(5)	113 (2)	112 (1)
Si(5)-N(4)-B(2)	118.4 (1)	118.5 (2)			
Si(6)-N(5)-B(2)	137.8 (2)	138.7 (2)			
X-B(1)-N(2)	121.9 (2)	124.1 (2)	X-B(2)-N(4)	117.8 (2)	117.2 (2)
X-B(1)-N(3)	118.8 (2)	115.5 (2)	X-B(2)-N(5)	119.9 (2)	120.3 (2)
N(2)-B(1)-N(3)	119.3 (2)	120.4 (2)	N(4)-B(2)-N(5)	122.3 (2)	122.5 (2)
N(2)-Si(1)-C(11)	108.9 (1)	109.1 (1)	N(4)-Si(4)-C(41)	109.9 (1)	109.3 (1)
N(2)-Si(1)-C(12)	112.6 (1)	111.8 (1)	N(4)-Si(4)-C(42)	113.1 (1)	113.4 (2)
N(2)-Si(1)-C(13)	111.8 (1)	111.8 (1)	N(4)-Si(4)-C(43)	111.5 (1)	111.3 (1)
C(11)-Si(1)-C(12)	107.3 (1)	107.3 (2)	C(41)-Si(4)-C(42)	106.0 (2)	106.8 (2)
C(11)-Si(1)-C(13)	108.7 (1)	108.7 (2)	C(41)-Si(4)-C(43)	109.1 (1)	109.1 (2)
C(12)-Si(1)-C(13)	107.5 (1)	107.9 (2)	C(42)-Si(4)-C(43)	107.0 (2)	106.7 (2)
N(2)-Si(2)-C(21)	108.6 (1)	108.2 (1)	N(4)-Si(5)-C(51)	113.1 (1)	113.0 (1)
N(2)-Si(2)-C(22)	111.0 (1)	111.1 (1)	N(4)-Si(5)-C(52)	111.6 (1)	112.0 (1)
N(2)-Si(2)-C(23)	113.1 (1)	112.7 (2)	N(4)-Si(5)-C(53)	109.6 (1)	109.4 (1)
C(21)-Si(2)-C(22)	108.7 (1)	109.0 (2)	C(51)-Si(5)-C(52)	107.1 (1)	106.5 (2)
C(21)-Si(2)-C(23)	107.4 (2)	107.3 (2)	C(51)-Si(5)-C(53)	107.5 (2)	108.1 (2)
C(22)-Si(2)-C(23)	107.8 (1)	108.4 (1)	C(52)-Si(5)-C(53)	107.7 (2)	107.7 (2)
N(3)-Si(3)-C(31)	108.3 (1)	107.7 (1)	N(5)-Si(6)-C(61)	113.2 (1)	112.7 (1)
N(3)-Si(3)-C(32)	110.9 (1)	110.1 (1)	N(5)-Si(6)-C(62)	110.8 (1)	110.6 (1)
N(3)-Si(3)-C(33)	108.5 (1)	108.3 (1)	N(5)-Si(6)-C(63)	106.9 (1)	106.7 (1)
C(31)-Si(3)-C(32)	109.1 (1)	110.1 (2)	C(61)-Si(6)-C(62)	108.0 (1)	108.7 (2)
C(31)-Si(3)-C(33)	110.0 (1)	108.9 (2)	C(61)-Si(6)-C(63)	109.0 (1)	108.9 (2)
C(32)-Si(3)-C(33)	110.1 (2)	111.7 (2)	C(62)-Si(6)-C(63)	108.9 (1)	109.2 (2)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figures 2 and 3.

105 °C. No phase transition responsible for these endotherms could be visually observed on heating. These endotherms were of higher intensities than those caused by melting. Both materials, on remelting in air, exhibited the same melting point, attesting to their thermal, oxidative, and hydrolytic stabilities.

Mass Spectral Data. The mass spectral breakdown patterns were also very similar for the two compounds, with the exception that the peaks were one mass unit higher in the case of the oxygen-bridged material, as evident from the compilations given in Table VI. The processes responsible for the production of several of the major fragments could be identified from the metastables. In the case of iminobis{[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane} these are

$$533^+ \text{ (M)} \rightarrow 518^+ + 15\ [CH_3] \quad m^*\ 503.4$$

$$518^+ \rightarrow 429^+ + 89\ [H_2NSi(CH_3)_3] \quad m^*\ 355.3$$

$$429^+ \rightarrow 341^+ + 88\ [HNSi(CH_3)_3] \quad m^*\ 271.0$$

$$429^+ \rightarrow 316^+ + 113\ [BNHNSi(CH_3)_3] \quad m^*\ 232.8$$

In view of the absence of the additional proton, the equivalent of the 341^+ ion, namely the 342^+ ion, would not be expected to

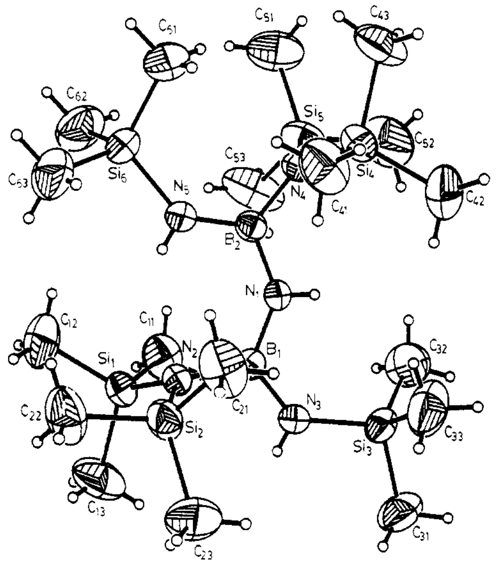


Figure 2. Perspective drawing of $C_{18}H_{57}N_5Si_6B_2$ (**2**) with non-hydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity.

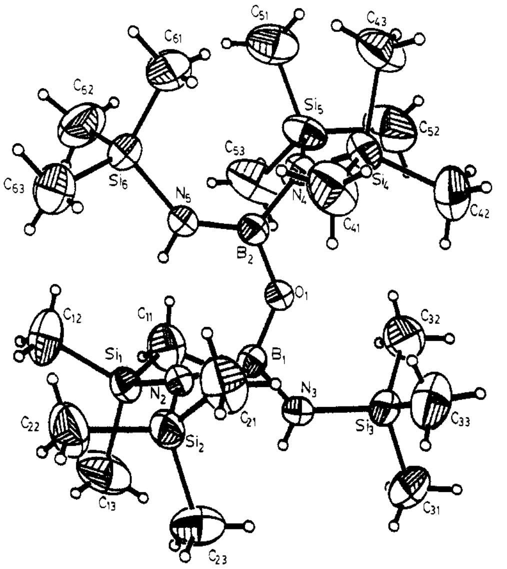


Figure 3. Perspective drawing $C_{18}H_{56}N_4OSi_6B_2$ (**3**) with non-hydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity.

be formed to any significant extent in the case of the oxygen-bridged compound. The fragmentation pattern confirms it, and no metastable for this process was found. In the oxygen-bridged compound, metastables were observed at *m/e* 504.5, 357.5, 213, and 82.5. The processes responsible have been identified as

$$534^+ \rightarrow 519^+ + 15\ [CH_3] \quad m^*\ 504.4$$

$$519^+ \rightarrow 430^+ + 89\ [H_2NSi(CH_3)_3] \quad m^*\ 356.3$$

$$519^+ \rightarrow 332^+ + 187\ [B(NHSi(CH_3)_3)_2] \quad m^*\ 212.4$$

Crystal Structures. The structure of **2** (Figure 2) confirms the presence of a central, essentially planar, N_2BNBN_2 skeleton with a B(1)–N(1)–B(2) angle of 135.9 (2)°. The B(1)–O–B(2) angle in **3** (Figure 3) is 135.5 (2)°. The B–N bond distances in **2** range from 1.405 (3) to 1.487 (3) Å; the shortest bonds are to nitrogens bonded to one silicon, whereas the longest are to nitrogens bonded to two silicons. The central B–N bonds are of intermediate length due to mutual competition of B(1) and B(2) for π-electron density on N(1). The shortest B–N distance for **2** (1.405 (3) Å) is not as short as the shortest distance (1.394 (3) Å) for the recently reported 1,3,5,7-tetra-*tert*-butyl-2,4,6,8-tetramethyl-1,3,5,7,2,4,6,8-tetrazatetraborocine,[17] while the longest B–N distance for **2** (1.487 (3) Å) is not as long as the longest distance reported for the above compound (1.518 (4) Å).

Table VI. Mass Spectral Breakdown Patterns of Iminobis{[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane} (**2**) and Oxybis{[bis(trimethylsilyl)amino][(trimethylsilyl)amino]borane} (**3**)[a]

	% intens			% intens			% intens	
m/e	**2**	**3**	*m/e*	**2**	**3**	*m/e*	**2**	**3**
73	43.2	47.8	244	27.5	14.5	355	11.8	
74	22.2	13.6	245	13.9	14.7	356	20.9	
98	22.1	13.1	252	20.4		357	33.1	
130	46.5	34.4	258	40.1	38.4	358	16.7	
131	19.0	10.8	259	68.6	100.0	359	10.5	
132	12.9		260	49.9	52.2	413	13.4	
146	57.5		261	27.7	42.5	414	10.1	
147	19.8	16.8	262	11.7	14.8	427	14.9	
148	11.1		268	16.2		428	53.9	
155	12.5		269	20.9		429	100.0	15.3
170	12.6		275	14.1		430	57.7	29.3
171	30.2	17.3	284	10.6		431	44.9	17.3
172	11.8		300	19.1		432	20.4	11.6
186	10.3		301	15.1		433	10.0	
187	21.1	13.9	316	14.4		505	15.0	
188	10.7		324	10.0		517	27.1	
202	12.5		325	16.3		518	50.4	16.3
203	29.8	12.4	326	11.3		519	30.4	31.0
204	13.7		331		13.9	520	19.4	21.4
207	23.2		332		38.9	521	10.1	14.1
227	12.5		333		20.3	532	21.7	
228	18.3		334		11.8	533	42.9	15.3
229	13.2		340	14.3		534	25.4	29.4
242	13.1		341	23.8		535	15.9	20.3
243	39.4	24.0	342	14.5		536		12.7

[a] Peaks having intensities lower than 10% of the base peak and lower than *m/e* 73 are not reported.

Since **2** and **3** crystallize isomorphously, the two molecules should experience nearly identical packing forces in the solid state. This permits us to assess the electronic and/or structural effects of replacing the NH group in **2** by oxygen in **3**. The only significant differences in bond lengths or bond angles between the two compounds involve the bridging group or an atom directly bonded to it. There is, however, a trend toward slightly shorter B–N distances for **2** than for **3**.

Acknowledgment. Support of this research from the Strategic Defense Sciences Office through Contract N00014-85-C-0659 from the Office of Naval Research is gratefully acknowledged.

Registry No. **1**, 10078-93-0; **2**, 113678-60-7; **3**, 113678-61-8; $[(CH_3)_3Si]_2NB(NH_2)NHSi(CH_3)_3$, 7266-80-0; $[(CH_3)_3Si]_2NB(NH_2)N[Si(CH_3)_3]_2$, 114862-57-6; hexamethyldisilazane, 999-97-3; ammonia, 7664-41-7.

Supplementary Material Available: Tables SI–SV, listing anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates for hydrogen atoms, and least-squares planes (12 pages); structure factor tables (42 pages). Ordering information is given on any current masthead page.

---

[17] Franz, T.; Hanecker, D.; Nöth, H.; Stocker, W.; Storch, W.; Winter, G. *Chem. Ber.* **1986**, *119*, 900.