The Stereochemistry of Polynuclear Compounds of the Main Group Elements.[1a] XII. The Preparation and Structure of the Ethyleniminodimethylaluminum Trimer[1b]

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Abstract: Ethyleniminodimethylaluminum trimer, $[(CH_3)_2AlN(CH_2)_2]_3$, synthesized by the reaction of ethylenimine with trimethylaluminum, has been structurally characterized by the analysis of three-dimensional X-ray data. The compound crystallizes in the monoclinic system with four trimers in a unit cell of dimensions $a = 13.063$, $b = 9.834$, $c = 15.050$ Å, $\beta = 96.70°$, with $\rho_{calcd} = 1.03$ g/cc. Full-matrix, least-squares refinement of the 303 observed F values for a structure in the space group C2/c, with the carbon and nitrogen atoms of the ethylenimino groups treated as isotropically vibrating atoms constrained in a rigid body, led to a discrepancy factor of 12.8%. Full-matrix, least-squares refinement of the same diffractometer data, with all atoms refined independently and anisotropically, gave a discrepancy factor of 7.8%. The trimers are located on crystallographic twofold axes and consist of $(CH_3)_2Al$ units bridged by ethylenimino groups to form a puckered six-membered ring. The average interior Al–N–Al angle is 119.9 ± 0.5°, while the corresponding N–Al–N angle is 102.0 ± 0.5°. The importance of the bridging group in determining the polynuclear geometry is discussed.

The reaction of organoaluminum compounds with reagents containing one acidic hydrogen almost always leads to the formation of dimeric or trimeric species.[2] It has been suggested that the glassy form of $(CH_3)_2AlN(CH_3)_2$ obtained by heating the dimeric form is a mixture of cyclic oligomers and polymers.[3,4] The only other well-documented exceptions are the reaction products of HCN with alkylaluminum compounds. Presumably, the cyanide ion bridges through both the carbon and the nitrogen atoms and thus facilitates ring expansion to tetrameric and higher membered ring systems.[5]

After a consideration of a number of associated organoaluminum compounds, Coates[2] has assessed the relative importance of entropy and steric factors for both dimeric and trimeric molecules. Entropy terms favor dimers (the largest number of molecules). Ring strain considerations favor trimer formation, but steric interference between substituent groups is more severe in a trimer than in the corresponding dimer. However, studies of systems in which the relative importance of these factors can be assessed are lacking. While the dimethylamino derivative was reported to be a dimer,[6] the much smaller steric requirement of the ethylenimino group left the nature of the molecular composition of ethyleniminodimethylaluminum in doubt.

An additional point of interest concerned the heterocyclic ligand, ethylenimine. It was hoped that a structural study of the geometry of a system in which one of the atoms in the three-membered strained ring is a bridging atom might give some information about the electron distribution within the ring.

Experimental Section

Ethylenimine was purified by distillation prior to use. In a glove box 0.02 mole of ethylenimine was added to 0.02 mole of trimethylaluminum. Methane was vigorously evolved; there was no indication of the formation of a solvated intermediate. Clear, colorless crystals were subsequently sublimed out of the brown-white residue. Single crystals of the oxygen and water-sensitive compound were sealed in thin-walled glass capillaries.

Preliminary unit cell parameters were determined by precession (Mo Kα) photographs. The crystal system is monoclinic. Systematic absences allow the space group to be C2/c or Cc. The lattice parameters as determined from a least-squares refinement of $(\sin \theta/\lambda)^2$ values of 12 reflections are: $a = 13.063 \pm 0.007$, $b = 9.834 \pm 0.006$, $c = 15.050 \pm 0.007$ Å, $\beta = 96.70 \pm 0.03°$, $V = 1290$ Å^3. A satisfactory observed density could not be obtained because of difficulty in separating the compound from an amorphous accompanying product. The calculated density is 1.03 g cm^{-3} with four trimers per unit cell.

Data were taken with Ni-filtered copper radiation. The diffracted intensities were collected by the θ–2θ scan technique with a take-off angle of 1.5° and a scan rate of 1° min^{-1}. The peak profiles were broad, and a scan of 2° was necessary to encompass all of the intensity. All reflections were carefully centered with respect to χ and φ before measurement. Data were collected only to $2\theta = 80°$, since at higher angles few peaks could be observed. Standard reflections were checked periodically to monitor possible crystal decomposition and electronic stability factors. A total of 303 independent reflections were observed ($I_{obs} > 3\sigma(I)$). The linear absorption coefficient (μ) for this compound is 16.55 cm^{-1} with Cu Kα radiation. This gives a maximum calculated value of 0.248 for μR for the crystal used, and absorption corrections were deemed unnecessary. The maximum error in the intensities due to this omission was estimated to be 9%. Fourier calculations were made with the Sly, Shoemaker, and Van den Hende ERFR[7] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program, ORFLS.[8] The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction or anomalous dispersion. Neutral atom scattering factors were taken from the compilations of Ibers[9] for C, N, and Al. Final

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bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE[10] program. The program ORTEP[11] was used for the crystal structure illustrations.

Nmr spectra were measured on a Varian A-60A spectrometer.

Structure Determination and Refinement

In the space group C2/c there are eightfold general positions and fourfold special positions, while in Cc there are only fourfold general positions. Thus, preliminary considerations suggested that the compound must exist in a trimeric configuration and lie on a fourfold special position in C2/c or in a general position in Cc. Since it is statistically more likely that a space group will be centric than acentric, C2/c was chosen initially. The fourfold special positions consist of four sites with $\bar{1}$ symmetry and one set with twofold symmetry. A cyclic trimer could not have a center of inversion, but twofold symmetry is possible.

The Patterson map showed peaks consistent with the configuration of a cyclic trimer. Assignment of vectors between equivalent aluminum atoms was not unambiguous, but did allow placement of one of the two aluminum atoms in the asymmetric unit. The reliability index was 45%, and a Fourier synthesis phased on the single aluminum atom showed peaks consistent, again, with a cyclic trimer. Placement of the remaining atoms and subsequent isotropic least-squares refinement (several cycles) led to a reliability index ($R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$) of 14.1%. Because of the limited amount of data available, refinement was continued with the ethylenimino rings (nitrogen and carbon atoms) treated as rigid groups. The bond distances in the ring were taken from a microwave spectroscopic study on ethylenimine by Turner, *et al.*[12] Isotropic refinement of the rigid group atoms and methyl carbon atoms, together with anisotropic refinement of the aluminum atom parameters, led to a final unweighted R value of 12.8%. A difference Fourier map did not show peaks which could be ascribed to hydrogen atoms. Unit weights were used at all stages of refinement and unobserved data were not included. A check of $|F_o - F_c|$ *vs.* F_o was interpreted to indicate that no significant improvement would result from the application of an empirical weighting scheme. A least-squares analysis was made in the acentric space group Cc; however, the results were not significantly different from those obtained by the centric refinement.

Refinement was also attempted with all atoms anisotropic and independent. The R value dropped to 10.1%. A difference Fourier showed peaks which were in chemically reasonable positions for hydrogen atoms but which were not significantly larger than background ($^1/_{10}$th to $^1/_5$th the carbon atom peak heights). Inclusion of hydrogen atoms ($B = 4.5$) in these positions and further refinement of the nonhydrogen atom parameters led to a final R factor of 7.8%.

The results obtained by the latter refinement are probably not too significant in view of the unsatisfactory ratio of refined parameters to observations (82/303). The parameters derived from the rigid-body refinement are accordingly presented in Tables I–IV. For comparison, and to give some idea of the effects on bond lengths and angles, Table III also contains the interatomic distances and angles obtained from the unconstrained refinement.

Table I. Final Observed and Calculated Structure Factor Amplitude

H	K	OBS	CAL
******* L = 0 *******			
1	1	41.1	51.4
1	2	16.1	46.9
5	1	12.5	1.6
1	1	10.9	11.2
3	2	19.1	16.7
4	2	20.3	11.1
6	2	23.9	27.6
8	2	26.1	28.1
1	1	21.1	17.1
3	1	42.7	42.3
5	1	55.1	56.5
1	1	60.6	61.5
5	1	16.2	15.1
0	4	11.6	16.1
2	4	10.4	44.1
4	4	44.0	50.1
8	4	34.1	19.1
1	5	21.4	26.2
1	1	19.4	22.2
******* L = 1 *******			
-1	1	142.8	141.2
1	1	19.1	68.1
-8	1	11.0	21.6
5	1	61.8	21.7
-5	1	55.9	80.8
1	1	15.9	21.6
-1	1	49.0	52.1
7	1	14.1	19.8
3	3	18.8	12.4
2	2	62.2	15.0
-2	2	41.8	18.0
-4	2	12.8	15.9
4	2	11.2	27.1
-6	2	11.1	12.4
6	2	28.8	25.4
-8	2	48.0	14.1
1	1	80.8	19.1
-1	1	29.5	14.6
1	1	21.2	16.1
-5	1	40.5	40.1
-1	1	55.2	51.1
1	1	12.9	14.1
-7	1	11.4	11.2
0	4	28.9	12.4
-2	4	11.5	18.2
6	4	12.4	10.9
1	5	11.0	20.6
-1	5	12.1	16.5
0	6	10.4	10.7
-4	6	21.4	29.2
******* L = 2 *******			
0	0	101.6	118.1
-2	0	164.5	120.5
2	0	51.1	52.1
-4	0	112.1	102.4
4	0	11.4	62.1
-6	0	22.1	24.3
6	0	12.1	10.6
-8	0	16.1	22.9
-11	0	20.9	24.6
-1	1	69.5	16.2
1	1	6.8	11.9
-1	1	6.9	2.6
5	1	16.2	9.5
-5	1	8.2	1.9
-2	1	16.2	11.1
7	1	10.2	1.6
9	1	13.1	12.5
0	2	10.4	64.1
-2	2	115.7	102.2
2	2	15.6	1.1
4	2	41.5	45.1
-6	2	12.2	13.1
6	2	42.1	45.5
10	2	12.8	11.9
1	1	10.4	26.5
1	1	21.1	20.6
-1	1	16.9	22.4
-5	1	54.6	41.6
5	1	51.5	55.9
-1	3	15.9	12.5
1	3	29.1	15.9
-9	1	25.6	44.1
9	1	26.6	6.7
0	4	14.4	1.6
2	4	45.2	46.4
-4	4	24.6	11.8
-6	4	11.4	19.2
-1	5	11.5	21.5
1	5	20.1	10.6
5	5	29.4	15.6
1	5	29.5	11.2
0	6	16.6	16.9
-2	6	10.9	11.9
2	6	18.1	23.2
******* L = 3 *******			
-1	1	55.2	48.1
1	1	112.8	106.0
-3	1	41.2	17.1
-5	1	40.1	40.2
5	1	21.7	20.5
1	1	18.7	42.7
-9	1	14.6	10.6
0	2	13.4	22.6
-2	2	45.7	16.5
2	2	51.6	86.8
-1	2	14.4	15.8
1	2	20.1	26.5
5	2	12.2	11.8
-1	2	11.1	36.2
-1	1	50.2	55.4
1	1	18.1	22.6
-1	1	41.2	45.4
1	1	26.1	15.9
-5	1	25.1	15.8
-1	1	14.5	15.5
1	1	16.5	10.1
7	1	27.0	25.1
3	4	29.4	24.1
1	4	15.1	14.4
5	4	64.6	25.1
1	5	27.1	12.1
-1	5	16.1	42.1
-1	5	61.2	19.8
8	5	45.1	11.9
-7	5	14.0	17.5
1	1	21.1	20.1
1	1	21.7	11.6
7	5	21.8	14.6
******* L = 4 *******			
1	0	55.1	56.5
1	0	11.2	64.5
-1	0	14.1	18.4
5	0	54.5	46.5
-5	0	11.4	7.4
-1	1	20.2	21.1
1	1	42.2	45.9
-1	1	42.2	50.2
1	1	12.9	21.9
-5	1	61.4	54.4
-8	1	45.2	17.8
8	1	11.5	15.1
-1	1	10.0	11.8
1	1	21.5	25.5
1	2	112.5	106.4
-2	2	11.7	14.0
-1	2	22.9	62.8
1	2	22.5	12.2
-1	2	65.1	61.8
6	2	12.1	19.6
-1	2	14.1	15.6
3	2	41.4	19.8
-11	2	15.6	9.9
-1	1	11.2	12.5
1	1	21.8	21.0
-5	3	25.2	25.9
-9	3	12.4	14.4
1	4	11.5	11.1
-5	4	16.3	14.5
-1	4	21.9	29.7
1	4	22.2	19.8
-1	5	12.1	28.1
1	5	50.2	51.1
-7	5	31.1	35.1
3	5	40.6	41.5
-5	5	11.5	27.2
5	5	14.4	15.1
0	6	46.1	44.1
-4	6	14.9	14.6
4	6	20.9	11.1
-1	2	18.4	11.4
1	1	11.1	9.2
******* L = 5 *******			
1	1	65.2	25.9
1	1	51.6	59.2
-5	1	55.1	59.8
5	1	11.6	14.4
-2	1	11.9	12.2
1	6	46.1	51.1
-7	2	21.8	16.2
1	2	24.8	25.0
-9	2	21.2	22.1
-1	1	11.9	11.8
1	1	31.9	11.6
-1	1	33.8	14.4
3	3	21.6	21.2
-1	1	41.7	42.6
-1	1	42.7	19.6
1	4	30.6	15.9
3	4	22.5	21.6
-2	4	12.1	15.2
-4	4	21.9	25.3
7	4	25.5	25.1
-1	4	14.9	11.4
-1	5	16.1	41.1
1	5	40.4	20.9
-1	5	46.1	11.2
1	5	19.5	11.1
-1	5	23.6	21.8
******* L = 6 *******			
-1	0	20.4	20.1
-1	0	8.1	9.1
5	0	67.6	14.1
-1	0	24.9	25.1
1	1	16.1	20.6
-11	1	11.6	5.5
-1	1	24.4	11.8
1	1	21.0	19.5
-1	1	12.8	10.5
-1	1	52.1	54.5
1	1	21.1	22.4
-9	1	21.4	25.9
3	2	51.8	51.0
-3	2	40.8	42.6
2	2	51.8	50.1
4	1	10.9	11.1
-8	2	51.9	53.2
-6	2	40.8	55.1
-1	2	67.1	65.1
0	2	11.1	1.7
-1	3	36.5	16.2
1	1	19.1	15.4
-1	3	9.6	31.5
-5	1	17.1	12.0
5	3	10.9	9.3
7	1	12.9	11.9
1	4	41.3	51.8
-1	4	11.9	10.9
-4	4	21.1	16.9
-5	4	11.0	11.1
-1	1	44.1	52.9
1	5	34.5	34.3
-1	5	13.7	25.9
-5	5	25.8	21.1
-1	5	11.8	11.1
7	6	29.6	23.6
-2	6	11.1	17.3
2	6	15.0	14.1
******* L = 7 *******			
1	1	15.4	16.5
5	1	27.1	27.0
1	1	28.5	23.6
3	2	14.7	0.9
-2	2	13.9	20.1
-4	2	19.1	26.6
7	2	23.1	23.9
-1	1	22.1	21.4
1	1	25.1	22.7
-3	5	12.9	15.9
******* L = 8 *******			
3	3	11.9	45.0
3	0	10.9	16.1
-2	0	26.5	29.1
4	0	55.1	69.1
-4	0	61.0	49.1
-6	0	41.4	46.4
6	0	34.4	56.1
-8	0	15.5	16.3
5	1	12.2	11.7
-1	1	15.4	14.8
0	2	11.5	6.9
-2	2	11.1	15.0
2	2	22.5	14.1
-6	2	11.6	18.4
-1	3	41.5	11.9
1	1	19.1	11.1
-3	1	10.1	12.2
1	1	23.1	16.1
-5	3	11.2	23.7
5	1	25.1	18.2
-1	1	11.5	19.1
3	4	55.1	48.4
-2	4	50.1	44.5
3	4	11.0	19.9
-6	4	11.9	17.7
-8	4	11.5	12.2
******* L = 9 *******			
-1	1	22.2	21.2
1	1	48.1	47.5
-1	1	16.1	15.8
1	1	11.5	19.1
-5	1	25.9	26.6
5	1	18.5	21.1
-7	1	18.1	11.5
-2	2	21.5	29.7
-4	1	21.6	12.6
-6	2	15.1	22.7
-1	1	21.5	24.6
1	1	11.7	9.2
-3	3	11.6	24.8
-5	1	30.1	13.7
-1	3	18.5	11.0
******* L = 10 *******			
3	3	41.1	42.8
-2	0	23.8	11.1
2	0	45.7	44.5
-4	0	41.1	45.5
4	0	30.1	11.6
-6	0	25.5	24.0
-4	2	12.4	6.4
-1	1	20.8	14.5
1	1	14.6	14.6
-3	1	24.6	25.6
1	1	10.1	14.1
-5	3	21.3	21.8
2	4	19.3	12.5
0	4	11.4	1.6
-2	4	21.5	15.0
-1	4	24.3	27.2
******* L = 11 *******			
-4	2	11.6	17.0
******* L = 12 *******			
0	2	20.1	22.4
-2	2	10.9	12.3

Discussion

The molecular structure, shown in Figure 1, is the first determined for a trimeric aluminum compound. Figure 2 shows the configuration of the ring viewed down the twofold axis and Figure 3 shows the unit cell contents as viewed in the same direction as Figure 2. It is evident that the external groups are essentially perpendicular to the plane of the ring. The inferior quality of the crystals which could be obtained for this study led to relatively large standard deviations for the bond lengths and angles; however, the general structural features are unambiguous. The average aluminum–nitrogen bond length of 1.91 Å is shorter than that found (2.01 Å) in the four-membered ring system in $(CH_3)_5Al_2N(C_6H_5)_2$.[13] In addition, the aluminum–nitrogen–aluminum bond angle of 119–120° is significantly greater than the tetrahedral value. These results suggest the possibility of sp^2 hybridization of the nitrogen atom, with one hybrid orbital directed into the ethylenimino ring. The mean aluminum–carbon bond length of 1.96 Å is typical of terminal distances reported in other organoaluminum compounds.[14,15] Carbon–aluminum–

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Table II. Final Atomic Positional Parameters and Temperature Factors

Atom	x/a	y/b	z/c	B
Al(1)	0.0000	0.5142 (13)	0.2500	a
Al(2)	−0.0109 (6)	0.2245 (10)	0.1373 (6)	b
N(1)	0.0000	0.1249	0.2500	5.52 (74)
N(2)	0.0731	0.3897	0.3339	6.26 (54)
C(1)	0.1309 (21)	0.2591 (29)	0.1031 (18)	8.26 (77)
C(2)	−0.1007 (23)	0.1233 (34)	0.0463 (20)	9.94 (99)
C(3)	0.0945 (22)	0.6258 (30)	0.1856 (18)	8.42 (83)
C(4)	0.0546	−0.0058	0.2417	8.34 (84)
C(5)	0.1873	0.3950	0.3396	8.88 (87)
C(6)	0.1337	0.4645	0.4082	8.04 (82)

Group	x/a	y/b	Rigid Group Parameters[c] z/c	ϕ	θ	ρ
1	0.0000	0.1249 (24)	0.2500	0.000	0.000	0.168 (40)
2	0.0731 (14)	0.3897 (20)	0.3339 (13)	−1.219 (25)	0.481 (22)	0.894 (31)

[a] β_{11} = 0.0081 (10), β_{22} = 0.0182 (23), β_{33} = 0.0081 (9), β_{12} = 0.0, β_{13} = 0.0037 (7), β_{23} = 0.0. [b] β_{11} = 0.0055 (7), β_{22} = 0.0235 (19), β_{33} = 0.0090 (6), β_{12} = −0.0012 (9), β_{13} = 0.0001 (5), β_{23} = −0.0034 (9). [c] As described by C. Scheringer in *Acta Cryst.*, **16**, 546 (1963).

Table III. Bonded Interatomic Distances (Å) and Angles (deg)

	Rigid body	Anisotropic with hydrogen atoms
Al(1)–N(2)	1.93 (2)	1.91 (2)
Al(2)–N(1)	1.95 (1)	1.94 (1)
Al(2)–N(2)	1.90 (2)	1.88 (2)
Al(1)–C(3)	1.99 (3)	1.96 (2)
Al(2)–C(1)	2.01 (3)	1.98 (2)
Al(2)–C(2)	1.97 (3)	1.94 (2)
N(2)–C(5)		1.48 (2)
N(2)–C(6)		1.52 (2)
C(5)–C(6)		1.46 (3)
N(1)–C(4)		1.41 (2)
C(4)–C(4)		1.46 (3)
N(2)–Al(1)–N(2)′	101.0 (0.9)	100.8 (1.2)
N(1)–Al(2)–N(2)	103.0 (0.8)	102.4 (1.0)
C(3)–Al(1)–C(3)′	112.8 (1.1)	114.6 (1.0)
Al(2)–N(1)–Al(2)′	119.5 (0.4)	120.4 (0.9)
Al(1)–N(2)–Al(2)	120.2 (0.6)	121.2 (1.0)
C(1)–Al(2)–C(2)	113.7 (1.2)	114.4 (1.1)
C(5)–N(2)–C(6)		58.1 (1.3)
C(6)–C(5)–N(2)		62.4 (1.3)
C(5)–C(6)–N(2)		59.5 (1.3)
C(4)–N(1)–C(4)		62.7 (1.5)
C(4)–C(4)–N(1)		58.7 (1.5)

Table IV. Nonbonded Interatomic Distances (Å)

C(1)–C(2)	3.33 (4)	C(3)–C(3)′	3.31 (3)
C(3)–C(5)	3.37 (3)	C(2)′–C(5)	3.44 (3)
C(1)–C(5)	3.79 (3)	C(2)′–C(6)	3.47 (3)
C(3)–C(6)	3.68 (3)	C(3)′–C(6)	3.53 (3)

carbon bond angles range from 112.8 to 113.7°, and as such are smaller than the corresponding angles in electron-deficient organoaluminum compounds.[14,15]

The closest approach of methyl carbon atoms to ethylenimino carbon atoms is 3.37 Å. In order to evaluate the steric interaction of such nonbonded groups, the ethylenimino groups were replaced by dimethylamino groups. (Parameters for the latter were taken from a study of bis(dimethylamino)beryllium.[16]) The assumption was made that the theoretical dimethylaminodimethylaluminum trimer would have essentially the same configuration as the ethyleniminodimethylaluminum trimer. Distance calculations show that in the dimethylamino trimer the closest approach between aluminum methyl carbon atoms and dimethylamino carbon atoms is 3.16 Å. Thus, nonbonded steric interactions are certainly less severe in the case of the ethylenimino trimer, but the electron distribution about the bridging nitrogen atom may well prove important to the dimer–trimer stability.

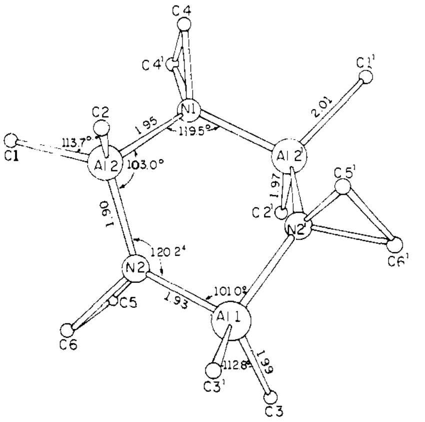

Figure 1. Molecular structure of the ethyleniminodimethylaluminum trimer.

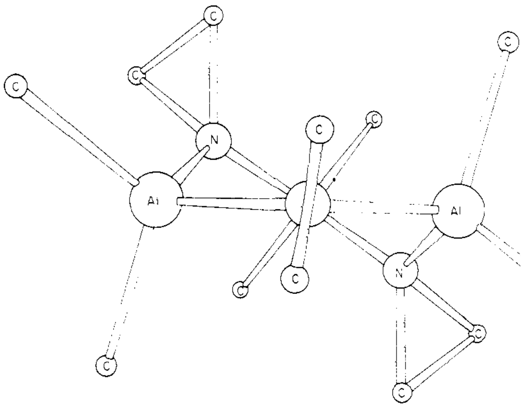

Figure 2. Molecular configuration of the ethyleniminodimethylaluminum trimer viewed down the crystallographic twofold axis.

(14) R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.,*. **89**, 3121 (1967).

(15) J. L. Atwood and G. D. Stucky, *ibid.*, **91**, 2538 (1969)9

(16) J. L. Atwood and G. D. Stucky, *ibid.*, **1**, 4426 (1969).

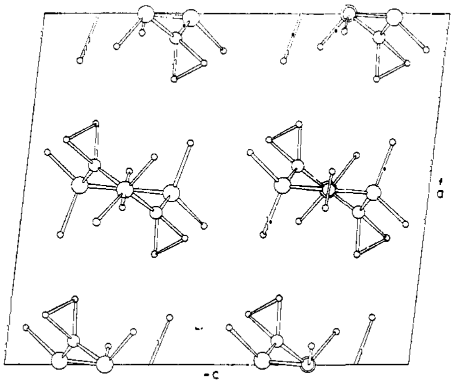

Figure 3. Packing in $[(CH_3)_2AlN(CH_3)_2]_3$ crystals as viewed along [010].

Table V. Association of Organoaluminum Compounds

Dimers (Four-Membered Ring Systems)	
$[(CH_3)_2Al\cdot N(CH_3)_2]_2$[a]	$[(C_2H_5)_2Al\cdot N(C_2H_5)_2]_2$[b]
$[(i\text{-}C_4H_9)_2Al\cdot N(CH_3)_2]_2$[b]	$[(CH_3)_2Al\cdot N(C_6H_5)_2]_2$[c]
$[(CH_3)_2Al\cdot NC(t\text{-}C_4H_9)(CH_3)]_2$[d]	$[(CH_3)_2Al\cdot NC(C_2H_5)(CH_3)]_2$[d]
$[(CH_3)_2Al\cdot NHSi(CH_3)_3]_2$[e]	$[(CH_3)_2Al\cdot OSi(CH_3)_3]_2$[f]
$[(C_2H_5)_2Al\cdot OC_2H_5]_2$[g]	$[(C_2H_5)_2Al\cdot OC_4H_9]_2$[g]
$[(C_2H_5)_2Al\cdot P(C_2H_5)_2]_2$[h]	$[(CH_3)_2Al\cdot P(C_6H_5)_2]_2$[c]
$[(C_2H_5)_2Al\cdot P(C_6H_5)_2]_2$[h]	$[(CH_3)_2Al\cdot SCH_3]_2$[a,m]
$[(CH_3)_2Al\cdot As(C_6H_5)_2]_2$[c]	
Trimers (Six-Membered Ring Systems)	
$[(CH_3)_2Al\cdot N(CH_2)_2]_3$[i]	$[H_2Al\cdot N(CH_3)_2]_3$[j]
$[(C_2H_5)_2Al\cdot NH_2]_3$[k]	$[(CH_3)_2Al\cdot OCH_3]_3$[a]
$[(C_2H_5)_2Al\cdot OCH_3]_3$[g]	$[H_2Al\cdot P(C_2H_5)_2]_3$[l]
$[(CH_3)_2Al\cdot P(CH_3)_2]_3$[a]	

[a] See ref 8. [b] W. P. Newmann, *Ann.*, **667**, 1 (1963). [c] G. E. Coates and J. Graham, *J. Chem. Soc.*, 233 (1963). [d] G. E. Coates, "Organometallic Compounds," Methuen, London, 1967, p 311. [e] H. Schmidbaur and M. Schmidt, *Angew. Chem. Intern. Ed.*, **1**, 327 (1962). [f] H. Schmidbaur, *ibid.*, **4**, 152 (1965). [g] E. G. Hoffmann, *Ann.*, **629**, 104 (1960). [h] K. Issleib and H. J. Deylig, *Z. Naturforsch.*, *B*, **17**, 198 (1962). [i] This study. [j] J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 1798 (1961). [k] M. Cohen, J. K. Gilbert, and J. D. Smith, *J. Chem. Soc.*, 1092 (1965). [l] G. Fritz and G. Trenczek, *Z. Anorg. Allgem. Chem.*, **331**, 206 (1964). [m] See ref 18.

The arguments of Coates[2] concerning the role of entropy and steric factors in determining the final association of organoaluminum compounds seem well founded as illustrated in Table V. Gillespie[17] has recently suggested that ring strain is not so important in compounds of elements of the second or third period as with those of first-row elements. This appears to be true in $[(CH_3)_2AlSCH_3]_2$, reportedly a dimer in the gas phase (but see ref 18), where steric interactions would not preclude the formation of a trimer or higher polymer as observed for its congener, $[(CH_3)_2AlOCH_3]_3$. The question then arises as to why the opposite associations are observed for $[(CH_3)_2AlN(CH_3)_2]_2$ and $[(CH_3)_2AlP(CH_3)_2]_3$.

The proton magnetic resonance spectrum of the ethyleniminodimethylaluminum trimer in cyclopentane shows two peaks (τ 8.14 and 11.00) in the expected ratio 2:3. At room temperature, there is no evidence that the methyl groups of the complex exchange with those of trimethylaluminum in a mixture of the two compounds.

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(17) R. S. Gillespie, *Angew. Chem. Intern. Ed.*, **6**, 819 (1967).

(18) In the solid state, $(CH_3)_2AlSCH_3$ is not a dimer but an infinite polymer. This structure is described in ref 1.