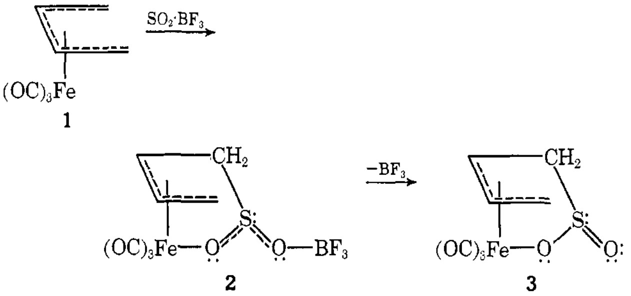
carbonyl has been the subject of electrophilic attack (either by SO_2 itself or by the $SO_2 \cdot BF_3$ adduct, which is stable below ambient temperatures[45]). The product is probably best considered as an intermediate (2) in the hypothetical Friedel–Crafts sulfination reaction **1** → **3**. [It should be emphasized that complexes of type **3** have yet to be reported. However, a complex of type **2** containing the Lewis acid SbF_5, rather than BF_3, has been prepared by Kaesz and coworkers.[18]]



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An Electron Diffraction Study of the Molecular Structure of Tetrakis(trimethylsilyl)silane[1]

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Gas-phase $Si[Si(CH_3)_3]_4$ possesses Si–Si and Si–C bond lengths of 2.361 ± 0.003 and 1.889 ± 0.003 Å, including estimated standard errors, respectively, and Si–Si–C and Si–C–H angles of 110.9 ± 0.6 and 109.3 ± 1.7°. The $(CH_3)_3Si$ groups appear to undergo cooperative torsional displacements of about 14° from T_d symmetry in order to relieve nonbonded interactions between methyl groups.

Introduction

The first successful preparation of tetrakis(trimethylsilyl)silane, $Si[Si(CH_3)_3]_4$, was reported in 1964 by Gilman and Smith.[3] Quite stable and unreactive, the yellow solid melts at 261–263°. The proton nmr exhibits a sharp singlet at τ 9.79, indicating that all protons are equivalent. Tetrakis(trimethylsilyl)silane presented a favorable opportunity to extend studies of the influence of nonbonded repulsions on molecular structure[4] to an analog of tetrakis(*t*-butyl)methane.

Experimental Section

The electron diffraction apparatus employed has been described elsewhere.[5] Except for the special heated nozzle assembly necessitated by the relatively nonvolatile sample, diffraction patterns were recorded and measured by the usual techniques.[6] Least-squares structure refinements upon the experimental leveled intensity were based on the elastic scattering factors of Cox and Bonham[7] and the inelastic scattering factors of Tavard[8] and did not differ significantly from procedures described elsewhere.[9] Comparison between experimental and theoretical points was carried out utilizing a weighting function proportional to the scattering variable for the composite reduced molecular intensity curve, $M(s)$. Asymmetry constants a were estimated[10] to be 2.5 $Å^{-1}$ for C–H distances and 2.0 $Å^{-1}$ for Si–Si and Si–C distances and were taken to be 1.0 $Å^{-1}$ for all nonbonded distances. No correction was made for shrinkage effects.[11]

Results

Figure 1 shows the molecular intensity curve determined for $Si[Si(CH_3)_3]_4$ by blending together data from the individual camera distances. The index of resolution was 0.95 for each of the three experimental camera ranges. Fourier inversion of the molecular intensity produced the radial distribution function illustrated in Figure 2. The results of our structural refinement are summarized in Table I. Experimental data were analyzed by least-squares fittings of the molecular intensity, and a representation of the error matrix determined during the final runs is reproduced in Table II. Listings of the experimental leveled intensity and the background used in data analysis at regular intervals of the scattering variable are given in Table III. Table

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(1) This work was supported by a grant from the National Science Foundation.

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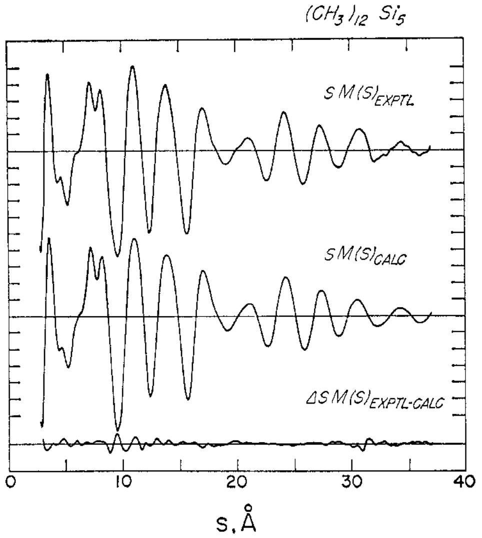

Figure 1.—Molecular intensity curves determined for Si[Si(CH$_3$)$_3$]$_4$.

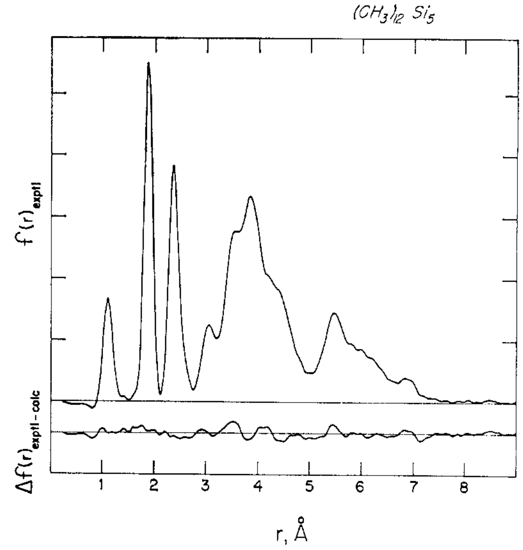

Figure 2.—Experimental radial distribution curve determined for Si[Si(CH$_3$)$_3$]$_4$.

IV compares parameters determined in this investigation with parameters for related molecules.

Discussion

The Si–Si and Si–C distances in Si[Si(CH$_3$)$_3$]$_4$ are nearly the same as the corresponding distances in elemental silicon[12] and in silicon carbide,[13] respectively. The C–Si–C bond angle determined is slightly less (~1.6°) than the tetrahedral angle, in accordance with simple Gillespie–Nyholm considerations.

Two somewhat approximate assessments, one experimental and one theoretical, were made of the possible consequences of intermethyl repulsions in the molecule. In the first, least-squares analyses of the experimental intensities were run at various fixed torsional displacements from T_d symmetry. These displacements moved all corresponding groups equally, preserving T symmetry. For sake of calculation, angular displacements about the Si–C bonds were taken to be equal to the displacements about the Si–Si bonds and were in a sense to augment the interhydrogen avoidance. This constraint for the Si–C rotations to follow the Si–Si rotations surely imposes far too great a methyl twist, as we shall see, but has only a secondary influence on the diffraction analyses. The methyl twists in-

TABLE I

PARAMETERS FOR (CH$_3$)$_{12}$Si$_5$[a]

Parameter	r_g, Å	l_g, Å	Angle, deg
Si–Si	2.361 ± 0.003	0.065 ± 0.003	
Si–C	1.889 ± 0.003	0.055 ± 0.003	
C–H	1.117 ± 0.004	0.071 ± 0.004	
∠Si–Si–C			110.9 ± 0.6
∠Si–C–H			109.3 ± 1.7
(CH$_3$)$_3$Si torsion[b]			11 ± 3.6
Si···Si[c]	3.855	0.135 ± 0.015	
C···C(1,3)[c]	3.054	0.116 ± 0.018	

[a] Uncertainties are estimated standard errors including the effects of known systematic errors. See L. S. Bartell in "Physical Methods in Chemistry," A. Weissberger and B. W. Rossiter, Ed., 4th ed, Interscience, New York, N. Y., in press. [b] See text for meaning. [c] Distance which is a dependent parameter.

TABLE II

ERROR MATRIX FOR (CH$_3$)$_{12}$Si$_5$[a]

	r(Si–Si)	r(Si–C)	r(C–H)	∠Si–Si–C	∠Si–C–H	Rotn[b]	l(Si–Si)	l(Si–C)	l(C–H)	l(Si···Si)	l(C···C)[c]	R
r(Si–Si)	5.7	−0.5	−1.1	−4.8	−5.4	−2.5	0.8	−1.0	−1.3	3.3	3.5	−4.6
r(Si–C)		3.1	−1.1	−2.2	−4.6	3.5	−1.8	−1.3	−2.4	−2.3	−1.9	−8.7
r(C–H)			4.7	1.8	−4.0	−4.1	0.9	1.2	0.4	0.5	1.9	4.4
∠Si–Si–C				6.2	5.4	3.3	2.0	2.0	2.9	−3.7	4.7	10.0
∠Si–C–H					18.9	−8.5	−2.9	3.2	5.5	7.1	−5.1	19.2
Rotn[b]						42.3	−4.9	−4.7	−6.6	−23.8	−14.0	−22.7
l(Si–Si)							3.9	1.6	2.2	1.8	3.0	7.7
l(Si–C)								2.5	2.2	2.1	1.9	7.5
l(C–H)									6.1	3.1	2.7	11.1
l(Si···Si)										18.8	9.3	11.0
l(C···C)[c]											20.0	9.4
R												38.8

[a] Values are ×10^3. Based on 110 intensity values interpolated from 297 data points. Units for the distances and amplitudes are ångströms; those for the angles are radians; the index of resolution R is dimensionless. Matrix elements are given by $\sigma_{ij} = \mathrm{sign}[B_{ij}^{-1}] \cdot \{|B_{ij}^{-1}|\mathbf{v}'\mathbf{w}\mathbf{v}/(n - m)\}^{1/2}$, where the notation corresponds to that of O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957). Since the elements are based on a diagonal (nonoptimum) weight matrix, they do not represent *bona fide* standard errors. [b] Rotation of the (CH$_3$)$_3$Si groups from tetrahedral symmetry. See text. [c] l(C···C) for (CH$_3$)$_3$Si group.

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TABLE III

EXPERIMENTAL LEVELED INTENSITY AND BACKGROUND DATA USED FOR $Si[Si(CH_3)_3]_4$[a]

s	$I_o(s)$	B(s)	s	$I_o(S)$	B(S)	s	$I_o(S)$	B(S)
2.862	0.6556	0.9210	6.091	1.0181	1.0184	9.307	1.0848	1.1632
2.986	0.7107	0.9332	6.215	1.0195	1.0192	9.431	1.0876	1.1714
3.111	0.8113	0.9440	6.339	1.0258	1.0208	9.554	1.0931	1.1799
3.235	0.9318	0.9536	6.463	1.0331	1.0235	9.677	1.1035	1.1887
3.359	1.0477	0.9622	6.587	1.0429	1.0266	9.800	1.1192	1.1977
3.484	1.1286	0.9697	6.711	1.0557	1.0302	9.924	1.1384	1.2071
3.608	1.1644	0.9763	6.835	1.0727	1.0342	10.047	1.1624	1.2167
3.732	1.1487	0.9821	6.959	1.0944	1.0387	10.170	1.1908	1.2267
3.857	1.0993	0.9872	7.082	1.1155	1.0436	10.293	1.2227	1.2369
3.981	1.0388	0.9918	7.206	1.1311	1.0489	10.416	1.2541	1.2475
4.105	0.9851	0.9961	7.330	1.1377	1.0545	10.539	1.2835	
4.229	0.9523	0.9998	7.454	1.1370	1.0605	10.662	1.3092	
4.354	0.9417	1.0031	7.578	1.1293	1.0666	10.785	1.3331	
4.478	0.9488	1.0060	7.701	1.1229	1.0730	10.908	1.3515	
4.602	0.9601	1.0084	7.825	1.1231	1.0795	11.031	1.3651	
4.726	0.9649	1.0105	7.949	1.1304	1.0858	11.154	1.3774	
4.850	0.9596	1.0124	8.072	1.1461	1.0922	11.277	1.3862	
4.974	0.9457	1.0140	8.196	1.1587	1.0987	11.400	1.3920	
5.099	0.9319	1.0153	8.319	1.1655	1.1053	11.523	1.3951	
5.223	0.9248	1.0163	8.443	1.1635	1.1120	11.645	1.3955	
5.347	0.9329	1.0172	8.567	1.1506	1.1189	11.768	1.3940	
5.471	0.9489	1.0179	8.690	1.1329	1.1259	11.891	1.3900	
5.595	0.9719	1.0180	8.814	1.1132	1.1330	12.013	1.3860	
5.719	0.9922	1.0179	8.937	1.0989	1.1402	12.136	1.3832	
5.843	1.0063	1.0179	9.060	1.0899	1.1477	12.259	1.3841	
5.967	1.0153	1.0180	9.184	1.0849	1.1553	12.381	1.3947	

s	$I_o(S)$	B(S)	s	$I_o(S)$	B(S)	s	$I_o(S)$	B(S)
4.354	3.3865		9.800	3.4083	3.7433	15.188	3.7579	3.8486
4.478	3.4090	3.6634	9.924	3.4583	3.7437	15.309	3.7313	3.8517
4.602	3.5055	3.6693	10.047	3.5274	3.7442	15.431	3.7056	3.8548
4.725	3.5242	3.6749	10.170	3.6067	3.7448	15.552	3.6895	3.8579
4.850	3.5138	3.6801	10.293	3.6990	3.7455	15.674	3.6852	3.8609
4.974	3.4537	3.6849	10.416	3.7841	3.7464	15.795	3.6950	3.8539
5.099	3.3745	3.6895	10.539	3.8605	3.7474	15.916	3.7149	3.8669
5.223	3.3516	3.6936	10.662	3.9198	3.7485	16.037	3.7456	3.8698
5.347	3.3848	3.6978	10.785	3.9545	3.7497	16.159	3.7825	3.8727
5.471	3.4298	3.7016	10.908	3.9888	3.7511	16.280	3.8195	3.8756
5.595	3.5170	3.7052	11.031	4.0002	3.7525	16.401	3.8582	3.8786
5.719	3.5906	3.7087	11.154	3.9986	3.7541	16.522	3.8957	3.8815
5.843	3.6415	3.7119	11.277	3.9844	3.7558	16.643	3.9226	3.8844
5.967	3.6582	3.7149	11.400	3.9567	3.7577	16.764	3.9463	3.8874
6.091	3.6774	3.7178	11.523	3.9171	3.7596	16.884	3.9620	3.8904
6.215	3.6912	3.7204	11.645	3.8460	3.7617	17.005	3.9728	3.8934
6.339	3.6652	3.7229	11.768	3.8085	3.7639	17.126	3.9792	3.8964
6.463	3.5988	3.7252	11.891	3.7423	3.7664	17.247	3.9809	3.8995
6.587	3.7509	3.7273	12.013	3.6739	3.7691	17.367	3.9790	3.9026
6.711	3.7835	3.7293	12.136	3.6148	3.7719	17.488	3.9740	3.9057
6.835	3.8488	3.7311	12.259	3.5728	3.7746	17.609	3.9655	3.9089
6.959	3.9285	3.7328	12.381	3.5606	3.7772	17.729	3.9584	3.9121
7.082	3.9593	3.7343	12.504	3.5734	3.7798	17.850	3.9506	3.9153
7.206	4.0465	3.7356	12.626	3.6078	3.7816	17.970	3.9411	3.9185
7.330	4.0548	3.7369	12.748	3.6604	3.7828	18.090	3.9365	3.9217
7.454	4.0222	3.7380	12.871	3.7140	3.7840	18.211	3.9315	3.9250
7.578	3.9653	3.7389	12.993	3.7674	3.7853	18.331	3.9290	
7.701	3.9264	3.7398	13.115	3.8124	3.7867	18.451	3.9317	
7.825	3.9194	3.7405	13.238	3.8493	3.7885	18.571	3.9262	
7.949	3.9250	3.7410	13.360	3.8809	3.7908	18.691	3.9265	
8.072	3.9675	3.7413	13.482	3.9083	3.7950	18.811	3.9255	
8.196	3.9980	3.7416	13.604	3.9323	3.7996	18.931	3.9223	
8.319	4.0012	3.7418	13.726	3.9488	3.8044	19.051	3.9256	
8.443	3.9565	3.7419	13.848	3.9647	3.8094	19.171	3.9328	
8.567	3.8711	3.7420	13.970	3.9704	3.8145	19.291	3.9361	
8.690	3.7351	3.7420	14.092	3.9682	3.8194	19.410	3.9425	
8.814	3.6597	3.7421	14.214	3.9602	3.8235	19.530	3.9519	
8.937	3.5693	3.7421	14.336	3.9482	3.8270	19.650	3.9585	
9.060	3.4962	3.7422	14.458	3.9256	3.8303	19.769	3.9670	
9.184	3.4519	3.7423	14.580	3.9086	3.8334	19.889	3.9730	
8.307	3.4178	3.7424	14.701	3.8813	3.8365	20.008	3.9774	
9.431	3.3949	3.7425	14.823	3.8550	3.8394	20.127	3.9857	
9.554	3.3841	3.7427	14.945	3.8215	3.8424	20.247	3.9941	
9.677	3.3892	3.7430	15.066	3.7920	3.8455	20.366	4.0051	

s	$I_o(S)$	B(S)	s	$I_o(S)$	B(S)	s	$I_o(S)$	B(S)
6.971	4.4081		18.178	4.2249	4.2147	28.929	4.2789	4.3018
7.203	4.5130		18.403	4.2111	4.2144	29.142	4.2815	4.3059
7.434	4.4715		18.628	4.2010	4.2142	29.355	4.2927	4.3101
7.666	4.4302		18.852	4.1915	4.2140	29.568	4.3040	4.3143
7.897	4.4024		19.077	4.1875	4.2140	29.780	4.3174	4.3187
8.128	4.4678		19.301	4.1881	4.2141	29.992	4.3304	4.3230
8.359	4.4410		19.524	4.1970	4.2143	30.203	4.3379	4.3273
8.590	4.2934		19.748	4.2066	4.2146	30.415	4.3511	4.3317
8.821	4.1289		19.971	4.2146	4.2150	30.625	4.3499	4.3361
9.052	3.9606		20.195	4.2208	4.2154	30.835	4.3526	4.3406
9.283	3.8752		20.418	4.2242	4.2160	31.047	4.3529	4.3451
9.513	3.8351		20.640	4.2324	4.2167	31.257	4.3482	4.3496
9.744	3.8356		20.863	4.2356	4.2175	31.467	4.3727	4.3541
9.974	3.9263		21.085	4.2421	4.2184	31.676	4.3555	4.3586
10.205	4.1073		21.307	4.2404	4.2194	31.885	4.3532	4.3631
10.435	4.2746		21.529	4.2349	4.2205	32.094	4.3547	4.3676
10.665	4.4093	4.2483	21.751	4.2249	4.2216	32.303	4.3608	4.3721
10.895	4.4817	4.2395	21.972	4.2151	4.2229	32.511	4.3652	4.3767
11.125	4.4949	4.2328	22.194	4.1985	4.2242	32.719	4.3733	4.3812
11.355	4.4516	4.2279	22.415	4.1870	4.2255	32.927	4.3814	4.3857
11.584	4.3666	4.2240	22.635	4.1787	4.2270	33.135	4.3843	4.3901
11.814	4.2296	4.2210	22.856	4.1821	4.2285	33.342	4.3891	4.3944
12.043	4.0537	4.2188	23.076	4.1947	4.2301	33.549	4.3991	4.3987
12.272	3.9904	4.2172	23.296	4.2140	4.2318	33.755	4.4041	4.4031
12.501	4.0042	4.2162	23.516	4.2365	4.2336	33.961	4.4110	4.4075
12.730	4.0740	4.2155	23.736	4.2612	4.2356	34.167	4.4168	4.4121
12.959	4.1824	4.2151	23.955	4.2804	4.2377	34.373	4.4265	4.4167
13.188	4.2700	4.2151	24.174	4.2958	4.2398	34.578	4.4309	4.4215
13.416	4.3297	4.2153	24.393	4.2992	4.2420	34.783	4.4315	4.4265
13.645	4.3683	4.2158	24.612	4.2916	4.2443	34.987	4.4380	4.4317
13.873	4.3847	4.2163	24.830	4.2760	4.2457	35.192	4.4407	4.4370
14.101	4.3779	4.2169	25.048	4.2595	4.2491	35.396	4.4437	4.4425
14.329	4.3453	4.2171	25.266	4.2401	4.2514	35.599	4.4430	4.4482
14.557	4.2908	4.2171	25.484	4.2247	4.2538	35.803	4.4507	4.4541
14.784	4.2373	4.2171	25.701	4.2115	4.2562	36.008	4.4539	4.4602
15.012	4.1617	4.2171	25.918	4.2105	4.2586	36.208	4.4597	4.4666
15.239	4.0979	4.2171	26.135	4.2187	4.2611	35.411	4.4694	4.4733
15.465	4.0393	4.2171	26.351	4.2322	4.2637	36.613	4.4781	4.4803
15.693	4.0243	4.2170	26.568	4.2517	4.2663	36.814	4.4856	4.4874
15.920	4.0528	4.2169	26.784	4.2731	4.2690	37.015	4.4990	4.4947
16.147	4.1180	4.2168	27.000	4.2909	4.2717	37.217	4.5067	
16.373	4.1940	4.2167	27.215	4.3049	4.2745	37.418	4.5202	
16.600	4.2557	4.2166	27.430	4.3132	4.2774	37.618	4.5314	
16.826	4.2923	4.2164	27.645	4.3089	4.2805	37.818	4.5439	
17.052	4.3040	4.2162	27.860	4.3046	4.2836	38.018	4.5481	
17.277	4.3049	4.2160	28.074	4.3002	4.2868	38.217	4.5546	
17.503	4.2842	4.2157	28.289	4.2899	4.2902	38.415	4.5539	
17.728	4.2599	4.2153	28.502	4.2795	4.2940	38.515	4.5575	
17.953	4.2368	4.2150	28.716	4.2800	4.2978	38.813	4.5751	

[a] R^2, 21-cm camera data (above); R^3, 21-cm camera data (center); R^3, 11-cm camera data (bottom). The function $M(s)$ is given by $[(I_0/B) - 1]$.

TABLE IV

STRUCTURAL PARAMETERS FOR SILICON DERIVATIVES

Distance, Å, or angle, deg	$Si[Si(CH_3)_3]_4$[a]	Si[b]	SiC[c]	$Si(CH_3)_4$[d]	Si_2H_6[e]
Si–Si	2.361 ± 0.003	2.352	...	...	2.32 ± 0.03
Si–C	1.889 ± 0.003	...	1.885	1.888 ± 0.02	...
C–H	1.117 ± 0.004	...	...	1.10 ± 0.05	...
∠C–Si–C	107.9 ± 0.5	...	...	109.5	...
∠Si–C–H	109.3 ± 1.7	...	...	110 ± 3	...

[a] This work. [b] M. E. Straumanis and E. Z. Aka, *J. Appl. Phys.*, **23**, 330 (1952). [c] N. W. Thibault, *Amer. Mineral.*, **29**, 249, 327 (1944); L. S. Ramsdell, *ibid.*, **29**, 431 (1944); **30**, 519 (1945). [d] W. F. Sheehan, Jr., and V. Schomaker, *J. Amer. Chem. Soc.*, **74**, 3956 (1952). [e] L. O. Brockway and J. Y. Beach, *ibid.*, **60**, 1836 (1938); G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1107 (1957).

volve only interactions with the weakly scattering hydrogens, whereas the $Si–Si(CH_3)_3$ twists involve carbon displacements. All important molecular parameters were allowed to vary. The results of the least-squares analyses are shown in Figure 3 where the mean value of

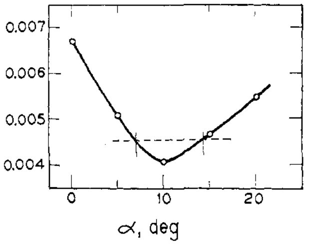

Figure 3.—Minima achieved in least-squares cycling as a function of the distortion of $Si[Si(CH_3)_3]_4$ from T_d symmetry.

α [over the skewed minimum between the $\pm\sigma(\alpha)$ limits] indicates a twist of 11° of the trimethylsilyl groups away from a reference T_d structure. A smaller imposed methyl twist would probably have increased this value slightly.

A simplified molecular mechanics model was investigated which incorporated only Si–Si and Si–C torsions (denoted as α and β, respectively) and the closest intermethyl nonbonded H · · · H interactions (set A including 12 interactions at a distance R). If the torsional potential energy for 4 Si–Si and 12 Si–C bonds is assumed to be

$$V_t(\alpha, \beta) = 4V_\alpha^0 \sin^2(3\alpha/2) + 12V_\beta^0 \sin^2(3\beta/2) \approx 9V_\alpha^0\alpha^2 + 27V_\beta^0\beta^2 \qquad (1)$$

and if $V_H(R)$ is the potential energy associated with a nonbonded pair of hydrogens, it can be shown for this model that, at static equilibrium

$$\alpha/\beta = (3V_\beta^0/V_\alpha^0)(\partial R/\partial\alpha)/(\partial R/\partial\beta) \qquad (2)$$

and

$$\partial V_t/\partial\alpha = -12(\partial V_H/\partial R)(\partial R/\partial\beta) \qquad (3)$$

If the approximate barrier values $V_\alpha^0 \approx 1$ kcal/mol[14] and $V_\beta^0 \approx 2.3$ kcal/mol[15] are inserted into eq 2 in the

[14] A. P. Cox and R. Varma, *J. Chem. Phys.*, **44**, 2619 (1966).

[15] J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).

vicinity of $\alpha \approx 10°$, a ratio of $\alpha/\beta \approx 25$ is obtained, implying that the methyl twist, β, must be small. If the crude $V_H(R)$ function of Bartell[4] is inserted into eq 3, the equation is satisfied for $\alpha \approx 18°$.

If the next most important H···H interactions (set B with six H···H pairs) are introduced into the calculation, the angle α is reduced to 16° at equilibrium, at which point the hydrogens of set A are 2.6 Å apart (a distance 0.5 Å *longer* than at $\alpha = \beta = 0°$). The hydrogens of set B resist a larger twist than 16° and nestle down to a 2.6-Å distance, also, at equilibrium (a distance 1.1 Å *shorter* than at $\alpha = \beta = 0°$). The remaining hydrogens play a much smaller role. In essence, then, the cooperative displacements just described have the effect of rotating the $Si(CH_3)_3$ groups until the hydrogen bumps on any given group are centered on the hollows between the methyls of the adjacent groups.

According to the model, the equilibrium structure is governed more by the interhydrogen interactions than by the relatively weak bond torsional potential function, $V(\alpha)$. This is underscored by comparing the total effective torsional force constant for concerted rotations, $(\partial^2 V(\alpha)/\partial\alpha^2)_{16°} \approx 34 \times 10^{-12}$ ergs/radian^2, including H···H interactions, with the "intrinsic" contribution $\partial^2 V_t(\alpha)/\partial\alpha^2 \approx 18 V_\alpha^0(\alpha = 16°) = 1.3 \times 10^{-12}$ ergs/radian^2, excluding H···H interactions. Such a large value of $\partial^2 V(\alpha)/\partial\alpha^2$ implies that thermal amplitudes of torsional oscillations are small.[16] The model also yields a potential energy lowering of 6.9 kcal/mol upon deformation from T_d symmetry, a value much larger than thermal disordering energy. It stems almost entirely from the decrease in $V_H(R)$ for the closest 12 hydrogens. Although the methyl–methyl interactions appreciably reduce the torsional freedom, they do not restrict the internal rotation so severely that the proton nmr signal is split.

The above experimental and calculated results are rather rough, at best. Nevertheless, they both suggest that the trimethylsilyl groups twist in a correlated manner, by perhaps 14°, in order to relieve intermethyl repulsions.

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[16] Hence it seems reasonable to interpret the results of Figure 3 in terms of a torsional deformation instead of "torsional shrinkage effects" of the sort discussed by L. S. Bartell and D. A. Kohl, *J. Chem. Phys.*, **39**, 3097 (1963).

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Electron Diffraction Determination of the Molecular Structure of Dimethylaminodichloroborane[1]

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Dimethylaminodichloroborane, $(CH_3)_2NBCl_2$, was found to have a planar C_2NBCl_2 skeleton. The B–N distance of 1.379 ± 0.006 Å is the shortest B–N bond so far measured and suggests that the boron and nitrogen are linked by a double bond. The Cl–B–N and C–N–B angles were 122.1 ± 0.3 and 123.2 ± 0.4°, respectively. Root-mean-square amplitudes of vibration were determined. The structural parameters are discussed in the light of results for related molecules.

Introduction

Dimethylaminodichloroborane and its bromide analog were first prepared by Brown and Osthoff.[3] The dichloride is a colorless liquid with a freezing point of −43° and a vapor pressure of about 20 Torr at 20°. Above its melting point the compound spontaneously dimerizes to form an insoluble solid with a low vapor pressure (about 1 Torr at 91°)[4] and was the first known example of self-association of an aminoborane.[5] The crystal structure of the cyclic dimer has been determined[6] and the monomer has been studied in the infrared and Raman regions by Whitmer.[7]

An electron diffraction study of monomeric $(CH_3)_2NBCl_2$ was undertaken to investigate the character of the B–N bond.

Experimental Section

Dimethylaminodichloroborane was prepared by the procedure of Brown and Osthoff[3] and Whitmer,[7] and the purity was checked by infrared spectroscopy. Except while being used, the sample container was stored at −78° to prevent formation of the unwanted dimer.

The diffraction apparatus and the procedure for obtaining the experimental leveled intensity from the 21- and 11-cm camera

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[2] Author to whom correspondence should be addressed.

[3] C. A. Brown and R. C. Osthoff, *J. Amer. Chem. Soc.*, **74**, 2340 (1952).

[4] H. E. Clark, Ph.D. Thesis, The University of Michigan, 1968.

[5] E. L. Muetterties, Ed., "The Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967, Chapter 7.

[6] H. Hess, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **118**, 361 (1963).

[7] J. C. Whitmer, Ph.D. Thesis, The University of Michigan, 1965.