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

IV*. THE PREPARATION AND CRYSTAL STRUCTURE OF $[H(HAlN\text{-}i\text{-}Pr)_5AlH_2]\cdot LiH/Et_2O$

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Summary

The compound $[H(HAlN\text{-}i\text{-}Pr)_5AlH_2]\cdot LiH/Et_2O$ has been prepared, and its crystal and molecular structure has been determined from single-crystal, three-dimensional X-ray diffractometer data. The molecular structure is a pseudo-hexameric cage, consisting of a five-membered fragment, Al—N—Al—N—Al, crosslinked to a six-membered cyclohexane type ring, $(AlN)_3$. The hydrogen atom of LiH is indistinguishable from the other hydridic hydrogens, so that the *N*-isopropyliminoalane part of the molecule may be considered as an anion with a formal charge of −1. The lithium cation is linked to two adjacent molecules through three Li—H—Al bridges, the fourth position of its tetrahedral coordination being occupied by the oxygen of diethyl ether. Large distortions of the tetrahedral valence angles occur, both on the aluminum atoms and on the nitrogen atoms, together with a noticeable spread of the Al—N bond lengths, averaging 1.919(4) Å. Colourless crystals of the compound have the following crystal data: orthorhombic space group $Pna2_1$; $a = 19.76(2)$, $b = 10.38(1)$, $c = 16.60(2)$ Å; $Z = 4$; calculated density 1.048 g/cm^3. The structure has been refined by block-matrix least-squares methods, using 2487 independent reflections, to an usual R factor of 5.9%.

Introduction

As part of our research program on the stereochemistry of poly(*N*-alkyliminoalanes), abbreviated PIA, an X-ray structural analysis of the title compound,

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[*] For parts I, II and III, see refs. 9, 1 and 6.

referred to as PIALIH, was undertaken, with the aim of clarifying the mode of bonding in complexes formed by the cage molecule of PIA with alkaline hydrides. Chemical analysis indicated a pseudo-hexameric cage (consisting of 6 Al and 5 N atoms), plus one molecule of LiH and one molecule of diethyl ether. Because LiH is a component of the reaction mixture, the compound was believed to be a precursor of the hexameric cage molecule $(HAlN\text{-}i\text{-}Pr)_6$, previously studied [1]. Therefore, it was hoped that knowledge of its structure would give some indication of the mechanism of formation of PIA.

Experimental

Synthesis

A molar excess of LiH suspended in diethyl ether was treated with $AlCl_3 \cdot Et_2O$ (Li/Al = 4) during 1 h at room temperature. To the suspension of AlH_3 polymer thus formed, isopropylamine was added during 30 min, in a molar ratio $H_2N\text{-}i\text{-}Pr/AlH_3$ 0.87. The mixture was stirred for 6 h at room temperature and solid material filtered off. The residue remaining after removal of diethyl ether from the filtrate was washed with anhydrous heptane and then dissolved in a mixture of diethyl ether and hexane. This solution, was set aside for a day, and the crystals were removed, dried and analyzed. (Found: C, 42.5; N, 12.8; Al, 29.8; Li, 1.6%; H_{active}/Al, 1.52. $H_8N_5Al_6(iso\text{-}C_3H_7)_5 \cdot LiH/Et_2O$ calcd.: C, 42.46; N, 13.03; Al, 30.12; Li, 1.29%; H_{active}/Al, 1.5.)

X-ray analysis

Single crystals of PIALIH are colourless, and roughly prismatic. The space group and preliminary lattice constants were determined from Weissenberg photographs. From the systematic absences and presumed density, the space group $Pna2_1$ was assigned, and subsequently confirmed by successful refinement. More accurate unit cell parameters were obtained from measurements of the setting angles of 22 reflections on the diffractometer. Crystal data are summarized in Table 1.

Intensities were collected on a computer-operated Siemens AED diffractometer by a procedure described in a previous paper [1], using Zr-filtered Mo-K_α radiation. A crystal, with approximate dimensions 0.5 × 0.7 × 0.8 mm, was sealed in a thin-walled glass capillary under nitrogen and was aligned with the *c* axis along the ϕ axis of the diffractometer. A total of 3443 reflections having

TABLE 1

CRYSTAL DATA FOR $[H(HAlN\text{-}i\text{-}Pr)_5AlH_2] \cdot LiH/Et_2O$

Molecular formula:	$\{H[HAlN(iso\text{-}C_3H_7)]_5AlH_2\} \cdot LiH/(C_2H_5)_2O$
Molecular weight:	537.5
Space group:	$Pna2_1$
Molecules/unit cell:	4
Calculated density:	1.048 g/cm^3
Cell constants: (Mo-K_α radiation, λ = 0.71069 Å)	a = 19.76(2), b = 10.38(1), c = 16.60(2) Å
Cell volume:	3404.0 Å^3

$(\sin\theta)/\lambda < 0.62$ Å^{-1} were collected, and of these, 2487 having intensities above $2.5\,\sigma\,(I)$, $\sigma^2\,(I) = [\text{total counts} + (0.005\,I)^2]$, were utilized throughout. A standard reflection (6 0 0), checked every 15 reflections, showed a 5% decay in intensity during the data collection run; a correction factor varying continuously from 1.0 to 1.05 was therefore applied to the measured intensities. The absorption correction was disregarded ($\mu R < 0.2$ for Mo-K_α radiation).

Structure amplitudes were put on an absolute scale by Wilson's statistical method and normalized structure factors $|E|$ were calculated.

Structure determination and refinement

The structure was solved by means of direct methods, using the program MULTAN by Main et al. [2]. The 442 largest and the 50 smallest $|E|$ values were used as input data. The program selected a starting set composed of 6 reflections, three fixing the origin (13 3 0, 0 1 7, 2 5 6) and three with variable phase (1 4 0 with restricted phase, 8 1 3 and 19 3 4 with general phase). A total of 32 combinations of initial phases were processed and after phase refinement by means of a weighted tangent formula [2], the third most probable combination (on the basis of the 'figures of merit' ABS FOM = 1.64 and PSI ZERO = 1265) was found to be correct.

All the aluminum atoms were located from an E-map, and after three cycles of Fourier synthesis, phased by structure factor calculations, the position of the nitrogen, oxygen and carbon atoms were determined. The residual R over all observed reflections was 0.31 with the aluminum atoms only and 0.18 including all the other atoms mentioned above. The coordinates of these 31 atoms were refined by block-diagonal least-squares methods, using isotropic thermal parameters. The function minimized was $\Sigma w(F_o - F_c)^2$, using Cruickshank's weighting scheme [3]. After five cycles the residual R was reduced to 0.12. The lithium atom and most of the hydrogen atoms bonded to aluminum were then located from a ΔF-map; for some of the hydrogens, however, the coordinates were adjusted slightly in order to maintain the tetrahedral geometry of aluminum and a value of 1.5 Å for the Al—H bond length [1]. The hydrogen peaks of the isopropyl groups were so broad and weak that they were placed in calculated tetrahedral positions (C—H, 1.1 Å). The hydrogen atoms of the ether molecule were disregarded owing to the large thermal motions of the ether carbon atoms. In the later least-squares cycles the hydrogen positional and (isotropic) thermal parameters were refined, but with the reduction of the calculated shifts by a 'damping factor' of 0.2. The final R value was 0.059. The atomic scattering factors used throughout were calculated from the regression formula suggested by V. Vand et al., using Moore's numerical values [4]. All the calculations were performed on a IBM 360 computer using programs written by one of us (A. I.) [5].

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

Results and discussion

The molecular structure of PIALIH can be regarded as derived from that of

TABLE 2

FINAL ATOMIC FRACTIONAL COORDINATES (X 10^4) AND THERMAL PARAMETERS (X 10^2 A^2) FOR $[H(HAlN\text{-}i\text{-}Pr)_5AlH_2]\cdot LiH/Et_2O^a$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al(1)	1053(1)	-1684(2)	472(2)	314(9)	365(9)	339(9)	16(8)	14(8)	-1(9)
Al(2)	2634(1)	-1824(2)	121(2)	326(8)	386(9)	347(9)	-41(8)	-20(8)	-28(9)
Al(3)	1681(1)	-4264(2)	-198(2)	307(8)	283(8)	366(9)	-12(7)	3(8)	62(8)
Al(4)	590(1)	-3341(2)	-954(2)	303(9)	415(10)	438(11)	-22(8)	-49(9)	-25(9)
Al(5)	1974(1)	-1889(2)	1245(1)	341(8)	307(8)	280(8)	-50(7)	-9(8)	41(8)
Al(6)	3139(1)	-3877(2)	-640(2)	309(8)	414(10)	405(11)	13(8)	17(9)	-5(9)
N(1)	1780(3)	-1111(6)	-199(4)	374(26)	318(26)	354(27)	-41(21)	-10(24)	71(24)
N(2)	2514(3)	-3642(6)	242(4)	288(24)	372(27)	375(30)	33(21)	-12(22)	34(24)
N(3)	868(3)	-3417(6)	153(4)	305(25)	290(25)	416(28)	-23(21)	21(24)	110(25)
N(4)	1517(3)	-3510(6)	-1251(4)	311(23)	316(24)	208(24)	-7(19)	-4(22)	-12(23)
N(5)	2901(3)	-2200(6)	-975(4)	321(25)	420(29)	343(28)	-47(22)	46(24)	70(24)
C(1)	1881(4)	358(8)	-197(6)	628(37)	322(36)	553(38)	26(29)	-10(34)	-78(34)
C(2)	1434(6)	1006(10)	-788(7)	894(51)	377(53)	911(60)	81(44)	68(48)	106(47)
C(3)	1792(5)	920(10)	666(7)	928(48)	434(47)	623(52)	-1(39)	-45(42)	-185(41)
C(4)	2597(4)	-4351(8)	1049(5)	549(37)	585(38)	416(40)	108(31)	-44(32)	103(33)
C(5)	2846(7)	-3482(13)	1687(9)	1363(72)	817(73)	458(81)	4(62)	-273(63)	123(64)
C(6)	3003(6)	-5608(12)	924(9)	1011(67)	919(72)	764(76)	400(57)	12(62)	299(61)
C(7)	397(5)	-4178(9)	693(6)	400(43)	630(43)	754(47)	-41(36)	221(38)	261(38)
C(8)	-289(6)	-3515(10)	749(7)	435(56)	972(56)	974(60)	123(46)	157(49)	368(48)
C(9)	667(7)	-4564(13)	1437(9)	720(78)	1389(76)	909(86)	63(64)	70(70)	600(70)
C(10)	1677(4)	-4166(8)	-2044(5)	511(33)	499(33)	357(35)	-48(27)	-33(29)	-104(29)
C(11)	1236(5)	-3606(9)	-2721(6)	708(43)	656(44)	426(47)	-57(36)	-176(38)	-18(38)
C(12)	1583(5)	-5619(9)	2016(7)	938(48)	393(49)	652(49)	-35(39)	-53(41)	-125(41)
C(13)	3474(5)	-1585(9)	1446(6)	477(42)	633(44)	678(49)	-120(35)	186(33)	107(38)
C(14)	3484(5)	-2129(10)	-2288(7)	727(53)	862(53)	521(56)	-95(44)	236(46)	12(45)
C(15)	3440(5)	-162(10)	-1458(7)	661(50)	600(51)	847(56)	-191(42)	237(44)	161(45)

Atom	x	y	z	B	Atom	x	y	z	B
O(1)	-281(5)	955(9)	-1203(6)	990(23)	C(18)	-354(12)	926(20)	-2012(16)	1776(77)
C(16)	-538(9)	2121(17)	-818(12)	1261(50)	C(19)	41(12)	173(22)	-2533(16)	1565(61)
C(17)	-381(10)	2133(18)	8(14)	1343(53)	Li	-181(7)	-623(14)	-608(10)	531(27)
H'(Al1)	1250(45)	-1649(94)	1393(64)	655(231)	H'''(C6)	2778(61)	-6223(120)	547(82)	882(331)
H''(Al1)	446(43)	-826(78)	305(52)	382(194)	H(C7)	303(48)	-5272(96)	438(63)	640(252)
H(Al2)	3066(42)	-1050(88)	729(58)	489(213)	H'(C8)	-635(57)	-4059(123)	1063(80)	1060(353)
H(Al3)	1636(44)	-5667(82)	-132(61)	434(194)	H''(C8)	-574(56)	-3253(113)	175(74)	778(306)
H'(Al4)	298(43)	-1980(83)	-1165(59)	479(206)	H'''(C8)	-218(58)	-2534(103)	1031(69)	772(291)
H''(Al4)	162(43)	-4414(84)	-1216(60)	545(208)	H'(C9)	331(65)	-5145(125)	1726(88)	1224(426)
H(Al5)	1849(44)	-1013(89)	2063(61)	494(218)	H''(C9)	809(74)	-3620(154)	1706(101)	1443(451)
H'(Al6)	3934(43)	-3834(87)	-433(57)	452(220)	H'''(C9)	1133(64)	-5036(126)	1273(84)	1037(390)
H''(Al6)	2945(41)	-4959(80)	-1198(57)	406(187)	H(C10)	2176(42)	-4025(81)	2197(53)	360(195)
H(C1)	2395(49)	613(94)	-432(65)	712(253)	H'(C11)	1343(48)	-4034(94)	-3289(61)	615(248)
H'(C2)	1525(56)	2010(102)	-759(72)	762(275)	H''(C11)	1312(52)	-2562(94)	-2779(62)	656(253)
H''(C2)	901(51)	754(98)	-632(71)	628(255)	H'''(C11)	719(48)	-3728(100)	2553(65)	627(251)
H'''(C2)	1501(53)	666(99)	-1344(70)	794(284)	H'(C12)	1704(45)	-5993(95)	2552(66)	544(235)
H'(C3)	1935(52)	1861(108)	664(73)	767(298)	H''(C12)	1102(44)	-5777(88)	-1855(57)	400(221)
H''(C3)	2142(56)	516(104)	979(71)	820(289)	H'''(C12)	1880(45)	-5944(92)	-1547(63)	482(230)
H'''(C3)	1306(52)	796(105)	832(68)	753(288)	H(C13)	3969(46)	-1805(86)	1154(65)	544(228)
H(C4)	2087(45)	-4602(85)	1215(55)	378(204)	H'(C14)	3889(51)	-1801(102)	2600(65)	640(273)
H'(C5)	2859(65)	-3952(125)	2259(85)	1041(358)	H''(C14)	3087(51)	-1935(96)	-2571(65)	521(258)
H''(C5)	2526(63)	-2729(106)	1872(75)	875(345)	H'''(C14)	3541(57)	-3059(112)	-2284(71)	741(279)
H'''(C5)	3305(67)	-3174(139)	1396(100)	1325(418)	H'(C15)	3794(54)	67(107)	-1787(71)	774(294)
H'(C6)	3075(55)	-6041(114)	1577(79)	742(328)	H''(C15)	3503(45)	140(92)	-877(62)	488(229)
H''(C6)	3500(61)	-5243(122)	750(80)	928(339)	H'''(C15)	3018(56)	135(107)	-1643(67)	699(275)

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[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.

the hexamer, $(HAlN\text{-}i\text{-}Pr)_6$, previously designated as PIAHEX, by replacing one $\geqslant$N-i-Pr group with two hydrogen atoms and by adding a molecule of LiH. It may be seen from Fig. 1 that in the LiH derivative, only one of the two six-membered cyclohexane-like rings, $(AlN)_3$, which form the cage of PIAHEX, is fully preserved; the second, broken by the loss of a nitrogen atom, is reduced to the fragment Al(4)—N(4)—Al(5)—N(5)—Al(6). This fragment is joined to the six-membered ring in a special way: in contrast with the situation for the hexameric

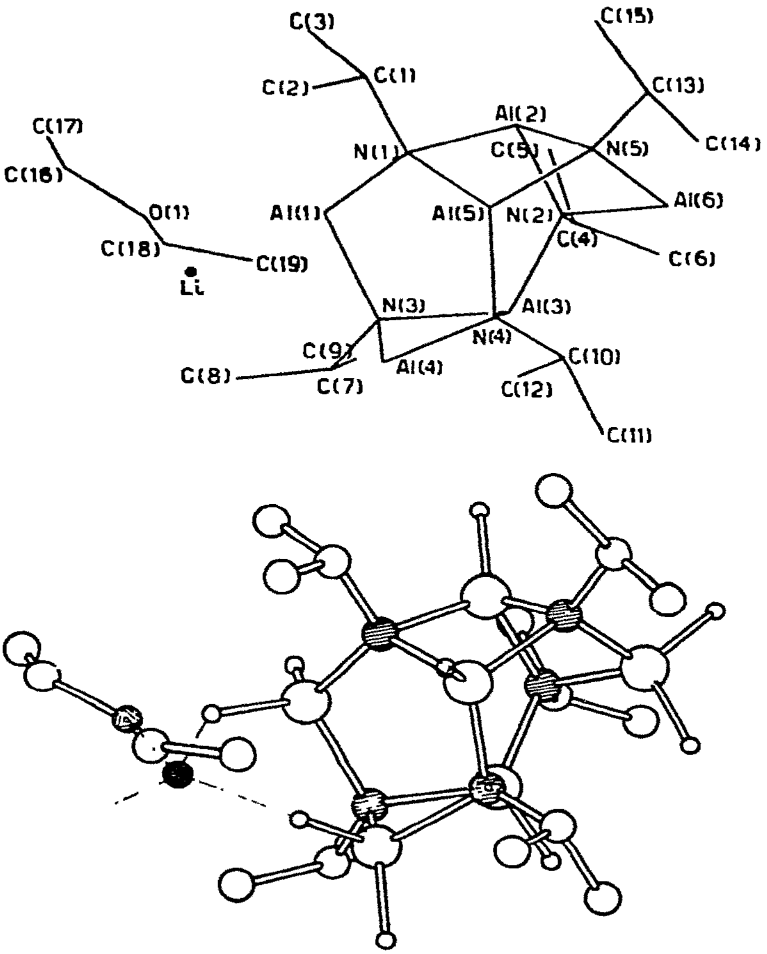

Fig. 1. Perspective view and labelling scheme for the molecule of $[H(HAlN\text{-}i\text{-}Pr)_5AlH_2]\cdot LiH/Et_2O$.

cage molecule, the N(4) atom is bonded not to Al(6) in the adjacent position on the ring but rather to Al(5), which is located on the opposite side of the ring from N(4). The conformation of the six-membered ring is clearly of the skew-boat type (see in Table 3 the internal rotation angles). The largest displacements from the mean plane towards the other part of the molecule occur for the N(1) (0.57 Å) and Al(3) (0.42 Å) atoms, which form part of the central bridge N(1)—Al(5)—N(4)—Al(3).

For the three aluminum atoms Al(1), Al(4) and Al(6), each of which is linked to two nitrogen atoms only, the tetrahedral coordination is completed by a pair of hydrogen atoms. Since one of these must be furnished by the LiH molecule, the distorted cage may be considered as an anion with a formal charge of −1. In the crystal, the lithium cation is linked through three hydrogen bridges with Al(1), Al(4) and Al(6)′ (the latter atom belonging to an adjacent molecule); the fourth position of its tetrahedral coordination is occupied by the oxygen of diethyl ether. Thus, as shown in Fig. 2, the crystal structure of PIALIH is built

(continued on p. 50)

TABLE 3

GEOMETRICAL PARAMETERS FOR $[H(HAlN\text{-}i\text{-}Pr)_5AlH_2]\cdot LiH/Et_2O$.

Bond lengths (Å) and angles (°) involving hydrogen atoms

Al(1)-H'(Al1)	1.58(11)	Al(1)-H''(Al1)	1.52(8)	Al(2)-H(Al2)	1.55(9)
Al(3)-H(Al3)	1.46(8)	Al(4)-H'(Al4)	1.56(9)	Al(4)-H''(Al4)	1.46(9)
Al(5)-H(Al5)	1.65(10)	Al(6)-H'(Al6)	1.61(9)	Al(6)-H''(Al6)	1.51(9)
Li-H''(Al1)	1.98(9)	Li-H'(Al4)	1.93(9)	Li-H'(Al6)	1.85(9)
Al(1)-H''(Al1)-Li	134.5(12)	Al(4)-H'(Al4)-Li	137.0(14)	Al(6)-H'(Al6)-Li	151.0(14)
O(1)-Li-H''(Al1)	123.5(20)	O(1)-Li-H'(Al4)	115.1(22)	H''(Al1)-Li-H'(Al4)	89.0(25)
H'(Al4)-Li-H'(Al6)	108.3(26)	H'(Al6)-Li-H''(Al1)	116.0(23)	O(1)-Li-H'(Al6)	104.0(27)

(H'(Al6) refers to the equivalent position $x-\frac{1}{2}$, $-y-\frac{1}{2}$, z)

Internal rotation angles (°)

Al(1)-N(1)-C(1)-C(2)	274.8	Al(1)-N(1)-C(1)-C(3)	40.5	Al(2)-N(1)-C(1)-C(2)	151.2
Al(2)-N(1)-C(1)-C(3)	276.8	Al(5)-N(1)-C(1)-C(2)	60.0	Al(5)-N(1)-C(1)-C(3)	185.7
Al(2)-N(2)-C(4)-C(5)	354.2	Al(2)-N(2)-C(4)-C(6)	223.8	Al(3)-N(2)-C(4)-C(5)	221.6
Al(3)-N(2)-C(4)-C(6)	91.3	Al(6)-N(2)-C(4)-C(5)	105.6	Al(6)-N(2)-C(4)-C(6)	335.3
Al(1)-N(3)-C(7)-C(8)	59.5	Al(1)-N(3)-C(7)-C(9)	287.5	Al(3)-N(3)-C(7)-C(8)	193.8
Al(3)-N(3)-C(7)-C(9)	61.7	Al(4)-N(3)-C(7)-C(8)	294.8	Al(4)-N(3)-C(7)-C(9)	162.8
Al(3)-N(4)-C(10)-C(11)	156.5	Al(3)-N(4)-C(10)-C(12)	33.7	Al(4)-N(4)-C(10)-C(11)	48.2
Al(4)-N(4)-C(10)-C(12)	285.4	Al(5)-N(4)-C(10)-(11)	280.7	Al(5)-N(4)-C(10)-C(12)	157.9
Al(2)-N(5)-C(13)-C(14)	182.2	Al(2)-N(5)-C(13)-C(15)	306.8	Al(5)-N(5)-C(13)-C(14)	293.0
Al(5)-N(5)-C(13)-C(15)	57.5	Al(6)-N(5)-C(13)-C(14)	77.4	Al(6)-N(5)-C(13)-C(15)	202.0
Al(1)-N(1)-Al(2)-N(2)	49.3	N(1)-Al(2)-N(2)-Al(3)	12.7	Al(2)-N(2)-Al(3)-N(3)	307.2
N(2)-Al(3)-N(3)-Al(1)	26.5	Al(3)-N(3)-Al(1)-N(1)	32.3	N(3)-Al(1)-N(1)-Al(2)	284.5
Al(3)-N(4)-Al(5)-N(5)	55.3	N(4)-Al(5)-N(5)-Al(6)	351.6	Al(5)-N(5)-Al(6)-N(2)	299.2
N(5)-Al(6)-N(2)-Al(3)	89.7	Al(6)-N(2)-Al(3)-N(4)	311.2	N(2)-Al(3)-N(4)-Al(5)	332.8
Al(1)-N(1)-Al(5)-N(4)	342.7	N(1)-Al(5)-N(4)-Al(4)	51.1	Al(5)-N(4)-Al(4)-N(3)	275.7
N(4)-Al(4)-N(3)-Al(1)	89.0	Al(4)-N(3)-Al(1)-N(1)	298.0	N(3)-Al(1)-N(1)-Al(5)	23.2

Bond lengths (Å)

Al(1)-N(1)	1.914(7)	Al(1)-N(3)	1.910(6)	Al(2)-N(1)	1.918(7)
Al(2)-N(2)	1.912(7)	Al(2)-N(5)	1.936(7)	Al(3)-N(2)	1.914(7)
Al(3)-N(3)	1.922(7)	Al(3)-N(4)	1.942(7)	Al(4)-N(3)	1.921(8)
Al(4)-N(4)	1.906(6)	Al(5)-N(1)	1.953(8)	Al(5)-N(4)	1.910(6)
Al(5)-N(5)	1.914(7)	Al(6)-N(2)	1.930(7)	Al(6)-N(5)	1.886(7)
N(1)-C(1)	1.537(8)	N(2)-C(4)	1.538(9)	N(3)-C(7)	1.514(10)
N(4)-C(10)	1.516(8)	N(5)-C(13)	1.518(9)	C(1)-C(2)	1.482(14)
C(1)-C(3)	1.558(14)	C(4)-C(5)	1.476(17)	C(4)-C(6)	1.545(15)
C(7)-C(8)	1.525(14)	C(7)-C(9)	1.405(18)	C(10)-C(11)	1.537(13)
C(10)-C(12)	1.520(13)	C(13)-C(14)	1.507(15)	C(13)-C(15)	1.478(14)
O(1)-Li	1.922(17)	O(1)-C(16)	1.46(2)	O(1)-C(18)	1.35(3)
C(16)-C(17)	1.41(3)	C(18)-C(19)	1.40(3)		

Bond angles (°)

N(1)-Al(1)-N(3)	105.9(1)	N(1)-Al(2)-N(2)	107.5(1)	N(1)-Al(2)-N(5)	93.3(1)
N(2)-Al(2)-N(5)	86.2(1)	N(2)-Al(3)-N(4)	110.6(1)	N(3)-Al(3)-N(4)	87.1(1)
N(2)-Al(3)-N(3)	116.7(1)	N(3)-Al(4)-N(4)	88.2(1)	N(1)-Al(5)-N(4)	106.0(1)
N(1)-Al(5)-N(5)	92.8(1)	N(4)-Al(5)-N(5)	107.8(1)	N(2)-Al(6)-N(5)	87.0(1)
Al(1)-N(1)-Al(2)	112.3(1)	Al(1)-N(1)-Al(5)	122.5(1)	Al(2)-N(1)-Al(5)	85.1(1)
Al(1)-N(1)-C(1)	113.8(3)	Al(2)-N(1)-C(1)	105.5(3)	Al(5)-N(1)-C(1)	112.7(4)
Al(2)-N(2)-Al(3)	113.5(1)	Al(2)-N(2)-Al(6)	88.1(1)	Al(3)-N(2)-Al(6)	102.6(1)
Al(2)-N(2)-C(4)	123.4(4)	Al(3)-N(2)-C(4)	105.3(3)	Al(6)-N(2)-C(4)	122.1(4)
Al(1)-N(3)-Al(3)	110.8(1)	Al(1)-N(3)-Al(4)	106.4(1)	Al(3)-N(3)-Al(4)	88.1(1)
Al(1)-N(3)-C(7)	116.4(4)	Al(3)-N(3)-C(7)	117.0(4)	Al(4)-N(3)-C(7)	114.4(4)
Al(3)-N(4)-Al(4)	88.0(1)	Al(3)-N(4)-Al(5)	105.7(1)	Al(4)-N(4)-Al(5)	111.8(1)
Al(3)-N(4)-C(10)	124.5(4)	Al(4)-N(4)-C(10)	117.8(4)	Al(5)-N(4)-C(10)	107.6(3)
Al(2)-N(5)-Al(5)	85.7(1)	Al(2)-N(5)-Al(6)	88.6(1)	Al(5)-N(5)-Al(6)	117.6(1)
Al(2)-N(5)-C(13)	127.2(5)	Al(5)-N(5)-C(13)	121.5(5)	Al(6)-N(5)-C(13)	110.7(4)
N(1)-C(1)-C(2)	111.7(3)	N(1)-C(1)-C(3)	111.0(3)	C(2)-C(1)-C(3)	111.8(4)
N(2)-C(4)-C(5)	111.6(3)	N(2)-C(4)-C(6)	110.0(3)	C(5)-C(4)-C(6)	116.0(5)
N(3)-C(7)-C(8)	110.3(3)	N(3)-C(7)-C(9)	115.9(3)	C(8)-C(7)-C(9)	114.3(6)
N(4)-C(10)-C(11)	110.3(3)	N(4)-C(10)-C(12)	112.8(3)	C(11)-C(10)-C(12)	109.4(4)
N(5)-C(13)-C(14)	109.3(3)	N(5)-C(13)-C(15)	113.1(3)	C(14)-C(13)-C(15)	111.3(4)
C(16)-O(1)-C(18)	114.6(10)	O(1)-C(16)-C(17)	111.0(8)	O(1)-C(18)-C(19)	124.5(11)

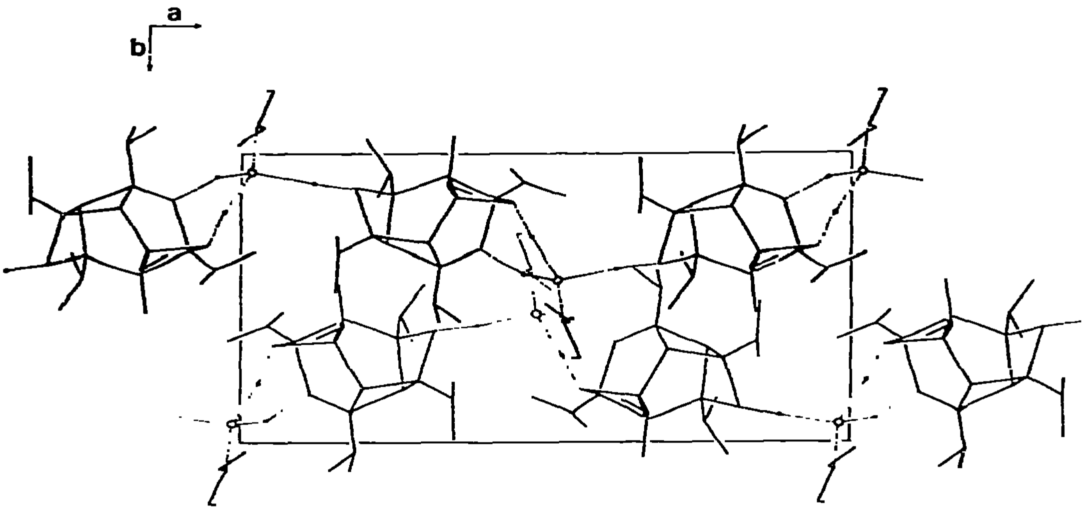

Fig. 2. A representation of the packing of [H(HAlN-i-Pr)$_5$AlH$_2$] · LiH/Et$_2$O; projection along the *c* axis.

up of chains of molecules held together by these hydrogen bridges and running approximately along the *a* axis. This feature accounts for the insolubility of the compound in non-polar solvents. The lateral packing of the chains is controlled by methyl—methyl contacts of the alkyl substituents, all of which are greater than 3.78 Å.

Owing to the multiple ring configuration large distortions of the tetrahedral valence angles occur for both the aluminum and nitrogen atoms, together with a noticeable spread of Al—N bond lengths, although the e.s.d.'s derived for the bond lengths from the least-squares refinement are in many cases too large to allow detailed comparisons. The overall average Al—N bond distance is 1.919(4) Å, with single values falling in the range 1.886 to 1.953 Å. It is interesting to note however that the largest distances, averaging 1.936(6) Å, occur for the Al—N bonds joining the six-membered ring to the five atom fragment as described above. This feature is quite analogous to those observed and discussed previously for the structure of PIAHEX [1] and its adduct, (HAlN-i-Pr)$_6$AlH$_3$ (PIAHAL) [6].

The Al—N—Al bond angles range from 85.1° to 122.5° and N—Al—N bond angles from 86.2° to 116.7°. Here too, the trend of these angles is similar to that remarked in the above cited structures: thus, in spite of a few outlying single values, in the six-membered ring the average Al—N—Al bond angle is a little larger than the average N—Al—N bond angle [112.2(9)° and 110.0(40)° respectively] whereas in the four-membered rings the corresponding angles average 87.3(6)° and 89.1(14)°. The average Al—H bond distance is 1.54(3) Å, slightly larger than the average observed in PIAHEX [1.49(1) Å] and in PIAHAL [1.51(1) Å]; however the e.s.d. of the mean indicates the difference to be scarcely significant. The average Li—H$_b$ bond distance is 1.92(4) Å, a value comparable to the 2.04 Å found in LiH, where the metal is hexacoordinated [7]; the corresponding Al—H$_b$ average is 1.56(3) Å. The spread of the values of the bond lengths is also observed for the N—C and C—C bonds, for which the resulting averages are 1.525(6) and 1.503(15) Å respectively. The torsion angles about the

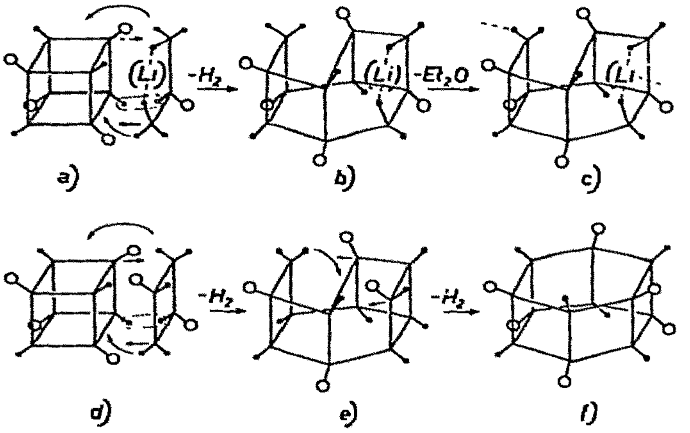

Fig. 3. A scheme proposed for the mechanism of formation of [$H(HAlN$-i-$Pr)_5AlH_2$] LiH/Et_2O (*a,b,c*) and the hexamer, ($HAlN$-i-$Pr)_6$ (*d,e,f*). Lithium atoms to which diethyl ether molecules are attached are enclosed in parentheses. Hydridic hydrogens are indicated with black filled circles, hydrogen atoms bonded to nitrogen atoms with small open circles and alkyl groups with large open circles.

N—C bonds, unlike those in the parent cage structures, do not in general correspond to staggered conformations. This can probably be ascribed to the presence in this structure of the intermolecular hydrogen bridges, which constrain some isopropyl groups to be bent away from the staggered conformation in order to achieve better distances between the methyl groups of adjacent molecules. For example, the C(5) and C(6) methyls which belong to an almost eclipsed isopropyl group, display some of the shortest methyl—methyl contacts (3.85 and 3.88 Å respectively).

One of the major interests of this structure resides in the information it may provide about the mechanism of formation of cage molecule of poly(*N*-alkyliminoalanes). Cucinella et al. have recently found that in the synthesis of PIA by a new method [8], tetramers are formed; these oligomers can be converted into more stable hexamers such as PIAHEX when isopropylamine and AlH_3 are added to their solution. Thus, since dimers are quite probable precursors of tetramers, we suggest the scheme shown in Fig. 3 as a possible mechanism of formation of PIALIH as well of the hexameric cage molecules. It is hoped that additional information on this aspect will emerge from our research now in progress.

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