Acta Cryst. (1964). 17, 1573

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

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(Received 6 December 1963)

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

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

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,

$$[(CH_3)_2N-CH_2-CH_2-N(CH_3)_2]-AlH_3$$

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:

hkl no absences

0k0 absent when k=2n+1

00*l* absent when l=2n+1

The possible space groups are thus  $P22_12_1$   $(D_2^3)$  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:

## $a = 9.554 \pm 0.004, b = 17.241 \pm 0.009,$ $c = 11.866 \pm 0.006$ Å.

The density calculated for eight formula weights per unit cell is 1.01 g.cm<sup>-3</sup>, 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  $P2_12_12_1$  ( $D_2^4$ ).

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 pulseheight 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:

if 
$$F(\text{obs}) < 40$$
,  $\forall w = F(\text{obs})/40$ ;  
if  $F(\text{obs}) > 200$ ,  $\forall w = 200/F(\text{obs})$ ;  
if  $40 \le F(\text{obs}) \le 200$ ,  $\forall w = 1.0$ 

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(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 103, the bond distance, and the peak height on the second difference map

				Dis-	$\mathbf{Peak}$
				tance	height
$\mathbf{Atom}$	$\boldsymbol{x}$	$\boldsymbol{y}$	z	(Å)	(e.Å-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<sup>4</sup>. The temperature factor for an atom is of the form  $\exp\left[-(\beta_{11}h^{2}+\beta_{22}k^{2}+\beta_{22}l^{2}+\beta_{12}hk+\beta_{12}hl+\beta_{22}kl)\right]$ 

			I L () II	1 22 1 00	112 113	1 40 /			
	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
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	0009	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  $3 \times 3$  blocks for positional parameters and with  $6 \times 6$  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  $\Sigma w \varDelta F(\partial |F_c|/\partial G)$  by  $\Sigma w (\partial |F_c|/\partial G)^2$ . Three cycles reduced R to 8.9% and  $\Sigma w \varDelta F^2$  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  $163 \times 163$  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-CH<sub>3</sub>, (3) N-CH<sub>2</sub>-, and (4) -CH<sub>2</sub>-CH<sub>2</sub>-. 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  $1.517 \pm 0.010$  Å, not significantly different from the value of  $1.533 \pm 0.003$  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 monohydro-chloride monohydrate was  $1.524 \pm 0.003$  Å, also in agreement with our value.

The twelve N-C bonds can be divided into two classes, the N-CH<sub>3</sub> bonds and the N-CH<sub>2</sub>- 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

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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	81 -0 -XX 6 244 1 -1 -0 7 325 21 0 -21 8 176 0 226 10 11 11 -411 0 12 17 204 0 205 13 100	220 211 -61 280 -81 268 147 -140 44 226 -196 113 100 44 -88 141 -147 34 160 -49 140 101 -191 -8	0         64         67         -37         55           10         157         160         -40         -145           11         38         36         -35         7           12         13         7         0         -7           13         69         62         -18         -59           14         79         72         -41         -59           15         69         73         -68         54	HE 2+L2 4 0 240 212 212 0 1 404 417 -151 384 2 414 811 -807 197	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	14. 85 91 -66 -63 16. 68 69 -61 32 17. 68 70 -67 -50 18. 115. 110 -23 -108 19. 84. 84 -70 48 20. 34. 41 23 34	8 50 34 2 -36 9 58 58 1 48 10 66 74 17 74 11 28 44 18 -70 H+ 1+[+]3 0 11 23 -0 13
2 131 1 211 1 211 H= 01(* 3 1 111 114 0 115 5 128 2 202 205 205 -00 6 11 3 96 111 0 111 7 70 4 09 111 111 -0 8 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	174 - 39 - 171 116 -70 - 93 128 - 60 - 112 51 - 12 - 50 87 - 14 - 81 52 - 31 - 42 23 - 21 - 10	H* 1+L+11 0 14 11 0 -13 1 40 43 31 29 2 227 229 9 229 3 16 22 -3 -22 4 18 25 -3 -15	3 496 514 -115 408 4 107 108 -71 81 5 276 108 42 305 6 167 359 -274 231 7 78 54 -53 -8 8 225 234 -277 79 . 9 205 206 20 20 707 10 131 10 -25 127	12 124 120 -107 53 13 62 69 39 57 14 33 43 -60 -14 H= 24L±12 0 234 227 227 -0 1 29 76 -68 36	H: 3+L: 4 0 877 867 0 867 1 45 40 70 2 203 222 -220 13 3 102 104 70 81 4 173 103 47 100 5 151 163 148 -68	0 31 07 07 -57 2 202 180 2 -180 3 84 72 51 51 4 42 35 -31 -17 5 106 93 87 -32 6 67 60 -18 -57 7 30 36 25 25
6         50         51 </td <td>178 -178 0 52 0 52 176 136 -0 не 14 6 -0 6 0 12 164 -164 0 1 12 54 0 -44 2 28 74 74 0 3 12</td> <td>2 106 -106 -0 140 -72 -120 1 271 -197 189 2 118 10 -118</td> <td>5 37 42 -20 3A 6 171 179 138 133 7 120 116 37 110 8 93 87 -31 81 9 18 22 17 12 10 28 24 24 4 11 54 47 23 40</td> <td>11 202 104 -107 26 12 101 304 -298 60 13 80 93 86 37 14 211 223 223 -1 15 74 74 44 -62 16 118 123 -119 33 17 53 47 33 33</td> <td>2 46 40 30 R 3 92 82 30 77 4 238 234 233 -19 5 14 14 15 -5 6 51 40 45 -15 7 80 80 40 43 8 33 23 16 -15</td> <td>6 103 02 -36 R4 7 47 44 -7 44 8 65 6A 6 65 9 167 168 112 124 10 224 227 -122 192 11 100 100 12 -99 12 144 144 24 -142</td> <td>8 62 57 16 -54 9 54 58 57 13 Ha 3-(1214 0 20 23 -23 -0 1 59 56 -48 27 2 68 67 25 -63</td>	178 -178 0 52 0 52 176 136 -0 не 14 6 -0 6 0 12 164 -164 0 1 12 54 0 -44 2 28 74 74 0 3 12	2 106 -106 -0 140 -72 -120 1 271 -197 189 2 118 10 -118	5 37 42 -20 3A 6 171 179 138 133 7 120 116 37 110 8 93 87 -31 81 9 18 22 17 12 10 28 24 24 4 11 54 47 23 40	11 202 104 -107 26 12 101 304 -298 60 13 80 93 86 37 14 211 223 223 -1 15 74 74 44 -62 16 118 123 -119 33 17 53 47 33 33	2 46 40 30 R 3 92 82 30 77 4 238 234 233 -19 5 14 14 15 -5 6 51 40 45 -15 7 80 80 40 43 8 33 23 16 -15	6 103 02 -36 R4 7 47 44 -7 44 8 65 6A 6 65 9 167 168 112 124 10 224 227 -122 192 11 100 100 12 -99 12 144 144 24 -142	8 62 57 16 -54 9 54 58 57 13 Ha 3-(1214 0 20 23 -23 -0 1 59 56 -48 27 2 68 67 25 -63
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 25 5 10 6 12 55 -0 -55 7 13 6 6 8 -0 8 29 71 -0 71 9 11 119 -119 0 10 17	1 748 116 -219 9 99 -61 -90 8 117 -271 141 2 120 -24 10 -296 6 110 -125 17 2 144 -128 86	12 130 124 -65 117 13 29 10 -28 -6 14 39 40 -28 -42 H# 1+L=12 0 43 48 48 0 1 41 45 43 -13	18 41 90 82 -37 19 24 20 4 -19 20 24 30 -22 30 H* 2+L= 5 5 94 103 -0 102 1 105 118 -0 118	9 22 23 20 13 10 85 87 82 6 11 45 45 -15 42 12 35 41 -36 15 He 2(11) 0 35 35 0 25	14 123 131 -31 129 15 66 64 -43 -47 16 69 65 7 -55 17 73 70 -6 69 18 94 91 -0 91 19 32 34 -17 -30	3 52 54 42 17 4 55 58 -18 55 H+ 4+L+ 0 0 565 512 512 -0 1 60 57 -57 0
21 73 82 -0 -8 6 19 7 32 82 -0 -8 6 19 7 32 81 -0 -8 6 19 1 10 -10 - 10 - 10 - 10 - 10 - 10 - 10	27         -22         0         12         16           30         -0         30         13         17           135         -135         0         14         14           34         0         34         15         16           1         1         0         16         15         16           34         0         34         15         16         10           34         0         34         15         16         10           34         0         34         15         16         10           34         0         34         15         16         10           34         0         34         15         16         10           34         0         34         17         17         17	0 174 -32 -174 6 179 -164 -72 8 143 -78 -120 1 173 -103 139 5 102 95 -37 5 122 -121 9 5 141 20 -139	2 132 134 -112 74 3 88 95 -65 -69 4 36 34 19 -31 5 25 24 17 17 6 123 122 8 121 7 27 19 -0 19 8 30 26 4 -26	2 240 244 -217 97 3 65 67 67 -0 4 287 247 747 -144 5 94 107 24 104 6 510 534 -538 -0 7 165 165 -58 151 8 165 165 -5	1         52         43         -39         25           2         54         44         -26         -35           3         27         14         9         -11           4         139         127         117         -40           5         63         57         -26         60           6         78         69         -61         -27           7         43         43         21         35	Ht 3+L 6 0 228 210 -210 -0 1 117 123 -122 10 2 261 264 42 -261 3 111 117 -108 35 4 304 320 -17 317 4 304 320 -17 317	2 78 74 -74 -0 3 180 172 172 -0 4 192 193 193 -0 5 161 121 121 0 6 48 59 59 -0 7 86 60 6° 0 8 231 234 235 -0
3 241 241 0 241 13 40 4 38 52 -52 0 14 81 5 55 40 0 -60 6 274 274 -736 -736 0 7 605 600 0 600 Hz 041 8 68 67 -67 -0 0 133 9 27 26 0 26 1 44	14 0 15 19 1 85 -86 0 20 4 нт 1 117 117 -0 1 18 44 -0 45 2 13	7 71 -72 -9 7 41 8 40 6 404 6 404 5 181 272 -267 1 121 121 -20	0 41 14 -10 28 10 147 140 22 138 11 -16 14 12 8 12 43 46 -29 36 Ha 1.(=13	9 161 163 -116 114 10 463 463 -64 60 11 116 127 -113 46 12 124 111 -67 -100 13 57 48 41 -23 14 60 68 -65 -20 15 110 123 -55 100	8 117 114 116 4 9 20 20 -13 14 HE 241=14 0 173 156 -156 0 1 123 111 12 -110 2 2 2 0 -23	6 147 147 23 -147 7 294 294 -166 274 8 410 401 -72 394 9 299 287 -242 -145 10 175 183 -70 -169 11 26 34 -29 21 12 127 138 4 126	10         160         145         145         -0           11         49         50         50         0           12         31         24         24         0           13         117         117         17         0           14         229         244         244         -0           14         229         244         244         -0           14         129         3         -3         0           16         109         103         -03         0
10 11 11 11 0 2 36 11 31 120 0 320 3 50 12 246 244 -248 0 4 14 13 108 105 0 104 5 -24 14 29 40 -49 0 6 62 15 168 171 0 171 7 6 16 183 184 -184 -0 8 100 19 27 0 22	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 267 176 200 6 429 40 426 2 160 71 143 5 202 41 194 6 129 123 38 5 190 96 164 4 124 90 85	1 86 84 76 17 2 139 110 -34 -126 3 86 85 32 -79 4 66 57 57 4 5 99 84 81 22 6 87 77 32 -70 7 66 67 23 -48	10 144 241 276 411 17 36 34 36 -6 18 35 26 -8 25 19 35 33 -6 32 20 135 144 -155 -20 19 241 6	1 96 91 -24 -87 4 57 57 -57 -0 5 48 46 6 -46 6 35 43 4 -42 H1 2-1-0	13 78 84 -79 -26 14 107 107 -8 107 15 37 35 -10 33 16 68 61 37 55 17 39 38 22 18 120 127 -8 126 19 28 37 -12 -31	17 44 46 -46 -0 18 114 111 111 -0 19 19 23 23 0 20 14 13 -13 -0 H+ 441+1
18 33 30 30 -0 10 155 19 18 1 -0 1 11 38 20 61 61 -61 0 12 -15 H= 0st 7 5 1 56 24 0 -26 1 71	121 121 -0 11 45 0 45 12 4 -8 -0 13 12 14 24 14 24 13 17 0 70 16	1 114 11 11 116 0 47 32 33 6 38 -16 -13 4 124 -23 121 9 265 55 259 8 35 35 -4 3 73 11 -72 6 4 -55	8 51 51 11 -40 9 76 79 79 3 10 79 33 -33 -2 H= 1+L=14 0 26 29 -29 0	0 35 47 43 0 1 281 270 178 -207 2 454 594 486 10h 3 108 104 -54 -90 4 26 21 19 -9 5 142 157 136 78 6 382 392 352 173	1 54 67 0 -43 2 231 208 0 208 3 202 141 0 -181 4 240 252 0 252 5 473 422 422 6 531 543 0 543 7 18 5 0 -5	H= 3+LT 7 n 407 410 -n -410 1 124 125 107 63 2 140 64 8 64 1 177 190 177 -68	0 352 350 0 -350 1 87 98 8 98 2 138 134 -133 25 3 249 247 163 -198 4 358 319 276 -154 5 221 242 -247 6 191 170 169 -23 1 10 10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	47 -47 0 18 0 19 0 -18 19 4 46 46 -0 20 12 0 -12 5 51 -51 0 24 0 -25 н+ 1 89 89 0 0 1	10 31 -16 -24 10 31 -16 -24 10 31 -16 -24 11 -16 -24	1 20 20 -2 -20 2 24 23 -17 -16 3 37 34 20 -26 4 40 44 3 44 5 37 13 15 -30 6 82 80 -3 -80 7 25 20 29 1	7 212 199 169 -120 8 178 174 173 19 9 93 84 -14 79 10 60 67 -6 42 11 125 144 119 -34 12 238 249 236 -36 13 86 102 -17 100 13 86 102 -17 100	B         263         228         0         228           9         131         134         -0         135           10         435         424         0         424           11         41         37         0         37           12         257         247         0         247           13         171         173         -0         -173           14         140         341         0         351	4 272 292 -0 202 5 01 03 03 0 6 124 127 43 -110 7 105 103 102 -0 8 207 274 -128 -140 9 146 148 -72 -140 10 306 304 62 -297 11 106 114 106 48	7 100 100 100 100 100 9 137 122 -105 -62 13 9 89 19 -67 11 87 81 80 14 12 777 268 237 125 13 -24 9 6 7 14 161 105 161 -77
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	*14 17 -17 -0 6 14 -0 16 7 14 -0 16 7 14 -0 0 6	5 106 31 101 1 118 87 79 2 160 48 152 3 244 -100 224 1 115 110 -33 6 81 3 -81 10 39 39 -2	H+ 2+L= 0 0 1228 1354-1364 -0 1 34 20 -20 0 2 127 101 101 -0 3 449 430 -430 0 4 266 194 196 -0	14 80 94 89 10 15 99 94 89 10 16 76 74 74 -12 17 37 11 -6 11 18 61 49 -67 -11 19 50 44 -19 43	16 258 267 0 267 17 11 5 -0 -4 18 75 70 0 79 19 54 57 -0 57 20 191 191 0 191	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	15 167 182 -68 168 16 103 102 84 58 17 56 62 60 14 18 186 174 176 -26 19 36 19 -37 12 20 32 32 -20 25
17 61 80 0 80 3 4 18 37 19 -39 0 4 8 19 56 54 -3 0 56 4 3 20 128 139 -139 0 6 -1 7 61 HE 01L = 6	4 0 -48 0 10 8 -81 -81 0 10 6 7 -16 -0 -16 11 5 - 8 -8 0 12 28 0 -74 -0 -78 13 1 14 1 15 - 15 - 15	1 306 -16 107 17 174 114 137 17 33 27 84 18 49 -39 30 10 283 -139 261 14 48 44 -20 10 121 -40 114 17 99 -37 -9	5 55 61 -61 0 6 10 101 101 -0 7 63 70 -70 0 8 97 50 -69 -0 9 268 247 -242 0 10 401 607 607 -0 11 221 223 -223 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H: 3.(* ) 0 -23 37 D -17 1 241 257 75 -247 2 570 522 73 -516 3 70 04 -03 -10 4 133 143 140 -15 5 366 330 338 -35	HE 34LE B 0 33 52 52 0 1 49 59 52 7 2 47 49 -37 33 3 106 108 -8 -108	H= 4.L= 2 0 671 699 -699 0 1 992 399 285 -279 2 109 115 46 106 1 636 614 -348 -506 4 224 273 -218 -43 5 101 112 24 -100
0 1/7 24 26 -0 H H 14 1 247 261 3 261 1 13 2 106 146 136 -0 2 46 3 101 104 3 106 3 4 4 63 56 56 0 4 54 5 -22 10 0 -19 5 12 6 82 101 101 -0 6 33	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	18 81 -17 72 51 49 -15 47 51 176 -19 175 52 41 -21 -16	12 151 140 140 -0 13 17 11 11 0 14 292 293 793 -0 15 59 67 -62 0 16 34 24 26 0 17 94 154 165 0 18 70 75 75 -0	6 243 270 257 - P4 7 136 141 - 135 41 8 68 53 - 28 57 9 158 153 - 28 57 9 158 155 67 138 10 173 158 267 45 11 128 135 - 111 75 12 33 44 39 - 10	6 250 364 -44 -361 7 216 202 -53 194 8 194 201 192 -53 194 9 190 178 171 51 10 138 115 23 -112 11 157 151 123 -84 12 168 157 -53 -145	4 37 34 12 31 5 142 141 133 -45 6 142 141 133 -45 1 7 36 35 16 52 9 45 51 40 -72 136 9 45 51 40 -72 1 0 143 151 130 57 1 10 25 23 6 22 10 25 23 6 22	6 114 94 64 70 7 380 367 -99 -353 8 353 347 -114 -108 9 243 246 -196 -141 10 249 240 -243 54 11 178 184 -36 -180 12 384 193 180 -46
7 186 174 0 178 7 7 8 290 272 72 - $n$ 8 $a$ 0 9 59 56 - $-7$ 56 9 $-7$ 8 $-10$ 5 10 107 94 94 $-n$ 10 56 11 96 100 0 100 11 29 12 200 201 70 $-0$ 12 3 13 46 57 $-55$ 0 $-52$ 12 22	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	75 307 -0 -307 72 183 163 82 22 209 -2017 25 23 211 183 -104 56 283 102 -264 56 74 58 45	19 62 65 -65 0 20 -17 1 -1 0 21 42 44 46 -0 H* 2+L+ 1 0 1048 1149 0 1149 1 364 369 -276 -244 2 207 203 203 203 1	11 91 10K -30 100 14 53 50 49 K 15 48 44 -14 23 16 149 136 124 42 17 99 47 -30 92 18 -16 7 4 6	14 40 47 10 72 14 60 47 10 72 15 99 107 102 13 16 122 107 17 17 17 17 45 40 -14 73 18 26 21 -13 13 19 57 40 38 -24 20 18 27 -10 -2	11         00         07         03         14           13         141         138         137         -11           14         40         137         -28         -24           7         14         154         127         122         3           7         16         61         40         -13         -49           6         17         51         58         57         -16	13 241 251 250 14 14 97 94 -96 -16 15 65 76 -19 -74 14 76 70 62 -32 17 106 104 -88 -59 18 115 107 -107 2 19 50 40 -33 23
15 -22 25 -0 27 16 242 217 237 -0 16 16 17 17 6 0 -617 12 18 21 12 -12 018 19 28 14 -0 -18 19 20 18 21 9	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		3 121 108 -101 66 4 108 280 154 233 5 58 42 -10 154 233 6 527 540 -528 111 7 196 151 -145 -41 8 253 251 250 18 9 81 108 -74 78 10 170 174 53 155	H= 2+L* 8 0 81 84 86 -0 1 91 77 -18 -75 2 257 267 -262 4 3 188 194 -2 -194 4 200 201 79 184 5 276 279 37 -276	H= 1+L= 2 0 469 4P4 4B4 1 122 114 -P1 -12 2 487 4B4 -274 -10 3 61 48 -54 11 - 14	H= 3+LT 9 0 51 64 =0 -66 1 75 74 -29 -66 4 2 105 104 -53 -90 8 3 9C 84 -15 -80 8 4 58 71 22 -66 5 73 73 -55 -55	20 37 39 38 -5 H4 4+Le 3 0 12 26 0 -26 1 123 103 -99 -30 2 259 217 -6 -237 3 193 183 -48 -177 4 190 100 100 100 100 100
L 298 318 0 -318 2 225 227 227 0 H+ 1. 3 76 88 0 86 0 4 4 51 56 -56 0 1 21 5 -23 8 0 8 2 100	14 16 17 17 17 18 18 18 110A - 654 - 965	44 34 _0 34 72 64 -30 63 66 49 58 6 54 53 -21 -48	11 147 140 -4 140 12 349 347 278 -224 13 191 187 -18 181 14 143 139 138 14 15 59 62 34 51	0 61 10 -65 38 7 127 124 121 -14 8 204 211 -66 102 9 144 143 -51 +144 13 67 64 27 41	4 17- 171 4-11 4 140 17A 70 -14 6 158 144 14 -14 7 57 57 -18 4 8 195 217 214 3	7 6 104 177 67 44 9 7 121 120 -127 1 9 8 78 82 44 -64 9 23 124 -121 -41	5 136 157 152 -4C 6 203 209 202 43 7 170 189 -125 -142 8 325 317 -317 0

GUS J. PALENIK Table 3 (cont.)

$1 \text{ able 4. } I \mathcal{U} \mathcal{U} \mathcal{U} \mathcal{U} \mathcal{U} \mathcal{U} \mathcal{U} \mathcal{U}$	nces un	i unqu	es
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		v	
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)-A1(2)-N(4)	176.5
A1(2) - N(2)	2.192		
A1(2) - N(4)	$2 \cdot 200$	Al(1)-N(1)-C(1)	108.3
(-) ()		Al(1)-N(1)-C(2)	109.3
N(1) - C(1)	1.477	Al(1)-N(3)-C(7)	107.2
N(1) - C(2)	1.477	Al(1)-N(3)-C(8)	109.1
N(2) - C(3)	1.472	Al(2)-N(2)-C(3)	107.8
N(2) - C(4)	1.479	Al(2)-N(2)-C(4)	107.6
N(3) - C(7)	1.463	Al(2)-N(4)-C(9)	111.1
N(3) - C(8)	1.469	Al(2)-N(4)-C(10)	106.6
N(4) - C(9)	1.482		
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	A1(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
Probable erro	ors	N(1)-C(5)-C(6)	113.7
Al–N	+0.004	N(2)-C(6)-C(5)	114.1
N-C	$\frac{-}{+}0.007$	N(3) - C(11) - C(12)	112.5
C-C	+0.008	N(4) - C(12) - C(11)	113.8

The average N-CH<sub>3</sub> distance is  $1.474 \pm 0.005$  Å and the average N-CH<sub>2</sub>- is  $1.495 \pm 0.008$  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-CH<sub>2</sub>- 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 electronegativity difference between  $-CH_3$  and  $-CH_{2-}$ . A view down the N-C bond in the N-CH<sub>2</sub>- 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-CH<sub>2</sub>-, compared with a N-CH<sub>3</sub> bond. Another possible explanation would be the difference between a methyl group and the  $-CH_2$ - group. The methyl group is generally considered to be the most electronegative of the alkyl groups.



Fig. 2. Views down various bonds in the molecule: (a) the N(2)-C(6) bond, (b) the N(2)-A1(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  $2.18 \pm$ 0.01 Å reported by Heitsch, Nordman & Parry (1963) for  $H_3Al[N(CH_3)_3]_2$  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-CH<sub>3</sub> 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

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

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

\* Values times 10<sup>3</sup>, in Ångström units.

 $\dagger$  Values times 10<sup>4</sup> (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  $N-CH_3$  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)	$\boldsymbol{A}$	2.53 Å	
H(8) - C(1)	H(24) - C(7)	D	2.67	
H(9) - C(1)	H(5) - Al(2)	C	2.57	
H(10) - C(2)	H(1) - Al(1)	B	2.39	
H(10) - C(2)	H(37) - C(12)	B	2.60	
H(12)-C(2)	H(34) - C(10)	B	$2 \cdot 62$	
H(16) - C(4)	H(26) - C(8)	B	2.69	
H(19) - C(5)	H(5) - Al(2)	C	2.38	
H(23) - C(7)	H(28) - C(8)	D	2.62	
H(25)-C(7)	H(28) - C(8)	D	2.27	
H(29) - C(9)	H(4) - Al(2)	E	2.69	
H(30) - C(9)	H(6) - Al(2)	E	2.58	
H(32) - C(10)	H(5) -Al(2)	E	2.56	
H(33) - C(10)	H(5) -Al(2)	E	2.57	
H(35)-C(11)	H(6) -Al(2)	E	2.58	
H(38) - C(12)	H(5) -Al(2)	E	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:

$\boldsymbol{A}$	$-x, \frac{1}{2}+y, \frac{1}{2}-z$	D	$\frac{1}{2} + x$ , $\frac{1}{2} - y$ , $1 - z$
B	$\frac{1}{2} + x, \frac{1}{2} - y, -z$	E	$\frac{1}{2} - x - 1$ , $-y$ , $\frac{1}{2} + z$
C	$\frac{1}{2} - x, -y, \frac{1}{2} + z$		

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  $H_3Al[N(CH_3)_3]_2$ 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 hydrogenbridges 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.

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