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The Crystal Structure of the Aluminum Hydride-*N,N,N',N'*-Tetramethylethylenediamine Adduct

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The aluminum hydride-*N,N,N',N'*-tetramethylethylenediamine adduct crystallizes as clear, colorless, needle-like orthorhombic crystals. The cell dimensions are:

$$a = 9.554 \pm 0.004, \quad b = 17.241 \pm 0.009, \quad c = 11.866 \pm 0.006 \text{ \AA}.$$

The space group is $P2_12_12_1$ and there are eight formula weights per unit cell. A total of 2300 reflections was measured with the use of a proportional counter and copper radiation. The structure was refined by least-squares methods to a final residual R of 6.4%.

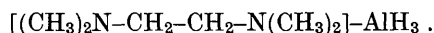
The crystal is composed of infinite chains of alternating aluminum hydride and diamine units. The aluminum atom is pentacoordinated with three hydrogen atoms (in the equatorial plane) and two nitrogen atoms at the corners of a trigonal bipyramid. The bidentate diamine unit is in the *trans* configuration.

Introduction

Recently an interest has arisen in the amine adducts of both aluminum hydride (or alane) and trimethylaluminum. The increased activity in this area has produced a number of interesting compounds in which aluminum apparently has fivefold coordination. The only direct evidence available for this unusual coordination for aluminum is the crystal structure determination of bis-trimethylamine alane by Heitsch, Nordman & Parry (1963). Unfortunately, there was disorder in the crystal and the structure could not be determined with high precision.

The Chemistry Division of the Naval Ordnance Laboratory, Corona, California has prepared a number of amine and substituted hydrazine adducts of both trimethylaluminum and alane. Since a number of these compounds were readily available, we decided to investigate the structures of several of the adducts. The final goals were: a better understanding of the bonding in these adducts, elucidation of the apparent fivefold coordination for aluminum, and a precise determination of the aluminum-nitrogen bond distance under varying conditions.

The following is a study of the structure of the *N,N,N',N'*-tetramethylethylenediamine-alane adduct,



This compound was first prepared by Davidson & Wartik (1960). They proposed a hydrogen-bridged dimer for the structure of the adduct in which the aluminum was six-coordinate. This proposal made it unnecessary to invoke fivefold coordination for the aluminum. The structure proposed by Davidson & Wartik (1960) is actually only one of several possible isomers. The structure of this compound appeared

to be of definite interest and thus was chosen for further study.

Experimental

The adduct was prepared by repeated treatment of bis-trimethylamine alane with *N,N,N',N'*-tetramethylethylenediamine. Because of the reactive nature of the alane adducts, all operations were carried out in a standard vacuum apparatus. The adduct sublimes readily, and clear prismatic crystals formed on the sides of the sealed and evacuated sample tube. The sample tube was opened in a glove box in an atmosphere of dry nitrogen and several small crystals were transferred to Lindemann-glass capillaries. The open ends of the capillaries were covered with stopcock grease. The capillaries were removed from the glove box and immediately sealed by fusing the glass below the grease-covered ends.

Weissenberg photographs of one of the crystals indicated that the crystals are orthorhombic. The systematic absences observed for a crystal rotating about what was later called the a axis were:

$$\begin{aligned} hkl & \text{ no absences} \\ 0k0 & \text{ absent when } k=2n+1 \\ 00l & \text{ absent when } l=2n+1 \end{aligned}$$

The possible space groups are thus $P2_12_12_1$ (D_2^3) or $P2_12_12_1$ (D_2^4).

The unit-cell dimensions and intensity measurements were carried out by means of a General Electric single-crystal orienter with copper radiation ($\alpha_1 = 1.54051$ and $\alpha_2 = 1.54433$ Å). The unit-cell dimensions were determined by using a narrow beam with a narrow slit at the counter window. The averages of these measurements are given below:

$$a = 9.554 \pm 0.004, \quad b = 17.241 \pm 0.009, \\ c = 11.866 \pm 0.006 \text{ \AA}.$$

The density calculated for eight formula weights per unit cell is 1.01 g.cm^{-3} , a reasonable value for a substance of this type. The experimental density could not be determined because of the reactive nature of the compound.

A survey of the $h00$ reflections using the goniostat indicated that they were absent if $h=2n+1$. Therefore, the most probable space group appeared to be $P2_12_12_1 (D_2^5)$.

The crystal used for the intensity measurements was approximately 0.4 mm by 0.2 mm by 0.2 mm . A proportional counter and reverter (a simple pulse-height selector) were employed in measuring the intensity of 2300 reflections with $2\theta \leq 150.0^\circ$. Of these, 2269 were greater than 1.1 times the background and were regarded as observed reflections. The experimental details have been described more fully elsewhere by the author (Palenik, 1963).

Determination of the structure

Three three-dimensional Patterson syntheses were computed: (1) a sharpened synthesis with the origin peak intact, (2) a sharpened synthesis with the origin peak removed and (3) a synthesis with no sharpening and the origin peak intact. The Harker sections for the second synthesis were plotted and carefully studied. Several peaks were consistent with the three Harker sections, but two in particular were quite outstanding. A comparison of the origin peak in the third synthesis with these Harker peaks indicated that they were possible Al-Al interactions. Using these two peaks, the vectors between non-equivalent aluminum atoms were also located in the second synthesis.

One aluminum atom had x approximately equal to 0, while the other aluminum atom had z approximately equal to $\frac{1}{4}$. It appeared that any superpositions using only equivalent aluminum atoms would retain a false mirror plane in the resulting minimum function. Therefore, three superpositions were carried out; one on an Al(1)-Al(1') vector, one on an Al(1)-Al(2) vector, and the last on an Al(1)-Al(2') vector. The two diamine molecules were easily located in the resulting minimum function.

Refinement of the structure

The first Fourier synthesis was computed from all 2269 observed reflections, the phases being calculated with the use of the contribution of all eighteen of the heavier atoms. The scattering factors for neutral aluminum from Tomiie & Stam (1958), for nitrogen and carbon from Hoerni & Ibers (1954), and for hydrogen from McWeeny (1951) were used in this and

all subsequent computations. The usual residual R (after adjustment of the scale factor) was 27.0%. A second set of positional parameters was obtained by the method described by Booth (1948). A second Fourier synthesis was calculated and a third set of positional parameters was obtained in the same way.

Least-squares refinement was started with the third set of parameters. Individual isotropic thermal parameters were used for each atom, and the full matrix was computed for each cycle. The function minimized was $\sum w \Delta F^2$ where the weighting scheme was:

$$\begin{aligned} \text{if } F(\text{obs}) < 40, \quad w &= F(\text{obs})/40; \\ \text{if } F(\text{obs}) > 200, \quad w &= 200/F(\text{obs}); \\ \text{if } 40 \leq F(\text{obs}) \leq 200, \quad w &= 1.0 \end{aligned}$$

where the limits 40 and 200 are on the scale used in Table 3. The above weighting scheme reflects our prejudice regarding the accuracy of the values of $F(\text{obs})$ and was used in all least-squares calculations. Four cycles of least-squares refinement dropped the

Table 1. Probable hydrogen positions

The hydrogen atom is given followed by the atom to which it is bonded, the position parameters times 10^3 , the bond distance, and the peak height on the second difference map

Atom	x	y	z	Dis- tance (\AA)	Peak height (e.\AA ⁻³)
H(1)-Al(1)	-068	229	144	1.61	0.3
H(2)-Al(1)	088	279	329	1.60	0.3
H(3)-Al(1)	123	156	310	1.50	0.3
H(4)-Al(2)	021	094	-239	1.68	0.4
H(5)-Al(2)	080	-068	-197	1.65	0.3
H(6)-Al(2)	-120	028	-066	1.61	0.3
H(7)-C(1)	428	235	176	1.03	0.4
H(8)-C(1)	322	289	258	0.98	0.5
H(9)-C(1)	333	206	263	0.86	0.4
H(10)-C(2)	271	299	004	1.01	0.4
H(11)-C(2)	101	291	016	1.00	0.4
H(12)-C(2)	165	329	078	0.80	0.2
H(13)-C(3)	257	-014	086	0.94	0.4
H(14)-C(3)	120	-035	096	0.99	0.3
H(15)-C(3)	201	-066	-008	0.96	0.3
H(16)-C(4)	294	082	-180	0.92	0.4
H(17)-C(4)	314	005	-152	0.83	0.4
H(18)-C(4)	366	057	-078	0.84	0.5
H(19)-C(5)	275	120	159	1.10	0.5
H(20)-C(5)	338	163	040	0.99	0.5
H(21)-C(6)	104	149	-051	0.88	0.4
H(22)-C(6)	044	120	029	0.93	0.3
H(23)-C(7)	-049	183	487	0.81	0.3
H(24)-C(7)	-171	204	517	0.76	0.3
H(25)-C(7)	-057	248	519	0.99	0.3
H(26)-C(8)	-209	314	348	1.03	0.3
H(27)-C(8)	-276	273	252	0.96	0.4
H(28)-C(8)	-345	256	396	1.10	0.3
H(29)-C(9)	-252	-072	202	0.90	0.3
H(30)-C(9)	-170	-019	298	0.93	0.3
H(31)-C(9)	-143	-021	173	0.90	0.4
H(32)-C(10)	-463	048	111	0.87	0.4
H(33)-C(10)	-431	-020	086	0.82	0.4
H(34)-C(10)	-331	046	045	1.02	0.5
H(35)-C(11)	-284	110	402	0.84	0.4
H(36)-C(11)	-150	090	371	0.98	0.3
H(37)-C(12)	-223	127	187	0.89	0.5
H(38)-C(12)	-369	133	226	0.93	0.4

Table 2. *Final positional and thermal parameters and the estimated standard deviations for the heavier atoms*

All values have been multiplied by 10^4 . The temperature factor for an atom is of the form $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al(1)	0236	2144	2457	0089	0018	0047	-0011	-0004	-0001
Al(2)	-0043	0124	-1630	0081	0018	0054	-0007	-0002	-0015
σ	0001	0001	0001	0001	0001	0001	0001	0002	0001
N(1)	2106	2235	1396	0086	0016	0043	-0009	-0010	-0002
N(2)	1696	0429	-0510	0079	0019	0047	0002	-0007	-0012
N(3)	-1636	2024	3577	0113	0024	0046	-0026	0017	-0010
N(4)	-3294	0237	2200	0084	0018	0056	-0009	0008	0006
σ	0004	0002	0003	0004	0001	0003	0004	0006	0003
C(1)	3311	2422	2128	0090	0031	0088	-0030	-0032	-0024
C(2)	1916	2873	0578	0136	0022	0062	-0015	0050	0019
C(3)	1830	-0191	0336	0167	0027	0086	-0017	-0076	0021
C(4)	2979	0471	-1205	0083	0039	0067	-0005	-0004	-0038
C(5)	2500	1498	0797	0082	0025	0063	0001	-0003	-0022
C(6)	1355	1186	0021	0086	0021	0060	0003	-0045	-0020
C(7)	-1149	2117	4738	0219	0065	0040	-0098	0006	-0011
C(8)	-2642	2641	3308	0136	0032	0117	0016	0082	-0013
C(9)	-2071	-0290	2270	0096	0032	0122	0017	0062	0011
C(10)	-3890	0189	1059	0142	0037	0051	-0022	-0006	-0001
C(11)	-2293	1243	3510	0142	0029	0060	-0049	0023	0019
C(12)	-2850	1065	2350	0101	0023	0060	-0019	0003	0022
σ	0006	0003	0005	0007	0002	0004	0006	0010	0005

residual R from 22.9 to 11.7% and the weighted sum of the residuals from 17751.3 to 7318.5.

Anisotropic thermal parameters were introduced at this point, and the full matrix was approximated by 3×3 blocks for positional parameters and with 6×6 blocks for the thermal parameters. Partial shifts of 0.75 and 0.50 were used for the positional and thermal parameters, respectively. Since the isotropic refinement had included the interaction between scale and temperature factors, the scale factor (G) was shifted by 0.25 of the amount calculated by dividing $\sum w \Delta F (\partial |F_c| / \partial G)$ by $\sum w (\partial |F_c| / \partial G)^2$. Three cycles reduced R to 8.9% and $\sum w \Delta F^2$ to 4299.9. At this point it seemed reasonable to include the contribution of the 38 hydrogen atoms in the calculation.

A difference Fourier synthesis was calculated and used as a guide to locating the hydrogen atoms. It was assumed that hydrogen atoms bonded to carbon atoms would surround the atom tetrahedrally with an average C-H distance of 1.0 Å. In the case of hydrogen atoms bonded to aluminum atoms, the only assumption was that the Al-H distance would be about 1.5 Å. The hydrogen atoms were all placed in high positive areas in the difference map using the above assumptions. In the majority of the cases, the hydrogen atoms appeared as resolved peaks.

The hydrogen atoms were included in the structure factor calculation for the subsequent least-squares calculations, but their positional and thermal parameters (isotropic B of 6.0) were not refined. Six least-squares cycles using the block approximation were calculated followed by one cycle in which the entire 163×163 matrix was computed.

A second difference Fourier synthesis was calculated

and a final set of hydrogen positions was obtained. These hydrogen atom positions together with their approximate peak heights are given in Table 1. The distance of each hydrogen atom from the atom to which it is bonded is also given in Table 1. One additional least-squares cycle was computed using the full matrix. The final parameters for the heavier atoms are given in Table 2. The standard deviations were obtained from the inverse of the full matrix; the individual values for a given type of atom were averaged and are given in Table 2. The structure factors computed with the parameters given in Tables 1 and 2 are presented in Table 3. The final residual R is 6.4% for the observed reflections.

Results and discussion

While there are 18 independent non-hydrogen atoms in the asymmetric unit of this structure, there are only four chemically distinct types of intramolecular distances: (1) Al-N, (2) N-CH₃, (3) N-CH₂-, and (4) -CH₂-CH₂-. The various intramolecular distances have been calculated and are tabulated in Table 4. In addition the atomic numbering and the distances are illustrated in Fig. 1. The agreement between chemically equivalent distances is good.

The average of the two C-C single bonds is 1.517 ± 0.010 Å, not significantly different from the value of 1.533 ± 0.003 Å suggested by Bartell (1959) for a C-C single bond. Wright & Marsh (1962) found that the average C-C single bond in L-lysine monohydrochloride monohydrate was 1.524 ± 0.003 Å, also in agreement with our value.

The twelve N-C bonds can be divided into two classes, the N-CH₃ bonds and the N-CH₂- bonds.

Table 3. Observed and calculated structure factors

The five columns in each group contain the values, reading from left to right, of k, 10F_o, 10F_c, 10A_c, 10B_c. A negative F_o indicates an unobserved reflection which was not included in the least-squares refinement

Table with multiple columns of numerical data representing structure factors for various reflections. The table is organized into groups, each with a header (e.g., H=0110, H=0111) and five columns of values. The values are integers, some positive and some negative, representing the observed and calculated structure factors.

Table 3 (cont.)

9 84 73 66 -31	2 94 07 97 7	5 144 154 127 -80	13 133 113 111	6 50 40 -16 41	13 14 94 -82 44	11 66 56 -0 -40	6 74 64 61 -51
10 188 104 95 161	3 59 07 -60 10	6 230 214 -104 214	14 60 48 -0 -0	7 11 10 10 -0	14 14 11 -0 -0	7 12 11 -0 -0	7 12 11 -0 -0
11 200 211 -44 -104	4 67 07 08 1	7 370 354 -144 -144	15 144 144 -144 -0	8 35 32 32 -11	15 14 31 -05 32	8 12 11 -0 -0	8 12 11 -0 -0
12 38 14 34 -11 0	5 102 114 -11 -13	8 108 117 -11 108	16 144 144 -144 -0	9 22 130 65 -1	16 14 31 -05 32	9 12 11 -0 -0	9 12 11 -0 -0
13 121 121 121 -11 0	6 121 114 -11 108	9 114 114 -11 108	17 144 144 -144 -0	10 30 30 30 -0	17 14 31 -05 32	10 12 11 -0 -0	10 12 11 -0 -0
14 64 64 -02 -00	7 102 114 -11 108	10 114 114 -11 108	18 25 22 22 0	11 51 40 -42 24	18 14 31 -05 32	11 12 11 -0 -0	11 12 11 -0 -0
15 64 64 -02 -00	8 90 92 -01 14	11 114 114 -11 108	19 114 114 -11 108	12 51 40 -42 24	19 14 31 -05 32	12 12 11 -0 -0	12 12 11 -0 -0
16 64 64 -02 -00	9 80 92 -01 14	12 114 114 -11 108	20 114 114 -11 108	13 51 40 -42 24	20 14 31 -05 32	13 12 11 -0 -0	13 12 11 -0 -0
17 58 52 -1 -42	10 50 57 50 27	13 114 114 -11 108	21 114 114 -11 108	14 51 40 -42 24	21 14 31 -05 32	14 12 11 -0 -0	14 12 11 -0 -0
18 58 52 -1 -42	11 50 57 50 27	14 114 114 -11 108	22 114 114 -11 108	15 51 40 -42 24	22 14 31 -05 32	15 12 11 -0 -0	15 12 11 -0 -0
19 82 84 1 -84	12 64 74 -00 -41	15 114 114 -11 108	23 114 114 -11 108	16 51 40 -42 24	23 14 31 -05 32	16 12 11 -0 -0	16 12 11 -0 -0

Table 4. *Intramolecular distances and angles*

Atoms	Distance	Atoms	Angle
Al(1)-N(1)	2.192 Å	N(1)-Al(1)-N(3)	178.0°
Al(1)-N(3)	2.238	N(2)-Al(2)-N(4)	176.5
Al(2)-N(2)	2.192		
Al(2)-N(4)	2.200	Al(1)-N(1)-C(1)	108.3
N(1)-C(1)	1.477	Al(1)-N(1)-C(2)	109.3
N(1)-C(2)	1.477	Al(1)-N(3)-C(7)	107.2
N(2)-C(3)	1.472	Al(1)-N(3)-C(8)	109.1
N(2)-C(4)	1.479	Al(2)-N(2)-C(3)	107.8
N(3)-C(7)	1.463	Al(2)-N(2)-C(4)	107.6
N(3)-C(8)	1.469	Al(2)-N(4)-C(9)	111.1
N(4)-C(9)	1.482	Al(2)-N(4)-C(10)	106.6
N(4)-C(10)	1.471	Al(1)-N(1)-C(5)	114.5
		Al(1)-N(3)-C(11)	112.9
N(1)-C(5)	1.505	Al(2)-N(2)-C(6)	107.5
N(2)-C(6)	1.486	Al(2)-N(4)-C(12)	113.5
N(3)-C(11)	1.488		
N(4)-C(12)	1.500	C(5)-N(1)-C(1)	105.5
		C(5)-N(1)-C(2)	110.4
C(5)-C(6)	1.527	C(6)-N(2)-C(3)	111.5
C(11)-C(12)	1.507	C(6)-N(2)-C(4)	112.0
		N(1)-C(5)-C(6)	113.7
Probable errors		N(2)-C(6)-C(5)	114.1
Al-N	± 0.004	N(3)-C(11)-C(12)	112.5
N-C	± 0.007	N(4)-C(12)-C(11)	113.8
C-C	± 0.008		

The average N-CH₃ distance is 1.474 ± 0.005 Å and the average N-CH₂- is 1.495 ± 0.008 Å. These distances are in agreement with the generally accepted value of 1.479 Å (*International Tables for X-ray Crystallography*, 1962). Following the suggestion of Cruickshank & Robertson (1953), the difference of 0.021 Å between the two types of N-C bonds is on the borderline (*t*₀ = 2.6) of being significant. The lengthening of the N-CH₂- bond can be explained

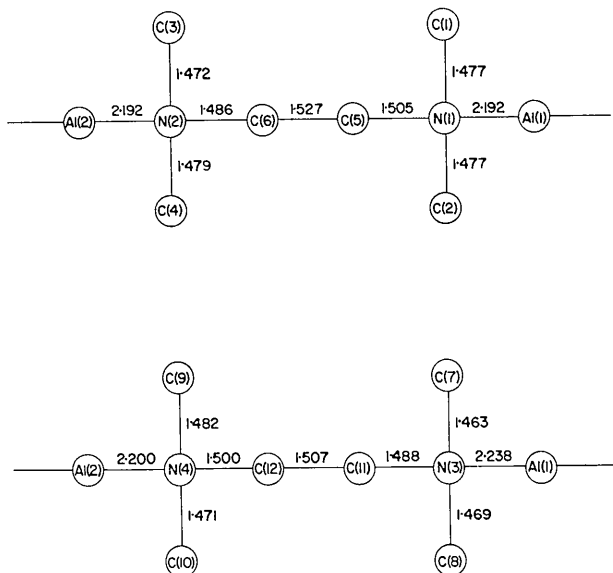


Fig. 1. The atom numbering and bond distances in the two crystallographic tetramethylethylenediamine units.

either by a steric repulsion effect or by an electro-negativity difference between -CH₃ and -CH₂-. A view down the N-C bond in the N-CH₂- case is given in Fig. 2(a). It is interesting to note that the Al(2) atom is *trans* to C(5), the position of minimum repulsion. Repulsion between C(5) and both C(3) and C(4) could cause a slight elongation of the bond, N-CH₂-, compared with a N-CH₃ bond. Another possible explanation would be the difference between a methyl group and the -CH₂- group. The methyl group is generally considered to be the most electro-negative of the alkyl groups.

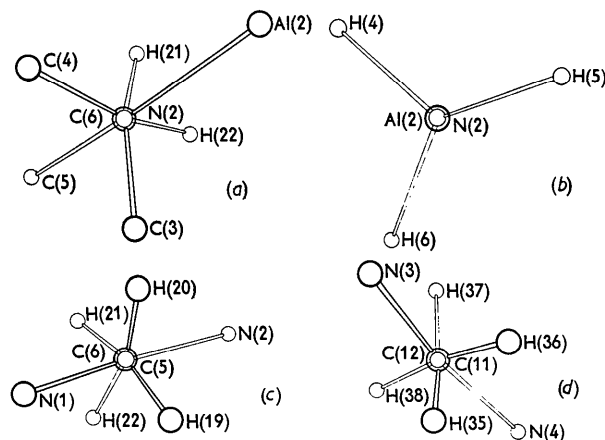


Fig. 2. Views down various bonds in the molecule: (a) the N(2)-C(6) bond, (b) the N(2)-Al(2) bond, (c) the C(5)-C(6) bond and (d) the C(11)-C(12) bond.

The Al-N bonds are the most precisely determined bond distances in the present study, but unfortunately present certain difficulties. Three of the four bonds are in good agreement with the average distance of 2.195 ± 0.004 Å. The fourth bond distance of 2.238 Å is significantly longer. The Al-N distance of 2.18 ± 0.01 Å reported by Heitsch, Nordman & Parry (1963) for H₃Al[N(CH₃)₃]₂ is in agreement with the shorter Al-N distance. There appears to be no reason to expect the fourth bond to be longer and it is felt that this value should be regarded with suspicion. It should be noted that while the Al(1)-N(3) distance is the longest of the Al-N bonds, the N(3)-C(7) and N(3)-C(8) bonds are the shortest of the N-CH₃ bonds. It is possible that there is a strong interaction in this group of atoms and the block approximation is inadequate in this case. While it would be interesting to repeat the refinement using only the full matrix, it is questionable whether the expenditure of time and effort would be profitable.

The thermal parameters given in Table 2 were converted to mean-square displacements and direction cosines and are tabulated in Table 5. The displacements are not unusual for a covalent type molecule. As expected, the methyl groups have the highest

Table 5. Root-mean-square displacements calculated from the thermal parameters

Atom	$(r^2)^{\frac{1}{2}}*$	Direction cosines†			Atom	$(r^2)^{\frac{1}{2}}$	Direction cosines		
Al(1)	207	9487	-2829	-1412	C(4)	271	-0248	7969	-6036
	183	1330	-0480	9900		198	-9530	1630	2551
	160	2868	9580	0080		179	-3020	-5816	-7554
Al(2)	207	-1878	4935	-8492	C(5)	231	0497	5792	-8137
	194	-9639	0736	2559		195	9982	-0555	0214
	152	-1888	-8666	-4619		172	0327	8133	5809
N(1)	203	9541	-1835	-2366	C(6)	239	5786	3249	-7481
	175	1876	-2496	9500		185	7003	-6681	2515
	151	2334	9508	2037		150	4181	6694	6141
N(2)	198	6169	4215	-6646	C(7)	375	-7182	6943	-0456
	187	7860	-3728	4932		244	-6950	-7126	0962
	155	0399	8267	5613		166	-0344	-1008	-9943
N(3)	243	-8605	4472	-2441	C(8)	314	5424	-0379	8393
	182	-4629	-4862	7412		239	6008	7158	-3560
	168	-2128	-7508	-6254		196	5873	-6973	-4110
N(4)	205	-6360	-0024	-7716	C(9)	308	3475	1617	9236
	197	-7153	3771	5884		220	3214	9048	-2793
	156	-2895	-9262	2416		190	8809	-3940	-2624
C(1)	264	1013	4336	-8954	C(10)	267	-8614	5067	0343
	237	7118	-6604	-2393		225	-5008	-8587	1088
	160	6951	6131	3755		190	-0846	-0765	-9935
C(2)	266	-8798	0162	-4751	C(11)	279	8589	-5120	0130
	215	-3534	6462	6764		225	2628	4623	8469
	150	-3179	-7630	5628		155	4397	7239	-5316
C(3)	309	-7858	2154	5798	C(12)	231	5779	-5748	-5794
	220	-6120	-4072	-6780		215	7577	1141	6426
	190	-0900	8876	-4517		156	3032	8103	-5014

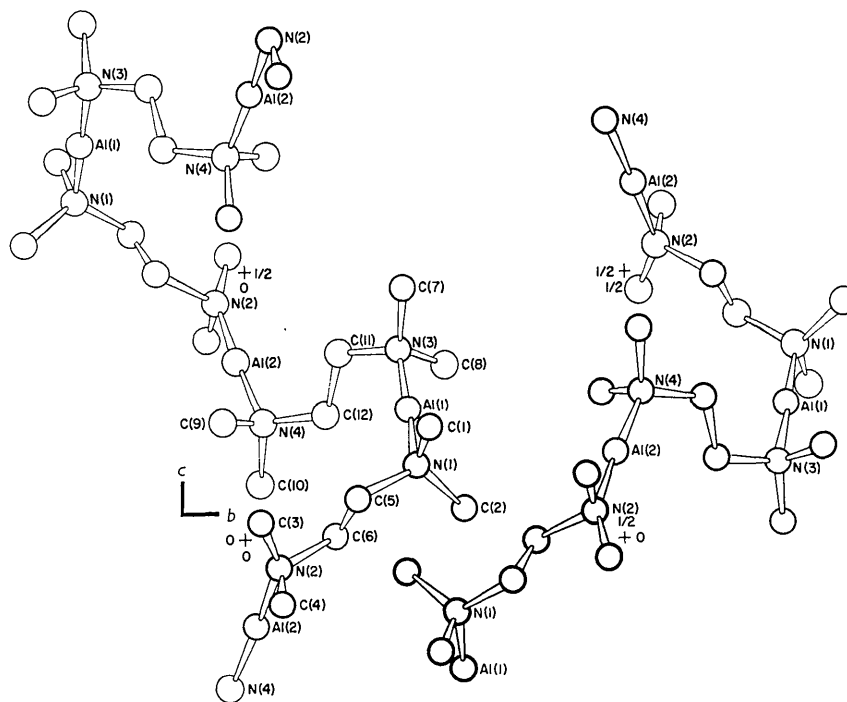
* Values times 10^3 , in Ångström units.† Values times 10^4 (cosines are given with respect to **a**, **b**, **c**).

Fig. 3. Projection on the (100) plane illustrating the relationship of two of the infinite chains.

mean square displacement, since they are restrained only by the one N-CH₃ bond.

In the solid state the complex forms infinite chains of alternating aluminum hydride and *N,N,N',N'*-tetramethylethylenediamine units. Portions of two of these chains projected onto the (100) plane are illustrated in Fig. 3. All the intermolecular distances less than 4.0 Å were computed. As expected for a compound of this type, the van der Waals contacts between the chains are between hydrogen atoms. The hydrogen-hydrogen contacts of less than 2.7 Å are tabulated in Table 6. Except for three short contacts, the distances average 2.61 Å, in reasonable agreement with the 2.4 Å value suggested by Pauling (1960).

Table 6. *Intermolecular distances*

X	Y	Molecule	Distance
H(8)-C(1)	H(29)-C(9)	<i>A</i>	2.53 Å
H(8)-C(1)	H(24)-C(7)	<i>D</i>	2.67
H(9)-C(1)	H(5)-Al(2)	<i>C</i>	2.57
H(10)-C(2)	H(1)-Al(1)	<i>B</i>	2.39
H(10)-C(2)	H(37)-C(12)	<i>B</i>	2.60
H(12)-C(2)	H(34)-C(10)	<i>B</i>	2.62
H(16)-C(4)	H(26)-C(8)	<i>B</i>	2.69
H(19)-C(5)	H(5)-Al(2)	<i>C</i>	2.38
H(23)-C(7)	H(28)-C(8)	<i>D</i>	2.62
H(25)-C(7)	H(28)-C(8)	<i>D</i>	2.27
H(29)-C(9)	H(4)-Al(2)	<i>E</i>	2.69
H(30)-C(9)	H(6)-Al(2)	<i>E</i>	2.58
H(32)-C(10)	H(5)-Al(2)	<i>E</i>	2.56
H(33)-C(10)	H(5)-Al(2)	<i>E</i>	2.57
H(35)-C(11)	H(6)-Al(2)	<i>E</i>	2.58
H(38)-C(12)	H(5)-Al(2)	<i>E</i>	2.48

The distances quoted are from X in the molecule specified by the parameters in Table 1 to Y in the molecule specified by the letters *A-E*. Molecules *A-E* are located as follows:

<i>A</i>	$-x, \frac{1}{2}+y, \frac{1}{2}-z$	<i>D</i>	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$
<i>B</i>	$\frac{1}{2}+x, \frac{1}{2}-y, -z$	<i>E</i>	$\frac{1}{2}-x-1, -y, \frac{1}{2}+z$
<i>C</i>	$\frac{1}{2}-x, -y, \frac{1}{2}+z$		

The conformation around the aluminum atoms is that of a trigonal bipyramid. Two nitrogen atoms from two different diamine molecules occupy the axial positions with N-Al-N angles of 178.0 and 176.5°. The hydrogen atoms around Al(2) were easily located from the difference Fourier synthesis and are located in the three equatorial positions. A view down the Al(2)-N(2) bond is given in Fig. 2(b), illustrating the approximate threefold symmetry of the hydrogen atoms. While the hydrogen atoms around Al(1) were not as well resolved in the difference Fourier synthesis,

the positive areas were located around Al(1) with threefold symmetry.

Joining the aluminum hydride groups is the bifunctional diamine chain in the *trans* configuration. Views down the two C-C bonds are given in Fig. 2(c) and (d) and illustrate the *trans* configuration. This is a departure from the usual *cis* or *gauche* forms of the diamine found when it acts as a bifunctional group.

At least in the solid state the hydrogen-bridged dimer proposed by Davidson & Wartik (1960) is incorrect. Both in this structure and in the H₃Al[N(CH₃)₃]₂ structure, aluminum has fivefold coordination with no hydrogen bridges. In either case a hydrogen bridge could easily provide octahedral coordination for the aluminum atom. It appears that hydrogen-bridges in aluminum compounds may not be as common as expected. If one assumes an Al-H (bridge) distance of 1.7 Å and an Al-H-Al angle of 90°, the Al-Al distance would be 2.4 Å. This Al-Al distance is just twice the single-bond radius for aluminum and might be too short for appreciable stability. This Al-Al distance can be increased slightly by increasing the Al-H-Al angle, but then the hydrogen atoms begin to approach each other with nearly van der Waals contact. It is true that boron in its various hydrides has very close B-B contacts but it is possible that aluminum finds this situation intolerable. It is hoped that further structural work on other aluminum complexes will provide more knowledge in this regard.

References

- BARTELL, L. S. (1959). *J. Amer. Chem. Soc.* **81**, 3497.
 BOOTH, A. D. (1948). *Fourier Technique in X-ray Organic Structure Analysis*, p. 64. Cambridge Univ. Press.
 CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.
 DAVIDSON, J. M. & WARTIK, T. (1960). *J. Amer. Chem. Soc.* **82**, 5506.
 HEITSCH, C. W., NORDMAN, C. E. & PARRY, R. W. (1963). *Inorg. Chem.* **2**, 508.
 HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
International Tables for X-ray Crystallography (1962). Vol. III. p. 276. Birmingham: The Kynoch Press.
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
 PALENK, G. J. (1963). *Acta Cryst.* **16**, 596.
 PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd ed. p. 260. Ithaca: Cornell Univ. Press.
 TOMIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126.
 WRIGHT, D. A. & MARSH, R. E. (1962). *Acta Cryst.* **15**, 54.