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# Group 13 Azatranes: Synthetic, Conformational, and Configurational Features

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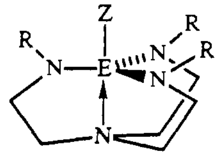
**Abstract:** The monomeric azatranes $\overline{\mathrm{E(RNCH_2CH_2)_3N}}$ **7** (E = B, R = Me), **8** (E = B, R = $SiMe_3$), and **9** (E = Al, R = $SiMe_3$) can be synthesized from $E(NMe_2)_3$ and $(HRNCH_2CH_2)_3N$ in low yields (6–37%). The azatrane **10** (E = Al, R = Me), formed in 64% yield by the analogous reaction, is a stable dimer featuring a four-membered $\mathrm{Me\overline{NAlNMeAl}}$ ring in which the aluminum is five-coordinate as shown by $^1H$, $^{13}C$, and $^{27}Al$ NMR spectroscopic techniques (including two-dimensional ones). Compound **7** can be made in 30% yield by reacting **10** with $B(OMe)_3$. Compound **8**, in contrast to **7** and **9**, exists as rigid enantiomers that interconvert slowly at room temperature on the NMR time scale owing to steric repulsion of the $Me_3Si$ groups. VT $^1H$ and $^{11}B$ NMR studies provide evidence for a concerted (rather than a stepwise) racemization mechanism ($\Delta H^\ddagger$, 61 ± 5 kJ·mol$^{-1}$; $\Delta S^\ddagger$, −36 ± 13 J·mol$^{-1}$ K$^{-1}$) involving a symmetric ($C_{3v}$) transition state that retains the transannular bond.

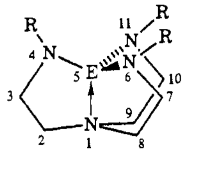
## Introduction

Azatrane structures such as **1–6** are members of an interesting class of compounds. Compounds of this type (including those wherein Z = OEt, for example) offer an interesting opportunity to study relative reactivities of the upper axial and the equatorial substituents to protonation and methylation, for example.[6] By increasing the bulk of R in these compounds to $Me_3Si$ (when E = Si and Z = Me), the transannular bond can be essentially broken.[7] Compounds of type **1–6** are volatile and may therefore also be potential MOCVD precursors to nitride films of E, since carbon retention may be minimized by the absence of C–E bonds and by a higher number of N–E bonds than is required by the normal valence of E.

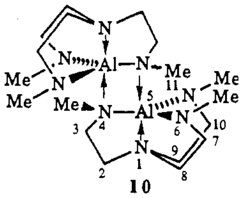


| | E | Z | R |
|---|---|---|---|
| 1[1] | Si | $NMe_2$ | Me |
| 2[2] | Ge | $NMe_2$ | Me |
| 3[3] | Sn | $NMe_2$ | Me |
| 4[4] | Ti | $NMe_2$ | Me |
| 5[3] | V | N-*t*-Bu | Me |
| 6[5] | Mo | N | Me |

Here we report the synthesis of the novel azatranes **7–9** in which boron and aluminum are four-coordinate and **10** in which aluminum occurs in a five-coordinate dimeric structure.[8] We further demonstrate that whereas **7** and **9** are nonrigid in solution on the NMR time scale, **8** is rigid at room temperature. Moreover, as suggested by the configuration shown for **10**, we demonstrate by NMR spectroscopy that this compound does not possess a mirror plane.



| | E | R |
|---|---|---|
| 7 | B | Me |
| 8 | B | $SiMe_3$ |
| 9 | Al | $SiMe_3$ |



**10**

## Experimental Section

All reactions were carried out under argon with the strict exclusion of moisture using Schlenk or dry box techniques.[9] Solvents were dried over and distilled from Na/benzophenone under nitrogen. Deuterated benzene and toluene were dried over and distilled from $CaH_2$ under an argon atmosphere. The starting materials $(MeHNCH_2CH_2)_3N$[10] (**11**) and $(Me_3SiHNCH_2CH_2)_3N$[11] (**12**) were prepared using our procedures published earlier. $B(NMe_2)_3$ was purchased from Aldrich and was used as received. $[Al(NMe_2)_3]_2$ (**13**) was prepared using the published procedure[12a] and was characterized by $^1H$, $^{13}C$, and $^{27}Al$ NMR spectroscopy.[12b] $B(OMe)_3$ was purchased from Aldrich and was purified by distillation from Na before using.

NMR spectra were recorded on a Varian VXR 300 with deuterated solvents as an internal lock. $^1H$ (299.94 MHz) spectra were referenced to the residual proton signal of the deuterated solvent (7.15 ppm for benzene-$d_6$ and 2.09 ppm for toluene-$d_8$). $^{13}C$ (75.429 MHz) spectra were also referenced to solvent signals (128.0 ppm in benzene-$d_6$ and 20.4 ppm in toluene-$d_8$). $^{11}B$ (96.233 MHz) spectra were referenced to $BF_3{\cdot}Et_2O$ in $C_6D_6$ (50% volume solution) as an external standard, $^{27}Al$ (78.157 MHz) spectra were measured at 25 and 70 °C and were referenced to the external standard 0.2 M $Al(ClO_4)_3$/0.1 M $HClO_4$ in $H_2O$ with the coaxial capillary containing benzene-$d_6$ as a lock medium. $^{29}Si$ (59.591 MHz) spectra were referenced to a 30% volume solution of $Me_4Si$ in benzene-$d_6$ as an external standard. Pulses of 90° and a relaxation delay of 25 s were used for acquisition of the $^{29}Si$ spectra. Variable temperature NMR spectra were measured in toluene-$d_8$ from −110 °C to +110 °C on Varian VXR 300 and Bruker WM 200 spectrometers with an accuracy

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of ±1 °C. Coalescence temperatures were evaluated from a series of spectra taken with 1 °C increments.

Frequency differences $\Delta\nu_{AB}$ were measured at several (5–6) temperatures in the slow exchange region and were extrapolated to the corresponding $T_c$. $^1$H,$^1$H DQF COSY spectra were recorded on a Varian Unity 500 instrument.

Mass spectra were recorded on a Finnigan 4000 low-resolution (70 eV EI, $NH_3$ CI) and a Kratos MS-50 high-resolution instrument. The masses are reported for the most abundant isotope present. IR spectra were taken on an IBM IR-98 FTIR spectrometer (4000–400 cm$^{-1}$) using Nujol mulls between KBr discs or as KBr pellets.

Elemental analyses were carried out by Galbraith Laboratories or Desert Analytics. Melting points (uncorrected) were measured in sealed capillaries.

**Trimethylboraazatrane,**[13] **7.** *Method A.* A solution of tetramine **11** (19 g, 0.10 mol) and $B(NMe_2)_3$ (16 g, 0.11 mol) in 350 mL of THF and a catalytic amount of vacuum dried $(NH_4)_2SO_4$ was refluxed for 99 h at which time the detectable evolution of $HNMe_2$ ceased. The yellowish solution was filtered and 3/4 of the solvent was removed under vacuum. The white crystalline solid was filtered, washed with 2 × 2.5 mL portions of THF, and dried under vacuum. Further evaporation of the filtrate gave a second crop crystals providing a total yield of 7.4 g (37%). The product was further purified by sublimation at 65 °C at 5 × 10$^{-3}$ Torr.

*Method B.* A solution of **10** (0.411 g, 0.970 mmol) and $B(OMe)_3$ (0.201 g, 1.93 mmol) in 50 mL of toluene was heated to 70–90 °C for 48 h with stirring. All volatiles were then removed under vacuum, and the residue was sublimed at 70–80 °C at 5 × 10$^{-3}$ Torr yielding 0.11 g (30%) of **7**: mp 135.0–135.5 °C; $^1$H NMR ($C_6D_6$) $\delta$ 2.67 (s, 3 H, $CH_3$, $^1J_{CH}$ = 130.6 Hz, $^{13}$C satellites), 2.58 (bt, 2 H, MeNC$H_2$, $^3J_{HH}$ = 5.6 Hz), 2.13 (t, 2 H, $N(CH_2)_3$, $^3J_{HH}$ = 5.6 Hz); $^{13}$C NMR ($C_6D_6$) $\delta$ 37.1 (qt, $CH_3$, $^1J_{CH}$ = 130.3 Hz, $^3J_{CNCH}$ = 2.2 Hz), 52.4 (tqt, $MeNCH_2$, $^1J_{CH}$ = 134.2 Hz, $^3J_{CNCH}$ = 6.0 Hz, $^2J_{CCH}$ = 2.0 Hz), 57.1 (tm, $N(CH_2)_3$, $^1J_{CH}$ = 140.0 Hz); $^{11}$B NMR ($C_6D_6$) $\delta$ 10.1 (bs, $\Delta\nu_{1/2}$ = 34 Hz); HRMS (EI) calcd for $C_9H_{21}N_4B$ ($M^+$) *m/z* 196.18593, found 196.18605; LRMS (EI) *m/z* (ion, rel intensity) 196 ($M^+$, 58), 152 (100), 138 (87), 124 (58); CIMS (negative ion detection) *m/z* 195 (M – $H^-$, 36), 213 (M + $NH_3^-$, 100), 231 (43), 253 (15); CIMS (positive ion detection) *m/z* 197 (M + $H^+$, 100); IR (KBr pellet, 4000–400 cm$^{-1}$) $\nu$ 2987, 2949, 2919, 2872, 2856, 2830, 2769, 2646, 1474, 1455, 1444, 1411, 1357, 1341, 1325, 1274, 1265, 1233, 1208, 1188, 1163, 1151, 1098, 1040, 1005, 972, 960, 923, 867, 844, 768, 761, 609, 511, 444. Anal. Calcd for $C_9H_{21}N_4B$: C, 55.12; H, 10.79; N, 28.57. Found: C, 55.35; H, 10.65; N, 28.10.

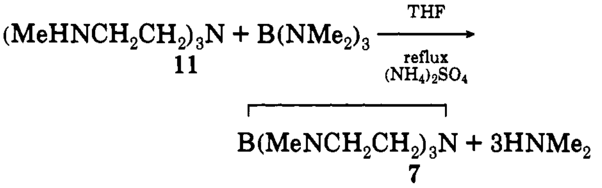
**Tris(trimethylsilyl)boraazatrane,**[14] **8.** A mixture of tetramine **12** (3.1 g, 8.5 mmol) and $B(NMe_2)_3$ (1.6 g, 11 mmol) and a catalytic amount of $(NH_4)_2SO_4$ was heated to 150 °C and the temperature held there for 40 h by which time the detectable evolution of $HNMe_2$ had ceased. Evacuation of residual volatiles under vacuum at room temperature was followed by sublimation at 100 °C at 5 × 10$^{-3}$ Torr, yielding 0.2 g (6% yield) of a white solid: mp 82–85 °C; $^1$H NMR (toluene-$d_8$) $\delta$ 0.23 (s, 9 H, $SiCH_3$, $^1J_{CH}$ = 117.3 Hz, $^{13}$C satellites, $^2J_{SiH}$ = 6.3 Hz, $^{29}$Si satellites), 1.72 (ddd, 1 H, $N(CH_2)_3$, $^2J_{HH}$ = $^3J_{HH(trans)}$ = 11.5 Hz, $^3J_{HH(gauche)}$ = 5.9 Hz), 2.16 (dd, 1 H, $N(CH_2)_3$, $^2J_{HH}$ = 11.2 Hz, $^3J_{HH(gauche)}$ = 3.9 Hz), 2.69 (b dd, 1 H, $Me_3SiNCH_2$, $^2J_{HH}$ = 12.2 Hz, $^3J_{HH(gauche)}$ = 5.9 Hz), 2.82 (ddd, 1 H, $Me_3SiNCH_2$, $^2J_{HH}$ = $^3J_{HH(trans)}$ = 12.2 Hz, $^3J_{HH(gauche)}$ = 3.8 Hz); $^{13}$C NMR (APT, toluene-$d_8$) $\delta$ 1.7 ($SiCH_3$, $^1J_{SiC}$ = 57.5 Hz, $^{29}$Si satellites), 44.4 ($Me_3SiNCH_2$), 60.2 ($N(CH_2)_3$); $^{11}$B NMR ($C_6D_6$) $\delta$ 16.1 (bs, $\Delta\nu_{1/2}$ = 100 Hz); $^{29}$Si NMR ($C_6D_6$, 25 °C) $\delta$ –2.37; HRMS (EI) calcd for $C_{15}H_{39}N_4Si_3B$ ($M^+$) *m/z* 370.25757, found 370.25683; LRMS (EI) *m/z* 370 ($M^+$, 64), 355 (M – $CH_3^+$, 18), 268 (88), 254 (67), 240 (19), 180 (23), 73 ($SiMe_3^+$, 100), 59 (32). Anal. Calcd for $C_{15}H_{39}N_4Si_3B$: C, 48.62; H, 10.61; N, 15.12. Found: C, 49.74; H, 9.91; N, 16.49.

**Tris(trimethylsilyl)alumaazatrane,**[15] **9.** A solution of tetramine **12** (39.76 g, 0.1096 mol) in 130 mL of toluene was added dropwise to a solution of $Al(NMe_2)_3$ (17.43 g, 0.1095 mol) in 350 mL of toluene. The reaction mixture was refluxed for 10 h with stirring. Removal of the solvent under vacuum left an amber-colored oil which solidified upon standing overnight. Although this material appeared to be pure **9** by $^1$H NMR spectroscopy, the product was recrystallized from pentane to give 7.7 g (18% yield) of a white crystalline solid: mp 62–63 °C; $^1$H NMR ($C_6D_6$) $\delta$ 0.24 (s, 9 H, $SiCH_3$, $^1J_{CH}$ = 117.0 Hz, $^{13}$C satellites, $^2J_{SiC}$ = 6.3 Hz, $^{29}$Si satellites), 2.00 (t, 2 H, $N(CH_2)_3$, $^3J_{HH}$ = 5.4 Hz, $^1J_{CH}$ = 137.3 Hz, $^{13}$C satellites), 2.76 (t, 2 H, $Me_3SiNCH_2$, $^3J_{HH}$ = 5.3 Hz, $^1J_{CH}$ = 135.0 Hz); $^{13}$C NMR ($C_6D_6$) $\delta$ 1.3 (q, $SiCH_3$, $^1J_{CH}$ = 116.6 Hz, $^1J_{SiC}$ = 55.3 Hz, $^{29}$Si satellites), 41.4 (tt, $Me_3SiNCH_2$, $^1J_{CH}$ = 135 Hz, $^2J_{CH}$ = 2.2 Hz, $^1J_{CC}$ = 37 Hz, $^{13}$C satellites), 58.7 (tm, $N(CH_2)_3$, $^1J_{CH}$ = 137 Hz, $^1J_{CC}$ = 37 Hz, $^{13}$C satellites); $^{27}$Al NMR ($C_6D_6$) $\delta$ 133 ($\Delta\nu_{1/2}$ = 3100 Hz at 25 °C, 1860 Hz at 70 °C); $^{29}$Si NMR ($C_6D_6$, 25 °C) $\delta$ –1.24; HRMS (EI) calcd for $C_{15}H_{39}N_4Si_3Al$ ($M^+$) *m/z* 386.22979, found 386.22937. Anal. Calcd for $C_{15}H_{39}N_4Si_3Al$: C, 46.59; H, 10.16; N, 14.19. Found: C, 46.04; H, 10.19; N, 14.72.

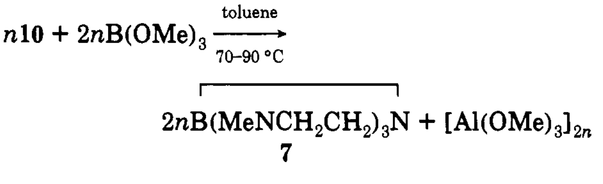
**Trimethylalumaazatrane Dimer, 10.** A solution of tetramine **11** (7.71 g, 40.9 mmol) in 50 mL of THF was added dropwise to a solution of $Al(NMe_2)_3$ (6.26 g, 39.3 mmol) in 350 mL of THF. The reaction mixture was heated at 90 °C with stirring for 8 h. After cooling to room temperature, the solvent was removed under vacuum to give a solid product which was recrystallized from THF to give 10.4 g (64% yield) of **10**: mp 104–106 °C; $^1$H NMR (500 MHz, $C_6D_6$) $\delta$ 1.88 (dd, 1 H, *J* = 13.2, 4.9 Hz), 2.12 (dd, 1 H, *J* = 13.1, 5.0 Hz), 2.24 (m, 1 H), 2.31 (m, 1 H), 2.44 (ddd, *J* = 13.3, 13.3, 5.1 Hz), 2.56–2.67 (m, 2 H), 2.65 (s, 3 H, $CH_3$), 2.78–2.85 (m, 2 H), 2.87 (s, 3 H, $CH_3$), 2.91 (s, 3 H, $CH_3$), 2.96 (m, 1 H), 3.04 (m, 1 H), 3.42 (ddd, 1 H, *J* = 13.1, 13.1, 4.9 Hz); $^{13}$C NMR ($C_6D_6$) $\delta$ 39.8 (qdd, $CH_3$, $^1J_{CH}$ = 133.8 Hz, $^3J_{CH}$ = 10.2, 4.5 Hz), 40.8 (qdd, $CH_3$, $^1J_{CH}$ = 129.1 Hz, $^3J_{CH}$ = 4.3, 2.7 Hz), 41.9 (qdd, $CH_3$, $^1J_{CH}$ = 129.1 Hz, $^3J_{CH}$ = 3.6, 2.2 Hz), 52.5, 53.2, 53.6, 53.7, 54.3, 56.0 ($CH_2$ groups); $^{27}$Al NMR ($C_6D_6$) $\delta$ 83 ($\Delta\nu_{1/2}$ = 950 Hz at 25 °C, 560 Hz at 70 °C); HRMS (EI) calcd for $C_{18}H_{42}N_8Al_2$ ($M^+$) *m/z* 424.31630, found 424.31628; calcd for $C_9H_{21}N_4Al$ ($M^+/2$) *m/z* 212.15815, found 212.15808; LRMS (EI) *m/z* 424 ($M^+$, 2%), 409 (M – $CH_3^+$, 5), 368 (61), 337 (6), 311 (15), 267 (7), 232 (4), 213 (M/2 + $H^+$, 98), 212 ($M^+$/2, 74), 211 (23), 197 (17), 168 (65), 156 (29), 140 (70), 126 (100). Anal. Calcd for $C_{18}H_{42}N_8Al_2$: C, 50.92; H, 9.97; N, 26.39. Found: C, 50.44; H, 10.05; N, 25.59.

## Discussion

**Syntheses.** The synthesis of trimethylboraazatrane **7** occurs in 37% and 30% yields according to reactions 1 and 2, respectively. The small amount of white precipitate formed during reaction 1 and the substantial amount of oily (polymeric?) residue remaining after sublimation of the crude product were not investigated further. Reaction 2 is an example of a novel type of transmetalation in which the rigid dimeric structure of **10** is disassembled and the ligand is reassembled around a new neutral atom. The driving force in this reaction is the formation of insoluble polymeric $[Al(OMe)_3]_n$ possessing strong polar Al–O bonds. Byproducts in reaction 2, probably containing partially transmetalated products, are currently under investigation. In the absence of moisture, **7** is stable for months in the solid and solution state and it is quite soluble in THF, toluene, and pentane.

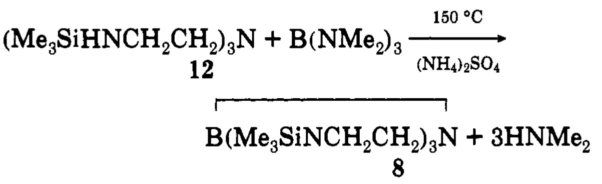


$$\underset{\mathbf{11}}{(MeHNCH_2CH_2)_3N} + B(NMe_2)_3 \xrightarrow[\text{reflux}\ (NH_4)_2SO_4]{THF} \underset{\mathbf{7}}{\overline{B(MeNCH_2CH_2)_3N}} + 3HNMe_2 \tag{1}$$



$$n\mathbf{10} + 2nB(OMe)_3 \xrightarrow[70\text{–}90\ °C]{toluene} \underset{\mathbf{7}}{\overline{2nB(MeNCH_2CH_2)_3N}} + [Al(OMe)_3]_{2n} \tag{2}$$

Tris(trimethylsilyl)boraazatrane **8** was synthesized via reaction 3. The large amount of glassy residue left upon sublimation of



$$\underset{\mathbf{12}}{(Me_3SiHNCH_2CH_2)_3N} + B(NMe_2)_3 \xrightarrow[(NH_4)_2SO_4]{150\ °C} \underset{\mathbf{8}}{\overline{B(Me_3SiNCH_2CH_2)_3N}} + 3HNMe_2 \tag{3}$$

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[13] 4,6,11-Trimethyl-1,4,6,11-tetraaza-5-boratricyclo[3.3.3.0$^{1,5}$]undecane.

[14] 4,6,11-Tris(trimethylsilyl)-1,4,6,11-tetraaza-5-boratricyclo[3.3.3.0$^{1,5}$]undecane.

[15] 4,6,11-Tris(trimethylsilyl)-1,4,6,11-tetraaza-5-alumatricyclo[3.3.3.0$^{1,5}$]undecane.

Table I. $^{11}B$ NMR Chemical Shifts for Selected Boron Compounds

| compound | $\delta$ $^{11}B$(ppm) | solvent | ref |
|---|---|---|---|
| $B(CH_2CH_2CH_2)_3N$, **14** | 9.40 | $CS_2$ | 22 |
| $B(OCRCH_2)_3N$ | | | |
| **15a**, R = H | 14.2 | *a* | 40 |
| | 10.7 | $H_2O$ | 39 |
| | 11.2 | $CHCl_3$ | 39 |
| **15b**, R = Me | 14.2 | *a* | 40 |
| $B(CHCXCH_2)_3N$ | | | |
| **16a**, X = Cl | 14.6 | $CH_2Cl_2$ | 17 |
| **16b**, X = Br | 12.1 | $CH_2Cl_2$ | 17 |
| $B(NRCH_2CH_2)_3N$ | | | |
| **7**, R = Me | 10.1 | $C_6D_6$ | this work |
| **8**, R = $Me_3Si$ | 16.1 | $C_6D_6$ | this work |

[a] No solvent given.

**8** in low yield (6%) from the reaction product suggests that a polymer formed during the reaction rather than upon sublimation, since the former process occurred at a higher temperature (150 °C) than the latter (100 °C). Polymer formation may be favored over cage formation by the bulky $Me_3Si$ groups (see later). The solubility properties of **8** are similar to those of **7**. The transmetalation reaction of **9** with $B(OMe)_3$ did not yield the expected product **8**, suggesting that the bulk of the $Me_3Si$ groups also disfavors a reaction analogous to reaction 2.

In contrast to the low yield of **8**, **9** is formed in essentially quantitative yield in reaction 4 without benefit of catalyst. The

$$\underset{\mathbf{12}}{(Me_3SiHNCH_2CH_2)_3N} + \underset{\mathbf{13}}{{}^1/_2[Al(NMe_2)_3]_2} \xrightarrow[\text{reflux}]{\text{toluene}} \underset{\mathbf{9}}{Al(Me_3SiNCH_2CH_2)_3N} + 3HNMe_2 \quad (4)$$

absence of polymer in this preparation is due at least in part to reduced steric hindrance among the $Me_3Si$ groups in **9** (see later). Compound **9** is soluble in nonpolar hydrocarbon solvents and it was recrystallized in 18% yield from pentane, although the crystals were not suitable for X-ray analysis.

The highly ordered rigid dimer of trimethylalumaazatrane, **10**, is easily assembled in reaction 5, giving a 64% yield.

$$\underset{\mathbf{11}}{2(MeHNCH_2CH_2)_3N} + \underset{\mathbf{13}}{2Al(NMe_2)_3} \xrightarrow[\text{reflux}]{\text{THF}} \underset{\mathbf{10}}{[Al(MeNCH_2CH_2)_3N]_2} + 6HNMe_2 \quad (5)$$

**Structural Considerations.** The monomeric nature of **7**–**9** is supported by their $^1H$ and $^{13}C$ NMR spectra which reflect the 3-fold symmetry of these molecules. There is also considerable precedent for transannular tricyclic structures of this type in the literature (Table I), two of which (**15a**[16] and **16a**[17]) have been established by X-ray diffraction. The single $^{11}B$ resonance for **7** at 10.1 ppm is also consistent with a monomeric transannulated structure (see Table I) possessing a tetracoordinated boron atom.[18] The possibiltiy of head-to-tail oligomeric structures involving an extended $\sigma$-type overlap of p orbitals in solutions of a closely related compound **14** was disproven by an IR study[19] in various solvents. Association of **14** in solution is ascribed to dipolar attractions involving the transannulated structure.

Compound **7** is an adduct of the type $(R_2N)_3BNR_3$. No examples of such an adduct could be found in the literature, though the related salt $Li[B(NHMe)_4]$ was reported[20] as well as several adducts of the type $(RO)_3BNR_2H$.[21] The upfield $^{11}B$ chemical shift of $Li[B(NHMe)_4]$ (0.2 ppm) relative to **7** may reflect the shielding effect of the negative charge on the $B(NHMe)_4^-$ ion. Also consistent with a stable monomeric tricyclic cage structure for **7** is its stability to cleavage of the transannular bond via nucleophilic attack on boron by diisopropylamine, $F^-$ and $t$-$BuO^-$, as judged by the constancy of its $^1H$ and $^{11}B$ NMR spectra in the presence of these bases. The $^1H$ NMR spectrum of **7** consists of a methyl singlet and two methylene triplets. The breadth of the singlet and the downfield triplet is approximately twice that of the high field triplet. We attribute this broadening to quadrupolar interactions of the $CH_3N$ and the $MeNCH_2$ protons with the $^{11}B$ nucleus.[22] Although the $N(CH_2)_3$ as well as the $MeNCH_2$ protons are separated from the boron nucleus by an equal number of bonds, the latter protons are connected to the boron by essentially planar $NR_2$ groups[23] which possess a higher degree of s-character in their bonds ($sp^2$) than the $N(CH_2)_3$ nitrogen ($sp^3$).

The value of $^3J_{HH}$ in the methylene proton triplets (5.6 Hz) is consistent with conformational mobility of the five-membered rings of **7** on the NMR time scale even down to −110 °C, although some peak broadening occurs at lower temperatures. This broadening occurs more rapidly with decreasing temperature for the $N(CH_2)_3$ protons than for the $MeNCH_2$ protons, suggesting that the latter (as expected) have greater motional freedom owing to their position on the "flap" carbon of a five-membered ring as in **15a**.[16] The $^{13}C$ APT NMR spectrum allows the assignment of the $CH_3$ versus the $CH_2$ carbons. Moreover the $^{13}C$–H coupled spectrum reveals that the high field $CH_2$ carbon peak is split into a quartet by scalar interaction with the $CH_3$ protons ($^3J_{CH}$), while the low-field $CH_2$ carbon resonance is split into an unresolved multiplet by protons on other $N(CH_2)_3$ carbons. The high field position of the $MeNCH_2$ carbons relative to the $N(CH_2)_3$ carbons may result from the lone-pair electron density present on the ($sp^2$) nitrogen of the former which is absent on the latter ($sp^3$), thus rendering the $N(CH_2)_3$ nitrogen more electronegative. This is also demonstrated in the magnitudes of the $^1J_{CH}$ coupling constants. Greater s-character in the CH bonds of $N(CH_2)_3$ is manifested as a larger coupling constant of 140.0 Hz in contrast to smaller value of 134.2 Hz observed for $MeNCH_2$. Finally, the $CH_2$ proton and carbon NMR assignments were rendered consistent by sequential irradiation of the proton triplets, leading to the collapse of the corresponding $^{13}C$ resonances to singlets. Two vibrations in the IR spectrum of **7** at 1098 and 1040 $cm^{-1}$ (intensity ratio roughly 1:4) can be tentatively assigned to the $^{10}B$–N and $^{11}B$–N stretch, respectively.[19]

The room temperature $^1H$ NMR spectrum of **8** contrasts that of **7** in that the protons on each of the $CH_2$ groups are diastereotopic (Figure 1). The four multiplets of equal intensity for these hydrogens in **8** indicate that the conformational mobility of the three five-membered rings of **7** is suppressed in **8** by the steric hindrance imposed by the presence of the $Me_3Si$ groups. Thus racemization of the two enantiomers is slow at room temperature on the NMR (300 MHz) time scale. At elevated temperatures, racemization is accelerated and the two downfield multiplets coalesce at 81 °C while the two higher field ones do so at 100 °C. The broadening of one of the pair of downfield multiplets in Figure 1 (probably caused by quadrupolar and

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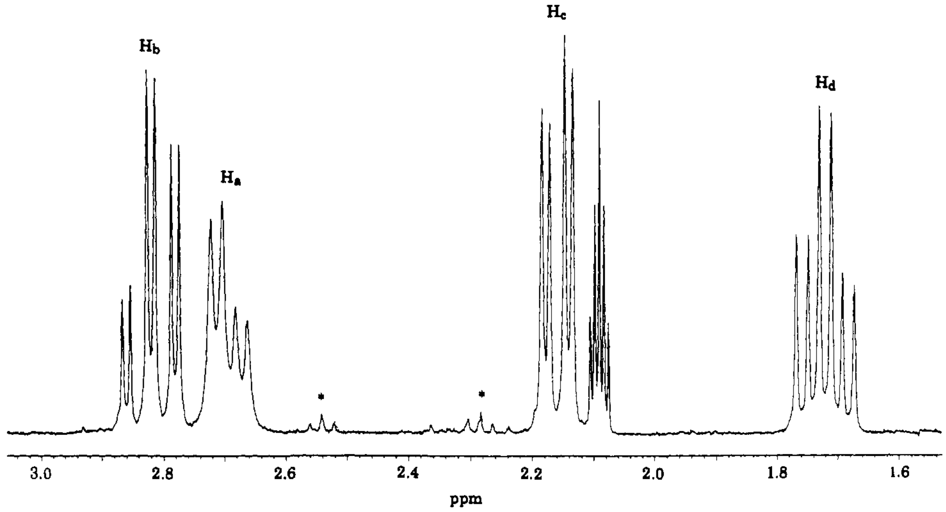
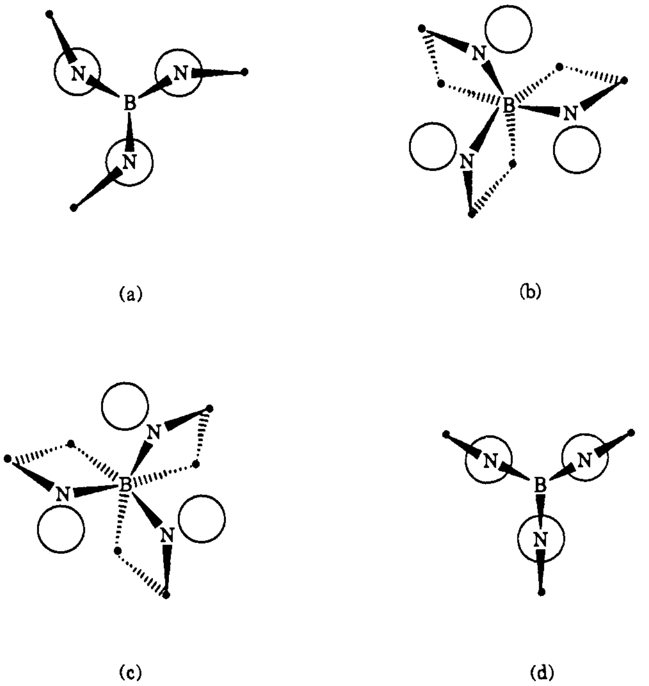


**Figure 1.** The methylene region of the $^1H$ NMR spectrum of **8** at room temperature. Asterisks denote impurities and the quintet at 2.09 ppm comes from the solvent, toluene-$d_8$.



(a) (b)

(c) (d)

**Figure 2.** View down the B–N transannular bond axis of **8** showing an eclipsed conformation of the bonds on these atoms (a), enantiomeric staggered conformations (b) and (c), and a proposed transition state in which all the atoms in the framework of the five-membered rings are coplanar (d). The circles represent the $Me_3Si$ groups bonded to the adjacent trigonal nitrogen.

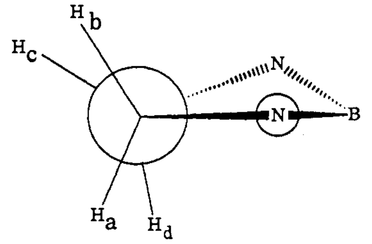
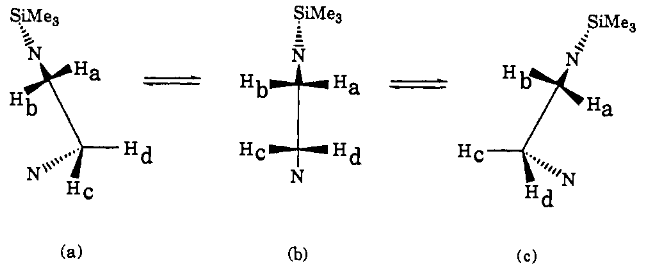


**Figure 3.** Newman projection of the ethylene portion of the five-membered rings in one of the enantiomers **8** revealing the four different environments of the protons and showing the axial nitrogen in the "flap" position. The circle represents the $Me_3Si$ group.



(a) (b) (c)

**Figure 4.** Depictions of a portion of the five-membered rings in **8** showing the four different methylene proton environments in the two enantiomers (a) and (c) and the two environments experienced by these protons during the racemization process.

unresolved scalar interactions with the $^{11}B$ nucleus) and the lower coalescence temperature for this pair of multiplets strongly suggest their assignment to $Me_3SiNCH_2$ protons. The higher coalescence temperature for the upfield pair of multiplets corresponds to the slower narrowing of the $N(CH_2)_3$ proton resonance in **7** (compared with its $MeNCH_2$ protons) upon raising the temperature from −100 °C. Thus the $N(CH_2)_3$ methylene groups in both **7** and **8** possess less motional freedom than the methylene moieties residing at the "flap" positions of the five-membered rings.

The rigidity on the NMR time scale of the enantiomers of **8** at room temperature undoubtedly arises from steric repulsions of the $Me_3Si$ groups, which distort the structure from the nearly eclipsed conformation (as viewed down the B–N axis in Figure 2a) encountered in the crystallographically determined structures of $\overline{B(OCH_2CH_2)_3N}$[16] and $ClV[(Me_3SiNCH_2CH_2)_3N]$[24] to a more staggered one (Figure 2b). This process (shown as a clockwise twist in Figure 2) reduces the congestion among the $Me_3Si$ groups by increasing the distance between them, and it changes the conformation of the five-membered rings from one in which the $Me_3SiNCH_2$ methylene carbon is in the "flap" position (Figure 2a) to one in which the $N(CH_2)_3$ nitrogen occupies this position. The latter location of the flap is not obvious from Figure 2b but becomes clear in Figure 3.

Some pyramidalization of the $Me_3SiN$ nitrogens may also result from the repulsions of the $Me_3Si$ groups. In order for the enantiomer in Figure 2b to racemize to that in Figure 2c, a counterclockwise twist around the BN axis is required, during which the $Me_3Si$ groups must temporarily crowd one another in an eclipsed conformation of the cage (Figure 2d) before separating again as conformation c in Figure 2 is approached. As depicted in Figure 4 (parts b and c), the protons on each methylene carbon exchange environments during racemization. At higher temperatures this exchange becomes rapid on the NMR time scale, providing an averaged spectrum of two signals.

The free energies of activation $\Delta G_{Tc}^{\ddagger}$ for racemization at the coalescence (Table II) were calculated from both the $Me_3SiNCH_2$

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**Table II.** Free Energies of Activation for Racemization of **8**

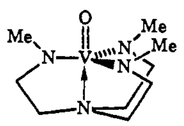
| $^1$H resonance | $T_c$ (K) | $\Delta\nu_{AB}^{T_c}$ (Hz) | $\Delta G_{T_c}{}^{\ddagger}$ (kJ·mol$^{-1}$) |
|---|---|---|---|
| $Me_3SiNCH_2$ | 350$^a$ | 21.2$^c$ | 73.4 |
| | 354$^b$ | 33.9$^c$ | 73.7 |
| $N(CH_2)_3$ | 366$^a$ | 94.8$^d$ | 74.0 |
| | 373$^b$ | 139.5$^d$ | 74.3 |

$^a$ At 200 MHz. $^b$ At 300 MHz. $^c$ Treated as an AB spin system: $J_{AB} = 12.2$ Hz, $k_c = \pi(\Delta\nu_{AB}^2 + 6J_{AB}^2)^{1/2}/2^{1/2}$. $^d$ $k_c = \pi\Delta\nu_{AB}/2^{1/2}$.

and the $N(CH_2)_3$ $^1$H NMR coalescence temperatures at two different magnetic fields.[25] The higher values of $\Delta G_{Tc}{}^{\ddagger}$ than those for azastannatranes (33–36 kJ·mol$^{-1}$) or for azametallatranes **6** and **17** (40.8 and 41.0 kJ·mol$^{-1}$ [5]) can be attributed to steric repulsions among the $Me_3Si$ groups. Thus the absence of $\pi$ bonding in the three BN amido bonds is in contrast to that likely to be of importance in favoring a structure resembling that in Figure 2d for azametallatranes **6** and **17**. Not unexpectedly, a rather low value of $\Delta G_{Tc}{}^{\ddagger}$ (8.4 kJ·mol$^{-1}$) was measured for substituted boratranes[26] and the same value was calculated for **14**.[19]

A stepwise mechanism for ring flipping during racemization was substantiated by a $^1$H NOESY experiment in the case of substituted silatranes.[27] On the other hand, a very small energy difference (8.4 kJ·mol$^{-1}$) between a stepwise and concerted pathway was calculated for **14**.[19] Owing to the bulkiness of the $Me_3Si$ groups, the synchronous mechanism is more plausible for boraazatrane **8**. Synchronous processes in polycyclic systems are known to possess higher barriers to interconversion, and this factor may also contribute to the high value of $\Delta G_{Tc}{}^{\ddagger}$ for **8**. For a series of 1,5-diazabicyclo[3.3.3]decane derivatives, the energy barriers increase as the bridgehead atoms are pushed further apart.[28] This can be accomplished in molecule **8** if breakage of the transannular B–N bond is involved in the racemization process. But as can be seen from the variable temperature $^{11}$B NMR spectra,[29] the chemical shift is rather temperature insensitive (shifting 0.4 ppm downfield from 25 to 110 °C) and remains in the region characteristic for tetracoordinated boron[18] (16.2 ppm in toluene-$d_8$). Supporting evidence for a concerted racemization mechanism is the negative value of the activation entropy $\Delta S^{\ddagger}$ (−36 ± 13 J·mol$^{-1}$·K$^{-1}$) which was evaluated together with the activation enthalpy $\Delta H^{\ddagger}$ (61 ± 5 kJ·mol$^{-1}$) by the linear regression of the plot $\Delta G_{Tc}{}^{\ddagger}$ versus $T_c$ ($r = 0.984$) (Table II). The negative value of $\Delta S^{\ddagger}$ is expected if the transition state in the racemization process is more symmetrical than both enantiomers. This can be accomplished, for example, if a $C_3$ enantiomer passes through the $C_{3v}$ transition state shown in Figure 2d.

**17**



$[MeAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$

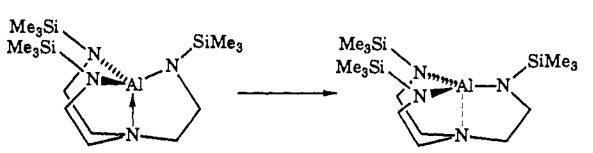
**18**

Analysis of the coupling patterns and magnitudes in the $^1$H NMR spectrum of **8** permits an assignment of each of the four multiplets in Figure 1. The presence of only two coupling constants in the two doublet of doublets at 2.16 and 2.69 ppm indicates that the vicinal coupling constant between them is close to zero owing to a dihedral angle of approximately 90°. Based on the assignment of the broadened multiplet (2.69 ppm) to one of the protons in the $Me_3SiNCH_2$ methylene group, the signals at 2.69 and 2.16 ppm are assigned to $H_a$ and $H_c$ in Figure 3, respectively. The appearance of two larger coupling constants (geminal and trans vicinal) of very similar values, and a smaller one (gauche vicinal) in the apparent pseudodoublet of triplets at 1.72 and 2.82 ppm are confirmatory of the assignments of these protons to $H_d$ and $H_b$, respectively, in Figure 3. Using selective proton decoupling techniques, the peaks at 44.4 and 60.2 ppm in the $^{13}$C NMR spectrum of **8** were assigned to $Me_3SiNCH_2$ and $N(CH_2)_3$, respectively.

The $^{11}$B NMR chemical shift of **8** at 16.1 ppm is shifted 6 ppm downfield from that of **7**. This may be ascribed to competition for the lone pair density on the adjacent nitrogens by the Lewis acidic $Me_3Si$ groups, which deshield the boron nucleus. This phenomenon is also manifested in the series $B(NMe_2)_3$, $B(NMe_2)_2(NMeSiMe_3)$, and $B(NMeSiMe_3)_3$ in which $\delta$ $^{11}$B increases from 27.3 to 28.7 to 33.8 ppm, respectively.[30]

The $^1$H NMR spectrum of **9** consists of two methylene triplets and a $Me_3Si$ singlet at 0.24 ppm.[31] Crowding of the $Me_3Si$ groups, causing the conformational rigidity observed for the boron derivative **8**, is relieved in the case of **9** by the larger size of the central aluminum atom. As for **7**, rapid racemization is observed in the $^1$H spectrum down to −70 °C. By analogy with **7** and **8**, the upfield and downfield triplets were assigned to the $N(CH_2)_3$ and $Me_3SiNCH_2$ protons, respectively. In accord with the corresponding assignments for **7** and **8**, the selectively decoupled $^{13}$C NMR spectrum of **9** permitted ascribing the methylene signals at 41.4 and 58.7 ppm to $Me_3SiNCH_2$ and $N(CH_2)_3$, respectively.

The $^{27}$Al NMR chemical shift at 133 ppm confirmed the tetrahedral coordination of the central aluminum atom of **9** (Table III). The signal is at lower field than that for tetrahedral aluminum with four surrounding nitrogens as in **13**.[12b] The downfield shift of **9** can be attributed to the large size of the aluminum atom, which distorts the coordination sphere of the central atom in **9** from tetrahedral toward trigonal-monopyramidal (TMP) with a weakened transannular Al–N bond (reaction 6). Such a TMP configuration has recently been observed by X-ray crystallographic means for a related V(III) analogue.[32] As expected, the $^{27}$Al chemical shift for **9** is at higher field than that for alumazine **18**, which possesses trigonally coordinated aluminum.[33] On the other hand $\delta$ $^{27}$Al for **9** is at lower field than those for compounds **19**,[34] **20**,[35] and **21**,[35] in which each possesses a pentacoordinate aluminum.



(6)

In contrast to the simple appearance of the $^1$H NMR spectra of compounds **7–9**, twelve multiplets and three methyl singlets are observed in the case of **10** (Figure 5a). Moreover, six methylene and three methyl signals can be observed in its $^{13}$C APT NMR spectrum. These results are consistent with a dimeric structure for **10**. Also, its HRMS gives evidence for a dimer stable in the gas phase, as is the case for alumatrane **22**.[36] The formation of the dimeric structure **10** renders three methyl groups and three $CH_2CH_2$ arms inequivalent. Moreover, all four methylene protons become diastereotopic. There are two possible

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(31) For $Al[N(SiMe_3)_2]_3$ $\delta$ ($^1$H) is 0.244 ppm in $CCl_4$ (Pump, J.; Rochow, E. G.; Wannagat, U. *Angew. Chem., Int. Ed. Engl.* **1963**, *5*, 264).

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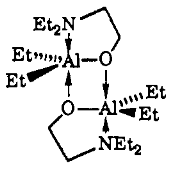
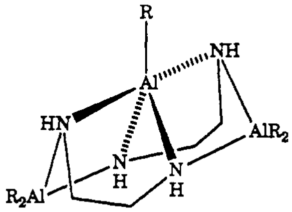
**Table III.** $^{27}$Al NMR Chemical Shifts for Selected Aluminum Compounds

| compound | $\delta^{27}$Al (ppm) | coordination no. | $\Delta\nu_{1/2}$ (Hz) | ref |
|---|---|---|---|---|
| **9** | 133[a] | 4 | 3100 at 25 °C<br>1860 at 70 °C | this work |
| **10** | 83[a] | 5 | 950 at 25 °C<br>560 at 70 °C | this work |
| **13** | 107[a] | 4 | 840 | 12b |
| | 107[a] | | 980 at 25 °C<br>620 at 70 °C | this work |
| **18** | 168[a] | 3 | 8800 | 33 |
| **19** | 112[b] | 5 | 7200 at 27 °C | 34 |
| **20** | 104[a] | 5 | broad[c] | 35 |
| | 156[a] | 4 | broad[c] | |
| **21** | 104[a] | 5 | broad[c] | 35 |
| | 158[a] | 4 | broad[c] | |
| **23** | 40.5[a] | 6 | sharp[c] | 37 |
| | 159.5[a] | 4 | broad[c] | |

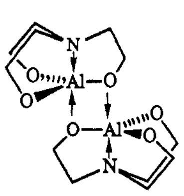
[a] Benzene-$d_6$ solution. [b] Toluene-$d_8$ solution. [c] Value of $\Delta\nu_{1/2}$ not given; room temperature.



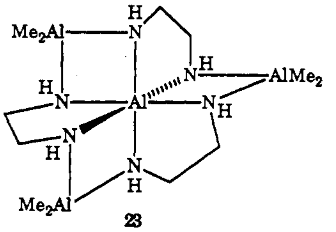
**19**



| | R |
|---|---|
| **20** | Me |
| **21** | Et |

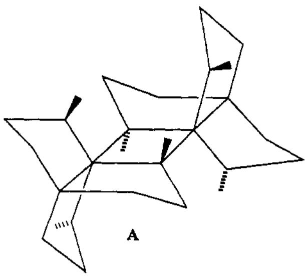


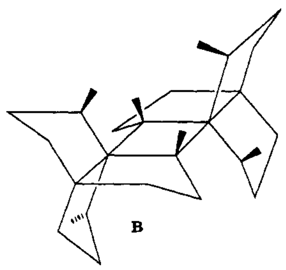
**22**



**23**

diastereomers for dimeric **10**. The diastereomer possessing an inversion center as the only symmetry element (schematically shown below as A) features a trans configuration of the methyl groups on the central four-membered ring. The other diastereomer (B) exists as an enantiomeric pair and possesses a $C_2$ axis as the only symmetry element, and the configuration of the methyls on the central ring is cis. The $^1$H NMR spectrum of **10** is clearly interpretable in terms of the presence of only one diastereomer. When an equimolar amount of the chiral shift reagent Eu(fod)$_3$ is added, the $^1$H NMR spectrum in CDCl$_3$ shows broadening and some shifting of the peaks downfield. However no peak doubling is observed, even of peaks that have widths at half-height of only 4 Hz. This result militates against structure B, whose lack of a center of inversion gives rise to enantiomers, and favors structure A which possesses a center of inversion. These observations do not rule out B, however. The proposed conformation of the five-membered rings in A and B is based on the fact that barriers to ring flipping are generally low for [3.3.3] systems, and the conformation is governed by a steric repulsion of substituents rather than by a mutual repulsion of rings.[26]





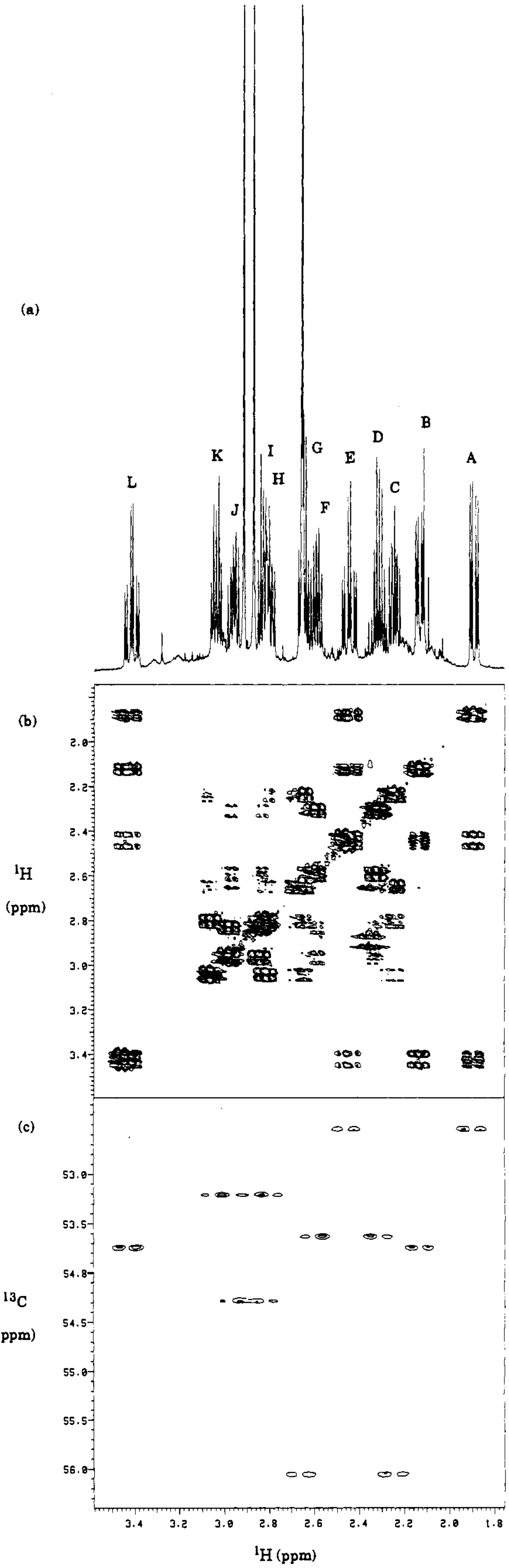


**Figure 5.** $^1$H NMR (500 MHz) spectrum of **10** showing twelve methylene multiplets A to L and three strong methyl singlets (a), the $^1$H $^1$H-DQF COSY 2D NMR spectrum (500 MHz) of **10** (b), and the $^1$H $^{13}$C-heterocorrelated 2D NMR spectrum (300 MHz) of **10** showing only the methylene region (c).

Distinguishing between the methyl group on the central Al$_2$N$_2$ ring (Me-4) and two other methyls (Me-6, 11) in **10** becomes possible from an analysis of its $^{13}$C H-coupled NMR spectrum. The nitrogens of the central ring are tetracoordinated and each

**Table IV.** Results of H-H and H-C NMR Correlatioin Experiments with **10**

| $\delta^{13}C$ (ppm) | $\delta^{1}H$ (ppm), assignment |
|---|---|
| 39.8 | 2.65, Me-4 |
| 40.8 | 2.87, Me-6 or 11 |
| 41.9 | 2.92, Me-11 or 6 |
| 52.5 | 1.89, A; 2.45, E |
| 53.7 | 2.12, B; 3.42, L |
| 53.2 | 2.78–2.82, H; 3.04, K |
| 56.0 | 2.24, C; 2.62–2.67, G |
| 53.6 | 2.56–2.62, F; 2.31, D |
| 54.3 | 2.82–2.85, I; 2.96, J |

bears a formal positive charge, while the other four methyl-bearing nitrogens are tricoordinated and possess lone electron pairs. Thus, the nitrogen in the four-membered ring is relatively more electronegative than the other two and attracts more p character into the N–C(Me-4) bond. This in turn leaves more s character in the C–H bonds and increases the value of the $^{1}J_{CH}$ coupling to 133.8 Hz for the signal at 39.8 ppm in contrast to 129.1 Hz for the other two methyl groups at 40.8 and 41.9 ppm.

The analysis of the cross-peak pattern in the $^{1}H$ DQF COSY spectrum of **10** (Figure 5) allows the sorting of 12 $CH_2$ proton signals into three groups belonging to three inequivalent arms namely, A, B, E, L; C, G, H, K; and D, F, I, J. The $^{1}H$–$^{13}C$ heterocorrelated 2D spectrum shows the connectivities between the proton and carbon signals by cross-peaks (Table IV), and each methylene carbon signal is seen to bear two diastereotopic protons (Figure 5c). The information from both the COSY and $^{1}H$–$^{13}C$ correlated spectra completely identifies the three inequivalent $CH_2CH_2$ arms. The remarkable rigidity of the dimer **10** is preserved up to 110 °C in solution, as was judged from its variable temperature $^{1}H$ and $^{13}C$ NMR spectra. The $^{27}Al$ NMR chemical shift of 83 ppm (Table III) confirms pentacoordination of the aluminum atom even at 70 °C. This value is at higher field than those for compounds **19**, **20**, and **21**, which are the closest examples of the few pentacoordinated aluminum compounds whose $^{27}Al$ NMR spectra have been measured.[34,35] Alumaazatranes **9** and **10**, together with the amide **13** and compound **23**[37] possess only nitrogen atoms in their coordination spheres and they clearly display a trend in their $^{27}Al$ chemical shifts toward higher field in the order of increasing coordination numbers, namely, $AlN_4 \rightarrow AlN_5 \rightarrow AlN_6$ (Table III). This trend is analogous to that observed for oxo and alkyl aluminum species.[38]

## Conclusions

Azatranes of boron and aluminum are stable transannulated molecules. In the case of boron they are monomeric (**7** and **8**), whereas for aluminum they can be monomeric (**9**) or dimeric (**10**), depending upon the size of the substituent on the nitrogen in the three bridging moieties of the transannulated cage structure. Steric crowding among the $Me_3Si$ groups in **8** leads to enantiomers sufficiently long-lived to be observed at room temperature on the NMR time scale. These enantiomers apparently racemize by a concerted mechanism rather than the step-wise process found for silatranes.[27]

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