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Dimethylalane, [Me_2AlH]$_n$, in the Vapor Phase and in Hydrocarbon Solution: Gas-Phase Electron Diffraction, Spectroscopic, Colligative, and ab Initio Studies

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The nature of dimethylalane, [Me_2AlH]$_n$, in the vapor phase and in hydrocarbon solutions has been reinvestigated experimentally by gas electron diffraction (GED), IR and mass spectrometric, and vapor pressure depression measurements, and also by quantum chemical calculations. The predominant vapor species at low pressures and temperatures near 470 K is the dimer ($n = 2$), but at temperatures near 330 K the vapor consists of a mixture of the dimer and a smaller proportion (ca. 30%) of the trimer ($n = 3$). The results of the GED measurements have been analyzed, together with those of ab initio calculations, using the SARACEN method to determine the most reliable structures of the doubly hydrogen-bridged dimer, $Me_2Al(\mu\text{-}H)_2AlMe_2$, and singly hydrogen-bridged trimer, $Me_2Al(\mu\text{-}H)Me_2Al(\mu\text{-}H)Me_2Al(\mu\text{-}H)$. Salient structural parameters in the r_a structures were thus found to be (a) for the dimer, r(Al−H) 177.6(7), r(Al−C) 195.2(2), r(Al···Al) 262.5(6), r(C−H) 111.4(2) pm; ∠C−Al−C 117.7(4), ∠Al−H−Al 95.3(6), ∠Al−C−H 108.9(7)°; and (b) for the trimer, r(Al−H) 171.1(23), r(Al−C) 195.8(3), r(Al···Al) 315.3(8) pm; ∠Al−H−Al 134.3(36), ∠Al−C−H 110.1(31)°. However, solution studies indicate the presence of an oligomer [Me_2AlH]$_n$ with $n > 3$, in addition to the dimer and, probably, the trimer.

Introduction

The dialkylalanes, [R_2AlH]$_n$, have attracted attention, not only as important reducing agents in organic chemistry[1,2] but also for their potential as precursors or intermediates in MOCVD processes giving rise to aluminum films.[3] Simplest of these is dimethylalane, [Me_2AlH]$_n$, which was first described in detail in 1942[4] and to which access can be conveniently gained by the reaction between trimethylaluminum and $LiAlH_4$.[5] High viscosity and low vapor pressure (ca. 1 Torr) at room temperature suggest that the compound is strongly associated in the liquid state. Vapor pressure depression measurements on isopentane solutions at 293 K gave a molecular weight, M, of ca. 178 for dimethylalane.[5] The conclusion drawn from this result, that the alane adopts a *trimeric* structure (M_{calc} 174) in hydrocarbon solutions, has remained virtually unchallenged ever since. By contrast, vapor density measurements[5] imply that the vapor consists of a *mixture* of oligomers. At high temperature (ca. 440 K) the measured molecular weight (M 118.5) suggests that the dimer (M_{calc} 116) is the dominant vapor species, a conclusion supported by electron-diffraction measurements reported in 1972.[6] At 355 K, however, the vapor was found to give M 141.6, and this has been taken to indicate a mixture of dimeric and trimeric oligomers (in roughly equal proportions).[5] Such is the basis on which the vibrational spectra of dimethylalane have been interpreted,[7−9] and it has

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(1) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 1, p 555. Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Housecroft, C. E., Ed.; Elsevier Science: Oxford, U.K., 1995; Vol. 1, p 431. Zietz, J. R., Jr.; Robinson, G. C.; Lindsay, K. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 7, p 365. Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; McKillop, A., Ed.; Elsevier Science: Oxford, U.K., 1995; Vol. 11, p 277.

(2) Miller, J. A. In *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Blackie: Glasgow, U.K., 1993; p 372.

(3) Russsell, D. K. *Coord. Chem. Rev.* **1992**, *112*, 131.

(4) Stecher, O.; Wiberg, E. *Chem. Ber.* **1942**, *75B*, 2003.

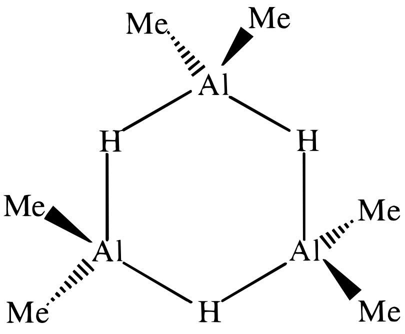
(5) Wartik, T.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1953**, *75*, 835.

(6) Almenningen, A.; Anderson, G. A.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 2315.

(7) Hoffmann, E. G.; Schomburg, G. *Z. Elektrochem.* **1957**, *61*, 1101, 1110.

10.1021/om990811f CCC: $19.00

become almost an axiom that the more highly associated oligomer is $[Me_2AlH]_3$, presumably with the structure **I** based on a six-membered $[Al(\mu\text{-}H)]_3$ ring akin to that in $[Bu^t{}_2AlH]_3$ identified in the crystal structure of di-*tert*-butylalane.[10] The vapor has been analyzed by mass spectroscopy,[11] but, although mass peaks corresponding to dimeric fragments such as $Al_2Me_3H_2^+$ are prominent, there is little to guide the identification of any heavier oligomer.



I

Here we report the results of a new investigation into the nature of dimethylalane, $[Me_2AlH]_n$, in the vapor phase and in hydrocarbon solution. The vapor has been reexamined at different temperatures by reference to its infrared and mass spectra and to its gas electron diffraction (GED) pattern. All the results are consistent with the original conclusions[5,6] that the dimer $[Me_2AlH]_2$ is the predominant vapor species at low pressures (0.1–10 Torr) and high temperatures (>400 K), but that it exists in equilibrium with a significant partial pressure of the trimer $[Me_2AlH]_3$ at lower temperatures. Ab initio calculations at HF and MP2 levels of theory have played an important part in modeling the optimum geometries and harmonic force fields of the dimer and trimer molecules. The SARACEN method[12] has then been used to refine the structures of the two molecules from the primary input of the experimental GED results. Parameters that cannot be refined independently on the basis of these results alone are made subject to restraints determined by an array of ab initio calculations; all geometric parameters and significant amplitudes of vibration are then refined as a matter of principle. Hence we have improved the reliability of the structure determined for the diborane-like dimer $Me_2Al(\mu\text{-}H)_2AlMe_2$ and achieved the first structural characterization of the trimer as represented in **I**, despite its being only a secondary source of scattering intensity. Dimethylalane exists also in hydrocarbon solutions as a mixture of oligomers, with the dimer prevailing at low concentrations and high temperatures. However, the combination of vapor pressure depression and NMR measurements implies a significant contribution from an oligomer $[Me_2AlH]_n$ with a nuclearity n greater than 3. The results may thus have some important lessons for the structures favored by other group 13 metal hydrides in the condensed phases to add to those learned, for example, from the compounds $[GaBH_6]_n$,[13] $[Me_2AlBH_4]_n$,[14] $[MeZnBH_4]_n$,[15] and $[Me_2InB_3H_8]_n$.[16]

Experimental Section

Synthesis. Dimethylalane was prepared by the reaction between trimethylaluminum (Aldrich) and freshly recrystallized $LiAlH_4$ (Aldrich), according to the procedure described previously.[5] The reaction took place at room temperature under solvent-free conditions, typically over a period of 72 h. The volatile product of the reaction was subsequently fractionated in vacuo, being collected in a trap held at 242 K. The best yields were secured by warming the reaction vessel to ca. 330 K during distillation, as this aided the desorption of the alane from the solid residue. The authenticity of the sample was checked by reference (i) to the IR spectra of the vapor[9,17,18] and of the solid condensate formed at 77 K[17,18] and (ii) to the ^1H, ^{27}Al, and ^{13}C NMR spectra of the compound dissolved in toluene-d_8[18] (see Table 2).

Spectroscopic Measurements. NMR measurements were made on toluene-d_8, methylcyclohexane-d_{14}, and isopentane-d_{12} solutions of dimethylalane at temperatures between 213 and 293 K using a Bruker model AM300 spectrometer. ^1H spectra were recorded at 300, ^{27}Al spectra at 78.2, and ^{13}C spectra at 75.5 MHz.

IR spectra were recorded using either a Perkin-Elmer model 580A dispersive spectrophotometer or a Mattson Galaxy FT-IR instrument. Vapor samples of the alane for studies at different temperatures were contained in a Pyrex-bodied cell to which silicon windows were sweated[19] giving a path-length of ca. 10 cm; the cell was placed in a metal chamber equipped with CsI outer windows and through which heated nitrogen gas could be passed. Solid films of the alane were presented for spectroscopic analysis by causing the vapor to condense on a CsI window contained in an evacuated glass shroud and maintained at 77 K.

Mass spectra were recorded using a Hiden HAL/3F residual gas analyzer equipped with an evacuable all-glass inlet system, with ionization effected by electron impact. Variation of the electron energy in the range 0–100 eV was possible so that the degree of molecular fragmentation could be reduced by lowering this energy. Spectra were in fact recorded at an electron energy of 50 eV.

Vapor Pressure Depression Measurements. The molecular weight of dimethylalane in isopentane solution was determined by vapor pressure depression measurements, using the same method as employed previously by Wartik and Schlesinger.[5] The vapor pressures of the solutions and the pure solvent were measured by means of a U-shaped mercury manometer, the levels in which were read to the nearest 0.05

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(8) Schrötter, H. W.; Hoffmann, E. G. *Ber. Bunsen-Ges. Phys. Chem.* **1964**, *68*, 627.

(9) Grady, A. S.; Puntambekar, S. G.; Russell, D. K. *Spectrochim. Acta, Part A* **1991**, *47A*, 47.

(10) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37.

(11) Tanaka, J.; Smith, S. R. *Inorg. Chem.* **1969**, *8*, 265. Chambers, D. B.; Coates, G. E.; Glockling, F.; Weston, M. *J. Chem. Soc. A* **1969**, 1712.

(12) Blake, A. J.; Brain, P. T.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Phys. Chem.* **1996**, *100*, 12280. Brain, P. T.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 4589.

(13) Pulham, C. R.; Brain, P. T.; Downs, A. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1990**, 177. Downs, A. J.; Parsons, S.; Pulham, C. R.; Souter, P. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 890.

(14) Aldridge, S.; Blake, A. J.; Downs, A. J.; Gould, R. O.; Parsons, S.; Pulham, C. R. *J. Chem. Soc., Dalton Trans.* **1997**, 1007.

(15) Aldridge, S.; Blake, A. J.; Downs, A. J.; Parsons, S.; Pulham, C. R. *J. Chem. Soc., Dalton Trans.* **1996**, 853.

(16) Aldridge, S.; Downs, A. J.; Parsons, S. *J. Chem. Soc., Chem. Commun.* **1996**, 2055.

(17) Baxter, P. L. D.Phil. Thesis, University of Oxford, U.K., 1984.

(18) Jones, L. A. D.Phil. Thesis, University of Oxford, U.K., 1993.

(19) The cell was made by Mrs. T. McGrady, Inorganic Chemistry Laboratory, University of Oxford; see: McGrady, T. *Br. Soc. Sci. Glassblowers J.* **1998**, *36*, 65.

Table 1. Nozzle-to-Plate Distances, Weighting Functions, Correlation Parameters, Scale Factors, and Electron Wavelengths Used in the Electron-Diffraction Study

sample temperature/K	nozzle-to-plate distance/mm	weighting functions/nm^{-1}					correlation parameter	scale factor/k[a]	electron wavelength[b]/pm
		Δs	s_{min}	sw_1	sw_2	s_{max}			
470	258.45	2	20	40	140	164	0.4695	0.828(17)	5.683
	95.10	4	80	100	248	300	−0.0905	0.623(19)	5.682
327	258.52	2	20	40	140	164	0.4887	0.859(11)	5.683
	95.14	4	80	100	248	300	−0.2763	0.716(15)	5.682

[a] Figures in parentheses are the estimated standard deviations. [b] Determined by reference to the scattering pattern of benzene vapor.

Table 2. Optimized Geometries for [Me$_2$AlH]$_n$ Molecules, where $n = 2$ or 3 (r_e/pm, ∠/deg, E/Hartrees)

parameter	dimer (D_{2h})		trimer (D_{3h})[a]	
	HF/6-31G*	MP2(fc)/6-31G*	HF/6-31G*	MP2(fc)/6-31G*
Al−C	197.2	196.5	197.2	196.6
Al···Al	266.3	263.8	327.1	322.1
Al−H$_b$	175.7	175.3	171.5	170.5
C−H (plane)	108.7	109.4	108.8	109.5
C−H (nonplane)	108.9	109.5	108.9	109.6
Al−Al−C	116.9	116.5	112.8	112.2
C−Al−C	126.2	127.1	126.8	128.2
Al−C−H (plane)	112.8	112.4	112.6	112.0
Al−C−H (nonplane)	111.3	111.3	111.5	111.6
H−C−H (plane)	107.2	107.3	107.1	107.2
H−C−H (nonplane)	106.8	106.9	106.8	107.0
Al−H$_b$−Al	98.5	97.6	145.0	141.2
H$_b$−Al−Hb	81.5	82.4	95.0	98.3
Al/H$_b$−Al−C−H (nonplane)[b]	±120.5	±120.4	±120.4	±120.2
absolute energy	−643.4591069	−644.1045016	−965.1993265	−966.1670315

[a] Geometry optimized in C_3 symmetry. [b] Dihedral angle for Al−Al−C−H for $n = 2$ and H$_b$−Al−C−H for $n = 3$.

mm by means of a cathetometer. Each of the samples was maintained at 273 K using an ice/water bath.

Electron-Diffraction Measurements. Electron-scattering patterns were recorded photographically on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus.[20] Camera distances were ca. 95 and 258 mm, and the accelerating voltage approximated to 44 kV, giving an electron wavelength near 5.7 pm. The precise camera distances and electron wavelengths were determined from scattering patterns for benzene vapor recorded immediately before or after the sample patterns. Details are given in Table 1, together with the weighting functions used to set up the off-diagonal weight matrixes, the s range, scale factors, and correlation parameters.

Patterns were recorded with the alane vapor at two temperatures, viz. 327 and 470 K. In both sets of experiments the sample of dimethylalane was maintained at ca. 320 K and the vapor heated to the desired temperature before it entered the diffraction chamber by means of a heating jacket surrounding the nozzle. Each exposed plate was left under pumping for 24 h before removal, washed, and left in the air for 24 h before being developed. These steps minimized, but did not eliminate, the effects of fogging caused by the action of the strongly reducing vapor on the photographic emulsion.

Details of the electron-scattering patterns were collected in digital form using a computer-controlled Joyce-Loebl MDM6 microdensitometer. Standard programs were used for the data reduction[21] and least-squares refinement,[22] the scattering factors being those listed by Ross et al.[23]

Ab Initio Calculations. All ab initio calculations were performed on a DEC Alpha APX 100A workstation using the Gaussian 94 program suite.[24] The geometries of [Me$_2$AlH]$_n$ were optimized in the point groups D_{nh} (where $n = 2-4$). Final geometries were obtained using the standard basis sets 6-31G* at the HF level, with those of the smaller oligomers ($n = 2$ or 3) also being calculated at the MP2 level of theory.

Vibrational frequencies were calculated from analytic second derivatives at the HF/6-31G* and MP2/6-31G* ($n = 2$ or 3 only) levels to verify that the structures deduced corresponded to minima on the potential energy surfaces. The force constants determined for the dimer and trimer in the higher level calculations were subsequently used to construct harmonic force fields with the aid of the ASYM40 program.[25] These force fields then served as a basis for estimating amplitudes of vibration (u) for inclusion in the GED refinements.

Results

Vapor Studies. (a) IR Spectra. IR spectra have been measured for [Me$_2$AlH]$_n$ and [Me$_2$AlD]$_n$ with reference (i) to the vapors at temperatures in the range 270−370 K (pressure ca. 1 Torr), (ii) to the vapor species trapped in solid argon or nitrogen matrixes at ca. 20 K,[17,18] and (iii) to annealed solid films of the compound formed by condensation of the vapor at 77 K.[17,18] Frequencies given in parentheses hereafter refer to the monodeuterated version of the compound. The results are similar in all important respects to those described in detail by Grady et al.[9] Certain bands maintain more or less constant frequencies and relative intensities

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(20) Huntley, C. M.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 954.

(21) Cradock, S.; Koprowski, J.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *77*, 113.

(22) Boyd, A. S. F.; Laurenson, G. S.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *71*, 217.

(23) Ross, A. W.; Fink, M.; Hilderbrandt, R.; Wang, J.; Smith, V. H., Jr. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, Boston, MA, and London, 1995; Vol. C, p 245.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision C.2; Gaussian Inc.: Pittsburgh, PA, 1995.

(25) *ASYM 40*, version 3.0, update of program *ASYM 20*: Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

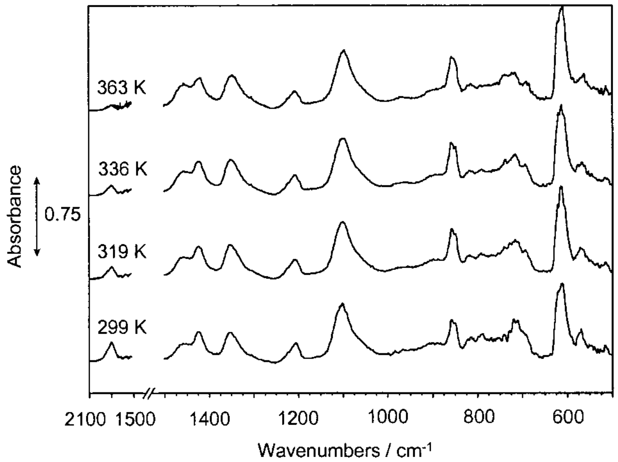

Figure 1. IR spectrum of dimethylalane vapor (pressure ca. 1 Torr) at different temperatures.

irrespective of the conditions; occurring near 2900, 1420, 1200, 850, 800, 700, and 570 cm^{-1}, these are clearly attributable to vibrational fundamentals mainly localized in the Me_2Al fragments.[7-9] The most significant features of the different spectra are those associated with what are primarily the Al−H(D)−Al stretching vibrations of the alane molecules. These give rise to prominent absorptions near 1400 (1000) cm^{-1} plainly associated with the major component **X** of the vapor. In addition, there is a broad absorption at 1786 (1279) cm^{-1} and a weaker one at 939 (733) cm^{-1} equally plainly associated with a less abundant component **Y** in equilibrium with **X**. As illustrated in Figure 1, if the pressure of the vapor is kept roughly constant (at ca. 1 Torr), raising the temperature from 299 to 363 K causes the bands due to **X** to grow at the expense of those due to **Y**. Unfortunately the low volatility and high reactivity of the compound precluded any reliable studies of how the spectrum varies with pressure at a particular temperature. On the evidence of the present and earlier[5-9] experiments, however, there can be little doubt that **X** is the dimer $[Me_2AlH]_2$. Using the integrated areas, *A*, under the bands at 1357 and 1786 cm^{-1} as measures of the partial pressures of **X** and **Y**, respectively, we have sought to analyze the results on the assumption that only these two components are in equilibrium (eq 1). On the basis of the van't Hoff isochore, a plot of $-\ln[A_Y{}^2/A_X{}^n]$ vs $1/T$ should then give a straight line, the slope of which offers an estimate of the enthalpy change ΔH associated with reaction 1. Figure 2 shows that the best fit to such a straight line is achieved by setting n equal to 3 ($R = 0.985$), as first suggested by Wartik and Schlesinger,[5] although the fit achieved with $n = 4$ ($R = 0.973$) is only marginally worse. For $n = 3$ reaction 1 is then found to have $\Delta H = -46 \pm 3$ kJ mol^{-1}, a value in pleasing agreement with that of −51.5 kJ mol^{-1} deduced from the calculated absolute energies of the dimer and trimer at the MP2 level (vide infra).

$$\underset{\mathbf{X}}{n\,[Me_2AlH]_2} \rightleftharpoons \underset{\mathbf{Y}}{2\,[Me_2AlH]_n} \qquad (1)$$

The IR spectrum reported by Schrötter and Hoffmann[8] for a cyclohexane solution of the alane features an intense band at 1780 cm^{-1}. The resemblance to the vapor spectrum gives grounds for believing that **Y** is present in appreciable concentration under these conditions too. Annealed solid films are characterized by ν-[Al−H(D)−Al] bands at the following wavenumbers (in cm^{-1}; s = strong, m = medium, v = very, sh = shoulder): 1820/1727 (1319/1244) vs, br and 975 (762) m. Again, the resemblance to the spectrum of **Y** is noteworthy, as is the absence of features diagnostic of **X**. Hence, although the solid has so far defied structural characterization,[26] it would appear to be composed of oligomeric or polymeric units with hydrogen-bridged linkages akin to those in **Y**.

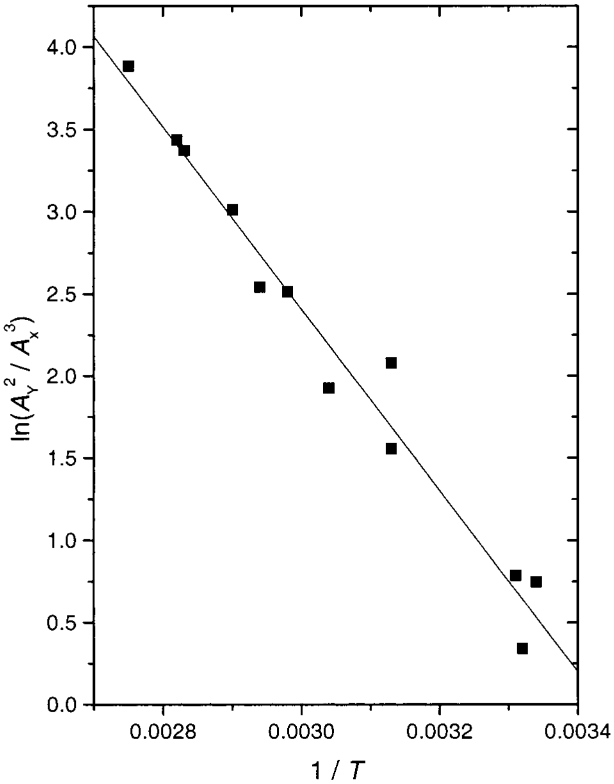

Figure 2. Plot of $-\ln[A_Y{}^2/A_X{}^3]$ vs $1/T$ (A_X = area under the band at 1357 cm^{-1}; A_Y = area under the band at 1786 cm^{-1}; **X** = $[Me_2AlH]_2$; **Y** = $[Me_2AlH]_3$).

If the absorptions characteristic of **Y** at 1786 and 939 cm^{-1} are ascribed to the antisymmetric and symmetric ν(Al−H−Al) fundamentals, respectively, a rough measure of the Al−H−Al bond angle can be made.[27,28] The value indicated is on the order of 125°, i.e., substantially wider than the 102.6(16)° deduced from earlier GED measurements[6] for the doubly hydrogen-bridged dimer $Me_2Al(\mu\text{-}H)_2AlMe_2$. The most plausible interpretation is that *single* Al−H−Al bridges link the Me_2Al units in **Y**. By extension, similar linkages occur in at least one of the species present in solution and also as the exclusive binding principle in the amorphous solid.

(b) Mass Spectrum. Earlier mass spectrometric studies of dimethylalane vapor gave no hint of any species containing more than two aluminum atoms.[11] The findings can be explained in two ways: either the alane exists in the vapor phase exclusively as the dimer,

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[26] Parsons, S.; Pulham, C. R., unpublished results.

[27] Howard, M. W.; Jayasooriya, U. A.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Chem. Commun.* **1979**, 18.

[28] Pulham, C. R.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Am. Chem. Soc.* **1991**, *113*, 5149.

$[Me_2AlH]_2$, regardless of the evidence of vapor density measurements,[5] or any oligomers of higher nuclearity are fragmented under the conditions of electron impact used for ionization. The second possibility is known to arise with other mixed metal hydrides, e.g., $MeZnBH_4$[29] and $[Me_2GaH]_n$.[17,30]

Our experiments carried out with a Hiden HAL/3F residual gas analyzer analyzed the vapor over a sample of dimethylalane held at a temperature of ca. 293 K. In addition to the peak at $m/z = 116$ due to $[Me_2AlH]_2^+$, the spectrum also showed peaks corresponding to the molecular ion $[Me_2AlH]_3^+$ ($m/z = 174$) and to other fragments containing *three* aluminum atoms. However, there was no sign of a peak corresponding to a species containing more than three aluminum atoms. Even the peaks due to the trialuminum species could not be detected in the spectrum of the vapor above the liquid at 263 K, although they were observed to grow relative to those of the dialuminum species, implying that the vapor became richer in the higher oligomer, as the temperature of the sample was raised.

That the proportion of trimer in the vapor should *increase* as the temperature of the liquid is raised may at first appear counterintuitive. The explanation lies in the following thermodynamic argument. If we denote the enthalpies of vaporization of the dimer and trimer as ΔH_D and ΔH_T, respectively,

$$2\ Me_2AlH(l) \rightarrow [Me_2AlH]_2(g)\ \Delta H_D \qquad (2)$$

$$3\ Me_2AlH(l) \rightarrow [Me_2AlH]_3(g)\ \Delta H_T \qquad (3)$$

and the enthalpy for the conversion of trimer to dimer as ΔH_R ($= -{}^1/_2\Delta H$ for reaction 1)

$$[Me_2AlH]_3(g) \rightarrow {}^3/_2[Me_2AlH]_2(g)\ \Delta H_R \qquad (4)$$

then it may be shown using the Clausius–Clapeyron equation that

$$\frac{\mathrm{d}\ln\left(\dfrac{p_{\mathrm{trimer}}}{p_{\mathrm{dimer}}}\right)}{\mathrm{d}T} = \frac{\dfrac{1}{3}\Delta H_T - \dfrac{2}{3}\Delta H_D}{RT^2} \qquad (5)$$

where the right-hand side will be positive if $\Delta H_T > 2\Delta H_R$. We have estimated ΔH_R to be 23 kJ mol^{-1} and therefore might expect the partial pressure of the trimer to grow more rapidly with temperature than does the partial pressure of the dimer if ΔH_T is on the order of 46 kJ mol^{-1} or greater. This seems a reasonable condition given the low vapor pressure of dimethylalane at room temperature. At appreciably higher temperatures—approaching 500 K,[5,6] and so outside the regime of the saturated vapor—the dimer becomes the dominant species, as expected.

(c) Ab Initio Calculations. All the experimental evidence accumulated to date suggests that only two oligomers have a significant presence in the dimethylalane vapor, namely the dimer $[Me_2AlH]_2$ and the trimer $[Me_2AlH]_3$. The vibrational spectra[7-9] and previously reported GED[6] studies of the dimer attest to a diborane-like structure $Me_2Al(\mu\text{-}H)_2AlMe_2$ analogous to those of the corresponding boron[33] and gallium[34] compounds. As yet, there is little information about the structure of the trimer, although the crystal structure of the corresponding *tert*-butyl compound[10] provides a useful precedent.

We have therefore performed ab initio calculations on both molecules to verify the symmetries of their optimum geometries and also to investigate the effects of changing the theoretical method; the details are presented in Table 2. Using the 6-31G* basis sets, we are thus able to confirm the overall D_{2h} and D_{3h} geometries of the dimer and trimer, respectively, as local minima on the potential energy surfaces. The trimer is built on a planar ring of aluminum atoms linked together through single hydrogen bridges (see **I**). As revealed by the results listed in Table 2, altering the theoretical treatment from HF to MP2 evoked only minor changes in the values calculated for the various molecular parameters. The biggest structural change observed for both conformers upon improving the level of theory was a shortening of the Al···Al distance, which is presumably correlated to the widening of the H_b-Al-H_b angle.

Similar calculations have also been carried out on the tetramer $[Me_2AlH]_4$, which cannot altogether be ruled out as a component of the vapor, at least on the evidence on hand. The geometry was optimized in D_{4h} symmetry, which gave rise to one imaginary frequency (6i cm^{-1}) at the HF/6-31G* level, corresponding to the butterfly bending motion of the Al_4 framework. Subsequent reoptimizations in the lower symmetry grouping C_{2v} failed to generate a minimum. It is unclear whether a higher level of theory is required, but with an imaginary frequency of only 6 cm^{-1} it is clear that the potential energy surface for this molecule is very flat, and any distinction between a planar or bent geometry for such a floppy molecule will be purely academic. The optimized geometry obtained for the tetramer is an eight-membered Al_4H_4 ring similar to that predicted in the hypothetical $[AlH_3]_4$ molecule.[35] Of particular interest is the Al···Al distance, which comes out to be 341.3 pm for the tetramer, versus 322.1 pm according to the MP2/6-31G* treatment of the trimer. The significance of this will become clear when we consider the GED pattern of dimethylalane vapor measured at the lower temperature of 327 K (q.v.), but as in essence it indicates the presence of the tetramer in the vapor state to be unlikely, higher level calculations for the tetramer were not pursued. A full set of coordinates for the HF/6-31G* optimization of the tetramer is also available in the Supplementary Information.

(d) Gas Electron Diffraction (GED) Measurements. Throughout the following discussion, the GED measurements made on dimethylalane vapor at 327 and 470 K will be referred to as the "low-temperature" and "high-temperature" set, respectively. At the low temperature the vapor may be expected to contain significant partial pressures of *both* the oligomers implied by vapor density[5] and IR and mass spectrometric studies.

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[29] Aldridge, S.; Downs, A. J.; Hofmann, M.; Pulham, C. R.; Schleyer, P. v. R. *J. Mol. Struct.* **1998**, *444*, 29.

[30] Goode, M. J. D.Phil. Thesis, University of Oxford, U.K., 1987.

[31] Cook, T. H.; Morgan, G. L. *J. Am. Chem. Soc.* **1970**, *92*, 6487.

[32] Borlin, J. J.; Gaines, D. F. *J. Am. Chem. Soc.* **1972**, *94*, 1367.

[33] Carroll, B. L.; Bartell, L. S. *Inorg. Chem.* **1968**, *7*, 219.

[34] Baxter, P. L.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1990**, 2873.

[35] Shen, M.; Liang, C.; Schaefer, H. F., III. *Chem. Phys.* **1993**, *171*, 325.

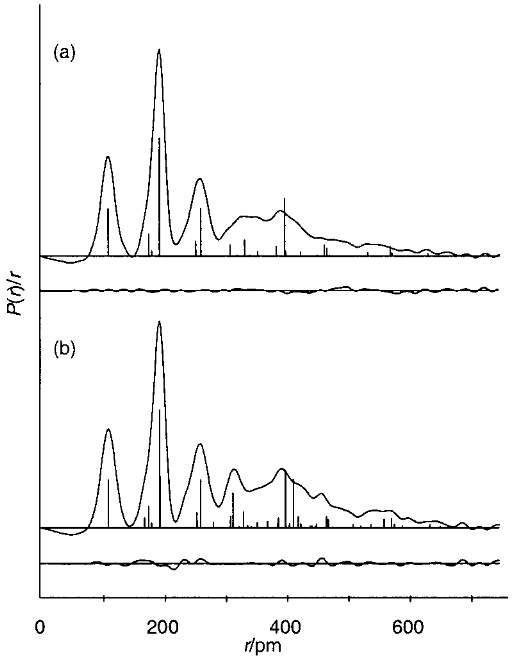

Figure 3. Observed and final weighted difference radial-distribution curves (a) for the high-temperature GED data set and $[Me_2AlH]_2$ and (b) for the low-temperature GED data set and a $[Me_2AlH]_2/[Me_2AlH]_3$ mixture. Before Fourier inversion the data were multiplied by $s \exp[(-0.00002s^2)/(Z_{Al} - f_{Al})(Z_C - f_C)]$.

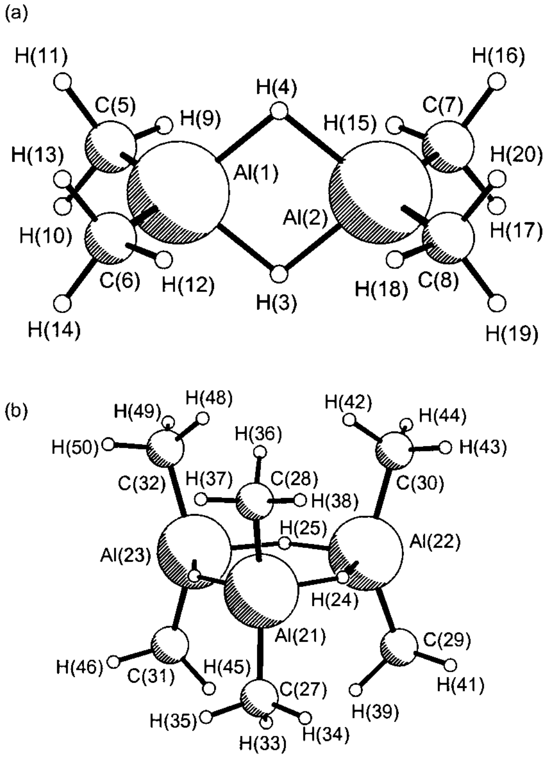

Figure 4. Views of the molecules (a) $[Me_2AlH]_2$ and (b) $[Me_2AlH]_3$ in the optimum refinements of the GED data.

To characterize the heavier oligomer, however, it was necessary first to measure the scattering pattern, and so redetermine the structure of the *lighter* oligomer on the basis of the experiments carried out with the vapor at 470 K, a temperature at which there is every reason to suppose the *dimer* to be the dominant species.[5,6]

(i) High-Temperature Results. The radial-distribution curve determined from the scattering pattern of the vapor at 470 K (Figure 3a) does not differ significantly from that reported previously[6] for the vapor at ca. 440 K. Guided by the conclusions drawn from the vapor density,[5] IR and mass spectra, and earlier GED[6] studies, we have sought to match the high-temperature GED results with the scattering from a single molecular source, namely $[Me_2AlH]_2$. According to the present ab initio calculations, the evidence of the vibrational spectrum,[7-9] and the precedents set by the structures deduced for the analogous boron[33] and gallium[34] compounds, this molecule is expected to have a diborane-like structure $Me_2Al(\mu\text{-}H)_2AlMe_2$. The $C_2Al(\mu\text{-}H)_2AlC_2$ skeleton conforms strictly to D_{2h} symmetry, and this is retained if, as indicated by the calculations, one C−H bond of each methyl group is disposed syn to the Al⋯Al core (see Figure 4a). Initial refinements were therefore based on such a model. Each of the $Al-CH_3$ fragments was assumed to comply with C_{3v} symmetry, the ab initio calculations (Table 2) having predicted differences at the MP2 level of no more than 0.2 pm between the in-plane and out-of-plane C−H distances and of no more than 1.1° between the corresponding Al−C−H angles. Six independent structural parameters then sufficed to define the geometry, viz. r(Al−C), r(Al⋯Al), $r(Al-H_b)$, r(C−H), ∠Al−C−H, and ∠Al⋯Al−C. During the course of the refinements, the effects of three other independent parameters were explored. These entailed (a) *rotation* of the methyl groups about the local C_3 axis in a number of different ways; (b) *tilting* of the methyl groups such that the local C_3 axis remains in the Al_2C_4 plane but becomes noncoincident with the Al−C bond; and (c) *wagging* of the methyl groups such that the local C_3 axis again becomes noncoincident with the Al−C bond, but now moving in a plane *perpendicular* to the Al_2C_4 plane and containing the adjacent Al−C bond.

Scattering from C−H bonded pairs is then responsible for the prominent peak at 110 pm in the radial-distribution curve (Figure 3a), whereas Al−C and $Al-H_b$ pairs combine to give the intense peak near 200 pm. Scattering from Al⋯Al and Al⋯H nonbonded pairs accounts for the third distinct peak near 260 pm. The diffuse feature extending from ca. 300 to 450 pm correlates mainly with scattering from Al⋯C and C⋯C but with contributions also from Al⋯H and C⋯H nonbonded pairs.

An r_a geometry for $[Me_2AlH]_2$ was refined, starting with the values for the geometrical and vibrational parameters afforded by the computations undertaken at the MP2/6-31G* level. All six independent geometrical parameters defining the molecule in D_{2h} symmetry could be refined simultaneously without restraint. An R-factor loop for the methyl rotation indicated a minimum for the D_{2h}, syn configuration. On the other hand, attempts to refine parameters specifying the tilting and wagging of the methyl groups revealed the diffraction pattern as containing no useful information.

It was possible also to refine 19 amplitudes of vibration, representing all distances associated with scattering intensity greater than 2% of that due to the principal scatterer. Dynamic motion of the molecule at the temperature of the experiment was evident from the disparity between the refined experimental values for many of the amplitudes and those computed from the ab initio

Table 3. Structural Parameters and Amplitudes of Vibration for the Dimer $Me_2Al(\mu\text{-}H)_2AlMe_2$ Determined from GED Measurements on the Vapor at 470 K[a]

		this work		ref 6[b]		
	parameter	distance, r_a/pm, or angle, ∠/deg	amplitude, u/pm	distance, r_a/pm, or angle, ∠/deg	amplitude, u/pm	MP2/6-31G* calculations distance, r_e/pm, or angle, ∠/deg
			(a) Independent Parameters			
p_1	C−H	111.4(2)	7.5(3)	111.7(5)	7.7(4)	109.5[c]
p_2	Al−C−H	109.0(7)		108.8(17)		111.7[c]
p_3	CH_3 tilt[d]	0[e]		0[e]		0
p_4	Al−C	195.2(2)	5.6(2)	194.7(3)	6.1[e]	196.5
p_5	Al⋯Al−C	121.2(2)		120.8(5)		116.5
p_6	Al−H_b	177.6(7)	6.1(9)	167.6(19)	11.1(15)	175.3
p_7	Al⋯Al	262.5(6)	10.6(5)	261.7(6)	7.9(4)	263.8
p_8	CH_3 twist[f]	0[e]		0[e]		0
p_9	CH_3 wag[g]	0[e]		0[e]		0
			(b) Dependent Parameters			
p_{10}	Al(2)⋯C(5)	400.1(5)	24.3(12)	398.3(13)	23.6(17)	393.0
p_{11}	Al(1)⋯H(10)	254.3(10)	20.6(12)	254.1(30)	22.8(21)	257.9
p_{12}	Al(2)⋯H(9)	386.1(15)	13.1(19)	383.9(25)	14.1(21)	380.5
p_{13}	Al(2)⋯H(10)	469.1(9)	24.0(27)	467.6(11)	26.3(21)	464.7
p_{14}	C(5)⋯C(6)	334.2(7)	9.0(15)	335.0(28)	16.7(29)	351.9
p_{15}	C(5)⋯C(7)	464.5(11)	47(12)	464.2(72)	29.1(75)	438.8
p_{16}	C(6)⋯C(7)	572.2(6)	26.2(37)	561.8(30)	16.0(22)	562.5
p_{17}	C(5)⋯H(3)	310.1(5)	10.3(16)			304.1
p_{18}	C(6)⋯H(10)	355.7(11)	10.5(77)			380.4
p_{19}	H(9)⋯H(10)	182.5(9)	11.3(39)			176.4
p_{20}	C−Al−C	117.7(4)		118.5(9)		127.1
p_{21}	Al−H_b−Al	95.3(6)		102.6(16)		97.6
p_{22}	H_b−Al−H_b	84.7(6)		77.4(16)		82.4
p_{23}	H−C−H	110.0(7)		110.1(17)		107.1[c]

[a] For atom-numbering scheme see Figure 4a. Figures in parentheses are the estimated standard deviations. [b] Vapor temperature 433 K. [c] Average for in-plane and out-of-plane units (see Table 2). [d] Angle subtended by C_3 axis of CH_3 group to Al−C bond in the Al_2C_4 plane. [e] Fixed. [f] Angle of twist of CH_3 group with respect to D_{2h}, syn configuration. [g] Angle subtended by C_3 axis of CH_3 group to Al−C bond in a plane perpendicular to the Al_2C_4 plane.

force field. For this reason, where restraints were necessary, for 10 amplitudes in total, uncertainties were assigned not at the normal level of 10% but at 30% of the absolute values.

Cutting the experimental data for the short camera distance to $s = 300\ \text{nm}^{-1}$ led to no significant change in the values of the refined parameters but to a decrease in the esd's, a finding commensurate with the poor quality of the wide-angle data, which were judged therefore to be superfluous. The final R_G factor for the refinement calculations was 0.091 ($R_D = 0.062$). Values for selected dimensions and vibrational amplitudes are given in Table 3; the optimized experimental structure is depicted in Figure 4a. The most significant elements of the least-squares correlation matrix are listed in Table 4a, while Figure 5a illustrates the observed and final difference curves for the molecular-scattering intensities.

To determine an r_α structure for the molecule, we would need a set of perpendicular amplitudes of vibration (K values). However, these cannot be estimated reliably from ASYM 40 or similar programs, being grossly overestimated when the molecule exhibits large-amplitude, low-frequency motions. For $Me_2Al(\mu\text{-}H)_2AlMe_2$ there are no less than 11 vibrational fundamentals estimated to have frequencies below 200 cm^{-1}, with six of these expected to fall below 100 cm^{-1}. These circumstances deny access to reliable K values and hence to a meaningful r_α structure. Were there but a single mode of vibration, e.g., the $Al(\mu\text{-}H)_2Al$ butterfly motion, giving rise to the large-amplitude motion of the molecule, it could be modeled explicitly, as in the case of the analogous $Ga(\mu\text{-}Cl)_2Ga$ motion of the $H_2Ga(\mu\text{-}Cl)_2GaH_2$ molecule.[36] For $Me_2Al(\mu\text{-}H)_2AlMe_2$, however, it would be necessary to model not only the butterfly motion (with an associated frequency near 61 cm^{-1} at the MP2/6-31G* level) but also the C−Al−C scissoring modes (at ca. 90 and 92 cm^{-1}), the other low-frequency motions being associated with the methyl groups. Such a complex model is not tenable given the experimental input

Table 4. Least-Squares Correlation Matrixes (×100)[a]

(a) High-Temperature GED Data Set with Dimer Model

u_1	u_{10}	u_{11}	u_{17}	u_{18}	u_{19}	k_1	k_2	
					−62			p_4
	50							p_5
						−59	−58	p_6
		−58						p_7
						51	61	u_1
51						57	75	u_4
					−55			u_6
			66	62				u_{14}
							64	k_1

(b) Low-Temperature GED Data Set with Dimer/Trimer Model

p_{25}	p_{27}	p_{29}	u_6	u_{30}	u_{33}	k_2	
	−64						p_4
		−60	−58				p_6
−51							p_7
			76				p_{29}
						53	u_4
					58		u_{11}
				−51			u_{17}

[a] Only elements with absolute values ≥ 50% are listed; k is a scale factor.

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(36) Johnsen, E.; Downs, A. J.; Greene, T. M.; Souter, P. F.; Aarset, K.; Page, E. M.; Rice, D. A.; Richardson, A. N.; Brain, P. T.; Rankin, D. W. H.; Pulham, C. R. *Inorg. Chem.*, in press.

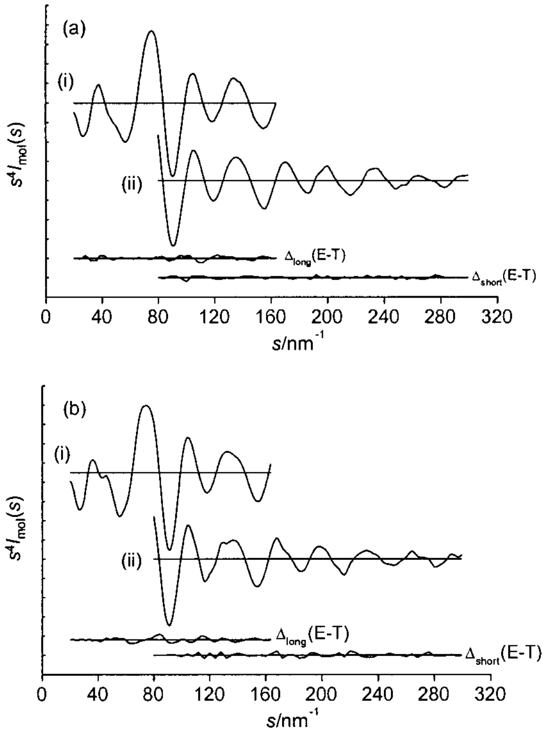

Figure 5. Observed and final weighted difference molecular-scattering intensity curves (a) for the high-temperature GED data set and $[Me_2AlH]_2$ with nozzle-to-plate distances of (i) 258.45 and (ii) 95.10 mm and (b) for the low-temperature GED data set and a $[Me_2AlH]_2/[Me_2AlH]_3$ mixture with nozzle-to-plate distances of (i) 258.52 and (ii) 95.14 mm.

of the current GED data. In these circumstances, an r_a structure is the only one we can realistically target.

(ii) Low-Temperature Results. The radial-distribution curve derived from the scattering pattern of the vapor at ca. 327 K is very similar to that for the high-temperature measurements at distances shorter than 300 pm (see Figure 3). However, the curve for the low-temperature data exhibits a new and distinctive peak at ca. 315 pm, as well as increased intensity in the region 400−500 pm. The GED pattern, like the IR and mass spectra, thus imply the presence of both the dimer and one or more higher oligomers.

Theoretical MP2/6-31G* investigations of the trimer, $[Me_2AlH]_3$, indicate a structure along the lines of **I** with an Al⋯Al distance of 322.1 pm and Al⋯C distance of 436.3 pm for the potential energy minimum with D_{3h} symmetry for the $[C_2AlH]_3$ skeleton; other distances are similar to the corresponding dimensions in the dimer (see Table 2). Since the mass and IR spectra point to the trimer as the only higher oligomer with a significant partial pressure at total vapor pressures on the order of 1 Torr, it seemed entirely reasonable to simulate the low-temperature GED results on the basis of a model consisting of a mixture of dimeric and trimeric forms of dimethylalane. The possibility of a higher oligomer with a nuclearity greater than 3 has been explored, notably through computations on a tetrameric form $[Me_2AlH]_4$. In this case the Al⋯Al distance is predicted to be significantly longer (ca. 340 pm) than in the trimer. Since the additional peak near 315 pm in the radial-distribution curve is most plausibly identified with scattering from Al⋯Al atom pairs of the higher oligomer, the theoretical treatments clearly favor the trimer as the second component of the vapor at low temperatures.

The model adopted for refinement calculations drawing on the low-temperature GED data was then made up as follows. Parameters defining the dimer were those used in the analysis of the high-temperature data. The trimer was assumed to have D_{3h} symmetry overall, with local C_{3v} symmetry for each of the $Al-CH_3$ units and C−H distances identical to those of the dimer. On this basis, the trimer geometry was defined by five independent geometrical parameters, consisting of r(Al−C), r(Al−H$_b$), r(Al⋯Al), ∠Al−C−H, and ∠H$_b$−Al−C. Finally, the molar fraction of dimer in the vapor could be varied independently.

For both the dimer and trimer r_a geometries were then refined. Starting values for the dimer structure were taken from the analysis of the high-temperature data. For the trimer, geometrical parameters were taken from the theoretical optimization at the MP2/6-31G* level, and vibrational amplitudes were derived from the harmonic force field computed at the HF/6-31G* level. To allow for changes in the dimer structure with the lowering of the vapor temperature, the relevant geometrical and vibrational parameters were refined initially using restraints and uncertainties based on the values refined in the context of the high-temperature data. In this way it was possible to refine freely all of the independent geometrical parameters for the trimer except the H$_b$−Al−C angle and to secure an initial estimate of the proportions of dimer and trimer in the vapor. Thereafter the uncertainties associated with restraints for parameters defining the dimer structure were relaxed to ±2 pm for distances and ±2° for angles. With the value of ∠H$_b$−Al−C for the trimer refining freely, the refinement became unstable. This parameter was subsequently refined using a restraint of 111.3 ± 3.0°, a value and uncertainty based on the difference between experiment and theory for the analogous Al⋯Al−C parameter in the refinements of the high-temperature data. Amplitudes of vibration, u, for the principal scattering pairs of the trimer were tied to those for the dimer, with the exception of u(Al−C), u(Al⋯Al), and u(Al⋯C), which were allowed to refine freely.

By considering the variation of R_G with the fraction of dimer, the vapor composition was shown to comprise 70(4)% of the dimer, based on a Hamilton test. The final R_G, at 0.098 (R_D = 0.074), was comparable with that for the analysis of the high-temperature data. The success of the analysis can also be gauged by the differences (a) between the experimental and calculated radial-distribution curves (Figure 3b) and (b) between the experimental and calculated molecular intensity curves (Figure 5b). Table 4b gives the most significant elements of the least-squares correlation matrix. Selected dimensions and vibrational amplitudes for the trimer are listed in Table 5; the optimized experimental structure is illustrated in Figure 4b.

Attempts were made also to analyze the low-temperature GED measurements on the basis of two alternative models. One involving the assumption of an exclusively dimeric form was quickly dismissed as giving a poor account of the measured scattering, for the reasons made manifest by the differences between the radial-

Table 5. Structural Parameters and Amplitudes of Vibration for the Dimer $[Me_2AlH]_2$ and Trimer $[Me_2AlH]_3$ Determined from GED Measurements on the Vapor at 327 K[a]

	parameter	distance, r_a/pm, or angle, ∠/deg	amplitude, u/pm	MP2/6-31G* calculations distance, r_e/pm, or angle, ∠/deg
		(a) Independent Parameters for $[Me_2AlH]_2$		
p_1	C−H[b]	112.0(2)	8.1(2)	109.5[c]
p_2	Al−C−H	109.7(9)		111.7[c]
p_3	CH_3 tilt[d]	0[e]		0
p_4	Al−C	195.6(2)	5.9(1)	196.5
p_5	Al···Al−C	121.7(3)		116.5
p_6	Al−H_b	177.8(10)	5.6(8)	175.3
p_7	Al···Al	262.3(8)	10.2(4)	263.8
p_8	CH_3 twist[d]	0[e]		0
p_9	CH_3 wag[d]	0[e]		0
		(b) Dependent Parameters for $[Me_2AlH]_2$		
p_{10}	Al(2)···C(5)	401.3(8)	23.6(10)	393.0
p_{11}	Al(1)···H(10)	256.0(12)	18.3(8)	257.9
p_{12}	Al(2)···H(9)	389.5(20)	10.4(14)	380.5
p_{13}	Al(2)···H(10)	471.4(13)	20.8(19)	464.7
p_{14}	C(5)···C(6)	332.7(10)	9.4(12)	351.9
p_{15}	C(5)···C(7)	468.1(16)	42(10)	438.8
p_{16}	C(6)···C(7)	574.3(9)	24.6(31)	562.5
p_{17}	C(5)···H(3)	311.2(7)	10.4(15)	304.1
p_{18}	C(6)···H(10)	355.1(15)	7.6[e]	380.4
p_{19}	H(9)···H(10)	182.7(11)	11.3[e]	176.4
p_{20}	C−Al−C	116.5(6)		127.1
p_{21}	Al−H_b−Al	95.0(8)		97.6
p_{22}	H_b-Al−H_b	85.0(8)		82.4
p_{23}	H−C−H	109.3(9)		107.1[c]
		(c) Independent Parameters for $[Me_2AlH]_3$		
p_{24}	C−H[b]	112.0(2)	8.1(2)	109.6[c]
p_{25}	Al−C−H	110.1(31)		111.8[c]
p_{26}	CH_3 tilt[d]	0[e]		0
p_{27}	Al−C	195.8(3)	5.7(2)	196.6
p_{28}	H_b−Al−C	108.3(14)		106.6
p_{29}	Al−H_b	171.1(23)	5.1[f]	170.5
p_{30}	Al···Al	315.3(8)	8.2(7)	322.1
p_{31}	mol fraction dimer	0.695[e]		
		(d) Dependent Parameters for $[Me_2AlH]_3$		
p_{32}	Al(22)···C(27)	414.0(30)	43.9(57)	436.3
p_{33}	Al(21)···H(33)	256.9(22)	16.9(10)	258.4
p_{34}	C−Al−C	143.3(27)		128.2
p_{35}	Al−H_b−Al	134.3(36)		141.2
p_{36}	H_b−Al−H_b	105.7(36)		98.3
p_{37}	H−C−H	108.8(16)		107.1[c]

[a] For atom-numbering scheme see Figures 4,a and 4,b. Figures in parentheses are the estimated standard deviations. [b] Assumed to be the same in $[Me_2AlH]_2$ and $[Me_2AlH]_3$. [c] Average for in-plane and out-of-plane units (see Table 2). [d] Defined as in Table 3. [e] Fixed. [f] Tied to u_6 of $[Me_2AlH]_2$.

distribution curves in parts a and b of Figure 3. The other consisted of a mixture of the dimeric and tetrameric forms. With the guidance of quantum chemical calculations at the HF/6-31G* level, we have tried to refine the r_a structure of such a tetramer together with a variable proportion of the dimer, but the optimum match, with $R_G = 0.14$, while superior to that achieved with the dimer alone, was distinctly inferior to that achieved with the dimer/trimer model. Even with the best fit, many refined parameters assumed unrealistic values when compared with those computed ab initio.

Solution Studies. Cooling liquid dimethylalane results in a marked increase in viscosity with solidification ultimately to give a glass.[26] In the absence of any definitive information about the nature of the solid, we have investigated the behavior of the alane in hydrocarbon solution by measuring the ^1H, ^{13}C, and ^{27}Al NMR spectra and also the vapor pressure depression of isopentane solutions, with the following results.

NMR Spectra. As recorded in Table 6, the ^1H NMR spectrum of a toluene-d_8 solution of dimethylalane at 293 K consists, as expected, of two resonances, a sharp one at $\delta_H = -0.48$ and a broad one at $\delta_H = 2.89$, with relative intensities of 6:1. These clearly correspond to the protons of the Me_2Al and Al−H groups, respectively. Cooling the solution to 213 K was observed to yield at least *two* and probably three resonances for the Al−H protons near δ_H 2.8 (see Figure 6). The relative intensities of these resonances showed a marked dependence on the concentration of the solution, clearly suggesting that they are to be ascribed to dimethylalane in at least two different oligomeric forms. The ^{13}C NMR spectrum of the solution over this temperature range exhibited only a quartet at δ_C −11.5 with $^1J_{CH} = 117$ Hz. The ^{27}Al NMR spectrum of the solution at 293 K consisted of a singlet at δ_{Al} 158, a chemical shift characteristic of a methyl-substituted tetracoordinated aluminum center (δ_{Al} 129−178);[37] cooling the solution resulted only in broadening of the resonance.

Similar results were found for methylcyclohexane-d_{14} and isopentane-d_{12} solutions of dimethylalane (see Table 6). To probe further the nature of the solute species in

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(37) Akitt, J. W. *Prog. Nucl. Magn. Reson. Spectrosc.* **1989**, *21*, 1.

Table 6. NMR Properties of Dimethylalane in Solution

	AlH			CH_3		
solvent	δ_H (293 K)	δ_H (213 K)	δ_{Al} (293 K)[b]	δ_H (293 K)	δ_C (213 K)	$^1J_{CH}$/Hz
toluene-d_8	2.89	2.83[a] 2.68	158	−0.48	−11.5	117
methylcyclohexane-d_{14}	3.05	3.06 2.84[a]	c	−0.59	c	c
isopentane-d_{12}	3.15	3.12 2.94[a]	161	−0.42	c	c

[a] Increases in relative intensity with respect to the neighboring resonance when overall concentration of solution is increased. [b] Measured with reference to $[Al(OH_2)_6]^{3+}$. [c] Not measured.

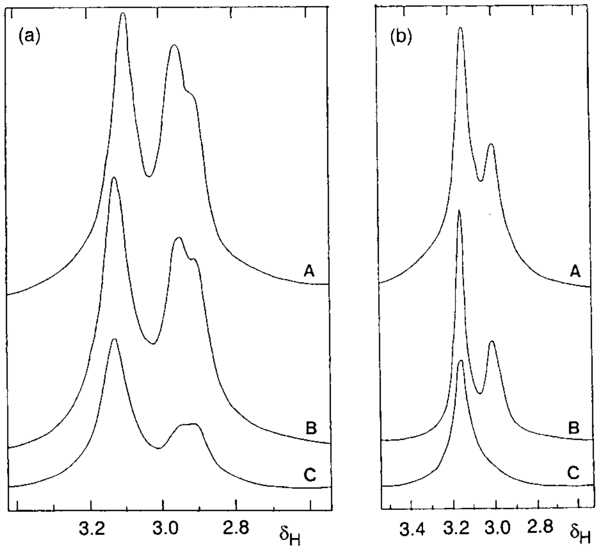

Figure 6. AlH region of the ^1H NMR spectrum of dimethylalane in isopentane-d_{12} solution: (a) ^1H spectra of solutions **A**, **B**, and **C** at 213 K and (b) $^1H\{^{27}Al\}$ spectra of solutions **A**, **B**, and **C** at 273 K. The concentrations of the solutions (in mol Me_2AlH dm^{-3}) were as follows: **A** 1.03, **B** 0.71, and **C** 0.15.

isopentane solutions, for which molecular weight measurements have previously been made,[5] ^1H NMR measurements were made on three isopentane-d_{12} solutions of the alane having the concentrations listed in Figure 6, where the Al−H regions of the ^1H and $^1H\{^{27}Al\}$ spectra displayed by each solution are reproduced. Broad-band ^{27}Al decoupling revealed that there are typically two distinct components to the Al−H resonance, whether at low temperature (213 K) or at high temperature (273 K). The resonance at lower frequency was observed to gain in intensity relative to that at higher frequency as the concentration of the solution increased. It follows that this resonance is most plausibly ascribed to one or more higher oligomers of $[Me_2AlH]_n$, where $n > 2$. Such findings are at odds with the previous interpretation of the apparent molecular weight of the alane in isopentane solution.[5] It seemed appropriate therefore to reinvestigate the vapor pressure depression of dimethylalane in isopentane solution.

Vapor Pressure Depression of Dimethylalane in Isopentane Solution. Vapor pressure depression measurements were made on dimethylalane in isopentane solution at three different concentrations. With the solutions at 273 K, the results were as listed in Table 7. Hence the apparent molecular weight, M, was found to increase as the solution became more concentrated, taking the value $M = 105 \pm 16$ at the lowest concentration (0.25 mol monomer dm^{-3}) and rising to $M = 178 \pm 16$ at the highest concentration (1.09 mol monomer dm^{-3}). The findings therefore support the conclusion that dimethylalane exists as a mixture of oligomers in isopentane solution; at the same time they are consistent with the earlier results of Wartik and Schlesinger,[5] which spanned a narrower range of concentration (see Table 7).

Table 7. Vapor Pressure Depression Measurements on Isopentane Solutions of Dimethylalane

temp/K	mass of solvent/g	mass of solute/g	conc of solute/ mol Me_2AlH dm^{-3}	calculated MW of solute	ref
273	0.5076	0.0519	1.09	178	a
	0.9811	0.0545	0.59	146	a
	1.4075	0.0325	0.25	105	a
293.5	0.2315	0.0697	3.22	206	b
	0.493	0.0697	1.51	187.5	b
	0.891	0.0697	0.84	182	b

[a] This work. [b] Ref 5.

Combined Analysis of the NMR and Vapor Pressure Depression Measurements. The ^1H NMR measurements, when analyzed in conjunction with the apparent molecular weight of the alane in isopentane solution, allow certain conclusions to be drawn as regards the nature of the solute species. The molecular weight of the alane in the most dilute solution studied, $M = 105$, corresponded within experimental error to the predominant presence of the dimer, $[Me_2AlH]_2$ (M_{calc} 116). The $^1H\{^{27}Al\}$ NMR spectrum of a solution at a comparable concentration exhibited a single Al−H resonance at δ_H 3.15 with only a hint of a shoulder near δ_H 3.0 (Figure 6), so that a molecular weight near 105 should indeed approximate to that of a single oligomer of dimethylalane. It is reasonable therefore to conclude that the lighter oligomer, which gives rise to the Al−H resonance at higher frequency, is the dimer $[Me_2AlH]_2$.

At a concentration of 1.09 mol monomer dm^{-3} dimethylalane has an apparent molecular weight $M = 178$. This might seem to imply that the predominant species is now the trimer $[Me_2AlH]_3$ (M_{calc} 174), in keeping with the conclusion drawn by Wartik and Schlesinger.[5] However, the $^1H\{^{27}Al\}$ NMR spectrum of a solution of similar concentration exhibited two distinct Al−H resonances (Figure 6), indicating the presence of at least two oligomers. The lighter one of these is plainly the dimer, and so the measured M value means that the trimer cannot be the sole heavier oligomer and that there must be a major contribution from an oligomer $[Me_2AlH]_n$ with $n > 3$. Although the NMR spectrum suggests some variation in the relative proportions of the species responsible for the two Al−H signals as a function of temperature, the indications are that they are present in comparable proportions at 273 K. Hence it may well be that the low-frequency resonance arises at least in part from a *tetramer*, $[Me_2AlH]_4$ (M_{calc} 232), although more highly associated species cannot be ruled out. We can therefore account for the earlier vapor pressure depression measurements and the finding that the apparent molecular weight of dimethylalane in solution exceeded that of the trimer and that it increased as the solution became more concentrated.

The ^1H spectra of solutions at lower temperatures (e.g., 213 K; see Figure 6) suggest indeed that a third oligomer is present, so that dimer, trimer, and tetramer species are probably in equilibrium with one another. The results are neither complete nor precise enough to give much insight into the effect of temperature. There are qualitative signs that, as expected, the proportion of dimer decreases as the temperature falls (witness Figure 6, for example), but any estimate of the associated enthalpy change or changes must await more elaborate studies.

Discussion and Conclusions

For the distances r(Al−H), r(Al−C), r(Al⋯Al), and r(C−H) in the gaseous molecule $Me_2Al(\mu\text{-}H)_2AlMe_2$, the final refined values were 177.6(7), 195.2(2), 262.5(6), and 111.4(2) pm, respectively, compared with the ab initio values [MP2(fc)/6-31G*] of 175.3, 196.5, 263.8, and 109.5 pm; for the angles ∠Al−C−H and ∠A⋯Al−C, the refined values were 109.0(7)° and 121.2(2)°, respectively, versus the ab initio values of 111.3/112.4° and 116.5°. In the case of the trimer, $[Me_2AlH]_3$, the final refined values for the independent geometrical parameters were as follows, with the ab initio values [also MP2(fc)/6-31G*] being given alongside in square brackets, distances being in pm, angles in deg: r(Al−H) 171.1(23) [170.5], r(Al−C) 195.8(4) [196.6], r(Al⋯Al) 315.3(8) [322.1], ∠Al−C−H 110.1(31) [111.6/112.0], and $\angle H_b$−Al−C 108.3(14) [111.3].

There is generally reasonable agreement between the experimental and theoretical values, with few of the differences exceeding four standard deviations. The chief discrepancy for the dimer concerns the angle ∠Al⋯Al−C, the refined value of which gives ∠C−Al−C = 117.7(4)° [cf. the ab initio value of 127.1°]. In the case of the trimer, the refined value of 108.3(14)° for $\angle H_b$−Al−C and the dependent value of 143.3(27)° for ∠C−Al−C diverge still further from the corresponding optimized values of 115.9° and 128.2° delivered by the ab initio calculations. The refined Al⋯Al distance in the trimer is also about 8 standard deviations shorter than the ab initio one. Even allowing for the generous esd's carried by some of the experimental values, these discrepancies between experiment and theory are substantial. However, as noted previously, the dimer is a comparatively “floppy” molecule, the $C_2Al(\mu\text{-}H)_2AlC_2$ skeleton possessing three vibrational fundamentals estimated to have frequencies < 100 cm^{-1}. The trimer is even more floppy: at the HF/6-31G* level, it is predicted to have no less than 18 vibrational modes with frequencies $<$ 200 cm^{-1}, half of them at frequencies < 100 cm^{-1}. The mode lowest in energy, corresponding to puckering of the six-membered Al_3H_3 ring, is forecast to lie at just 19 cm^{-1}, with the three C−Al−C scissoring modes at or near 97 cm^{-1}. In these circumstances, the differences between experiment and theory must, to a large extent, be attributable to “shrinkage” effects associated with the vibrational averaging of the GED measurements over these large-amplitude motions. It follows that, where such differences arise, the ab initio estimates must be regarded as giving a closer approximation to the equilibrium geometries of the molecules.

At 177.6 pm, the $Al-H_b$ distance determined for $[Me_2AlH]_2$ in the present investigation is some 10 pm longer than that determined in the earlier study.[6] There are few molecules containing $Al(\mu\text{-}H)_2X$ bridges with which meaningful comparisons can be made. Certainly the $Al-H_b$ bonds are appreciably longer than the $Al-H_t$ bonds found in molecules such as $Me_3N\cdot AlH_3$ (156 pm),[38a] $[Me_2NAlH_2]_3$ (155 pm),[38b] and $[HAlNPr^i]_6$ (149 pm).[38c] Rather surprisingly they are also somewhat longer than the $Ga-H_b$ bonds [170.8(14) pm] in the isostructural gallane, $[Me_2GaH]_2$,[34] a result that goes against the trend of near-equality of Al−X and Ga−X distances in compounds of this sort. Ab initio calculations on the fugitive molecule Al_2H_6 give $Al-H_b$ distances ranging, according to the sophistication of the level of theory and basis set used, from 171 to 177 pm,[39] in keeping with the present experimental and theoretical results for $[Me_2AlH]_2$. The $Al-H_b$ distance we have determined is also close to those in the molecules $Al(BH_4)_3$ (180 pm)[40] and Me_2AlBH_4 (177 pm)[41] containing unsymmetrical Al-$(\mu\text{-}H)_2B$ bridges. The Al⋯Al separation deduced for $[Me_2AlH]_2$ in the present study [262.5(6) pm] is not significantly different from that determined previously [261.7(6) pm][6] or from the corresponding separation in the structurally related $[Me_3Al]_2$ (262 pm).[42] This means that the $Al-H_b-Al$ angle determined for $[Me_2AlH]_2$ in the present study [95.3(6)°] is rather smaller than that determined previously [102.6(16)°], but closer to the theoretical mark [MP2/6-31G*] of 97.6°. How close the dimensions of the $Al(\mu\text{-}H)_2Al$ core of $[Me_2AlH]_2$ come to anticipating the corresponding unit of the parent hydride Al_2H_6 is difficult to judge, but ab initio calculations on this molecule[39] indicate an Al⋯Al distance in the range 258−271 pm and an $Al-H_b-Al$ angle never far from 98°.

The structure determined for trimeric $[Me_2AlH]_3$ resembles that of $[Bu^t{}_2AlH]_3$ in crystalline di-*tert*-butylalane,[10] being built on a planar six-membered Al_3H_3 ring. Somewhat fortuitously perhaps, the measured $Al-H_b$ distance of 171(2) pm in the methyl compound is very similar to that of 172.6(5) pm (measured by X-ray diffraction) in the *tert*-butyl compound. It is also about 6 pm shorter than that in the dimer, as anticipated by theory. The change is consistent with the move from a double to a single hydrogen bridge and with

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[38] (a) Almenningen, A.; Gundersen, G.; Haugen, T.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 3928. (b) Downs, A. J.; Duckworth, D.; Machell, J. C.; Pulham, C. R. *Polyhedron* **1992**, *11*, 1295. (c) Cesari, M.; Perego, G.; Del Piero, G.; Cucinella, S.; Cernia, E. *J. Organomet. Chem.* **1974**, *78*, 203.

[39] Liang, C.; Davy, R. D.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1989**, *159*, 393. Lammertsma, K.; Leszczyński, J. *J. Phys. Chem.* **1990**, *94*, 2806. Duke, B. J.; Liang, C.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1991**, *113*, 2884. Shen, M.; Schaefer, H. F., III. *J. Chem. Phys.* **1992**, *96*, 2868.

[40] Almenningen, A.; Gundersen, G.; Haaland, A. *Acta Chem. Scand.* **1968**, *22*, 328.

[41] Barlow, M. T.; Downs, A. J.; Thomas, P. D. P.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1793.

[42] Almenningen, A.; Halvorsen, S.; Haaland, A. *Acta Chem. Scand.* **1971**, *25*, 1937.

the widening of the Al−H$_b$−Al angle [134(4)°, cf. the ab initio value of 141.2°]. In this respect, the trimer is not very different from the aluminum hydride polymer $[AlH_3]_n$ (where Al−H$_b$ = 172 pm, as measured by neutron diffraction, and ∠Al−H$_b$−Al = 141°).[43] The relatively long Al···Al distance of 315.3 pm in $[Me_2AlH]_3$ provides the principal feature discriminating between the trimer and dimer through the medium of their GED patterns. The Al−H$_b$−Al angle is not very well defined, but appears to fall in the range 130−140°, thus being somewhat narrower than the corresponding angle in $[Bu^t{}_2AlH]_3$ [151(1)°].[10] By contrast, the dimensions of the Me_2Al moiety in the $[Me_2AlH]_n$ oligomers do not appear to vary significantly as a function of n, and indeed comparisons with related molecules such as $[Me_2AlCl]_2$,[44a] $[Me_2Al(OMe)]_3$,[44b] $[Me_3Al]_2$,[42] and $[Me_2AlF]_4$[44c] suggest that they are also comparatively insensitive to the nature of the bridging atom.

The results of our investigations leave little doubt that dimethylalane exists in the vapor at temperatures between 300 and 400 K and pressures near 1 Torr as a mixture of dimeric and trimeric forms. On the other hand, the consensus of the evidence provided by colligative and NMR measurements on hydrocarbon solutions of the alane is that the dimer is here accompanied by an oligomer $[Me_2AlH]_n$ with $n > 3$. It seems likely that this is the tetramer, $[Me_2AlH]_4$, presumably with the structure computed ab initio (q.v.). The difference between the vapor and solution phases must be presumed to reflect the change in molecular concentration of the alane and the different temperature regimes (300−500 K for the vapor, 200−300 K for the solutions), and possibly also the solvating influence of the hydrocarbon media. With such a fine balance between the stabilities of different oligomers, it need cause no surprise that the pure liquid alane becomes increasingly viscous on cooling and ultimately solidifies not as crystals but as a glass.[26]

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(43) Turley, J. W.; Rinn, H. W. *Inorg. Chem*. **1969**, *8*, 18.

(44) (a) Brendhaugen, K.; Haaland, A.; Novak, D. P. *Acta Chem. Scand*. **1974**, *28A*, 45. (b) Drew, D. A.; Haaland, A.; Weidlein, J. *Z. Anorg. Allg. Chem*. **1973**, *398*, 241. (c) Gundersen, G.; Haugen, T.; Haaland, A. *J. Organomet. Chem*. **1973**, *54*, 77.