Stereochemistry of Polynuclear Compounds of the Main Group Elements.[1] IX. Structure of Bis(dimethylamino)beryllium and Its Reaction with Trimethylaluminum[2]

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Abstract: The molecular structure of bis(dimethylamino)beryllium, $\{Be[N(CH_3)_2]_2\}_3$, has been determined by three-dimensional X-ray crystallographic techniques. The intensities of 506 independent reflections were measured on a counter diffractometer; full-matrix, least-squares refinement of isotropic thermal parameters for hydrogen atoms and anisotropic parameters for the remaining atoms gave a final weighted discrepancy index of 0.080. The compound crystallizes in the space group Fddd with unit cell dimensions a = 20.564 (12), b = 4.073 (8), c = 13.312 (8) Å; ρ(obsd) 0.95 g cm^{-1}, ρ(calcd), assuming $z = 8$ trimeric units, 1.01 g cm^{-2}. The linear trimeric molecules possess D_{2d} symmetry with two structurally nonequivalent metal atoms. The central beryllium atom is bound to four nitrogen atoms, while the two terminal beryllium atoms are three-coordinate. The terminal dimethylamino nitrogen atoms are coplanar with the attached methyl carbon atoms and a beryllium atom.

Bis(dimethylamino)beryllium has been shown to exist in both solution[4] and the solid state[5] as a linear trimer containing three- and four-coordinate beryllium atoms. The crystal structure of the compound indicated features which could be attributed to π bonding between the terminal beryllium and terminal nitrogen atoms. However, the film data did not permit the location of the hydrogen atoms. Thus, there was a basic uncertainty in the bond distances and angles which was not altogether reflected in the calculated standard deviations. Counter data have now been collected, and the results of this investigation are reported here. In addition, studies of the products of the reaction of trimethylaluminum and bis(dimethylamino)beryllium are discussed.[6]

Experimental Section[7]

Preliminary unit cell dimensions were determined from Weissenberg (Cu Kα) and precession (Mo Kα) photographs of a small polyhedral crystal of $Be[N(CH_3)_2]_2$. The compound belongs to the orthorhombic crystal system. Systematic absences determined the space group uniquely to be Fddd. The unit cell parameters as determined from the least-squares refinement of the sin θ/λ values of 12 independent reflections carefully centered and measured on a Picker diffractometer are: $a = 20.564 \pm 0.012$ Å, $b = 14.073 \pm 0.008$ Å, $c = 13.312 \pm 0.008$ Å, $V = 3852$ Å^3, Cu Kα_1, λ 1.54046, 24°, with eight trimers per unit cell. The measured density of 0.95 g/cm^3 agrees favorably with the calculated value of 1.01 g/cm^3.

Counter data were collected with Ni-filtered copper radiation. The diffracted intensities were measured by the θ-2θ scan technique with a take-off angle of 3° and a scan rate of 1° min^{-1}. Intensity data were collected up to 100° in 2θ for a total of 506 independent reflections of which 57 were unobserved ($I_{obsd} < 3\sigma(I)$). Unobserved reflected were given a raw intensity of $\sigma(I)$ = (total counts + background counts)$^{1/2}$. The linear absorption coefficient (μ) for this compound is 4.68 cm^{-1} with Cu Kα radiation. This gives a maximum calculated value of 0.070 for μR for the crystal used with a maximum estimated error of less than 5% in the corrected intensity, and absorption corrections were deemed unnecessary. Fourier calculations were made with the Sly–Shoemaker–Van den Hende ERFR3[8] program. The full-matrix least-squares refinement was carried out using the Busing and Levy program ORFLS.[9] No corrections were made for extinction or anomalous dispersion. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized. Neutral atom-scattering factors were taken from the compilations of Ibers[10] for H, Be, C, and N. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFEE[11] program. Johnson's program ORTEP[12] was used for the crystal structure illustrations.

Nmr spectra were measured on either a Varian A-60A or HA-100 spectrometer.

Structural Refinement

A structure factor calculation using the final coordinates from the film solution yielded an R_1 value of 25% for the counter data. Subsequent refinement did not reduce this value to below 20%. It thus became apparent that a satisfactory solution could not be accomplished without inclusion of hydrogen atom contributions (22% of the electrons in this compound are from the hydrogen atoms).

The question of the minimum energy configuration for the hydrogen atoms was considered in some detail. In the terminal dimethylamino groups, as a first approximation, only the two interacting methyl groups on the same nitrogen atom were considered. The potential function used consists of a simple sum of van der Waals repulsive terms

$$V(\phi_1,\phi_2) \sum_i = A_i \exp(-r_i/p_i)$$

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(1) Previous paper: V. R. Magnuson and G. D. Stucky, *Inorg. Chem.*, 8, 1427 (1969).

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(5) J. L. Atwood and G. D. Stucky, *Chem. Commun.*, 1169 (1967).

(6) F. M. Peters and N. R. Fetter, *J. Organometal. Chem.*, 4, 181 (1965).

(7) A sample of bis(dimethylamino)beryllium was kindly supplied by Dr. N. R. Fetter.

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(11) W. R. Busing, K. O. Martin, and H. A. Levy, Report No. ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

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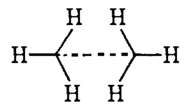
Table I. Final Observed and Calculated Structure Factors[a]

H	K	OBS	CAL
******L= 0********			
4	0	243.7	258.3
8	0	86.0	83.7
12	0	130.7	127.8
16	0	20.5	19.1
20	0	30.6	30.2
2	2	281.0	296.8
6	2	53.8	53.8
10	2	29.0	30.6
14	2	16.3	18.3
18	2	49.6	47.7
22	2	6.7	14.1
0	4	95.8	97.6
4	4	27.7	28.3
8	4	95.3	84.8
12	4	47.0	44.1
16	4	42.9	40.7
20	4	3.0	14.7*
2	6	57.4	55.2
6	6	91.4	88.6
10	6	88.0	93.0
14	6	55.2	56.8
18	6	9.4	10.3
0	8	125.7	125.8
4	8	10.3	11.6
8	8	72.3	70.1
12	8	101.2	106.8
16	8	33.5	33.2
2	10	14.6	15.7
6	10	41.6	39.1
10	10	54.9	54.9
14	10	46.5	45.9
0	12	54.6	53.9
4	12	53.1	51.2
8	12	20.7	19.8
12	12	2.6	7.6*
2	14	29.6	31.6
6	14	3.8	13.4*
******L= 1********			
1	1	120.7	124.8
3	1	118.7	122.4
5	1	141.0	140.9
7	1	94.3	94.8
9	1	26.6	23.3
11	1	19.3	23.2
13	1	45.6	45.9
15	1	24.5	24.3
17	1	31.6	30.4
19	1	5.8	11.9*
21	1	2.2	6.4*
1	3	38.7	44.6
3	3	217.5	220.7
5	3	29.8	30.1
7	3	31.5	31.4
9	3	88.6	91.9
11	3	21.2	21.7
13	3	14.7	12.4
15	3	40.8	36.9
17	3	5.3	2.8*
19	3	21.6	19.0
1	5	7.4	3.6
3	5	112.3	113.1
5	5	7.4	6.2
7	5	32.5	31.2
9	5	10.6	5.5
11	5	35.1	29.7
13	5	20.8	20.6
15	5	23.0	23.5
17	5	24.3	24.1
19	5	10.5	5.9
21	5	3.3	1.4*
1	7	10.2	9.4
3	7	34.7	32.6
5	7	56.6	57.8
7	7	4.7	5.0*
9	7	37.7	35.5
11	7	14.4	8.2
13	7	21.3	16.8
15	7	22.4	20.8
17	7	12.2	12.7
19	7	2.5	4.7*
1	9	44.4	46.9
3	9	32.5	31.5
5	9	22.4	16.4
7	9	12.5	11.9
9	9	27.7	24.2
11	9	22.0	19.7
13	9	25.5	22.2
15	9	13.7	13.2
1	11	11.5	3.3
3	11	40.3	37.9
5	11	14.5	16.1
7	11	36.5	36.1
9	11	20.5	22.0
11	11	16.8	15.1
1	13	22.0	20.1
3	13	5.4	4.7*
5	13	16.4	16.8
7	13	12.7	6.0
******L= 2********			
2	0	21.8	20.8
6	0	59.5	61.4
10	0	58.4	56.4
14	0	36.8	39.5
18	0	5.3	1.6*
0	2	53.3	52.1
2	2	148.4	149.7
4	2	100.0	102.9
6	2	34.2	36.8
8	2	42.3	42.5
10	2	64.3	66.6
12	2	39.8	41.2
14	2	31.7	31.1
16	2	12.7	9.4
18	2	15.8	14.0
2	4	65.4	67.7
4	4	29.3	26.1
6	4	60.4	61.2
8	4	49.3	50.2
10	4	26.6	25.4
12	4	4.7	4.7*
14	4	14.3	13.7
16	4	40.2	39.9
18	4	5.2	7.3*
0	6	47.7	49.5
2	6	68.6	68.4
4	6	36.2	34.6
6	6	14.9	16.7
8	6	25.0	23.3
10	6	23.9	20.6
12	6	12.5	10.4
14	6	24.4	24.4
16	6	11.8	10.4
18	6	9.7	4.0
2	8	52.3	53.1
4	8	25.3	26.4
6	8	20.8	21.8
8	8	16.2	15.8
10	8	9.4	5.9
12	8	19.5	22.3
14	8	5.3	1.4*
16	8	5.2	4.0*
0	10	32.0	34.3
2	10	26.6	28.5
4	10	18.3	19.3
6	10	38.5	38.1
8	10	10.7	11.1
10	10	16.8	15.0
12	10	5.2	2.3*
14	10	11.9	6.6
2	12	9.2	5.2
4	12	17.9	19.0
6	12	9.3	9.9
4	12	11.1	10.1
10	12	11.9	12.0
******L= 3********			
1	1	101.7	96.8
3	1	25.8	26.6
5	1	150.8	154.4
7	1	72.6	74.4
9	1	24.2	24.8
11	1	29.8	23.3
13	1	16.6	13.4
15	1	21.6	21.2
17	1	24.1	21.5
19	1	5.3	2.1*
1	3	10.7	5.1
3	3	205.0	209.8
5	3	18.2	20.0
7	3	62.5	57.2
9	3	69.5	70.4
11	3	30.2	30.4
13	3	14.2	12.2
15	3	37.9	38.2
17	3	21.4	23.0
19	3	11.2	10.4
1	5	21.0	20.6
3	5	89.4	90.9
5	5	40.0	34.2
7	5	10.6	4.0
9	5	32.8	30.3
11	5	8.9	6.3
13	5	11.9	6.9
15	5	39.9	40.8
17	5	17.6	21.5
1	7	41.9	33.2
3	7	58.4	38.4
5	7	48.1	48.5
7	7	31.5	30.1
9	7	11.4	9.8
11	7	30.5	31.2
13	7	11.7	7.9
15	7	9.5	7.5
17	7	15.7	14.3
1	9	12.8	11.8
3	9	17.4	15.9
5	9	15.7	15.6
7	9	28.1	28.1
9	9	5.1	.3*
11	9	5.3	5.7*
13	9	5.2	3.9*
15	9	8.9	2.7
1	11	11.3	11.4
3	11	36.1	34.6
5	11	30.7	37.0
7	11	28.3	32.2
9	11	30.1	30.5
11	11	5.3	6.3*
1	13	9.1	5.8
3	13	10.4	7.1
5	13	9.6	8.5
******L= 4********			
0	0	516.2	492.6
4	0	54.1	32.0
8	0	28.0	24.7
12	0	130.1	129.6
16	0	27.2	21.2
2	2	48.5	34.4
4	2	127.7	128.2
6	2	82.5	76.1
8	2	66.6	65.8
10	2	41.6	38.5
12	2	5.0	4.1*
14	2	54.7	54.8
16	2	28.5	28.5
18	2	16.8	13.7
20	2	2.7	6.4*
22	2	3.9	3.2*
0	4	50.0	48.2
2	4	80.2	79.2
4	4	95.9	92.7
6	4	59.1	56.1
8	4	19.6	12.5
10	4	28.0	27.8
12	4	18.0	15.4
14	4	30.9	32.6
16	4	5.4	3.4*
18	4	19.7	18.8
20	4	3.3	3.4*
2	6	41.1	39.7
4	6	47.4	48.7
6	6	17.6	6.1
8	6	27.6	29.5
10	6	17.3	11.0
12	6	5.3	2.7*
14	6	10.1	11.3
16	6	22.5	22.7
18	6	2.5	8.6*
0	8	134.7	131.1
2	8	9.4	7.6
4	8	47.0	46.7
6	8	9.7	1.6
8	8	12.5	4.7
10	8	10.2	8.0
12	8	38.9	41.7
14	8	5.2	3.7*
16	8	1.7	7.8*
2	10	52.1	52.8
4	10	34.0	35.5
6	10	11.3	6.7
8	10	30.4	31.5
10	10	11.7	12.6
0	12	13.3	10.9
2	12	19.4	15.9
4	12	18.3	13.8
6	12	23.5	24.0
8	12	9.6	6.4
******L= 5********			
1	1	166.3	160.5
3	1	70.8	73.1
5	1	35.8	38.4
7	1	21.0	22.8
9	1	10.7	8.3
11	1	32.1	35.2
13	1	60.6	59.2
15	1	24.2	22.0
17	1	5.3	14.3*
1	3	16.9	14.8
3	3	72.6	73.6
5	3	9.1	1.4*
7	3	14.0	6.6
9	3	38.1	38.6
11	3	15.3	15.1
13	3	9.4	7.4
15	3	5.4	3.5*
17	3	10.8	10.2
1	5	8.4	8.1
3	5	28.3	32.5
5	5	10.6	6.9
7	5	32.9	32.7
9	5	19.8	14.4
11	5	20.0	19.6
13	5	5.2	3.1*
15	5	5.3	1.3*
17	5	5.2	5.4*
1	7	21.2	23.7
3	7	19.4	17.2
5	7	24.2	20.7
7	7	10.6	10.4
9	7	23.6	21.3
11	7	12.9	14.8
13	7	21.5	20.3
15	7	11.4	11.8
1	9	56.3	57.1
3	9	28.8	27.9
5	9	9.3	5.2
7	9	5.2	1.5*
9	9	13.5	13.7
11	9	21.9	22.2
13	9	25.9	24.9
1	11	9.2	1.6
3	11	14.0	12.3
5	11	9.3	4.4
7	11	11.5	11.6
9	11	12.5	7.0
1	13	13.8	14.8
******L= 6********			
2	0	62.8	54.4
6	0	33.3	35.8
10	0	46.0	46.6
14	0	51.7	54.2
18	0	9.6	5.6
0	2	18.8	7.8
2	2	32.7	35.6
4	2	69.8	73.8
6	2	12.3	8.7
8	2	22.6	20.8
10	2	20.2	19.0
12	2	42.8	45.3
14	2	5.5	5.9*
16	2	9.3	4.8
2	4	43.8	43.2
4	4	13.8	15.6
6	4	37.7	40.2
8	4	44.9	42.0
10	4	14.8	12.8
12	4	10.0	5.6
14	4	13.9	11.2
16	4	19.7	19.1
0	6	21.3	23.6
2	6	13.7	15.9
4	6	12.5	13.3
6	6	32.2	25.0
8	6	14.6	10.4
10	6	10.3	7.4
12	6	11.2	4.8
14	6	12.0	8.4
16	6	15.2	11.8
2	8	52.4	56.2
4	8	15.9	15.7
6	8	16.3	14.3
8	8	11.3	10.9
10	8	5.2	2.4*
12	8	12.7	12.7
14	8	11.4	7.3
0	10	38.1	42.0
2	10	9.3	4.2
4	10	15.6	16.4
6	10	19.1	15.9
8	10	9.7	7.9
10	10	5.3	5.1*
2	12	5.2	4.0*
4	12	5.2	6.2*
******L= 7********			
1	1	44.3	47.6
3	1	26.0	28.4
5	1	11.7	12.9
7	1	63.5	67.7
9	1	33.9	34.5
11	1	74.8	76.4
13	1	37.1	37.1
15	1	15.3	14.1
17	1	22.1	18.8
1	3	38.6	38.4
3	3	22.7	24.8
5	3	52.7	54.9
7	3	21.3	18.4
9	3	47.2	54.1
11	3	14.9	10.0
13	3	22.0	22.7
15	3	35.7	35.8
1	5	34.9	37.9
3	5	65.6	70.6
5	5	29.0	26.7
7	5	9.7	10.4
9	5	16.4	12.9
11	5	15.2	16.4
13	5	12.7	9.5
15	5	16.2	15.8
1	7	83.0	81.9
3	7	23.2	20.1
5	7	45.9	48.0
7	7	5.2	4.1*
9	7	15.7	14.2
11	7	22.6	24.5
13	7	11.1	4.7
1	9	40.0	41.9
3	9	34.6	34.0
5	9	27.4	28.1
7	9	5.3	2.4*
9	9	5.2	1.2*
11	9	9.5	6.1
13	9	1.2	5.7*
1	11	13.5	8.5
3	11	33.3	30.5
5	11	11.4	14.0
******L= 8********			
0	0	51.0	58.6
4	0	9.8	3.5
8	0	9.0	3.8
12	0	28.7	31.1
16	0	16.2	16.0
2	2	10.4	11.3
4	2	86.8	90.8
6	2	30.4	33.0
8	2	55.0	55.3
10	2	10.3	6.0
12	2	13.4	12.1
14	2	20.8	24.9
16	2	28.6	29.5
0	4	14.7	19.0
2	4	59.5	60.0
4	4	36.7	43.1
6	4	43.9	43.4
8	4	11.2	11.4
10	4	26.9	28.6
12	4	12.1	12.4
14	4	29.2	31.5
2	6	9.4	8.0
4	6	43.7	44.6
6	6	11.3	9.3
8	6	26.2	25.9
10	6	11.6	12.1
12	6	5.3	6.2*
0	8	28.0	29.9
2	8	12.4	13.2
4	8	16.7	18.7
6	8	5.3	4.5*
8	8	11.0	11.3
10	8	11.6	10.4
2	10	22.8	24.6
4	10	34.4	35.9
6	10	5.2	9.2*
******L= 9********			
1	1	43.3	41.2
3	1	14.2	15.4
5	1	13.9	21.4
7	1	27.8	26.5
9	1	11.8	9.9
11	1	29.1	32.2
13	1	43.5	45.8
15	1	15.3	16.9
1	3	29.5	30.3
3	3	9.1	27.9
5	3	45.1	41.9
7	3	21.6	18.7
9	3	5.4	10.0*
******L=10********			
2	0	62.3	62.8
6	0	16.8	13.1
10	0	14.9	10.4
0	2	37.3	39.9
2	2	5.2	4.4*
4	2	12.2	6.8
6	2	15.1	11.3
8	2	25.1	24.4
10	2	13.7	2.0
12	2	5.2	3.6*
2	4	10.4	8.3
4	4	13.0	14.4
6	4	16.3	11.4
8	4	25.8	24.1
10	4	23.0	18.5
12	4	15.8	4.6
0	6	29.7	26.4
2	6	5.5	4.6*
4	6	29.9	27.2
6	6	23.5	19.7
8	6	20.8	16.0
10	6	13.5	1.9
2	8	9.1	5.4
4	8	14.4	7.0
6	8	17.1	11.9
******L=11********			
1	1	63.2	67.7
3	1	31.8	35.9
5	1	24.0	23.8
7	1	10.5	9.3
9	1	5.2	3.7*
11	1	20.4	23.4
1	3	19.1	21.5
3	3	20.2	21.6
5	3	22.0	16.9
7	3	9.7	2.8
9	3	16.2	11.2
1	5	12.1	8.3
3	5	13.2	9.9
5	5	5.2	1.0*
7	5	36.3	32.6
1	7	9.2	19.9
3	7	9.6	4.5
******L=12********			
0	0	22.1	23.2
4	0	11.7	9.4
8	0	16.2	14.8
2	2	15.2	13.2
4	2	33.7	36.6
6	2	5.2	4.8*
8	2	26.2	25.2
0	4	5.2	1.5*
2	4	24.4	27.0
4	4	5.2	8.8*
6	4	14.1	11.8
******L=13********			
1	1	17.8	15.4
3	1	11.6	10.8

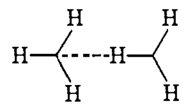
[a] Unobserved reflections are indicated by an asterisk.

where r_i is the separation in ångströms of the ith pair of hydrogen atoms, and the constants $A_i = 9.57 \times 10^2$ (kcal/mole) and $p_i = 0.3917$ (Å) are those given by Howlett.[13] The angles ϕ_1 and ϕ_2 give the rotational orientation of the methyl groups with respect to the plane of the dimethylamino group (carbon and nitrogen atoms). Rotations were done in intervals of 15°.

The results of the calculations show the minimum energy configuration as given below.



For the bridge dimethylamino groups, the situation is complicated by the close approach of methyl groups from dimethylamino units in other parts of the molecule. However, the minimum energy calculation for the interaction of one methyl group with the nearest nonbonded methyl group leads to the same configuration which was obtained by consideration of the interactions within a dimethylamino group. Subsequent calculations on the simultaneous interaction of three neighboring groups led, again, to the opposed configuration. A difference Fourier was calculated and showed electron density approximately 20% above background which was consistent with the opposed configuration of hydrogen atoms as determined above. Attempts to refine the structure with the hydrogen atoms in positions as shown below led to divergence of the



least-squares refinement. With the former hydrogen configuration, however, refinement proceeded smoothly and the hydrogen atom positional parameters were varied in the latter stages. The final R values were $R_1 = 9.0\%$ ($R_1 = \Sigma \, ||F_o| - |F_c|| / \Sigma F_o$) and $R_2 = 8.0\%$ ($R_2 = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$). Unit weights were used; a check of Cruickshank's criterion[14] that $W(|F_o| - |F_c|)^2$ be independent of F_o indicated no divergence except for 16 of the most intense reflections. These reflections were weighted one-ninth the weight of all other reflections in order to satisfy the above criterion. Subsequent refinements produced bond distances and angles which agreed within a standard deviation to those corresponding to unit weights. A final difference Fourier calculation showed no residual electron density greater than approximately 0.4 e/Å^3. The final calculated and observed structure factors are listed in Table I. Final atomic parameters and standard deviations are tabulated in Table II. Anisotropic thermal parameters are shown in Table III. Bond distances, angles, and errors are shown in Table IV.

Discussion

The molecule, shown in Figure 1, lies at the intersection of three twofold axes and possesses D_{2d} symmetry. Figure 2 shows the molecular packing in the crystal. The gross structural features are the same as given before.[5] A reason for the stabilization of the coordination number of three for the terminal beryllium atoms is suggested by a consideration of the geometry about the terminal nitrogen and terminal beryllium atoms. A terminal beryllium atom, the nitrogen atoms to which the beryllium atom is coordinated, and the carbon atoms of the methyl groups on the terminal nitrogen atom are coplanar (Table V). Essentially unhybridized p orbitals on both the terminal nitrogen and beryllium atoms are then free to form a dative π

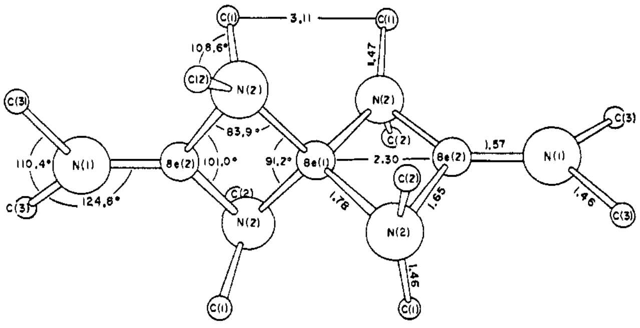


Figure 1. The molecular structure of bis(dimethylamino)beryllium.

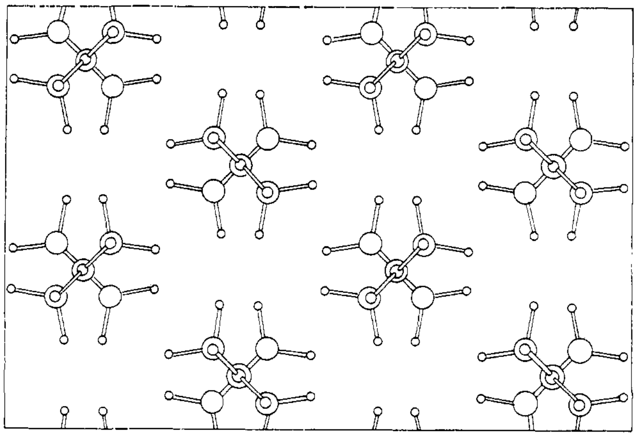


Figure 2. The packing in a unit cell of bis(dimethylamino)beryllium viewed along [001].

Table II. Final Atomic Positional Parameters

Atom	x/a	y/b	z/c
Be(1)	−0.1250	−0.1250	−0.1250
Be(2)	−0.1250	−0.1250	0.0478 (7)
N(1)	−0.1250	−0.1250	0.1660 (5)
N(2)	−0.0812 (2)	0.1892 (3)	−0.0312 (3)
C(1)	−0.0933 (5)	−0.2908 (4)	−0.0189 (6)
C(2)	−0.0114 (3)	−0.1717 (7)	−0.0186 (6)
C(3)	−0.0856 (5)	−0.1880 (5)	0.2287 (5)
H1(C(1))	−0.1451 (28)	−0.3243 (39)	−0.0131 (42)
H2(C(1))	−0.0711 (30)	−0.3319 (45)	−0.0486 (48)
H3(C(1))	−0.0731 (28)	−0.3194 (44)	0.0342 (54)
H4(C(2))	0.0013 (28)	−0.0880 (42)	−0.0136 (44)
H5(C(2))	0.0053 (28)	−0.1989 (40)	0.0443 (46)
H6(C(2))	0.0140 (29)	−0.2022 (43)	−0.0598 (45)
H7(C(3))	−0.0519 (27)	−0.2423 (42)	0.2013 (42)
H8(C(3))	−0.0533 (27)	−0.1465 (40)	0.2697 (43)
H9(C(3))	−0.1215 (29)	−0.2393 (40)	0.2621 (42)

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(13) K. E. Howlett, *J. Chem. Soc.*, 1055 (1960).

(14) D. W. J. Cruickshank, "Computer Methods in the Phase Problem," Pergamon Press, Oxford, 1961.

Table III. Anisotropic Temperature Factors ($\times 10^4$)[a]

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Be(1)	31 (4)	68 (9)	54 (10)	0	0	0
Be(2)	30 (3)	57 (6)	34 (6)	2 (4)	0	0
N(1)	38 (2)	67 (4)	59 (5)	4 (3)	0	0
N(2)	23 (1)	48 (3) q	52 (3)	3 (1)	−3 (1)	1 (2)
C(1)	67 (3)	48 (4) q	75 (5)	6 (3)	−9 (3)	14 (4)
C(2)	22 (2)	150 (8)	73 (5)	5 (3)	−8 (2)	10 (5)
C(3)	47 (2)	90 (5)	63 (5)	9 (3)	−9 (3)	1 (4)

[a] Anisotropic temperature factors are of the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl]$.

Table IV. Interatomic Distances (Å) and Angles (deg)

	Bonded		
Be(1)–Be(2)	2.300 (9)	C(1)–H2	0.84 (6)
Be(1)–N(2)	1.785 (4)	C(1)–H3	0.91 (6)
Be(2)–N(2)	1.653 (7)	C(2)–H4	1.20 (6)
Be(2)–N(1)	1.573 (11)	C(2)–H5	0.98 (6)
N(2)–C(1)	1.460 (7)	C(2)–H6	0.88 (6)
N(2)–C(2)	1.466 (7)	C(3)–H7	1.09 (6)
N(1)–C(3)	1.462 (7)	C(3)–H8	1.05 (6)
C(1)–H1	1.16 (6)	C(3)–H9	1.12 (6)
	Nonbonded Intramolecular Distances		
C(1)–C(2)	2.38 (1)	$C(2)–C(2)_2$	3.12 (2)
$C(3)–C(3)_2$	2.40 (1)	$C(1)–C(1)_2$	3.11 (2)
	Nonbonded Intermolecular Distances		
C(3)–C(3)′	4.25 (2)		
	Bond Angles		
Be(1)–N(2)–Be(2)	83.9 (3)	C(1)–N(2)–C(2)	108.6 (6)
$N(2)–Be(1)–N(2)_2$	91.2 (2)	$C(3)–N(1)–C(3)_2$	110.4 (5)
$N(2)–Be(2)–N(2)_2$	101.0 (3)	Be(2)–N(1)-C(3)	124.8 (3)

Table V. Mean Plane[a] for Bis(dimethylamino)beryllium

Atom	Distance, Å	Atom	Distance, Å
Be(2)	0.000 (0)	N(1)	0.000 (0)
N(2)	−0.012 (4)	C(3)	0.040 (8)
N(2)′	0.012 (4)	C(3)′	−0.040 (8)

[a] Equation of the plane is $-0.7149x - 0.6993y + 0.000z - 3.0677 = 0$. Weights are given by w (atom i) = $[\sigma^2(x_i) + \sigma^2(y_i) + \sigma^2(z_i)]^{-1}$; calculated according to the procedure of D. M. Blow, *Acta Cryst.*, **13**, 168 (1960).

bond. In the terminal dimethylamino group, the observed carbon–nitrogen–carbon angle of 111.7° is smaller than the expected angle if the nitrogen atom is assumed to exhibit sp^2 hybridization, but this may be accounted for, in part, by electrostatic repulsion arguments. The Be(terminal)–N(terminal) bond length of 1.57 Å may be compared with distances of 1.65 Å for Be(terminal)–N(bridge) and 1.78 Å for Be(central)–N(bridge). This trend is in the expected direction if π-bonding effects are considered. The nitrogen–carbon bond lengths (1.46 Å) are the same in both bridge and terminal dimethylamino groups to within a standard deviation.

Since arguments often hinge on the observed bond distances and angles, a comparison was made of the values found for three different refinements of this structure. With film data, the hydrogen atoms could not be located; with counter data, the hydrogen coordinates were found and refined. In order to verify the initially observed reluctance of the data to refine without hydrogen atoms, the final atomic parameters excluding hydrogen atoms as determined from the counter data were used as a starting point for a least-squares refinement. Full-matrix, anisotropic least-squares treatment of all Be, C, and N parameters would not give values of R_2 below 16.1% and R_1 below 15.6%. Table VI contains the results of the comparison. For the film structure, the calculated standard deviations all were less than 0.02 Å, *vs.* 0.01 Å for the counter structure. The distances and angles (film data *vs.* counter data) do not vary in a straightforward manner: one carbon–nitrogen–carbon angle changed only 1.7°, while the other changed 8.2°. In addition, the beryllium–beryllium distance changed by 0.10 Å. It is interesting to note that inclusion of hydrogen atom parameters in the counter-data refinement does not always give predictable results. For example, the two Be–N distances are changed by 0.0 and 0.06 Å, respectively, and the Be–Be distance is, if anything, slightly lengthened (2.28 *vs.* 2.30 Å). The decrease in the bond angle is expected and is experimentally the same (1.35°) for the two unique C–N–C bond angles. The data reemphasize the fact that in light atom structures proper treatment of the hydrogen atoms is necessary if any faith is to be placed in the reported distances and angles.

Table VI. Comparison of Selected Distances (Å) and Angles (deg) for Different Least-Squares Refinements

	Film data (no hydrogen atom contribution)	Counter data (hydrogen atoms refined)	Counter data (no hydrogen atom contribution)
Be(1)–Be(2)	2.18 (2)	2.30 (1)	2.28 (1)
Be(1)–N(2)	1.76	1.78	1.80
Be(2)–N(2)	1.61	1.65	1.65
Be(2)–N(1)	1.56	1.57	1.63
N–C	1.53	1.46	1.49
C(1)–N(2)–C(2)	108.2	108.6	109.9
C(3)–N(1)–C(3)	103.6	110.4	111.8

Bis(dimethylamino)magnesium[15] is believed to be an infinite polymer. At the outset of this study, the question of why bis(dimethylamino)beryllium, on the other hand, is a trimer was subject to debate. Now, however, the answer is apparent. Consideration of the nonbonded methyl–methyl distances shows that between the bridge groups the approach is 3.11 Å. Normally a methyl–methyl distance of 4.0 Å is expected, and even in electron-deficient compounds the value is not less than 3.25 Å. A considerable distortion of these groups away from the center of the molecule was necessary to attain even this separation. If this substance were an infinite polymer, such a distortion would not be possible, and nonbonded methyl–methyl distances would have to be less than 3.11 Å. It seems safe to conclude that bis(methylamino)beryllium terminates its chain at three because of steric requirements of groups exterior to the four-membered rings.

(15) G. E. Coates and D. Ridley, *J. Chem. Soc., A*, 56 (1967).

Nuclear magnetic resonance spectra of bis(dimethylamino)beryllium show two resonances in benzene (τ 7.55 and 6.96) and in cyclohexane (τ 7.55 and 7.40). In both solvents, the resonance associated with the protons on the terminal groups is shifted downfield with respect to the resonance associated with the bridge groups. The C^{13}–H coupling constants, redetermined in benzene from HA-100 data and taken at room temperature, are 129 ± 1 cps for the terminal group and 133 ± 1 cps for the bridge group. Drago and Matwiyoff[16] have drawn a correlation between $J(C^{13}\text{–H})$ and τ from a number of observations. This relationship affords a means of determining the existence of large nonlocal contributions to the proton chemical shifts. While a quantitative comparison of the two environments in bis(dimethylamino)beryllium cannot be made, the anisotropic contribution appears to be larger for the terminal groups than for the bridge groups. The fact that τ values of the terminal protons are solvent shifted upfield in benzene relative to cyclohexane implies that a significant portion of the anisotropic contribution may be due to the interaction of the benzene molecules with the terminal amino group. We were unable to obtain C^{13}–H coupling constants in cyclohexane.

The reaction of trimethylaluminium with bis(dimethylamino)beryllium[6] in various molar ratios, and subsequent sublimation at low temperatures, yields a mixture of materials. Principal among these are two crystalline substances (multiple plates and very small needles) and an amorphous solid. The plate-like material can be initially separated, but upon successive sublimations a variety of compounds are again obtained. Attempts to mount fragments of the plates for X-ray structural analysis did not produce satisfactory results. However, single crystals of the needle-like substance were mounted and preliminary X-ray data were taken. Space group and unit cell determination showed that this compound was dimethylberyllium.[17] The presence of dimethylberyllium could be accounted for by a reaction such as

$$2\text{Al}(\text{CH}_3)_3 + \text{Be}[\text{N}(\text{CH}_3)_2]_2 \rightleftarrows \text{Be}(\text{CH}_3)_2 + [(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2 \quad (1)$$

Previous studies with this system indicated that neutral addition complexes such as $\text{Al}(\text{CH}_3)_3 \cdot \text{Be}(\text{N}(\text{CH}_3)_2)_2$ and $(\text{Al}(\text{CH}_3)_3)_2 \cdot \text{Be}(\text{N}(\text{CH}_3)_2)_2$ were formed.[6] However, the expected severe steric interaction for these compounds together with the complex spectra reported (three to four resonances in the Al–CH_3 area and three resonances in the –$N(CH_3)_2$ area) shed doubt as to their actual nature. If one views the spectra as the result of a redistribution equilibrium process,[18] then compounds with more favorable stereochemistries may be expected. Indeed, we have found that in a typical nmr spectrum of the plate-like substance, two of the resonances may be assigned to the $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ compound. It is believed that by a systematic study of compounds related to the parent species in eq 1, the nature of the redistribution equilibrium could be fully understood.

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[16] R. S. Drago and N. A. Matwiyoff, *J. Organometal. Chem.*, 3, 62 (1965).

[17] A. I. Snow and R. E. Rundle, *Acta Cryst.*, 4, 348 (1951).

[18] K. Moedritzer, *Advan. Organometal. Chem.*, 6, 171 (1968).

The Structure of Aquomagnesium Tetraphenylporphyrin[1]

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Abstract: The crystal and molecular structure of aquomagnesium tetraphenylporphyrin, (H_2O)MgTPP, has been solved using X-ray crystallographic techniques. The crystals are tetragonal (a = 13.46, c = 9.68 Å) and the space group was fixed to be I4/m with two molecules per unit cell. Since the magnesium atom does not lie in the mirror plane (±0.273 Å), the crystal structure was concluded to be disordered, similar to that of ClFeTPP and (H_2O)ZnTPP. The magnesium atom proved to be hydrated and possesses approximate square-pyramidal coordination. The porphyrin molecule is characteristic of other porphyrins and metalloporphyrins.

Most of the metalloporphyrin structures that have been reported thus far consist of metals of the first transition series or beyond.[3] Of the metalloporphyrins preceding the first transition series, magnesium-containing porphyrins are probably of the most interest because of their possible relationship to chlorophyll and its related compounds. Thus, during the course of a continuing study of the structure of porphyrin molecules, we have determined the crystal and molecular structure of magnesium tetraphenylporphyrin (MgTPP), which we now wish to summarize here.

Experimental Section

Crystals of MgTPP suitable for X-ray study and displaying pseudo-octahedral morphology were grown by slow evaporation of chloroform solutions seeded with very small crystals of MgTPP

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[2] NSF Undergraduate Summer Participant, 1967, 1968.

[3] For extensive reviews of structural studies of porphyrins, see T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Am. Chem. Soc.*, 87, 2305 (1965); L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, 43, 3100 (1965), and references contained therein.