

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN AND THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

## The Molecular Structures of the Dimers of Aluminum Dimethyl Chloride, Aluminum Dimethyl Bromide, and Aluminum Trimethyl and of Hexamethyldisilane

BY L. O. BROCKWAY AND N. R. DAVIDSON<sup>1</sup>

The problem of the nature of the binding in aluminum trimethyl in the vapor state has aroused the interest of structural chemists since vapor density measurements indicated the existence of double molecules. The most recent vapor density determinations<sup>2</sup> show that the trimethyl is completely dimerized at temperatures below 70° and pressures close to the saturation values, while the triethyl compound is 12% associated at 150.6°. The present electron diffraction investigation was undertaken in order to compare the structures of the double molecules of aluminum dimethyl chloride and bromide with that of aluminum trimethyl and of the latter with the molecule hexamethyldisilane, since it appeared possible that these two substances would have similar geometrical structures. For the latter compound a new preparation and vapor tension data are reported. A previous electron diffraction study of aluminum trimethyl was made in another laboratory on a sample prepared by one of the present authors<sup>3</sup> but a reinvestigation with the aid of photographs extending to larger scattering angles is reported here.

### Experimental

Aluminum trimethyl was prepared in the manner described by Laubengayer and Gilliam.<sup>2</sup> The preparation of aluminum dimethyl chloride and bromide and the vapor density determinations which show that these substances in the vapor state near room temperature exist as double molecules are described in detail elsewhere.<sup>4</sup>

Hexamethyldisilane has been prepared previously from hexachlorodisilane and the methyl Grignard reagent.<sup>5,6</sup> An attempt was made to adapt the method of Friedel and Ladenburg,<sup>7</sup> who prepared hexaethylidisilane by gently warming a mixture of zinc diethyl and hexaiododisilane. We observed that zinc dimethyl does not react with hexachlorodisilane even at 130°; in the presence of ethyl ether, however, the reaction proceeds smoothly at 80°.

(1) Present address: Dept. of Chemistry, University of Michigan, Ann Arbor, Michigan.

(2) Laubengayer and Gilliam, *THIS JOURNAL*, **63**, 477 (1941).

(3) Davidson, Hugill, Skinner and Sutton, *Trans. Faraday Soc.*, **36**, 1212 (1940).

(4) Brown and Davidson, *THIS JOURNAL*, forthcoming publication.

(5) For early preparations, see Krause and Von Grosse, "Die Chemie der metall-organischen Verbindungen," Gebrüder Borntraeger, Berlin, 1937, p. 268.

(6) Schumb and Saffer, *THIS JOURNAL*, **61**, 363 (1939).

(7) Friedel and Ladenburg, *Ann.*, **203**, 251 (1880).

To 3.71 g. of freshly distilled Si<sub>2</sub>Cl<sub>6</sub> was added a 31% excess (1216 cc. S. T. P.) of zinc dimethyl vapor and 222 cc. (S. T. P.) of diethyl ether.<sup>8</sup> The reaction tube containing the mixture was sealed off and heated for several hours at 85°. A grayish-black, finely divided powder, having the appearance of zinc dust, and two liquid layers formed. After reconnection to the vacuum line, the mixture was distilled off, leaving a large volume of white solid, which probably consisted chiefly of the ether complex of zinc chloride, ((C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O)<sub>2</sub>ZnCl<sub>2</sub>. The hexamethyldisilane was separated by repeated distillations from a 20° bath through a trap at -50° into a receiver at -80°. The final sample was tensimetrically homogeneous as shown by careful vapor tension measurements on various fractions. The yield was 1.49 g. or 74% of the theoretical. The vapor tension data are given in Table I.

TABLE I  
VAPOR TENSION AND THERMAL DATA ON HEXAMETHYLDISILANE

<i>t</i> , °C.	20.3	26.4	32.9	38.9	42.2	44.0	47.0	54.5	61.2
<i>P</i> , mm.	22.9	31.2	42.4	56.9	66.2	70.4	80.6	109.1	141

$\log_{10} p = -1920/T + 7.907$ ; mean dev. of calcd. *p* from expt. *p* = 0.8%; b. p. (extrapolated) = 109°;  $\Delta H$  (vaporization) = 8.8 kcal.; m. p. (observed) = 14.0-14.4°; Trouton constant = 23.1.

The boiling point has been reported<sup>8</sup> as 112.5°. The molecular weight observed for a 89.5-mg. sample occupying 13.4 cc. (S. T. P.) was 149 ( $M_{\text{calcd.}} = 146.6$ ).

The electron diffraction photographs were made in an improved camera<sup>9</sup> with a plate distance of 10.34 cm. and an electron wave length of 0.0592 Å. The four compounds were photographed at temperatures of 20 to 30°, with vapor pressures of 5 to 15 mm. for the three aluminum compounds and of about 25 mm. for silicon hexamethyl. At these temperatures and pressures the three aluminum compounds exist in the vapor state entirely in the form of double molecules, *i. e.*, with two Al atoms per molecule.

In the following presentation of results the observed *s*<sub>0</sub> values (equal to  $4\pi (\sin \theta/2)/\lambda$ ) for each measured maximum and minimum are tabulated together with the coefficients, *c*<sub>*k*</sub>, derived from the visually estimated intensities, *I*<sub>*k*</sub>. The radial distribution functions,  $D(r) = \sum c_k (\sin s_k r)/s_k r$ , were calculated with  $c_k = s_k^2 \exp(-as_k^2) I_k$  and with  $\exp(-as^2) = 0.1$  for the largest ring. The resulting curves shown in Fig. 1 have a series of maxima which represent various interatomic distances in the respective molecules. In general the

(8) The vacuum apparatus and techniques required in this preparation are described in ref. 4.

(9) Eyster, Gillette and Brockway, *THIS JOURNAL*, **62**, 3236 (1940)

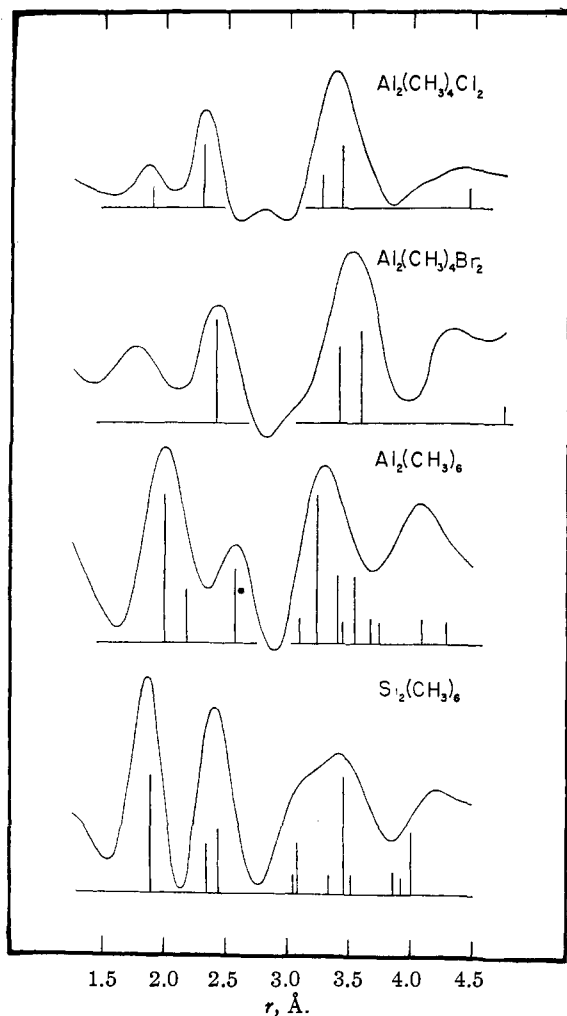


Fig. 1.—Radial distribution functions. The vertical lines show the relative scattering power associated with the interatomic distances in the final models.

values obtained from the two most prominent peaks are reliable to one or two per cent. The tables also show the ratios of  $s_{\text{theor}}/s_{\text{obs}}$  for the measured rings where the values of  $s_{\text{theor}}$  are taken from the indicated intensity curves calculated with the atomic scattering factors replaced by the atomic numbers. The average values of these ratios for the better models of each compound are multiplied by the assumed interatomic distances to give the experimental values reported. The agreement between the photographs and the simplified type of intensity curve used here has been shown by tests on molecules of known structure to be good for rings with  $s$  values larger than about 4.0. For that reason rings with lower  $s$  values are excluded in calculating the average  $s_{\text{theor}}/s_{\text{obs}}$  values.

**Aluminum Dimethyl Chloride.**—Nine maxima were measured on the photographs of aluminum dimethyl chloride with  $s_0$  values ranging out to 19.7. The experimental data in Table II give a radial distribution curve showing strong peaks at 2.32 and 3.37 Å. A consideration of the number of terms and their relative coefficients in the scattering function suggests that these two distances probably belong to Al-Cl and to a mean value of the C-Cl and Cl-Cl terms.

TABLE II

ALUMINUM DIMETHYL CHLORIDE (DIMER)								
Max. Min.	$s_0$	$C_k$	$s_2/s_0$	$s_4/s_0$	$s_6/s_1$	$s_7/s_0$	$s_9/s_0$	
1	2.29	10						
2	3.07	-4						
2	4.06	30	0.958	0.956	0.965	0.968	0.968	
3	5.12	-45	.988	.980	.982	.973	.980	
3	6.03	+44	1.011	1.005	1.003	.998	1.001	
4	7.05	-41	0.997	0.999	0.994	.984	1.000	
4	7.94	+35	1.002	.999	1.015	1.020	1.031	
5	8.76	-10						
5	9.67	16		.998	0.998			
6	10.50	-34	0.983	1.006	.997	0.985	0.985	
6	11.53	36	1.000	1.000	.997	.989	.985	
7	12.68	-46	0.990	0.986	.987	.984	.982	
7	14.04	24	.972	.964	.964	.992	1.004	1.003
8	15.47	-17	1.022	1.005	1.018	1.014	1.025	
8	16.87	11	1.014	1.009	1.013	1.002	1.002	
9	18.41	-4	0.989	0.984	0.984			0.972
9	19.71	4	.969	1.010		1.009		
Average			.992	0.993	0.996	0.994	0.995	
Average deviation			.015	.014	.011	.014	.016	
Al-Cl, Å.			2.301	2.304	2.311	2.306	2.308	
C-Cl, Å.			3.383	3.416	3.426	3.459	3.423	
Al-C = 2.31 ± 0.03 Å.				Al-C = 1.85-2.00 Å.				
C-Cl = 3.43 ± 0.05 Å.				∠ CAIC = 120-135°				
∠ CAICl = 89 ± 4°.								

The principal models considered were based on the bridged structure having a four-membered ring of two Al and two Cl atoms as reported for  $\text{Al}_2\text{Cl}_6$ ,  $\text{Al}_2\text{Br}_6$  and  $\text{Al}_2\text{I}_6$  vapors.<sup>10</sup> Two methyl groups (with C-H = 1.09 Å. and  $\angle \text{HCH} = 109.5^\circ$ ) were attached to each aluminum in a plane normal to the four-membered ring. Preliminary calculations showed that of the terms involving scattering by hydrogen atoms only those associated with the shortest C-H and Al-H distances had any detectable effect on the intensity curves, and only those hydrogen terms were included in calculating the curves. The models also were chosen to have strong scattering terms associated with the distances 2.32 and 3.37 Å. as required by the radial distribution function. Within this limitation a range of parameter values was tested as shown in Table III.

The extreme values of the bridge angle at the aluminum atom, *i. e.*, 100 and 80°, both give unsatisfactory agreement with the photographs

(10) Palmer and Elliot, *THIS JOURNAL*, **60**, 1852 (1938).

TABLE III  
BRIDGED MODELS OF ALUMINUM DIMETHYL CHLORIDE  
(DIMER)

Model	$\angle \text{ClAlCl}$	$\angle \text{CAIC}$	Al-C, Å.
1	100°	120°	1.87
2	93	128	1.84
3	93	128	1.90
4	90	148	2.10
5	90	136	2.00
6	90	125	1.90
7	90	120	1.90
8	90	117.2	1.80
9	86	127.6	1.90
10	80	139.4	1.85

In all models, Al-Cl = 2.32 Å. and C-H = 1.09 Å.

since for the 100° model the fourth and fifth maxima (near  $s = 8$  and 9) are shown to be about equal, while in the 80° model the fifth maximum is missing. The best agreement is obtained for the 90° bridge angles with the C-Al-C angle lying between 120 and 135° (Models 5, 6, and 7, Fig. 2). Models 3 and 9 with bridge angles of 93 and 86° are almost as good, although Model 9 gives poorer agreement than 3 at the seventh maximum near  $s = 14$ . The quantitative comparisons of the theoretical and observed positions of the maxima and minima are given in Table II for Models 3, 5, 6, 7, and 9. At the foot of the table are shown the average values of the ratios of theoretical and observed  $s$  values and the values of the two strongest scattering terms obtained by multiplying the observed ratios by the distances assumed in the various models. The resulting parameter values are: Al-Cl =  $2.31 \pm 0.03$  Å., C-Cl (non-bonded) =  $3.43 \pm 0.05$  Å.,  $\angle \text{ClCCl} = 89 \pm 4^\circ$  with the Al-C bond length probably lying between 1.85 and 2.00 Å. and the C-Al-C angle between 120 and 135°.

One intensity curve was calculated for an ethane-like model in which each aluminum atom is bonded to two methyl groups, one chlorine atom and one aluminum atom, and the qualitative and quantitative agreement with the observed pattern were both poor. A systematic test of models of this type was not made for the chlorine compound, but was made for the bromine compound. We believe that the unsatisfactory character of the ethane-like models in the latter case makes such models improbable in the chlorine compound.

**Aluminum Dimethyl Bromide.**—Photographs of aluminum dimethyl bromide showed eight rings of which the fourth and fifth form a partially resolved doublet with the fifth much weaker than the fourth. The radial distribution

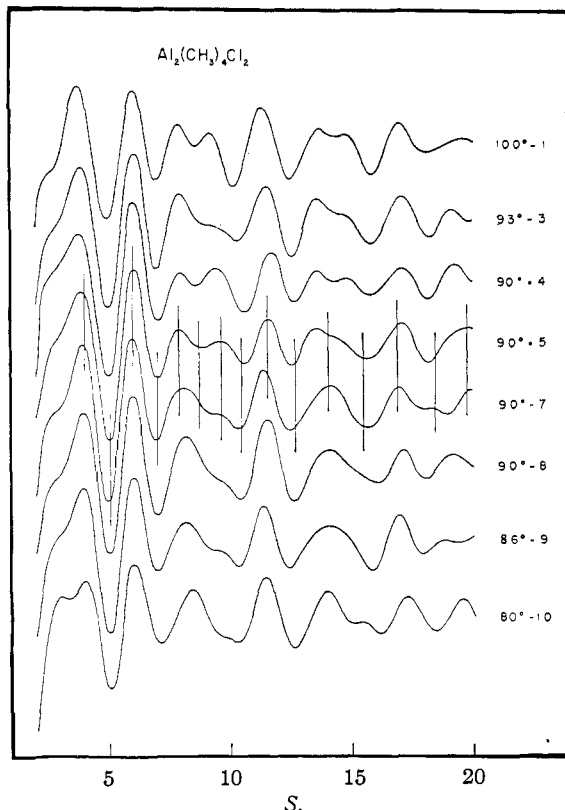


Fig. 2.—Theoretical intensity curves for models of  $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$  (see Table III). The vertical lines show the observed  $s_0$  values compared with the maxima and minima of the best molecular models.

curve based on the data of Table IV shows two strong maxima at 2.42 and 3.52 Å.

Models based on the bridged structure have the most important contributions to the diffraction pattern associated with the Al-Br bond distances and the non-bonded C-Br and Br-Br distances. The first of these is fixed at 2.42 Å. by the radial distribution function and the average of the other two was made equal to 3.52 Å. in each of the models listed in Table V, except Model 9, for which the corresponding values were taken at 2.35 and 3.55 Å.

The models with the  $\angle \text{BrAlBr}$  smaller than 90° lead to curves showing only one maximum near  $s = 8$  (e. g., Curve 8, Fig. 3) where two are observed on the photographs. Curves based on models with a bridge angle larger than 90° show an extra ring at  $s = 14$  (Curve 2, Fig. 3). A value of 90° for the bridge angle leads to a set of qualitatively correct curves with C-Al-C angles ranging from 115 to 130°. Outside of this range the appearance of the doublet near  $s = 8$  no longer agrees with the observed pattern.

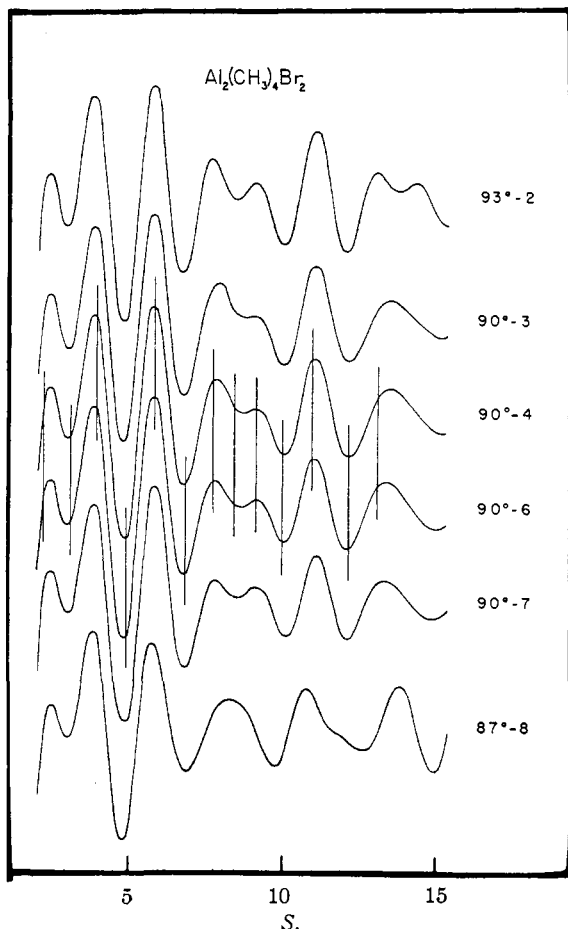


Fig. 3.—Theoretical intensity curves for models of  $\text{Al}_2(\text{CH}_3)_4\text{Br}_2$  (see Table V).

An ethane-like model formed by joining the aluminum atoms of two  $\text{Al}(\text{CH}_3)_2\text{Br}$  groups was considered as a possibility because a model of this type is reported for  $\text{Al}_2(\text{CH}_3)_6$ . The range of values of the molecular parameters is limited by the following considerations based chiefly on the radial distribution curve. The 2.42 Å. distance is again taken to represent the Al-Br bond length and the peak at 3.52 Å. is due to Br-Br, C-Br and the non-bonded Al-Br distances. The Al-Al distance ought to lie between 2.0 and 2.4 Å. with C-Al-Br angles somewhat larger than  $110^\circ$  as in the case of the corresponding parameters in aluminum trimethyl. The Br-Br distance then lies between a minimum value in the *cis* configuration of  $3.0 \pm 0.2$  Å. and a maximum value in the *trans* configuration of  $5.6 \pm 0.2$  Å. The radial distribution curve allows an intermediate value of about 3.5 Å., which fixes the molecule with one end rotated about  $40^\circ$  from the *cis* position. In this model

two Al-Br distances occur, 2.42 and 3.54 Å., and also two C-Br distances, 3.50 and 5.20 Å. The first three values agree well with the positions of the two most prominent peaks in the radial distribution curve, but for this model the second of these peaks should be more than three times as strong as the first according to the relative scattering power associated with each.

The intensity curve based on the model just described shows a series of regular maxima and minima whose positions agree fairly well with those of the measured rings on the photographs, but the distinctive qualitative features of the observed pattern do not appear at all in the curve. In particular, the double maximum near  $s = 8$  (as in Curve 4, Fig. 3) appears as two completely resolved maxima with the second stronger than the first. A further test was made by using another ethane-like model in which the distances at 2.42 Å. and near 3.50 Å. were retained in order to preserve the agreement with the radial distribution function, but the bond angles all were set at  $109.5^\circ$ , the Br atoms in the *cis*-position, the Al-C bond distances and the Al-Al bond at 1.89 Å. The resulting curve is indistinguishable from the foregoing one. This will be true for any other ethane-like model which agrees with the radial distribution function because the major part of the scattering power of the molecule is associated with the two important maxima in this function, and any variations among the remaining terms have no appreciable effect on the calculated intensity curves. A bridged model, on the other hand, has been found which not only gives agreement with positions of the peaks in the radial distribution curve but also better represents their relative importance as well as showing good quantitative and qualitative agreement with the calculated intensity curves. We believe, therefore, that the ethane-like models must be rejected in favor of a bridged model with  $90^\circ$  angles.

The quantitative comparison of Table IV leads to the final results: Al-Br =  $2.42 \pm 0.03$  Å.; C-Br =  $3.59 \pm 0.05$  Å.;  $\angle \text{Br-Al-Br} = 90 \pm 3^\circ$ ;  $\angle \text{C-Al-C} = 115\text{--}130^\circ$  and Al-C = 1.90–2.05 Å.

**Aluminum Trimethyl.**—The two innermost maxima were very strong, the second being a little broader than the first and showing a slight asymmetry on the outer edge. The third and fourth were only partially resolved with the latter somewhat weaker. The fifth ring was sharp and

TABLE IV  
 ALUMINUM DIMETHYL BROMIDE (DIMER)

Max.	Min.	$s_0$	$c_k$	$s_4/s_0$	$s_5/s_0$	$s_6/s_0$
1		2.19	9	(1.106)	(1.110)	(1.106)
	2	3.07	-9	(0.961)	(0.977)	(0.961)
2		3.95	24	.977	.980	.972
	3	4.92	-38	.979	.986	.981
3		5.83	37	.988	1.000	.995
	4	6.85	-45	.987	0.993	.990
4		7.74	33	1.019	1.013	1.007
	5	8.43	-4			
5		9.13	11	0.997	1.014	0.999
	6	10.00	-30	1.006	1.010	1.007
6		10.97	30	1.008	1.013	1.008
	7	12.16	-14	1.003	0.999	0.995
7		13.17	13	1.025	1.015	1.019
8		15.36	3			
Average				0.999	1.002	0.997
Average deviation				0.013	0.011	0.011
Al-Br, Å.				2.418	2.424	2.414
C-Br				3.597	3.576	3.589

Al-Br = 2.42 ± 0.03 Å.      Al-C = 1.90-2.05 Å.  
 C-Br = 3.59 ± 0.05 Å.      ∠C-Al-C = 115-130°  
 ∠Br-Al-Br = 90 ± 3°

TABLE V

BRIDGED MODEL	OF	ALUMINUM DIMETHYL BROMIDE	
Model	∠Br-Al-Br	∠C-Al-C	Al-C, Å.
1	95°	120°	1.83
2	93.4	120	1.90
3	90	109	1.85
4	90	115	1.90
5	90	120	1.90
6	90	126	2.00
7	90	136	2.10
8	86.5	113	1.95
9	87	115	1.95

Models 1-8, Al-Br = 2.42, C-H = 1.09 Å.  
 Model 9, Al-Br = 2.35, C-H = 1.09 Å.

well-defined, while the sixth was rather broad. A seventh ring was observed, but measurements on it were not reproducible. The observed  $s_0$  values are shown in Table VI. The first nine values correspond to the maxima and minima reported by Sutton,<sup>3</sup> whose values average about 0.5% smaller than ours. Our radial distribution function based on twelve maxima and minima shows two strong peaks at 2.01 and 3.30 Å., with a weaker intermediate one at 2.58 Å. (Fig. 1).

The first tests were made on models of the ethane type with trigonally symmetrical aluminum trimethyl groups joined by the aluminum atoms. Changes in the relative orientation of the two trimethyl groups about the axis of the molecule had no effect on the intensity curves. For that reason in all but three models a single orientation was used, *i. e.*, with the carbon atoms at one end of the molecule lying in planes through the axis which bisected the C-Al-C angles at the other end. The long C-H distances were usually neglected since their contributions had no detectable effect on the intensity curves. The models calculated are described in Table VII in terms of two parameters, the C-Al-Al bond angle and the ratio of the Al-Al to Al-C bond lengths, following the scheme used by Sutton. The absolute scale was fixed in these models by assuming an Al-C bond distance of 2.00 Å. as suggested by the radial distribution curve. Intensity curves for Models 1 to 8 are shown in Fig. 4. All of these curves except 5 show the partially resolved third and fourth maxima although only in 1, 2, 6 and 7 is the fourth ring weaker than the third as ob-

 TABLE VI  
 ALUMINUM TRIMETHYL (DIMER)

Max.	Min.	$s_0$	$c_k$	$s_6/s_0$	$s_7/s_0$	$s_{11}/s_0$	$s_{12}/s_0$	$s_{18}/s_0$
1		2.20	7	(1.082)	(1.068)	(1.105)	(1.077)	(1.109)
	2	2.89	-8	(1.059)	(1.038)	(1.100)	(1.067)	(1.090)
2		3.73	19	(1.085)	(1.067)	(1.080)	(1.072)	(1.094)
	3	5.33	-28	0.976	0.957	0.970	0.947	0.964
3		6.31	29	1.038	1.022	1.017	.995	1.005
	4	7.14	-7	1.018	1.001	1.008	.983	1.003
4		7.88	27	0.977	0.983	0.977	.983	0.996
	5	8.98	-44	0.991	0.989	0.980	.978	0.997
5		10.00	37	1.030	1.018	1.027	1.030	1.305
	6	11.43	-24	1.020	0.983	1.010	0.993	1.008
6		12.72	9	1.037	1.019	1.018	1.038	1.060
7		(17.39)	3					
Average				1.013	1.002	1.005	1.000	1.015
Average deviation				0.020	0.015	0.015	0.019	0.019
Al <sub>1</sub> -C				2.026	2.004	2.010	2.000	2.030
Al <sub>2</sub> -C <sub>1</sub>				3.252	3.296	3.196	3.260	3.258
Al <sub>1</sub> -C <sub>1</sub> = 2.01 ± 0.04 Å.								
Al <sub>2</sub> -C = 3.24 ± 0.06 Å.								
∠C-Al-Al = 100 ± 5°.								

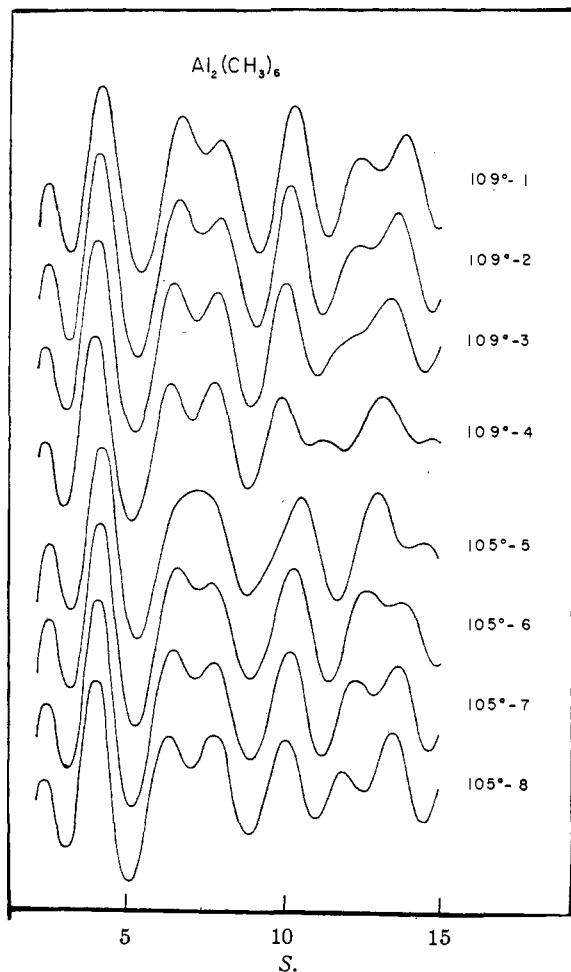


Fig. 4.—Theoretical intensity curves for 109° and 105° models of  $\text{Al}_2(\text{CH}_3)_6$  (see Table VII).

served in the photographs. The 109.5° curves all show an extra ring between the observed fifth and sixth. Curves 6 and 7 are somewhat better in this region, but the double maximum shown here appears on the plates as a single broad ring. From these observations we conclude that the C-Al-Al angle is definitely less than 109.5° and probably less than 105°.

In Fig. 5 some of the curves for 100 and 95° models are shown. Curves 9 and 10 do not show the third and fourth maxima resolved. Curves 11 and 12 give the best reproduction of the characteristic features of the diffraction pattern of all the calculated curves. In curve 13 the fourth maximum is too much stronger than the third. Of the 95° curves number 15 is the best, but the sixth ring here is less like the photographs than is the corresponding ring in curves 11 and 12.

From the foregoing comparisons it appears that

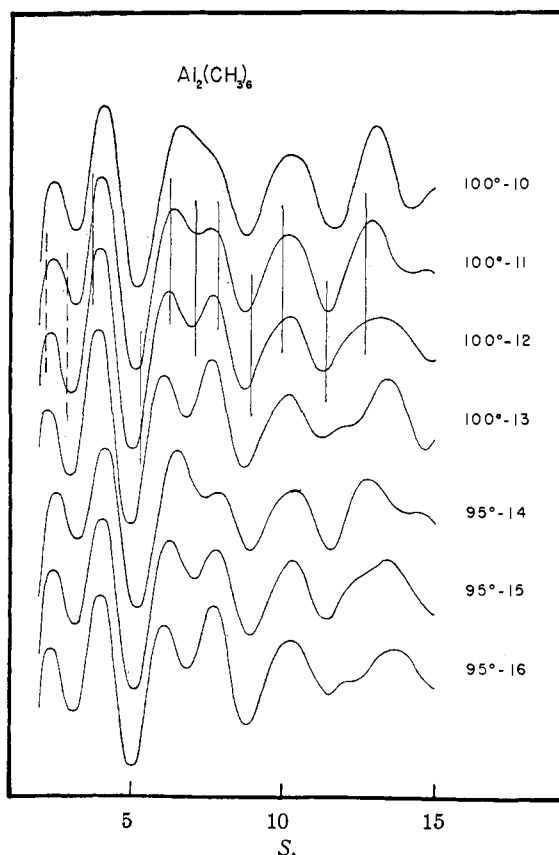


Fig. 5.—Theoretical intensity curves for 100° and 95° models of  $\text{Al}_2(\text{CH}_3)_6$  (see Table VII).

for a given angle better curves are obtained with small values of the Al-Al/Al-C bond length ratio when the angle is large and with larger length ratios when the angle is smaller. It is found that the more satisfactory curves for the various angles all have nearly the same value of the ratio of the non-bonded Al-C distance to the bonded Al-C distance, *i. e.*,  $\text{Al}_2\text{-C}_1/\text{Al}_1\text{-C}_1 = 1.61 \pm 0.02$ . For the ethane-like models these two terms represent about two-thirds of the total scattering power of the molecule. The 90° model indicated in Table VII was chosen to have the same value of

TABLE VII  
ETHANE-LIKE MODELS FOR ALUMINUM TRIMETHYL  
(DIMER)

$\angle \text{C-Al-Al}$ Al-Al/Al-C	90°	95°	100°	105°	109.5°
0.975			9	5	1
1.025			10	6	2
1.075			11	7	3
1.125		14	12	8	4
1.175		15	13		
1.225		16			
1.25	17				

the last mentioned ratio as the most promising curve in the  $100^\circ$  group, but it fails to reproduce the observed third and fourth rings. A consideration of the qualitative agreement between the photographs and the curves based on ethane-like models leads to a model having  $\angle C-Al-Al = 100^\circ$  and a ratio of the two Al-C distances equal to 1.61.

The difficulty of accounting for the existence of the ethane-like molecule in terms of existing bond theories led to the testing of other possible models. In particular, it was decided to test the bridged structure found in the  $Al_2(CH_3)_4X_2$  models. Two Al and two C atoms were placed in a four-membered ring with two additional methyl groups attached to each Al atom in a plane perpendicular to the ring. Three models were calculated using parameters suggested by the results on the halogen substituted molecules: *i. e.*, using a square ring, an external C-Al-C angle of  $125$  or  $120^\circ$  and the following Al-C bond lengths in the ring and external to the ring: Model A — 1.90, 1.90 Å.; B — 1.80, 1.90 Å.; C — 1.90, 1.80 Å. The corresponding intensity curves show extremely poor agreement with the observed pattern. In A, the fourth ring is missing, but two extra rings appear near the fifth and sixth; in B the second ring is doubled, the fifth is much too weak, while the sixth appears as an inner shelf on a strong seventh.

A second group of bridged models was chosen to give at least fair agreement with the strong radial distribution peaks at 2.01 and 3.30 Å. The average of the bonded Al-C distances was set at 2.00 Å., while the average of the other two important terms, the separation of non-bonded Al and C atoms and of C atoms in the ring and outside the ring, was kept near 3.3 Å. The resulting C-Al-C bridge angle is about  $120^\circ$  so that the two Al atoms approach each other within about 2.1 Å. This close approach of non-bonded Al atoms is very unreasonable but it is not possible to avoid this difficulty in any bridged model with distances required by the radial distribution curve. Three of the six models were calculated with C-Al-C bridge angles of  $120^\circ$  and external C-Al-C angles of  $125^\circ$ . The external and internal Al-C bond lengths were equal in the first at 2.00 Å. and were set at 1.90 and 2.10 Å. in the second and at 1.80 and 2.20 Å. in the third. A fourth model with a  $120^\circ$  bridge angle was calculated with an external angle of  $135^\circ$  and Al-C bond lengths of 1.90 Å and 2.10 Å. None of these five models gave curves reproducing the observed pattern,

particularly in the region of the distinctive third and fourth maxima. The parameters of the sixth model were chosen to reduce as much as possible the difference between the two terms averaging 3.3 Å. while maintaining an average Al-C bond length of 2.00 Å. The resulting values were C-C = 3.18 Å. and Al-C = 3.38 Å. with Al-C bond lengths of 1.90 and 2.10 Å. a bridge angle of  $126^\circ$  and an external angle of  $110^\circ$ . The scattering curve fits the third and fourth maxima quite well but the positions of the sixth minimum and maximum were in error by three and seven per cent., respectively. This model is also unsatisfactory in bringing non-bonded Al atoms within 1.9 Å. of each other.

The bridged models giving reasonable agreement with the radial distribution curve lead to unsatisfactory scattering curves (as well as giving improbable values to some of the interatomic separations). Since any other models would necessarily give poor quantitative fit with the photographs, there is little hope of finding a satisfactory bridged model on the basis of the present data and we conclude that the most probable structure is represented by the ethane-like model described above.

The final parameter values are determined by comparisons for the better models as shown in Table VI. The first three measured  $s_0$  values fall below 4.0 and are excluded from the final average because (as usual for the smallest rings) they do not give results in agreement with those from the larger rings. The final values are Al-C (bonded) =  $2.01 \pm 0.04$  Å.; Al<sub>2</sub>-C (non-bonded) =  $3.24 \pm 0.06$  Å.;  $\angle C-Al-Al = 100 \pm 5^\circ$ ; Al-Al =  $2.20 \pm 0.15$  Å.

**Hexamethyldisilane.**—Seven maxima and five minima were measured in a range of  $s$  values from 4.1 out to 20.6. The third ring is stronger than the second, the fourth is sharp, while the fifth ring is broad and appears to be a double ring, but not well enough resolved to afford measurements on the components. In Table VIII the value shown for the fifth ring is the measured center of the doublet. The radial distribution curve based on the data in Table VIII shows strong peaks at 1.87 and 2.41 Å. with a broad peak ranging from 3.25 to 3.50 Å.

A series of ethane-like models was calculated for the values of bond angles and bond length ratios shown in Table IX. The scale was fixed by assuming Si-Si = 1.94 Å. in each model. As in the case of the aluminum methyl compound, fairly

TABLE VIII

HEXAMETHYLDISILANE						
Max.	Min.	$s_0$	$c_k$	$s_2/s_0$	$s_4/s_0$	$s_6/s_0$
1		4.07	23	(0.943)	(0.939)	(0.929)
	2	5.17	-12	0.977	0.961	0.948
2		6.18	22	1.021	1.010	1.003
	3	6.98	-26	0.984	0.978	0.974
3		7.91	45	.978	.964	.967
	4	9.56	-56	.946	.953	.968
4		10.91	62	1.011	1.001	.993
	5	12.26	-46	0.982	0.972	.965
5		13.94	34	.986	.976	.971
	6	15.60	-13	.990	.981	.977
6		16.97	12	.974	.966	.958
7		20.59	4	.983	.976	.976
Average				.985	.976	.973
Average deviation				.013	.012	.011
Si <sub>1</sub> -C <sub>1</sub>				1.911	1.893	1.888
Si <sub>2</sub> -C <sub>1</sub>				3.448	3.465	3.493

Si<sub>1</sub>-C<sub>1</sub> (bonded) = 1.90 ± 0.02 Å.

Si<sub>2</sub>-C<sub>1</sub> (non-bonded) = 3.47 ± 0.04 Å.

∠C-Si-Si = 109 ± 4°.

Si-Si = 2.34 ± 0.10 Å.

satisfactory intensity curves were obtained with bond angles covering an eight degree range if the ratio of the two strongest scattering terms is kept nearly constant (at a value of 1.82 for the silicon compound).

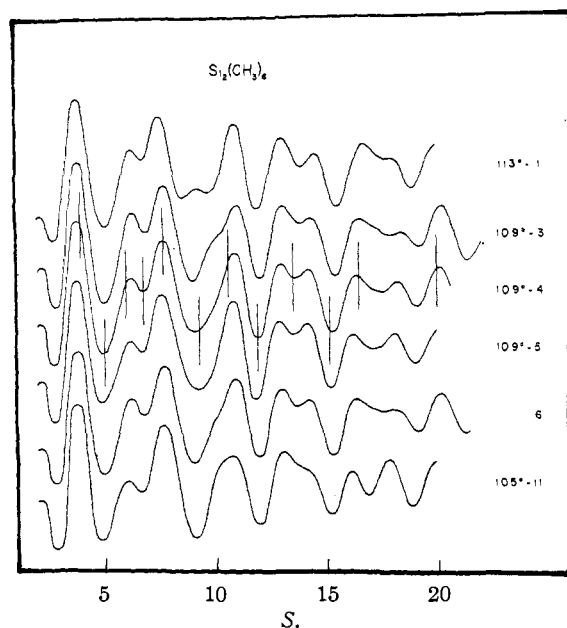


Fig. 6.—Theoretical intensity curves for models of Si<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> (see Table IX). The observed  $s_0$  values have been multiplied by 0.976, the scale factor obtained for Model 4 in Table VIII.

Among the 109°28' models whose intensity curves were calculated first the best reproduction of the observed pattern is given by 4 with 3 and 5

TABLE IX

ETHANE-LIKE MODELS FOR HEXAMETHYLDISILANE					
∠C-Si-Si	105°	107°	108°45'	109°28'	113°
Si-Si/Si-C					
1.154	8			2	
1.185					1
1.206	9	7		3	
1.232			6	4	
1.258	10			5	
1.294	11				

almost as good. Model 6 with a bond angle of 108°45' was chosen to have the value of the ratio of the two Si-C distances determined from Model 4 and to show the best possible agreement with the radial distribution function. The intensity curves for Models 4 and 6 are almost indistinguishable, and therefore a change of only a degree in the bond angle cannot be detected experimentally. Model 1 with a bond angle of 113° and Si<sub>2</sub>-C<sub>1</sub>/Si<sub>1</sub>-C<sub>1</sub> = 1.82 gives a curve quite similar to that of Model 4, but a little less satisfactory in the neighborhood of the third and fourth maxima. Model 11, the best of those having 105° bond angles, is also only a little less satisfactory than Model 4.

The final results for hexamethyldisilane and the estimated uncertainties are as follows: Si-C (bonded) = 1.90 ± 0.02 Å.; Si-C (non-bonded) = 3.47 ± 0.04 Å.; ∠C-Si-Si = 109 ± 4°; Si-Si = 2.34 ± 0.10 Å. The relatively large uncertainty in the length of the Si-Si bond is due to the small proportion of the total scattering represented by this term.

### Discussion

The results for the four compounds are collected in Table X together with the corresponding values previously reported for Al<sub>2</sub>Cl<sub>6</sub> and Al<sub>2</sub>Br<sub>6</sub>.<sup>10</sup> The Al-C bond distances and angles in the substances Al<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> and Al<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>Br<sub>2</sub> are given as ranges of values because within each range there is no experimental reason for preferring one value over another. These two compounds have the bridged structure involving a ring of two metal and two halogen atoms found in the Al<sub>2</sub>X<sub>6</sub> molecules,<sup>11</sup> as

(11) The possibility of ethane-like molecules was not considered in the investigation by Palmer and Elliot. We calculated three intensity curves based on ethane-like models of Al<sub>2</sub>Cl<sub>6</sub> with distances indicated by the two strong peaks in the radial distribution function. The qualitative agreement with the pattern described by the authors was not very good. For Al<sub>2</sub>Br<sub>6</sub>, however, we found that an ethane-like model with an Al-Br bond length of 2.28 Å., Al-Al 1.90 Å. and Br-Al-Al bond angles of 105° gave excellent qualitative and quantitative agreement with the observed pattern. Photographs extending to larger scattering angles would be required for distinguishing between the bridged and ethane-like structures on the basis of electron diffraction data. The bridge structure seems more likely in view of the present result on Al<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>Br<sub>2</sub> and of the number of other halogen compounds known to have such structures.



TABLE X

	Al-X	C-X	Al-C	$\angle$ X-Al-X	$\angle$ C-Al-C
$\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$	$2.31 \pm 0.03 \text{ \AA.}$	$3.43 \pm 0.05 \text{ \AA.}$	$1.85\text{--}2.00 \text{ \AA.}$	$89 \pm 4^\circ$	$120\text{--}135^\circ$
$\text{Al}_2(\text{CH}_3)_4\text{Br}_2$	$2.42 \pm 0.03$	$3.59 \pm 0.05$	$1.90\text{--}2.05 \text{ \AA.}$	$90 \pm 3^\circ$	$115\text{--}130^\circ$
$\text{Al}_2\text{Cl}_6^{11}$	2.21			$80^\circ$	$(118^\circ)$
$\text{Al}_2\text{Br}_6^{11}$	2.33			$87^\circ$	$(115^\circ)$
	M <sub>1</sub> -C	M <sub>2</sub> -C	M <sub>1</sub> -M <sub>2</sub>	$\angle$ CMM	
$\text{Al}_2(\text{CH}_3)_6$	$2.01 \pm 0.04 \text{ \AA.}$	$3.24 \pm 0.06 \text{ \AA.}$	$2.20 \pm 0.15 \text{ \AA.}$	$100 \pm 5^\circ$	
$\text{Si}_2(\text{CH}_3)_6$	$1.90 \pm 0.02$	$3.47 \pm 0.04$	$2.34 \pm 0.10 \text{ \AA.}$	$109 \pm 4^\circ$	

well as in other metallic halides such as the dimeric diethyl auric bromide,  $\text{Au}_2(\text{C}_2\text{H}_5)_4\text{Br}_2$ ,<sup>12</sup> and the crystalline polymer of palladous chloride,  $\text{PdCl}_2$ .<sup>13</sup> The Al-X distances appear to be longer in the methyl substituted compounds, in which also there is no evidence for any deviation from  $90^\circ$  angles in the bridge. Since the bonds are probably partially covalent, the formation of the bridge in the  $\text{Al}_2(\text{CH}_3)_4\text{X}_2$  molecules presumably involves the occurrence of four electron-pair bonds on aluminum, in one of which both the electrons have been supplied by a halogen atom. Because of the many examples of this type of polymerization no new problem is raised here.

In the case of  $\text{Al}_2(\text{CH}_3)_6$  the present results confirm the ethane-like structure reported by Sutton and co-workers.<sup>3</sup> Our values for the Al-C bond length and the bond angle are given with smaller uncertainties than theirs ( $2.05 \pm 0.10 \text{ \AA.}$  and  $105 \pm 10^\circ$ ) because the extra ring observed and measured on our photographs made it possible to eliminate certain models. Our consideration of the possibility of bridged models has made the correctness of the ethane-like structures more probable. It is interesting to note that the C-Al-Al bond angle is definitely less than  $109^\circ$  (the value observed for C-Si-Si). It seems probable that the monomer  $\text{Al}(\text{CH}_3)_3$  has the coplanar structure observed in  $\text{B}(\text{CH}_3)_3$ <sup>14</sup> with  $120^\circ$  angles. When two  $\text{Al}(\text{CH}_3)_3$  molecules are united, the C-Al-C angle decreases only to about  $115^\circ$ .

The dielectric constants and polarizations of the vapors of  $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$  and  $\text{Al}_2(\text{CH}_3)_6$  have been measured by Wiswall and Smyth.<sup>15</sup> The latter compound was about 10% dissociated at the temperatures of the measurements and the authors conclude that the monomer  $\text{Al}(\text{CH}_3)_3$  must have a dipole moment of about  $1.4D$ . The calculations leading to the moment values in the third column of their Table I (p. 353) are based

(12) Buraway, Gibson, Hampson and Powell, *J. Chem. Soc.*, 1690 (1937).

(13) Wells, *Z. Krist.*, **100**, 189 (1938).

(14) Lévy and Brockway, *THIS JOURNAL*, **59**, 2085 (1937).

(15) Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941).

on the differences between the observed total polarizations and estimated electronic polarizations. These differences are 21 cc. for  $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$  and 11 cc. for  $\text{Al}_2(\text{CH}_3)_6$ , and we believe that they are not sufficient to prove the existence of a permanent dipole moment. In  $\text{Au}_2(\text{C}_2\text{H}_5)_4\text{Br}_2$  the excess of total polarization over electron polarization is 36.3 cc.<sup>12</sup> although an X-ray investigation<sup>12</sup> has shown the molecule to have a symmetrical bridged structure (similar to that of  $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$  except for the planar coordination around the Au atoms) incompatible with the existence of a permanent moment. In  $\text{Al}_2\text{Br}_6$  measured in  $\text{CS}_2$  solutions at concentrations which contain almost exclusively double molecules the excess of total over electron polarization is about 12 cc.<sup>16</sup> The probable explanation of these abnormal atom polarizations has been discussed by Coop and Sutton,<sup>17</sup> who expect to find anomalous polarizations in molecules containing groups with large individual moments opposed to each other and in which the individual groups have relatively low force constants with respect to their bending motions. In view of the number of substances cited by Coop and Sutton for their anomalous behavior and the observations by Wiswall and Smyth of excess polarizations for  $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$  and  $\text{Al}_2(\text{CH}_3)_6$  at temperatures where the samples are composed mainly of double molecules there is still considerable doubt of the existence of permanent moments. A test of the structure of the monomer  $\text{Al}(\text{CH}_3)_3$  by measuring the temperature coefficient of polarization at high temperatures is perhaps not feasible, but we hope to make an electron diffraction investigation of the monomer.

For hexamethyldisilane only the ethane-like structure was tested because it is in accord with all of the observed structures of compounds containing four coordinated silicon and because this model gave quite satisfactory agreement with the electron diffraction data. The silicon-silicon bond length is reported as  $2.34 \text{ \AA.}$  with an uncer-

(16) Nespital, *Z. physik. Chem.*, **B16**, 153 (1932).

(17) Coop and Sutton, *J. Chem. Soc.*, 1269 (1938).

tainty of 0.10 Å. because of the relative unimportance of this term in the scattering function. The reported value is probably more reliable than indicated, however, since the same bond in  $\text{Si}_2\text{H}_6$  was observed to be  $2.32 \pm 0.03$  Å.<sup>18</sup> The Si-C bond length observed here ( $1.90 \pm 0.02$  Å.) may be compared with the value  $1.93 \pm 0.03$  Å., reported for  $\text{Si}(\text{CH}_3)_4$ .<sup>19</sup> The difference may not be real, but the investigation of  $\text{Si}(\text{CH}_3)_4$  is being repeated on the present apparatus as a further test. The radius sum for a single covalent Si-C bond is 1.94 Å., while Schomaker and Stevenson<sup>20</sup> propose a modification of the use of atomic radii based on the relative electronegativity of the bonded atoms which gives for Si-C a calculated value of 1.88 Å. The bond angles do not differ from the tetrahedral value by as much as 4°, the experimental uncertainty.

The hexamethyl derivatives of both aluminum and silicon show the same ethane-like structure, but the molecules are differently proportioned. The ratio of the two metal-carbon distances is 1.61 in the Al compound and 1.83 in the Si compound. The Al-Al bond is about 10% longer than the Al-C bond whereas the Si-Si bond is about 25% longer than the Si-C bond. If from the Si-C bond length we subtract a carbon atom radius of 0.77 Å., a Si radius of 1.13 Å. is left. This is to be compared with  $1.17 \pm 0.05$  Å., *i. e.*, half of the observed Si-Si bond. (The agreement here would be better if the difference in the relative electronegativities in the two bonds were allowed for by the Schomaker-Stevenson scheme.) In  $\text{Al}_2(\text{CH}_3)_6$ , subtracting the carbon radius leaves 1.24 Å. for Al<sup>21</sup> whereas half of the observed Al-Al bond length is  $1.10 \pm 0.08$  Å. If the bonds in  $\text{Si}_2(\text{CH}_3)_6$  are single electron pair bonds, then in the Al compound the Al-C bond is too long relative to Al-Al for both to be electron pair bonds.

The existence of double molecules of  $\text{Al}(\text{CH}_3)_3$  requires some modification of our bond theories, but the best manner of describing the binding forces in this molecule is by no means clear. The deficiency of two electrons below the number required for electron-pair bonds throughout the molecule suggests that the Al-Al bond should have less than two electrons on the average, but the Al-Al bond is apparently 0.1 Å. shorter than

the Si-Si bond. Aluminum forming normal covalent bonds in an octet should be larger than Si. An electron deficiency could scarcely shorten the bond, although it may be noted that if the electron deficiency does not occur at all in the Al-Al bond but is concentrated in the Al-C bonds, the Al-Al bond might then be shorter than the normal octet bonds because the average number of electrons per Al atom would be less than eight. Structures involving only three occupied orbitals ( $sp^2$ ) on aluminum would have bonds shorter than the octet bonds. At the same time the Al-C bonds would be relatively longer because of the deficiency there. These suggestions are not very satisfactory because the loss of energy in the electron-deficient Al-C bonds would probably be greater than the energy gained in the formation of the double molecule. The heat of the reaction of dissociation is observed to be about 20 kilocalories per mole. That the bond holding the two aluminum atoms together should be predominantly ionic or polar is unlikely because of the symmetry of the molecule, but electron deficiency in the Al-C bonds would increase their polar character and indeed help to account for the abnormal atom polarization of the substance.

**Acknowledgments.**—The assistance of the Horace H. Rackham Foundation and of the Midgley Foundation which made possible the construction of the diffraction apparatus is gratefully acknowledged. We are indebted to Dr. H. C. Brown for suggesting the comparison of  $\text{Al}_2(\text{CH}_3)_6$  with  $\text{Si}_2(\text{CH}_3)_6$  and for help in the preparation of the latter substance, and to Miss Charlys-Marion Lucht for special assistance in the preparation and interpretation of the photographs. One of us (N. R. D.) wishes further to acknowledge helpful advice and criticism from Professor H. I. Schlesinger.

### Summary

1. A new preparation of  $\text{Si}_2(\text{CH}_3)_6$  is described, and the vapor pressure has been measured over a range of temperature from 20 to 60°.
2. The structures of  $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$ ,  $\text{Al}_2(\text{CH}_3)_4\text{Br}_2$ ,  $\text{Al}_2(\text{CH}_3)_6$  and  $\text{Si}_2(\text{CH}_3)_6$  have been determined by means of electron diffraction with the results shown in Table X.
3. The two methyl aluminum halides have the bridged structure of two metal and two halogen atoms in a ring observed in other similar compounds and the ring angles are close to 90°.

(18) Brockway and Beach, *THIS JOURNAL*, **60**, 1836 (1938).

(19) Brockway and Jenkins, *ibid.*, **58**, 2036 (1936).

(20) Schomaker and Stevenson, *ibid.*, **63**, 37 (1941).

(21) The tetrahedral covalent radius for Al is given by Pauling ("Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 167) as 1.26 Å.

4.  $\text{Al}_2(\text{CH}_3)_6$  and  $\text{Si}_2(\text{CH}_3)_6$  have ethane-like structures. The silicon compound has the bond lengths and angles expected for a normal covalent structure. In the aluminum compound the C-Al-C bond angles are  $115^\circ$  or larger. The Al-Al

bond is surprisingly short in comparison with the Si-Si bond length.

5. The structural question of what makes two  $\text{Al}(\text{CH}_3)_3$  molecules join is still a question.

ANN ARBOR, MICHIGAN

RECEIVED AUGUST 4, 1941

[CONTRIBUTION OF THE FERTILIZER RESEARCH DIVISION, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

## The Catalytic Decomposition of Ammonia over Iron Synthetic Ammonia Catalysts

BY KATHARINE S. LOVE AND P. H. EMMETT<sup>1</sup>

The catalytic decomposition of ammonia has been studied by many workers. In only a few instances, however, have such studies been concerned with the decomposition over iron synthetic ammonia catalysts. The present work had as its primary object the elucidation of the kinetics of ammonia decomposition over several of the many iron catalysts prepared and studied in the U. S. Department of Agriculture. The results obtained point toward a complexity of the ammonia synthesis and decomposition reactions over iron that heretofore has not been recognized. The present work is believed to represent progress in unravelling some of the many complex aspects of these reactions over iron but much additional painstaking work is needed for a complete understanding of ammonia catalysts.

### Apparatus and Procedure

The apparatus and procedure were similar to those described by E. Winter.<sup>1a</sup> A flow system at approximately atmospheric pressure was employed. Mixtures of hydrogen, nitrogen and ammonia were led over the hot catalyst. In a few experiments helium was substituted for nitrogen. The undecomposed ammonia was absorbed in half normal sulfuric acid and the excess acid titrated with standard alkali. The rate of decomposition was estimated as the difference between the ammonia flow at the entrance and at the exit. Each entering gas was measured by a separate flowmeter. Through a multiple capillary arrangement each flowmeter could accurately cover the range 50 to 500 cc. of gas per minute. All of the capillaries were thermostated at  $30^\circ$ . By thus keeping the temperature constant and correcting for pressure changes, satisfactory precision could be obtained. The manometer measuring the flow of ammonia was made from tubing 12 mm. in diameter. It was long enough to allow a pressure difference of 100 cm. of nujol and was kept at constant temperature. Mercury was used in the auxiliary manometers for measuring the pressure at the exit of each flowmeter.

(1) Present address: Department of Chemical and Gas Engineering, The Johns Hopkins University, Baltimore, Maryland.

(1a) E. Winter, *Z. physik. Chem.*, **B13**, 401 (1931).

Synthetic ammonia which had been selected for its purity was dried over fused potassium hydroxide. The hydrogen was electrolytic. The nitrogen was atmospheric (Linde) and was purified by passage first through one tube of hot copper and after mixing with the hydrogen stream through a second. The hydrogen-nitrogen mixtures were then passed through tubes containing soda lime, through a trap immersed in liquid air and finally through a phosphorus pentoxide tube. The copper had been reduced at  $800^\circ$  and then oxidized and reduced again at a lower temperature. The temperature of the catalyst was measured by a thermocouple placed in a glass well extending through the body of the catalyst.

Most of the results reported here are on the decomposition over three iron synthetic ammonia catalysts: Catalyst 931, doubly promoted with 1.3%  $\text{Al}_2\text{O}_3$  and 1.59%  $\text{K}_2\text{O}$ ; Catalyst 954 singly promoted with 10.2%  $\text{Al}_2\text{O}_3$ ; and pure iron Catalyst 973, containing 0.15%  $\text{Al}_2\text{O}_3$  as impurity. The decomposition was also measured over iron supported on  $\text{Al}_2\text{O}_3$ .

### Experimental Results

**Decomposition on Catalyst 931.**—The initial period of reduction of each sample of 931 included about twenty-four hours at  $400^\circ$  and twenty-four to seventy hours at 430 to  $450^\circ$ . The space velocities during reduction were 15,000, 3600, 2400 and 1000 for samples A, B, C and D, respectively. Immediately before each run on this and other catalysts, the catalyst was reduced at the temperature of the run for at least one hour. Between runs the cold catalyst stood in hydrogen at a pressure 1.5 cm. of mercury higher than atmospheric. Unless stated otherwise, the data on the decomposition over all of the catalysts were obtained under conditions of temperature and gas composition which preclude formation of the iron nitrides.<sup>2,3</sup>

An apparent energy of activation of  $43,800 \pm$

(2) Emmett, Hendricks and Brunauer, *THIS JOURNAL*, **53**, 1456 (1930).

(3) Brunauer, Jefferson, Emmett and Hendricks, *ibid.*, **53**, 1778 (1931).