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

II*. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE HEXAMER, $(HAlN\text{-}i\text{-}Pr)_6$

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Summary

The crystal and molecular structure of the hexamer, $(HAlN\text{-}i\text{-}Pr)_6$, has been solved by direct-methods from single crystal three-dimensional X-ray diffraction data obtained on an automatic diffractometer. The molecule consists of an hexagonal cage, formed by two almost planar six-membered rings, $(AlN)_3$, joined together by six transverse Al—N bonds. The unit cell contains four independent molecules, related to inversion centres, presenting two conformers which arise from different rotation angles around the N—C bond of the isopropyl groups. The main average bond lengths are: Al—N, 1.898 (2) Å in six-membered rings and 1.956(2) Å in transverse bonds; Al—H, 1.49(1) Å and N—C, 1.514(2) Å. The hexamer crystallizes as colourless prisms with the following crystal data: triclinic space group, $P\bar{1}$; $a = 17.18(2)$, $b = 10.68(2)$, $c = 20.09(2)$ Å, $\alpha = 123.5(4)°$, $\beta = 90.0(5)°$, $\gamma = 93.5(5)°$; $Z = 4$; calculated density 1.106 g/cm^3. The structure has been refined by the block-matrix least-squares method, using 6491 independent reflections, to an R factor of 5.0%.

Introduction

There has been little structural information obtained to date on the stereochemistry of alane derivatives. To our knowledge, structural data are available

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* For part I see ref. 5.

only for a stable polymeric form of $(AlH_3)_x$ (I) [1], the adduct $AlH_3 \cdot 2NMe_3$ (II) [2], the complex $[AlH_3 \cdot (Me_2NCH_2CH_2NMe_2)]_x$, (III) [3], and more recently for the trimer $(H_2AlNMe_2)_3$ (IV) [4]. The aluminum atom shows tetrahedral coordination only in compound IV, while in the others the coordination is five, with trigonal bipyramidal geometry; moreover, the crystal stuctures of II and IV are poorly refined.

A distinct absence of structural works is apparent for the class of poly(*N*-alkyliminoalanes), for which the identification of a single compound has turned out to be a major problem. Our interest in this field, indicated in a previous paper [5], led us to carry out X-ray structural analyses of various compounds of this and closely related classes, which new and improved preparative methods yielded in the form of single crystals. As a result of these studies, the crystal structures of the following compounds have been solved and refined: $(HAlN\text{-i-Pr})_6$ (labelled as PIAHEX), $HAlN\text{-i-Pr})_6 \cdot AlH_3$ (PIAHAL), $[(HAlN\text{-i-Pr})_2(H_2AlNH\text{-i-Pr})_3]$ (PIAPEN), $[H(HAlN\text{-i-Pr})_5AlH_2] \cdot LiH/Et_2O$, (PIALIH). The use of the isopropyl group as alkyl substituent derives from the excellent properties in polymerization, and the good solubility and crystallizability that this group confers on many product

In the present paper we report the crystal structure of PIAHEX. Among the poly(*N*-alkyliminoalanes), which are generally obtained as a mixture of compounds with different degrees of polymerization, hexamers have been found to be commonest except when the substituent is excessively bulky, e.g. the tert-butyl group. Recently, syntheses carried out in these laboratories [5], yielded poly(*N*-isopropyliminoalanes) as the almost pure hexamers and many preparations allowed the separation of single crystals in a form suitable for an X-ray structural analysis.

Experimental

Colourless crystals of PIAHEX, highly sensitive to moisture, crystallize as well shaped prisms, elongated along the *b* axis. Weissenberg photographs showed triclinic symmetry; the $P\bar{1}$ space group was chosen and confirmed subsequently by successful refinement. The final cell dimensions were determined by a least-squares fit to the setting angles measured for 19 high-angle reflections. A summary of the crystal data is given in Table 1. Three dimensional intensity data were collected from a crystal with approximate dimensions 0.35 × 0.45 × 0.9 mm, sealed in a thin-walled glass capillary, mounted with *b* axis along the spindle axis of a on-line Siemens AED diffractometer, using Zr-filtered Mo-K_α radiation. A total of 9560 reflections were measured [max. $(\sin\theta/\lambda) = 0.58$ Å^{-1}] following the θ—2θ scan method and "five-points" technique [6]; 6491 reflections with intensity greater than 2.5 $\sigma(I)$, $\{\sigma^2(I) = [\text{total counts} + (0.005\ I)^2]\}$, were used for the structure determination. A correction, based on a simple linear interpolation, was applied for intensity decay, monitored by a standard reflection measured every 15 reflections; the maximum long-term variation was ca. 6%.

The intensities were corrected for Lorentz and polarization effects and then scaled by Wilson's statistical method. The values obtained were used for the calculation of structure factor amplitudes $|F|$ and normalized structure factors $|E|$. Correction for absorption was neglected owing to the low value of μR (< 0.2 for Mo-K_α).

TABLE 1

CRYSTAL DATA FOR $(HAlN\text{-}i\text{-}Pr)_6$

Molecular formula:	$[HAlN(iso\text{-}C_3H_7)]_6$
Molecular weight:	510.5
Sapce group:	Triclinic, $P\bar{1}$
Molecules/unit cell:	4
Calculated density:	1.106 g/cm^3
Cell constants:	a = 17.18(2), b = 10.68(2), c = 20.09(2)Å;
(MoKα radiation, λ = 0.71069 Å)	α = 123.5(4)°, β = 90.0(5)°, γ = 93.5(5)°
Cell volume:	3064.8 Å^3

Structure determination and refinement

The structure was solved by direct methods by means of the computer program MULTAN written by Main et al. [7]. In the first computing run, using as input data the 500 highest (>1.47) and the 50 lowest $|E|$ values, the program stopped after having difficulty in finding origin-defining reflections. It was believed that this failure might depend on the systematically higher $|E|$ values of the *hkl* reflections with *l* even, compared with those with *l* odd. Both sets were then scaled independently to $\langle E^2 \rangle = 1$ and a further run was attempted. This led successfully to 64 phased sets of $|E|$, whose 18th set, having the 'figures of merit' ABS FOM = 1.33 and PSI ZERO = 2012, allowed the solution of the structure.

The starting reflections were phased as: 405(+), $1\bar{4}10$(+), $1\bar{1}0$(+), fixing the origin, and 2012(—), $11\bar{2}$(+), 002(+), $3\bar{4}7$(+), $11\bar{3}10$(—), 136(+). Only the phase of $3\bar{4}7$ was changed in the course of the refinement using a weighted tangent formula [7]. From the corresponding E-map all the 12 aluminum and 12 nitrogen atoms were located. The residual R computed with these coordinates was 0.33. From the next Fourier synthesis the positions of the 36 independent carbon atoms were deduced and the value R = 0.21 was obtained.

Refinement was then carried out by block-diagonal least-squares methods, using isotropic temperature factors. When R was reduced to 0.11 a ΔF-map was computed which gave the location of almost all the hydrogen atoms; in a few cases however, with those bonded to carbon atoms, the coordinates were adjusted following the usual carbon geometry. In the last two cycles the hydrogen atoms were refined using isotropic thermal parameters and a 'damping' factor of 0.5 to reduce the calculated shifts. The final value of R was 0.050. The function minimized was $\Sigma w(F_o - F_c)^2$ using Cruickshank's [8] weighting scheme. The atomic scattering factors used, assuming that no atoms are changed, were those of Moore [9].

Except for the program MULTAN, all other computer programs, which were run on an IBM 360 computer, were written by Immirzi [10]. Positional and thermal parameters for non-hydrogen atoms are given in Table 2 and for hydrogen atoms in Table 3. A list of structure factors may be obtained from the authors on request.

(continued on p. 208)

TABLE 2

FINAL FRACTIONAL COORDINATES (X 10^4) AND THERMAL PARAMETERS (X 10^2Å^2) FOR NONHYDROGEN ATOMS OF $(HAlN\text{-}i\text{-}Pr)_6$

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

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Molecule I									
Al(1)	4263(1)	3386(1)	-1017(1)	313(5)	375(5)	351(5)	42(4)	-27(4)	172(4)
Al(2)	4529(1)	7083(1)	356(1)	315(5)	356(5)	414(5)	79(4)	12(4)	231(4)
Al(3)	6057(1)	5089(1)	-547(1)	291(5)	426(6)	406(5)	60(4)	51(4)	262(5)
N(1)	3878(2)	5291(3)	-299(2)	279(13)	396(15)	392(15)	71(11)	-17(11)	231(13)
N(2)	5608(2)	6945(3)	162(2)	331(14)	361(14)	466(16)	31(11)	20(12)	267(13)
N(3)	5360(2)	3356(4)	-1172(2)	338(14)	390(15)	313(14)	89(11)	30(11)	162(12)
C(1)	3130(2)	5649(5)	-545(2)	312(17)	473(20)	474(20)	123(15)	-29(15)	259(17)
C(2)	2457(3)	4557(6)	-682(3)	362(20)	764(30)	700(28)	-8(20)	-121(19)	443(25)
C(3)	3257(3)	5750(7)	-1255(3)	587(27)	886(35)	704(29)	102(24)	-84(22)	568(28)
C(4)	6047(3)	8206(5)	140(3)	459(22)	499(23)	786(30)	1(18)	72(20)	440(23)
C(5)	5979(4)	9726(6)	915(4)	704(33)	487(26)	970(38)	-83(23)	-15(28)	375(27)
C(6)	5759(4)	8181(7)	-578(4)	784(34)	797(34)	991(40)	-30(27)	111(29)	715(33)
C(7)	5539(3)	2283(5)	-2040(2)	591(25)	539(24)	331(18)	164(19)	103(17)	174(18)
C(8)	6333(4)	1661(7)	-2147(3)	777(34)	827(36)	586(28)	379(29)	298(25)	323(27)
C(9)	5443(4)	2991(7)	-2501(3)	913(37)	919(38)	448(25)	218(30)	92(24)	416(27)
Molecule II									
Al(1)	518(1)	1368(1)	1181(1)	324(5)	414(5)	356(5)	30(4)	6(4)	215(4)
Al(2)	816(1)	-1690(1)	-617(1)	306(5)	390(5)	420(5)	91(4)	59(4)	233(5)
Al(3)	237(1)	1381(1)	-461(1)	347(5)	407(5)	414(5)	45(4)	41(4)	272(5)
N(1)	848(2)	-612(4)	517(2)	282(13)	446(16)	425(15)	69(11)	1(11)	281(14)
N(2)	575(2)	-612(4)	-1073(2)	312(14)	416(15)	384(15)	52(11)	82(11)	231(13)
N(3)	284(2)	2351(3)	664(2)	335(14)	346(14)	414(15)	16(11)	13(11)	213(13)
C(1)	1540(3)	-993(7)	811(3)	376(20)	843(34)	761(31)	85(20)	-83(20)	565(29)
C(2)	1414(4)	-958(8)	1538(4)	734(35)	1189(47)	970(40)	-31(32)	-226(30)	805(39)
C(3)	2270(3)	-120(7)	821(3)	360(20)	791(33)	694(29)	61(21)	-69(19)	422(27)
C(4)	1037(3)	-865(5)	-1775(3)	454(21)	605(25)	455(21)	90(18)	167(17)	317(20)
C(5)	992(4)	-2493(7)	-2465(3)	753(33)	790(34)	504(26)	178(27)	200(23)	314(25)
C(6)	1079(3)	-227(7)	-1498(4)	551(27)	934(38)	802(34)	52(26)	267(25)	535(32)
C(7)	567(3)	3994(5)	1178(3)	520(22)	400(20)	459(21)	-65(16)	-10(17)	221(17)
C(8)	135(3)	4963(5)	985(3)	843(34)	402(22)	656(29)	30(22)	6(24)	294(22)
C(9)	1439(3)	4184(7)	1116(4)	534(26)	686(30)	810(34)	-169(22)	-13(23)	421(28)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Molecule III									
Al(1)	567(1)	-1317(1)	5333(1)	402(6)	381(5)	422(6)	14(4)	-33(4)	237(5)
Al(2)	-1178(1)	-940(1)	4772(1)	336(5)	398(6)	446(6)	-32(4)	-29(4)	231(5)
Al(3)	410(1)	-888(1)	3816(1)	417(6)	438(6)	344(5)	23(5)	21(4)	199(5)
N(1)	-532(2)	-1298(4)	5402(2)	422(16)	385(16)	470(17)	-41(13)	-14(13)	268(14)
N(2)	-690(2)	-876(4)	3941(2)	394(16)	396(16)	331(14)	-4(12)	-54(12)	187(13)
N(3)	1000(2)	-1234(4)	4481(2)	381(15)	344(15)	394(15)	66(12)	36(12)	179(13)
C(1)	-954(3)	-2368(6)	5572(3)	545(25)	608(27)	786(31)	-72(21)	-12(22)	523(26)
C(2)	-654(4)	-2244(8)	6299(4)	885(40)	990(43)	815(38)	-78(33)	31(30)	677(36)
C(3)	-911(4)	-4005(7)	4821(4)	863(38)	570(30)	1032(43)	-165(37)	-148(32)	514(31)
C(4)	-1124(3)	-1730(6)	3144(3)	629(28)	587(27)	497(25)	0(22)	-242(21)	185(22)
C(5)	-1849(5)	-1132(9)	3140(5)	975(47)	939(46)	898(44)	63(37)	-403(36)	359(38)
C(6)	-1176(4)	-3393(6)	2798(3)	713(32)	555(28)	539(28)	-94(24)	-150(23)	145(23)
C(7)	1660(3)	-2289(6)	4121(3)	450(22)	529(25)	576(25)	154(19)	77(19)	261(21)
C(8)	2246(4)	-1791(8)	3723(4)	585(31)	955(41)	851(38)	245(29)	238(27)	481(34)
C(9)	1321(4)	-3889(7)	3539(4)	875(40)	540(30)	774(37)	229(28)	118(30)	213(27)
Molecule IV									
Al(1)	4741(1)	6463(2)	6240(1)	377(6)	498(6)	311(5)	-15(5)	33(4)	143(5)
Al(2)	4360(1)	2973(1)	4671(1)	406(6)	380(6)	434(6)	-59(5)	-24(5)	220(5)
Al(3)	6190(1)	4499(1)	5056(1)	334(5)	431(6)	415(6)	14(4)	-4(4)	196(5)
N(1)	4046(2)	4744(4)	5605(2)	346(15)	531(18)	370(15)	-65(13)	37(12)	245(14)
N(2)	5441(2)	2851(4)	4466(2)	418(17)	357(16)	463(17)	23(13)	-10(14)	160(14)
N(3)	5815(2)	6227(4)	5975(2)	337(14)	420(16)	299(14)	-42(12)	-34(11)	141(13)
C(1)	3431(3)	4369(6)	6021(3)	453(23)	792(32)	509(24)	-131(21)	49(18)	364(24)
C(2)	2918(3)	5662(8)	6533(4)	542(29)	1093(45)	733(35)	63(29)	220(26)	453(34)
C(3)	3811(4)	3835(9)	6497(4)	952(43)	1150(48)	761(36)	-64(36)	193(31)	679(37)
C(4)	5684(3)	1301(6)	4191(4)	641(30)	441(25)	914(38)	125(22)	-90(26)	275(26)
C(5)	6363(4)	842(7)	3647(5)	857(43)	613(34)	1029(48)	322(31)	87(36)	145(33)
C(6)	5852(5)	1242(8)	4929(5)	1050(49)	799(41)	1220(53)	128(36)	-57(40)	683(41)
C(7)	6332(3)	7008(6)	6729(3)	463(22)	645(27)	404(21)	-141(19)	-133(17)	237(20)
C(8)	7125(3)	7533(7)	6602(4)	551(28)	809(36)	687(33)	-162(25)	-134(24)	306(29)
C(9)	6385(4)	6008(8)	7042(4)	745(35)	1009(41)	605(30)	-66(30)	-154(26)	513(31)

TABLE 3

FINAL FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS FOR HYDROGEN ATOMS ($\times 10^2$ Å^2) OF $(\text{HAlN-i-Pr})_6$

	x	y	z	B		x	y	z	B
Molecule I					Molecule III				
H(Al1)	3772(25)	2278(49)	-1779(26)	401(99)	H(Al1)	962(28)	-2260(53)	5496(28)	356(112)
H(Al2)	4156(28)	8444(54)	499(25)	267(115)	H(Al2)	-2009(28)	-1655(53)	4612(28)	325(114)
H(Al3)	6731(26)	5100(50)	-984(26)	326(102)	H(Al3)	661(27)	-1599(51)	2987(27)	346(106)
H(C1)	3034(28)	6681(53)	-71(28)	294(111)	H(C1)	-1556(30)	-1972(57)	5840(30)	481(125)
H'(C2)	2022(35)	4724(67)	-891(35)	601(158)	H'(C2)	-46(38)	-2271(72)	6319(38)	775(176)
H''(C2)	2389(29)	4440(56)	-233(30)	445(121)	H''(C2)	-699(35)	-1220(68)	6751(36)	708(162)
H'''(C2)	2574(32)	3580(61)	-1061(32)	537(139)	H'''(C2)	-1047(36)	-3093(70)	6353(37)	660(170)
H'(C3)	2758(30)	6059(59)	-1420(31)	478(133)	H'(C3)	-1158(40)	-4079(75)	5051(40)	953(190)
H''(C3)	3299(31)	4752(60)	-1710(31)	491(133)	H''(C3)	-345(38)	-4341(73)	4667(38)	828(179)
H'''(C3)	3582(29)	6507(56)	-1136(29)	424(119)	H'''(C3)	-1154(37)	-4004(71)	4333(38)	785(172)
H(C4)	6678(27)	8138(52)	120(27)	279(112)	H(C4)	-771(46)	-1575(88)	2718(47)	548(232)
H'(C5)	6302(38)	10232(73)	709(38)	566(181)	H'(C5)	-2076(46)	-1804(88)	2475(47)	1379(232)
H''(C5)	6109(35)	9916(67)	1418(35)	757(158)	H''(C5)	-1674(45)	142(85)	3355(44)	1353(223)
H'''(C5)	5358(35)	9970(68)	1008(36)	770(162)	H'''(C5)	-2257(44)	-1506(84)	3512(44)	1282(217)
H'(C6)	6138(35)	8933(68)	-596(35)	1149(162)	H'(C6)	-1447(34)	-4000(66)	2256(34)	642(152)
H''(C6)	5165(31)	8372(60)	-530(31)	500(132)	H''(C5)	-1435(37)	-3661(72)	3096(38)	863(174)
H'''(C6)	5775(35)	7373(67)	-1016(36)	732(161)	H'''(C6)	-751(36)	-3621(70)	2661(36)	819(171)
H(C7)	5212(26)	1254(50)	-2269(26)	335(104)	H(C7)	2031(29)	-2180(56)	4589(30)	398(122)
H'(C8)	6456(34)	981(65)	-2760(34)	902(152)	H'(C8)	2673(39)	-2575(75)	3520(39)	733(184)
H''(C8)	6286(38)	1054(72)	-1890(38)	665(175)	H''(C8)	2502(39)	-732(74)	4111(39)	904(184)
H'''(C8)	6746(36)	2590(69)	-1916(36)	734(167)	H'''(C8)	2000(39)	-1988(75)	3197(39)	823(180)
H'(C9)	5536(44)	2316(85)	-3061(44)	760(221)	H'(C9)	1724(38)	-4681(72)	3269(38)	795(176)
H''(C9)	5800(31)	3896(60)	-2312(32)	514(137)	H''(C9)	952(36)	-3884(69)	3065(36)	700(165)
H'''(C9)	4888(35)	3286(66)	-2453(35)	668(158)	H'''(C9)	996(35)	-4226(66)	3783(35)	657(153)
Molecule II					Molecule IV				
H(Al1)	899(23)	2358(44)	1995(23)	149(86)	H(Al1)	4672(31)	7481(60)	7135(32)	310(135)
H(Al2)	1444(26)	-2825(51)	-1002(26)	371(106)	H(Al2)	3937(27)	1543(51)	4470(27)	553(104)
H(Al3)	475(26)	2245(50)	-793(26)	321(102)	H(Al3)	6989(27)	4169(51)	5167(27)	274(106)
H(C1)	1616(39)	-2099(75)	339(39)	525(187)	H(C1)	3103(30)	3581(57)	5620(30)	377(126)
H'(C2)	1992(39)	-1536(75)	1600(39)	952(187)	H'(C2)	2807(40)	5315(77)	6764(40)	918(192)
H''(C2)	836(44)	-1516(84)	1538(44)	1314(219)	H''(C2)	2696(36)	6045(68)	6202(36)	630(163)
H'''(C2)	1367(39)	397(75)	1868(40)	996(189)	H'''(C2)	3262(34)	6450(66)	7035(35)	639(155)
H'(C3)	2799(38)	-386(72)	1043(38)	717(175)	H'(C3)	3367(36)	3458(69)	6726(37)	713(167)
H''(C3)	2294(32)	805(61)	1100(32)	571(139)	H''(C3)	3955(39)	4789(74)	6915(39)	769(181)
H'''(C3)	2449(31)	-332(59)	331(31)	515(132)	H'''(C3)	4128(38)	2970(72)	6172(38)	725(177)
H(C4)	761(24)	-379(46)	-2029(24)	233(93)	H(C4)	5213(27)	432(51)	3736(27)	729(105)
H'(C5)	1268(33)	-2493(63)	-2851(33)	549(146)	H'(C5)	6508(37)	-213(70)	3442(37)	979(173)
H''(C5)	425(34)	-2948(65)	-2615(34)	647(150)	H''(C5)	6883(33)	1604(65)	3955(34)	864(150)
H'''(C5)	1251(33)	-3106(64)	-2301(34)	634(151)	H'''(C5)	6368(36)	1034(69)	3204(36)	823(166)
H'(C6)	2156(36)	-389(69)	-1950(36)	721(166)	H'(C6)	6108(37)	880(72)	4513(38)	1088(175)
H''(C6)	2110(34)	-885(66)	-1366(35)	701(155)	H''(C6)	5478(36)	1579(69)	5300(36)	783(161)
H'''(C6)	1899(36)	822(69)	-1014(36)	747(167)	H'''(C6)	6352(30)	2035(59)	5269(31)	900(129)
H(C7)	411(25)	4365(48)	1728(25)	223(97)	H(C7)	6166(36)	8107(70)	7201(37)	198(163)
H'(C8)	350(34)	5884(66)	1274(34)	619(157)	H'(C8)	7377(41)	8227(79)	7201(41)	821(200)
H''(C8)	-405(33)	4809(63)	965(33)	542(145)	H''(C8)	7093(40)	8234(76)	6362(40)	634(188)
H'''(C8)	314(30)	4686(58)	442(30)	440(130)	H'''(C8)	7390(37)	6442(72)	6209(38)	656(174)
H'(C9)	1574(34)	5291(65)	1491(34)	650(152)	H'(C9)	6801(41)	6764(79)	7624(42)	723(200)
H''(C9)	1542(28)	3795(53)	572(28)	406(114)	H''(C9)	6640(37)	5134(71)	6669(37)	696(174)
H'''(C9)	1731(29)	3588(55)	1235(29)	373(119)	H'''(C9)	5831(40)	5713(77)	7144(40)	430(191)

Results and discussion

The molecular structure of PIAHEX consists essentially of an hexagonal cage as shown in Fig. 1, which is built up from two six-membered $(AlN)_3$ rings joined together by six transverse Al—N bonds, forming six four-membered $(AlN)_2$ rings. Each aluminum atom is tetrahedrally bonded to three nitrogen atoms and vice versa. The hydridic hydrogens and isopropyl groups point away from the cage, giving the molecule a somewhat spherical shape. In the crystal there are four independent molecules lying on centres of symmetry. Three of them (indicated I, II, III in the tables) have a nearly identical conformation which is

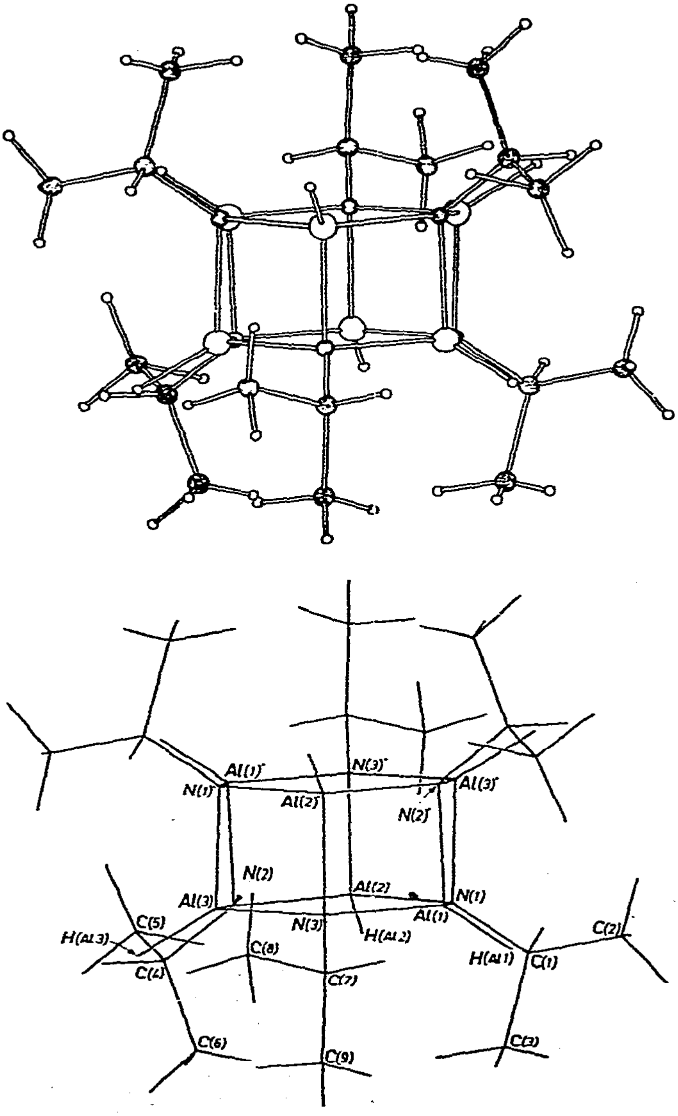

Fig. 1. A perspective view of a cage molecule of $(HAlN\text{-}i\text{-}Pr)_6$ with a scheme for labelling. The independent molecular unit I is represented.

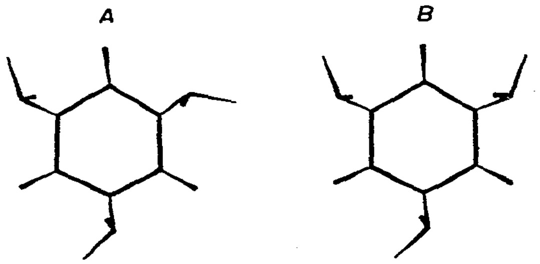

Fig. 2. Schematic diagram of the conformers found in the crystal of $(HAlN\text{-}i\text{-}Pr)_6$. Only one half of the molecule is shown, the second half being related by a centre of symmetry. The conformer of the type A shows a pseudo-symmetry $\bar{3}$ ($\bar{3}$ axis passes through the centres of the six-membered rings), which disappears in the conformer of type B.

related, although not rigorously, to a $\bar{3}$ symmetry. The conformation of the fourth molecule (IV) derives from the former by a rotation of 120° around the N—C bond of one of the isopropyl groups. These two conformers are schematically illustrated in Fig. 2. The presence in the crystal of these conformers does not seem to be required by any particular constraint of packing, but, as will be discussed later, it is a consequence of their similar potential energies. The packing, of which a diagrammatic view is shown in Fig. 3, is essentially determined by methyl—methyl contacts, most of which are longer than 3.8 Å, the shortest being 3.65 Å.

Bond distances and angles are reported in Table 4 and corresponding mean values in Table 5. The mean N—C bond distance [1.514(2)Å] is in good agree-

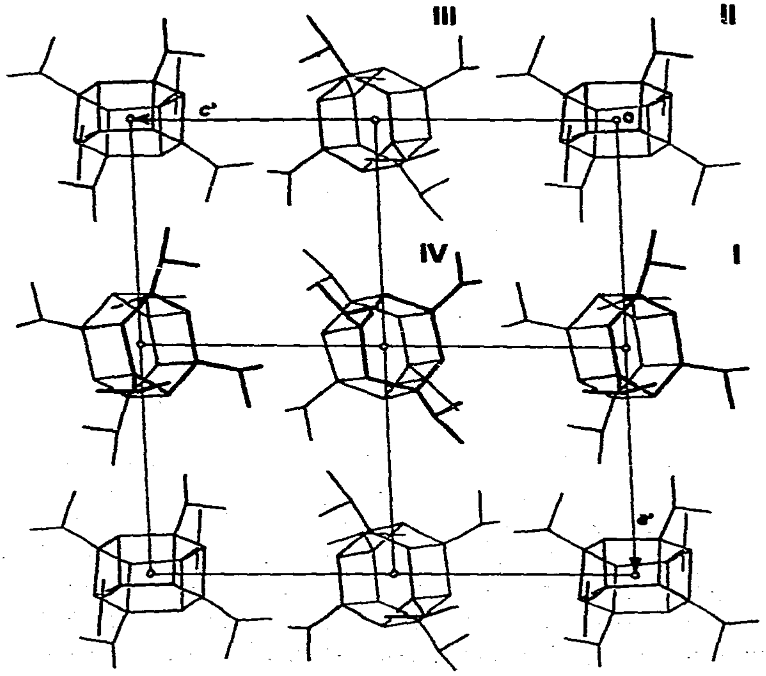

Fig. 3. A representation of the packing of $(HAlN\text{-}i\text{-}Pr)_6$. Projection along the b axis.

TABLE 4

GEOMETRICAL PARAMETERS FOR (HAlN-i-Pr)$_6$

Molecule	I	II	III	IV
Bond angles (°)				
C(2) – C(1) – C(3)	112.5(2)	115.6(3)	110.8(3)	112.1(3)
C(5) – C(4) – C(6)	112.3(4)	111.8(3)	115.0(3)	112.1(4)
C(8) – C(7) – C(9)	111.9(2)	111.0(2)	111.4(3)	113.0(3)
N(1) – C(1) – C(2)	111.9(2)	114.2(3)	114.1(3)	112.9(3)
N(1) – C(1) – C(3)	110.5(2)	110.4(2)	108.1(3)	110.1(2)
N(2) – C(4) – C(5)	111.5(3)	112.8(3)	114.1(3)	112.8(4)
N(2) – C(4) – C(6)	109.5(2)	109.8(2)	110.6(3)	109.2(3)
N(3) – C(7) – C(8)	113.0(3)	112.8(2)	111.8(3)	111.4(3)
N(3) – C(7) – C(9)	110.7(3)	110.3(3)	109.7(3)	110.4(2)
N(1) – Al(1) – H(Al1)	117.6(30)	117.6(25)	118.8(19)	121.5(30)
N(3) – Al(1) – H(Al1)	113.7(19)	115.3(16)	113.1(17)	110.3(24)
N(2)' – Al(1) – H(Al1)	122.0(25)	119.2(20)	121.0(18)	122.0(27)
N(1) – Al(2) – H(Al2)	111.8(22)	113.3(26)	115.0(16)	115.6(31)
N(2) – Al(2) – H(Al2)	118.3(21)	118.1(20)	118.0(21)	115.0(22)
N(3)' – Al(2) – H(Al2)	123.5(22)	121.4(23)	118.8(19)	120.4(26)
N(2) – Al(3) – H(Al3)	118.2(28)	112.2(18)	115.6(25)	117.6(17)
N(3) – Al(3) – H(Al3)	112.6(18)	118.7(20)	116.3(22)	114.3(23)
N(1)' – Al(3) – H(Al3)	122.8(24)	123.3(19)	122.2(23)	122.9(20)
Internal rotation angles (°)				
Al(1) – N(1) – C(1) – C(2)	60.0	64.5	54.3	56.1
Al(1) – N(1) – C(1) – C(3)	293.9	292.2	290.5	290.1
Al(2) – N(1) – C(1) – C(2)	209.1	212.3	203.8	204.7
Al(2) – N(1) – C(1) – C(3)	82.9	80.0	80.0	78.7
Al(3)' – N(1) – C(1) – C(2)	311.1	316.0	305.3	307.2
Al(3)' – N(1) – C(1) – C(3)	184.9	183.8	181.5	181.2
Al(2) – N(2) – C(4) – C(5)	57.7	57.1	65.9	151.3
Al(2) – N(2) – C(4) – C(6)	292.8	291.6	294.5	276.6
Al(3) – N(2) – C(4) – C(5)	205.9	207.2	213.5	299.4
Al(3) – N(2) – C(4) – C(6)	81.0	81.7	82.1	64.8
Al(1)' – N(2) – C(4) – C(5)	308.7	309.2	318.0	48.9
Al(1)' – N(2) – C(4) – C(6)	183.9	183.7	186.6	174.2
Al(3) – N(3) – C(7) – C(8)	58.2	52.2	55.7	59.3
Al(3) – N(3) – C(7) – C(9)	291.8	287.4	291.6	292.9
Al(1) – N(3) – C(7) – C(8)	207.5	203.2	205.3	208.6
Al(1) – N(3) – C(7) – C(9)	81.3	78.4	81.2	82.1
Al(2)' – N(3) – C(7) – C(8)	309.8	303.7	306.6	311.0
Al(2)' – N(3) – C(7) – C(9)	183.4	178.9	182.5	184.5

Deviation of atoms from their least-squares planes (Å)
(Planes through Al(1), N(1), Al(2), N(2), Al(3) and N(3))

Molecule	Al(1)	N(1)	Al(2)	N(2)	Al(3)	N(3)
I	0.041	– 0.040	0.037	– 0.036	0.038	– 0.040
II	0.040	– 0.042	0.041	– 0.039	0.037	– 0.038
III	0.040	– 0.043	0.042	– 0.039	0.037	– 0.038
IV	0.038	– 0.043	0.045	– 0.042	0.036	– 0.035

ment with the values observed, e.g., in complexes of organoaluminum compounds [11]. The values observed in this structure for the Al—H single bond distance, although inherently of low accuracy, could represent the first reliable experimental data for this bond: the average length, over twelve bond distances, is 1.49(1) Å with individual values ranging from 1.47 to 1.52 Å. A value of 1.50 Å has been calculated [12] from the tetrahedral covalent radius of aluminum and the covalent radius of hydrogen with Pauling's revised version of the Schomaker—Stevenson rule. There is a significant difference between the average Al—N bond distances in the six-membered ring and in the transverse bonds

TABLE 5

AVERAGE GEOMETRICAL PARAMETERS FOR $(\mathrm{HAlN}\text{-}i\text{-}\mathrm{Pr})_6$

		Molecule I	II	III	IV	I, II, III	all
Bond lengths (Å)							
Al—N	in six-memb. rings	1.898(3)	1.898(3)	1.897(5)	1.898(4)	1.897(2)	1.898(2)
	in transverse bonds	1.955(3)	1.963(3)	1.956(5)	1.948(6)	1.958(2)	1.956(2)
Al—H		1.50(2)	1.49(3)	1.48(3)	1.50(1)	1.49(1)	1.49(1)
N—C		1.519(4)	1.509(5)	1.513(10)	1.514(1)	1.514(3)	1.514(2)
C—C		1.508(4)	1.506(11)	1.505(19)	1.522(6)	1.506(7)	1.510(5)
Bond angles (°)							
N—Al—N	in six-memb. rings	116.6(3)	116.5(3)	116.4(1)	116.3(9)	116.5(1)	116.4(2)
	in four-memb. rings	91.4(2)	91.4(3)	91.4(2)	91.4(2)	91.4(1)	91.4(1)
Al—N—Al	in six-memb. rings	123.1(4)	123.1(3)	123.3(1)	123.3(8)	123.2(1)	123.2(2)
	in four-memb. rings	88.5(2)	88.5(3)	88.5(2)	88.5(1)	88.5(1)	88.5(1)
Al(2)′—N(3)—C(7)	type	123.8(3)	123.1(13)	123.9(10)	124.2(4)	123.6(4)	123.8(3)
Al(3)—N(3)—C(7)	type	117.8(1)	118.0(5)	117.6(10)	117.4(5)	117.8(3)	117.7(2)
Al(1)—N(3)—C(7)	type	110.5(7)	110.7(3)	110.5(4)	110.5(5)	110.5(2)	110.5(2)

joining these rings (belonging therefore to four-membered rings). In the former case the average of 1.898(2) Å is somewhat smaller than the average of 1.956(2) observed in the latter. This difference may be simply explained by the geometry of the molecule which forces three bond angles of nitrogen to open up with respect to ideal tetrahedral sp^3 hybridization: this causes more *s* character to be used in these bonds, which are shorter, and more *p* character to be left in the fourth, which is longer.

Other important differences occur in the Al—N—Al and N—Al—N bond angles in the two types of rings: in the six-membered rings, the average N—Al—N bond angle is 116.4(2)° which is smaller than the average Al—N—Al bond angle of 123.2(2)°, while in four-membered rings the former is 91.4(1)°, which is slightly greater than the latter of 88.5(1)°. The six-membered rings are little puckered and their chair shape is apparent from the deviations of the atomic positions from their mean planes (see Table 4): these deviations are 0.04 Å away from the cage for the three nitrogen atoms, and 0.04 Å toward the centre of the cage for the three aluminum atoms (these figures are identical for all the four molecules).

The Al—N—C bond angles, quite similar for all four molecules, are divided to three types. By referring to Fig. 1, type I may be exemplified by Al(2)′—N(3)—C(7), type II by Al(3)—N(3)—C(7) and type III by the Al(1)—N(3)—C(7) bond angle. The angles of type I, averaging 123.8(3)°, are most responsible for allowing good contacts between the methyls of isopropyl groups at opposite corners of the four-membered rings. The angles of type II are larger than those of type III, averaging 117.2(2)° and 110.5(2)° respectively, and this difference clearly results from the lengthening of the distance between the methyl group [C(8) in the example] and the hydrogen at the nearest aluminum atom [Al(3)]. In this way, the hydridic hydrogens are spaced out from the nearest carbon atoms by distances which fall in the range 3.0 to 3.5 Å.

The distinction between the two type of conformers, A and B has been neglected because, as is seen in Table 4, they do not present any significant differences both as regards bond lengths and bond angles. The same close similarity is found for the non-bonded distances, the comparatively shorter methyl—methyl contacts (but greater than 4.0 Å) being scarcely relevant in conformer B. It is therefore believed that the potential energy of the more symmetrical conformer A is only slightly lower than that of conformer B. Consequently, the presence in the crystal of the two conformers could be attributed to entropic factors. Many other conformers, obtainable by arranging the alkyl groups in staggered conformations about the N—C bond, could possess potential energies equal to or higher than that of conformer B. On the basis of the molecular structure observed in the solid state we find it difficult to believe that in solution free rotation around the N—C bonds occurs, as is suggested by NMR spectroscopy. It is certain that large oscillations around conformation equilibria take place quite readily. Whether or not these rotations occur freely, the volume swept out by the alkyl groups seems large enough to determine the so-called 'front strain' [13], which accounts for the high solubility of the compound even in non polar solvents. That the corresponding methyl derivative is quite insoluble in these solvents supports this hypothesis. Nevertheless this effect does not minimize the space around the hydridic hydrogens where there is room enough, especially on the side of six-membered rings, so that a small molecule or an external functional group of a big molecule, might approach the hydrogen and aluminum atoms and react with them.

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