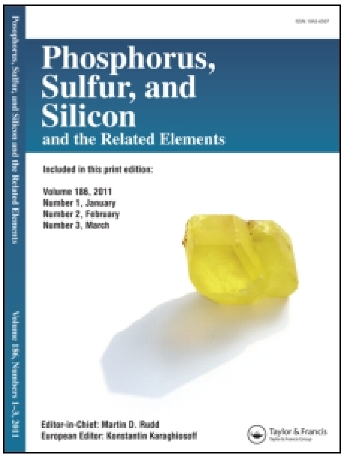

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CYCLIC $(AlN)_n$ COMPOUNDS AS PRECURSORS TO ALUMINUM NITRIDE: SYNTHESIS AND STRUCTURE OF $[(CH_3)_2AlNH_2]_3$ AND THE PLANAR SPECIES $[(t\text{-}C_4H_9)_2AlNH_2]_3$

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Abstract The crystal and molecular structures of the title compounds, $[(CH_3)_2AlNH_2]_3$ 1 and $[(t\text{-}C_4H_9)_2AlNH_2]_3$ 2, have been determined in connection with their investigation as possible precursors to aluminum nitride. Both compounds have an $(AlN)_3$ ring-structure with distorted tetrahedral geometries for the ring Al and N atoms. The distortion from tetrahedral geometry is most pronounced for the N atoms where the endocyclic Al-N-Al bond angles average 125.3 for 1 and 134.2 for 2. The $(AlN)_3$ ring in 1 is in a skew-boat conformation with no unusual intra- or intermolecular contacts. Compound 2 on the other hand exhibits an unprecedented planar $(AlN)_3$ ring as required by a crystallographic three-fold symmetry axis. The effects of the Al and N substituents on the $(AlN)_3$ ring size and conformation, as well as on the endocyclic Al-N-Al bond angles, are discussed in the context of the structural results obtained for these and other $(AlN)_n$ ring compounds.

INTRODUCTION

The products of the reaction of alkylaluminum compounds with ammonia and primary and secondary organic amines have been the subject of considerable interest for many years, yielding a rich variety of intermediate amide and imide compounds with novel ring and cage structures[1-8]. Surprisingly, until quite recently, the least investigated members of this class of compounds have been the derivatives of the trialkylaluminum compounds with ammonia. In 1948 the work of Wiberg on the reaction of trimethyaluminum with ammonia was reported briefly in a review of WWII German science;[1] however, the structures and properties of the amide and imide intermediates observed in the thermal conversion of the initially formed Lewis acid-base adduct, $(CH_3)_3Al:NH_3$, to the reported end product, aluminum nitride (Scheme 1, $R = CH_3$), were not specified in detail.

Scheme 1

$$R_3Al + NH_3 \longrightarrow R_3Al:NH_3$$

$$R_3Al:NH_3 \longrightarrow R_2AlNH_2 + RH$$

$$R_2AlNH_2 \longrightarrow RAlNH + RH$$

$$RAlNH \longrightarrow AlN + RH$$

The interest in these and related trialkylaluminum/ammonia derivatives has been enhanced recently by the discovery of their potential utility as precursors to aluminum nitride powder[9], thin films[10] and fiber[11]. As part of a detailed investigation of the structures and reactions of these compounds we have isolated and determined the crystal and molecular structures of the dialkylaluminum amides, R_2AlNH_2 , where $R = CH_3$ and $t\text{-}C_4H_9$. The latter compound apparently has not been previously investigated whereas the $(CH_3)_2AlNH_2$ derivative was reported by Wiberg to be a dimer in liquid ammonia solution.[1]

SYNTHESES

The compound, $[(CH_3)_2AlNH_2]_3$ **1**, was obtained by bubbling excess ammonia through a refluxing solution of trimethylaluminum in benzene. After removal of the solvent in vacuum and purification by vacuum sublimation, crystals suitable for x-ray diffraction were obtained by slow cooling of a heptane solution. The $[(t\text{-}C_4H_9)_2AlNH_2]_3$ compound (2) was obtained in an analogous manner from a refluxing xylene mixture. In this case the crystals obtained by slow cooling of the original xylene solution were used directly for x-ray diffraction studies. Details of the crystal structure determination of these two compounds are reported elsewhere.[12]

CHARACTERIZATION

$[(CH_3)_2AlNH_2]_3$ (1)

Infrared spectrum (KBr disk): ν(N-H) 3314, 3304, and 3252 cm^{-1} (N-D) 2468, 2458, and 2390 cm^{-1}; ν(Al-N) 705 cm^{-1}. H^1-NMR (C_6D_6 solution): 0.68 (2H, NH_2), -0.95 (6H, CH_3); Mass spectrum (E.I., relative intensities): 219 (3.2%, M [trimer]), 204 (100%, M-15).

$[(t\text{-}C_4H_9)_2AlNH_2]_3$ (2)

Infrared spectrum (KBr disk): ν(N-H) 3357, 3278, and 3170 cm^{-1}. H^1-NMR (C_6D_6 solution): 1.07 (18 H, CH_3), 0.68 (2H, NH_2). Mass spectrum (E.I., relative intensities): 472 (0.5%, M [trimer]), 456 (3.2%, M-15), 414 (100%, M-57), and 257 (10%, M-214). Elemental analysis (C, H, and N): Calculated: 61.09, 12.84, 8.91; Found: 61.42, 13.05, 8.77.

RESULTS

Formation and Thermal Stability of the Amides

Studies in our laboratory[13] have shown that the two organoaluminum amides described herein are formed in exothermic processes from the corresponding Lewis acid-base adducts, $R_3Al{:}NH_3$. The heat evolved in both cases is consistent with the enthalpy change anticipated for the following bond breaking/formation process: C-Al + N-H $\longrightarrow$ C-H + Al-N. These results, along with previous structural studies of analogous alkylaluminum amides[2-8], suggest that oligomerization through the formation of additional Al-N bonds accompanies the conversion of these adducts to the amides.

Mass spectral and NMR studies indicate that the predominant form for these oligomers in the gas phase and in solution is a trimer. In addition to a weak peak at m/e corresponding to the trimer, the most abundant peak in the mass spectra of both compounds occurs at the m/e expected for the trimer minus one alkyl group. There was no evidence in either mass spectrum for a dimeric mass peak.

Description of Molecular Structures

$[(CH_3)_2AlNH_2]_3$ (1)

The structure of **1**, as is illustrated in Figure 1, consists of alternating $(CH_3)_2Al$ and NH_2 units which form a six membered $(AlN)_3$ ring in a skew-boat conformation.

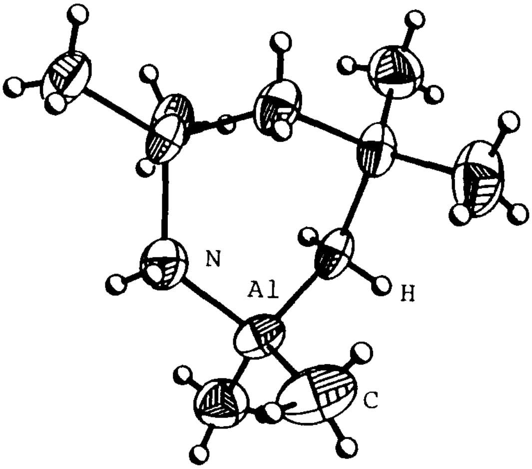

Figure 1. Molecular Structure of $[(CH_3)_2AlNH_2]_3$

The closest intramolecular 1-3 methyl-methyl $(CH_3)Al$ nonbonded carbon distance is 3.89 A and is within reasonable limits of the expected van der Waal's radii for two methyl groups (*ca.* 4.0 A). The Al and N atoms exhibit distorted tetrahedral geometries, with the distortion from tetrahedral symmetry most apparent for N.

$[(t\text{-}C_4H_9)_2AlNH_2]_3$ (2)

The structure of 2 is illustrated in Figure 2. The most conspicuous feature of 2 is the planar nature of the six-membered $(AlN)_3$ ring which has D_{3h} symmetry. All of the Al and N atoms in this structure are coplanar and exhibit distorted tetrahedral geometries. The distortion about N is particularily severe with an Al-N-Al bond angle of 134.3^0. Nonbonded 1-3 diaxial *t*-butyl-methyl carbon distances are greater than 4.0 A in this structure while the shortest 1-2 methyl carbon-to-hydrogen on nitrogen distance is 2.90 A (van der Waal's distance = 3.2 A).

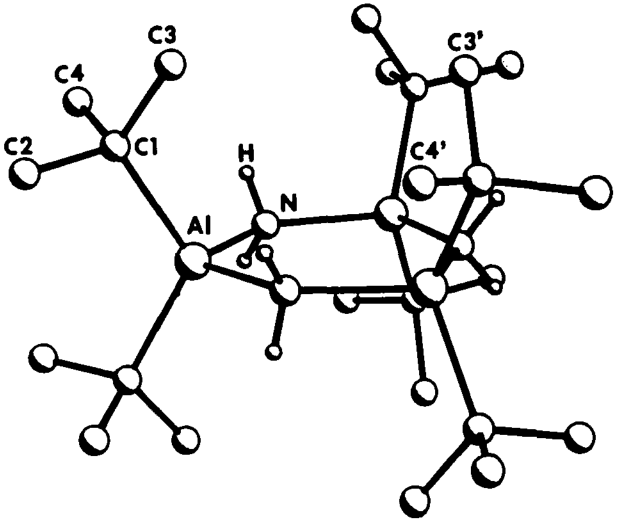

Figure 2. Molecular Structure of $[(t\text{-}C_4H_9)_2AlNH_2]_3$

DISCUSSION

The trimeric association observed for these two dialkylaluminum amides extends the number of structurally characterized examples of $(AlN)_3$ ring structures from four to six, allowing a more detailed assessment of the role of Al and N substituents in determining ring size in this class of compounds. Most of the previously studied examples of dialkylaluminum amides have been shown to have dimeric formulae with planar $(AlN)_2$ rings[7]. In fact, with one exception to be discussed subsequently, these latter compounds are all derivatives of organic primary or secondary amines with either one large substituent or two organic groups on N. With alkyl groups also on aluminum, the 1-2 Al-N substituent interactions would clearly be greater in the case of the alternative 6-membered ring structure, where the bond angles and geometrical arrangement of substituents in any ring conformation would place these substituents in closer proximity.

As has been discussed previously by Coates[14] and others[15], the choice of ring size among the dialkylaluminum amides is determined by both enthalpic and entropic factors with entropy favoring the formation of the dimer (larger number of molecules per empirical formula) and both ring strain (favoring the trimer) and substituent interactions contributing to the enthalpy differences. In the case where both N substituents are organic groups (*i.e.*, organic amines), steric interactions between the 1-2 Al-N substituents generally prevail over ring strain to yield dimeric units. Among the few exceptions are the derivatives of organic cyclic amines where a structure solution of the ethylenimine derivative, $(CH_3)_2Al\overline{NCH_2C}H_2$ has revealed a trimeric unit with a skew-boat conformation for the 6-membered $(AlN)_3$ ring[3] and ^{1}H NMR studies have suggested that the corresponding $(CH_3)_2Al\overline{NCH_2CH_2C}H_2$ compound exists in solution as an equilibrium mixture of the dimer and trimer.[16] Similarly, replacement of the aluminum alkyl substituents by hydrogen (*i.e.*, in $H_2AlN(CH_3)_3$) allows formation of a trimer with two organic groups on N.[3] When one of the two nitrogen subsituents is hydrogen both trimeric ($[(CH_3)_2AlNHCH_3]_3$[2]) and dimeric ($[(CH_3)_2AlNHSi(CH_3)_3]_3$[17]) species have been identified depending, apparently, on the steric bulk of the N and Al substituent.

The observation of a trimeric structure for the $(CH_3)_2AlNH_2$

compound is therefore quite understandable in the context of prior observations on $(AlN)_n$ ring compounds. The original report of a dimeric structure for this compound in liquid ammonia solution by Wiberg[1] may be in error or due to a reaction of the amide with ammonia to form lower molecular weight linear oligomers.

On the other hand, the 6-membered ring structure of the $(t\text{-}C_4H_9)_2AlNH_2$ compound stands in distinct contrast to the results of earlier work. In particular, a structural study of the closely related $[(CH_3)_3Si]_2AlNH_2$ compound has revealed a dimeric structure with a planar $(AlN)_2$ ring.[5] The larger size of the trimethylsilyl groups may render the 1-3 or 1-2 substituent interactions untenable in the hypothetical 6-membered ring structure of this compound; alternatively, the mutual interaction of these two large groups on the aluminum atom may force a larger R-Al-R bond angle, thereby reducing the N-Al-N angle to a value more consistent with that found in the 4-membered $(AlN)_2$ ring. The observation of a 123° angle for the Si-Al-Si bond in this dimer as compared to the 118.2° value found in the case of the $[(t\text{-}C_4H_9)_2AlNH_2]_3$ compound is at least consistent with this supposition. Alternatively, it is quite possible that the differences in these two structures arise from changes in the electronic structure of the Al atoms resulting from the differing electronegativity of the respective substituents. In accordance with Bent's rule,[18] the greater electronegativity of C relative to Si may lead to the use of hybrid orbitals with a larger amount of s-character in the bonding of the Al atoms in $[(t\text{-}C_4H_9)_2AlNH_2]_3$ to N, thus favoring the larger N-Al-N angle of the 6-membered ring structure over that required by a 4-membered $(AlN)_2$ ring.

The extraordinarily large Al-N-Al bridge-bond angles found for the $[(t\text{-}C_4H_9)_2AlNH_2]_3$ compound as well as its planar structure also make this compound most unusual among organoaluminum amides. The planar structure is unprecedented among this class of compounds and highly unusual among any main group heterocycles involving four-coordinate ring atoms. The only close relative among Group 13-15 compounds is the compound, $[(CH_3)_2InAs(CH_3)_2]_3$, which was determined by x-ray crystallography to have two different $(InAs)_3$ units in the same structure. One has a nearly planar $(InAs)_3$ ring while the other has a puckered ring conformation.[19]

The conformation of the $[(t\text{-}C_4H_9)_2AlNH_2]_3$ compound might be appropriately viewed as the extreme extension of a distortion from a chair configuration brought about by 1-3 Al-Al substituent interactions and facilitated by an unusually flexible Al-N-Al bridge. In this case the expansion in the Al-N-Al bond angle to 134.3° allows achievement of a planar configuration with only a slight adjustment in the endocyclic N-Al-N bond angle relative to that in the $[(CH_3)_2AlNH_2]_3$ compound (Table I). The unusual flexibility in the Al-N-Al bond angle relative to all of the other endo- and exocyclic bond angles in the aluminum amide compounds summarized in Table I is obvious. This angle ranges from 115° in the $[H_2AlN(CH_3)_2]_3$ structure to 125.3° in the case of $[(CH_3)_2AlNH_2]_3$ and finally to the 134.3° of $[(t\text{-}C_4H_9)_2AlNH_2]_3$.

TABLE I Comparison of $(AlN)_n$ Ring Structures

Compound	Form (Ref.)	Average Distances and Angles Al-N	C-Al-C	N-Al-N	Al-N-Al
$[H_2AlN(CH_3)_2]_3$	tr, c.(4)	1.93	---	108	115
$[(CH_3)_2AlNCH_2CH_2]_3$	tr, s.b.(3)	1.91	114.6	100.8	120.4
$t\text{-}[(CH_3)_2AlNHCH_3]_3$	tr, s.b.(2)	1.90	117.7	101.7	119.9
$c\text{-}[(CH_3)_2AlNHCH_3]_3$	tr, c.(2)	1.94	117.6	101.7	125.3
$[(CH_3)_2AlNH_2]_3$	tr, s.b.(12)	1.935	117.9	101.7	125.3
$[(t\text{-}C_4H_9)_2AlNH_2]_3$	tr, p.(12)	1.951	118.0	106.0	134.3
$[\{(CH_3)_3Si\}_2AlNH_2]_2$	di, p.(5)	1.954	123.6(Si)	86.9	93.1

tr = trimer, di = dimer; c. = chair, s.b. = skew boat, p. = planar

It is likely that the small spatial requirements of the two hydrogen substituents along with the high degree of ionic character in the Al-N bonds contribute to this unusual flexibility. The appreaciable electronegativity difference between Al and N implies a high degree of Al-N bond ionicity; this should lead to relaxation in the constraint of sp^3 hybridization and greater flexibility in this angle. In this respect these compounds are perhaps more appropriately viewed as relatives of halide or OR bridged Al compounds rather than as analogs of carbon-based ring compounds. Indeed, Al-X-Al bond angles of this magnitude have been observed in prior studies of halide[20] and oxygen-bridged[21,22] $(AlX)_n$ rings, where the bridging species has either no or only one terminal substituent. As is suggested by the persistence of these trimer units in the gas phase as well as the preliminary results of DSC measurements[13], the bonding in the 6-membered ring structure of the R_2AlNH_2 ($R = CH_3$, $t\text{-}C_4H_9$) compounds is sufficiently effective even at bridge angles of up to 134° to favor this structure strongly over the alternative dimeric one.

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