

## THE CHEMISTRY AND THE STEREOCHEMISTRY OF POLY(*N*-ALKYL-IMINOALANES)

### V\*. THE PREPARATION AND CRYSTAL STRUCTURE OF THE PENTAMER [(HAIN-*i*-Pr)<sub>2</sub>(H<sub>2</sub>AlNH-*i*-Pr)<sub>3</sub>]

G. PEREGO, G. DEL PIERO, M. CESARI, A. ZAZZETTA and G. DOZZI

*Snamprogetti S.p.A., Direzione Ricerca e Sviluppo, 20097 San Donato Milanese, Milano (Italy)*

(Received October 1st, 1974)

#### Summary

The compound [(HAIN-*i*-Pr)<sub>2</sub>(H<sub>2</sub>AlNH-*i*-Pr)<sub>3</sub>] has been prepared and the crystal and molecular structure determined by an X-ray analysis, carried out with three-dimensional data collected on a diffractometer. The molecule is made up of a cyclohexane-type ring, [(HAIN-*i*-Pr)<sub>2</sub>(H<sub>2</sub>AlNH-*i*-Pr)], in skew-boat conformation, on each side of which is bonded an —H<sub>2</sub>AlNH-*i*-Pr— bridging unit between a nitrogen atom and an aluminum atom of the ring. The molecule lies on a binary axis of the crystal, but this symmetry is fulfilled only by a statistical orientation of the asymmetric molecular units (the statistical model is not however completely defined). The Al—N bond lengths range from 1.901 to 1.985 Å; the average N—C bond length is 1.527(9) Å. Main crystal data are: monoclinic space group *C2/c*; *a* = 10.15(2), *b* = 21.64(3), *c* = 12.84(2) Å, *β* = 111.9(5)°; *Z* = 4; calculated density 1.095 g/cm<sup>3</sup>. The structure was solved by direct methods and block-matrix least-squares converged to an *R* value of 5.6%.

#### Introduction

The synthesis and structural resolution of the title compound, subsequently referred to as PIAPEN, have been carried out as part of our study of poly(*N*-alkyliminoalanes), (PIA) [1–4]. Probably the formation of a true pentakis(*N*-alkyliminoalane), (HAIN-*i*-Pr)<sub>5</sub>, is very difficult or impossible, if tetracoordination on aluminum and nitrogen atoms is to be preserved; therefore, although PIAPEN contains *N*-isopropylaminoalane groups, —H<sub>2</sub>AlNH-*i*-Pr—, we prefer to consider this compound as the pentameric form of PIA.

\* For parts I–IV see refs. 1–4.

## Experimental

### Synthesis

The title compound was separated from a mixture of products from the reaction between  $\text{AlH}_3$  and  $i\text{-C}_3\text{H}_7\text{NH}_2$  ( $\text{AlH}_3$  was synthesized in situ via  $\text{NaAlH}_4$ ). A solution of  $\text{AlCl}_3$  (348 mmol) in diethyl ether (150 ml) was added dropwise to a stirred suspension of  $\text{NaH}$  (1045 mmol) in boiling diethyl ether/hexane (300 ml, in volume ratio 60/40) containing small amounts of  $\text{AlEt}_3$  (10 mmol). The mixture was initially heated, but subsequently the boiling temperature was maintained by regulation of the  $\text{AlCl}_3$  addition. The  $\text{AlCl}_3$  solution was added in two stages: after addition of the amount corresponding to the formation of  $\text{NaAlH}_4$ , the reaction mixture was stirred for 1 h at the boiling temperature, and then the remaining  $\text{AlCl}_3$  was added. Finally the reaction was completed, as confirmed by the disappearance of chlorine in the solution, by further refluxing for 2 h. Isopropylamine (325 mmol) in diethyl ether (50 ml) was then added dropwise; hydrogen was evolved and the reaction mixture was refluxed for 8 h. The mixture was filtered and the solvent was evaporated from the solution in vacuo and replaced by diethyl ether. The ether solution was cooled to about  $5^\circ$ . After 50 h the crystals which formed were separated by decantation, dried, and analyzed (the yield was 4.5 g). (Found: Al, 29.80; N, 15.89;  $H_{\text{active}}$ , 18.40.  $\text{C}_{15}\text{H}_{46}\text{N}_5\text{Al}_5$  calcd.: Al, 31.25; N, 16.22;  $H_{\text{active}}$ , 18.55%.)

### X-ray analysis

Crystals of PIAPEN, colourless and prismatic in shape, were sealed in thin-walled glass capillaries under dry nitrogen because of their instability to moisture. From Weissenberg photographs, the monoclinic space groups  $C2/c$  or  $Cc$  were deduced; the former was confirmed by subsequent successful refinement.

Accurate cell dimensions were determined by least-squares refinement of 18 carefully centered reflections on the diffractometer; they are given with other pertinent data in Table 1.

Intensity data were collected from a crystal of approximate dimensions  $0.4 \times 0.5 \times 0.75$  mm, mounted with the  $a$  axis parallel to the spindle axis of a computer-operated Siemens AED diffractometer. Intensities were measured using Zr-filtered  $\text{Mo-K}\alpha$  radiation by a procedure described in a previous paper [2]. A total of 2718 independent reflections up to  $(\sin \theta/\lambda)$   $0.62 \text{ \AA}^{-1}$  were collected, of which 1826 with intensities greater than  $2.5\sigma(I)$  where  $\sigma^2(I) = [\text{total counts} + (0.005 I)^2]$  were used in the structure determination. The variation of

TABLE 1

CRYSTAL DATA FOR  $[(\text{HAlN}(i\text{-Pr}))_2(\text{H}_2\text{AlNH}(i\text{-Pr}))_3]$ 

Molecular formula:	$[\text{HAlN}(i\text{-C}_3\text{H}_7)]_2[\text{H}_2\text{AlNH}(i\text{-C}_3\text{H}_7)]_3$
Molecular weight:	431.5
Space group:	monoclinic, $C2/c$
Molecules/unit cell:	4
Calculated density:	$1.095 \text{ g/cm}^3$
Cell constants:	$a = 10.15(2)$ , $b = 21.64(3)$ , $c = 12.84(2) \text{ \AA}$ .
$\text{Mo-K}\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$	$\beta = 111.9(5)^\circ$
Cell volume:	$2615.9 \text{ \AA}^3$

the intensity of a selected standard reflection, measured every 15 reflections, reached a maximum of 8% during the experiment; the scale factor was adjusted on the assumption that all other intensities varied at the same rate. A correction for Lorentz and polarization factors was applied, but the absorption effect was neglected owing to the low value of the transmission factor ( $\mu R < 0.2$ ). Structure amplitudes were put on an absolute scale by Wilson's statistical method, and  $|E|$  values were computed.

### Structure determination and refinement

The structure was solved by application of direct methods, using the program MULTAN written by Main et al. [5]. The greatest 200  $|E|$  values ( $> 1.6$ ) and the smallest 50 were used, assuming the acentric  $Cc$  space group. The starting reflections chosen by the program were:  $3\ 13\ \bar{2}$  and  $4\ 6\ \bar{1}$  fixing the origin,  $10\ 12\ \bar{4}$  fixing the enantiomorph; those, with variable phases were  $10\ 12\ \bar{4}$ ,  $8\ 2\ \bar{3}$  and  $5\ 7\ \bar{7}$ . The program gave 32 independent solutions, of which the 32nd, having 'figures of merit' ABS FOM = 1.225 and PSI ZERO = 2561, led to correct solution of the structure.

From the  $E$ -map, all the aluminum and nitrogen atoms were located, and from the next Fourier synthesis the positions of all the carbon atoms were deduced; the  $R$  residual was 0.21. Thus far, the image of the molecule shown by the Fourier map gave very strong evidence of a binary axis, suggesting  $C2/c$  as the correct space group. Refinements carried out at the beginning for both  $Cc$  and  $C2/c$  space groups indicated that the former was to be definitely rejected. After five block-diagonal least-squares cycles with isotropic thermal parameters, the  $R$  factor was reduced to 0.12. A  $\Delta F$ -map was then computed, which allowed the location of almost all the hydrogen atoms. However for those bonded to Al(1), N(1), C(1) and C(2), which occupy two sets of nearby positions, only mean positions were found. After four cycles with anisotropic thermal parameters and fixed contributions of the hydrogen atoms, the  $R$  factor dropped to 0.059. Three more cycles in which the hydrogen atoms were isotropically refined led to a final  $R$  value of 0.056.

Atomic scattering factors are those of Moore [6], for neutral atoms. All computer programs, with the exception of MULTAN, were those written by Immirzi [7]. The final values of positional and thermal parameters are reported in Table 2. A list of structure factors is obtainable from the authors on request.

### Results and discussion

Bond lengths and angles, including torsion angles, are reported in Table 3. A skeletal picture of the molecular structure, showing the statistical positions of some of the atoms, is given in Fig. 1. A perspective view of the molecule is shown in Fig. 2.

The molecule is essentially built up of a six-membered ring,  $[(\text{HAlN-}i\text{-Pr})_2(\text{H}_2\text{AlNH-}i\text{-Pr})]$ , crossed on either side by a bridging unit  $-\text{H}_2\text{AlNH-}i\text{-Pr}-$ , each one giving rise to two more secondary six-membered rings,  $(\text{AlN})_3$ . The molecule possesses only a pseudo-binary axis, passing approximately through Al(1) and N(1). However, as may be seen in Fig. 3, the molecules in

(continued on p. 59)

TABLE 2

FINAL ATOMIC FRACTIONAL COORDINATES ( $\times 10^4$ ) AND THERMAL PARAMETERS ( $\times 10^3 \text{ \AA}^2$ ) FOR  $[(\text{HAIN}+\text{Pr})_2(\text{H}_2\text{AINH}+\text{Pr})_3]_d$ .

Atom	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$D_{12}$	$D_{13}$	$D_{23}$
Al(2)	1857(1)	3840(0)	4536(1)	390(4)	666(5)	483(4)	0(3)	157(3)	10(4)
Al(3)	1270(1)	3386(0)	2073(1)	359(3)	417(3)	550(4)	6(3)	238(3)	-20(3)
N(2)	1615(2)	4085(1)	3036(2)	319(9)	448(10)	493(10)	-17(8)	177(8)	-13(9)
N(3)	-118(3)	3714(1)	4375(2)	443(11)	548(12)	501(11)	45(9)	239(9)	82(9)
C(2)	932(5)	1869(1)	2113(3)	898(25)	411(14)	892(24)	90(15)	497(21)	10(15)
C(3)	2969(3)	4387(2)	3004(3)	388(12)	577(16)	665(17)	-82(11)	206(12)	21(13)
C(4)	3102(4)	5065(2)	3324(4)	558(19)	781(23)	974(27)	-197(16)	275(19)	-92(20)
C(5)	4313(4)	4048(3)	3722(4)	386(14)	877(23)	850(23)	-33(15)	239(15)	1(19)
C(6)	-232(4)	3482(2)	5449(3)	607(17)	785(20)	552(16)	52(15)	314(14)	67(15)
C(7)	-1653(5)	3676(2)	5494(4)	876(26)	830(24)	936(27)	8(20)	631(23)	-36(21)
C(8)	-29(5)	2805(2)	5566(4)	950(27)	712(21)	789(23)	67(20)	465(21)	131(18)

Atom	x	y	z	Atom	x	y	z	B
Al(1)	-26(3)	4636(1)	2365(2)	N(1)	-176(5)	2865(2)	2262(3)	370(8)
C(1)	341(6)	2242(2)	2835(4)					
H <sup>1</sup> (Al1)	79(88)	4976(33)	3365(67)	H <sup>1</sup> (Al1)	-144(97)	4968(37)	1287(72)	745(220)
H <sup>1</sup> (Al2)	2438(38)	4318(16)	5377(30)	H <sup>1</sup> (Al2)	2571(34)	3198(14)	4804(26)	327(69)
H <sup>1</sup> (Al3)	2457(37)	3073(16)	1955(29)	H(N1)	-873(97)	2576(39)	1518(77)	771(234)
H(N3)	-339(36)	4062(16)	4339(29)	H(C1)	878(101)	2572(41)	3477(81)	821(250)
H <sup>1</sup> (C2)	1546(41)	2069(19)	1986(32)	H <sup>1</sup> (C2)	1271(46)	1561(19)	2523(37)	720(108)
H <sup>1</sup> (C2)	301(56)	1607(21)	1537(43)	H(C3)	2923(36)	4560(15)	2220(28)	355(72)
H <sup>1</sup> (C4)	3142(49)	5066(20)	4099(38)	H <sup>1</sup> (C4)	2289(53)	5308(21)	2679(41)	838(120)
H <sup>1</sup> (C4)	4087(46)	5215(18)	3293(37)	H <sup>1</sup> (C5)	4421(39)	4145(17)	4473(32)	433(88)
H <sup>1</sup> (C5)	4351(44)	3386(17)	3502(34)	H <sup>1</sup> (C5)	5181(38)	4232(16)	3619(32)	484(89)
H(C6)	680(32)	3531(13)	6256(24)	H <sup>1</sup> (C7)	-2271(36)	3390(15)	4933(27)	337(76)
H <sup>1</sup> (C7)	-1417(52)	3541(20)	6245(40)	H <sup>1</sup> (C7)	-1765(45)	4121(19)	5382(37)	740(113)
H <sup>1</sup> (C8)	-878(51)	2585(19)	4872(40)	H <sup>1</sup> (C8)	930(47)	2644(18)	5491(36)	718(109)
H <sup>1</sup> (C8)	-267(42)	2651(17)	6278(34)					

$\sigma_{\text{Anisotropic}}$  thermal factor defined by  $\exp[-\frac{1}{2}(B_{11}x^2 + B_{22}y^2 + B_{33}z^2 + 2D_{12}xy + 2D_{13}xz + 2D_{23}yz)]$ . Standard deviations in parentheses, in this and following tables, refer to the last digit.

TABLE 3. GEOMETRICAL PARAMETERS FOR  $[\text{HAIN-Pr}_2(\text{H}_2\text{AINH-Pr})_3]$ 

Bond lengths (Å) and angles (°)					
Al(1)-N(2)	1.967(4)	Al(1)-N(2)'	1.915(4)	Al(2)-N(2)	1.922(3)
Al(2)-N(3)	1.956(3)	Al(3)-N(2)	1.901(2)	Al(3)-N(3)'	1.925(2)
Al(3)-N(1)	1.935(5)	Al(3)''-N(1)	1.985(5)	N(1)-C(1)	1.533(8)
N(2)-C(3)	1.537(4)	N(3)-C(6)	1.512(5)	C(1)-C(2)	1.511(6)
C(1)-C(2)'	1.546(6)	C(3)-C(4)	1.517(6)	C(3)-C(5)	1.519(7)
C(6)-C(7)	1.524(6)	C(6)-C(8)	1.480(6)		
N(2)-Al(1)-N(2)'	103.4(1)	N(2)-Al(2)-N(3)	100.9(1)	N(2)-Al(3)-N(1)	110.2(1)
N(2)''-Al(3)''-N(3)''	99.7(1)	N(2)-Al(3)''-N(3)''	103.5(1)	N(1)-Al(3)''-N(3)''	96.9(1)
N(1)-Al(3)''-N(3)''	112.9(1)	Al(3)''-N(1)-Al(3)''	107.2(1)	Al(3)''-N(1)-C(1)	115.6(2)
Al(3)''-N(1)-C(1)	116.0(2)	Al(1)-N(2)-Al(2)	112.1(1)	Al(1)-N(2)''-Al(2)''	102.8(1)
Al(1)-N(2)-Al(3)	106.1(1)	Al(1)-N(2)''-Al(3)''	112.8(1)	Al(2)-N(2)-Al(3)	110.9(1)
Al(1)-N(2)-C(3)	110.5(1)	Al(1)-N(2)''-C(3)''	113.6(1)	Al(2)-N(2)-C(3)	111.2(1)
Al(3)-N(2)-C(3)	105.7(1)	Al(2)-N(3)-Al(3)''	112.5(1)	Al(2)-N(3)-C(6)	112.0(1)
Al(3)''-N(3)-C(6)	122.2(2)	C(2)-C(1)-C(2)'	106.1(2)	C(2)-C(1)-N(1)	108.6(2)
C(2)''-C(1)-N(1)	109.8(2)	N(2)-C(3)-C(4)	113.3(2)	N(2)-C(3)-C(5)	112.9(2)
C(4)-C(3)-C(5)	109.5(2)	N(3)-C(6)-C(7)	109.8(2)	N(3)-C(6)-C(8)	111.5(2)
C(7)-C(6)-C(8)	111.5(2)				
Bond lengths (Å) and angles (°) involving hydrogen atoms					
Al(1)-H'(Al1)	1.45(8)	Al(1)-H''(Al1)	1.52(10)	Al(2)-H'(Al2)	1.45(4)
Al(2)-H''(Al2)	1.54(4)	Al(3)-H(Al3)	1.44(4)	N(1)-H(N1)	1.14(11)
N(3)-H(N3)	0.78(4)				
H'(Al1)-Al(1)-H''(Al1)	121.4(30)	N(2)-Al(1)-H''(Al1)	98.8(20)	N(2)-Al(1)-H''(Al1)	116.8(40)
N(2)''-Al(1)-H''(Al1)	109.1(30)	N(2)''-Al(2)-H''(Al2)	106.0(30)	H'(Al2)-Al(2)-H''(Al2)	116.6(15)
N(2)-Al(2)-H''(Al2)	114.4(17)	N(2)''-Al(2)-H''(Al2)	110.2(12)	N(3)-Al(2)-H''(Al2)	107.1(14)
N(3)-Al(2)-H''(Al2)	106.0(11)	N(2)-Al(3)-H(Al3)	118.9(13)	N(1)-Al(3)-H(Al3)	116.4(14)
N(1)-Al(3)''-H(Al3)''	113.8(14)	N(3)''-Al(3)''-H(Al3)''	107.6(15)	Al(3)''-N(1)-H(N1)	118.5(56)
Al(3)''-N(1)-H(N1)	113.6(55)	C(1)-N(2)-H(N1)	85.0(39)	Al(2)-N(3)-H(N3)	97.6(25)
Al(3)''-N(3)-H(N3)	103.9(25)	C(6)-N(3)-H(N3)	104.8(28)		
Internal rotation angles (°)					
Al(1)-N(2)-Al(3)-N(1)	285.8	N(2)-Al(3)-N(1)-Al(3)'	21.1	Al(1)-N(2)-C(3)-C(5)	167.9
Al(3)-N(1)-Al(3)''-N(2)''	48.0	N(1)-Al(3)''-N(2)''-Al(1)	279.3	Al(2)-N(2)-C(3)-C(5)	42.6
Al(3)''-N(2)''-Al(1)-N(2)	29.9	N(2)''-Al(1)-N(2)-Al(1)	44.5	Al(3)-N(2)-C(3)-C(5)	282.2
Al(1)-N(2)-Al(2)-N(3)	39.6	N(2)-Al(2)-N(3)-Al(3)'	35.0	Al(2)-N(3)-C(6)-C(8)	277.2
Al(2)-N(3)-Al(3)''-N(2)''	282.8	N(3)-Al(3)''-N(2)''-Al(1)	35.8	Al(3)''-N(3)-C(6)-C(8)	55.1
Al(3)''-N(2)''-Al(1)-N(2)	29.9	N(2)''-Al(1)-N(2)-Al(1)	283.4	Al(1)-N(2)-C(3)-C(4)	42.8
N(3)-Al(2)-N(2)-Al(3)	281.3	Al(2)-N(2)-Al(3)-N(1)	47.8	Al(2)-N(2)-C(3)-C(4)	77.6
Al(3)-N(1)-Al(3)''-N(3)	298.8	N(1)-Al(3)''-H(3)-Al(2)	29.6	Al(3)-N(2)-C(3)-C(4)	57.2
Al(3)-N(1)-C(1)-C(2)	297.7	Al(3)-N(1)-C(1)-C(2)'	182.1	Al(2)-N(3)-C(6)-C(7)	153.1
Al(3)''-N(1)-C(1)-C(2)	170.8	Al(3)''-N(1)-C(1)-C(2)''	55.3	Al(3)''-N(3)-C(6)-C(7)	291.0

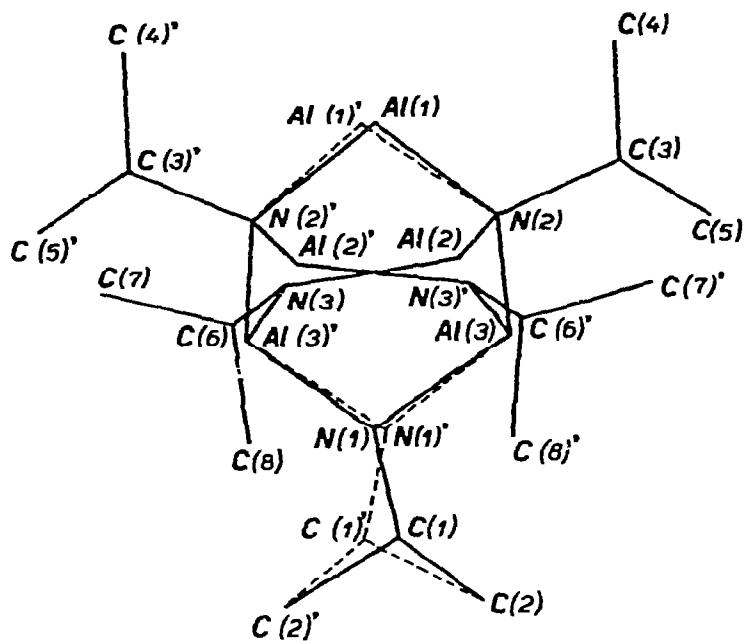


Fig. 1. A skeletal picture of the molecular structure of  $[(\text{HAlN-}i\text{-Pr})_2(\text{H}_2\text{AlNH-}i\text{-Pr})_3]$ . The splitting of the positions of Al(1), N(1) and C(1) arises from the two orientations of the molecule in the crystal, as required by the two-fold axis.

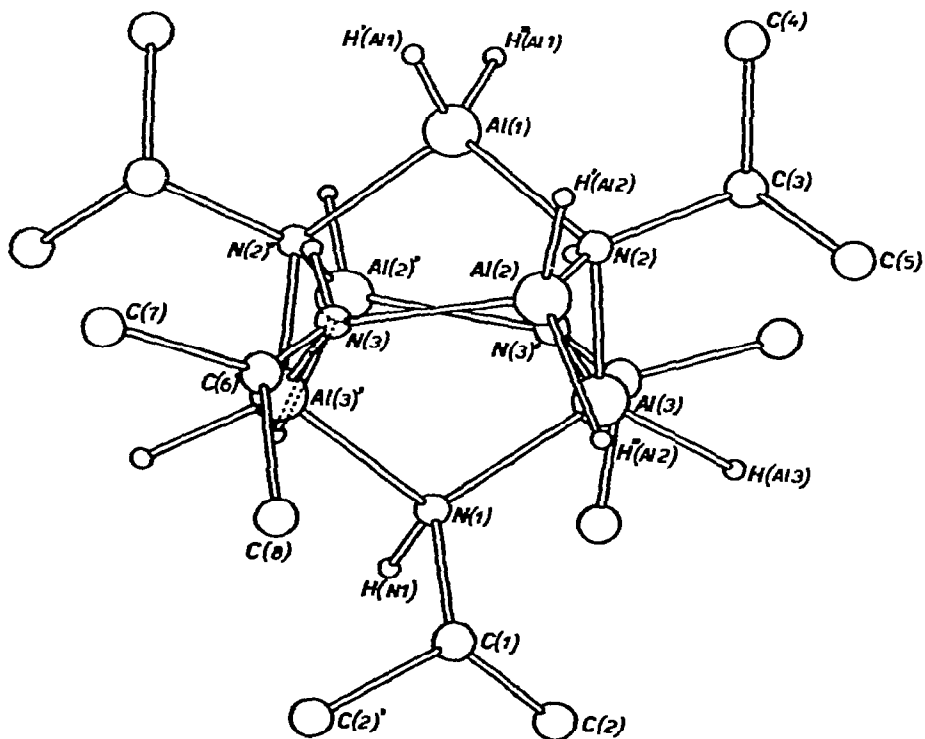


Fig. 2. A perspective view of the molecule of  $[(\text{HAlN-}i\text{-Pr})_2(\text{H}_2\text{AlNH-}i\text{-Pr})_3]$ .

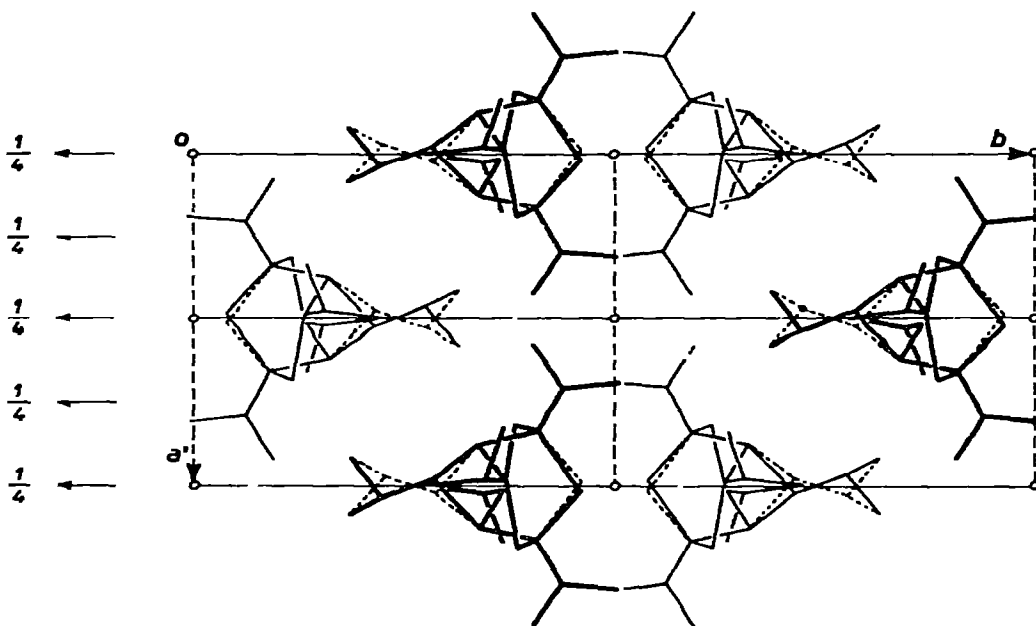


Fig. 3. A representation of the packing of  $[(\text{HAlNH-}i\text{-Pr})_2(\text{H}_2\text{AlNH-}i\text{-Pr})_3]$ ; projection along the  $c$  axis.

the crystal actually lie on a two-fold axis of the space group. The rigorous binary symmetry thus required is achieved by splitting of the positions of Al(1), N(1) and C(1) and of the related hydrogen atoms, as shown in Fig. 1. This statistical occupancy is possible because it does not affect the positions of the methyl groups, which determine the packing in the crystal. Although the quality of the refinement leaves no doubt about the existence of this splitting, some difficulties do arise for the interpretation of the true molecular structure. From Fig. 1 it will be seen that the connection of N(1) with C(1) and consequently of N(1)' with C(1)' is directly imposed by the requirement of a C—N bond distance close to 1.5 Å [N(1)—C(1) and N(1)'—C(1)', 1.533(8) Å]. The crucial point is now to connect one of these positions [i.e. N(1), C(1) or N(1)', C(1)'] to those related to Al(1) and Al(1)'. These two positions of the aluminum atom, both unaffected by any steric constraints of the packing, should be equally probable, so that even a dynamic-statistical occupancy must be considered. Such a model would, however, produce important changes in bond lengths (about 0.05 Å) and bond angles (about 6°), and would thus probably involve a considerable activation energy. Therefore, we have preferred to choose a definite structural model, as sketched in Fig. 1, which occupies statistically the crystallographic sites according to the two orientations required by the two-fold axis. The choice of this model has been made on the basis of the greatest possible alternation of short and long Al—N bond distances on the six-membered ring. Unfortunately true alternation of these bond distances is not possible because of the identity of the two bonds Al(3)—N(2) and Al(3)'—N(2)'. The question therefore remains largely unsettled. This uncertainty precludes very detailed consideration of the geometrical parameters of the molecule, especially with regard to the Al—N bond distances. It is noteworthy, however, that the shortest Al—N bond distance, 1.901

Å, is observed for the Al(3)–N(2) bond, the only one involving aluminum and nitrogen atoms, linked respectively to three nitrogen and three aluminum atoms, while the longest, 1.985(5) Å, is found for the Al(3)'–N(1) bond. All other mean bond distances are in good agreement with the values found in the structures of the analogous compounds previously studied [2–4] [Al–H, 1.48(2); N–C, 1.527(9); C–C, 1.516(9) Å].

Only six-membered rings (AlN)<sub>3</sub> are present in the compound, and here too the rule established for previous structures [2–4] of this series concerning the Al–N–Al and the N–Al–N bond angles is obeyed: i.e. in four-membered rings (AlN)<sub>2</sub>, Al–N–Al bond angles are a little smaller than the N–Al–N angles, whereas in six-membered rings the opposite order is found. In the present case Al–N–Al bond angles average 109.2(16)° and N–Al–N ones average 103.9(23)°.

The packing, a view of which is given in Fig. 3, is established by methyl–methyl contacts, the shortest distance being 3.68 Å.

The structure of PIAPEN gives further insight into possible mechanisms of formation of poly(*N*-alkyliminoalanes) under various conditions; in this case, the formation of cyclohexane-type rings, (AlN)<sub>3</sub>, in an intermediate product is demonstrated. This finding is significant, because most of the evidence collected so far for other conditions of preparation [8] favours formation of dimers and tetramers as intermediates.

### Acknowledgements

We thank Dr. M. Bruzzone and A. Mazzei for useful discussions and their interest in this work and the management of Snamprogetti for allowing publication.

### References

- 1 S. Cucinella, T. Salvatori, C. Busetto, G. Perego and A. Mazzei, *J. Organometal. Chem.*, **78** (1974) 185.
- 2 M. Cesari, G. Perego, G. Del Piero, S. Cucinella and E. Cernia, *J. Organometal. Chem.*, **78** (1974) 203.
- 3 G. Perego, M. Cesari, G. Del Piero, A. Balducci and E. Cernia, *J. Organometal. Chem.*, **87** (1975) 33.
- 4 M. Cesari, G. Perego, G. Del Piero, A. Immirzi and M. Corbellini, *J. Organometal. Chem.*, **87** (1975) 43.
- 5 P. Main, M.M. Woolfson and G. Germain, *Computer Program Multan*, 1971; G. Germain, P. Main and M.M. Woolfson, *Acta Crystallogr. Sect. B*, **26** (1970) 274.
- 6 F.H. Moore, *Acta Crystallogr.*, **16** (1963) 1169.
- 7 A. Immirzi, *Ric. Sci.*, **37** (1967) 847; *ibid.*, **850**; *J. Appl. Crystallogr.*, **6** (1973) 246.
- 8 S. Cucinella and G. Dozzi, results to be published.