Geometries and Relative Stabilities of AlN Four-Membered-Ring Compound Isomers: *Ab initio* Study

Sung Soo Park,[‡] Kee Hag Lee,[*] Youngsun Suh, Changhoon Lee, and Hans P. Lüthi[†]

Department of Chemistry, Wonkwang University, Iksan 570-749, Korea
[†]Laboratory of Physical Chemistry, ETH Zurich, 809 Zurich, Switzerland
Received October 10, 2001

Using ab initio method, we have studied the structural stabilities, the electronic structures and properties between the two isomers with C_{2h} and C_{2v} symmetry of AlN four-membered-ring single precursors $[Me_2AlNHR]_2$ (R = Me, ^{i}Pr, and ^{t}Bu). In the viewpoint of bond lengths in optimized structures, the N-C bonds are considerably affected by the change of the R groups bonded to nitrogen, but the bonding characters of the Al-N and Al-C bonds are little affected. Also the structural stabilities between the two isomers with C_{2h} and C_{2v} symmetry by using Hartree-Fock (HF) and the second order Moeller-Pleset (MP2) calculations agree well with the experimental results for the relative stability of bis(dimethyl-μ-isopropylamido-aluminum) (BDPA) and bis(dimethyl-μ-*t*-butylamido-aluminum) (BDBA), while the semiempirical AM1 and PM3 calculations for BDPA were reverse. Thus, our results may aid in designing an optimum precursor for a given process by explaining the experimental results through the elimination of the R groups bonded to nitrogen.

Keywords : AlN four-membered-ring, *Ab initio* calculation, Organometallic precursor.

Introduction

Aluminum nitride (AlN) has received widespread attention in recent years[1-4] because of its attractive thermal, electronic, and mechanical properties. A general route to synthesize nonoxide ceramic materials is the pyrolytic decomposition of a suitable organometallic precursor.[5,6] The single precursor organometallic chemical vapor deposition (OMCVD) has been shown to have a number of important advantages over the conventional CVD process.[6] Thus, amido- and imido-compounds of aluminium have received considerable attention.[7-11] The single precursor OMCVD method using compounds with the Al-N bonds was recently employed.[12-15] The advantage here is that the precursors have both Al and N atoms, and it is relatively easy to control reaction parameters.

The rationalization most commonly offered for the single-source precursors approach has been that the presence of covalent bonds between the required elements in the desired atomic ratio offers an efficient manner to transport multiple elements, with different volatilities, to the film growth surface. In addition to containing the desired elements, the single precursors should preferentially contain ligands that are readily removed during film growth and should be sufficiently volatile to allow vapor transport at appropriate temperatures.[16] Recently, quantum chemical studies of group 13-15 donor-acceptor adducts in light of their potential usage as single precursors for stoichiometry-controlled CVD were reported.[17,18]

For the preparation of the AlN thin films using a single precursor, it is important to understand the decomposition pathway of the Al-N, Al-C, and N-C bonds. Thus, AlN reaction pathway and Al-N bonding characters have been studied.[14,15] In the study of the deposition of AlN using $[Me_2AlNR_2]_2$ compounds,[15] with the change of the alkyl group (^{i}Pr, ^{t}Bu) bonded to N, optimum deposition temperatures were found to differ as follows: the deposition temperatures of bis(dimethyl-μ-isopropylamido-aluminum) (BDPA) and bis(dimethyl-μ-*t*-butylamido-aluminum) (BDBA) are about 770 K and 720 K, respectively. Also the amount of nitrogen in the film was found to be somewhat larger with BDBA than with BDPA indicating more favorable dissociation of the N-C bonds in the case of BDBA. In our previous semiempirical HF (MNDO, AM1, and PM3) studies of the AlN precursors, we were subject to limitations in our computational resources. The relative stability of BDPA isomers in these semiempirical calculations did not agree with the experimental x-ray and NMR results. In this work, we revisit the effect of terminal alkyl groups of the Al-N bond strength using *ab initio* method.

We have studied the electronic properties and atomic structures of selected precursors by using *ab initio* HF SCF theory (using 3-21G, 6-31G, and 6-31G* basis sets) in order to investigate the bonding characters of the Al-N, Al-C, and N-C bonds. Also we used the MP2 method to account for the electron correlation effect. Here selected precursors are *cis* and *trans* bis(dimethyl-μ-methylamido-aluminium) (BDMA), BDPA, and BDBA, which have different alkyl groups bonded to N.

Calculations

Ab initio HF methods were performed to the geometry optimization of *cis*- and *trans*-isomers in BDMA, BDPA,

---

[*] Corresponding author: E-mail: khlee@wonkwang.ac.kr

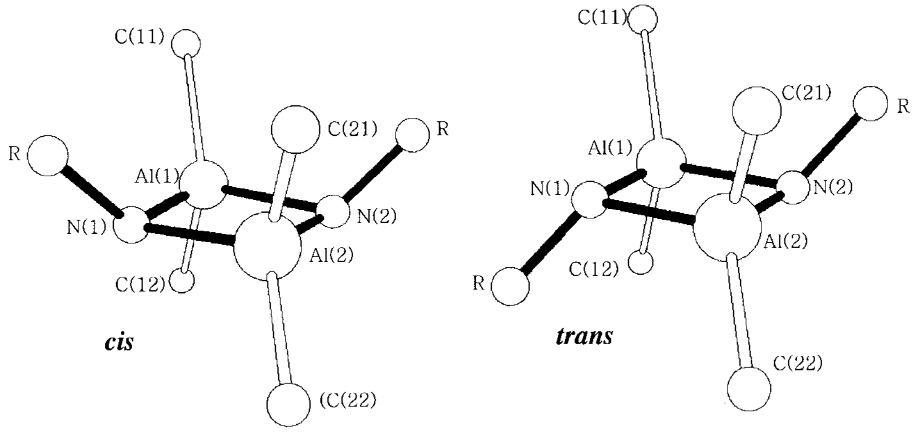
[‡] Present address: CAMD Research Center, Soong Sil Univ., Seoul 156-743, Korea

and BDBA to understand the effect of the alkyl substituents and the relative stability of the precursor isomers. Four basis sets STO-3G, 3-21G, 6-31G, and 6-31G* basis sets are used in this sequence for geometry optimizations in order to minimize computation time as well as to get energy values at different theory levels. The MP2 energetics with 6-31G* basis set were calculated at the geometries optimized at the level of HF/6-31G*. The *ab initio* calculations were carried out with the Gaussian98 suite[19] of programs on a Compaq XP-1000 workstation. No symmetry constraints were specified for the geometry optimization.

Results and Discussion

The structure of the precursors used in the calculations is schematically shown in Figure 1. The difference of the precursors is the R group (Me, ^{i}Pr, and ^{t}Bu) bonded to N atom as shown in the Figure 1.

The HF calculations with various basis sets (STO-3G, 3-21G, 6-31G, and 6-31G*) are applied to fully optimize the geometries for *cis*- and *trans*-isomers of BDBA, BDPA, and BDMA. In Table 1, we show the geometry parameters obtained from the HF calculations of BDBA, BDPA, and



R-groups are Methyl, iso-Propyl, and t-Butyl.

Figure 1. The structures of precursors used in this calculation. The BDMA isomers are the *cis* and *trans* $[AlMe_2NHMe]_2$ (a), the BDPA isomers are the *cis* and *trans* $[AlMe_2NH^iPr]_2$ (b), and the BDBA isomers are the *cis* and *trans* $[AlMe_2NH^tBu]_2$ (c). R-groups are Methyl, *iso*-Propyl, and *t*-Butyl.

Table 1. Bond lengths for *cis* and *trans* isomers of BDBA, BDPA, and BDMA from the HF calculations[a]

BDBA	STO-3G	3-21G	6-31G	6-31G*
Al(1)-Al(2)	2.787(2.792)	2.863(2.864)	2.901(2.901)	2.898(2.900)
Al(1)-N(1)	1.907(1.906)	1.975(1.975)	2.002(2.002)	1.994(1.994)
Al(1)-C(11)	1.905(1.907)	2.003(2.007)	1.998(2.002)	1.988(1.991)
Al(1)-C(12)	1.909(1.907)	2.010(2.007)	2.005(2.002)	1.995(1.991)
N(1)-C(10)	1.510(1.510)	1.513(1.513)	1.503(1.503)	1.492(1.492)

BDPA	STO-3G	3-21G	6-31G	6-31G*	Experiment[8]
Al(1)-Al(2)	2.752 (2.762)	2.819 (2.827)	2.856 (2.863)	2.852 (2.859)	2.800 (2.789)
Al(1)-N(1)	1.901 (1.902)	1.968 (1.969)	1.994 (1.995)	1.987 (1.988)	1.946 (1.959)
Al(1)-C(11)	1.905 (1.902)	2.004 (2.005)	1.999 (2.000)	1.989 (1.990)	1.956 (1.964)
Al(1)-C(12)	2.006 (2.005)	2.000 (2.000)	1.990 (1.990)	1.957 (1.964)	
N(1)-C(10)	1.498 (1.499)	1.506 (1.506)	1.492 (1.492)	1.480 (1.481)	1.502 (1.488)

BDMA	STO-3G	3-21G	6-31G	6-31G*
Al(1)-Al(2)	2.762(2.762)	2.828(2.828)	2.869(2.869)	2.860(2.860)
Al(1)-N(1)	1.900(1.902)	1.965(1.965)	1.992(1.992)	1.984(1.984)
Al(1)-C(11)	1.903(1.904)	2.002(2.003)	1.996(1.997)	1.986(1.987)
Al(1)-C(12)	1.905(1.904)	2.005(2.003)	1.999(1.997)	1.989(1.987)
N(1)-C(10)	1.491(1.491)	1.502(1.502)	1.483(1.483)	1.472(1.472)

[a] The values of parentheses are for *trans* isomers.

BDMA. As shown Table 1, the differences in the bond lengths between *cis*- and *trans*-isomers are quite small. The Al-N and Al-C bond lengths are negligibly changed when the R group is changed from Me through ^{i}Pr to ^{t}Bu. But, the N-C bond lengths in HF/STO-3G, HF/3-21G, HF/6-31G, and 6-31G* calculations increased by 0.012, 0.007, 0.011, and 0.012 Å, respectively, when the R group is changed from ^{i}Pr to ^{t}Bu. Also the N-C bond lengths in HF/STO-3G, HF/3-21G, HF/6-31G, and 6-31G* calculations increased by 0.003, 0.004, 0.009, and 0.008 Å, respectively, when the R group is changed from Me to ^{i}Pr. The increase of the N-C bond lengths can be interpreted as the weakening of the N-C bonds. It thus shows the same tendency to the experimental deposition temperature. Also, it suggests the steric effect of R groups for the deposition of N-C bonds. Table 2 shows the difference in total energy between *trans*- and *cis*-isomer, which represents the relative stability of the BDBA, BDPA, and BDMA isomers. The relative stability between *trans*-isomer and *cis*-isomer of BDBA in the HF and MP2 calculations is the same to the NMR results[20] for which the ratio of *trans*-isomer to *cis*-isomer is 2:1. In the NMR experiment, the net enthalpy change from *trans*-isomer to *cis*-isomer of BDBA in the isomerization process is 0.53 ± 0.02 kcal/mol. This experimental value properly agrees with the total energy difference of 0.56 (at the level of HF/3-21G), 0.26 (HF/6-31G*), and 0.33 kcal/mol (MP2/6-31G*//HF/6-31G*) between two isomers. Also, the HF calculation shows that *cis*-isomer of BDPA is more stable than *trans*-isomer. The relative stability of *cis* to *trans* isomers of BDPA in HF and MP2 calculations agrees with the NMR and X-ray study[8] in which the ratio of *cis* to *trans* isomer is close to 2:1, while the former semiempirical PM3 and AM1 calculations[18] did not agree with the NMR and X-ray experimental studies. In Table 3, the atomic charge represents properties of each atoms which constitute molecule. The atomic charges on Al of BDPA and BDBA show the same values at each of the HF/3-21G, HF/6-31G, and HF/6-31G* levels, but the values of BDMA shows a little smaller values than the others. The negative charge N in our calculations with various basis sets is almost constant. The positive charge on C atom bonded to N atom in our calculations is shown to increase in the following order: BDMA < BDPA < BDBA. Thus, the bond polarization between N and C in our calculations shows the tendency of increasing in the following order BDMA < BDPA < BDBA. The sum of atomic charges for $(AlN)_2$ fragment of BDMA shows almost the same value to them of BDPA and BDBA. Thus, the electron donor effect, which increases in the order Me < ^{i}Pr < ^{t}Bu in experimental organic chemistry might be not so effective, while the steric effect in these single precursors would be crucial. Therefore, our results support the previous suggestion from the semiempirical AM1 and PM3 calculations that C-N fission may be an important step in forming AlN films from these single precursors, since tendency of the experimental deposition temperature for the film formation agrees best with the variation of bond lengths of the C-N bonds in the bulky order of alkyl substituents. Also, they suggest that the HF calculations may be properly to predict the relative stability of AlN four-membered-ring compound isomers.

Table 2. Energy difference (ΔE) between *cis* isomer and *trans* isomer for BDBA, BDPA, and BDMA in the HF and MP2 calculations

	BDMA	BDPA	BDBA
PM3	-0.42	0.45	3.65
HF/3-21G	-0.02	-0.38	0.56
HF/6-31G	0.00	-0.40	0.30
HF/6-31G*	0.03	-0.40	0.26
MP2/6-31G*//HF/6-31G*	0.10	-0.42	0.33

ΔE = Energy (*cis* isomer) – Energy (*trans* isomer), ΔE is in kcal/mol.

Table 3. Atomic charge for BDBA, BDPA, and BDMA obtained from HF-SCF calculations[a]

BDBA	STO-3G	3-21G	6-31G	6-31G*
Al(1)	1.10(1.10)	1.57(1.57)	1.59(1.61)	1.17
N(1)	-0.59(-0.59)	-1.10(-1.09)	-1.28(-1.29)	-1.08
C(11)	-0.45(-0.45)	-1.11(-1.10)	-0.96(-0.95)	-0.85
C(12)	-0.45(-0.45)	-1.09(-1.10)	-0.93(-0.95)	-0.83
C(10)	0.13(0.13)	0.02(0.02)	0.16(0.16)	0.19

BDPA	STO-3G	3-21G	6-31G	6-31G*
Al(1)	1.11(1.11)	1.57(1.57)	1.59(1.58)	1.17(1.17)
N(1)	-0.59(-0.59)	-1.10(-1.10)	-1.28(-1.29)	-1.08(-1.08)
C(11)	-0.45(-0.45)	-1.12(-1.10)	-0.96(-0.94)	-0.85(-0.84)
C(12)	-0.45(-0.45)	-1.09(-1.10)	-0.93(-0.94)	-0.83(-0.84)
C(10)	0.06(0.06)	-0.08(-0.07)	0.06(0.07)	0.06(0.07)

BDMA	STO-3G	3-21G	6-31G	6-31G*
Al(1)	1.11(1.11)	1.55(1.55)	1.56(1.56)	1.15
N(1)	-0.59(-0.59)	-1.11(-1.11)	-1.28(-1.28)	-1.06
C(11)	-0.45(-0.45)	-1.10(-1.09)	-0.94(-0.94)	-0.83
C(12)	-0.448(-0.45)	-1.09(-1.09)	-0.93(-0.94)	-0.83
C(10)	-0.10(-0.10)	-0.38(-0.38)	-0.20(-0.20)	-0.27

[a] The values of parentheses are for *trans*-isomers.

Acknowledgment. This paper was supported by Wonkwang University in 2001. K. H. L. thanks the LG Yonam Foundation for a fellowship. This paper (KHL) is dedicated to Professor Kyung-Hoon Jung at KAIST on the occasion of his 65th birthday.

References

1. Gabe, E.; Le Page, Y. *Phys. Rev.* **1981**, *B24*, 5634.
2. Kobayashi, A.; Sankey, O. F.; Volz, S. M.; Dow, J. D. *Phys. Rev.* **1983**, *B28*, 935.
3. Olson, C. G.; Sexton, J. H.; Lynch, D. W.; Bevolo, A. J.; Shanks, H. R.; Harmon, B. N.; Ching, W. Y.; Wieliczka, D. M. *Solid State Commun*. **1985**, *56*, 35.
4. Awad, M. K.; Anderson, A. B. *Surface Sci*. **1989**, *218*, 543.
5. (a) Mayer, T. M.; Rogers, Jr., J. W.; Michalske, T. A. *Chem. Mater.* **1991**, *3*, 641. (b) Bartram, M. E.; Michalcke, T. A.; Rogers, Jr., J. W.; Mayer, T. M. *Chem. Mater.* **1991**, *3*, 953. (c) Gaskill, D. K.; Bottka, N.; Lin, M. C. *J. Cryst. Growth* **1986**, *77*, 418.

6. (a) Zanella, P.; Rossetto, G.; Brianese, N.; Ossola, F.; Porchia, M.; Williams, J. O. *Chem. Mater.* **1991**, *3*, 225. (b) Ho, K. L.; Jensen, K. F. *J. Cryst. Growth* **1991**, *107*, 376.
7. (a) Bowen, R. E.; Gosling, K. *J. Chem. Soc. Dalton Trans.* **1974**, 964. (b) Amirkhalili, S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc. Dalton Trans.* **1979**, 1206.
8. Amirkhalili, S.; Hitchcock, P. B.; Jenkins, A. D.; Nyathi, J. Z.; Smith, J. D. *J. Chem. Soc. Dalton Trans.* **1981**, 377.
9. Al-Wassil, A.-A. I.; Hitchcock, P. B.; Sarisaban, S.; Smith, J. D.; Wilson, C. L. *J. Chem. Soc. Dalton Trans.* **1985**, 1929.
10. Haiduc, I.; Sowerby, D. B. *The Chemistry of Inorganic Homo- and Heterocycles*; Academic Press: London, 1987; Vol 1.
11. (a) Sauls, F. C.; Interrante, L. V.; Jiang, Z. *Inorg. Chem.* **1990**, *29*, 2989. (b) Interrante, L. V.; Carpemter II, L. E.; Whitmarsh, C.; Lee, W.; GarbauskasSlack, G. A. *Mat. Res. Soc. Symp. Proc.* **1986**, *73*, 359.
12. Interrante, L. V.; Lee, W.; McConnell, M.; Lewis, N.; Hall, E. *J. Electrochem. Soc.* **1989**, *136*, 472 and references therein.
13. Boyd, D. C.; Haasch, R. T.; Mantell, D. R.; Schulze, R. K.; Evans, J. F.; Gladfelter, W. T. *Chem. Mater.* **1989**, *1*, 119.
14. (a) Park, J. T.; Lee, J.-K.; Kim, S.; Sung, M. M.; Kim, Y. *Bull. Korean Chem. Soc.* **1993**, *14*, 163 and references therein. (b) Park, S. M.; Boo, B. H.; Kim, Y.; Park, J. T.; Koyano, I. *Jpn. J. Appl. Phys.* **1995**, *34*, L933.
15. Sung, M. M.; Jung, H. D.; Lee, J.-K.; Kim, S.; Park, J. T.; Kim, Y. *Bull. Korean Chem. Soc.* **1994**, *15*, 79.
16. Stoll, S. L.; Barron, A. R. *Chem. Mater.* **1998**, *10*, 650.
17. (a) Ni, H.; York, D. M.; Bartolotti, L.; Wells, R. L.; Yang, W. *J. Am. Chem. Soc.* **1996**, *118*, 5732. (b) Okamoto, Y. J. *J. Crystal Growth* **1998**, *191*, 405. (c) Timoshkin, A. Y.; Suvorov, A. V.; Bettinger, H. F.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1999**, *121*, 5687. (d) Reinhardt, S.; Gastreich, M.; Marian, C. M. *Phys. Chem. Chem. Phys.* **2000**, *2*, 955. (e) Timoshkin, A. Y.; Bettinger, H. F.; Schaefer III, H. F. *J. Crystal Growth* **2001**, *222*, 170.
18. Lee, K. H.; Park, S. S.; Lee, H. M.; Park, S. J.; Park, H. S.; Lee, Y. S.; Kim, Y.; Kim, S.; Jo, C. G.; Eun, H. M. *Bull. Korean Chem. Soc.* **1998**, *19*, 1314.
19. 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 98*, Revision A.7; Gaussian, Inc.: Pittsburgh PA, 1998.
20. Park, J. T.; Oh, W. T.; Kim, Y. *Bull. Korean Chem. Soc.* **1996**, *17*, 1147.