On the Molecular Structure of Bis[di(trimethylsilyl)amino]-beryllium, [(((CH₃)₃Si)₂N]₂Be

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The molecular structure of bis[di(trimethylsilyl)amino]beryllium has been determined by electron diffraction. The bond distances are $Be-N = 1.562(24)$ Å, $N-Si = 1.722(7)$ Å, $Si-C = 1.876(4)$ Å and $C-H = 1.093(12)$ Å. The nitrogen atoms appear to form dative $p\pi$-$p\pi$ bonds to beryllium and dative $p\pi$-$d\pi$ bonds to silicon. The $Si_2NBeNSi_2$ skeleton has D_{2d} symmetry.

The degree of association of dialkylberyllium compounds is strongly dependent on the bulk of the alkyl groups: in dimethylberyllium the beryllium atoms obtain a coordination number of four through the formation of infinite methyl-bridged polymers,[1] while diethylberyllium[2] and diisopropylberyllium[3] are dimeric and di*tert*-butylberyllium is monomeric.[4]

One might therefore expect bisamino derivatives of beryllium to form infinite nitrogen-bridged polymers if the amino groups are sufficiently small, to form dimers or trimers if the amino groups are of intermediate size and to be monomeric if the amino groups are particularly bulky. Bis(dimethylamino)-beryllium is in fact a trimer in inert organic solvents.[3] The molecular structure of the trimer has recently been determined by Atwood and Stucky,[5] see Fig. 1A. It is clear that the chain is terminated after three units because of steric requirements of the dimethylamino groups.[5] The shortest distance between methyl groups in different bridging dimethylamino groups is only 3.11 Å, and it would have been even shorter if the amino groups had not been distorted in such a way as to increase the distance. Such a distortion would not have been possible in a polymer.

Since polymerization is not possible, the terminal beryllium atoms appear to achieve valence saturation through dative π-bonding to the terminal nitrogen atoms.[5] The Be−N (terminal) bond distance, 1.573(11) Å, and planar environment of the terminal nitrogen atoms supports this view.

Bis[di(trimethylsilyl)amino]beryllium (I), [(CH₃)₃Si]₂NBeN[Si(CH₃)₃]₂, first prepared by Bürger, Forker and Goubeau[6] is monomeric in organic
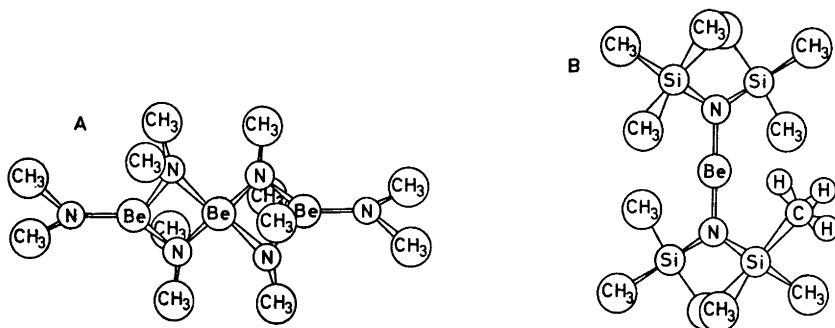

Fig.1. Molecular models of bis(dimethylamino)beryllium trimer (A) and bis[di(trimethyl-silyl)amino]beryllium (I) (B).

solvents. Indeed, a molecular model of the compound makes it clear that association is prevented by the extreme bulk of the substituents. One might therefore except the monomer to be stabilized by dative N−Be bonding.

EXPERIMENTAL AND CALCULATION PROCEDURE

The sample of bis[di(trimethylsilyl)amino]beryllium was a gift from Dr. Bürger and was used without further purification. The electron diffraction pattern from the gas was recorded on the Oslo electron diffraction unit [7] with a nozzle temperature of $100° \pm 10°C$. Exposures were made at nozzle to photo-
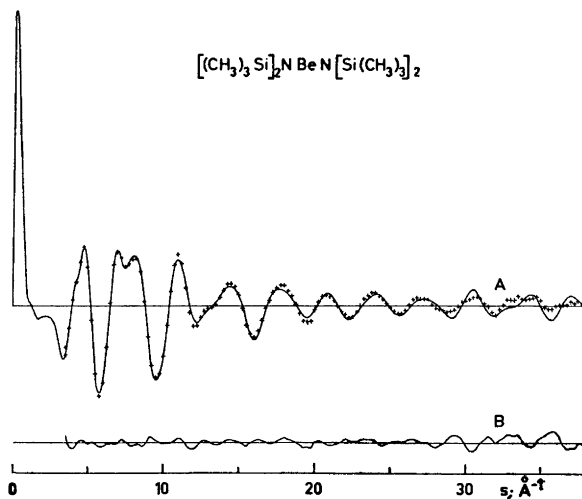

Fig. 2. A: theoretical modified molecular intensity curve for the best model of (I) with experimental values indicated by ×. B: difference curve.

graphic plate distances of about 48 cm and 20 cm. Four apparently faultless plates were photometered and the data processed in the usual way.[8] The resulting modified molecular intensity points are shown in Fig. 2. They extend from $s = 3.50$ Å^{-1} to $s = 38.00$ Å^{-1}. $s = (4\pi/\lambda)\sin(\theta/2)$ where λ is the electron wavelength (determined by diffraction from gaseous CO_2) and θ the diffraction angle. Below $s = 10.00$ Å^{-1} the point density is eight points per Å^{-1}, above 10.00 Å^{-1} the density is four points per Å^{-1}.

Theoretical intensity curves were calculated from:

$$I^{CC}(s) = \sum_{i \neq j} \frac{|f_i(s)| \cdot |f_j(s)|}{|f_{Si}(s)| \cdot |f_C(s)|} \cos(\eta_i(s) - \eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2)$$

$$= \sum_{i \neq j} g_{ij/SiC}(s) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2)$$

The sum extends over all atom pairs i,j in the molecule. R_{ij} is the internuclear distance, u_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)|\exp(i\eta_j(s))$ is the complex atomic scattering factor of atom j. It has been calculated for H, Be, C, N, and Si by the partial wave approximation with a program written by Peacher [9] from the scattering potentials listed by Strand and Bonham.[10]

Radial distribution functions were calculated by Fourier inversion of experimental or theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$.

STRUCTURE ANALYSIS

An experimental radial distribution curve is shown in Fig. 3. The peak at 1.1 Å clearly corresponds to the C−H bond distances, while the peak at 1.9 Å is the sum of peaks corresponding to the Be−N, N−Si, and Si−C bond
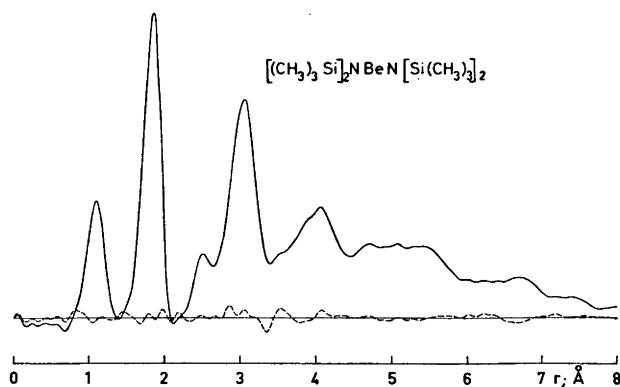

$[(CH_3)_3 Si]_2 N Be N [Si(CH_3)_3]_2$

Fig. 3. Full line: experimental radial distribution curve of (I). The artificial damping constant $k=0.002$ Å^2. Dashed line: difference between experimental curve and a theoretical curve calculated for the best model.

distances. The peak at 2.5 Å corresponds to distances between hydrogen and silicon atoms bonded to the same carbon atom. The peak at 3.0 Å is again highly composite, but the main contributions are peaks corresponding to distances between nitrogen and carbon atoms bonded to the same silicon atom ($N \cdots C$ and $C \cdots C$).

Refinements were first carried out on a model of overall D_{2d} symmetry (this implies that the amino groups are staggered) with a Si $-$ C bond in each trimethylsilyl group eclipsed with a Be $-$ N bond. Three additional assumptions were made: (i) the trimethylsilyl groups have C_{3v} symmetry and the threefold axes coincide with the Si $-$ N bonds, (ii) the methyl groups have C_{3v} symmetry and the threefold axes coincide with the Si $-$ C bonds, and (iii) the methyl groups themselves are in a staggered position with respect to the Si $-$ N and Si $-$ C bonds.

It became clear, however, that this model was incapable of yielding a satisfactory fit between experimental and calculated intensities, and that such a model would have prohibitively short distances between methyl groups bonded to different silicon atoms in one amino group. The model was therefore deformed in the following way: the D_{2d} (staggered) symmetry of the $Si_2NBeNSi_2$ skeleton was retained, but the trimethylsilyl groups were allowed to rotate about the Si $-$ N bonds in such a way that the distance between the methyl groups is increased. The overall molecular symmetry is thus lowered to S_4. See Fig. 1B.

The molecular structure is then determined by eight parameters: the Be $-$ N, N $-$ Si, Si $-$ C, and C $-$ H bond distances, the Be $-$ N $-$ Si, N $-$ Si $-$ C, and Si $-$ C $-$ H valence angles, and the angle of twist of the trimethylsilyl groups about the Si $-$ N bonds. This angle was defined as zero for the D_{2d} model described above.

The molecular structure was refined by least-squares calculations on the intensity data using a diagonal weight matrix.[8] The following simplifying assumptions were made: (iv) shrinkage effects [11] were neglected; (v) all vibrational amplitudes except the thirteen listed in Table 1 were fixed at reasonable values.

Full matrix least-squares refinement of the eight structure parameters and the thirteen vibrational amplitudes converged to give the parameter values listed along with their estimated standard deviations in Table 1. The latter have been obtained by multiplying the standard deviations obtained by least-squares calculations by a factor of four in order to compensate for estimated correlation in our intensity data [12] and for systematic errors introduced by assumptions (i) to (v) above.

A theoretical modified molecular intensity curve calculated from the parameters in Table 1 is shown in Fig. 2, a theoretical radial distribution curve in Fig. 3. The agreement with the experimental curves is seen to be very good.

Calculations were also made on models in which the amino groups are eclipsed (the Si_2NBeSi_2 trunk has symmetry D_{2h}) and on models in which the amino groups undergo nonhindered rotation. It became clear, however, that such models could not be brought into agreement with our data.

Table 1. Structure parameters of $[((CH_3)_3Si)_2N]_2Be$ with estimated standard deviations. The angles have not been corrected for shrinkage.

	R (Å)	u (Å)
Bond distances:		
Be—N	1.562 (24)	0.041 (52)
N—Si	1.722 (7)	.050 (12)
Si—C	1.876 (4)	0.060 (6)
C—H	1.093 (12)	0.091 (12)
Nonbonded distances between atoms in the same $(CH_3)_3Si$ group:		
Si···H	2.523 (25)	0.134 (21)
C···C	3.056 (19)	0.087 (57)
Nonbonded distances between atoms in the same $((CH_3)_3Si)_2N$ group:		
N···C	2.945 (16)	0.068 (15)
Si···Si	3.111 (21)	0.062 (25)
Si···C	3.732 (48)	0.132 (64)
Si···C	3.866 (43)	0.237 (120)
Si···C	4.631 (19)	0.25 (not refined
Other nonbonded distances:		
Be···Si	2.776 (22)	0.062 (28)
N···Si	4.164 (43)	0.111 (56)
Si···Si	5.100 (46)	0.198 (84)
SiNSi	129.2° (0.7°)	
NSiC	109.8° (0.9°)	
SiCH	109.8° (0.9°)	
SiCH	113.8° (2.0°)	
$(CH_3)_3Si$ twist	7.2° (3.5°)	

DISCUSSION

The very reasonable values obtained for the vibrational amplitudes of the N···C and Si···H distances listed in Table 1 show that assumptions (i) and (ii) above were warranted. Any significant deviation from the high local symmetry that was postulated would have resulted in abnormally large amplitudes for these two distances.

The Be—N bond distance obtained, 1.562(24) Å, is very similar to the terminal Be—N bond distance in the bis(dimethylamino)beryllium trimer, 1.573(11) Å.[5] The N—Si bond distance, 1.722(7) Å, is similar to N—Si bond distances found in molecules where dative $p\pi$-$d\pi$ bonding is postulated: in a recent study of $(SiH_3)_2NCH_3$, for instance, the heavy atoms were found to be coplanar and the N—Si bond distance was 1.726(3) Å.[13] It appears therefore that the nitrogen "lone pair" electrons are delocalized, giving partial double bond character to the Be—N and Si—N bonds.

This view is supported by the fact that the amino groups seem to be fairly rigidly held in the staggered conformation giving the $Si_2NBeNSi_2$ skeleton an allene-like structure: while the *tert*-butyl groups in di*tert*-butylberyllium

undergo nearly nonhindered rotation,[14] attempts to refine a nonhindered rotation model for (I) were not successful. Indeed, the relatively small value obtained for the amplitude of the long Si⋯Si distance by refinement on a staggered model suggests that the molecule is fairly rigid. (The reason for this rigidity cannot be steric interactions between the two amino groups: the shortest distance between carbon atoms in different amino groups is 4.5 Å.)

The angle of rotation of the trimethylsilyl groups from the position where one Si−C bond is eclipsed with the Be−N bond is 7.2° (3.5°). The shortest distance between carbon atoms in different trimethylsilyl groups is then 3.5 Å.

Table 2. Selected structure parameters of [((CH₃)₃Si)₂N]₂Be and some related compounds with estimated standard deviations.

	R(N−Si) (Å)	R(Si−C) (Å)	SiNSi
[((CH₃)₃Si)₂N]₂Be	1.722 (7)	1.876 (4)	129.2° (0.7°)
((CH₃)₃Si)₂NH [15]	1.735 (12)	1.867 (4)	125.5° (1.8°)
[((CH₃)₃Si)₂N]₃Al [16]	1.75 (2)	1.90 (2)	118.0° (1.5°)
[((CH₃)₃Si)₂N]₃Fe [17]	1.731 (3)	1.886 (12)	121.2° (0.4°)
(H₃Si)₂NCH₃ [13]	1.726 (3)	—	125.4° (0.4°)
(H₃Si)₂NH [18]	1.725 (3)	—	127.7° (0.1°)

In Table 2 we have set out the N−Si and Si−C bond distances and NSiN valence angles of (I) and a number of related compounds whose structure have been recently determined. ((CH₃)₃Si)₂NLi is not included since this compound forms a cyclic nitrogen-bridged trimer.[19] It is seen that the N−Si bond distances are remarkably constant. It does not appear that the formation of dative N−metal π-bonds weakens dative N−Si π-bonding.

Only two Si−C bond distances are accurately determined (in (I) and in ((CH₃)₃Si)₂NH). The two values are rather different, though not significantly so.

The most interesting variation is found among the values obtained for the SiNSi valence angles. It is tempting to regard the angles found in (H₃Si)₂NCH₃ and (H₃Si)₂NH as "normal" and to explain deviations from the value in these compounds as a result of strain or N-metal π-bonding. However, since the angle in (I) is significantly larger than "normal" and the angles in the derivitives of iron and aluminium are significantly smaller, it does not appear that the presence or absence of N−metal π-bonding is decisive. Rather it may be assumed that the angle in (I) is large because substitution of two (CH₃)₃Si groups for two H₃Si groups introduces strain that is relieved through opening of the SiNSi angle as well as by rotation of the trimethylsilyl groups. In the trisamino derivatives of iron and aluminium interaction between the amino groups may be sufficient to force a closing of the angle.

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