Separation and Identification of Some Stereoisomers of Cyclodi-μ-t-butylamido-di(ethylbromoaluminium). Spectral Studies of their Interconversion in Solution and the Similar Behaviour of Some Related Compounds [1]

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The preparation of the adducts Et_2XAl,NH_2Bu^t, X = Cl, Br, and I, is described and the n.m.r. spectra are analysed to show that there is no restriction of rotation about Al–C or N–C bonds at room temperature. Et_3Al,NH_2Bu^t has been restudied. Thermal decomposition of the adducts leads to dimers containing $(AlN)_2$ rings. Two crystalline stereoisomers of $(EtBrAlNHBu^t)_2$ have been isolated by fractional sublimation and are shown to isomerize in solution at room temperature, at different rates, to give an equilibrium mixture containing three principal isomers. A preliminary *X*-ray study indicates that the predominant and most stable isomer is 1α,3α-di-t-butyl-2α,4α-dibromo-1β,3β-dihydro-2β,4β-diethyl-cyclodialuminatazoniane. ^1H N.m.r. spectra (250 MHz) are used to show that the second crystalline isomer is 1α,3β-di-t-butyl-2α,4β-dibromo-1β,3α-dihydro-2β,4α-diethylcyclodialuminatazoniane and a third isomer, evident in solution, is probably 1α,3α-di-t-butyl-2α,4β-dibromo-1β,3β-dihydro-2β,4α-diethyl-cyclodialuminatazoniane. It is proposed that isomer stability is principally a function of steric interactions. N.m.r. studies indicate that mixtures of isomers are also present in solutions of $(EtXAlNHBu^t)_2$, X = Et, Cl, and I. Mass spectral studies are reported which show that exchange takes place in solution between the dimers $(EtBrAlNHBu^t)_2$ and $(EtIAlNHBu^t)_2$, and between $(EtBrAlNHBu^t)_2$ and $(EtBrAlNDBu^t)_2$, which points to a complex mechanism for the isomerization process.

THE preparation [2] and structures [3] of *cis*- and *trans*-stereoisomers of the six-membered $(AlN)_3$ ring compound cyclotri-μ-methylamido-tris(dimethylaluminium) $(Me_2AlNHMe)_3$ have been reported recently, but, although the existence of stereoisomers of certain four-membered $(AlN)_2$ ring compounds has been postulated,[4] they have

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[1] Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, April 1972.

[2] K. J. Alford, K. Gosling, and J. D. Smith, *J.C.S. Dalton*, 1972, 2203.

[3] G. M. McLaughlin, G. A. Sim, and J. D. Smith, *J.C.S. Dalton*, 1972, 2197.

[4] A. W. Laubengayer, J. D. Smith, and G. G. Ehrlich, *J. Amer. Chem. Soc.*, 1961, **83**, 542.

not previously been positively identified or isolated. ^1H N.m.r. studies have been cited as evidence for the presence of *cis*- and *trans*-isomers of the related four-membered ring compounds, $(H_2GaNHR)_2$[5] and $(RClBNMe_2)_2$,[6] but individual isomers were not separated. Here we report the isolation of two crystalline stereoisomers of the $(AlN)_2$ ring compound cyclodi-μ-t-butylamido-di-(ethylbromoaluminium), $(EtBrAlNHBu^t)_2$, and a study of their isomerization in solution to give a mixture containing three principal stereoisomers. Structure assignments are made on the basis of 250 MHz ^1H n.m.r. spectra and a preliminary single crystal *X*-ray study. We will show that the behaviour of this system is also typical of the related compounds $(EtXAlNHBu^t)_2$, X = Et, Cl, and I.

EXPERIMENTAL

Air and moisture were rigorously excluded from all reactions and samples through the use of vacuum line or Schlenk-tube techniques, or a dry-box filled with nitrogen which was constantly recirculated through Linde type 13X and 4A molecular sieves to remove solvent and water vapours, and B.A.S.F. copper catalyst to remove oxygen. Solvents and amines were distilled from calcium hydride and stored either under nitrogen, or under vacuum in ampoules fitted with high-vacuum Teflon stopcocks. Triethylaluminium (Texas Alkyls) was distilled slowly through a glass-packed column and the fraction distilling at 109—112 °C, 10^{-3} mmHg was used. t-Butylammonium chloride, bromide, and iodide were prepared in the vacuum line by condensing together equimolar quantities of dry hydrogen halide and t-butylamine at −196°, followed by warming to room temperature. Bu^tND_3Br was prepared by dissolving Bu^tNH_3Br in 99·8% D_2O, stirring the solution for 15 min, then removing the solvent under vacuum. The process was repeated five times and the product finally dried by prolonged pumping under vacuum. The mass spectrum indicated that deuteriation had been accomplished to better than 95%. Bu^tND_2 was prepared by shaking a sample of Bu^tNH_2 with double its volume of D_2O followed by removal of the amine by distillation below 65°. This procedure was repeated three times and the deuteriated amine finally distilled from sodium. The i.r. spectrum showed no absorption in the N–H stretching region. Routine sublimations were carried out in 200 mm long, 15 mm diameter, Pyrex tubes and the separation of isomers and final purification of compounds was accomplished using a special vacuum fractional sublimation apparatus.[7] Compounds were analysed by hydrolysing small samples with 2% sulphuric acid. Ethyl groups were estimated as ethane, aluminium as the 8-hydroxyquinolate, and halide by a modified Volhard method. Molecular weights were determined cryoscopically in benzene.

N.m.r. spectra were recorded with Varian HA 60 EL or T 60 spectrometers, or with a 250 MHz instrument at Carnegie-Mellon University, and are reported relative to tetramethylsilane as an external standard. For the 250 MHz spectra, the benzene solvent resonance at δ 7·270 was used as a lock signal. I.r. spectra were recorded on a Beckman IR 12 spectrometer from liquid films or Nujol and Fluorolube mulls, and mass spectra were obtained at 70 eV on a Nuclide 12 90 G spectrometer with samples being introduced *via* a direct-insertion probe. The principal peaks of the mass spectra are reported with the relative intensities in parentheses and some assignments based upon metastable ions are suggested.

Preparation of Adducts.—Diethylbromoaluminium–t-butylamine. Finely divided t-butylammonium bromide (5·26 g, 34·2 mmol) was added slowly from a rotatable side-arm to a stirred solution of triethylaluminium (3·75 g, 32·9 mmol) in dry hexane (25 ml) at 0 °C on the vacuum line. The gas evolved in the reaction passed a −130° trap, was measured (27·0 mmol), and identified as ethane by its vapour pressure (40 mmHg, −130°) and i.r. spectrum. The solvent was removed from the reaction mixture at room temperature on the vacuum line and the residue sublimed at 50°, 10^{-3} mmHg, to give Et_2BrAl,NH_2Bu^t, as a white crystalline solid, m.p. 59—60° (Found: Et, 23·8; Al, 11·4; Br, 34·1%; *M*, 246. $C_8H_{21}AlBrN$ requires Et, 24·4; Al, 11·4; Br, 33·6%; *M*, 238).

Diethyliodoaluminium–t-butylamine. This compound was prepared similarly to the bromo-derivative and was purified by recrystallizing three times from hexane to give Et_2IAl,NH_2Bu^t, as colourless needles, m.p. 79—80°.

Diethylchloroaluminium–t-butylamine. When t-butylamine (1·80 g, 24·7 mmol) was condensed on to diethylaluminium chloride (2·61 g, 21·7 mmol) in hexane (20 ml) at −196° and allowed to warm to room temperature, the excess of amine and ethane were evolved. The reaction was complete after 2 h and, after removal of the solvent, the residue sublimed at 45°, 10^{-3} mmHg, to give Et_2ClAl,NH_2Bu^t, as a white crystalline solid, m.p. 68—69°.

Triethylaluminium–t-butylamine. This was prepared as reported elsewhere,[8] except that the reaction was carried out in stirred hexane solution to provide better cooling. When ethane evolution had ceased, the solvent was removed on the vacuum line and the liquid product, triethylaluminium–t-butylamine, distilled slowly at 48—50°, 10^{-3} mmHg, without decomposition. There was no observable dissociation pressure at 20°, contrary to the earlier report (Found: Al, 15·1%, *M*, 188. $C_{10}H_{26}AlN$ requires Al, 14·5; *M*, 187).

Thermal Decomposition of Adducts.—Cyclodi-μ-t-butylamido-di(ethylbromoaluminium). A flask containing Et_2BrAl,NH_2Bu^t (3·49 g, 14·7 mmol) was attached to a closed section of the vacuum line under a pressure of 75 mmHg of nitrogen (this allowed the ethane evolution to be monitored whilst preventing the reactant or product from subliming). The flask was heated and gas evolution began at 110 °C. The reaction was complete after 13 h at 120° when 14·7 mmol of ethane had been collected. The solid product was contaminated with a viscous oil which sublimed together with the major product at 65°, 10^{-3} mmHg, but was removed when the product was recrystallized from hexane. A final sublimation gave *cyclodi-μ-t-butylamido-di(ethylbromoaluminium)* as colourless crystals, m.p. 83—92°. The m.p. was always ill defined and the range varied considerably with the isolation procedure (Found: Et, 13·0; Al, 13·6; Br, 38·5%; *M*, 410. $C_{12}H_{30}Al_2Br_2N_2$ requires Et, 13·9; Al, 13·0; Br, 38·5%; *M*, 416). The ^1H n.m.r. spectrum of this compound and the inconsistent m.p. indicated the presence of isomers. Partial separation was achieved by fractional

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[5] A. Storr and A. D. Penland, *J. Chem. Soc.* (*A*), 1971, 1237.

[6] H. Noth and P. Fritz, *Z. anorg. Chem.*, 1963, **324**, 270.

[7] K. Gosling and R. E. Bowen, *Analyt. Chem.*, 1973, **45**, 1574.

[8] K. Gosling, J. D. Smith, and D. H. W. Wharmby, *J. Chem. Soc.* (*A*), 1969, 1738.

recrystallization from hexane at −78° into more- and less-soluble fractions. The more-soluble fraction was fractionally sublimed under vacuum to give compound *A* as the less volatile component in the form of chunky block-like crystals, m.p. 87—100°. The broad melting range of the pure compound was observed when the temperature was raised very slowly. It is apparent that as soon as a liquid phase is present under these conditions, isomerization takes place leading to a mixture of isomers which results in poor definition of the melting point (Found: Et, 14·0; Al, 13·1; Br, 37·2%; *M*, 401. $\mathrm{C_{12}H_{30}Al_2Br_2N_2}$ requires Et, 13·9; Al, 13·0; Br, 38·5%; *M*, 416). The i.r. spectrum did not change over a period of 4 h and the mass spectrum was identical to that of the mixture of isomers.

The less-soluble fraction was fractionally sublimed under vacuum to give compound *B* as the more volatile component in the form of flat block-like crystals, m.p. 88—89° (fast) (Found: Et, 13·9; Al, 13·7; Br, 39·5%. $\mathrm{C_{12}H_{30}Al_2Br_2N_2}$ requires Et, 13·9; Al, 13·0; Br, 38·5%). The i.r. spectrum did not change over a period of 4 h and the mass spectrum was identical to that of the mixed isomers.

From one experiment, a second less volatile component was isolated from the less-soluble fraction in less than 5% yield. The 60 MHz n.m.r. spectrum of a *ca.* 10% solution in benzene (relative areas in parentheses) showed a broad resonance centered at δ 2·74 (2), ($\mathrm{N}H_2$), a triplet at δ 1·27 (3), ($\mathrm{AlCH_2}CH_3$), a singlet at δ 0·60 (9), ($\mathrm{NBu^t}$), and a quartet at δ 0·33 (2), ($\mathrm{Al}CH_2\mathrm{CH_3}$); *J* ($CH_2CH_3$) 8·0 Hz. The n.m.r. spectrum and the characteristic isotope pattern for a principal fragment containing two bromine atoms in the mass spectrum, indicate that this compound is $\mathrm{EtBr_2Al{\text -}NH_2Bu^t}$.

Cyclodi-μ-t-butyldeuterioamido-di(ethylbromoaluminium). $\mathrm{Bu^tND_2Br}$ was added from a rotatable side-arm to an equimolar quantity of $\mathrm{Et_3Al}$ in hexane at 0° under a nitrogen atmosphere. When the initial evolution of ethane had ceased, the solvent was removed under vacuum and the product was heated under nitrogen to 120° for 15 h. $\mathrm{(EtBrAlNDBu^t)_2}$ was purified by recrystallization from hexane followed by vacuum sublimation at 80 °C.

Cyclodi-μ-t-butylamido-di(ethylchloroaluminium). Diethylchloroaluminium–t-butylamine decomposed at 130—150° to liberate ethane over a period of 2 h. The solid product sublimed at 70° under vacuum to give white crystals of $\mathrm{(EtClAlNHBu^t)_2}$. The 60 MHz ^{1}H n.m.r. spectrum of a benzene solution showed single resonances at δ 1·08, 0·93, 0·92, and 0·80 ($\mathrm{Bu^t}$) and a series of quartets centered at δ 0·07 ($\mathrm{Al}CH_2\mathrm{CH_3}$). It was not possible to identify the N*H* or ($\mathrm{AlCH_2}CH_3$) resonances since they were masked by the $\mathrm{Bu^t}$ signals. Integration N*H*, $\mathrm{AlCH_2}CH_3$, and $\mathrm{N}Bu^t$: $\mathrm{Al}CH_2\mathrm{CH_3}$ = 13 : 2.

Cyclodi-μ-t-butylamido-di(ethyliodoaluminium). This compound was prepared by the thermal decomposition of diethyliodoaluminium–t-butylamine in decane solution at 150° under a nitrogen atmosphere. After 12 h no more ethane was evolved. The solvent was distilled off under vacuum and the solid product sublimed under vacuum at 75° to give $\mathrm{(EtIAlNHBu^t)_2}$, m.p. 96—115°. The n.m.r. spectrum of a benzene solution showed a broad peak centered at δ 1·95 (N*H*), single peaks at δ 1·09, 0·97, and 0·93 ($\mathrm{N}Bu^t$) and a complex series of quartets centered at δ 0·22. It was not possible to identify the $\mathrm{AlCH_2}CH_3$ resonances as they were hidden under the $\mathrm{Bu^t}$ signals. Integration, $\mathrm{AlCH_2}CH_3$ and $\mathrm{N}Bu^t$: $\mathrm{Al}CH_2\mathrm{CH_3}$ = 6 : 1.

Cyclodi-μ-t-butylamido-bis(diethylaluminium). The same procedure as reported earlier [8] was used to prepare this compound. It was purified by sublimation under vacuum at 80°.

Cyclodi-μ-t-butyldeuterioamido-bis(diethylaluminium). This compound was prepared similarly to $\mathrm{(Et_2AlNHBu^t)_2}$ except that $\mathrm{Bu^tND_2}$ was substituted for $\mathrm{Bu^tNH_2}$. $\mathrm{(Et_2AlNDBu^t)_2}$ was purified by vacuum sublimation at 80°.

Infrared and Mass Spectra.—I.r. spectra of the adducts $\mathrm{Et_2(X)Al,NH_2Bu^t}$ (X = Et, Cl, Br, and I) and of the amide $\mathrm{(EtBrAlNHBu^t)_2}$, compounds *A* and *B*, together with the mass spectra of the adducts $\mathrm{Et_2XAl,NH_2Bu^t}$ (X = Cl, Br, and I) and $\mathrm{EtBr_2Al,NHBu^t}$, and the amides $\mathrm{(EtBrAlNHBu^t)_2}$ and $\mathrm{(EtBrAlNDBu^t)_2}$ are reported in Supplementary Publication No. SUP 20937 (6 pp.).*

Exchange Reactions.—$\mathrm{(EtXAlNHBu^t)_2}$, X = Br *and* I. Approximately equimolar quantities of $\mathrm{(EtBrAlNHBu^t)_2}$ and $\mathrm{(EtIAlNHBu^t)_2}$ were stirred together in benzene solution at room temperature for 4 h. (This is the time needed for the most stable bromo-isomer to give the equilibrium mixture of isomers.) The solvent was removed and the mass spectrum of the residue was recorded. The principal high mass peaks observed were *m/e* 481(6) $\mathrm{EtI_2Al_2(NHBu^t)_2^+}$, 435(22) $\mathrm{Et^{81}BrIAl(NHBu^t)_2^+}$, 433(23) $\mathrm{Et^{79}BrIAl(NHBu^t)_2^+}$, 389(47) $\mathrm{Et^{81}Br_2Al(NHBu^t)_2^+}$, 387(100) $\mathrm{Et^{81}Br^{79}BrAl(NHBu^t)_2^+}$, and 385(45) $\mathrm{Et^{79}Br_2Al(NHBu^t)_2^+}$. The relative abundances of the $(P - \mathrm{Et})^+$ ions observed in the spectrum serve to demonstrate that exchange has taken place although the absolute intensities will depend upon the relative volatilities of the isomers.

$\mathrm{(EtBrAlNYBu^t)_2}$, Y = H *and* D. Approximately equimolar quantities of $\mathrm{(EtBrAlNHBu^t)_2}$ and $\mathrm{(EtBrAlNDBu^t)_2}$ were mixed in benzene solution at room temperature for 4 h. After removal of the solvent, the mass spectrum of the residue showed the following peaks at *m/e* 391(42) $\mathrm{Et^{81}Br_2Al_2(NDBu^t)_2^+}$, 390(51) $\mathrm{Et^{81}Br_2Al_2(NDBu^t)(NHBu^t)^+}$, 389(100) $\mathrm{Et^{81}Br_2Al_2(NHBu^t)_2^+}$, and $\mathrm{Et^{81}Br^{79}BrAl_2(NDBu^t)_2^+}$, 388(80) $\mathrm{Et^{81}Br^{79}BrAl_2(NHBu^t)(NDBu^t)^+}$, 387(98) $\mathrm{Et^{81}Br^{79}BrAl_2(NHBu^t)_2^+}$, and $\mathrm{Et^{79}Br_2Al_2(NDBu^t)_2^+}$, 386(49) $\mathrm{Et^{79}Br_2Al_2(NHBu^t)(NDBu^t)^+}$, and 385(46) $\mathrm{Et^{79}Br_2Al_2(NHBu^t)_2^+}$. For complete scrambling, the relative intensities would be respectively (24), (49), (75), (100), (76), (51), and (26) modified slightly by other isotope contributions. Although equilibrium had not been achieved in the time allowed, it is evident that exchange does take place at room temperature.

RESULTS AND DISCUSSION

t-Butylamine Adducts.—The adducts $\mathrm{Et_2XAl,NH_2Bu^t}$, X = Cl, Br, and I, were conveniently prepared according to equation (1), and the triethylaluminium adduct by direct combination with an equivalent of amine.[8]

$$\mathrm{Et_3Al + Bu^tNH_3X \longrightarrow Et_2XAl,NH_2Bu^t + EtH} \qquad (1)$$

Cryoscopic molecular weight studies and mass spectral data fail to reveal any dissociation of the adducts. The ^{1}H n.m.r. spectra (Table) are in complete accord with the formulation of the adducts. Each shows a single resonance due to the t-butyl protons indicating no coupling to the protons on the adjacent nitrogen and free rotation about the N–C bond at room temperature compared to

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, index issue; items less than 10 pp. are sent as full-size copies.

the n.m.r. time scale. Two quartets due to the methylene protons (H_x, H_y) of the ethyl groups [$AlCH_xH_yC(H_A)_3$] of the halogen-containing adducts arise because of their magnetic inequivalence, but further splitting of the methyl group triplets is not observed at 60 MHz due presumably to the closely similar coupling constants, J(AX) and J(AY). The triethylaluminium adduct exhibits a single quartet since the ethyl groups and their methylene protons are all magnetically equivalent and this provides good evidence for the free rotation of these groups at room temperature. The spectra of the adducts are distinctly solvent- and concentration-dependent, as has been shown previously for the adduct $Et_2IAl,NHMe_2$,[9] and all resonances shown an upfield shift in benzene relative to carbon tetrachloride solution. This is more marked for the N-protons and to a lesser extent the N-Bu^t protons, and points to the formation of a collision complex between the aromatic solvent and the nitrogen protons.

^{1}H N.m.r. spectra [a] of adducts Et_2XAl,NH_2Bu^t

Compound	$\delta(NH_2)$ [b]	$\delta(Bu^t)$ [c]	$\delta(AlCH_2CH_3)$ [d,e]	$\delta(AlCH_2CH_3)$ [e,f]
Et_3Al,NH_2Bu^t [g]	2·77	1·61	1·33	0·09
$Et_2Cl,AlNH_2Bu^t$ [h]	3·64	1·82	1·45	0·37, 0·33
$Et_2Br,AlNH_2Bu^t$ [h]	4·07	2·00	1·62	0·58, 0·56
$Et_2Br,AlNH_2Bu^t$ [i]	2·60	0·61	1·22	0·12, 0·10
Et_2IAl,NH_2Bu^t [h]	3·77	1·92	1·48	0·55, 0·52

[a] δ-Values in p.p.m. downfield from tetramethylsilane at 0·00. [b] Broad signal. [c] Singlet. [d] Triplet. [e] $J(CH_2CH_3)$ 8·0 Hz for all spectra. [f] Quartets. [g] Neat liquid. [h] *Ca.* 10% solution in CCl_4. [i] *Ca.* 10% solution in C_6H_6.

The isolation of a small quantity (<5%) of the ethylaluminium dibromide adduct $EtBr_2Al,NH_2Bu^t$, during the isomer separation of one sample, was unexpected. That it had escaped decomposition at 120° is in accord with the increased decomposition temperatures required for the adducts as ethyl groups are substituted by halogen atoms, *e.g.* Et_3Al,NH_2Ph (0°), Et_2ClAl,NH_2Ph (25°), and $EtCl_2Al,NH_2Ph$ (120°).[10] Examination of the mass spectrum of unpurified Et_2BrAl,NH_2Bu^t indicated the presence of a small proportion of $EtBr_2Al,NH_2Bu^t$, so that it appears to be formed during the initial reaction between triethylaluminium and t-butylammonium bromide at 0°. It could result from (a) a redistribution reaction (2), or (b) the attack of a second mole of Bu^tNH_3Br on the adduct, followed by loss of Bu^tNH_2 (3), although this type of reaction has not been reported.

$$2Et_2BrAl,NH_2Bu^t \rightleftharpoons Et_3Al,NH_2Bu^t + EtBr_2Al,NH_2Bu^t \quad (2)$$

$$\begin{array}{l} Et_2BrAl,NH_2Bu^t + Bu^tNH_3Br \longrightarrow [EtBr_2Al(NH_2Bu^t)_2] + EtH \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad EtBr_2Al,NH_2Bu^t + Bu^tNH_2 \quad (3) \end{array}$$

Both reactions (2) and (3) would result in the formation of Et_3Al,NH_2Bu^t and this is also probably present in the mass spectrum of the crude adduct, so that an unequivocal explanation for the formation of the ethylaluminium dibromide adduct cannot be made at this time.

Cyclodi-μ-t-butylamido-di(ethylbromoaluminium).— The decomposition of diethylbromoaluminium–t-butylamine takes place rapidly at 120° with quantitative elimination of ethane, reaction (4). The analysis, cryoscopic mole-

$$2Et_2BrAl,NH_2Bu^t \xrightarrow{120^\circ} (EtBrAlNHBu^t)_2 + 2EtH \quad (4)$$

cular weight, and mass spectral information indicate that the product of decomposition is the dimer $(EtBrAlNHBu^t)_2$. However, the broad melting range and the complex n.m.r. spectrum (Figure 1) which exhibits three, or possibly four, signals due to the N-*Bu*^{t} protons, suggests that a mixture of three (of four) isomers is present. In the following, these compounds will be referred to as compounds *A*, *B*, *C*, and *D*. It is unlikely that these compounds contain bromine bridges with the superior donor t-butylamido groups in terminal positions, since it has been shown that the chlorine bridges in $(Me_2AlCl)_2$ are split by relatively weak donors such as ethers, and also that the bridging strength decreases in the order Cl > Br > I.[11] It is also possible to exclude mixed-bridge molecules since the 250 MHz n.m.r. spectra do not show a compound with two inequivalent t-butyl groups in the ratio 1 : 1 which would be required for N-Bu^t groups in both bridging and terminal positions. Assuming that all the isomers contain the $(AlN)_2$ ring system, there are five possible stereoisomers (Figure 2). Although the all-*trans*-isomer (II)

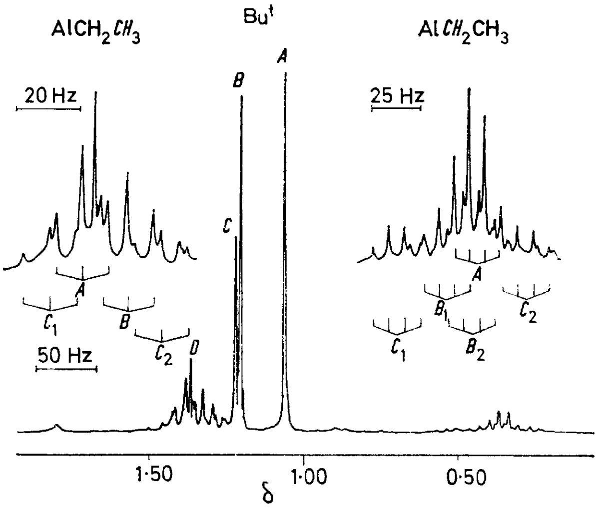

FIGURE 1 The 250 MHz ^{1}H n.m.r. spectrum of the mixture of isomers of $(EtBrAlNHBu^t)_2$ in benzene solution. Signals due to compounds *A*, *B*, *C*, and *D* are indicated. Chemical shifts for compound *C*: δ 1·441, 1·302 ($AlCH_2CH_3$), δ 1·242 (Bu^t), and δ 0·536, 0·268 ($AlCH_2CH_3$); $J(CH_2CH_3)$ 8·16 Hz. δ-Values are downfield from tetramethylsilane. The nitrogen proton resonance was not resolved

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[9] K. Gosling and A. L. Bhuiyan, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 329.

[10] J. K. Gilbert and J. D. Smith, *J. Chem. Soc.* (*A*), 1968, 233.

[11] C. A. Smith and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1967, 7.

might be expected to have a planar ring, models indicate that steric interactions between ethyl and t-butyl groups in the remaining isomers would be considerably reduced if the ring were non-planar. Planar $(AlN)_2$ rings have been indicated by single crystal *X*-ray studies of the symmetrical $Al_2(\mu\text{-}NMe_2)_2Me_4$ [3,12] and $[Al_2(\mu\text{-}(p\text{-}BrC_6H_4)PhC{:}N)_2Ph_4],2C_6H_6$ [13] (trigonal nitrogen) compounds, and a non-planar $\overline{\text{Al–C–Al–N}}$ ring was found in $Al_2(\mu\text{-}NPh_2)(\mu\text{-}Me)Me_4$ [14] which was attributed to steric interactions between the Ph groups and the terminal Me groups on the aluminium atoms. Similarly, steric factors and crystal packing forces have been deemed responsible for the non-planarity of $(AlC)_2$ rings in $Al_2(\mu\text{-}Ph)_2Me_4$ [15] and $Al_2(\mu\text{-}cyclopropyl)_2(cyclopropyl)_4$.[16]

Careful fractional sublimation of $(EtBrAlNHBu^t)_2$ resulted in the isolation of two distinct crystalline compounds, *A* and *B*. A single crystal of *A* suitable for *X*-ray studies was obtained and a preliminary investigation [17] indicates that this is the all-*cis*-isomer (I), 1α,3α-di-t-butyl-2α,4α-dibromo-1β,3β-dihydro-2β,4β-diethyl-cyclodialuminatazoniane, in which the bromine atoms and t-butyl groups are on the same side of the $(AlN)_2$ ring. The ring is non-planar so as to give maximum separation of the t-butyl groups without creating close bromine–bromine interactions.

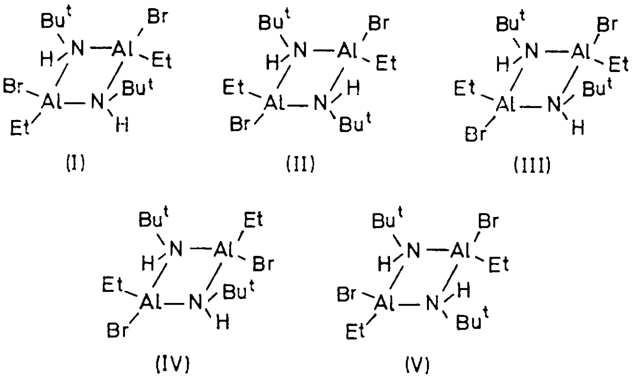

FIGURE 2 The five possible stereoisomers of $(EtBrAlNHBu^t)_2$

The corroboration of the structure of compound *A* and the identification of the structure of compounds *B* and tentatively that of *C* is provided by their 250 MHz ^1H n.m.r. spectra. The following arguments are based upon the observation, discussed later, that the isomers interconvert slowly on the n.m.r. time scale and that there is no restriction of rotation about Al–C or N–C bonds. This latter point is in agreement with the interpretation of the n.m.r. spectra of the adducts and is also verified by scale models of the molecules.

The n.m.r. spectrum of compound *A* (Figure 3), recorded as soon as possible after dissolution, is simple, as would be expected for isomer (I) in which the t-butyl protons and nitrogen protons are equivalent and lead to single resonances, and the ethyl groups are equivalent and give rise to a triplet and a quartet for the methyl and methylene protons, respectively.

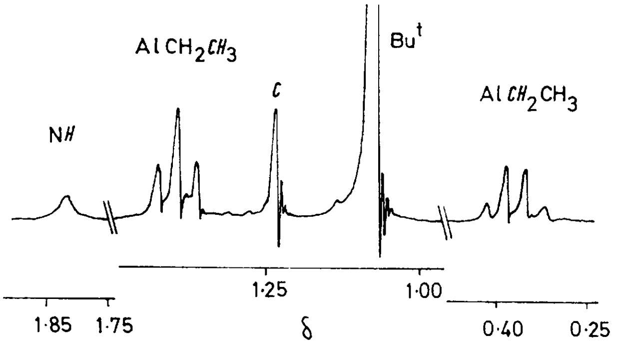

FIGURE 3 The 250 MHz ^1H n.m.r. spectrum of compound *A* in benzene solution. Chemical shifts: δ 1·818 (N*H*), δ 1·401 ($AlCH_2CH_3$), δ 1·085 (Bu^t), and δ 0·370 ($AlCH_2CH_3$); $J(CH_2CH_3)$ 8·00 Hz. The appearance of compound *C* is shown by its Bu^t proton resonance at δ 1·242. δ-Values are downfield from tetramethylsilane

The n.m.r. spectrum of compound *B* (Figure 4), recorded rapidly following dissolution, shows single resonances for the nitrogen protons and the t-butyl protons and a triplet and two equal intensity quartets for the methyl and methylene protons of the ethyl groups. Isomer (V) would be expected to show two distinct t-butyl proton resonances in the ratio 1 : 1 since one t-butyl group is adjacent to two bromine atoms whilst the other is in close proximity to two ethyl groups. Isomer (IV) would be expected to show a single triplet and quartet for the ethyl group protons since the ethyl groups and the methylene protons are equivalent. Isomer (III) has

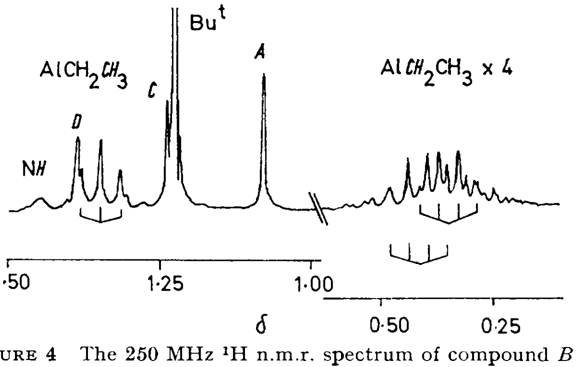

FIGURE 4 The 250 MHz ^1H n.m.r. spectrum of compound *B* in benzene solution. Chemical shifts: δ 1·445 (N*H*), δ 1·345 ($AlCH_2CH_3$), δ 1·228 (Bu^t), and δ 0·433, 0·383 ($AlCH_2CH_3$); $J(CH_2CH_3)$ 8·05 Hz. The appearance of the t-butyl signals from compounds *A*, *C*, and *D* is indicated. δ-Values are downfield from tetramethylsilane

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ethyl groups in different environments, but each has equivalent methylene protons and would be expected to show two quite distinct triplets for the methyl protons of the ethyl groups [as described later for the *cis*-isomer of $(Et_2AlNHBu^t)_2$] and two quartets for the methylene protons. This leaves isomer (II), the all-*trans*-molecule, in which the t-butyl protons are equivalent, the nitrogen protons are equivalent and the ethyl groups are equivalent, but the latter contain inequivalent methylene protons. The ethyl groups could give rise to a complex A_3XY pattern, but if $J(AX) = J(AY)$ and $J(XY) = 0$, or if $J(AX) = J(AY)$ and $J(XY)/\Delta\nu(XY)$ is large (*ca.* 1 or larger), then this would be reduced to a triplet and two quartets. [Since neither $J(XY)$ nor $\Delta\nu(XY)$ can be deduced accurately from the observed spectrum, and geminal coupling constants are notably sensitive to the electronegativity of the adjacent atom and to bond lengths and angles, a precise interpretation is not possible.] Compound *B* is thus assigned as isomer (II), 1α,3β-di-t-butyl-2α,4β-dibromo-1β,3α-dihydro-2β,4α-diethylcyclodialuminatazoniane.

The third compound observed in the n.m.r. spectrum of the solution of isomers is compound *C*. By subtracting the spectra of compounds *A* and *B* from the spectrum of the mixture (Figure 1), the remainder is found to contain a single t-butyl proton resonance, two well separated triplets for the methyl protons of the ethyl group, and two quartets for the methylene protons.

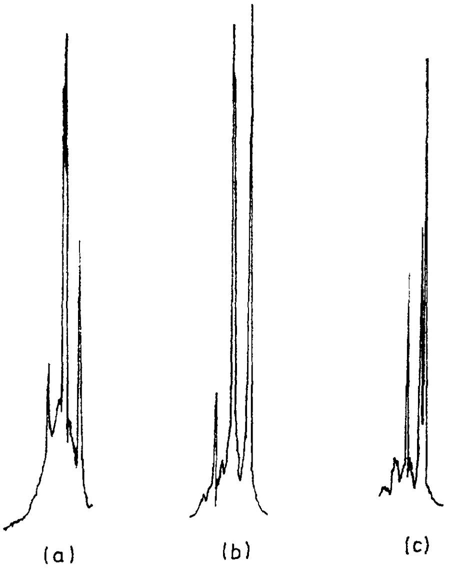

FIGURE 5 The 60 MHz ^1H n.m.r. spectra of the t-butyl proton signals of the mixtures of isomers: (a), $(EtClAlNHBu^t)_2$; (b), $(EtBrAlNHBu^t)_2$; and (c), $(EtIAlNHBu^t)_2$ in benzene solution. The base-line is complicated by the underlying ethyl group methyl signals

Isomers (IV) and (V) are again disqualified for the reasons noted earlier, which leaves compound *C* to be tentatively assigned as isomer (III), 1α,3α-di-t-butyl-2α,4β-dibromo-1β,3β-dihydro-2β,4α-diethylcyclodialuminatazoniane.

The sharp resonance at δ 1·385 seen in the spectrum of the benzene solution of the mixture cannot be attributed to the methyl protons of the ethyl groups of any of the assigned isomers and is absent from the initial spectra of the isolated compounds. The signal moves downfield together with the other t-butyl proton signals in carbon tetrachloride solution and it may therefore be due to the t-butyl signal of a small quantity of another isomer, *D*, but there is insufficient data to justify an assignment.

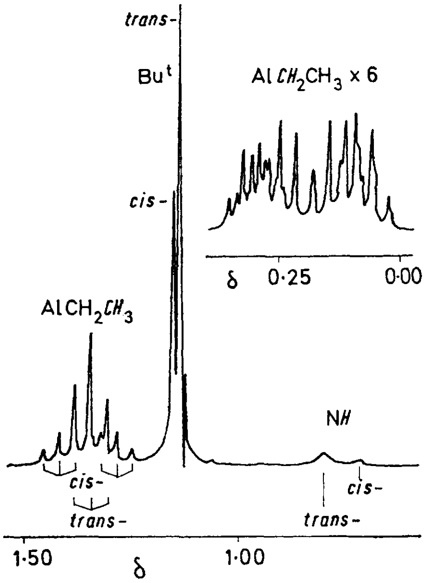

FIGURE 6 The 250 MHz n.m.r. spectrum of the mixture of *cis*- and *trans*-isomers of $(Et_2AlNHBu^t)_2$ in benzene solution. Chemical shifts: *cis*-isomer, δ 1·426, 1·313 ($AlCH_2CH_3$), δ 1·194 (Bu^t), and δ 0·817 (NH); $J(CH_2CH_3)$ 7·9 Hz; *trans*-isomer, δ 1·365 ($AlCH_2CH_3$), δ 1·178 (Bu^t), and δ 0·861 (NH); $J(CH_2CH_3)$ 8·2 Hz. δ-Values are downfield from tetramethylsilane. The spectrum of $(Et_2AlNDBu^t)_2$ is identical except for the absence of the nitrogen proton signals

Evidence for Isomers of $(EtClAlNHBu^t)_2$, $(EtIAlNHBu^t)_2$, *and* $(Et_2AlNHBu^t)_2$.—The t-butyl proton resonance regions of the 60 MHz n.m.r. spectra of $(EtClAlNHBu^t)_2$ and $(EtIAlNHBu^t)_2$ (Figure 5) show considerable similarity to that of the mixed bromo-isomers and all exhibit at least three inequivalent t-butyl proton resonances. Partial separation of compounds with distinct t-butyl proton signals was achieved during routine sublimation of the iodo-compound and it seems reasonable to suppose that these compounds also exist as mixtures of isomers in solution, but no attempt has been made to study them in detail.

The n.m.r. spectrum of $(Et_2AlNHBu^t)_2$ has been reported.[8] Previously, it was considered that a mixture of *cis*- and *trans*-isomers was unlikely and the presence of two signals, attributed to the t-butyl protons and separated by *ca.* 1 Hz, was due to the splitting of the resonance by the proton on the adjacent nitrogen atom in the *trans*-isomer. We have recorded the 250 MHz n.m.r. spectrum of $(Et_2AlNHBu^t)_2$ (Figure 6), and find that the two t-butyl proton signals are of unequal intensity and that their separation is now 4·0 Hz, suggesting that inequivalent t-butyl groups are present. We have also prepared the deuteriated compound $(Et_2AlNDBu^t)_2$ and find that in this compound the two t-butyl proton resonances are unchanged and conclude that both *cis*- and *trans*-isomers are indeed present, but in unequal proportions at room temperature.

Although the methylene proton resonance region of $(Et_2AlNHBu^t)_2$ is complex, it is possible to assign the rest of the spectrum to specific isomers. The *cis*-isomer has magnetically equivalent nitrogen and t-butyl protons and both should result in single resonances. However, there are two magnetically inequivalent types of ethyl groups in the molecule of the dimer, although in each type the methylene protons are equivalent. This should give rise to two triplets and two quartets for the methyl and methylene protons, respectively, of the ethyl groups. The two triplets can be discerned in the spectrum shown in Figure 6. The total area under these peaks, determined using a planimeter, compares to the area under the low field t-butyl proton signal in the ratio 2 : 3, leading to the assignment of these resonances to the *cis*-isomer. Similarly, the smaller, higher field, nitrogen proton resonance is assigned to the *cis*-isomer and is consistent with the greater shielding experienced by these protons in the non-planar ring compound.

The *trans*-isomer also contains equivalent nitrogen protons and t-butyl protons and all ethyl groups are equivalent. However, the methylene protons of each ethyl group are not magnetically equivalent[8] and this could give rise to a complex A_3XY pattern with two triplets in the methyl proton region and possibly 16 lines in the methylene proton region of the spectrum. But if $J(AX) = J(AY)$, such a complex pattern would not be observed and a single triplet would be evident for the methyl protons. Thus the larger triplet observed in the methyl region of the spectrum is assigned to the *trans*-isomer as also is the larger high-field t-butyl proton signal, and the larger low-field nitrogen proton resonance. Integration of these peaks is in total agreement with that expected for $(Et_2AlNHBu^t)_2$. Also, integration of the t-butyl proton signals allows the ratio of *cis*-to-*trans*-isomers in benzene solution at 25° to be estimated as 1 : 2.

Stereoisomer Interconversion.—Complete conversion of isomers (I) and (II) to the equilibrium mixture of isomers takes place in benzene solution at room temperature in 150 and 50 min, respectively, and was observed by their changing n.m.r. spectra. The slower rate for isomer (I) and its predominance in the equilibrium mixture [approximate relative proportions, (I) : (II) : (III) = 1·8 : 1·6 : 1·0] reflects the greater stability of this stereoisomer. From scale models of the isomers, it is clear that isomer (I), with a non planar $(AlN)_2$ ring, has the least steric interactions between terminal ethyl and t-butyl groups, and bromine atoms. Such steric control of the relative stabilities of the stereoisomers agrees well with recent work in which steric factors were found to predominate in determining the respective stability of $(AlN)_2$ and $(AlN)_3$ rings. Valency angle strain appears to be much less important in $(AlN)_n$ rings considering the wide variations found in N–Al–N and Al–N–Al angles, respectively, in *cis*-$(Me_2AlNHMe)_3$ (102, 122°) and $(Me_2AlNMe_2)_2$ (88·3, 91·7°).[3]

A qualitative study on the rate at which the partially separated isomers of the iodo-compound $(EtIAlNHBu^t)_2$, achieved equilibrium, indicated that the interconversion was appreciably slower than the bromo-compounds. In turn, these rates are considerably slower than for $(Me_2AlNHMe)_3$ for which it was found impossible to obtain spectra of the individual isomers, even when the solutions were cooled to −40° immediately after dissolution.[2] These results are consistent with the idea that the rate determining step in the interconversion reaction is the cleavage of the $(AlN)_2$ ring. The relative stability of $(AlN)_2$ rings should be a function of the acceptor properties of the aluminium atoms in the monomers and should follow the order $(EtXAlNHBu^t)_2$, X = Et < Cl < Br < I, which is in accord with a study of the acceptor properties of the diethylaluminium halides towards trimethylamine.[11]

All stereoisomers of $(EtBrAlNHBu^t)_2$ could interconvert through successive cleavages of an Al–N bridge, leading to an intermediate in which the terminal aluminium and nitrogen atoms are approximately trigonally co-ordinated. Rotation about a terminal Al–N bond and reformation of the ring leads to a different isomer. However, this simple mechanism is not confirmed by experiments in which the closely related compounds, $(EtBrAlNHBu^t)_2$ and $(EtIAlNHBu^t)_2$ were mixed in benzene solution at room temperature. After removal of the solvent, the mass spectrum of the residue showed that scrambling of bromine and iodine atoms had taken place as indicated in equation (5). Similarly, when

$$(EtBrAlNHBu^t)_2 + (EtIAlNHBu^t)_2 \rightleftharpoons EtBrAl(NHBu^t)_2AlIEt \quad (5)$$

$(EtBrAlNHBu^t)_2$ and $(EtBrAlNDBu^t)_2$ were mixed, scrambling of hydrogen and deuterium was evident as shown in equation (6).

$$(EtBrAlNHBu^t)_2 + (EtBrAlNDBu^t)_2 \rightleftharpoons (EtBrAl)_2(NHBu^t)(NDBu^t) \quad (6)$$

Although it is conceivable that halogen exchange could take place *via* halogen bridges between dimer molecules, involving five-co-ordinate aluminium atoms in the transition state, it is improbable that hydrogen–deuterium exchange at the nitrogen atoms could occur by a similar mechanism. Ring opening, followed by hydrogen–deuterium exchange at three-co-ordinate nitrogen atoms of different molecules, or exchange of $NHBu^t$ and $NDBu^t$ groups between molecules, seem more likely routes. Similarly, ring opening followed by halogen or EtAlX group exchange seems more plausible. Thus we can only deduce that the isomer interconversion reaction is complex and may involve many transient species which we have been unable to detect.

Mass Spectra.—The common feature of the mass spectra of the adducts Et_2XAl,NH_2Bu^t, X = Cl, Br, and I is that the parent ion is not observed, but that in all cases an ion resulting from the loss of ethyl from the parent is abundant. Characteristic isotope patterns of bromine and chlorine provide valuable confirmation of the number of these atoms in the ions and show that Al–X bonds persist in the fragmentation pattern down to the ion $HAlX^+$ in the monohalogenoadducts and $AlBr_2^+$ in the single dihalogenoadduct studied.

The base peak in the spectra of all the adducts occurs at *m/e* 58. This is also found to dominate the spectra of Bu^tNH_2[18] and Bu^tNH_3Br, whilst the correspondingly intense peak occurs at *m/e* 60 in Bu^tND_3Br. This suggests the ion $Me_2C=NH_2^+$ (or $Me_2C=ND_2^+$) which could arise through the loss of a methyl radical by the characteristic cleavage at the α-carbon atom,[18] of Bu^tNH_2 (or Bu^tND_2). Further fragmentation of this ion occurs through the loss of NH_3 and leads to a peak at *m/e* 41, $C_3H_5^+$. This ion is also found in the spectrum of Bu^tND_3Br and would arise through similar loss of NHD_2. These eliminations are supported by metastable peaks and peaks due to NH_3 or NHD_2.

No parent peak is observed for the dimers, but again the ion resulting from the loss of ethyl from the dimer is observed. There is no evidence for the breakdown of the dimers into monomers in the gas phase, as has been shown to be the predominant reaction in the case of $(Me_2AlNHMe)_3$,[2] $(Et_2AlNHMe)_3$, and $(Et_2AlNHBu^t)_2$,[8] since neither monomer ions nor ions due to the loss of ethyl from the monomer, are observed. Unlike the adducts, the base peak for the dimers $(EtBrAlNHBu^t)_2$ and $(EtBrAlNDBu^t)_2$ occurs at *m/e* 57, probably meaning that simple loss of $C_4H_9^+$ is preferred.

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