

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF  
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## The Crystal Structure and Dipole Moment in Solution of the Compound $\text{AlH}_3 \cdot 2\text{N}(\text{CH}_3)_3$

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A single crystal X-ray study of  $\text{AlH}_3(\text{N}(\text{CH}_3)_3)_2$  shows that the compound is monomeric in the solid state. The two nitrogen atoms and the aluminum atom lie on a straight line with an N-Al distance of  $2.18 \pm 0.01 \text{ \AA}$ . These data strongly favor a trigonal bipyramidal structure with axial amine groups. The methyl groups of the two  $\text{N}(\text{CH}_3)_3$  ligands are disordered about the N-Al-N axis. The solid undergoes a phase transition between room temperature and  $-35^\circ$ . The measured molar polarization of the molecule in benzene, cyclohexane, and dioxane solutions corresponds to an apparent dipole moment ranging in the different solvents from 1.2 to 1.6 D., if normal atomic polarization estimates are used. Since a dipole moment is not expected for the trigonal bipyramidal model, the observation is most logically rationalized in terms of a high value for the atomic polarization.

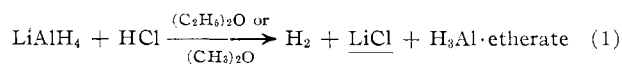
The compound  $\text{H}_3\text{Al} \cdot 2\text{N}(\text{CH}_3)_3$  was first reported by Wiberg and co-workers,<sup>1</sup> who postulated a trigonal bipyramidal structure to account for the monomeric nature of the substance in freezing benzene and boiling ether. This structure was also supported by Schomburg and Hoffmann<sup>2</sup> on the basis of their assignment of the infrared bands. On the other hand such spectral evidence is far from conclusive, and these same authors found an apparent dipole moment of about 1.3 D. in cyclohexane solution. To achieve consistency between the measured polarization and the symmetrical trigonal bipyramidal model a very high atomic polarization was assigned to the compound.

Davidson and Wartik<sup>3</sup> synthesized the related compound  $\text{H}_3\text{Al} \cdot (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$  and found that it was a dimer in the vapor phase. A marked similarity in the infrared spectrum of their new compound and that of  $\text{H}_3\text{Al} \cdot 2\text{N}(\text{CH}_3)_3$  suggested that the bis-trimethylamine alane might also be dimeric in the vapor state and in the solid; thus two octahedrally coordinated aluminums, held together by two hydrogen bridges, appeared as a reasonable possibility for solid and vapor phases of  $\text{H}_3\text{Al} \cdot 2\text{N}(\text{CH}_3)_3$ .

An independent X-ray and dipole study in this Laboratory,<sup>4</sup> coincident with much of the earlier work, now offers very strong support for the trigonal bipyramidal model in the solid. Additional evidence is thus offered in support of the atomic polarization arguments used by Schomburg and Hoffmann to rationalize their dielectric measurements.

### Experimental

1. Preparation of  $\text{H}_3\text{Al} \cdot 2\text{N}(\text{CH}_3)_3$ .—The following reactions were used

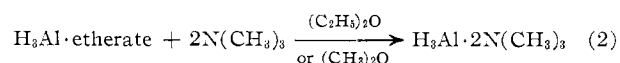


(1) (a) O. Stecher and E. Wiberg, *Chem. Ber.*, **75**, 2003 (1942); (b) E. Wiberg, H. Graf, M. Schmidt, and R. U. Lacial, *Z. Naturforsch.*, **7b**, 578 (1952); (c) E. Wiberg, H. Graf, and R. U. Lacial, *Z. anorg. allgem. Chem.*, **272**, 221 (1953).

(2) G. Schomburg and E. G. Hoffmann, *Z. Elektrochem.*, **61**, 1110 (1957).

(3) J. M. Davidson and T. Wartik, *J. Am. Chem. Soc.*, **82**, 5506 (1960).

(4) C. W. Heitsch, Ph.D. Dissertation, Univ. of Mich., 1959.



Commercial  $\text{LiAlH}_4$  (Metal Hydrides, Inc.) was purified by leaching with diethyl ether through a medium porosity frit in the vacuum system. A 3 to 20 mmole sample of pure  $\text{LiAlH}_4$  dissolved in 5 to 25 cc. of diethyl or dimethyl ether was frozen with liquid nitrogen in a vacuum line reaction tube. Somewhat less than a stoichiometric quantity of HCl (eq. 1) was frozen in; the system was then allowed to warm gradually, and as the ether melted, hydrogen evolution occurred. LiCl then was filtered off at  $-78^\circ$  in the vacuum filter system, and an excess of trimethylamine was added immediately to the filtrate (eq. 2) before insoluble  $\text{AlH}_3$  formed in the ether. The solvent was distilled away at  $-45^\circ$ ; then the  $\text{H}_3\text{Al} \cdot 2\text{N}(\text{CH}_3)_3$  was sublimed at room temperature in the vacuum system onto a cold finger. The yield based on HCl used was about 65%.

A second procedure, analogous to that of Wiberg,<sup>1</sup> involved generation of  $\text{AlH}_3$  from  $\text{AlCl}_3$  and  $\text{LiAlH}_4$  in dimethyl ether at  $-32^\circ$ . Because LiCl is somewhat soluble in the dimethyl ether, the solvent was removed at  $-32^\circ$  and the product was leached from the residue using diethyl ether. Removal of the ether gave the product in 70% yield.

*Anal.* Calcd. for  $\text{H}_3\text{Al} \cdot 2\text{N}(\text{CH}_3)_3$ : Al, 18.1; N, 18.8; H<sup>-</sup>, 2.03; mol. wt., 148. Found: Al, 18.1; N, 18.9; H<sup>-</sup>, 2.07; mol. wt. by vapor pressure depression in dimethyl ether at  $-30^\circ$ ,  $143 \pm 8$ . The above synthetic procedures are somewhat less convenient than those described by Ruff and Hawthorne.<sup>5</sup>

Although the X-ray powder data can be calculated from the single crystal data,  $d$  values, in  $\text{\AA}$ ., for a number of the more intense lines of the room temperature orthorhombic form are listed as an aid to compound identification: m, 6.47; s, 5.92; s, 5.05; s, 4.64; m, 4.42; m, 4.19; m, 3.98; m, 2.37.

2. Crystal Structure. Unit Cell and Space Group.—Two crystals of the compound, grown in Pyrex capillaries, were used to record three-dimensional X-ray data with a precession camera. A total of 241 independent reflections of measurable magnitude were recorded.

The crystals were found to be orthorhombic with cell parameters  $a = 10.10 \text{ \AA}$ .,  $b = 8.84 \text{ \AA}$ ., and  $c = 12.94 \text{ \AA}$ .. Assuming 4 molecules per unit cell, one calculates a density of 0.85 g./cc. It was found in preparing benzene solutions for the dipole moment measurements (Table IV) that the density of the compound was very close to that of benzene, 0.87 g./cc.

Systematic absences limited the possible space groups to  $Cmca$  ( $D_{2h}^{18}$ ) or  $C2cb$  ( $C_{2v}^{17}$ ), of which the former is centrosymmetric with 16 general positions and the latter non-centrosymmetric with 8 general positions in the unit cell.

(5) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960); **83**, 535 (1961).

A phase transition was observed when the crystal was cooled from room temperature to  $-35^\circ$ . The low-temperature modification has an  $a$  axis approximately five times as long as that of the room temperature modification, while the other axes and the apparent space group are unchanged.

**Structure Determination.**—Intensity data were obtained from the diffraction photographs by visual comparison with a series of timed exposures of spots of similar shape. Application of Lorentz and polarization factors yielded a set of raw values of the squares of the structure factors. For every spot observed in two different nets, the ratio of these raw  $|F|^2$  values was calculated and averaged to give the ratio of the scale factors to be applied to the two nets. Through appropriate averaging of such ratios, the scale factors themselves were found and the raw  $|F|^2$  values placed on a common scale.

The  $0kl$  projection of the structure is the same, and is centrosymmetric, in each of the two possible space groups. Furthermore, the four aluminum atoms must occupy the special fourfold positions  $x, 0, 0$ ;  $x, 1/2, 1/2$ ;  $1/2 + x, 1/2, 0$ , and  $1/2 + x, 0, 1/2$ , where  $x$  must equal zero if the space group is  $\text{Cmca}$ . The magnitudes of the structure factors  $F(hkl)$  with  $k + l$  even were, for all values of  $h$ , found to be larger, on the average, than those with  $k + l$  odd. Since Al dominates the scattering, this observation indicated that  $x$  must be zero or nearly so, consistent with  $\text{Cmca}$ .

A  $0kl$  electron density Fourier projection was computed employing only those  $F(0kl)$  structure factors for which  $k + l = 2n$ , and taking all signs positive, as required by the Al contribution. The result suggested the orientation of the  $\text{N}(\text{CH}_3)_3$  groups with respect to the aluminum atom, and was consistent with an essentially linear  $\text{N}-\text{Al}-\text{N}$  molecule lying approximately perpendicular to  $a$ . The space group  $\text{Cmca}$  was now tentatively assumed, placing the Al atoms at centers of symmetry and requiring the molecule to have  $\text{C}_{2h}$  symmetry, at least in a statistical sense.

Several models, differing in the orientation of the methyl groups about the  $\text{N}-\text{Al}-\text{N}$  axis, were now explored by least squares refinement methods. In addition to the ordered structures with one methyl group of each  $\text{N}(\text{CH}_3)_3$  lying in the mirror plane at  $x = 0$  and the other two symmetrically oriented on either side of it, several models with a disordered arrangement of methyl groups were tried. The presence of some form of disorder was suggested by the observed rapid fall off of intensities with increasing angle of diffraction, and by the phase transition observed on lowering the temperature.

The least squares refinement of each model was initially carried out in terms of the scale factor  $K$ , an over-all isotropic thermal parameter  $B$  in the temperature factor  $\exp(-B \sin^2 \theta / \lambda^2)$ , and the atomic coordinates not fixed by the space group. Specifically, the quantity

$$R' = \sum w(hkl) [K F_0(hkl) - F_c(hkl)]^2 / w(hkl) K^2 F_0^2(hkl)$$

was minimized, where the weight  $w(hkl)$  of each reflection was taken as  $3F_{\min} / F_c(hkl)$  if  $F_c(hkl) > 3F_{\min}$ , and equal to unity otherwise.

A disordered model corresponding to a superposition of two orientations,  $180^\circ$  apart, of the trimethylamine group (Fig. 1), and represented by a hexagon of six half-methyls, as shown in Fig. 2, soon proved to be most consistent with the data, and was retained for the subsequent calculations. Individual isotropic thermal parameters were introduced and the refinement continued, giving an agreement of  $R = \sum ||KF_c| - |F_c|| / \sum KF_c = 0.134$ . Next, a three-dimensional electron density plot and a  $(KF_0 - F_c)$  difference synthesis were computed, primarily to check for indications of lower symmetry than  $\text{Cmca}$ . Since no such indications were found, it can be concluded that the space group is  $\text{Cmca}$ , at least within the accuracy of this determination. The only features observed in the difference synthesis suggested the presence of the scattering matter not yet included in the calculations, namely the 21 hydrogen atoms.

Since it was not possible to locate the hydrogen atoms independently, their presence was assumed; three half-hydrogens around each half-carbon with tetrahedral angles and six half-

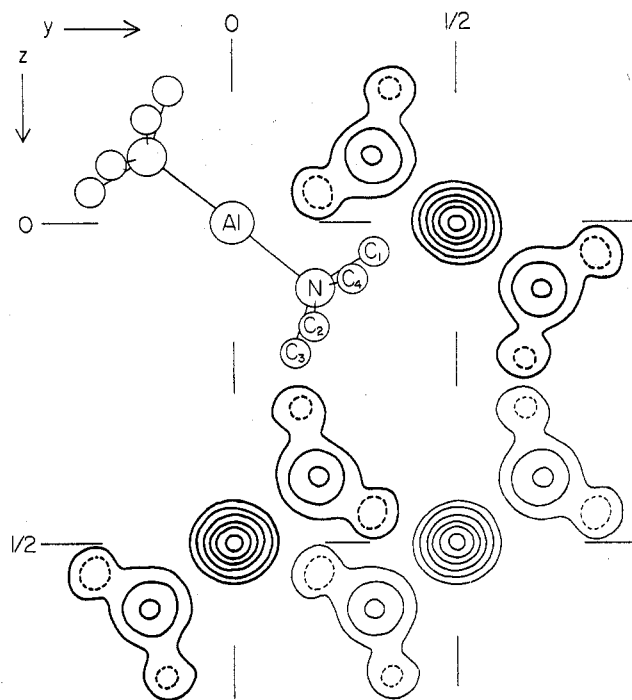


Fig. 1.—A portion of the crystal structure of  $\text{AlH}_3 \cdot 2\text{N}(\text{CH}_3)_3$  showing the packing of the molecules. Sections through the electron density function at  $x = 0.000$  (light contours) and  $0.500$  (heavy contours) are contoured at 1.0, 1.5 (broken), 2.5, 5.0, 7.5, 10.0, and 12.5 electrons/ $\text{\AA}^3$ . The carbon atoms are numbered as in Table II.

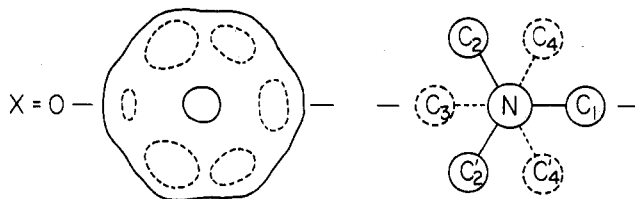


Fig. 2.—Left: Electron density section in the plane of the carbon atoms, perpendicular to the  $\text{N}-\text{Al}-\text{N}$  axis. Contour intervals as in Fig. 1. Right: Schematic interpretation of the electron density distribution in terms of a superposition of two orientations of the trimethylamine group.

hydrogens about the aluminum atom in a hexagonal array perpendicular to the  $\text{N}-\text{Al}-\text{N}$  axis. An isotropic thermal parameter  $B = 10.00$  was used for each half-hydrogen. The assumed coordinates and thermal parameters of the hydrogen atoms were held constant during the subsequent refinement. Several additional cycles of least-squares refinement of the heavy-atom parameters were carried out. The final agreement between observed and calculated structure factors is given by  $R = 0.114$  and  $R' = 0.026$ . The observed and final calculated structure factors are listed in Table I. A final difference synthesis in three dimensions using the quantities  $(KF_0 - F_c)$  as Fourier coefficients was almost featureless, and failed to reveal any significant anisotropy in the heavy atoms. The final coordinates and thermal parameters are given in Table II. Interatomic distances and bond angles, with estimated standard deviations, are given in Table III. The standard deviations were found by dividing the  $|F_0|$  data into four parts and refining each part independently.<sup>6</sup>

**Dipole Moment Measurements on  $\text{H}_3\text{Al} \cdot 2\text{N}(\text{CH}_3)_3$ .**—The total molar polarization of  $\text{H}_3\text{Al} \cdot 2\text{N}(\text{CH}_3)_3$  was obtained from dielectric constant measurements made on dilute solutions of the

(6) C. E. Nordman and C. Reimann, *J. Am. Chem. Soc.*, **81**, 3538 (1959).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS									
<i>hkl</i>	<i>KF<sub>0</sub></i>	<i>F<sub>0</sub></i>	<i>hkl</i>	<i>KF<sub>0</sub></i>	<i>F<sub>0</sub></i>	<i>hkl</i>	<i>KF<sub>0</sub></i>	<i>F<sub>0</sub></i>	
000	--	3360+	226	243	268+	515	91	97+	
002	463	401+	227	111	119+	517	114	108+	
004	132	112-	228	112	100+	518	35	38+	
006	95	88+	2.2.10	63	62+	519	126	126+	
008	210	248+	2.2.11	34	32-	5.1.10	40	38-	
0.0.10	136	182+	2.2.12	60	65+	5.1.11	39	51+	
020	699	594-	240	111	147+	531	70	88+	
021	535	553-	241	130	128+	533	200	197+	
022	238	282+	242	224	235+	535	249	248+	
023	231	108+	243	70	73+	537	126	105+	
024	668	653+	244	172	169+	551	188	170+	
025	184	148+	245	110	77-	553	79	75+	
026	296	315+	246	180	149+	557	44	64+	
027	52	42+	247	119	106-	559	73	81+	
028	74	100+	248	90	107+	573	84	67+	
0.2.10	52	42+	2.4.10	50	65+	575	75	62+	
0.2.12	59	62+	260	245	243+	600	326	351+	
040	152	147+	262	163	148+	602	214	203+	
041	177	172+	263	56	51-	604	59	82+	
042	292	342+	264	77	75+	606	59	55+	
043	34	50+	266	68	62+	608	116	108+	
044	148	157+	268	60	72+	6.0.10	60	73+	
045	191	166-	2.6.10	62	48+	620	77	63+	
046	120	105+	311	290	381+	621	59	63-	
047	74	41-	313	220	222+	622	139	129+	
0.4.8	148	134+	314	172	171-	623	72	37-	
0.4.10	70	83+	315	146	130+	624	173	168+	
060	305	316+	317	138	152+	626	152	134+	
062	168	148+	318	78	49+	627	60	62+	
064	71	63+	319	162	172+	628	43	54+	
066	90	103+	3.1.10	46	51-	640	135	94+	
084	79	95+	3.1.11	65	71+	641	59	53+	
111	589	555+	331	148	133+	642	131	111+	
112	1117	1125-	333	304	314+	643	64	50+	
113	79	110+	335	326	348+	644	109	88+	
114	72	116-	337	207	146+	646	85	82+	
115	295	295+	351	232	232+	647	49	57-	
116	83	106+	352	44	47+	660	100	110+	
117	166	189+	353	110	97+	662	77	78+	
118	77	82+	357	89	89+	664	44	41+	
119	181	162+	359	93	109+	711	180	147+	
1.1.10	50	34-	371	58	52+	712	132	138-	
1.1.11	72	89+	372	62	41-	713	124	82+	
1.1.12	43	41-	373	70	87+	715	99	88+	
1.1.13	40	40+	374	41	36-	717	84	74+	
131	272	233+	375	76	85+	719	61	62+	
132	220	160+	400	253	304+	731	66	72+	
133	618	633+	402	380	357+	732	33	33+	
134	132	98+	404	245	240+	733	136	154+	
135	295	274+	408	162	170+	735	108	105+	
136	140	91+	4.0.10	96	97+	737	40	53+	
137	138	138+	420	246	245+	751	91	89+	
138	31	32-	421	69	94-	753	49	40+	
139	35	53+	422	192	175+	800	268	275+	
1.3.11	45	42+	423	145	99-	802	112	102+	
151	214	229+	424	209	197+	806	62	45+	
152	128	117+	426	217	201+	808	61	58+	
153	85	80+	427	127	160+	821	32	46-	
155	82	79+	428	92	80+	822	95	76+	
157	144	131+	4.2.10	57	63+	824	128	117+	
159	82	96+	4.2.11	35	35-	826	72	76+	
1.5.11	44	54+	4.2.12	49	58+	840	69	54+	
171	102	100+	440	123	133+	842	69	71+	
172	102	88+	441	89	72+	844	64	50+	
173	93	74+	442	173	148+	846	42	35+	
174	33	21-	443	116	121+	848	43	35+	
175	87	88+	444	169	130+	860	56	74+	
177	34	49+	446	173	154+	911	97	78+	
191	33	33+	447	125	132-	912	82	76-	
192	33	28+	448	44	70+	913	63	42+	
193	53	56+	4.4.10	43	43+	915	56	48+	
200	1375	1395+	460	152	138+	917	36	40+	
202	454	489+	461	48	36-	931	32	39+	
204	256	137+	462	134	133+	951	47	47+	
206	35	86+	463	70	64-	10.0.0	107	104+	
208	192	212+	464	89	68+	10.0.2	76	53+	
2.0.10	132	143+	468	53	65+	10.2.2	35	36+	
221	254	234+	511	276	251+	10.2.4	50	52+	
222	259	275+	512	50	51-	10.2.6	54	36+	
223	55	34-	513	195	162+	11.1.1	54	35+	
224	378	376+	514	103	101-				

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Al	0	0	0	6.1
N	0	0.1874	0.1092	6.6
1/2C <sub>1</sub>	0	0.3255	0.0466	8.8
1/2C <sub>2</sub>	0.1186	0.1661	0.1715	9.6
1/2C <sub>3</sub>	0	0.1412	0.2172	11.4
1/2C <sub>4</sub>	0.1188	0.2909	0.1016	10.4

TABLE III

## MOLECULAR PARAMETERS AND THEIR STANDARD DEVIATIONS

(a) Distances in Å.		(b) Angles in deg.	
Al-N	2.18 ± 0.01	Al-N-C <sub>1</sub>	105 ± 2
N-C <sub>1</sub>	1.48 ± 0.02	Al-N-C <sub>2</sub>	105 ± 3
N-C <sub>2</sub>	1.46 ± 0.02	Al-N-C <sub>3</sub>	114 ± 4
N-C <sub>3</sub>	1.46 ± 0.03	Al-N-C <sub>4</sub>	115 ± 2
N-C <sub>4</sub>	1.51 ± 0.07	Al-N-C (av.)	110 ± 2
N-C (av.)	1.48 ± 0.03		

where<sup>7</sup> was used. The very reactive solute was sublimed under vacuum into a special removable flask of known weight, attached to the vacuum line.<sup>4</sup> The flask was filled with dry nitrogen, removed, weighed, and replaced on the line. Solvent was distilled in and the flask weighed again. Solution was removed from the flask with a hypodermic syringe for density or dielectric constant measurements. After each measurement of dielectric constant, a weighed aliquot of solution was withdrawn from the dielectric cell and analyzed for hydridic hydrogen by acid hydrolysis. Concentrations calculated from this analysis agreed with the concentrations calculated from the weight of the original components to within ±0.0001 mole fraction unit. The concentrations recorded are the average of the weight and analytical values. The density of each solution was determined using a special 5-cc. pycnometer with a 2-mm. constriction in the neck. Details are available elsewhere.<sup>4</sup> The total polarization of the solution was determined using the Clausius-Mosotti equation and additivity was assumed in calculating the contributions of solvent and solute to the total measured polarization. Data are summarized in Tables IV and V.

The Electronic polarization or molar refraction can be obtained if the square of the refractive index at infinite wave length,  $n_{\infty}^2$ , is substituted for the dielectric constant,  $\epsilon$ , in the Clausius-Mosotti equation. Values for the index of refraction of the benzene and dioxane solutions were determined using the sodium D line and the green and blue lines of the mercury arc. Extrapolation then provided values for  $n_{\infty}$ . For the hexane solution the values for the blue line were difficult to obtain. On the other hand, since for pure hexane  $nD^2 = \epsilon$ , the difference between  $nD$  and  $n_{\infty}$  compensates for the atomic polarization. In the hexane case, the polarization calculated directly from  $nD$  was assumed to be equal to both electronic and atomic polarizations, not just the electronic polarization as was obtained from values of  $n_{\infty}$  in the other two solvents. Data are shown in Table V.

The atomic polarization is very difficult to measure and is usually estimated as 10 to 20% of the electronic polarization; it is known, however, that such estimates may be in serious error, particularly for flexible molecules with polar bonds.<sup>8</sup>

The apparent dipole moments recorded in Table V are calculated using 10% of the electronic polarization for the atomic polarization. Any sizable increase in the atomic polarization will bring about a corresponding decrease in the orientation polarization and in the magnitude of the permanent dipole moment.

Calculations of moments using  $\partial E/\partial x$  and  $\partial n_{\infty}/\partial x$  in place of solution density were also carried out using the method of

(7) J. R. Weaver, S. G. Shore, and R. W. Parry, *J. Chem. Phys.*, **29**, 1 (1958).

(8) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 420.

compound using very dry dioxane, benzene, and *n*-hexane as solvents. A superheterodyne-beat instrument described else-

TABLE IV  
PROPERTIES OF SOLUTIONS OF THE COMPOUND  
 $\text{AlH}_3 \cdot 2\text{N}(\text{CH}_3)_3$

Concn.	Solvent	$\epsilon^a$	$d$ , g./cc.	$n_{D5892}^b$	$n_{D5461}^b$	$n_{D4985}^b$
0.0669	Dioxane	2.324	0.9915	1.42160	1.42352	1.43128
.0298	Dioxane	2.286	1.0081	1.42015	1.42206	1.42974
.0135	Dioxane	2.258	1.0171	1.41986	1.42176	1.42914
.0000	Dioxane	2.212	1.075	1.41963	1.42145	1.42873
.0543	Benzene	2.362	0.8613 <sup>c</sup>	1.48966	1.49347	1.51072 <sup>c</sup>
.0348	Benzene	2.336	0.8661 <sup>c</sup>	1.49241	1.49638	1.51353
.0151	Benzene	2.304	0.8704 <sup>c</sup>	1.49521	1.49911	1.51645
.0000	Benzene	2.274 <sup>d</sup>	0.8740	1.49722	1.50134	1.51898
.0399	Hexane	1.956	0.6598	1.37465	...	...
.0137	Hexane	1.909	0.6566	1.37305	...	...
.0065	Hexane	...	0.6559	1.37255	...	...
.0000	Hexane	1.897	0.6549	1.37205	...	...

<sup>a</sup>  $\epsilon$  = dielectric constant. <sup>b</sup>  $n_x$  = index of refraction for light of wave length  $x$  Å. <sup>c</sup> Extrapolated from solutions of similar concentrations. <sup>d</sup> Literature value used to calibrate dielectric cell. A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," Natl. Bur. Std. Circ. 514, Washington, D. C., August, 1951.

TABLE V  
POLARIZATION VALUES FOR  $\text{AlH}_3 \cdot 2\text{N}(\text{CH}_3)_3$

Solvent	$P_x^a$ cc.	$P_{ex}^b$ cc.	$P_{ox}^c$ cc.	$\mu,^d$ D.
Dioxane	110.6	51.6	53.8	1.6
Benzene	84.9	48.8	31.1	1.2
Hexane	99.5	50.6	48.9	1.6

<sup>a</sup> Total polarization. <sup>b</sup> Electronic polarization. <sup>c</sup> Apparent orientation polarization. <sup>d</sup> Apparent dipole moment.

P. Cohen-Henriquez.<sup>9</sup> Values obtained are the same as those listed to within 0.1 D. This method assumes that the atomic polarization of the solute will be comparable to that of the solvent which it displaces. Such an assumption is open to serious question in the present case.

## Discussion

Although disorder and thermal motion have precluded precise location of those hydrogen atoms bound to aluminum, certain structural features are revealed by the X-ray data and can eliminate unequivocally a number of structural possibilities. The space group requires that the compound be a *monomer* in the solid state. It is clear from the data that the aluminum atom is located at a center of symmetry. A center of symmetry in a dimer would have to be located between two aluminum atoms and not at either one of them. Even in the unlikely event that the space-group assignment is in error, the logical alternative assignment, C2cb, requires that the Al atoms lie on twofold axes and be separated along these axes by a distance of 10.10 Å. Such a distance is incompatible with a dimeric structure. Monomeric five-coördinate aluminum is indicated.

Although the hydrogens attached to aluminum could not be resolved, a linear N–Al–N pattern is unequivocal. Only two common coördination patterns for five ligands would be consistent with the linear N–Al–N arrangement. These are: (1) The trigonal bipyramid with the nitrogens in apical positions and the three hydro-

gens disordered about the N–Al–N axis [the disordering would be needed to satisfy the  $C_{2h}$  symmetry]; and (2) the improbable square pyramid with the Al atom in the center of the base of the pyramid and the nitrogen atoms in a *trans*-configuration in the base. The trigonal bipyramid is strongly favored. Without a group or unshared electron pair in the sixth octahedral position of the square pyramid, it is probable that the Al atom would be forced out of the plane, giving rise to an N–Al–N angle of less than  $180^\circ$ . The data indicate clearly that the N–Al–N axis is *not* bent by more than 3 or 4 degrees at the most. To be compatible with the space group requirement of a center of symmetry at the Al atom, the entire square pyramidal molecule would have to rotate, giving rise to a time average centrosymmetric structure. Such a rotation of an angular N–Al–N group should lead to distortion of the shapes of the aluminum and nitrogen atoms in the electron density plots. As can be seen in Fig. 2, the aluminum and nitrogen atoms appear to be perfectly spherical.

The obvious inference of a significant dipole moment is that the square pyramidal model is the better. Since the dielectric measurements were made in solution, it might be suggested that the configuration in solution is different from that in the crystal; for example, a molecule of solvent might be coördinated in the sixth position of the square pyramid. Thus the stronger the coördinating properties of the solvent, the larger the perturbation of  $\text{H}_3\text{Al} \cdot 2\text{N}(\text{CH}_3)_3$  should be, and the larger the measured dipole moment should be. One should then expect a variation in the measured moment which parallels the coördinating ability of the solvents [*i.e.*, dioxane > benzene > *n*-hexane]. The fact that the observed moment in *n*-hexane as well as dioxane is 1.6 D. while that in benzene is only 1.2 D. argues against this proposal.

A more probable explanation for the apparent dipole moment in the trigonal bipyramidal model is high atomic polarization. Such an argument is given strong support by the present data. Coop and Sutton<sup>10</sup> report a number of compounds where the atomic polarization runs as high as 30% of the total molar polarization. Since a high atomic polarization value would arise from facile bending modes, and since the peculiar geometry of this coördination number five would make bending vibration relatively intense, atomic polarization is indicated. The N–Al link should be highly polar and any distortion of the N–Al–N angle *in the field* would give rise to an electric moment of the size observed. A Raman line near  $100\text{--}200\text{ cm.}^{-1}$  has been tentatively assigned<sup>11</sup> to the low energy N–Al–N deformation mode. The earlier postulate of Schomburg and Hoffmann relative to high atomic polarization is strongly supported.

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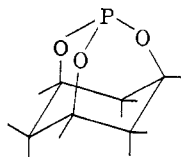
## Phosphorus Complexes of Group III Acids. III. Boron Acids and 2,8,9-Trioxa-1-phospha-adamantane

BY J. G. VERKADE AND C. W. HEITSCH

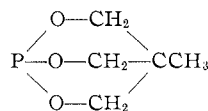
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One to one complexes of the bicyclic phosphite 2,8,9-trioxa-1-phospha-adamantane,  $C_6H_9O_3P$ , have been prepared with the acids  $BH_3$ ,  $B_2H_7$ ,  $B(CH_3)_3$ , and  $BF_3$ . The adduct  $C_6H_9O_3PBH_3$  has a melting point of  $247-251^\circ$  dec. and a measured dipole moment of  $8.82 \pm 0.05$  D. The higher moment of this compound compared to  $CH_3C(CH_2O)_3PBH_3$  ( $8.60 \pm 0.05$  D.) is expected in view of the higher moment of the ligand,  $C_6H_9O_3P$ , which was more accurately determined in this work to be  $4.51 \pm 0.05$  D.  $\Delta H$  for the process:  $C_6H_9O_3P(s) + B(CH_3)_3(g) = C_6H_9O_3PB(CH_3)_3(s)$  from pressure-temperature data was estimated to be  $-15.9 \pm 0.1$  kcal./mole. The foregoing dipole moment data and the value for  $\Delta H$  as well as the displacement of  $(CH_3)_3N$  from  $(CH_3)_3NBH_3$  indicate that  $C_6H_9O_3P$  is a better ligand than  $CH_3C(CH_2O)_3P$  toward  $BH_3$  and  $B(CH_3)_3$ .

The synthesis in 20% yield of the phosphite ester 2,8,9-trioxa-1-phospha-adamantane ( $C_6H_9O_3P$ ) was first reported by Stetter and Steinacker.<sup>1</sup> Brown, Verkade, and Piper recently reported an improved synthesis (70% yield)<sup>2</sup> by a *trans*-esterification procedure. The synthesis and properties of adducts of



boron Lewis acids and a phosphite having the caged structure



have been investigated previously.<sup>3</sup> It was decided, however, that a comparison of the ligand properties of the adamantane system toward some boron reference acids such as  $BH_3$  and  $B(CH_3)_3$  would be of interest. Since the change in steric requirements between the two phosphite ligands upon adduct formation will be quite small, any change in ligand properties will be more purely a function of the lone-pair electron availability on the phosphorus which in turn is determined largely by any change in O-P-O bond angle and inductive effects due to the variation in carbon skeletons.

### Experimental

**Preparation of  $C_6H_9O_3P$ .**—The phosphite,  $C_6H_9O_3P$ , was prepared by a method described previously.<sup>2</sup> Although  $C_6H_9O_3P$  is more stable to moisture than is  $CH_3C(CH_2O)_3P$ , a small amount of ether-insoluble material is formed on prolonged storage of the pure ester *in vacuo* over  $CaCl_2$  with intermittent exposure to the atmosphere for use. Final purification, therefore, was necessary before use in a reaction and this was effected by filtering a solution of  $C_6H_9O_3P$  in dry ether under an inert atmosphere.<sup>3</sup>

**Preparations and Analytical Data.**—The experimental procedures used to obtain diborane, tetraborane, boron trifluoride, boron trimethyl, trimethylamine, trimethylamineborane, the adducts formed with the boron acids, and the pure solvents used in this research, as well as the physical properties of the adducts discussed, are described elsewhere except where indicated.<sup>3</sup>

The method of purifying  $B(CH_3)_3$  reported by Brown was found to be tedious and wasteful since a significant portion of the  $B(CH_3)_3$  could not be recovered from the triethylamine complex.<sup>4</sup> Moreover, other workers have found this product to be impure.<sup>5</sup> The following improved purification procedure was developed, which proved to be markedly simpler than that previously reported.<sup>5</sup>

Approximately 15 g. of  $CH_3C(CH_2O)_3P$  was dissolved in 100 ml. of anhydrous ether and filtered to remove insoluble impurities. When attached to the vacuum line, about 2 l. (1 atm.,  $25^\circ$ ) of crude  $B(CH_3)_3$  gas was condensed into the solution and stirred. The  $CH_3C(CH_2O)_3PB(CH_3)_3$  complex formed as a precipitate. The volatile components of this system were removed at  $-23^\circ$  and the pure  $B(CH_3)_3$  removed at  $25^\circ$  and passed through a trap at  $-78^\circ$  to condense traces of  $CH_3C(CH_2O)_3P$ . The product so prepared was quite pure as shown by its infrared spectrum.<sup>6</sup> The residue of  $CH_3C(CH_2O)_3P$  then could be used repeatedly. This solid was found to absorb  $B(CH_3)_3$  rapidly so that in subsequent cycles the step involving ether solution could be eliminated.

The  $BH_3$  adduct of  $C_6H_9O_3P$  decomposed with melting from  $247-251^\circ$ .

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