Structure of Ammonia Trimethylalane (Me₃Al-NH₃): Microwave Spectroscopy, X-ray Powder Diffraction, and ab Initio Calculations

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Abstract: The structural parameters of the ground-state geometry of $Me_3Al\text{-}NH_3$ calculated by various ab initio methods (HF, B3LYP, and MP2) are presented. For the two isotopomers $Me_3Al\text{-}^{14}NH_3$ and $Me_3Al\text{-}^{15}NH_3$, the rotational transitions $J = 1 \leftarrow 0$ and $J = 2 \leftarrow 1$ were investigated by Fourier transform microwave spectroscopy (4−12 GHz). All transitions showed a complicated hyperfine structure consisting of a large number of lines, so that only partial assignment of the experimental data was possible. The best fit was achieved for the $J = 1 \leftarrow 0$ transition of the ^{15}N-marked sample ($Me_3Al\text{-}^{15}NH_3$), for which 17 of 42 observed components could be assigned by assuming a symmetric top with one quadrupole nucleus (^{27}Al) and three internal methyl group rotors. The combination of microwave spectroscopy and the calculated geometry of $Me_3Al\text{-}NH_3$ at the MP2(fc)/6-311G(2d,2p) level resulted in an Al−N bond length of 2.066(1) Å as the best estimate for the experimental value. These results are compared with those of the well-known isomer $H_3Al\text{-}NMe_3$ (Warner, H. E.; et al. *J. Phys. Chem.* **1994**, *98*, 12215. Atwood, J. L.; et al. *J. Am. Chem. Soc.* **1991**, *113*, 8183. Almenningen, A.; et al. *Acta Chem. Scand.* **1972**, *26*, 3928. March, M. B. C.; et al. *J. Phys. Chem.* **1995**, *99*, 195). The solid-state structure of $Me_3Al\text{-}NH_3$ was solved from X-ray powder diffraction data. The compound crystallizes in the orthorhombic space group *Ama*2 with four molecules per unit cell. There are significant differences between the structure of ammonia trimethylalane in the gas phase and in the solid state. The main differences could be understood on the basis of Onsager's theory using SCRF calculations (B3LYP/6-311++G(2d,p)) (Foresman, J. F.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996. Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486).

Group 13 nitrides are promising materials for advanced microelectronic and optoelectronic devices such as light-emitting diodes and lasers, high-temperature and high-power devices, as well as chemical sensors, acoustic surface wave conductors, and isolating passivation layers.[1,2] Modern metal organic chemical vapor deposition (MOCVD) of aluminum nitride is based on an early investigation of Wiberg.[3] He found that the thermolysis of ammonia trimethylalane, $Me_3Al\text{-}NH_3$, led to a loss of methane according to eq 1.

$$Me_3Al\text{-}NH_3 \xrightarrow{-CH_4} (Me_2AlNH_2)_x \xrightarrow{-CH_4}$$
$$(MeAlNH)_y \xrightarrow{-CH_4} AlN \quad (1)$$
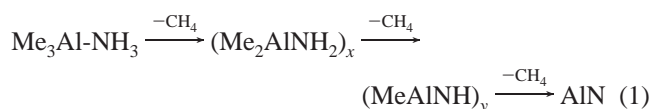
Usually, AlN films are obtained by MOCVD processes from Me_3Al and a large excess of NH_3 (typical ratios of ca. 1:2000),[1,2] but Jones et al. demonstrated that, even without an excess of ammonia, starting from the adduct $Me_3Al\text{-}NH_3$ as a single-source precursor, AlN films could be deposited from the gas phase.[4] From the molecular species depicted in eq 1, only the

structure of the aminoalane as the trimeric compound $(Me_2\text{-}AlNH_2)_3$ is known from a single-crystal analysis.[5] Recently, we had shown that monomeric Me_2AlNH_2 is accessible by photolysis of matrix-isolated $Me_3Al\text{-}NH_3$ in argon at 10 K (eq 2).[6]

$$Me_3Al\text{-}NH_3 \xrightarrow[\text{Ar (10 K)}]{h\nu} Me_2Al=NH_2 + CH_4 \quad (2)$$

Within this investigation, we characterized the starting material as well as the product by IR spectroscopy and ab initio calculations.[6] According to the calculations, ammonia trimethylalane is a C_{3v} symmetrical molecule (Figure 1).

In this article, we report on a detailed investigation of the molecular structure of ammonia trimethylalane. Results of microwave spectroscopy, X-ray powder diffraction, and ab initio calculations are discussed.

Results and Discussion

Ab Initio Calculations and Microwave Spectroscopy. The structural parameters of $Me_3Al\text{-}NH_3$, predicted by several methods and basis sets, are compiled in Table 1, which includes the results of the published MP2(fc)/6-31G(d) calculation.[6] On first sight, there are no significant changes of the bond lengths and angles, except for the Al−N distance, which varies between

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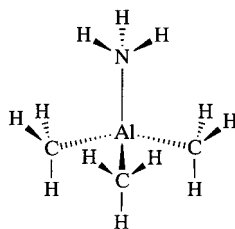(6) Müller, J. *J. Am. Chem. Soc.* **1996**, *118*, 6370.

Figure 1. C_{3v} symmetrical equilibrium geometry of Me₃Al-NH₃ deduced from ab initio calculations.

2.118 (B3LYP/6-311G(d,p) level) and 2.086 Å (MP2(fc)/6-311G(2d,p) level). As expected, the Al−N bond gets shorter as the number of polarization functions is increased.

The experimental gas-phase structure of Me₃Al-NH₃ is unknown in the literature. First, we tried to deduce the structure from gas-phase electron diffraction (GED), but the vapor pressure of the substance up to 50 °C was too low;[7] further heating resulted in the known decomposition of the adduct.[3] Fortunately, the volatility of Me₃Al-NH₃ is sufficiently high even without heating the sample for microwave spectroscopy, which was conducted with a Balle−Flygare type molecular beam Fourier transform microwave spectrometer[8] in the frequency range of 4−12 GHz. Beside the main isotopomer, Me₃Al-¹⁴-NH₃, we investigated the ¹⁵N-labeled compound Me₃Al-¹⁵NH₃; two rotational transitions, $J = 1 \leftarrow 0$ and $J = 2 \leftarrow 1$, for each isotopomer were found. All transitions show a complicated hyperfine structure consisting of a large number of lines (Table 2).[9] The interaction of the electric quadrupole moments of the nitrogen and aluminum nuclei with the surrounding electronic charge distribution results in a hyperfine structure of the rotational lines. Elimination of one quadrupolar nucleus, i.e., substitution of the ¹⁴N atom by a ¹⁵N atom, drastically reduces the amount of lines (Table 2). The hyperfine pattern of the $J = 1 \leftarrow 0$ transition of the main isotopomer, Me₃Al-¹⁴NH₃, with the two quadrupolar nuclei ¹⁴N and ²⁷Al should consist of 19 lines, from which for intensity reasons only ca. 50% should be detectable.[10] In contrast to this expectation, we found 43 lines for this rotational transition (Table 2). Therefore, it is clear that an additional fine structure has to be taken into account, which most probably is caused by internal rotation of the three methyl groups, a phenomenon that has been described in ref 11. However, one pattern of the quadrupole splitting could be identified at the high-frequency end of this transition (Table 3). Fitting the rotational and quadrupole coupling constants yielded $B = 2796.9697(7)$ MHz, $\chi_{zz}(\text{Al}) = 28.30(1)$ MHz, and $\chi_{zz}(\text{N}) = -2.77(1)$ MHz. The quadrupole coupling constants are in good agreement with those of the well-known "inverse" isomer H₃Al-N(CH₃)₃.[12] However, these results should be used with some care. It is not quite clear to which internal rotor state this special pattern belongs. Since a first-order treatment of nuclear quadrupole coupling depends directly on the expectation values of the squared angular momenta, which, in turn, slightly depend on the internal rotor state, these results should be

considered just as effective parameters. They just show that a consistent fit of theses lines is possible.

To simplify the quadrupole pattern, we carried out some measurements on the ¹⁵N isotopomer and tried to analyze the $J = 1 \leftarrow 0$ transition of Me₃Al-¹⁵NH₃ assuming a symmetric top with one quadrupolar nucleus (²⁷Al) and three internal methyl group rotors.[13] To do so, the hindering barrier of the internal rotation of a methyl group was estimated using the relation[14] of eq 3 with the (internal) rotational constant $F = 161$ GHz of one methyl group.

$$E_n = 3\sqrt{V_3 F} \tag{3}$$

E_n was estimated by taking the mean value of the two scaled (factor 0.93) harmonic frequencies, 109.1 (E mode) and 105.8 cm⁻¹ (A₂ mode), respectively, taken from the published MP2-(fc)/6-31G(d) calculation.[6] This gave a rotational barrier of 7160 GHz (2.86 kJ mol⁻¹).

With this information, 17 of 42 measured components of the $J = 1 \leftarrow 0$ transition of the ¹⁵N isotopomer could be assigned. The quadrupole coupling constants were found to be in good agreement with those of the "inverse" isomer H₃Al-NMe₃.[12] But still, this fit is not complete; some lines remained unassigned, and other lines which should be detectable were missing (Table 4). The results of this partial fit are compiled in Table 5. Obviously, the theoretical model, one quadrupole interaction with three internal rotors, is not sufficient to describe the measured rotational transitions of ammonia trimethylalane completely. Perhaps the internal rotation of the NH₃ part against the Me₃Al part has also to be taken into account. Unfortunately, first attempts to include NH₃ internal rotation were not successful.

The structure of trimethylamine alane (H₃Al-NMe₃), which is an isomer of ammonia trimethylalane (Me₃Al-NH₃), is well known by single-crystal X-ray analysis,[15] gas-phase electron diffraction,[16] microwave spectroscopy,[12] and ab initio calculations.[17] Within the microwave study,[12] six isotopomers were examined, and the rotational transitions $J = 1 \leftarrow 0$, $2 \leftarrow 1$, and $3 \leftarrow 2$ had been investigated. The authors were able to assign all of the measured lines on the basis of the theoretical model of a symmetric top with two quadrupole nuclei. That means that the hindering potential of the methyl groups of H₃Al-NMe₃ is much higher than that in the case of Me₃Al-NH₃; as a result, a large difference in the number of lines was found for a particular rotational transition; e.g., the $J = 1 \leftarrow 0$ transition consists of three lines for H₃Al-¹⁵NMe₃ and of 42 lines for Me₃-Al-¹⁵NH₃ (Table 2). The large difference in the hindering potential for the two compounds is not unexpected, because the respective carbon−element distances are quite different: C−N = 1.47 Å for H₃Al-NMe₃ (ab initio calculation)[17] and C−Al = 1.99 Å for Me₃Al-NH₃ (see Table 1). The calculated and experimental C−N rotational barriers are 18.0 kJ mol⁻¹ and between 15.2 and 21.3 kJ mol⁻¹, respectively.[12] We calculated the Al−C rotational barrier for Me₃Al-NH₃ at the MP2(fc)/6-311G(2d,2p) level of theory to be 3.1 kJ mol⁻¹.[18] The calculated

(7) We thank Prof. H. Oberhammer (Universität Tübingen) for the attempted gas-phase electron diffraction of Me₃Al-NH₃.

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(9) Probably there are more lines for the $J = 2 \leftarrow 1$ transition, but we focused our attention on the $J = 1 \leftarrow 0$ transition.

(10) Computer program SYM2Q, written by B. Kleiboemer, J. Kasten, and J. Gripp.

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(18) Calculated barrier without ZPVE correction; total energy, −417.860612 hartrees. The transition state for Me₃Al-NH₃ is reached by a rotation of one methyl group by 180°.

Table 1. Calculated Structural Parameters and Energies of Me$_3$Al-NH$_3$ (C_{3v} Symmetry)

method	basis set	Al−N	Al−C	N−H	C−H$_t$[a]	C−H$_g$[b]	total energy (hartrees)
HF	6-31G(d)	2.117	2.001	1.005	1.090	1.091	−416.977937
MP2(fc)	6-31G(d)[c]	2.106	1.993	1.020	1.097	1.098	−417.603566
	6-311G(d)	2.089	1.988	1.015	1.097	1.097	−417.704833
	6-311G(d,p)	2.098	1.987	1.017	1.097	1.098	−417.800478
	6-311G(2d,p)	2.086	1.988	1.018	1.095	1.096	−417.842158
	6-311G(2d,2p)	2.087	1.988	1.012	1.091	1.092	−417.861796
B3LYP	6-31G(d)	2.117	1.995	1.020	1.100	1.100	−418.777022
	6-311G(d)	2.114	1.994	1.017	1.098	1.098	−418.846453
	6-311G(d,p)	2.118	1.993	1.018	1.097	1.098	−418.867778
	6-311G(2d,p)	2.105	1.989	1.017	1.096	1.097	−418.872561
	6-311G++(2d,p)	2.106	1.989	1.018	1.096	1.097	−418.875488
	6-311G(2d,2p)	2.104	1.988	1.015	1.094	1.095	−418.879059
	6-311G(3df,2p)	2.099	1.986	1.016	1.095	1.095	−418.883622

method	basis set	N−Al−C	C−Al−C	H−N−Al	H$_t$-C−Al	H$_g$-C−Al	H$_g$-C−Al−N
HF	6-31G(d)	99.72	117.21	111.19	111.45	113.01	60.76
MP2(fc)	6-31G(d)	99.60	117.28	111.44	111.28	113.03	60.85
	6-311G(d)	99.64	117.25	111.27	111.69	113.10	60.87
	6-311G(d,p)	99.59	117.28	111.75	111.31	112.91	60.86
	6-311G(2d,p)	99.50	117.26	111.36	111.36	112.82	60.88
	6-311G(2d,2p)	99.40	117.39	111.38	111.43	112.84	60.78
B3LYP	6-31G(d)	99.70	117.22	111.35	110.98	113.40	61.07
	6-311G(d)	99.72	117.21	111.50	110.38	113.64	61.10
	6-311G(d,p)	99.77	117.18	111.39	110.87	113.28	61.11
	6-311G(2d,p)	99.77	117.18	111.39	111.02	113.18	61.03
	6-311G++(2d,p)	99.81	117.16	111.40	110.93	113.13	61.03
	6-311G(2d,2p)	99.75	117.19	111.32	111.05	113.16	60.99
	6-311G(3df,2p)	99.96	117.07	111.43	111.00	113.24	61.02

The table is divided under two spanning headers: "bond length (Å)" for the first block and "bond angle (deg)" for the second block.

[a] Three H atoms in trans positions relative to the Al−N bond (see Figure 1). [b] Six H atoms in gauche positions relative to the Al−N bond (see Figure 1). [c] Data taken from ref 6.

Table 2. Frequency Ranges (MHz) of Rotational Transitions of Ammonia Trimethylalane

	transition	
	$J = 1 \leftarrow 0$	$J = 2 \leftarrow 1$
Me$_3$Al-^{14}NH$_3$	5582.3−5599.0 (43 lines)	11148.4−11216.0 (70 lines)
Me$_3$Al-^{15}NH$_3$	5477.8−5519.5 (42 lines)	10935.0−11012.0 (31 lines)

Table 3. $J = 1 \leftarrow 0$ Transition of Me$_3$Al-^{14}NH$_3$: Partial Fit of the High-Frequency End

	frequency (MHz)		obsd − calcd
$F',F1' \leftarrow F,F1$[a]	observed	calculated	frequency (kHz)
$3/2,3/2 \leftarrow 3/2,5/2$	5589.8497	5589.8497	−0.0
$3/2,5/2 \leftarrow 5/2,5/2$	5598.0397	5598.0443	−4.6
$5/2,5/2 \leftarrow 5/2,5/2$	5599.0454	5599.0449	0.5
$5/2,7/2 \leftarrow 5/2,5/2$	5592.9541	5592.9554	−1.4
$7/2,5/2 \leftarrow 5/2,5/2$	5598.3406	5598.3366	4.0
$7/2,7/2 \leftarrow 5/2,5/2$	5592.1087	5592.1046	4.1
$9/2,7/2 \leftarrow 7/2,5/2$	5592.6608	5592.6634	−2.6

[a] F' is a quantum number according to the coupling scheme $F_1 = J + I_1$ and $F = F_1 + I_2$.

value of 3.1 kJ mol^{-1} matches with our rotational barrier of V_3 = 8051(11) GHz (3.213(5) kJ mol^{-1}; Table 5), deduced from the partial assignment of the $J = 1 \leftarrow 0$ transition of Me$_3$Al-^{15}NH$_3$ (Table 4).

One aim of the microwave spectroscopic studies was the determination of the gas-phase structure of ammonia trimethylalane. As discussed before, the spectra are too complex to allow a complete assignment and to deduce the complete molecular structure. Therefore, to get more information from the experimental data, we tried at least to estimate the Al−N bond length, which surely is the most uncertain and also the most interesting parameter of the molecular structure (Table 1). Therefore, we

Table 4. $J = 1 \leftarrow 0$ Transition of Me$_3$Al-^{15}NH$_3$: Partial Fit Performed with XIAM[13]

		frequency (MHz)		obsd − calcd
transition[a]		observed[b]	calculated	frequency (kHz)
AAA	$3/2 \leftarrow 5/2$	5481.8900[c]	5481.8768	13.2
AAA	$7/2 \leftarrow 5/2$	5484.5306	5484.5641	−33.5
EAA	$3/2 \leftarrow 5/2$	5490.7666	5490.7899	−23.5
EAA	$5/2 \leftarrow 5/2$	5498.8896	5498.8810	8.6
EAA	$7/2 \leftarrow 5/2$	5493.1903	5493.2015	11.2
EEA	$3/2 \leftarrow 5/2$	5489.9574[d]	5489.9390	18.4
EEA	$5/2 \leftarrow 5/2$	5497.9777	5497.9794	−1.7
EEA	$7/2 \leftarrow 5/2$	5492.3087	5492.3337	−25.1
EE′A	$3/2 \leftarrow 5/2$	5513.4323	5513.4174	−14.9
EE′A	$5/2 \leftarrow 5/2$	5506.3699	5506.3642	5.8
EE′A	$7/2 \leftarrow 5/2$	5508.4679	5508.4545	13.4
EEE	$3/2 \leftarrow 5/2$	5478.6009	5478.5667	34.2
EE′E	$3/2 \leftarrow 5/2$	5519.4720	5519.4743	−2.3
EE′E	$5/2 \leftarrow 5/2$	5512.7948	5512.8072	−12.4
EE′E	$7/2 \leftarrow 5/2$	5514.7804	5514.7793	1.1

[a] The transitions are designated by their torsional symmetry species (AAA, etc.) and the $F \leftarrow F$ quantum numbers. [b] When the measured frequencies were investigated, it seemed that some lines appeared as a doublet split by only a few kilohertz. This becomes obvious especially for the frequencies of the $J = 2 \leftarrow 1$ transitions. In the fit of Table 4, the components of the doublets were averaged to give a hypothetical center frequency. [c] Arithmetic mean of two doublet components: 5481.8238 and 5481.9562 MHz. [d] Arithmetic mean of two doublet components: 5489.8921 and 5490.0227 MHz.

used the following procedure: first, we took the calculated structure of Me$_3$Al-NH$_3$ at the highest ab initio level (MP2(fc)/6-311G(2d,2p). Second, with the exception of the Al−N distance, all other parameters of this calculated structure were fixed, and only the Al−N bond length was fitted so that the experimental rotational constants were reproduced. It can be shown that the choice of the rotational constant has a minor

Table 5.   Results of the Partial Fit of Table 4

parameter	value
$B_x = B_y$	2741.945(4) MHz
B_z	2588.13(5) MHz
χ_{zz}	29.86(5) MHz
V_3	8051(11) GHz
δ^a	74.5(6)

[a] δ is the angle between the internal rotation axis and the z-axis; this is the symmetry axis (for comparison, the ab initio calculation gave 80.6° (i.e., N−Al−C = 99.4°) for this angle).

Table 6.   Al−N Bond Lengths (Å) of $Me_3Al\text{-}NH_3$ and $H_3Al\text{-}NMe_3$

	$Me_3Al\text{-}NH_3$	$H_3Al\text{-}NMe_3$
[15]N isotopomer	2.067	2.050
[14]N and ^{15}N isotopomers[a]	2.065	2.050
all six isotopomers[b]		2.052
MP2(fc)/6-311G(2d,2p)	2.087	2.064
CISD/DZP[c]		2.063
GED[d]		2.063(7)

[a] For $Me_3Al\text{-}^{14}NH_3$, rotational constant $B = 2793.2$ MHz was used. [b] Data taken from ref 12; see text for discussion. [c] Data taken from ref 17. [d] Data taken from ref 16.
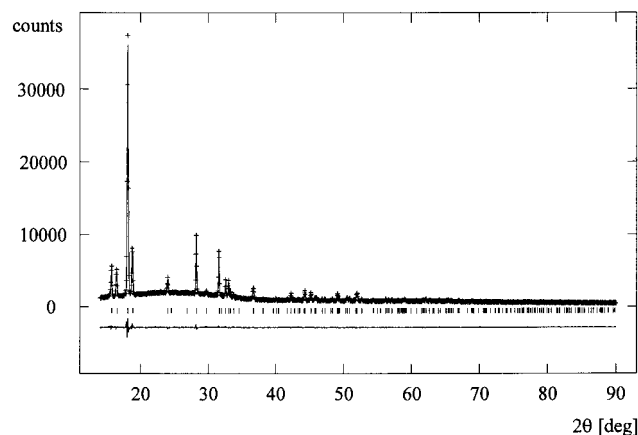

Figure 2. X-ray powder diffraction data of $Me_3Al\text{-}NH_3$. Depicted are the experimental (+) and the calculated profile (solid line), and the difference of both graphs. Vertical lines indicate the positions of reflections.

influence on the Al−N bond length; it makes no difference whether a frequency at the low-frequency end or at the high-frequency end of the "bands" of the $J = 1 \leftarrow 0$ transition is taken as the $2B$ value. A much larger influence arises from the choice of the other internal parameters, as small changes in the distances and angles lead to significant changes in the rotational constants. For test purposes, we applied the same procedure to the "inverse" isomer $H_3Al\text{-}NMe_3$, where the rotational constants of six isotopomers are known, and where the complete internal structure has been determined. The results of both compounds were found to be consistent (Table 6). The value of the ab initio bond length is always about 0.02 Å larger than the one obtained from the rotational constants. In the first row of Table 6, the results of a fit using the rotational constants of the ^{15}N isotopomers are given; in the second row the rotational constants of both the ^{14}N and ^{15}N isotopomers were used. For the hydride $H_3Al\text{-}NMe_3$, the complete structure could also be fitted using the rotational constants of six isotopomers; the resulting bond length of 2.052 Å must be regarded as the best one for $H_3Al\text{-}NMe_3$. Therefore, we recommend an Al−N bond length of 2.066(1) Å as a reliable value for ammonia trimethylalane, $Me_3Al\text{-}NH_3$.
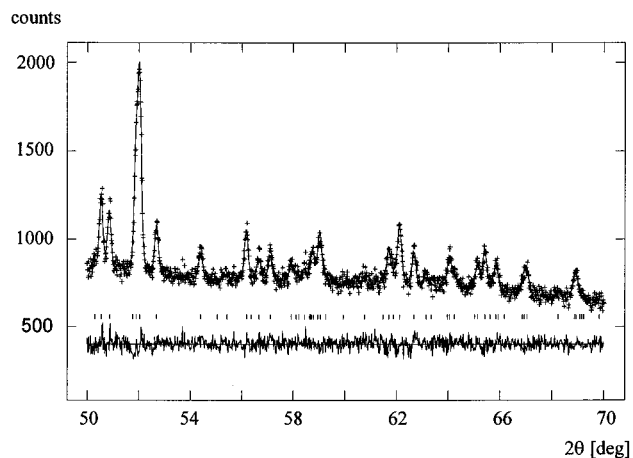

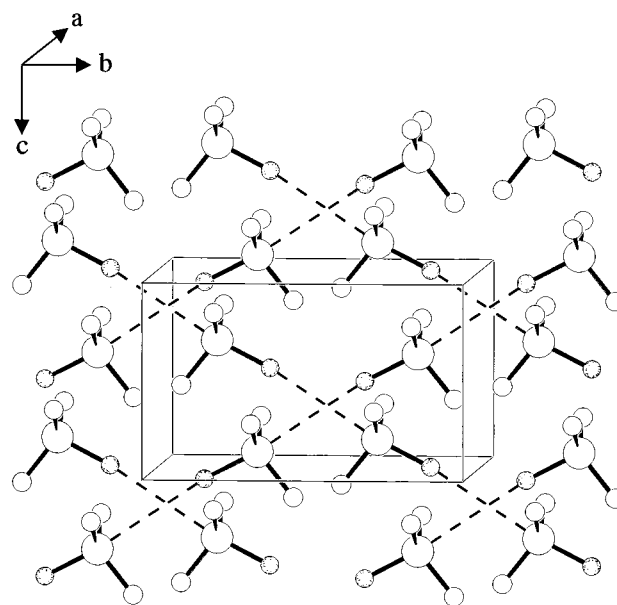**Figure 3.**   Enlarged high-angle range of the X-ray powder diffraction data in Figure 2.

Figure 4.   Packing of $Me_3Al\text{-}NH_3$ in the solid state.[31]

X-ray Powder Diffraction. To solve the molecular structure of $Me_3Al\text{-}NH_3$, we tried to crystallize the molecule from hexane solutions at various temperatures, but so far we have not succeeded in growing suitable crystals for a single-crystal X-ray analysis. Recently, we demonstrated that this compound can be obtained in an analytically pure form by sublimation in vacuo at ca. 30 °C in high yields.[6] The X-ray powder diffraction data of the resulting micro crystalline powder of $Me_3Al\text{-}NH_3$ measured at ambient temperature in the 2θ range of 14° and 90° are shown in Figure 2. The crystal structure of the title compound could be solved from these data by direct methods and was refined by applying the Rietveld method (see Experimental Section). The resulting refined profile is also given in Figure 2. The quality of the refinement can be seen in Figure 3, which enlarges the high-angle region of the powder pattern.

Ammonia trimethylalane crystallizes in the orthorhombic space group *Ama*2 with four molecules per unit cell. The molecules are lined up in a head-to-tail manner to form infinite chains with intermolecular contacts of the van der Waals type (Figure 4). The N, Al, and C1 atoms lie on the crystallographic mirror plane; i.e., the molecule exhibits C_s point group symmetry (Figure 5). As discussed before, ab initio calculations predicted a C_{3v} symmetrical equilibrium geometry for $Me_3Al\text{-}NH_3$ (Figure
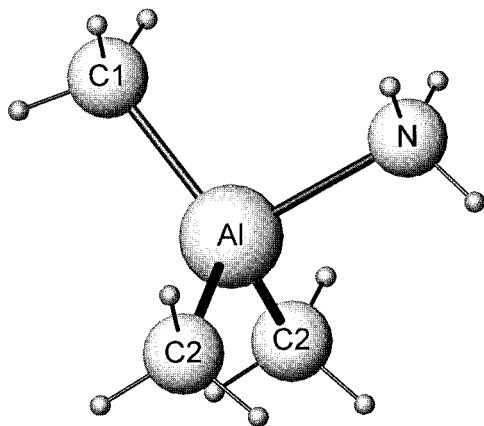
Figure 5. Molecular structure of Me₃Al-NH₃ in the solid state.

Table 7. Experimental Bond Lengths (Å) and Angles (deg) of Me₃Al-NH₃ in the Solid State

Al−N[a]	2.004(5)	N−Al−C1	101.1(2)
Al−C1	1.945(6)	N−Al−C2	103.0(2) 2×
Al−C2	1.976(3) 2×	C1−Al−C2	115.7(1) 2×
		C2−Al−C2	115.2(2)

[a] Intermolecular Al−N distance = 4.331(5) Å.

1 and Table 1). With respect to the point group symmetry, the geometry of the molecule in the crystal is not far from the calculated symmetry, as revealed by the small differences between the Al−C bond lengths, the N−Al−C angles, and the C−Al−C angles, respectively (Table 7).

Comparison of the Gas-Phase and the Solid-State Structures. There are significant differences between the structures of Me₃Al-NH₃ in the gas phase and in the solid state (Tables 1, 6, and 7). In the gas phase, the Al−N bond is longer and the C₃Al pyramid is flatter than those in the solid state. Similar trends are known from other donor−acceptor complexes; e.g., the B−N bond of H₃B−NH₃ decreases by 0.11 Å, judged on microwave data[19] in comparison with single-crystal X-ray data.[20] The structural differences can be quite enormous: F₃B-NCH shows differences of 0.84 Å for the B−N bond length and 14° for the F−B−N bond angle (microwave[21] and X-ray data[22]). The reasons for these findings are well understood. These donor−acceptor complexes are polar molecules, and the intermolecular forces in the crystalline state are mainly governed by dipole−dipole interactions. The higher the molecular dipole moment is, the higher the energy that is gained by the crystallization of the compound. Hence, a change of the molecular geometry resulting in an increase of the dipole moment can be thermodynamically favorable. Of course, the change of the molecular geometry alone causes an increase in energy, which must be compensated by the stronger interactions in the crystal.

Self-consistent reaction field (SCRF) calculations are commonly used to predict structures of molecules in polar environments.[23] For example, SCRF calculations based on Onsager's theory[23,24] reproduced the experimental molecular structures of

Table 8. Comparison of Structural Parameters of Me₃Al-NH₃[a]

	B3LYP/ 6-311++G(2d,p)	SCRF[b]/B3LYP/ 6-311++G(2d,p)	X-ray
Al−N	2.106	2.083	2.004(5)
Al−C	1.989	1.992	1.966[c]
N−Al−C	99.81	101.79	102.4[c]
C−Al−C	117.16	115.94	115.5[c]
H−N−Al	111.40	112.16	
Hₜ-C−Al	110.93	110.48	
Hg-C−Al	113.13	113.24	
Hg-C−Al−N	61.03	61.03	

[a] Bond lengths are given in angstroms; bond angles are given in degrees. [b] Onsager theory:[23,24] radius of the polar sphere = 3.99 Å and ϵ = 78.54. [c] Mean values from Table 7.

the solid state of the two compounds H₃B-NH₃ and F₃B-NCH, mentioned above, satisfactorily.[20,25] We optimized the geometry of Me₃Al-NH₃ in a simulated solvent with a polarity similar to that of water. Table 8 compares the results of the ab initio calculations, with and without the reaction field, and the experimental data. According to the SCRF calculation, Me₃Al-NH₃ has a shorter Al−N bond and a more pronounced AlC₃ pyramid in the polar surrounding, while the dipole moment increases from 4.89 to 6.35 D with respect to the B3LYP/6-311++G(2d,p) level of theory.[26] The N−Al−C angle of 101.79° and the C−Al−C angle of 117.16° from the SCRF calculation match well with the mean values from the X-ray powder diffraction of 102.4 and 115.5°, respectively. In contrast to the angles, there is not such a good match between the calculated Al−N distance of 2.083 Å and the value of 2.004(5) Å in the solid state (Table 8). As it was shown by ab initio calculations on various levels of theory (Table 1), the Al−N bond length is the most difficult structural parameter to calculate. The MP2(fc)/6-311G(2d,2p) level, the highest level applied in this investigation, gives an Al−N distance of 2.087 Å, whereas 2.066(1) Å was deduced from microwave spectroscopy (Table 7). The SCRF method predicts a 1.09% shortening of the Al−N bond by a polar environment. If the real Al−N distance of the gas-phase molecule were 2.087 Å, the polar effect should result in 2.064 Å; based on the results of the microwave spectroscopy, the shortening should give ca. 2.04 Å. Still, even with these estimations, a small difference between the measured and calculated Al−N bond length remains, probably for two main reasons. First, we applied a theoretical model which is relatively simple and, therefore, cannot describe the reality precisely. Second, bond lengths from X-ray diffraction investigations are usually shorter than the real nucleus-to-nucleus distances. The amount of the latter effect may be estimated by comparison of the measured and calculated Al−C bond lengths (Table 8): the Al−C distances, 1.989 and 1.992 Å, are uninfluenced by the polar environment, and the mean experimental value is ca. 0.02 Å shorter (1.966 Å).

In summary, the combination of microwave spectroscopy, X-ray powder diffraction, and ab initio calculations gives a detailed picture of the molecular structure of ammonia trimethylalane. The geometry of the molecule in the gas phase is distinctively different from that of the solid state, which can be understood on the basis of SCRF calculations.

Experimental Section

Me₃Al-NH₃ and Me₃Al-¹⁵NH₃ were synthesized and purified according to the literature methods.[6]

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(26) The dipole moment points from the Al to the N atom.

Microwave Spectroscopy. The microwave measurements were carried out using a pulsed molecular beam Fourier transform microwave spectrometer, which has been described before.[8] As the compound is very moisture sensitive, some precautions were necessary in order to avoid decomposition. After synthesis, the sample was kept under argon in a Schlenk flask. From this flask, it was filled in a helium flow into a reservoir upstream of the beam nozzle. The time the sample was exposed to air had to be kept as short as possible; however, the use of an argon box for filling the sample into the reservoir was not necessary. Nevertheless, the spectral lines were not detectable from the beginning; a time of about 30 min had to pass until the spectra could be recorded. Probably during this time, traces of water in the inlet line reacted with a part of the sample which was thereby removed. When the signals became weaker after several hours of measurements, simply stirring the sample with a spatula led to stronger lines again, so that the measurements could be continued. Most measurements were carried out at room temperature; heating the sample turned out to be not necessary.

X-ray Powder Diffraction. The crystal structure of Me_3Al-NH_3 was solved and refined from X-ray powder diffraction data. Freshly sublimed and carefully ground Me_3Al-NH_3 was sealed in a capillary (LINDE-MANN-glass, 0.3 mm diameter). The X-ray powder investigations were performed on a STOE Stadi P2 powder diffractometer (Cu $K\alpha_1$ radiation, Ge monochromator, PSD detector). All reflections could be indexed in an orthorhombic unit cell using the program DICVOL.[27] The systematic absences of reflections led to *Cmcm* (No. 63), *Cmc*21 (No. 36), and *Ama*2 (No. 40) as possible space groups. From an estimate of the volume of Me_3Al-NH_3, the conclusion was drawn that the unit cell contains four molecules of the title compound.

In a first step, integrated intensities were obtained by the Le Bail method[28] using the GSAS suite of programs.[29] Direct methods (SIR-POW.92)[30] gave the only reasonable structural solution with these intensities in the space group *Ama*2 (No. 40). All non-hydrogen atoms

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could be found in this step. Subsequently, the crystal structure was refined by applying the Rietveld method again with the GSAS package.[29] The hydrogen atoms were placed at calculated positions and constrained to ride on the respective atoms (N–H 0.90 Å, C–H 0.95 Å, $B_{iso}(H) = 1.1B_{iso}(C)$ and $1.1B_{iso}(N)$). All non-hydrogen atoms were refined isotropically. No absorption correction was applied to the data (*Ama*2 (No 40); $Z = 4$; $a = 9.8257(2)$ Å, $b = 10.7759(2)$ Å, $c = 6.6329(2)$ Å; $14° \leq 2\theta \leq 90°$; 172 reflections in the final refinement; $R_p = 0.0300$, w$R_p = 0.0393$, $R_{Bragg} = 0.0659$).

The quality of the refinement can be seen in Figures 2 and 3; the latter enlarges the high angle range of the powder pattern. Selected bond distances and angles are listed in Table 7. Figures 4 and 5 show the packing of the molecules in the solid state and the refined molecular structure of Me_3Al-NH_3, respectively. In the case of C1 and N, which lie on a crystallographic mirror plane, there are only two possible orientations for the H atoms, whereas the orientation of the C2 methyl groups is not restricted by symmetry. Therefore, we included both orientations for C1 and for N in our refinements by refining the respective occupancies. In both cases, only one orientation showed an occupancy of the respective positions close to 1. These hydrogen positions correspond to methyl group conformations which are similar to the ones calculated for the molecule in the gas phase (Figure 1).

Ab Initio Calculations. The Gaussian 94 package,[32] run on a cluster of workstations (Rechenzentrum der RWTH Aachen), was applied for all ab initio calculations. The calculations were conducted in redundant internal coordinates. The harmonic frequencies were checked on various levels of theory (HF/6-31G(d), MP2(fc)/6-31G(d), and B3LYP/6-311++G(2d, p)) to ensure that the C_{3v} symmetrical molecule corresponds to a local minimum. Following common practice, 0.5 Å was added to the computed molecular radius of the HF/6-31G(d) structure of Me_3Al-NH_3, giving an estimated value of 3.99 Å for the polar sphere for the SCRF calculation.[23] The polarity of the model solvent was chosen to be equal to that of water ($\epsilon = 78.54$).

Supporting Information Available: Complete list of the measured frequencies for the $J = 1 \leftarrow 0$ and $J = 2 \leftarrow 1$ transitions of the two isotopomers $Me_3Al-^{14}NH_3$ and $Me_3Al-^{15}NH_3$, and the positional and displacement parameters for Me_3Al-NH_3 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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