Inorg. Chem. **1990**, *29*, 4688-4692

Contribution from the Departments of Chemistry, Rensselaer Polytechnic Institute,
Troy, New York 12180-3590, and King's College, Wilkes-Barre, Pennsylvania 18711

Effects of Ring Substituents, Preferential Solvation, and Added Amine on the Trimer–Dimer Equilibrium in Cyclic Dialkylaluminum Amide Compounds

Frederick C. Sauls,*[1a] Corinna L. Czekaj,[1b,c] and Leonard V. Interrante*[1b]

Received December 14, 1989

Multinuclear NMR studies of the dialkylaluminum amides $[R_2AlNR'_2]_x$ (R = CH_3, C_2H_5, i-C_4H_9, t-C_4H_9; R'_2 = H_2, $(CH_3)_2$, $(CH_2)_2$) were carried out as a function of temperature and concentration in aromatic hydrocarbon solvents and in the presence of added RNH_2 (R = H, CH_3). Equilibrium constants, ΔH, and ΔS for the trimer–dimer (x = 3, 2) equilibria in solution were obtained. The results were interpreted in terms of steric interactions, ring strain, and preferential solvation. In addition to qualitative increases in the rates of trimer–dimer equilibration, rapid amine exchange was observed in the presence of added RNH_2. The effects of added amine were attributed to amine-catalyzed ring-opening reactions. The potential relevance of these observations to aluminum nitride synthesis via pyrolysis of such dialkylaluminum amides was noted.

Introduction

Compounds of the class $(R_2AlNR'_2)_x$ are known to form cyclic trimers or dimers, depending on the choice of the Al and N substituents R and R′. Several studies have addressed the structure of this class of compounds and the factors that determine the relative stability of the trimeric or dimeric forms.[2-7] These studies have been largely qualitative in nature and have generally applied thermodynamic arguments to rationalize the results of solid-state molecular structure determinations. A priori reasoning suggests that enthalpic changes are due to ring strain and steric interactions involving the ring 1,1-, the 1,2-, and 1,3-substituents. A six-membered ring (trimer) should have minimum ring strain but will have relatively large steric interactions between substituent groups. A four-membered ring (dimer) will have greater ring bond angle strain but reduced steric interference. Larger groups should thus favor the dimer over the trimer. Entropy is expected to favor the dimeric form over the trimer, as more independent molecules are present when the substance is dimeric.

These are some difficulties with this approach, however. There have been very few determinations of ΔH and ΔS for the trimer–dimer conversion for any of these compounds.[5] Instead, the substituents have been varied, and the trimeric or dimeric nature of the compounds has been determined in the crystalline state or in solution. Correlations between variations in R or R′ and changes in the structure were then sought. While these studies have contributed to the understanding of the structures of the organoaluminum amides, some problems are inherent in this approach. Molecular structure in the crystal does not necessarily reflect that in solution, as both crystal packing forces and solvation effects may be important. Ideally, if information regarding the *intrinsic* relative stabilities of different molecular forms is desired, studies should be conducted in the gas phase. When, as for most of the molecules examined in this study, this is impractical, solution structures may be compared cautiously, provided that information on solvation is obtained.

In the context of a series of investigations into the structure and chemistry of organoaluminum amides, we have investigated the solution behavior for a series of related alkylaluminum amides in aromatic solvents. The equilibrium constants, ΔH, and ΔS for the trimer–dimer transformation were determined. These compounds' reactivity toward polar solvents and their low solubility in alkanes preclude an extension to other solvents.

From the viewpoint of materials chemistry, these compounds are interesting as precursors to the useful ceramic AlN[7-10] and as prototypical examples of precursors to a wide range of III–V materials. They are intermediates in the series of reactions

$$R_3Al + NH_3 \rightarrow R_3AlNH_3 \xrightarrow{\Delta} (R_2AlNH_2)_x \xrightarrow{\Delta} (RAlNH)_n \xrightarrow{\Delta} AlN$$

each step accompanied by loss of RH.[7]

Production of pure crystalline AlN is not straightforward, however, as ammonia must be used in the final steps of the conversion of prevent incorporation of carbon.[8] We have partially addressed this effect of ammonia through studies of the interaction of ammonia and methylamine with the $(Me_2AlNH_2)_x$ intermediate. We report here the preliminary results of this investigation in addition to our findings relating to the equilibria between the different $(R_2AlNR'_2)_x$ species.

Information about these compounds' behavior will prove useful in understanding the mechanism of the R_3AlNH_3 to AlN conversion. It may also aid in designing the best precursor for a given process and for optimizing process conditions.

Experimental Section

All handling of alkylaluminum compounds was done in a nitrogen-filled glovebox, due to their sensitivity to oxygen and moisture. Alkylaluminum solutions were prepared gravimetrically. Solutions containing ammonia were prepared by bubbling NH_3 into the alkylaluminum solution; the NH_3 concentration was determined by NMR integration using the alkylaluminum as internal standard.

NMR measurements were made on a Varian XL-200 magnetic resonance spectrometer. ^1H NMR spectra were obtained at 200 MHz, with the residual protons in deuteriobenzene (δ = 7.15 ppm) or residual α-protons in deuteriotoluene (δ = 2.09 ppm) a reference. TMS was not used, as its resonance overlaps other peaks of interest. In cases where quantitation was important, appropriate delays between acquisitions were employed.[11] ^{13}C NMR spectra were obtained on the same instrument at 50.3 MHz. The benzene peak at δ = 128.0 ppm or the toluene peak at δ = 20.4 ppm was used as reference. ^{27}Al NMR spectrometry was performed at 52.1 MHz with external 1 M $AlCl_3$ in 0.1 M HNO_3 as reference. Temperatures were measured by inserting a sealed sample of ethylene glycol or methanol into the spectrometer probe, allowing thermal equilibration, and measuring the peak separation. An internal program computed the temperature using van Geet's equations.[12]

For $(Me_2AlNH_2)_3$, $(i\text{-}Bu_2AlNH_2)_3$, and $(Me_2AlN(CH_2)_2)_3$, equilibrium studies were performed as follows. A series of solutions of varying alkylaluminum amide concentration were prepared gravimetrically in

---

[1] (a) King's College. (b) Rensselaer Polytechnic Institute. (c) Current address: Department of Chemistry, Oklahoma State University, Stillwater, OK 74078.

[2] Coates, G. E. *Organometallic Compounds*; Methuen: London, 1967; p 397.

[3] Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: London, 1972; p 236.

[4] Cesari, M.; Cucinella, S. Aluminum-Nitrogen Rings and Cages. In *The Chemistry of Inorganic Homo and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; p 167.

[5] Storr, A.; Thomas, B. S. *J. Chem. Soc. A* **1971**, 3850.

[6] Interrante, L. V.; Sigel, G. A.; Garbauskas, M.; Hejna, C.; Slack, G. A. *Inorg. Chem.* **1989**, *28*, 252.

[7] Work of Wiberg, E. reported in: Bahr, G. *Inorganic Chemistry*; Klemm, W., Ed.; FIAT Review of German Science 1939–1946, Vol. 24; Dieterichsche Verlagsbuchhandlung: Wiesbaden, 1948; Part 2, p 155.

[8] Interrante, L. V.; Carpenter, L. E.; Whitmarsh, C.; Lee, W.; Slack, G. A. *Mat. Res. Soc. Symp. Proc.* **1986**, *73*, 986.

[9] Bolt, J. D.; Tebbe, F. Aluminum Nitride Fibers; Sintering and Microstructure. *Proc. Am. Ceram. Soc. Electronic Div.*, Oct. 19, 1987.

[10] Tebbe, F.; Bolt, J. D.; Young, R. J.; van Buskirk, O. R.; Mahler, W.; Reddy, G. S.; Chowdhry, U. Thermoplastic Organoaluminum Precursors of Aluminum Nitride. *Proc. Am. Ceram. Soc. Electronic Div.*, Oct. 19, 1987.

[11] Sauls, F. C.; Interrante, L. V.; Jiang, Z. *Inorg. Chem.* **1990**, *29*, 2989.

[12] van Geet, A. *Anal. Chem.* **1968**, *40*, 2227.

Table I. Equilibrium Calculations at 100 °C in Toluene-d_8

molarity	peaks $(M/L)^a$	$K_{32}{}^b$	$K_{31}{}^c$	$K_{21}{}^d$
A. $(Me_2AlNH_2)_x$				
0.237	1655/67.9	5.020×10^{-5}	2.75×10^{-4}	2.24×10^{-3}
0.126	1693/89.5	5.95×10^{-4}	1.71×10^{-4}	2.00×10^{-3}
0.0814	1839/109	6.4×10^{-5}	1.00×10^{-4}	1.62×10^{-3}
0.0348	1838/147	5.06×10^{-5}	0.432×10^{-4}	1.24×10^{-3}
0.0127	1266/160.5	7.75×10^{-5}	0.210×10^{-4}	1.09×10^{-3}
0.00476	881/160.3	8.20×10^{-5}	0.080×10^{-4}	0.80×10^{-3}
B. $(t\text{-}Bu_2AlNH_2)_x$				
0.719	53/190	27.0	31.4	12.1
0.330	34/189	29.1	35.3	9.45
0.141	21/191	35.1	11.3	6.8
0.0745	16/190	31.1	1.5	4.9
C. $(Et_3AlNH_2)_x$				
0.584	306/48	6.55×10^{-3}	7.95×10^{-2}	7.45×10^{-2}
0.215	340/82	8.20×10^{-3}	3.40×10^{-2}	6.03×10^{12}
0.0940	330/96	6.10×10^{-3}	1.06×10^{-2}	3.70×10^{-2}
0.0319	363/141	4.55×10^{-3}	0.09×10^{-2}	1.26×10^{-2}
0.0193	344/158	7.10×10^{-3}	0.027×10^{-2}	0.74×10^{-2}
D. $(i\text{-}Bu_2AlNH_2)_x$				
0.329	419/417	0.55	2.18	0.98
0.171	379/479	0.52	0.93	0.724
0.0981	295/484	0.56	0.494	0.600
0.0613	239/508	0.63	0.299	0.532
0.0178	142/494	0.57	0.0535	0.288
E. $(Me_2AlN(CH_2)_2)_x$				
0.397	1869/11	2.71×10^{-7}	2.57×10^{-6}	1.57×10^{-4}
0.183	1750/18	6.65×10^{-6}	2.89×10^{-6}	1.15×10^{-4}
0.0958	1920/23	5.50×10^{-7}	1.25×10^{-6}	0.82×10^{-4}
0.0419	1940/22	2.04×10^{-7}	0.203×10^{-6}	0.32×10^{-4}

[a] Peak heights in arbitrary units; more/less (M/L) aggregated forms. [b] For trimer–dimer equilibrium. [c] For trimer–monomer equilibrium. [d] For dimer–monomer equilibrium.

toluene-d_8 (a density of 0.94 g/mL was assumed) (Table I). Each solution was allowed to equilibrate in the NMR probe at 100 °C, and the spectrum was obtained at intervals. Initially, constancy of the spectrum was taken as evidence for the attainment of equilibrium. The ΔH determinations were performed on the most concentrated solutions of Table I by allowing equilibration at varying temperatures. For each compound, the spectra showed noticeable change with temperature. Alternate points on the ln K vs $1/T$ plot were obtained during upward and downward passage over the temperature range spanned. Because both sets of points fell on the same line, we consider that equilibration was achieved.

For $(Et_2AlNH_2)_3$ at temperatures near and above ambient, the peaks from the two species overlap so severely that quantitation is not feasible; modification of the above method was required. Samples were prepared in toluene-d_8, as above and allowed to equilibrate in NMR tubes at the temperature of interest. They were then rapidly cooled to −78 °C in a dry ice–isopropyl alcohol bath. Spectra were then obtained at −70 °C, where the species are resolved and equilibration is very slow.

$(t\text{-}Bu_2AlNH_2)_3$ equilibrates slowly, even at 100 °C. The procedure was therefore modified as follows. A series of toluene-d_8 solutions of $(t\text{-}Bu_2AlNH_2)_3$ in varying concentration were prepared. NMR tubes containing these solutions were then equilibrated for 14 h at 100 °C and ^1H NMR spectra obtained. In order to determine ΔH and ΔS for the equilibrium, the spectra were determined as above in tetrahydronaphthalene-d_{12} (bp 207 °C) over the temperature range 90–135 °C. At temperatures less than 90 °C equilibration is impractically slow; the boiling point of toluene (110.6 °C) is thus too low to give an adequate temperature range for ΔH determinations.

Mass spectra were obtained by using the direct-insertion probe of a Hewlett-Packard 5987A GC/MS system in the chemical ionization mode, with isobutane as reagent gas.

$(Me_2AlNH_2)_3$,[6] $(Et_2AlNH_2)_3$,[13] $(i\text{-}Bu_2AlNH_2)_3$,[14] $(t\text{-}Bu_2AlNH_2)_3$,[6] $(Me_2AlNHMe)_3$,[15] $(Me_2AlNMe_2)_2$,[16] and $(Me_2AlN(CH_2)_2)_3$[5] were prepared as previously described. For all compounds, the proton NMR spectra showed no extraneous peaks. Peak integrations gave the expected ratios.

Benzene-d_6, toluene-d_8, and tetrahydronaphthalene-d_{12} (99.5%, 99%, and 99% D, respectively) were used as received from Aldrich. NH_3 (USS Agrichemicals) was dried over sodium before use. NH_2Me (Matheson) was dried by passage over KOH.

Results

$(Me_2AlNH_2)_n$ is known to exist as a trimer in the crystal.[6] Initial qualitative proton NMR observations revealed a small peak 0.09 ppm downfield of the main methyl resonance at room temperature.[11] The relative intensity of this small peak increased with decreasing concentration and increased reversibly with temperature, implying the presence of an equilibrium.

The spectra obtained at 100 °C from the series of solutions of varying concentration were analyzed as follows. Peaks due to the more aggregated (M) and less aggregated (L) forms were identified, on the basis of the shift toward less aggregation with dilution. Peak heights of the two resonances were then measured (slight spectral overlap made this preferable to measurement of peak areas) and are shown in Table I.

If we assume the equilibrium

$$2(Me_2AlNH_2)_3 \overset{K_{32}}{\rightleftharpoons} 3(Me_2AlNH_2)_2$$

then M is the trimer and L the dimer. Thus

$$[(Me_2AlNH_2)_3] = RM/18 \tag{1}$$

$$[(Me_2AlNH_2)_2] = RL/12 \tag{2}$$

where R is the instrumental response per proton, constant for any particular spectrum, and M and L denote peak heights of the M and L forms. The total concentration, computed as if the compound were completely trimeric, is known (C_t) and must obey the relation

$$C_t = R(M + L)/18 \tag{3}$$

Combining eqs 1–3 yields

$$K_{32} = 3.375C_tL^3/(M^2(M + L)) \tag{4}$$

If we assume the equilibria

$$(Me_2AlNH_2)_3 \overset{K_{31}}{\rightleftharpoons} 3Me_2AlNH_2$$

$$(Me_2AlNH_2)_2 \overset{K_{21}}{\rightleftharpoons} 2Me_2AlNH_2$$

similar derivations yield the expressions

$$K_{31} = 27C_t^2L^3/(M(M + L)^2) \tag{5}$$

$$K_{21} = 6C_tL^2/(M(M + L)) \tag{6}$$

Upon test-fitting of the observed intensities to eqs 4–6, only K_{32} was reasonably constant; K_{31} and K_{21} showed significant trends with concentration (Table IA). We therefore conclude that the trimer–dimer equilibrium is being observed; the trimer is the dominant species. Implicit in all equilibria determined by this method is the approximation of thermodynamic activity by concentration.

Equilibration at various temperatures (30–100 °C) and computation of the associated K_{32} allowed determination of ΔH and ΔS for the transformation (Figure 1). This equilibration was rapid compared with the ~7-min NMR probe thermal equilibration time, indicating the lability of the dimer and trimer. The entire process was repeated by using benzene-d_6 (30–80 °C) instead of toluene-d_8, yielding essentially the same results (Table II).

The ^1H NMR shift values are given in Table III.

$(t\text{-}Bu_2AlNH_2)_n$. This compound was isolated from solution by slow cooling and crystallized as the cyclic trimer.[6] It was much less soluble in toluene than its analogues. Its ^1H NMR spectrum (0.1 M) at 30 °C comprised the expected two peaks (δ = 1.0, 9

---

(13) Cohen, M.; Gilbert, J. K.; Smith, J. D. *J. Chem. Soc.* **1965**, 1092.

(14) Czekaj, C. L.; Hackney, M. L. J.; Hurley, W. J., Jr.; Interrante, L. V.; Sigel, G. A.; Schields, P. J.; Slack, G. A. *J. Am. Ceram. Soc.* **1990**, *73*, 352.

(15) Interrante, L. V.; Lee, W.; McConnell, M.; Lewis, N.; Hall, E. *J. Electrochem. Soc.* **1989**, *132*, 472.

(16) Alford, K. J.; Gosling, K.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 2203.

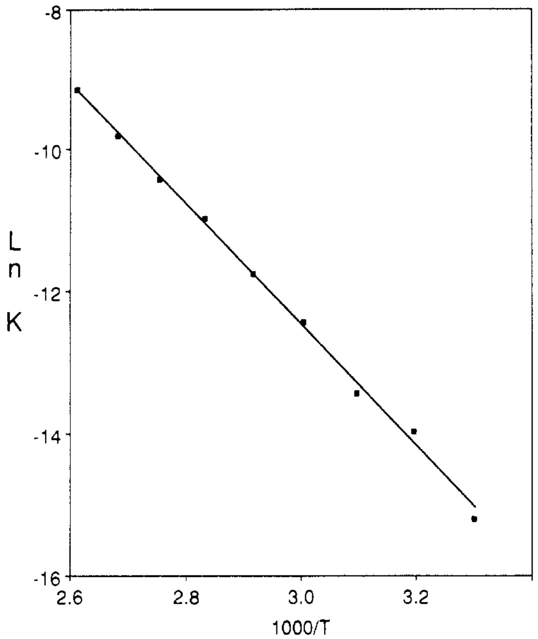


Figure 1. Determination of ΔH for the conversion of $(Me_2AlNH_2)_3$ to $(Me_2AlNH_2)_2$ in toluene-d_8 solution.

Table II. Summary of Thermodynamic Results for the Reaction

$$2(\text{trimer}) \rightleftharpoons 3(\text{dimer})$$

compd[a]	ΔH, kJ	ΔS, J/K	K[b]
$(Me_2AlNH_2)_3$[c]	38 ± 2	12	1×10^{-5}[d]
$(Me_2AlNH_2)_3$	36.0 ± 0.7	15	5.5×10^{-5}
$(Et_2AlNH_2)_3$	20 ± 2	5	2.8×10^{-3}
$(i\text{-}Bu_2AlNH_2)_3$	14 ± 2	30	4.25×10^{-1}
$(t\text{-}Bu_2AlNH_2)_3$	30 ± 3[e]	104[e]	1.65×10[e]
			2.5×10
$(Me_2AlN(CH_2)_2)_3$	69 ± 7	72	1.3×10^{-6}
$(Me_2AlN(CH_2)_3)_3$[c]	57.8[f]	162[f]	6.4×10^{-1}[g]

[a] In toluene-d_8 unless otherwise noted. [b] At 100 °C unless noted. [c] In benzene-d_6. [d] At 80 °C. [e] In tetrahydronaphthalene-d_{12}. [f] From ref 5. [g] At 55 °C.

H; $\delta = 0.8$, br, 2 H) from the *tert*-butyl and NH_2 groups, respectively. However, when the solution was heated at 100 °C, the sharp peak near $\delta = 1$ began to decrease and several other peaks appeared in this region. After the solution was heated for 1 h, only the original peak (now much reduced in intensity) and a large new peak (attributed to the dimer; see below) just upfield at $\delta = 0.99$ were present in this region, the intermediates in the conversion having disappeared (Figure 2). A broad peak near $\delta = 0.6$ ppm also appeared, replacing that near $\delta = 0.8$ ppm. When the solution was cooled to 25 °C, the sharp peak of the new species shifted to be nearly coincident with that of the trimer.

After equilibration at 100 °C, room-temperature $^{13}C\{^1H\}$ NMR spectra contained peaks at $\delta = 31.3$ ppm for the trimer and $\delta = 31.5$ ppm for the dimer. A broad peak at $\delta = 21$ ppm did not change as the conversion proceeded; we attribute this to the α-carbon in both forms, broadened by the quadrupolar ^{27}Al nucleus. ^{27}Al NMR (0.1 M) showed only a broad peak at $\delta = 140$ ppm, characteristic of tetrahedrally coordinated aluminum.[17] No peaks attributable to 3-, 5-, or 6-coordinate aluminum[17] were detected.

The sample was allowed to stand for several days at ambient temperature. $^{13}C\{^1H\}$ NMR demonstrated that the equilibrium had shifted partially back toward the trimer. Two weeks later, a precipitate of the trimer was noted in the NMR tube. The supernatant still contained principally the new species, which is much more soluble than the trimer. Efforts to isolate the new species by solvent removal failed; only crystalline trimer was recovered.

Table III. Summary of ^1H NMR Chemical Shift Data[a]

compound	aluminum substituent	nitrogen substituent
$(Me_2AlNH_2)_3$[b]	−0.78/−0.67 (s)	−0.27/... (br)
$(Me_2AlNH_2)_3$	−0.83/−0.71 (s)	−0.25/... (br)
$(Et_2AlNH_2)_3$	α −0.17/+0.03 (q)[c] β +1.21/+1.24 (t)	+0.10/... (br)
$(Et_2AlNH_2)_3$ (l)[d]	α −0.02 (q) β +1.16 (t)	+0.97 (br)
$(i\text{-}Bu_2AlNH_2)_3$	α −0.06/−0.01 (d) β +1.83/+1.87 (m) γ +1.035/+1.026 (d)	+0.31/+0.18 (br)
$(i\text{-}Bu_2AlNH_2)_3$ (l)[d]	α −0.25 (m) β +1.6 (m) γ +0.75 (m)	+0.42/+0.37 (br)
$(t\text{-}Bu_2AlNH_2)_3$[e]	+1.00/+0.99 (s)	+0.8/+0.6 (br)
$(Me_2AlNMe_2)_2$	.../−0.63 (s)	.../+2.08 (s)
$(Me_2AlN(CH_2)_2)_3$	−0.90/−0.73(s)	+1.53/... (s)
$(Me_2AlN(CH_2)_3)_3$[f]	−0.47/−0.61(s)	α +3.43/+3.30 (t) β +1.96/+1.73 (q)

[a] All data in δ (ppm) for trimer/dimer in toluene-d_8 at 30 °C unless noted otherwise. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. [b] In benzene-d_6. [c] AT −70 °C. [d] Neat liquid. Only one set of overlapping resonances was observed. [e] At 100 °C. [f] From ref 5.

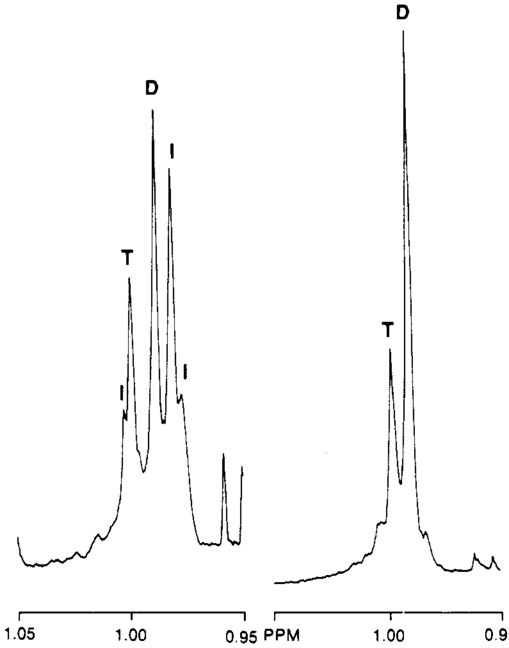


Figure 2. Proton NMR spectrum in the CH_3 region, showing the conversion of $(t\text{-}Bu_2AlNH_2)_3$ to $(t\text{-}Bu_2AlNH_2)_2$ at 100 °C in tetrahydronaphthalene-d_{12}. Note several intermediate peaks (I) present in the spectrum on the left, obtained after 10 min. The spectrum on the right, obtained after 1 h, shows the trimer (T) as the small peak to the left of the large dimer (D) resonance.

On the basis of the equilibrium calculations performed as for the methyl derivative, we identify the new species as the dimer. The results are shown in Tables IB and II.

Mass spectral data are in accord with this interpretation. The isobutane CI mass spectrum of the fused trimer (250 °C) shows only two peaks of significant intensity. They are at $M = 414$ (trimer minus an isobutyl group, 100%) and $M = 257$ (dimer minus an isobutyl group, 9%). Time vs intensity profiles for the $M = 414$ and $M = 257$ peaks were obtained. The peak we attribute to the dimer decreased in intensity at a more rapid rate than did that for the trimer, indicating that it is not due to trimer fragmentation but that it is from a separate, more volatile species.

$(Et_2AlNH_2)_n$, $(i\text{-}Bu_2AlNH_2)_n$, and $(Me_2AlN(CH_2)_2)_n$. Data were obtained and calculations performed in the same manner as those for $(Me_2AlNH_2)_3$. Trimer–dimer equilibria are again indicated (Tables IC–E and II). Spectra of the isobutyl compound, showing the effects of temperature increase on the equilibrium, are shown in Figure 3.

---

[17] Delpuech, J. J. Aluminum-27. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2.

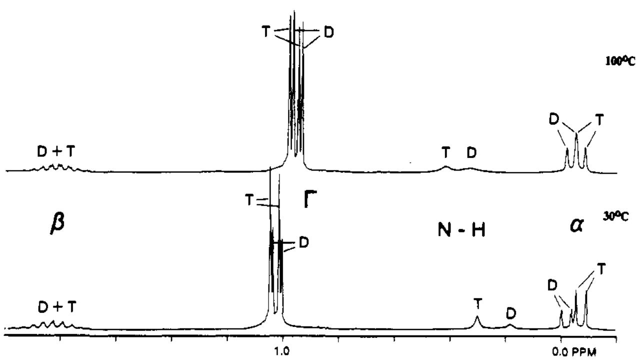


Figure 3. Proton NMR spectra of $(i\text{-Bu}_2\text{AlNH}_2)_x$ in toluene-d_8. The lower plot is at 30 °C; the upper, at 100 °C. Peaks labeled D are from the dimer; those labeled T, from the trimer.

$(\text{Me}_2\text{AlNMe}_2)_2$. Dissolution of this species in toluene-d_8 revealed no evidence for an equilibrium. Peaks attributable to only one species, known to be the dimer,[16] were detected.

$(\text{Me}_2\text{AlNHMe})_n$. The complexity due to the cis–trans isomerism prevented convincing identification of any peaks attributable to dimeric forms.

Efforts of Added NH_3 and MeNH_2 on the $(\text{R}_2\text{AlNH}_2)_n$ Trimer–Dimer Equilibria. The lability of the $(\text{Me}_2\text{AlNH}_2)_3$ ring toward ring opening and amine exchange was investigated by adding NH_2Me to the trimer in benzene-d_6. $(\text{Me}_2\text{AlNHMe})_3$, identified by comparison with the NMR spectrum of a known sample, formed nearly completely in less than 1 h at room temperature. At 70 °C, N–Me lines from free NH_2Me and from $(\text{Me}_2\text{AlNHMe})_3$ have broadened and shifted toward one another, indicating a substantial rate of exchange. Smith et al.[16] have noted that the NMR spectrum of $(\text{Me}_2\text{AlNHMe})_3$ shows structure in the Al–Me region due to the existence of cis and trans isomers. In the presence of methylamine this structure collapses, indicating that rapid interconversion of the isomers is catalyzed by the amine.

It is reasonable to expect ammonia to labilize the ring in the same manner, but as no cis–trans isomerism exists and the N–H resonances are broad, the effects are not readily observed.

When NH_3 is added to $(t\text{-Bu}_2\text{AlNH}_2)_3$ in toluene-d_8, the rate of trimer–dimer equilibration is dramatically increased. The *tert*-butyl peaks for the two forms are now also distinct at room temperature but superimposed at 100 °C. This difference in shift behavior implies substantial differences in solvation in the presence and absence of ammonia. We suspect this is caused by better hydrogen bonding to the dimer than to the trimer, although formation of $\text{H}_3\text{NAl}(t\text{-Bu})_2\text{NH}_2$ cannot be ruled out.

Discussion

Models based on tetrahedral coordination of the ring atoms show that the alkyl groups are farther apart in the dimer than in the trimer. Steric relief would therefore provide a driving force to overcome increased ring strain in the dimer; larger alkyl groups would cause a less endothermic conversion from trimer to dimer. Examination of the ΔH values for the series $(\text{R}_2\text{AlNH}_2)_3$ partially bears out this expectation. ΔH decreases along the series methyl > ethyl > isobutyl. The anomalous $(t\text{-Bu}_2\text{AlNH}_2)_3$ will be discussed separately below.

On the other hand, a close examination of the molecular structures for the various trimeric dialkylaluminum amides,[6] $(\text{R}_2\text{AlNH}_2)_3$, suggests that the concept of ring strain should be applied with some caution in the discussion of ring size preferences among the compounds of this class. In particular, large deviations from tetrahedral coordination have been observed for the ring atoms, with endocyclic Al–N–Al angles typically in the range 120–134°. Also, the conformations observed among these six-membered rings show wide deviations from the chair conformation usually exhibited by the corresponding cyclic hydrocarbons, ranging from skew-boat to even a planar $(\text{AlN})_3$ ring. These observations, along with the relatively high degree of ionic character presumably associated with the Al–N bonds, suggest that deviations from the idealized tetrahedral bond angles may be less costly in energy for these ring systems. Therefore, ring bond angle strain may be of lesser importance in determining ring size and conformation in dialkylaluminum amides than in analogous hydrocarbons.

Steric relief has the additional effect of making the N–H protons more accessible in the dimer than in the trimer. We assume that solvation effects are principally due to interaction of the solvent's aromatic π cloud with the relatively positive N–H protons.[14] Solvation is therefore expected to be more exothermic for the dimer than for the trimer. Thus, $\Delta H_{\text{solvation}}$ for the dimer will be larger than $\Delta H_{\text{solvation}}$ for the trimer, and differential solvation will stabilize the dimer relative to the trimer.

The extent of this relative stabilization of the dimer by solvation will depend on the alkyl groups. For very small susbtituents, there may be no interference with solvation of either trimer or dimer, hence no relative stabilization. If the alkyl groups are very large, the N–H protons will be inaccessible in both forms. Neither trimer nor dimer will be well solvated, and there will again be no differential solvation. It is only when the substituents are of intermediate size, large enough to interfere with the trimer N–H but small enough to allow access to the dimer N–H, that differential solvation will be significant.

Because the trend with size of differential solvation partially parallels that due to the steric interference already considered, the relative contributions of angle strain, steric crowding, and differential solvation cannot be easily quantitated. Several lines of evidence suggst that these differential solvation effects are by no means negligible, however.

Wiberg[7] has reported that $(\text{Me}_2\text{AlNH}_2)_x$ is apparently dimeric in liquid ammonia, in contrast to the trimeric form found in aromatic solvents. This may be understood in terms of the greater accessibility of dimer N–H protons. The dimer will more readily hydrogen-bond to the basic solvent than will the trimer, and will therefore gain in relative stability. Alternatively, the high Lewis basicity of ammonia may lead to a more complex set of equilibria involving ring-opening, Al–NH_3-coordinated species.

It was noted in all cases that the protons α to the aluminum showed a greater temperature dependence in shift for dimers than for the corresponding trimers. β- and γ-protons show similar, but smaller, effects. For those compounds whose trimer and dimer N–H ^{1}H resonances are distinguishable ($(i\text{-Bu}_2\text{AlNH}_2)_3$ and $(t\text{-Bu}_2\text{AlNH}_2)_3$), the dimer also shows the greater temperature dependence in shift (cf. Figure 3). These observations can also be understood in terms of less crowding in the dimer. Since the N–H protons of the dimer are more accessible for interaction with the aromatic π cloud of the solvent, stronger complexation and a correspondingly more temperature-dependent shift are expected consequences.

ΔS values for the trimer–dimer conversion in $(\text{Me}_2\text{AlN}(\text{CH}_2)_2)_2$ and $(\text{Me}_2\text{AlN}(\text{CH}_2)_3)_3$ are much higher than for the analogous NH_2-bridged compounds (except the anomalous $(t\text{-Bu}_2\text{AlNH}_2)_3$); the NH_2-bridged compounds have a smaller ΔS than expected. This can be explained by recognizing that if the dimer is better solvated than the trimer, then tighter organization of the solvent sphere on going from trimer to dimer will cause a *decrease* in entropy. This decrease will partially offset the increase in the solute entropy, rendering the net ΔS smaller than expected. Because $(\text{Me}_2\text{AlN}(\text{CH}_2)_2)_3$ and $(\text{Me}_2\text{AlN}(\text{CH}_2)_3)_3$ have no N–H groups, they will be less well solvated, and preferential solvation will be much less important. Their higher ΔS values follow, as there is little solvent reorganization.

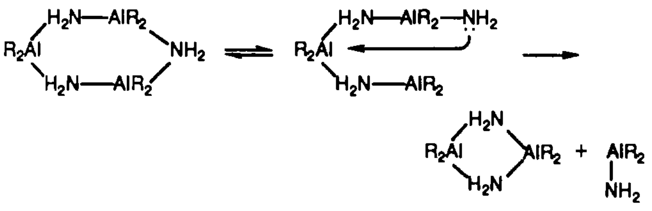
The anomalous ΔH, ΔS and N–H ^{1}H NMR shift values for $(t\text{-Bu}_2\text{AlNH}_2)_3$ can all be rationalized as consequences of the large bulk of the *tert*-butyl group. Models show that it is so large that it restricts the approach of an aromatic π cloud to the N–H in *both* the trimer and the dimer. Neither form is well solvated, so differential solvation is unimportant. Without differential solvation to stabilize the dimer, ΔH is unexpectedly large in comparison with the values for the methyl, ethyl, and isobutyl derivatives. Since solvent sphere reorganization is less important, ΔS is also large.

The N–H ^{1}H NMR shift values for this series of compounds are also in accord with this interpretation. Comparing the N–H resonance for neat $(Et_2AlNH_2)_3$ with that of $(Et_2AlNH_2)_3$ in toluene gives a substantial upfield shift (0.97 vs 0.10 ppm) due to π complexation. A similar but smaller upfield shift is evident for the less well-solvated $(i\text{-}Bu_2AlNH_2)_3$. The N-H proton resonances for both forms of the *tert*-butyl derivative are well downfield of the corresponding resonances for all the other compounds examined, indicating very poor π complexation of both the trimer and the dimer.

If we examine the series in which the Me_2Al group is held constant but NR_2 varies through the set $N(CH_2)_2$, $N(CH_2)_3$, and NMe_2, a progression of less endothermic ΔH values would be expected, indicating increasing preference for the dimeric form as substituent size increases. This is consistent with our observations, as ΔH values decrease in the order $N(CH_2)_2 > N(CH_2)_3$, with the $N(CH_3)_2$ compound occurring only in the dimeric form. Another factor that may contribute to this trend is the effect of $(AlN)_x$ ring size variation on the ring strain within the $N(CH_2)_n$ rings. In going from the trimer to the dimer, i.e. from a six- to a four-membered ring, the Al-N-Al bond angle tends to decrease, causing an increase in the R-N-R angle. If the R groups are bound in an already strained ring, this angular expansion will be strongly resisted, hence the preference for the more sterically crowded trimer over the more ring-strained dimer.

Qualitative observations indicate that the rate of trimer-dimer equilibration lies in the order methyl, ethyl > isobutyl ≫ *tert*-butyl, for substituents on aluminum. Uncatalyzed trimer to dimer conversion may occur via one of three basic pathways:

(1) Ring opening may be followed by an attack of the free NH_2 group's lone pair on an aluminum atom, resulting in a four-membered ring and a free monomer, which may dimerize.

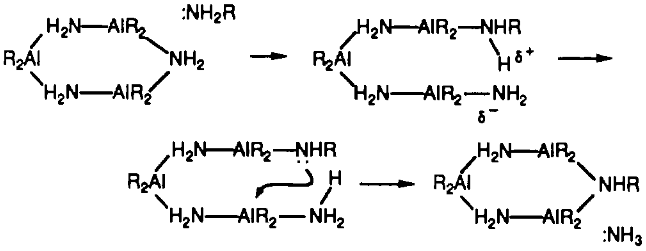


As larger alkyl groups cause slower equilibration, this is plausible only if the attack step is rate-determining. Larger alkyl groups would speed the ring opening due to steric relief but would slow the attack step because of crowding. This mechanism is in accord with kinetic evidence for presence of monomer,[11] as well as with the fact that mixing $(Me_2AlNH_2)_3$ and $(Et_2AlNH_2)_3$ rapidly produces mixed trimers $(Me_2AlNH_2)_x(Et_2AlNH_2)_{3-x}$ in an approximately statistical distribution.[11] The transient intermediates noted during conversion of $(t\text{-}Bu_2AlNH_2)_3$ to dimer may be the monomer and ring-opened forms of trimer or dimer.

(2) Dissociation to monomers and subsequent recombination may occur. This seems unlikely both because three Al-N bonds must be broken (a high-energy process) and because steric relief would make this route faster with larger substituents.

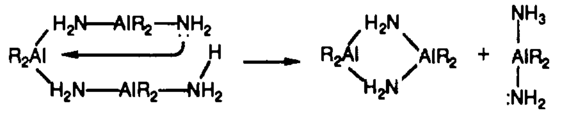
(3) Ring opening followed by attack on a neighboring ring, as proposed by Storr and Thomas,[5] is a further possibility. Rigorous discrimination among these possibilities is not possible with the information currently available.

Amine exchange is rapid, and trimer-dimer equilibration is catalyzed by amine. Amine exchange may occur by a ring-opening, proton-transfer, and reclosure mechanism:



Repetition of this process at each bridge yields complete exchange. Because no loss of Al-N bonds occurs during this process, it should be a relatively low energy pathway.

Catalytic conversion to the dimer is also explicable within this framework; the intermediate need not necessarily reattach to the same aluminum atom.



The last species may then lose NH_3 and dimerize or trimerize. Alternatively, two ammonia molecules may cleave the ring into monomer and open-chain dimer, each with an ammonia coordinated to the terminal aluminum atom. The fragments may then lose NH_3 and close into rings or recombine.

The ability of amines to open Al-N rings may partially explain why an ammonia atmosphere improves the purity and morphology of AlN prepared by precursor pyrolysis.[8] The initial stages of AlN formation by $(R_2AlNH_2)_3$ pyrolysis are suspected to proceed by linkage of individual rings into a network. If it probable that during this process, some Al-R groups are left without H atoms on neighboring nitrogens. In addition, regions may form in which the rings are misaligned, such that an aluminum atom of one ring is adjacent to an aluminum of the next ring rather than a nitrogen. Fusion of rings so aligned is not possible. Ammonia, by allowing ring opening, would facilitate skeletal rearrangement under mild conditions so that RH elimination can occur instead of pyrolysis of the R groups. It may also serve as an alternative source of hydrogen in the final stages of the conversion of $(RAlNH)_n$ to AlN, thereby circumventing the pyrolysis of isolated Al-R groups to carbon and hydrogen.[8] Improved AlN purity and crystallinity would naturally follow.

Acknowledgment. We thank Zhiping Jiang, Chris Warren, Wei Lee, and Gary Sigel for synthesis of the compounds used in this work. Mass spectra were obtained by Savely Goldin. This work was supported by the Air Force Office of Scientific Research (AFSC) and, in part, by a DARPA/ONR URI grant. F.C.S. thanks King's College for a sabbattical leave and the NSF for participation in the Summer Workshop in Solid-State Chemistry.