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New Insights into an Old Reaction. High-Resolution X-ray Powder Diffraction of Wiberg's Aminoalane Intermediate

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In accordance with the procedure described by E. Wiberg, $Me_3Al–NH_3$ was heated as a bulk material in inert atmosphere to give a colorless liquid which slowly loses methane. Close to the end of this elimination reaction, the melt crystallized to give a microcrystalline powder of $(Me_2AlNH_2)_x$. The structure of this intermediate has been solved by the method of high-resolution X-ray powder diffraction. The compound crystallizes in the monoclinic space group $C2/c$ with the cell parameters of $a = 15.0047(6)$ Å, $b = 8.7500(2)$ Å, $c = 24.4702(8)$ Å, and $\beta = 107.290(2)°$, with eight trimers $(Me_2AlNH_2)_3$ per unit cell. These trimers crystallize in a boat conformation in contrast to the known trimers of the same composition where a twist-boat conformation had been found by single crystal determination. Different conformers of $(Me_2AlNH_2)_3$ have been investigated by theoretical methods (HF/6-31G(d), B3LYP/6-31G(d), B3LYP/6-311G(d,p), MP2(fc)/6-31G(d), and MP2(fc)/6-311G(d,p)). The twist-boat and the chair conformer correspond to minima at the potential energy surface, whereas the boat conformer corresponds to a first-order transition state (relative energies of 0.45–2.56 kJ/mol (boat) and 6.66–11.91 kJ/mol (chair)). Relaxed scans of the potential energy surface at the HF/6-31G(d) and B3LYP/6-31G(d) levels have shown that the boat conformer (C_s symmetry) connects two enantiomers of the twist-boat form (C_2 symmetry).

Introduction

The nitrides AlN, GaN, and InN as well as the alloys $Al_xGa_yIn_{1-x-y}N$ can be used for micro- and optoelectronic devices; of particular interest are blue and ultraviolet laser diodes for high-density optical storage and other applications.[1–7] Usually, thin films of group 13 nitrides are deposited on suitable substrates by metal organic chemical vapor deposition techniques (MOCVD) using R_3M ($R = Me$, Et; $M = Al$, Ga, In) and a large excess of ammonia. The model reaction for these processes was found by E. Wiberg over 50 years ago, who has shown that ammonia trimethylalane heated as a bulk material loses methane to give amino- and iminoalane intermediates and finally aluminum nitride.[8]

$$Me_3Al{-}NH_3 \xrightarrow{-CH_4} (Me_2AlNH_2)_x \xrightarrow{-CH_4} (MeAlNH)_y \xrightarrow{-CH_4} AlN \quad (1)$$

At the time Wiberg investigated the condensation reaction (eq 1), only the crystal structure of the end material AlN was known from X-ray powder diffraction.[9] Recently, we began to determine the structures of compounds involved in Wiberg's reaction sequence with the aim of getting insights into the nitride deposition. We have shown that the starting compound $Me_3Al{-}NH_3$ can be obtained as an analytical pure, crystalline powder by sublimation in a vacuum.[10] The molecular structure was determined from X-ray powder diffraction data.[11] In the crystal lattice infinite chains are

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[‡] University of Saskatchewan.

(1) Jones, A. C.; Whitehouse, C. R.; Roberts, J. S. *Chem. Vap. Deposition* **1995**, *1*, 65−74.
(2) Akasaki, I.; Amano, H. *J. Cryst. Growth* **1995**, *146*, 455−461.
(3) Neumayer, D. A.; Ekerdt, J. G. *Chem. Mater.* **1996**, *8*, 9−25.
(4) Matsuoka, T. *Adv. Mater.* **1996**, *8*, 496−479.
(5) Ponce, F. A.; Bour, D. P. *Nature* **1997**, *386*, 351−359.
(6) Nakamura, S.; Fasol, G. In *The Blue Laser Diode, GaN Based Light Emitters and Lasers*; Springer: Berlin, Heidelberg, 1997.
(7) Nakamura, S. *Science* **1998**, *281*, 951−961.
(8) Bähr, G.; In *FIAT Review of WWII German Science, 1939−1946. Inorganic Chemistry*; Klemm, W., Ed.; Dieterichsche Verlagsbuchhandlung: Wiesbaden, Germany 1948; pp 155−179.
(9) Ott, H. *Z. Phys.* **1924**, *22*, 201−214.
(10) Müller, J. *J. Am. Chem. Soc.* **1996**, *118*, 6370−6376.
(11) Müller, J.; Ruschewitz, U.; Indris, O.; Hartwig, H.; Stahl, W. *J. Am. Chem. Soc.* **1999**, *121*, 4647−4652.

10.1021/ic026146b CCC: $25.00

formed by a head-to-tail association of the polar molecules with intermolecular contacts of the van der Waals type. In addition to the solid-state structure, the structure of the molecule in the gas phase has been investigated by microwave spectroscopy in combination with ab initio calculations.[11] The geometry of Me_3Al-NH_3 in the gas phase is distinctively different from that in the solid state. In the solid state, the Al−N bond is shorter, and the C_3Al pyramid is more pronounced than those in the gas phase. These differences are mainly due to the effect of a polar environment on a polar molecule; prominent examples of the same type are H_3B-NH_3[12,13] and F_3B-NCH.[14,15]

Cryoscopic measurements of the aminoalane $(Me_2AlNH_2)_x$ dissolved in liquid ammonia hinted to a dimeric aminoalane.[8] Thermolysis of Me_3Al-NH_3 from benzene solutions followed by crystallization from heptane solutions resulted in crystals of trimers $(Me_2AlNH_2)_3$ (single-crystal X-ray analysis).[16] Furthermore, amino(dimethyl)alane exists in an equilibrium of trimers and dimers. In solutions of benzene or toluene, the trimer is the main component of the equilibrium.[17,18] Kinetic measurements of the thermolysis reaction of Me_3Al-NH_3 in benzene suggested that monomers Me_2AlNH_2 are present in solution, but they were not observed directly.[18] We have shown that the monomer is an existing species by using matrix-isolation techniques. Irradiation of matrix isolated Me_3Al-NH_3 with UV light resulted in a loss of methane to give monomeric Me_2AlNH_2.[10]

In this paper, we report on the molecular and crystal structure of the aminoalane $(Me_2AlNH_2)_x$, the first intermediate of Wiberg's reaction sequence (eq 1). Results of high-resolution X-ray powder diffraction and theoretical calculations are discussed.

Results and Discussion

X-ray Powder Diffraction. In accordance with the known procedure,[8] Me_3Al-NH_3 was heated to 65−70 °C in argon atmosphere to give a colorless liquid which slowly loses methane. Close to the end of this elimination reaction, the water clear melt crystallized to give a microcrystalline powder. Laboratory X-ray powder diffraction data indicated that this aminoalane has a different crystal structure than the known trimer $(Me_2AlNH_2)_3$, whose crystal structure was determined from single-crystal X-ray analysis,[16] although we could not determine the space group. Therefore, we performed high-resolution X-ray powder diffraction at the European Synchrotron Radiation Facility (powder pattern see Figure 1). This time, the diffraction pattern could be indexed successfully on basis of a monoclinic lattice with lattice parameters given in Table 1.[19] According to extinction rules, the only possible space groups were determined as *Cc* and *C*2/*c* from which the latter could be confirmed by Rietveld refinement. The number of formula units per unit cell directly followed from geometrical considerations, suggesting a trimer.

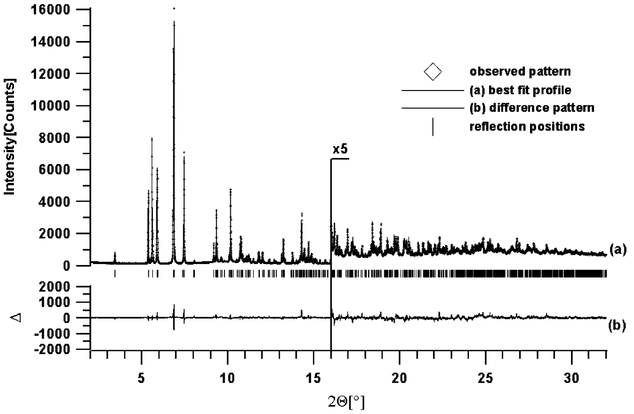

Figure 1. Scattered X-ray intensity for $(Me_2AlNH_2)_3$ at T = 295 K as a function of diffraction angle 2Θ. Shown are the observed pattern (diamonds), the best Rietveld-fit profile in C2/c (line a), the difference curve between observed and calculated profile (line b), and the reflection markers (vertical bars). The wavelength was $\lambda = 0.70011(2)$ Å. The higher angle part starting at 16° 2Θ is enlarged by a factor of 5.

Table 1. Lattice Parameters and Selected Details of the Refinement of $(Me_2AlNH_2)_3$. R-P, R-wp, R-F, and R-F^2 Refer to the Rietveld Criteria of Fit for Profile, Weighted Profile, and Structure Factor, Respectively[a]

a (Å)	15.0047(6)	temp (K)	295
b (Å)	8.7500(2)	R-p (%)	5.2
c (Å)	24.4702(8)	R-wp (%)	7.0
β (deg)	107.290(2)	R-F (%)	9.3
V (Å^3)	3067.5(2)	R-F^2 (%)	13.7
V/*Z* (Å^3)	383.44	no. of reflns	782
Z	8	no. of variables	126
space group	C 2/c	no. of refined atoms	36
ρ−calcd (g/cm^3)	0.949	wavelength (Å)	0.70011(2)
fw	1753.80	2Θ range (deg), counting time (h)	2−42, 6
μ (cm^{-1})	1.73	step size (2Θ)	0.003 (after rebinning)

[a] Defined in: Langford, I.; Louër, D. *Rep. Prog. Phys.* **1996**, *59*, 131−234.

As starting geometry for the simulated annealing procedure, we used a geometry of $(Me_2AlNH_2)_3$ in a chair conformation, which was calculated at the HF/6-31G(d) level of theory.[20] Because the conformation of the six-membered ring was unknown in advance, all angles and torsion angles

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(12) Thorne, L. R.; Suenram, R. D.; Lovas, F. J. *J. Phys. Chem.* **1983**, *78*, 167−171.

(13) Bühl, M.; Steinke, T.; von Ragué Schleyer, P.; Boese, R. *Angew. Chem.* **1991**, *103*, 1179−1181.

(14) Burns, W. A.; Leopold, K. R. *J. Am. Chem. Soc.* **1993**, *115*, 11622−11623.

(15) Reeve, S. W.; Burns, W. A.; Lovas, F. J.; Suenram, R. D.; Leopold, K. R. *J. Phys. Chem.* **1993**, *97*, 10630−10637.

(16) Interrante, L. V.; Sigel, G. A.; Garbauskas, M.; Hejna, C.; Slack, G. A. *Inorg. Chem.* **1989**, *28*, 252−257.

(17) Sauls, F. C.; Czekaj, C. L.; Interrante, L. V. *Inorg. Chem.* **1990**, *29*, 4688−4692.

(18) Sauls, F. C.; Interrante, L. V.; Jiang, Z. *Inorg. Chem.* **1990**, *29*, 2989−2996.

(19) Visser, J. W. *J. Appl. Crystallogr.* **1969**, *2*, 89−95.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1998.

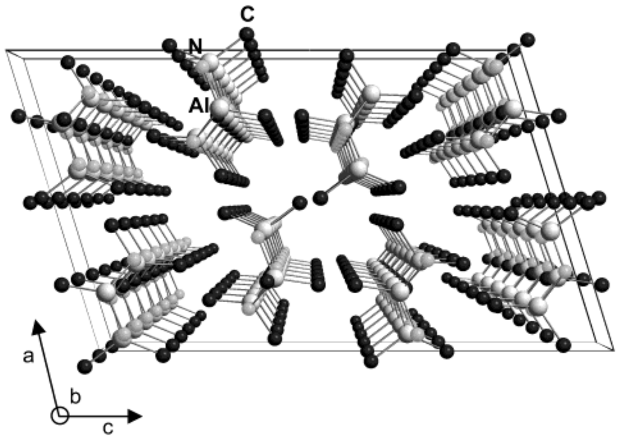

Figure 2. Perspective view along the *b*-axis of the packing of (Me$_2$AlNH$_2$)$_3$ at T = 295 K using a ball-and-stick representation. Figure produced using SCHAKAL 99 (Keller, E.; SCHAKAL 99, *A Computer Program for the Graphical Representation of Molecular and Crystallographic Models*; University of Freiburg, Germany, 2001).

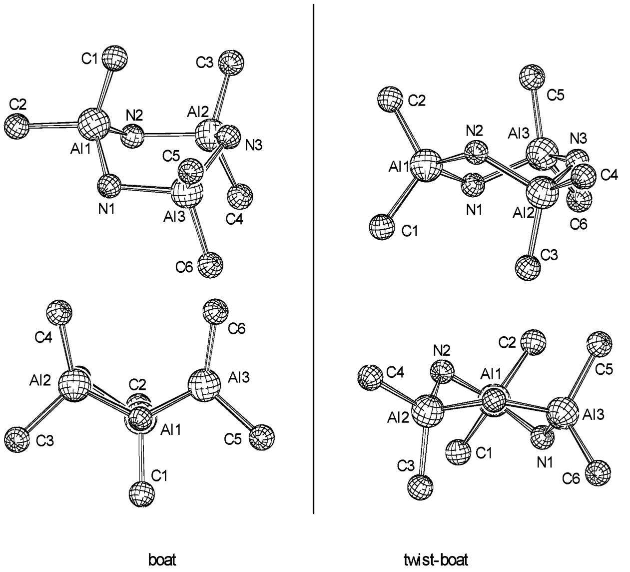

Figure 3. Two different views of the boat (this work) and twist-boat conformation[16] of (Me$_2$AlNH$_2$)$_3$ in the crystal lattice. Hydrogen atoms are omitted for clarity. Figure produced using SCHAKAL 99.

Table 2. Selected Bond Lengths (Å), Intramolecular Distances (Å), Angles (deg), and Torsion Angles (deg) of (Me$_2$AlNH$_2$)$_3$[a]

Al1−N1	1.96(2)	N1−Al1−N2	107(1)
Al1−N2	1.97(2)	N2−Al2−N3	111.6(9)
Al2−N2	1.99(2)	N3−Al3−N1	113.3(9)
Al2−N3	2.00(2)	C1−Al1−C2	113(1)
Al3−N1	1.98(2)	C3−Al2−C4	116(1)
Al3−N3	1.96(2)	C5−Al3−C6	117(1)
Al1−C1	1.98(3)	Al1−N2−Al2	110.7(9)
Al1−C2	1.99(2)	Al2−N3−Al3	111(1)
Al2−C3	1.99(2)	Al3−N1−Al1	110.5(9)
Al2−C4	1.98(3)	Al1−N2−Al2−N3	11(1)
Al3−C5	1.98(3)	Al2−N3−Al3−N1	−52(1)
Al3−C6	1.98(3)	Al3−N1−Al1−N2	60(1)
Al1−Al2	3.26(2)	N1−Al1−N2−Al2	−65(1)
Al1−Al3	3.24(2)	N2−Al2−N3−Al3	47(1)
Al2−Al3	3.26(2)	N3−Al3−N1−Al1	−2(1)
N1−N2	3.16(2)		
N2−N3	3.30(2)		
N1−N3	3.29(2)		

[a] The given esd's are Rietveld statistical estimates.

Table 3. Average Bond Lengths (Å), Intramolecular Distances (Å), and Angles (deg) of (Me$_2$AlNH$_2$)$_3$

parameter	boat[a]	twist-boat[b]
Al−N	1.98(2)	1.935(5)
Al−C	1.98(2)	1.958(7)
Al−Al	3.25(2)	3.382(3)
N−N	3.25(2)	2.99(1)
N−Al−N	110.6(9) (107−113.3)	101.4(2) (99.7−102.7)
Al−N−Al	110.7(9) (110.5−111)	122.1(2) (118.6−125.3)
C−Al−C	115(1) (113−117)	118.3(3) (117.0−120.0)

[a] This work. [b] Data were taken from ref 16.

between non-hydrogen atoms were flagged as variables in the simulated annealing procedure. The structure giving the best fit to the data obtained at the end of the simulated annealing run was (Me$_2$AlNH$_2$)$_3$ in a boat conformation, which could be verified by Rietveld refinement. Figure 2 shows the packing of (Me$_2$AlNH$_2$)$_3$ in the monoclinic cell. To illustrate the difference between the boat conformation and the known twist-boat conformation of (Me$_2$AlNH$_2$)$_3$, two different views for each molecule are depicted in Figure 3.

The Al−N and the Al−C bond lengths vary in the range of 1.96−2.00 and 1.98−1.99 Å (Table 2), respectively. Both types of bonds show the same average value of 1.98(2) Å (Table 3), whereas the average bond lengths of (Me$_2$AlNH$_2$)$_3$ in the known twist-boat conformation are 1.935(5) Å for Al−N and 1.958(7) Å for Al−C. If one takes into account that a realistic deviation for bond length can be obtained by multiplying the estimated standard deviations by a factor of 6,[21] the Al−N and the Al−C bond lengths, respectively, of the two different conformations are the same within the experimental error. In contrast to the bond lengths, there are some significant differences between angles of the boat and twist-boat isomer (Table 3). While the exocyclic C−Al−C angles of 115° (boat) and 118° (twist-boat) are quite similar, the endocyclic angles show average differences of 9° and 11° for N−Al−N and Al−N−Al, respectively (Table 3). Even though structure determinations from powder diffraction data are not as precise as those from single-crystal analyses, the differences between the endocyclic angles are far outside the experimental error.

It is noteworthy that along the crystallographic *b*- and *c*-direction a small anisotropic microstrain was detected (see Supporting Information). Because the microstrain is directly related to the elastic constants of the material, one can say that the compressibility along the stacks of the molecules (*b*-direction) and between these stacks in *c*-direction is much lower than in all other directions.

Theoretical Calculations. It is known that cyclohexane exists in a chair (D_{3d} symmetry) and a twist-boat conformation (D_2 symmetry), with the latter being 22−29 kJ/mol less stable.[22−29] The boat conformer (C_{2v} symmetry) corresponds

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(21) Hill, R. J.; Cranswick, L. M. D. *J. Appl. Crystallogr.* **1994**, *27*, 802−844.

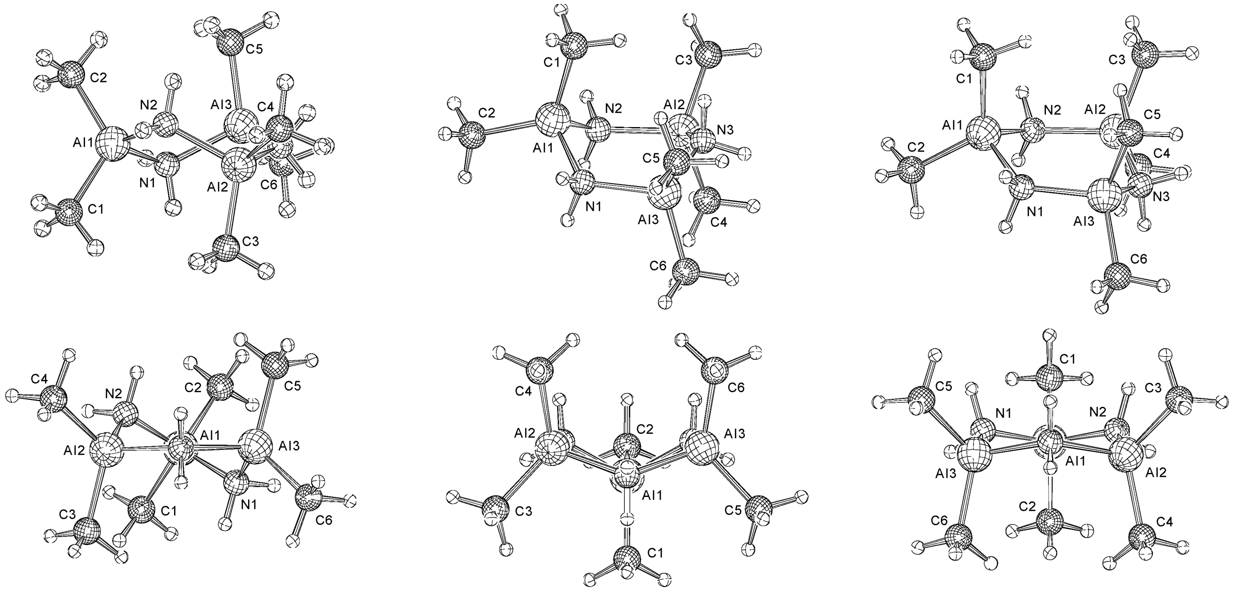
(22) For cyclohexane, see refs 23−29 and cited literature therein.

(23) Squillacote, M.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1975**, *97*, 3244−2346.

(24) Arnason, I.; Oberhammer, H. *J. Mol. Struct.* **2001**, *598*, 245−250.

(25) Offenbach, J. L.; Fredin, L.; Strauss, H. L. *J. Am. Chem. Soc.* **1981**, *103*, 1001−1006.

(26) Leong, M. K.; Mastryukov, V. S.; Boggs, J. E. *J. Phys. Chem.* **1994**, *98*, 6961−6966.



twist-boat boat chair

Figure 4. Ball and stick representation of the twist-boat, boat, and chair conformers of $(Me_2AlNH_2)_3$ calculated at the B3LYP/6-311G(d,p) level of theory. Figure produced using SCHAKAL 99.

Table 4. Relative Energies[a] [kJ/mol] of the Different Conformers of $(Me_2AlNH_2)_3$

level of theory	twist-boat	boat[b]	chair
HF/6−31G(d)	0.00	0.51	8.06
B3LYP/6−31G(d)	0.00	0.92	7.41
B3LYP/6−311G(d,p)	0.00	0.45	6.66
MP2(fc)/6−31G(d)	0.00	2.24	11.45
MP2(fc)/6−311G(d,p)	0.00	2.56	11.91

[a] Without ZPVE (see Experimental Section). [b] Corresponds to a transition state.

Table 5. Calculated Average Bond Lengths (Å), Intramolecular Distances (Å), and Angles (deg) of $(Me_2AlNH_2)_3$ at the B3LYP/6-311G(d,p) and MP2(fc)/6-311G(d,p) Level[a]

parameter	twist-boat	boat[b]	chair
Al−N	1.980 [1.971]	1.980 [1.971]	1.980 [1.972]
Al−C	1.981 [1.976]	1.981 [1.976]	1.981 [1.971]
Al−Al	3.471 [3.421]	3.493 [3.449]	3.550 [3.509]
N−N	3.076 [3.047]	3.097 [3.074]	3.145 [3.103]
N−Al−N	101.93 [101.89]	102.93 [102.53]	105.17 [103.76]
Al−N−Al	122.44 [120.40]	123.79 [122.16]	127.43 [125.69]
C−Al−C	119.60 [120.01]	120.04 [120.97]	120.45 [120.55]

[a] MP2(fc)/6-311G(d,p) results in square brackets. [b] Corresponds to a transition state (see Experimental Section).

to a transition state that connects two enantiomers of the twist-boat form at the potential energy surface (PES) with an activation energy of 4−6 kJ/mol. Against this background, our finding, a boat conformation for the cyclohexane derivative $(Me_2AlNH_2)_3$ in the solid state, was a surprise. Therefore, we have investigated the six-membered heterocycle by theoretical methods, i.e., HF, B3LYP, and MP2 with the standard basis sets 6-31G(d) and 6-311G(d,p) (see Experimental Section). The calculated structures are depicted in Figure 4; relative energies and selected structural parameters are compiled in Tables 4 and 5, respectively. At all levels of theory, the order of increasing energy is twist-boat, boat, and chair conformer (Table 4). Like for cyclohexane, only the twist-boat and chair conformer correspond to minima at the PES, whereas the boat conformer is a transition state with the imaginary frequency mode showing a twist of the boat. Figure 5 illustrates the results of relaxed PES scans where we have changed the Al2−N3−Al3−N1 torsion angle of the twist-boat conformer systematically in steps of 5°. The relaxed PES scans clearly show that the boat conformer is the transition state for two enantiomers of the C_2 symmetrical twist-boat conformer. The activation energies are very low and vary between 0.45 kJ/mol [B3LYP/6-311G(d,p)] and 2.56 kJ/mol [MP2(fc)/6-311G(d,p)].

The energetic order of the twist-boat and chair conformer of $(Me_2AlNH_2)_3$ is reverse with respect to cyclohexane. However, cyclohexane is not an ideal molecule to compare it with $(Me_2AlNH_2)_3$, because the ring sizes are quite different: C−C = 1.53 Å[30] compared with Al−N = 1.94−1.98 Å (Table 3). The ideal molecule for comparison would be the isoelectronic trisilacyclohexane $(Me_2SiCH_2)_3$, but to the best of our knowledge, details of the different conformers of this molecule are unknown. In contrast, the parent compound $(H_2SiCH_2)_3$ was investigated by theory and experiment. The Si−C bond length of 1.87 Å (GED)[24] in $(H_2SiCH_2)_3$ comes close to the Al−N bond lengths in $(Me_2AlNH_2)_3$ (1.94−1.98 Å). According to calculations, the chair conformer of $(H_2SiCH_2)_3$ is still more stable than the twist-boat conformer, but the energy difference is diminished to 9.2 kJ/mol[24] (22−29 kJ/mol for cyclohexane). A further increase of the size of the six-membered ring does not change the energy gap significantly; e.g., for cyclohexasilane (Si−

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(27) Weiser, J.; Golan, O.; Fitjer, L.; Biali, S. E. *J. Org. Chem.* **1996**, *61*, 8277−8284.

(28) Arnason, I.; Thorarinsson, G. K.; Matern, E. *Theochem-J. Mol. Struct.* **1998**, *454*, 91−102.

(29) Smith, B. J. *J. Phys. Chem. A* **1998**, *102*, 3756−3761.

(30) Dommen, J.; Brupbacher, T.; Grassi, G.; Bauder, A. *J. Am. Chem. Soc.* **1990**, *112*, 953−957.

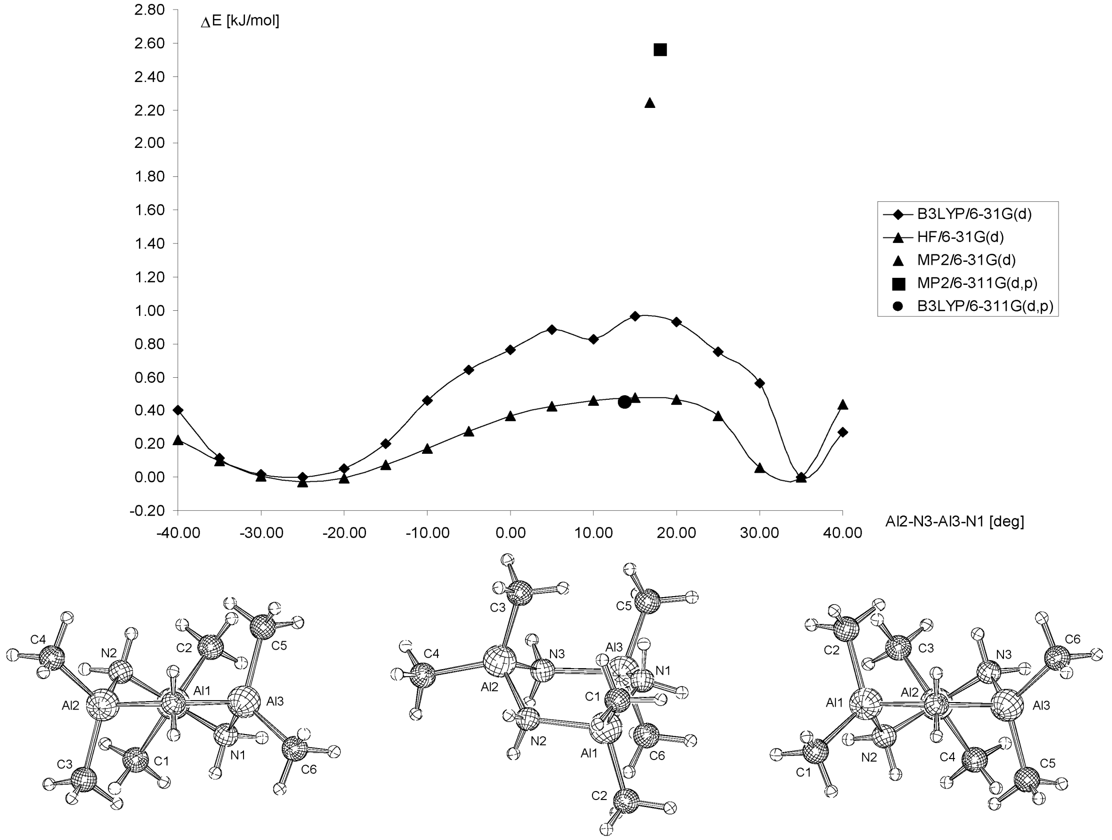

Figure 5. Relaxed scan of the PES and relative energies of the boat conformer at different levels of theory (see Table 4). Starting geometry is the twist-boat isomer of Figure 4 including the atom labels. This results in a boat conformer with different atom labels than the boat conformer shown in Figure 4.

Si = 2.34 Å GED)[31] the energy difference was calculated to be 7.9 kJ/mol.[24,26] Moreover, the energy of the boat conformer decreases with respect to the twist-boat form with increasing ring size: 6.3 kJ/mol for C_6H_{12} and 2.2 kJ/mol for Si_6H_{12} (both at the MP2/6-31G(d) level), which can be attributed to a reduction of the nonbonded interactions with increasing ring size.[26,32]

In the case of $(Me_2AlNH_2)_3$ the relative energies of the chair and twist-boat conformer are reversed. This is probably caused by 1−3 diaxial interactions of the methyl groups that energetically disfavors the chair conformer relative to the twist-boat and boat conformer.[33]

Conclusion

According to our calculations, the boat conformer of the aminoalane $(Me_2AlNH_2)_3$ is a transition state that connects two C_2 symmetrical twist-boat forms (Figure 5). The activation energies for the process are very low and these values should not be overrated (Table 4). However, because all methods HF, B3LYP, and MP2 show in principle similar results, we assume that the boat conformer of the isolated free aminoalane indeed corresponds to a transition state. It is noteworthy that we found boat conformers of $(Me_2AlNH_2)_3$ packed in the solid state. The molecular building blocks are severely distorted in comparison with the calculated structures of the isolated molecule (Tables 3 and 5). While the Al−N and Al−C distances agree very well, the endo- and exocyclic angles differ quite substantially. The most pronounced differences can be seen for the endocyclic angles (average values): 111° (exptd) versus 103° (calcd) for N−Al−N, and 111° (exptd) versus 123−124° (calcd) for Al−N−Al. In contrast to these findings, the known molecular structure of the twist-boat isomer[16] matches quite well with our calculated structures (Tables 3 and 5).

Most of the known aminoalanes crystallize as dimers, and the minority of this class of compounds forms trimers. Twist-boat conformers were determined for $[Me_2AlN(CH_2CH_2)]_3$,[34] *trans*-$(Me_2AlNHMe)_3$,[35] and $(Me_2AlNH_2)_3$,[16] chair conformers were determined for $(H_2AlNMe_2)_3$[36] and *cis*-$(Me_2AlNHMe)_3$,[35] and planar six-membered rings were determined for $[(Me_3Si)_2AlNH_2]_3$[37] and $(tBu_2AlNH_2)_3$.[16] With the latter two examples, the flexibility of six-membered Al−N heterocycles is demonstrated. Maximal distances between the bulky substituents Me_3Si and *t*Bu, respectively, are realized in planar heterocycles.

In summary, it seems that the transition state boat conformer of $(Me_2AlNH_2)_3$ is transformed into an equilibrium

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(31) Smith, Z.; Almenningen, A.; Hengge, E.; Kovar, D. *J. Am. Chem. Soc.* **1982**, *104*, 4362−4366.
(32) Hummel, J. P.; Stackhouse, J.; Mislow, K. *Tetrahedron* **1977**, *33*, 1925−1930.
(33) Hoffmann, R. W. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1124−1134.
(34) Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 285−288.
(35) McLaughlin, G. M.; Sim, G. A.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 2197−2203.
(36) Semenenko, K. N.; Lobkovskii, E. B.; Dorosinskii, A. L. *Zh. Strukt. Khim.* **1971**, *13*, 743−744.
(37) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1987**, *26*, 4341−4345.

geometry by the alignment of the molecules in a crystal lattice. This alignment is accompanied by a severe distortion of the heterocycles.

Experimental Section

Preparation of $(Me_2AlNH_2)_3$. Me_3Al-NH_3 (0.50 g, 5.61 mmol),[10,11] placed in a 25-mL Schlenk flask under argon, was slowly heated to an oil bath temperature of 65 °C. After ca. 10 min at an oil bath temperature of 65−70 °C, the melt crystallized completely. The sample was kept for another 10 min at the same temperature, and it was cooled to ambient temperature afterward. In a glovebox, the crystallized melt was grained with an agate mortar, and the powder was filled in a 0.7 mm lithium borate glass capillary (glass No. 50).

Theoretical Calculations. All calculations have been carried out using the GAUSSIAN 98 program package.[20] All geometry optimizations have been performed without constraints. As a hybrid HF-DFT method the three-parameter exchange functional of Becke[38] with the correlation functional by Lee, Yang, and Parr[39] has been used (B3LYP). All MP2 calculations have been performed with the frozen core (fc) approximation and 6-31G(d) and 6-311G-(d,p) basis sets have been applied. Analysis of the vibrational frequencies at the HF/6-31G(d), B3LYP/6-31G(d), and B3LYP/6-311G(d,p) levels confirmed that the twist-boat and the chair conformers correspond to local minima at the PES and that the boat conformers correspond to transition states. The absolute energies in Hartrees and the ZPVE in kJ/mol (values in braces) are as follows: twist-boat −1130.5107326 {836.80} [HF/6-31G-(d)], −1134.9337619 {790.87} [B3LYP/6-31G(d)], −1135.1469570 {783.32} [B3LYP/6-311G(d,p)], −1131.9832465 [MP2(fc)/6-31G-(d)], −1132.4167861 [MP2(fc)/6-31G(d)], boat −1130.5105396 {836.39} [HF/6-31G(d)], −1134.9334126 {789.70} [B3LYP/6-31G(d)], −1135.1467860 {782.46} [B3LYP/6-311G(d,p)], −1131.9823918 [MP2(fc)/6-31G(d)], −1132.4158100 [MP2(fc)/6-31G(d)], and chair −1130.5076631 {836.11} [HF/6-31G(d)], −1134.9309383 {789.36} [B3LYP/6-31G(d)], −1135.1444188 {782.28} [B3LYP/6-311G(d,p)], −1131.9788858 [MP2(fc)/6-31G-(d)], −1132.4122497 [MP2(fc)/6-31G(d)]. Quoted energies (Table 4) are relative energies without the inclusion of ZPVE and thermal corrections. The scans of the PES have been performed by changing the Al2−N3−Al3−N1 torsion angle of the twist-boat conformer from 40 to −40° in steps of 5° (Figure 5). At each point of the PES, only the Al2−N3−Al3−N1 torsion angle was kept constant, and all other geometrical parameters were optimized without constraints.

X-ray Powder Diffraction. Powder diffraction data were collected at the high-resolution powder diffractometer at the BM16 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). At the BM16, the X-rays from the bending magnet source are collimated vertically by a rhodium-coated silicon mirror before they are incident on the double crystal monochromator.[40] An Si 111 reflection was used to select an X-ray energy of 17.7 keV. The size of the beam was adjusted to 2×0.6 mm^2 using slits. The wavelength was determined to 0.70011(1) Å from a silicon standard. The sample was rotated around θ to improve randomization of the crystallites. The diffracted beam was analyzed with a nine crystal analyzer stage (nine Ge(111) crystals separated by 2° intervals) and detected with nine scintillation counters simultaneously. The incoming beam was monitored by an ion chamber for normalization for the decay of the primary beam. In this parallel beam configuration, the resolution is determined by the analyzer crystal instead of by slits.[41] Details of the experimental setup are described in the beamline handbook and on the Internet (http://www.esrf.fr/). Powder diffraction data for the structure determination and Rietveld refinement of $(Me_2AlNH_2)_3$ were collected at $T = 295$ K in continuous mode and later normalized and converted to step scan data from 2° to 43° in steps of 0.003° in 2θ. Low-angle diffraction peaks had a full width at half maximum of 0.01° in 2θ significantly broader than the resolution of the spectrometer, which is estimated to be as low as 0.002° in 2θ for the given energy (powder pattern see Figure 1). Data reduction was performed using the GUFI program.[42] The diffraction pattern could be indexed on the basis of a monoclinic lattice with lattice parameters given in Table 1.[19] According to extinction rules, the only possible space groups of $(Me_2AlNH_2)_3$ were determined as Cc or $C2/c$ from which the latter could be confirmed by Rietveld refinement. The number of formula units per unit cell (Z) directly followed from geometrical considerations, suggesting a trimer.

The crystal structure was solved with the DASH[43] structure solution package as follows. The measured powder pattern was subjected to a Pawley refinement[44] in space group $C2/c$ in order to extract correlated integrated intensities from the pattern. Good fit to the data was obtained. As a starting geometry for the simulated annealing procedure, a calculated geometry of $(Me_2AlNH_2)_3$ in a chair conformation (HF/6-31G(d) level of theory) was used in internal coordinates. All angles and torsion angles between non-hydrogen atoms were flagged as variables for refinement in the simulated annealing procedure. The position, orientation, and conformation of the ring in the refined unit cell were postulated, and the level of agreement between the trial structure and the experimental diffraction data quantified by

$$\chi^2 = \sum_h \sum_k \left[(I_h - c|F_h|^2)(V^{-1})_{hk}(I_k - c|F_k|^2)\right]$$

where I_h and I_k are Lorentz−polarization corrected, extracted, integrated intensities from the Pawley refinement of the diffraction data, V_{hk} is the covariance matrix from the Pawley refinement, c is a scale factor, and $|F_h|$ and $|F_k|$ are the structure factor magnitudes calculated from the trial structure. The trial structure was subjected to a global optimization,[45,46] in which the angles and torsion angles between the non-hydrogen atoms (19 parameters) were the only internal degrees of freedom and the external degrees of freedom consisted of three fractional coordinates describing the position and four quaternions[47] describing the orientation of the trimer. The structure giving the best fit to the data obtained at the end of the simulated annealing run was $(Me_2AlNH_2)_3$ in a boat conformation (Figures 2 and 3), which could be verified by Rietveld refinement. Rietveld refinement and LeBail extraction were performed using

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[38] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[39] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

[40] Fitch, A. N. *European Powder Diffraction: Epdic Iv, Pts 1 and 2* **1996**, *228*, 219−221.

[41] Cox, D. E. In *Handbook on Synchrotron Radiation*; Brown, G., Moncton, D. E., Eds.; Elsevier Science Publishers B.V., 1991; Vol. 3, p 155.

[42] Dinnebier, R. E. *GUFI, A Program for Measurement and Evaluation of Powder Pattern*; Heidelberger Geowiss. Abh. 68, 1993.

[43] David, W. I. F. *Simulated Annealing Program DASH*, 1999.

[44] Pawley, G. S. *J. Appl. Crystallogr.* **1981**, *14*, 357−361.

[45] Newsam, J. M.; Deem, M. W.; Freeman, C. M. *NIST Spec. Publ. No. 846* **1992**, 80−91.

[46] David, W. I. F.; Shankland, K.; Shankland, N. *Chem. Commun.* **1998**, 931−932.

[47] Leach, A. R. In *Molecular Modelling Principles and Applications*; Addison-Wesley Longman Limited: Reading, MA, 1996.

the program system GSAS.[48] In the analysis, a Pseudo-Voigt profile function[49] with a special function which accounts for the asymmetry due to axial divergence[50] was used. The powder pattern of ($Me_2AlNH_2)_3$ exhibits severe anisotropic peak broadening caused by lattice strain, which could be satisfactorily modeled by the phenomenological strain model of Stephens[51] as implemented in GSAS. Nine parameters were refined for the monoclinic crystal lattice. A three-dimensional representation of the isosurface of the microstrain at T = 295 K is given as Supporting Information. The background was modeled manually using GUFI.[42] To stabilize the refinements, slack soft constraints for the bond lengths and angles within the trimer were introduced and gradually removed during the refinement. In a final cycle of refinement of $(Me_2AlNH_2)_3$, all non-hydrogen atoms were turned loose. They remained close to their original positions, although small but meaningless changes occurred without improving the weighted profile *R*-factor. The best Rietveld refinement using weak soft constraints was achieved with the data set at T = 295 K, from which the agreement factors (*R*-values) are listed in Table 1, the coordinates are given in the Supporting Information, and a selection of intra- and intermolecular distances and angles is given in Table 2. Throughout the refinements, the hydrogen atoms were attached to the carbon atoms by strong restraints (riding model). The crystallographic data of $(Me_2AlNH_2)_3$ can be obtained from the Cambridge Crystallographic Data Centre using the compound number CCDC 192108 (www.ccdc.cam.ac.uk).

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Supporting Information Available: Positional parameters, three-dimensional representation of the microstrain, measured structural parameters (distances, angles, torsion angles), calculated structural parameters for the twist-boat, boat, and chair conformer at the B3LYP/6-311G(d,p) and MP2(fc)/6-311G(d,p) levels (distances, angles, torsion angles), Cartesian coordinates of all calculated molecular structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(48) Larson, A. C.; Von Dreele, R. B. *GSAS − General Structure Analysis System*; Los Alamos National Laboratory Report LAUR 86-748, 1994.

(49) Thompson, P.; Cox, D. E.; Hastings, J. B. *J. Appl. Crystallogr.* **1987**, *20*, 79−83.

(50) Finger, L. W.; Cox, D. E.; Jephcoat, A. P. *J. Appl. Crystallogr.* **1994**, *27*, 892−900.

(51) Stephens, P. W. *J. Appl. Crystallogr.* **1999**, *32*, 281−289.