754 *Inorg. Chem.* **1997,** *36,* 754−755

# Theoretical Study of the Dimerization of Multiply-Bonded Aluminum−Nitrogen Compounds

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*Received October 15, 1996*

For a long time, the only known group III−group V analogue of benzene was borazine, $B_3N_3H_6$; however, recently, $Al_3N_3R_6$ compounds were synthesized.[1] The rings are nearly planar and have nearly equal bond lengths, and the bond distances are indicative of multiple bonds. Alumazene has been studied theoretically by other groups.[2,3]

Attempts to synthesize compounds of the formula $R_2MNR'_2$ (M = Al, Ga, or In) usually result in cyclic oligomers of formula $[R_2MNR'_2]_n$ where $n = 2-4$. There is a rich variety of ring and cage structures found in aluminum−nitrogen chemistry, all of which show a strong tendency for the Al and N atoms to be *tetracoordinated*.[4] Compounds with Al−N double bonds were only recently reported in the literature because of their strong tendency to dimerize.[5,6] Molecules with the formula R−AlN−R′ have yet to be observed. Compounds with Al−N double and triple bonds are difficult to synthesize and isolate; bulky or electropositive substituents may be used to protect and stabilize Al−N multiple bonds in a manner similar to techniques used for Si═Si bonds.[7]

The Al−N analogs of acetylene and ethylene, $H_2AlNH_2$ and HAlNH, were previously investigated by *ab initio* quantum chemical techniques.[8] Theory predicts that the parent compounds are minima on the potential energy surface, which is a nontrivial result in light of the fact that $H_2SiSiH_2$ and HSiSiH are nonplanar and nonlinear, respectively.[9] This communication reports the results of an *ab initio* study of the dimerization of $H_2AlNH_2$ and HAlNH, which produces Al−N analogues of cyclobutane and cyclobutadiene, respectively. Further, the dimerization of $[HAlNH]_2$ to form the cubane analogue $[HAlNH]_4$ is studied at lower levels of theory.

The basis set used for the initial survey of the potential energy hypersurface was the 3-21G basis. For an improved basis of double-ζ plus polarization quality, the 6-31G* and 6-31G** basis sets were employed. A triple-ζ basis with two sets of polarization functions (TZ2P) was used for SCF and MP2 calculations.[10] Electron correlation was included through the use of second-order Møller−Plesset perturbation theory (MP2), the singly and doubly substituted coupled cluster (CCSD) wave functions, and the CCSD(T) wave function. The 1s, 2s, and 2p core orbitals of Al and the 1s orbitals of N were frozen in the CCSD and CCSD(T) wave functions. Geometry optimizations were performed at all of the levels of theory indicated in Figures 1 and 2. Harmonic vibrational frequencies were computed for the SCF and MP2 stationary points.

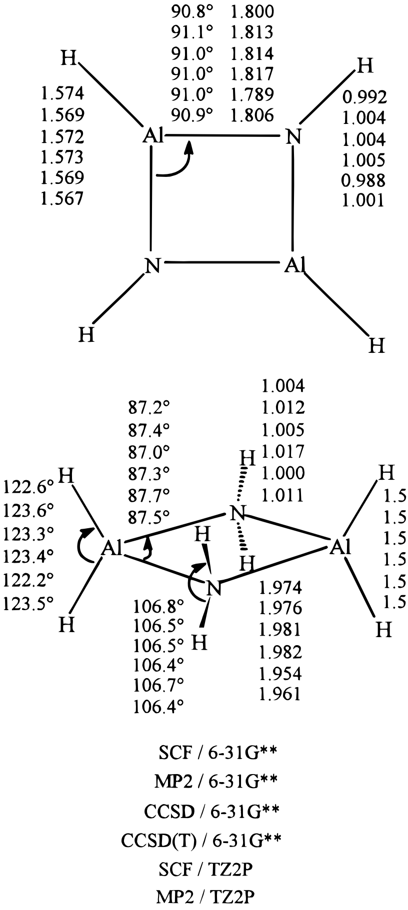

**Figure 1.** Optimized structures for the dimerization products of planar $H_2AlNH_2$ and linear HAlNH. Bond distances are in angstroms.

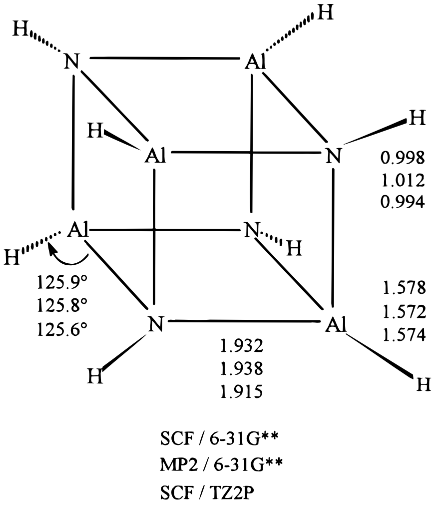

**Figure 2.** Theoretical geometries for $[HAlNH]_4$, a cubane analogue which is the expected dimerization product of $[HAlNH]_2$.

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S0020-1669(96)01248-7 CCC: $14.00

Our optimized geometry parameters for ethylene and acetylene Al−N analogs are similar to those reported by Davy.[8] $H_2AlNH_2$ is planar at all levels of theory, and HAlNH is linear at all levels of theory except for MP2, which predicts a *trans*-bending distortion to the bent HAlNH structure. The Al═N bond distance of 1.78 Å is only a little shorter than the 1.79 Å distance predicted in alumazine, $Al_3N_3H_6$ .[2] The $\pi$ bond energy in $H_2AlNH_2$ is 10−13 kcal/mol,[8] and the delocalization energy in alumazine is 2 kcal/mol.[2] The Al−N bond in HAlNH averages 1.63 Å, which could be interpreted as a triple-bond distance.

The optimized structures (at various levels of theory) of the dimerization product of $H_2AlNH_2$ are shown in Figure 1. The Al−N distances are those expected for single bonds in a slightly strained structure. The $Al_2N_2$ ring is planar (almost square), unlike the puckered conformation one might expect by analogy with cyclobutane. An experimental X-ray crystal structure for the octamethyl derivative has Al−N distances of 1.955 and 1.972 Å,[11] in close agreement with our best value (MP2/TZ2P) of 1.961 Å for $[H_2AlNH_2]_2$. The X-ray structure also has a planar ring. The Al−N distances are not the same due to lower symmetry and crystal packing forces for the octamethyl compound. The interior Al−N−Al and N−Al−N angles match within 1° for the experimental octamethyl and theoretical $[H_2AlNH_2]_2$ geometries.

The *trans*-bent HAlNH structure is greatly different from the linear one at the N atom. The N atom has a lone pair of electrons in the bent structure that would normally form the third $\pi$ bond. The Al−N distance increases by only 0.02 Å when the lone pair forms. This can be explained by the fact that the second $\pi$ bond (if it can be said to exist at all) is essentially the dative bond formed by a lone pair on N donating electron density into an empty p orbital on Al.

Figure 1 also shows the optimized Al−N cyclobutadiene analog which results from dimerization of HAlNH. The Al−N ring is also nearly square with equal Al−N distances as in the $[H_2AlNH_2]_2$ ring. The predicted Al−N distance of 1.81 Å is slightly longer than the Al−N bond length computed for alumazene, indicating that multiple-bond character is still present.

The theoretical geometry of the cubane analogue that results from the dimerization of $[HAlNH]_2$ is displayed in Figure 2. It has $T_d$ symmetry with equivalent Al−N bonds. The Al−N skeleton is nearly cubic, with Al−Al distances of 2.754 Å and N−N distances of 2.713 Å. The Al−N distances are single-bond distances, so further reaction is much less likely. Note that this structure has only tetracoordinated Al and N atoms. The Al−N distances compare well to the X-ray structures for $[MeAlNiPr]_4$ (1.92 Å)[12] and $[HAlNiPr]_4$ (1.91 Å).[13]

According to the concept of normal and dative bonds,[14] the amount of each kind of bonding is crudely expressed in the Al−N bond length as a weighted average of a dative bond (2.08 Å) and a normal bond (1.81 Å). The four-membered ring in the $[H_2AlNH_2]_2$ molecule comes from two intermolecular Al−N dative interactions of $H_2AlNH_2$ plus the original $\sigma$ (normal) bonds. Since the Al−N bonds in the four-membered ring are equivalent, each is half-normal and half-dative, and the expected Al−N distance is 1.945 Å, in good agreement with the X-ray structure and with theory. Each tricoordinate Al in $[HAlNH]_2$ has two normal Al−N bonds, so the resulting number of normal bonds in the cubane analogue is 8, with four dative bonds formed in the dimerization process. The expected distance is 1.90 Å, also in good agreement with X-ray structures and theory. The Al−N distances in $[HAlNH]_2$ are the same length as the normal Al−N bond, indicating very little change due to $\pi$ interactions in this molecule.

**Dimerization Energies.** The energy released upon forming $[HAlNH]_2$ from HAlNH is predicted to be 140 kcal/mol. This is an energy difference of 70 kcal/mol per Al−N bond formed. Since this is close to Haaland's estimated value of 84 kcal/mol for a normal Al−N bond,[14] it is misleading to think of HAlNH dimerizing through a double-dative reaction. The energy released upon dimerization of the doubly-bonded $[HAlNH]_2$ is 66 kcal/mol. The energy difference between each of the two $\pi$ bonds that disappear and the $\sigma$ bonds that are formed is only 33 kcal/mol, indicating a much stronger $\pi$ bond in $[HAlNH]_2$. This compares favorably to the thermodynamics of Al−N dative bonds in adducts, such as 26 kcal/mol in ammonia−alane.[15] The dimerization energy to form the cube is 125 kcal/mol; dividing by 4 gives a dative bond formation energy of 31 kcal/mol. This is very similar to the results for $[H_2AlNH_2]_2$ formation, so there appears to be little strain in this system, since the dimerization energy per double bond is the same for forming $[H_2AlNH_2]_2$ and $[HAlNH]_4$.

**Barriers to Dimerization.** Searches for transition states between the dimers and separated monomers (HAlNH and $H_2AlNH_2$) were futile. The dimerization evidently occurs without any energy barrier at all levels of theory up to CCSD/6-31G**. The Al−N multiple-bond dimerization is very facile, which is consistent with a double-dative-bond interaction between the approaching monomers. The $\pi$ bond is predominantly located on the N atom, just as a lone pair would be. The "lone pair" on the N can then datively bond with the "empty" p orbital on the other monomer's Al atom. Given the similarity between dimerization of $H_2AlNH_2$ and $[HAlNH]_2$, we speculate that the latter process occurs without an activation barrier also.

There are two standard approaches to preventing dimerization of multiply bonded compounds. One is to sterically hinder the two monomers from approaching each other close enough to form a bond. The other method is to strengthen the $\pi$ bond by having the N substituents push the electrons in the "lone pair" and having the Al substituents pull $\pi$-electron density from the N atom. Care must be taken that the electronegative substituent on the Al atom does not back-donate $\pi$ density.

As a final note, the SCF/TZ2P Al−N stretching frequencies cluster around 550 $cm^{-1}$, in good agreement with the observed IR band at 508 $cm^{-1}$.[16]

In conclusion, the multiply bonded Al−N hydrides spontaneously dimerize with zero energy of activation required. Substituents or isolation are required to observe structures which can be formally written as having Al═N bonds. The second $\pi$ bond in the Al−N triple bond is nonexistent, and R−AlN−R′ compounds are expected to be highly reactive. The $\pi$ bond in Al═N is much weaker than a $\sigma$ bond. The dimerization energies of compounds with formal Al═N bonds have dative-bond energies very similar to those in Al−N adducts.

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