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THE CHEMISTRY AND THE STEREOCHEMISTRY OF POLY(*N*-ALKYLIMINOALANES)

III*. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE ADDUCT $(HAlN\text{-}i\text{-}Pr)_6AlH_3$

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Summary

The crystal and molecular structure of the adduct $(HAlN\text{-}i\text{-}Pr)_6AlH_3$ has been determined from single-crystal and three dimensional X-ray diffraction data collected by counter methods. The cage-type molecular structure consists of two six-membered rings, $(AlN)_3$, joined together by four adjacent transverse Al—N bonds; the loss of two of these bonds allows the complexation of one alane molecule, with five-coordination of the aluminum (trigonal bipyramidal geometry), through two Al—N bonds and two Al—H—Al bridge bonds. The Al—N bond lengths range from 1.873 to 1.959 Å; the average Al—H bond length is 1.50(1) Å for the four-coordinated aluminum atoms; the average distance of the two apical hydrogens from the five-coordinated aluminum atom is 1.92(5) Å. Colourless prismatic crystals of the compound have the following crystal data: triclinic space group $P\bar{1}$; a = 17.13(2); b = 10.78(2); c = 10.20(2) Å α = 124.3(4), β = 92.0(4), γ = 92.1(5); Z = 2; calculated density 1.157 g/cm^3. The structure has been refined by block-matrix, least-squares methods using 4358 independent reflections to a standard unweighted R factor of 4.9%.

Introduction

The resolution of the crystal structure of the hexamer $(HAlN\text{-}i\text{-}Pr)_6$ was reported in a previous paper of this series [1] and we now describe the investigation of the structure of its adduct $(HAlN\text{-}i\text{-}Pr)_6AlH_3$. In the preparation of poly(*N*-alkyliminoalanes), (PIA), evidence was frequently obtained both from chemical analyses and spectroscopic (mass and NMR) investigations for the

* For parts I and II see refs. 7 and 1.

existence of adducts between cage molecules of PIA and molecules of alane, but attempts to separate and identify such compounds were until recently largely unsuccessful.

A crystalline powder of the title compound, referred to as PIAHAL, was isolated by one of us (A.B.) during a large-scale preparation of poly(*N*-isopropyliminoalane) from sodium hydride, aluminum chloride and isopropylamine using a mixture of diethyl ether and hexane (1/1) as solvent. Single crystals, suitable for X-ray analysis, were obtained from a solution of this powder in heptane at room temperature. Although there are strong indications that other adducts exist, some of which are highly unstable, it is hoped that determination of the structure of PIAHAL will give insight into the general features of the bonding between the alane molecule and the cage-type structures of PIA.

Experimental

Colourless crystals of PIAHAL, roughly prismatic in shape, were sealed in thin-walled glass capillary under an atmosphere of dry nitrogen and were first examined by Weissenberg photographs. In the absence of any lattice symmetry or systematic absences, the space group $P\bar{1}$ was assumed. The successful refinement confirmed this assignment. The unit cell parameters were refined by a least-squares fit to the setting angles measured for 23 reflections on the diffractometer. The crystal data are summarized in Table 1.

Intensity data were collected from a crystal of dimensions 0.25 × 0.4 × 0.75 mm, mounted with the *c* axis parallel to the axis of a Siemens AED automated diffractometer, using Mo-K_α radiation. Other experimental conditions were identical to those described in a previous paper of this series [1]. A total of 5430 reflections were collected within an hemisphere up to $(\sin\theta)/\lambda = 0.60$ Å^{-1}; 4358 reflections, whose intensities were greater than 2.5 $\sigma(I)$, where $\sigma(I)$ is defined as [total counts + $(0.005\ I)^2$]$^{1/2}$, were used for the structure determination. A standard reflection (6 0 0) measured every 15 reflections, monitored the intensity fluctuations, which did not exceed 6%. Intensities were corrected for this effect by means of a simple linear interpolation method. No absorption correction was applied in view of the low transmission factor ($\mu R < 0.2$ for Mo-K_α). The intensities were subjected to the usual Lorentz and polarization corrections and put on an absolute scale by Wilson's statistical method.

TABLE 1

CRYSTAL DATA FOR $(HAlN\text{-}i\text{-}Pr)_6AlH_3$

Molecular formula:	$[HAlN(iso\text{-}C_3H_7)]_6AlH_3$
Molecular weight:	540.5
Space group:	Triclinic, $P\bar{1}$
Molecules/unit cell:	2
Calculated density:	1.157 g/cm^3
Cell constants[a]:	a = 17.13(2), b = 10.78(2), c = 10.20(2) Å; α = 124.3(4)°, β = 92.0(4)°, γ = 92.1(4)°
Cell volume:	1550.7 Å^3

[a] Mo-K_α radiation, λ 0.71069 Å

The values obtained were used for the calculation of structure factor amplitudes $|F|$ and the normalized structure factor amplitudes $|E|$.

Structure determination and refinement

The solution of the structure was performed by direct methods, using the MULTAN program written by Main et al. [2]. The 400 strongest reflections, with $|E| > 1.74$ and the 50 lowest reflections were used as input data. The program gave 64 solutions, of which that having the 'figures of merit' ABS FOM = 1.195 and PSI ZERO = 3215, led to the correct solution of the structure. The set of the starting reflections were: 5 3 2, 2 $\bar{4}$ 7, 5 $\bar{4}$ 6 fixing the origin and 7 3 2, 1 $\bar{8}$ 5, 6 4 2, 11 $\bar{2}$ 2, 3 5 $\bar{5}$, 6 4 1 with variable phases. From an E-map all the seven aluminum and six nitrogen atoms were located, and a residual R 0.35 was calculated. The next Fourier synthesis allowed the location of all of the 18 carbon atoms, reducing the R value to 0.22. After four block-matrix least-squares cycles, with thermal isotropic parameters, a ΔF-map was calculated and the coordinates of all hydrogen atoms (51) were derived. The next five least-squares cycles, with anisotropic thermal factors for all the atoms excluding the hydrogen atoms, for which fixed thermal factors were used, led to an R factor of 0.055. After a few more cycles, with the inclusion of isotropic thermal refinement of the hydrogen atoms (the positional shifts were limited by a 'damping factor' of 0.5) a final R factor of 0.049 was obtained. The function minimized was $\Sigma w(F_o - F_c)^2$, using Cruickshank's weighting scheme [3]. The atomic scattering factors used, assuming that no atoms are charged, were those of Moore [4]. With the exception of the program MULTAN, all the other programs were those of Immirzi [5].

The final values of the positional and thermal parameters are given in Table 2. A list of the structure factors may be obtained from the authors on request.

Results and discussion

The molecular structure of PIAHAL derives directly from that of the previously described hexamer $(HAlN\text{-}i\text{-}Pr)_6$ (referred to as PIAHEX). A molecule of PIAHEX is able to bind to a molecule of AlH_3, with five-coordination of the aluminum atom, by the opening of two adjacent Al—N bonds, which join the two six-membered rings, $(AlN)_3$, of the hexagonal cage. The distortion needed for this bonding affects essentially only one half of the cage, as is schematically illustrated in Fig. 1. The partial deformation of the cage molecule of PIAHEX is shown by the values of the internal rotation angles around the Al—N bonds of the two six-membered rings, reported in Table 3, together with other geometrical parameters. While in PIAHEX all these angles average ca. ± 8°, here the torsion angles of the three adjacent bonds of the two six-membered rings (i.e. the pairs of bonds 1, 2 and 3 in Fig. 1b) average 35.7°, −48.5° and 23.4° respectively. Individual values of the internal rotation angles can be better discussed with the aid of the Fig. 2, which shows a labelled projection of the whole molecule. From this figure it is apparent also that the molecule possesses, at least approximately, a binary symmetry with a two-fold axis passing through the five-coordinated aluminum, [Al(7)], and the centre of the opposite four-mem-

TABLE 2

ATOMIC FRACTIONAL COORDINATES (× 10^4) AND THERMAL PARAMETERS (× 10^2 Å^2) FOR $(HAlN\text{-}i\text{-}Pr)_6AlH_3$[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al(1)	3120(0)	988(1)	6025(1)	333(3)	243(3)	270(3)	47(3)	8(3)	151(3)
Al(2)	1347(0)	1637(1)	5126(1)	299(3)	228(3)	263(3)	29(2)	17(2)	119(3)
Al(3)	2231(1)	1928(1)	8719(1)	403(4)	313(4)	272(3)	37(3)	37(3)	120(3)
Al(4)	2551(0)	464(1)	3267(1)	344(3)	229(3)	219(3)	43(3)	28(2)	106(3)
Al(5)	2044(1)	3789(1)	4211(1)	479(5)	271(3)	372(4)	15(3)	-41(3)	193(3)
Al(6)	3522(1)	3581(1)	6344(1)	351(4)	247(3)	277(3)	4(3)	-7(3)	139(3)
Al(7)	1858(1)	5255(1)	7305(1)	430(4)	237(3)	392(4)	65(3)	39(3)	133(3)
N(1)	2126(1)	301(2)	4913(2)	334(10)	205(8)	240(9)	20(7)	5(7)	118(7)
N(2)	1428(1)	3517(2)	7122(3)	330(10)	257(9)	307(10)	64(8)	36(8)	111(8)
N(3)	3163(1)	3047(2)	7780(2)	342(10)	260(9)	226(8)	20(7)	-26(7)	110(7)
N(4)	1788(1)	1801(2)	3478(3)	322(10)	258(9)	263(9)	19(7)	-24(7)	152(8)
N(5)	2795(1)	4734(2)	6110(3)	391(11)	205(9)	309(10)	19(8)	10(8)	130(8)
N(6)	3478(1)	1496(2)	4590(3)	301(10)	265(9)	288(9)	57(7)	43(7)	150(8)
C(1)	1748(2)	-1116(3)	4643(4)	447(14)	263(11)	417(14)	-39(10)	-25(11)	217(11)
C(2)	1627(2)	-925(4)	6207(5)	588(19)	467(17)	554(18)	39(14)	122(15)	366(15)
C(3)	2211(2)	-2470(4)	3574(5)	730(22)	270(13)	523(18)	58(13)	86(16)	205(13)
C(4)	669(2)	394(3)	7992(4)	384(14)	329(13)	406(14)	95(11)	125(11)	94(12)
C(5)	36(2)	4251(5)	7120(5)	417(17)	528(19)	695(22)	154(14)	83(15)	302(18)
C(6)	344(2)	2752(4)	8240(4)	474(18)	510(18)	465(17)	56(14)	143(14)	215(15)
C(7)	3808(2)	3424(4)	9059(4)	373(13)	426(14)	306(12)	20(11)	-44(10)	197(11)
C(8)	3925(2)	5125(4)	10304(4)	519(17)	442(16)	335(14)	-44(13)	-110(13)	111(13)
C(9)	3671(3)	2592(5)	9839(5)	676(22)	643(21)	436(17)	-6(17)	-71(15)	377(17)
C(10)	1227(2)	1036(4)	1980(4)	461(15)	356(13)	331(13)	-44(11)	-117(11)	181(11)
C(11)	516(2)	1946(5)	2249(5)	471(17)	640(21)	548(19)	69(15)	-131(15)	338(17)
C(12)	1621(3)	737(4)	537(4)	701(22)	509(18)	358(15)	-27(16)	-39(14)	236(14)
C(13)	3146(2)	61 5(3)	6325(4)	473(16)	284(12)	481(16)	-39(11)	-2(12)	229(12)
C(14)	3776(2)	5869(4)	5200(5)	664(22)	418(16)	559(19)	-73(15)	28(16)	307(15)
C(15)	3457(3)	7347(4)	8045(5)	676(22)	332(15)	513(18)	-87(14)	21(16)	156(14)
C(16)	4237(2)	1038(4)	3779(4)	305(12)	436(14)	372(13)	72(10)	85(10)	205(12)
C(17)	4266(2)	1444(5)	2554(5)	620(21)	613(20)	500(18)	50(16)	187(15)	348(17)
C(18)	4369(2)	-602(4)	3005(5)	477(17)	476(17)	547(18)	205(14)	152(14)	230(15)

Atom	x	y	z	B	Atom	x	y	z	B
H(Al1)	3563(20)	-66(39)	6240(41)	250(74)	H'''(C8)	4347(25)	5292(49)	10944(52)	425(103)
H(Al2)	560(21)	862(41)	4643(43)	282(80)	H''(C9)	3189(26)	2982(51)	10354(53)	467(108)
H'(Al3)	1994(24)	3815(47)	10052(50)	390(95)	H'''(C9)	3595(25)	1520(49)	9102(52)	451(106)
H'''(Al3)	2351(21)	5686(42)	9183(44)	265(79)	H'''(C9)	4150(27)	2793(54)	10431(57)	512(117)
H(Al4)	2621(20)	-863(40)	1659(42)	242(75)	H(C10)	1030(20)	5(39)	1752(42)	219(73)
H'(Al5)	2299(27)	4102(53)	3980(57)	565(113)	H''(C11)	245(24)	2159(47)	3036(49)	356(94)
H'''(Al5)	1417(24)	4730(46)	5225(50)	346(95)	H'''(C11)	720(25)	2842(49)	2375(51)	421(101)
H(Al6)	4350(22)	4279(43)	6800(45)	328(83)	H'''(C11)	107(25)	1306(46)	1298(50)	402(97)
H(Al7)	1478(23)	6828(44)	8174(47)	331(87)	H''(C12)	2121(26)	277(50)	347(53)	470(107)
H(C1)	1232(19)	-1320(37)	4161(40)	176(70)	H'''(C12)	1768(24)	1750(47)	827(50)	383(96)
H''(C2)	2075(23)	-746(44)	6752(47)	331(89)	H'''(C12)	1236(30)	83(58)	296(62)	672(139)
H'''(C2)	1292(25)	-229(48)	676(52)	449(102)	H(C13)	2725(20)	6525(39)	6068(42)	215(73)
H'''(C2)	1355(27)	-1804(54)	5913(57)	523(118)	H''(C14)	4226(23)	5601(45)	5446(48)	354(92)
H''(C3)	2722(24)	-2362(48)	3940(51)	419(100)	H'''(C14)	3581(24)	5195(45)	4200(48)	347(93)
H'''(C3)	2252(25)	-2601(47)	2582(50)	404(98)	H'''(C14)	3949(28)	6757(54)	5288(58)	536(118)
H'''(C3)	1924(26)	-3310(51)	3434(55)	491(110)	H''(C15)	3917(23)	6968(44)	8274(47)	382(90)
H(C4)	825(19)	4895(37)	9070(39)	164(68)	H'''(C15)	3054(26)	7589(49)	8748(53)	473(106)
H'(C5)	-91(24)	3411(46)	6134(49)	367(96)	H'''(C15)	3549(29)	8215(55)	8061(60)	611(131)
H''(C5)	239(25)	4891(49)	6852(52)	442(102)	H(C16)	4648(23)	1652(44)	4573(47)	332(88)
H'''(C5)	-388(28)	4038(55)	7832(58)	525(119)	H''(C17)	4718(27)	1170(52)	2142(57)	486(115)
H'(C6)	740(26)	2600(50)	8788(54)	472(108)	H'''(C17)	4228(27)	2550(52)	3156(55)	491(110)
H''(C6)	204(23)	1836(44)	7174(48)	336(90)	H'''(C17)	3888(25)	759(48)	1664(51)	418(101)
H'''(C6)	-188(28)	3081(56)	8907(60)	567(126)	H'(C18)	4011(25)	-1234(48)	2168(51)	418(101)
H(C7)	4285(20)	3167(39)	8535(41)	202(73)	H''(C18)	4345(24)	-861(47)	3702(50)	384(96)
H'(C8)	4082(22)	5662(44)	9824(47)	331(89)	H'''(C18)	4850(29)	-768(58)	2569(62)	608(131)
H''(C8)	3480(23)	5358(44)	10875(47)	313(86)					

[a] Anisotropic thermal factor defined by $\exp[-\frac{1}{4}[B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$. Standard deviations in parentheses in this and following tables, refer to the last digit quoted.

bered ring, [N(1)—Al(1)—N(6)—Al(4)]. It should be noted that an important effect on the hexameric cage, arising from the complexation of the molecule of alane, is the change in the Al—N bond distances in the six-membered rings, which in PIAHEX average uniformly 1.898(3) Å. In PIAHAL, short Al—N bond distances alternate with long ones, the two average lengths being 1.923(6) and

(continued on p. 40)

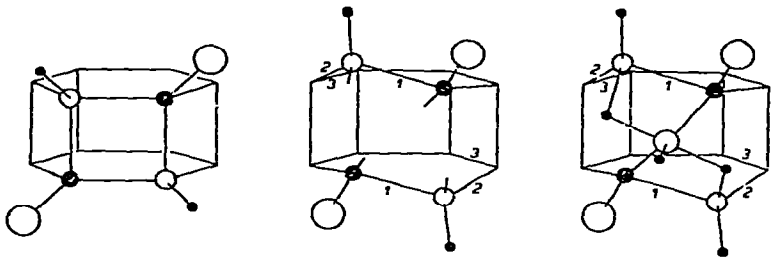

Fig. 1. Diagrammatic representation of formation of $(HAlN\text{-}i\text{-}Pr)_6AlH_3$ from the hexagonal cage molecule of $(HAlN\text{-}i\text{-}Pr)_6$. (This diagram is not meant to imply any chemical mechanism for the formation of the adduct.) For clarity, only the four-membered ring involved in the formation of the adduct is represented complete with its substituents.

TABLE 3

GEOMETRICAL PARAMETERS FOR $(HAlN\text{-}i\text{-}Pr)_6AlH_3$.

Bond lengths (Å)			
Al(1) - N(1)	1.889(2)	Al(4) - N(6)	1.901(3)
Al(2) - N(1)	1.925(3)	Al(6) - N(6)	1.926(4)
Al(2) - N(2)	1.894(4)	Al(6) - N(5)	1.892(3)
Al(3) - N(2)	1.932(3)	Al(5) - N(5)	1.940(3)
Al(3) - N(3)	1.885(3)	Al(5) - N(4)	1.873(3)
Al(1) - N(3)	1.908(4)	Al(4) - N(4)	1.906(3)
Al(1) - N(6)	1.938(3)	Al(4) - N(1)	1.945(3)
Al(6) - N(3)	1.958(3)	Al(2) - N(4)	1.959(3)
Al(7) - N(2)	1.933(3)	Al(7) - N(5)	1.948(4)
N(1) - C(1)	1.506(5)	N(6) - C(16)	1.509(5)
N(2) - C(4)	1.533(6)	N(5) - C(13)	1.537(5)
N(3) - C(7)	1.536(5)	N(4) - C(10)	1.536(5)
C(1) - C(2)	1.511(7)	C(16) - C(17)	1.525(6)
C(1) - C(3)	1.515(8)	C(16) - C(18)	1.525(8)
C(4) - C(5)	1.540(5)	C(13) - C(15)	1.532(8)
C(4) - C(6)	1.529(6)	C(13) - C(14)	1.507(8)
C(7) - C(8)	1.532(8)	C(10) - C(11)	1.525(7)
C(7) - C(9)	1.514(5)	C(10) - C(12)	1.506(7)
Al(1) - H(Al1)	1.50(4)	Al(4) - H(Al4)	1.46(6)
Al(2) - H(Al2)	1.47(4)	Al(6) - H(Al6)	1.51(4)
Al(3) - H'(Al3)	1.50(5)	Al(5) - H'(Al5)	1.52(6)
Al(3) - H''(Al3)	1.68(5)	Al(5) - H''(Al5)	1.56(6)
Al(7) - H''(Al3)	1.88(4)	Al(7) - H''(Al5)	1.96(6)
Al(7) - H(Al7)	1.55(6)		
Bond angles (°)			
N(1) - Al(1) - N(3)	112.7(1)	N(4) - Al(4) - N(6)	112.6(1)
N(1) - Al(2) - N(2)	113.6(1)	N(5) - Al(6) - N(6)	114.2(1)
N(2) - Al(3) - N(3)	111.0(1)	N(4) - Al(5) - N(5)	111.3(1)
N(1) - Al(1) - N(6)	90.9(1)	N(1) - Al(4) - N(6)	90.4(1)
N(1) - Al(4) - N(4)	92.7(1)	N(3) - Al(1) - N(6)	92.6(1)
N(1) - Al(2) - N(4)	91.7(1)	N(3) - Al(6) - N(6)	91.4(1)
N(2) - Al(2) - N(4)	111.2(1)	N(3) - Al(6) - N(5)	111.2(1)
N(2) - Al(7) - N(5)	107.0(1)		
Al(1) - N(1) - Al(2)	123.1(2)	Al(4) - N(6) - Al(6)	122.7(1)
Al(1) - N(1) - Al(4)	88.5(1)	Al(1) - N(6) - Al(4)	88.4(1)
Al(2) - N(1) - Al(4)	87.8(1)	Al(1) - N(6) - Al(6)	88.1(1)
Al(1) - N(1) - C(1)	117.3(2)	Al(4) - N(6) - C(16)	116.1(2)
Al(2) - N(1) - C(1)	110.9(1)	Al(6) - N(6) - C(16)	112.2(2)
Al(4) - N(1) - C(1)	125.0(2)	Al(1) - N(6) - C(16)	125.1(2)
Al(2) - N(2) - Al(3)	120.1(1)	Al(5) - N(5) - Al(6)	119.8(1)
Al(2) - N(2) - Al(7)	120.2(1)	Al(6) - N(5) - Al(7)	119.7(1)
Al(3) - N(2) - Al(7)	86.8(1)	Al(5) - N(5) - Al(7)	86.7(1)

(Table to be continued)

TABLE 3 (continued)

Bond angles (°)

Al(2) - N(2) - C(4)	114.3(2)	Al(6) - N(5) - C(13)	115.2(1)
Al(3) - N(2) - C(4)	104.7(1)	Al(5) - N(5) - C(13)	105.1(2)
Al(7) - N(2) - C(4)	106.9(1)	Al(7) - N(5) - C(13)	106.2(1)
Al(1) - N(3) - Al(3)	119.5(1)	Al(4) - N(4) - Al(5)	120.3(1)
Al(1) - N(3) - Al(6)	88.0(1)	Al(2) - N(4) - Al(4)	87.9(1)
Al(3) - N(3) - Al(6)	113.2(1)	Al(2) - N(4) - Al(5)	112.8(1)
Al(1) - N(3) - C(7)	112.5(2)	Al(4) - N(4) - C(10)	110.5(1)
Al(3) - N(3) - C(7)	110.7(1)	Al(5) - N(4) - C(10)	112.1(2)
Al(2) - N(4) - C(10)	111.0(2)	Al(6) - N(3) - C(7)	111.2(1)
N(1) - C(1) - C(2)	110.8(2)	N(6) - C(16) - C(17)	110.3(2)
N(1) - C(1) - C(3)	111.7(2)	N(6) - C(16) - C(18)	112.4(2)
C(2) - C(1) - C(3)	111.4(2)	C(17) - C(16) - C(18)	110.4(2)
N(2) - C(4) - C(5)	111.4(2)	N(5) - C(13) - C(15)	111.9(2)
N(2) - C(4) - C(6)	113.0(2)	N(5) - C(13) - C(14)	112.5(2)
C(5) - C(4) - C(6)	109.6(1)	C(14) - C(13) - C(15)	110.3(2)
N(3) - C(7) - C(8)	111.3(2)	N(4) - C(10) - C(11)	111.4(2)
N(3) - C(7) - C(9)	113.0(1)	N(4) - C(10) - C(12)	112.9(2)
C(8) - C(7) - C(9)	111.2(1)	C(11)- C(10) - C(12)	109.9(2)
N(1) - Al(1) - H(Al1)	118.3(10)	N(6) - Al(4) - H(Al4)	118.9(10)
N(6) - Al(1) - H(Al1)	119.7(10)	N(1) - Al(4) - H(Al4)	121.5(10)
N(3) - Al(1) - H(Al1)	117.2(10)	N(4) - Al(4) - H(Al4)	115.8(10)
N(1) - Al(2) - H(Al2)	110.8(10)	N(6) - Al(6) - H(Al6)	111.8(10)
N(2) - Al(2) - H(Al2)	114.7(10)	N(5) - Al(6) - H(Al6)	114.1(10)
N(4) - Al(2) - H(Al2)	112.7(10)	N(3) - Al(6) - H(Al6)	112.0(10)
N(2) - Al(3) - H'(Al3)	117.7(10)	N(5) - Al(5) - H'(Al5)	116.4(10)
N(3) - Al(3) - H'(Al3)	116.6(10)	N(4) - Al(5) - H'(Al5)	117.6(10)
N(2) - Al(3) - H''(Al3)	88.4(10)	N(5) - Al(5) - H''(Al5)	90.4(10)
N(3) - Al(3) - H''(Al3)	104.1(10)	N(4) - Al(5) - H''(Al5)	104.8(10)
H'(Al3) - Al(3) - H''(Al3)	115.0(10)	H'(Al5) - Al(5) - H''(Al5)	112.4(10)
N(2) - Al(7) - H''(Al5)	95.4(10)	N(5) - Al(7) - H''(Al3)	95.8(10)
N(2) - Al(7) - H(Al7)	124.7(10)	N(5) - Al(7) - H(Al7)	128.3(10)
N(5) - Al(7) - H''(Al5)	79.4(10)	N(2) - Al(7) - H''(Al3)	82.9(10)
H''(Al3) - Al(7) - H(Al7)	93.4(10)	H''(Al5) - Al(7) - H(Al7)	92.1(10)
H''(Al3) - Al(7) - H''(Al(5)	174.3(10)		

Internal rotation angles (°)

Al(1) - N(1) - C(1) - C(2)	50.0	Al(4) - N(6) - C(16) - C(17)	63.7
Al(1) - N(1) - C(1) - C(3)	295.2	Al(4) - N(6) - C(16) - C(18)	300.0
Al(2) - N(1) - C(1) - C(2)	271.5	Al(6) - N(6) - C(16) - C(17)	275.7
Al(2) - N(1) - C(1) - C(3)	146.7	Al(6) - N(6) - C(16) - C(18)	151.9
Al(4) - N(1) - C(1) - C(2)	169.0	Al(1) - N(6) - C(16) - C(17)	171.5
Al(4) - N(1) - C(1) - C(3)	44.2	Al(1) - N(6) - C(16) - C(18)	47.8
Al(2) - N(2) - C(4) - C(6)	56.0	Al(6) - N(5) - C(13) - C(14)	57.1
Al(2) - N(2) - C(4) - C(5)	292.1	Al(6) - N(5) - C(13) - C(15)	292.2
Al(3) - N(2) - C(4) - C(5)	158.7	Al(5) - N(5) - C(13) - C(15)	158.1
Al(3) - N(2) - C(4) - C(6)	282.6	Al(5) - N(5) - C(13) - C(14)	282.9
Al(7) - N(2) - C(4) - C(5)	67.6	Al(7) - N(5) - C(13) - C(15)	67.3
Al(7) - N(2) - C(4) - C(6)	191.5	Al(7) - N(5) - C(13) - C(14)	192.1
Al(3) - N(3) - C(7) - C(8)	306.6	Al(5) - N(4) - C(10) - C(11)	305.1
Al(3) - N(3) - C(7) - C(9)	72.3	Al(5) - N(4) - C(10) - C(12)	69.4
Al(1) - N(3) - C(7) - C(8)	170.1	Al(4) - N(4) - C(10) - C(11)	168.0
Al(1) - N(3) - C(7) - C(9)	295.8	Al(4) - N(4) - C(10) - C(12)	292.4
Al(6) - N(3) - C(7) - C(8)	73.3	Al(2) - N(4) - C(10) - C(11)	72.1
Al(6) - N(3) - C(7) - C(9)	199.0	Al(2) - N(4) - C(10) - C(12)	196.5
Al(1) - N(1) - Al(2) - N(2)	332.3	N(5) - Al(6) - N(6) - Al(4)	332.9
N(1) - Al(2) - N(2) - Al(3)	359.3	Al(5) - N(5) - Al(6) - N(6)	359.7
Al(2) - N(2) - Al(3) - N(3)	36.2	N(4) - Al(5) - N(5) - Al(6)	35.1
N(2) - Al(3) - N(3) - Al(1)	311.0	Al(4) - N(4) - Al(5) - N(5)	312.0
Al(3) - N(3) - Al(1) - N(1)	23.6	N(6) - Al(4) - N(4) - Al(5)	23.3
N(3) - Al(1) - N(1) - Al(2)	16.7	Al(6) - N(6) - Al(4) - N(4)	16.2
N(4) - Al(2) - N(2) - Al(7)	2.8	Al(7) - N(5) - Al(6) - N(3)	2.4
Al(2) - N(2) - Al(7) - N(5)	315.1	N(2) - Al(7) - N(5) - Al(6)	314.8
N(2) - Al(7) - N(5) - Al(5)	77.6	Al(3) - N(2) - Al(7) - N(5)	78.3
Al(7) - N(5) - Al(5) - N(4)	272.5	N(3) - Al(3) - N(2) - Al(7)	272.8
N(5) - Al(5) - N(4) - Al(2)	53.5	Al(6) - N(3) - Al(3) - N(2)	52.4
Al(5) - N(4) - Al(2) - N(2)	354.5	N(5) - Al(6) - N(3) - Al(3)	355.2

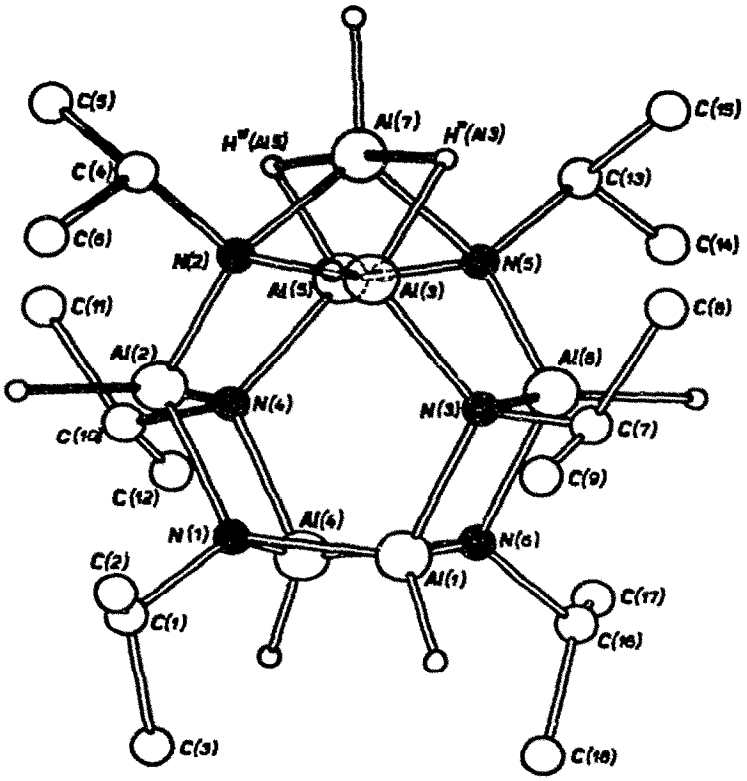

Fig. 2. A perspective view of a cage molecule of $(HAlN\text{-}i\text{-}Pr)_6AlH_3$.

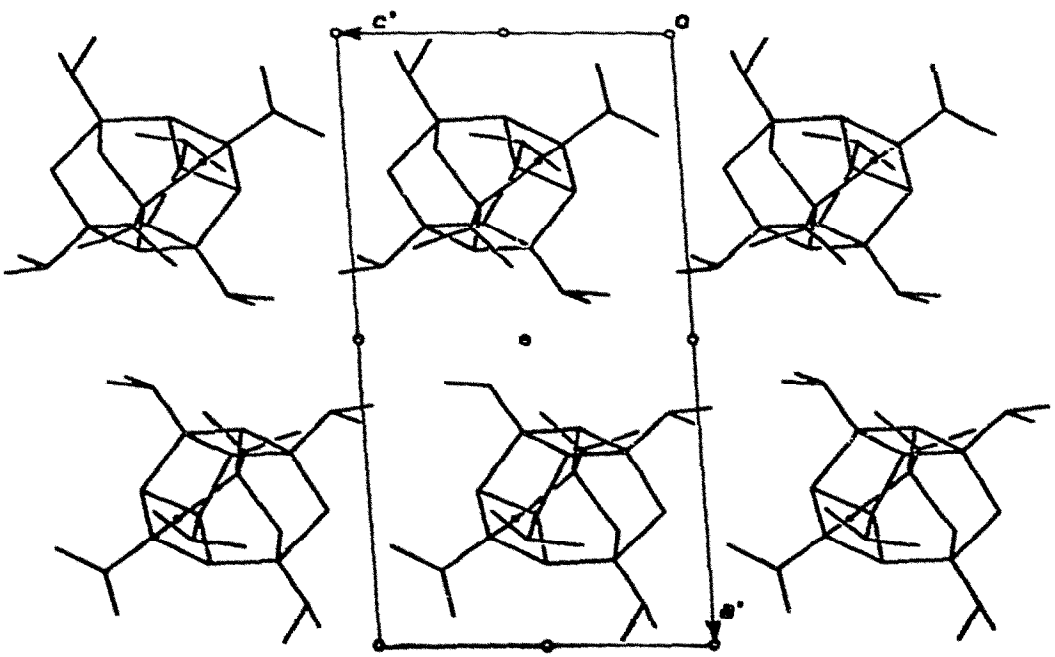

Fig. 3. A representation of the packing of $(HAlN\text{-}i\text{-}Pr)_6AlH_3$. Projection along the *b* axis.

1.889(4) Å respectively. A simple explanation of this could be the loss of planarity of the rings, with a consequent reduction, from a VB point of view, of a resonance effect between the extreme models of a pure covalent Al—N bond and of a pure semipolar Al—N bond. In contrast the average length of the transverse Al—N bond distance of 1.950(6) Å is in good agreement with that of 1.956(2) Å found in the hexamer. The difference between the two Al(7)—N bond lengths [1.933(3) and 1.948(4) Å] is difficult to explain, it should be noted that there is a relatively large dispersion of all the geometrical parameters of this deformed structure.

Two distinct values must be considered for the N—C bond distance: the first, involving N(1) and N(6) averages 1.508(2) Å and is comparable with the average found in PIAHEX [1.514(2) Å]; the second involving all other nitrogen atoms is a little greater averaging 1.536(1) Å. If the sum of the three C—N—Al bond angles is considered as an index of the *s* character used in the hybridized sp^3 C—N bond, it is of interest to note that in the first case this sum averages 353.3(2)° (i.e. more *s* character and a shorter bond length) and in the second 330.1(50)°.

The average Al—H bond distance for the four-coordinated aluminum atoms is 1.50(1) Å which is in good agreement with the average of 1.49(1) Å found in PIAHEX. The value of 1.55(5) Å found for the equatorial Al(7)—H cannot be regarded as significantly different. The two bridging hydrogen atoms at the apical positions of the trigonal bipyramidal arrangement around Al(7) average 1.92(5) Å from the central atom and 1.62(8) Å from the two four-coordinate aluminum atoms, Al(5) and Al(3); the Al—H—Al bond angles average 97.3(10)°. These values can be compared with those of 1.715 Å and 141.2° found in polymeric aluminum hydride structure [6], where the aluminum is hexacoordinate. The geometry around Al(7) is rather irregular: the N(2)—Al(7)—N(5) bond angle is only 107.0(1)° and the H_b—Al—H_b bond angle is a little bent (ca. 174°) inward toward the centre of the cage.

The other bond angles of the four-coordinate aluminum and nitrogen atoms, although more variable, are in line with the trends observed in PIAHEX: thus, in six-membered rings, $(AlN)_3$, the Al—N--Al bond angles are larger than the N—Al—N angles, ranging from 119.5° to 123.1° and from 112.0° to 114.2° respectively; and vice versa, in four-membered rings, $(AlN)_2$, they fall in the range 86.8 to 88.5° and 90.4 to 92.7° respectively.

The isopropyl groups attached to the nitrogen atoms are angled with staggered conformations around the N—C bonds, in such a way as to fulfill the binary symmetry mentioned above and to give methyl—methyl intramolecular contacts greater than 4.0 Å.

The packing, which is shown in Fig. 3, is determined essentially by methyl—methyl interactions, the shortest distance being 3.71 Å.

We believe that the structural characteristics established for the attachement of an alane molecule to the cage molecule in PIAHEX, will be found also for alane molecules complexed to many of the PIA cage molecules.

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