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

I. SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF POLY(*N*-ALKYLIMINOALANES)

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Summary

The structural features of poly(*N*-alkyliminoalanes) (PIA) and their dependence on the method of preparation as well as on the amine have been investigated. Different PIA have been synthesized from ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, *isobutyl*, *tert*-butyl and cyclohexylamine, and have been characterized by X-ray diffraction, mass spectrometry, ^1H and ^{13}C NMR. In general all the results agree with the formation of oligomers of $-\text{HAlNR}-$ units, with three dimensional structures made up by four and six membered rings. In particular a cage structure has been found for $(\text{HAlN-iso-C}_3\text{H}_7)_6$ by X-ray diffraction on a single crystal.

Introduction

The structural characterization of poly(*N*-alkyliminoalanes) (PIA) has received little attention relative to other alane derivatives, in spite of their interest as active polymerization cocatalysts [1].

The first synthesis of PIA was reported by Wiberg and May [2], who by reaction of aluminum hydride with equimolar amounts of methylamine in diethyl ether/dioxane, obtained an insoluble substance which was assumed to have a polymeric structure $(\text{HAlNR})_n$ (I).

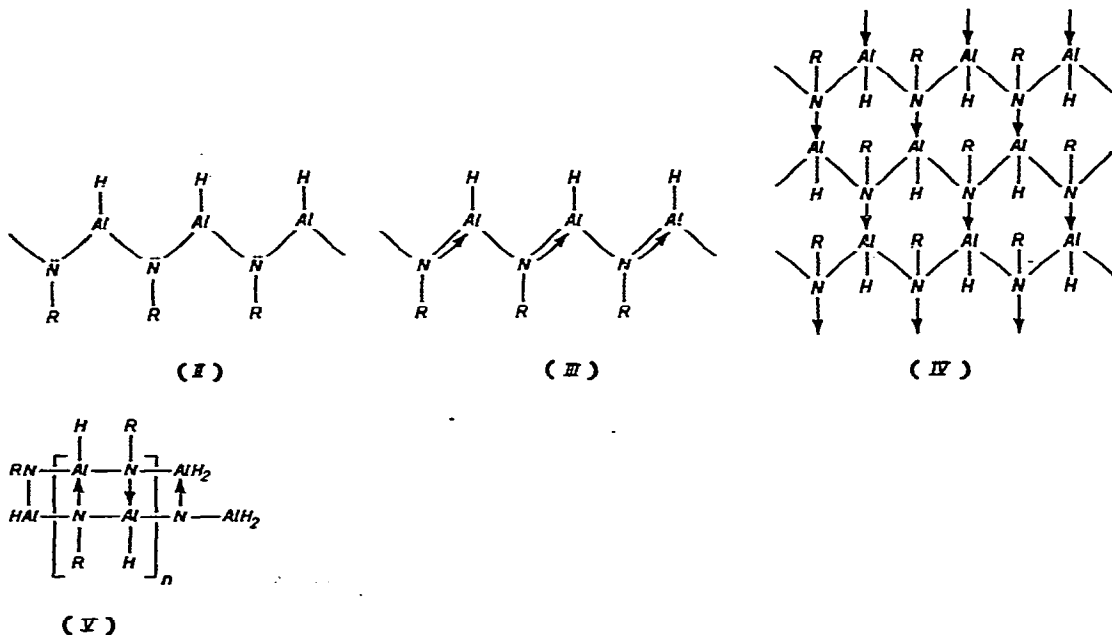
Later Ehrlich and co-workers [3] found that similar compounds containing aluminum–nitrogen backbones could be prepared by the reaction of trialkylaminoalane with ethylamine, acetonitrile or ethyleneimine or by the reaction of

* This current name is used although other general names could be more appropriate to indicate the oligomeric character of these compounds.

lithium aluminum hydride with ethylamine hydrochloride. These compounds were soluble in some organic solvents and contained from 3 to 35 monomer units.

Other synthetic methods based on the reaction of AlH_3 complexes or LiAlH_4 with aluminum amides of *n*-butylamine or isopropylamine were reported by Mazzei et al. [1]. Degrees of polymerization ranging from 5 to 7 for poly(*N*-isopropyliminoalane) (i-PrPIA) and 6 to 12 for poly(*N*-*n*-butyliminoalane) (n-BuPIA) were found in diethyl ether.

However only a few hypotheses have been put forward concerning the structure of PIA. Ehrlich et al. [3] suggested that structures such as II or III were less probable than IV or V, because of the inherently greater stability of



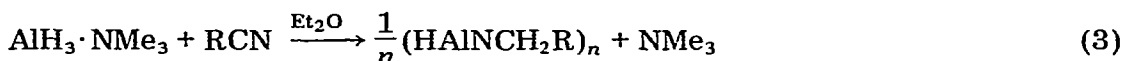
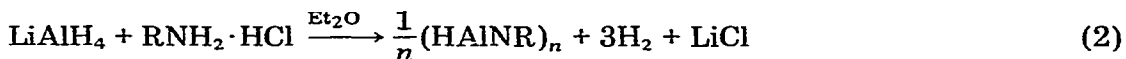
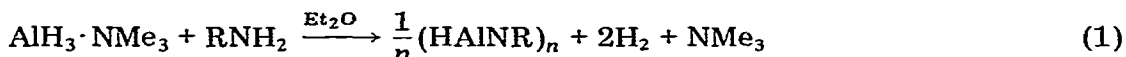
the network structures. In structures IV and V the aluminum would be tetra-coordinated by crosslinking with other chains through the lone pair electrons on the nitrogen atoms. The preparation [4] of the three dimensional cubic compound, $(\text{C}_6\text{H}_5\text{AlNC}_6\text{H}_5)_4$, from triphenylaluminum and aniline suggested [3] this type of structure might also apply to PIA. More recently the differences found by some of us in the catalytic behaviour in the polymerization of mono- and di-olefins [5] of PIA, prepared from different amines or under different reaction conditions, have suggested an influence of structure on activity. This prompted us to determine the structure of PIA obtained by different synthetic methods and with different amines.

Results and discussion

A. The influence of the synthetic method on the structure of poly(*N*-alkyliminoalanes)

Among the possible routes for the synthesis of PIA we have chosen reac-

tions 1–3, starting from iso-C₃H₇NH₂, n-C₃H₇NH₂, or C₂H₅CN and carried out in diethyl ether. The separation of crystalline products when possible was achieved by cooling the ethereal solution of the reaction products. We stress the fact that this crystallization was done only in order to obtain purified products suitable for analytical and physicochemical characterizations. In some cases the residue, after the complete elimination under vacuum of the solvent and of NMe₃, gave products which had the same structure as the separated crystals. In other cases different structures were found, as reported below.



Synthesis of PIA from isopropylamine and characterization. In Table 1 analytical, infrared and molecular weight data are reported for PIA from iso-C₃H₇NH₂ obtained by the reactions 1 and 2. Also the degree of polymerization obtained by different physicochemical methods (X-ray diffraction, mass spectrometry, ¹H and ¹³C NMR) is reported.

In reaction 1 the crystalline fraction (i-PrPIA1–C) obtained from the solution by cooling shows good agreement with the calculated analytical values for solvent-free (HAINR)_n. The infrared spectrum in Nujol shows ν(Al–H) absorption attributed to hydridic hydrogens linked to tetracoordinated aluminum atoms [6].

The molecular structure has been determined by X-ray diffraction on a single crystal. As shown in Fig. 1 a hexameric structure (VI) has been found [7] in which the aluminum and nitrogen atoms are linked to form a cage having ternary symmetry. In Table 2 the X-ray powder pattern is given.

Mass spectrometry data for i-PrPIA1–C are given in Table 3. The molecular ion M⁺ at m/e 510, corresponding to VI is present in low abundance, together with ions (M–H)⁺ at m/e 509 and (M–2H)⁺ at m/e 508. By far the most abundant ion in the spectrum is at m/e 495, derived from the molecular ion by loss of a methyl radical. The very low abundance of ions corresponding to lower polymers of the –HAINR– units is consistent with a stable hexameric structure. Moreover the more abundant fragments contain an equal number of aluminum and nitrogen atoms, showing the greater stability of these ions with respect to others having a N/Al atomic ratio different from 1. This breakage of the C–C linkage adjacent to a nitrogen atom also dominates the mass spectra of PIA from other amines.

The ¹H NMR spectrum of i-PrPIA1–C in benzene solution exhibits one doublet at τ 8.49 and one septet at τ 6.29, due to the CH₃ and the CH protons of the amine radical respectively (AX spectrum; Table 4). The coupling constant [J(H–C–C–H)] is 6.5 Hz. The equivalence of the alkyl protons indicates that in benzene solution the product has a symmetrical structure. This equivalence is maintained at low temperature in toluene, because no splitting of the signals

TABLE I
RESULTS OBTAINED FOR THE SYNTHESIS OF POLY(N-ISOPROPYLIMINOALANES) (i-PPIA)

Compound	Synthesis reaction ^d	Fraction		Chemical composition ^d			$\nu(\text{Al-H})^e$ (cm^{-1})	Mol. wt. ^f	n in ($\text{HAINR})_n$	Physicochemical data suggest:	
		Sample ^b	%	X-ray analysis ^c	Al (%)	N (%)					H_{act}
i-PPIA1	(1)	i-PPIA1-C	55	XX	30.67	16.24	11.48	1850	528	6.2	Closed hexamer
		i-PPIA1-R	45	XX	28.55	15.97	10.50	1850	495	5.8	Closed hexamer
i-PPIA2	(2)	i-PPIA2-C	30	XX	28.94	14.80	13.45	1850	505	5.9	Closed hexamer
		i-PPIA2-R	70	XX	29.77	15.93	15.30	1850	455	5.3	Predominantly open hexamer

^d(1): $\text{AlH}_3 \cdot \text{NMe}_3 + \text{iso-C}_3\text{H}_7\text{NH}_2$; (2) $\text{LiAlH}_4 + \text{iso-C}_3\text{H}_7\text{NH}_2 \cdot \text{HCl}$. ^b C = precipitated fraction at -50°C from the ethereal solution; R = residue to the separation of C. ^c As evidenced by the powder X-ray pattern; XX = crystalline. ^d H_{act} = hydridic hydrogen content indicated as meq/g. Calc. for $(\text{HAINC}_3\text{H}_7)_n$: Al, 31.71; N, 16.46; Hactive, 11.76. ^e in nujol mull. ^f By ebullometry in diethyl ether.

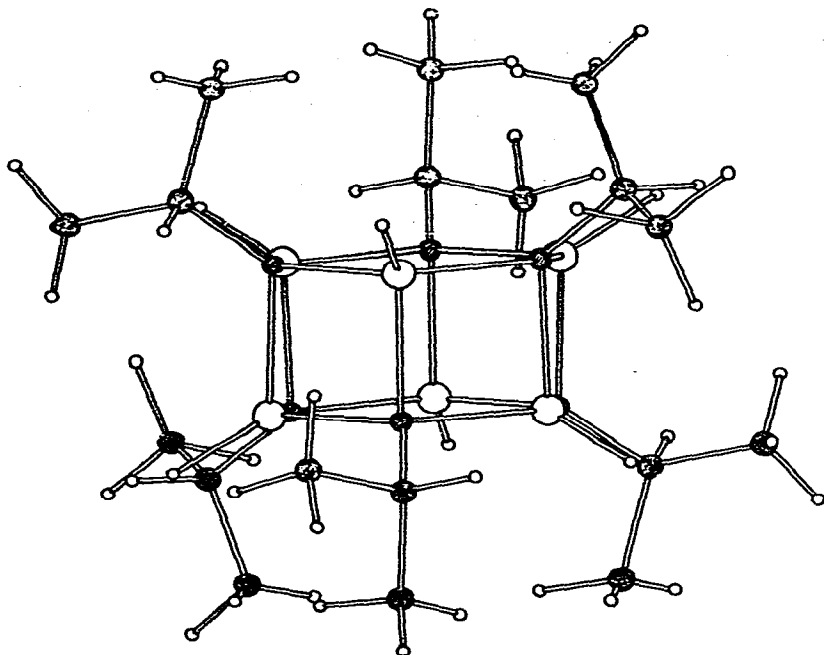


Fig. 1. Molecular structure of hexamer (HAIN-iso-C₃H₇)₆.

TABLE 2

X-RAY POWDER DATA^a OF POLY(*N*-ISOPROPYLMINOALANES)

i-PrPIA1-C ^b		i-PrPIA2-R ^b	
I	<i>d</i> (Å)	I	<i>d</i> (Å)
vs	8.12 ^c	vs	8.21 ^h
m	6.00 ^d	m	6.21
m	5.29 ^e	m	5.87
mw	4.84 ^f	mw	5.37
m	4.53 ^g	w	5.01
m	4.27	mw	4.80
mw	4.08	mw	4.61
m	3.87	mw	4.30
m	3.60	mw	3.95
m	3.39	mw	3.76
m	3.13	w	3.39
w	2.988	w	3.23
m	2.826	mw	3.11
mw	2.726	w	3.00
vw	2.667	w	2.926
vw	2.600	w	2.797
w	2.518	w	2.578
w	2.455	w	2.389
m	2.382		
m	2.276		

^aIn this table as well as in the following ones, visually estimated intensities are reported as: vs = very strong, s = strong, m = medium, ms = medium strong, mw = medium weak, w = weak, vw = very weak (Cu-K_α radiation, λ = 1.54178 Å). ^bReference is made to Table 1. ^cMultiplet with *d* from 8.7 to 7.6 Å. ^dMultiplet with *d* from 6.1 to 5.9 Å. ^eMultiplet with *d* from 5.39 to 5.19 Å. ^fMultiplet with *d* from 4.93 to 4.76 Å. ^gMultiplet with *d* from 4.63 to 4.44 Å. ^hMultiplet with *d* from 8.9 to 7.5 Å.

TABLE 3
 MASS SPECTRUM OF THE CLOSED HEXAMER POLY(*N*-ISOPROPYLMINOALANE)^a

<i>m/e</i>	Intensity ^b	Formula	Deviation from calc. (ppm)
510	3 ^b		
509.2744	4	C ₁₈ H ₄₇ N ₆ Al ₆	-1.3
508.2694	4	C ₁₈ H ₄₆ N ₆ Al ₅	+ 3.9
497	3		
496.2636	22	¹³ CC ₁₆ H ₄₅ N ₆ Al ₆	+ 1.5
495.2592	100	C ₁₇ H ₄₅ N ₆ Al ₆	-0.8
465.2112	3	C ₁₅ H ₃₉ N ₆ Al ₆	-3.0
451.1968	4	C ₁₄ H ₃₇ N ₆ Al ₆	-0.2
437	3		
380.1655	3	C ₁₂ H ₃₁ N ₅ Al ₅	+ 0.2
366	3		
339.1837	3	C ₁₂ H ₃₁ N ₄ Al ₄	+ 8.3
325.1212	4	C ₁₁ H ₂₉ N ₄ Al ₄	-6.5
295.1182	3	C ₉ H ₂₃ N ₄ Al ₄	0
240.1188	3	C ₈ H ₂₁ N ₃ Al ₃	+ 3.4
183.1023	4	C ₇ H ₁₇ N ₂ Al ₂	+ 0.7
169.0859	7	C ₆ H ₁₅ N ₂ Al ₂	-3.6
155.0710	3	C ₁₅ H ₁₃ N ₂ Al ₂	+ 1.0
45	3		
44	6		

^a Reference is made to *i*-PrPIA1—C of Table 1. ^b As % of the strongest peak.

was observed at 253 K. A broad signal at τ 5.43 appears at 213 K which we have ascribed to the hydridic hydrogen resonance. The hydridic hydrogen resonance for *i*-PrPIA1—C occurs at a particularly low chemical shift for a metal hydride, similar to the observation by Kovar and Ashby for HAl(NMe₂)₂ [8], and disappears at room temperature, probably because of the increased broadening caused by the large electric quadrupole moment associated with the ²⁷Al nucleus. Similar conclusions have been derived from the ¹³C NMR spectrum (Table 5). In benzene solution singlets at 79.3 ppm and 101 ppm from the solvent have been found which have been assigned to the α - and β -carbon atoms with respect to the nitrogen. The equivalence at low temperature has been confirmed in both toluene and diethyl ether solution.

The liquid separated from the fraction *i*-PrPIA1—C gave, on evaporation of the solvent in vacuo, the solid *i*-PrPIA1—R. In this case, as for some other products reported below, small amounts of complexed diethyl ether, which we were unable to remove in vacuo at room temperature, could account for the low values of the aluminum and nitrogen contents. However, for *i*-PrPIA1—R all the different physicochemical data (X-ray diffraction, mass spectrometry, ¹H and ¹³C NMR) supported the hexamer structure shown in Fig. 1.

In contrast some uncertainty arises in the interpretation of structural data for *i*-PrPIA obtained by reaction 2. By repeating the preparation we have not obtained identical results. In Table 1 typical results are given for *i*-PrPIA obtained by this route. Whereas the N/Al atomic ratio is not significantly different

TABLE 4

¹H NMR SPECTRAL PARAMETERS OF POLY(N-ALKYLIMINOALANES) FROM DIFFERENT AMINES IN BENZENE

Sample ^a	Compound	τ , multiplicity ^b	Relative area	Assignment
i-PrPIA1-C	(HAIN-iso-C ₃ H ₇) ₆	8.49 d	6.0	CH ₃
		6.29 sp	1.0	CH
		5.43 s	1.0	Al-H
n-PrPIA1-C	(HAIN-n-C ₃ H ₇) ₈	9.07 t	3.0	CH ₃
		7.96 m	2.0	nitrogen β -CH ₂
		6.74 t	2.0	nitrogen α -CH ₂
n-PrPIA2-C	(HAIN-n-C ₃ H ₇) ₆	9.07 t	3.0	CH ₃
		8.23 m	2.0	nitrogen β -CH ₂
		6.83 t	2.0	nitrogen α -CH ₂
s-BuPIA	(HAIN-sec-C ₄ H ₉) ₆	9.04 t	3.0	nitrogen γ -CH ₃
		8.40 d	3.0	nitrogen β -CH ₃
		8.06 m	2.0	CH ₂
		6.54 m	1.0	CH
i-BuPIA	(HAIN-iso-C ₄ H ₉) ₆	8.92 d	6.0	CH ₃
		7.96 m	1.0	CH
		6.80 d	2.0	CH ₂
t-BuPIA-H	(HAIN-tert-C ₄ H ₉) ₄	8.56 s		CH ₃
t-BuPIA-R	tert-C ₄ H ₉ NH- (HAIN-tert-C ₄ H ₉) ₃ AlH ₂	8.63 s	1.0	CH ₃ on NH group
		8.57 s	1.0	CH ₃ on nitrogen linked to three AlH groups
		8.39 s	2.0	CH ₃ on nitrogen linked to two Al-H and to one AlH ₂ groups

^a Reference is made to Tables 1, 7 and 9. ^b s = singlet, d = doublet, t = triplet, m = multiplet, sp = septet.

from unity as in reaction 1, the hydridic hydrogen content is considerably higher. This cannot be due to the possible presence of lithium hydride from LiAlH₄ (used as a reactant in this reaction) because the lithium content is very low (Li/Al \leq 0.05).

TABLE 5

¹³C NMR SPECTRAL PARAMETERS OF POLY(N-ISOPROPYLIMINOALANE) AND POLY-N-n-PROPYLIMINOALANE)

Sample ^a	Compound	Chemical shift (from benzene) (ppm)	Assignment
i-PrPIA1-C	(HAIN-iso-C ₃ H ₇) ₆	79.3	nitrogen α -C atoms
		101.0	nitrogen β -C atoms
n-PrPIA2-C	(HAIN-n-C ₃ H ₇) ₆	80	nitrogen α -C atoms
		91	nitrogen β -C atoms
		116	nitrogen γ -C atoms

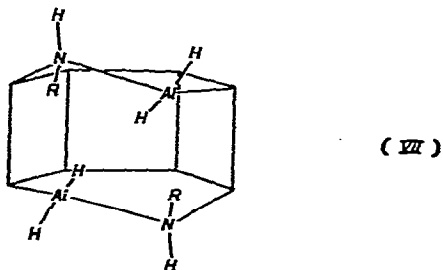
^a Reference is made to Tables 1 and 7.

In these samples ^1H NMR showed the presence of small amounts of complexed diethyl ether on the basis of a 0.14 ppm shift to higher fields of the characteristic signals of the $\text{O}-\text{CH}_2$ protons.

Physicochemical results for the crystallized fraction (i-PrPIA2-C) are generally consistent with the predominant presence of VI in spite of the abnormally high hydridic hydrogen content. This apparent discrepancy will be discussed later.

For the residual fraction (i-PrPIA2-R), the mass spectrum showed the presence of a mixture of oligomers. Besides the cage hexamer $[(M-\text{CH}_3)^+ \text{ at } m/e \text{ 495}]$, ions corresponding to a pentamer, probably $\text{H}-(\text{HAlNR})_5-\text{H}$ [m/e 427, 426, 425, 412 corresponding to M^+ , $(M-\text{H})^+$, $(M-2\text{H})^+$, $(M-\text{CH}_3)^+$] as well as a tetramer $[(M-\text{CH}_3)^+ \text{ at } m/e \text{ 325}]$ were observed. The abundance of the latter ion increased with the inlet temperature. From this, the formation of tetramer ions by thermal decomposition from more complex structures can be hypothesized.

The ^1H NMR spectrum showed a wide multiplicity of lines for both the CH_3 and the CH protons. In addition to the signals associated with VI, other doublets and septets are present. These signals indicated the formation of species in which isopropyl groups are not equivalent. Although mass spectrometry and ^1H NMR data show the presence of a certain amount of VI, the X-ray powder pattern (Table 2), excludes the presence of this component and by analogy with the i-PrPIA2-R and i-PrPIA1-C X-ray patterns, suggests the formation of intermediate hexamer structures, e.g. VII, in which terminal groups like AlH_2 and NHR



are present to give open cage structures. These open structures change into VI by ageing, by heating or on dissolution. This tendency of the open cages to close explains the discrepancy of chemical and physicochemical data for both i-PrPIA2-C and i-PrPIA2-R.

The occurrence of VII could be favoured in reaction 2 by the presence of LiH during the formation of PIA and by the tendency of LiH to complex aluminum atoms via hydrogen bridges. This would hinder the interaction between the lone pair of nitrogen with aluminum and the subsequent reaction (eqn. 4).

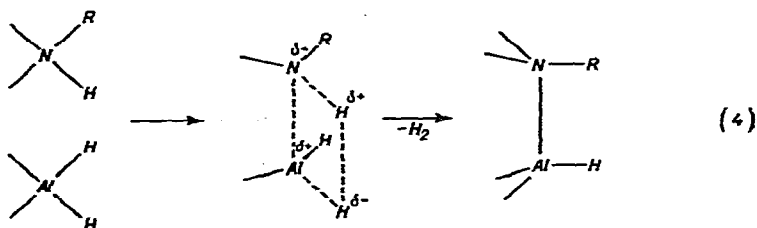


TABLE 6

FRACTIONATION RESULTS OF POLY(*N*-ISOPROPYLIMINOALANE) OBTAINED FROM THE REACTION OF LiAlH_4 WITH $\text{isoC}_3\text{H}_7\text{NH}_2^a$

Product	Temp. (°C)	Precipitate (%)	Chemical composition ^b				Physicochemical data suggest:
			Al (%)	N (%)	H _{act.}	H _{act./Al} atomic ratio	
Initial product			29.30	15.93	14.5	1.33	
1st fraction	20	6.5	30.65	16.22	11.55	1.02	Decamer
2nd fraction	-5	12.0	30.78	16.66	11.73	1.03	Decamer
3rd fraction	-20	15.5	30.24	16.26	12.40	1.10	Closed hexamer
4th fraction	-40	14.0	30.46	15.89	11.95	1.06	Closed hexamer
5th fraction	-60	13.5	28.19	14.24	12.90	1.23	Predominantly closed hexamer
6th fraction	-78	6.0	29.83	15.96	11.06	1.00	Predominantly closed hexamer
Residue		34	28.95	15.41	13.50	1.29	Closed hexamer and other unidentified species

^a 8.7 g of initial product were dissolved in 50 ml of diethyl ether. Then the solution, filtered from the 1st fraction, was cooled subsequently to the indicated temperature. The precipitate fraction was separated by removing the overstanding liquid, dried (10 h, 10^{-3} mm Hg, room temperature) and analyzed.

^b Calc. Values for $(\text{HAlNC}_3\text{H}_7)_n$: Al, 31.71; N, 16.46; H_{act.}, 11.75. H_{act.} is the hydridic hydrogen content indicated as meq/g.

Unfortunately our attempts to isolate the hypothesized open cage structures by fractional crystallization of *i*-PrPIA2-R have been unsuccessful. Most of the resulting fractions contained VI (Table 6). This confirms the aforementioned instability of the open structures. Similar results have been obtained by heating toluene solutions of *i*-PrPIA2-R at 70–80°.

Synthesis and characterization of PIA from n-propylamine. The results are reported in Table 7. It was impossible to separate crystalline fractions by cooling the resulting solution from reaction 3. Generally, from the different routes 1, 2 and 3 a mixture of oligomers has been obtained containing hexamer, heptamer, octamer and for reaction 3 also a nonamer. In some cases the separation and characterization of single oligomers has been successful. For example the insoluble fraction obtained at room temperature from reaction 1 (*n*-PrPIA1-P) consists essentially of the heptamer, as shown by the mass spectrum which exhibits the most abundant ion $(M-\text{Et})^+$ at m/e 566. The corresponding X-ray powder pattern is reported in Table 8.

By cooling the residual solution, a crystalline fraction (*n*-PrPIA1-C) containing mainly an octamer was obtained, and the ion $(M-\text{Et})^+$ at m/e 651 dominates the mass spectrum. The ¹H NMR spectrum shows the typical signals of equivalent alkyl groups on nitrogen atoms indicating a symmetrical structure. A triplet at τ 9.07, a multiplet centered at τ 7.96 and a triplet at τ 6.74 due to CH₃, β -CH₂, α -CH₂ protons with respect to nitrogen are present. The latter triplet shows two singlets near the central line, which together with the line multiplicity of the β -CH₂ protons is consistent with an AB spectrum.

TABLE 7
RESULTS OBTAINED FOR THE SYNTHESIS OF POLY(*N*,*n*-PROPYLIMINOALANES) (*n*-PrPIA)

Compound	Synthesis reaction ^d	Fraction	Chemical composition ^d			$\nu(\text{Al-H})^e$ (cm^{-1})	Mol. wt. / (HAINR) _n	Physicochemical data suggest:	
			Sample ^b	%	X-ray analysis ^c				Al (%)
n-PrPIA1	(1)	n-PrPIA1-P	10	XX	28.82	16.01	11.47	1.07	Heptamer Octamer A mixture containing hexamer, heptamer, octamer and unidentified products
		n-PrPIA1-C	30	XX	29.77	16.03	11.85	1.07	
		n-PrPIA1-R	60	A	30.08	15.81	13.60	1.22	
n-PrPIA2	(2)	n-PrPIA2-C	35	XX	30.68	16.67	12.20	1.07	Hexamer A mixture containing hexamer, heptamer and octamer
		n-PrPIA2-R	65	A	30.28	16.27	11.66	1.03	
n-PrPIA3	(3)	n-PrPIA3-P	10	A	27.44	15.04	10.01	0.98	A mixture containing hexamer, heptamer, octamer and nonamer
		n-PrPIA3-R	90	A	27.50	16.23	10.40	1.02	

^a (1): $\text{AlH}_3 \cdot \text{NMe}_3 + n\text{-C}_3\text{H}_7\text{NH}_2$; (2): $\text{LiAlH}_4 + n\text{-C}_3\text{H}_7\text{NH}_2 \cdot \text{HCl}$; (3) $\text{AlH}_3 \cdot \text{NMe}_3 + \text{C}_2\text{H}_5\text{CN}$. ^b P = insoluble fraction in diethylether at room temperature; C = precipitated fraction at -50° from the ethereal solution; R = residue to the separation of C. ^c As evidenced by the powder X-ray pattern; XX = crystalline; A = amorphous. ^d H_{act.} = hydride hydrogen content indicated as meq/g. Calc. for (HAINR)_n: Al, 31.71; N, 16.46; H_{act.}, 11.75. ^e In nujol mull. ^f By ebulliometry in diethyl ether.

TABLE 8
X-RAY POWDER DATA OF POLY(*N*-*n*-PROPYLIMINOALANES)

n-PrPIA2-C ^a		n-PrPIA1-P ^a		n-PrPIA1-C ^a	
I	d (Å)	I	d (Å)	I	d (Å)
w	9.61	vs	10.22	ms	10.22
vs	8.59	vs	9.46	s	9.21
vs	7.94	w	8.47	m	8.39
w	7.53	m	7.50	m	7.53
mw	6.36	w	6.44	mw	6.73
m	5.81	ms	5.85	mw	6.33
w	5.02	m	5.14	mw	5.44
vs	4.80	m	4.82	mw	4.61
w	4.58	w	4.40	m	4.38
w	4.34	m	4.15	w	4.10
ms	4.19	m	3.82	vw	3.92
vw	4.03	vw	3.63	m	3.76
vw	3.87	m	3.47	m	3.60
m	3.73	w	3.14	vw	2.894
w	3.63	w	2.973	w	2.809
w	3.41	m	2.772	w	2.710
s	3.17	w	2.578	w	2.637
vw	3.01	vw	2.475	mw	2.505
vw	2.908	mw	2.301	w	2.433
mw	2.803	w	2.206	w	2.374
w	2.743	w	1.817	vw	2.304
mw	2.648			vw	2.270
mw	2.522			w	2.178
vw	2.426			vw	2.067
ms	2.383			w	1.943
m	2.330			w	1.804
mw	2.290				
w	2.212				
vw	2.168				
vw	2.144				
mw	2.092				

^a Reference is made to Table 7.

The residual fraction n-PrPIA1-R is a complex mixture of oligomers, i.e. hexamer [(*M*-Et)⁺ at *m/e* 481], heptamer [(*M*-Et)⁺ at *m/e* 566], octamer [(*M*-Et)⁺ at *m/e* 651] and unidentified compounds having higher molecular weights.

The prevailing presence of hexamer in the fraction n-PrPIA2-C from reaction 2 is supported by physicochemical data. The most abundant ion in the mass spectrum is at *m/e* 481 corresponding to (*M*-Et)⁺. The ¹H NMR spectrum is in agreement with a structure having equivalent alkyl groups: the CH₃ protons give a triplet at τ 9.07, the nitrogen β-CH₂ protons a multiplet at τ 8.23, and the nitrogen α-CH₂ protons a triplet at τ 6.83. The spectrum in this case is also of the AB type. ¹³C NMR supports the equivalence of the alkyl groups: three signals appear at 80 ppm, 91 ppm and 116 ppm from benzene corresponding to nitrogen α-C, β-C and γ-C respectively. In Table 8 the X-ray powder pattern is reported.

Also for reaction 2, the residue (n-PrPIA2-R) from the hexamer separation consists of oligomers of different molecular weights.

The presence of a nonamer in relatively small amount in the product from reaction 3 has been demonstrated by mass spectrometry [$(M-Et)^+$ at m/e 736].

B. The influence of the nature of the amine on the structure of poly(N-alkyliminoalanes)

The influence of the nature of the amine on the structure of PIA obtained by the same preparation method has been demonstrated above: reaction 1 gives the hexamer VI from iso-C₃H₇NH₂ but a mixture of oligomers from n-C₃H₇NH₂.

This prompted us to extend our investigations on the chemical and physico-chemical properties of PIA from other amines. PIA have been synthesized from ethyl, n-butyl, sec-butyl, isobutyl, tert-butyl and cyclohexylamine by reaction 1.

In Table 9 the results of the syntheses and characterizations are reported. The discrepancies of analytical data for the aluminum and nitrogen contents, with respect to the calculated analytical values for (HAINR)_n, could be ascribed to small amounts of complexed diethyl ether, and the high hydridic hydrogen contents of some PIA can be reasonably attributed to the formation of open structures probably due to the steric effects of the alkyl groups in the intermediate steps of the reaction. These open structures would also have some tendency to give closed structures as demonstrated by poly(N-tert-butyliminoalane).

The influence of the nature of the amine on the corresponding PIA structure can be summarized as follows: (i) tetramers have been obtained from tert-butylamine (t-BuPIA); (ii) hexamers have been obtained predominantly from sec-butyl (s-BuPIA), isobutyl (i-BuPIA) and cyclohexylamine (c-HexPIA); (iii) mixtures of oligomers have been obtained from ethyl (EtPIA) and n-butylamine (n-BuPIA).

Ions corresponding to tetramers [$(M-CH_3)^+$ at m/e 381] are very abundant in the mass spectra of t-BuPIA. Ions derived from hexamers dominate the mass spectra of s-BuPIA [$(M-Et)^+$ at m/e 565], of i-BuPIA [$(M-C_3H_7)^+$ at m/e 551] and of c-HexPIA [M^{++} at m/e 750; $(M-C_6H_{11})^+$ at m/e 667]. On the other hand ions derived from oligomer mixtures have been observed for n-BuPIA [hexamer, $(M-C_3H_7)^+$ at m/e 551; heptamer, $(M-C_3H_7)^+$ at m/e 650; octamer, $(M-C_3H_7)^+$ at m/e 749] and for EtPIA [hexamer, M^{++} at m/e 426; heptamer, M^{++} at m/e 497; octamer, M^{++} at m/e 568].

Generally, the ¹H NMR spectra (Table 4) agree with these structures having equivalent alkyl groups for s-BuPIA, i-BuPIA and for t-BuPIA heated for some time at 70–80°. In the case of c-HexPIA the ¹H NMR spectrum shows broad signals due to the structural features of the cyclohexyl groups; this does not allow us to show the eventual equivalence of cycloalkyl groups. For n-BuPIA and EtPIA the signal multiplicity is consistent with complex mixtures.

It is noteworthy that by heating a toluene solution of t-BuPIA–R at 70–80°, which originally had a H_{active}/Al atomic ratio equal to 1.27, a product was obtained which exhibits a H_{active}/Al value of 1 (t-BuPIA–H). For this last compound the ¹H NMR spectrum shows a single signal for all CH₃ protons at τ 8.56. The NMR spectrum of the initial t-BuPIA–R shows three CH₃ proton signals at τ 8.63, τ 8.57 and τ 8.39 having relative intensities 1/1/2, according to their different nitrogen environments. By comparison with the spectrum of t-BuPIA–H, we have assigned the τ 8.57 resonance to the protons of the tert-butyl group on the nitrogen linked to three AlH groups. The τ 8.39 resonance could be due to

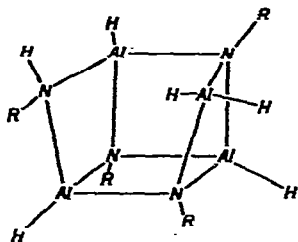
TABLE 9

RESULTS OBTAINED FOR THE SYNTHESIS OF POLY(N-ALKYLIMINOALANES) FROM DIFFERENT AMINES^a

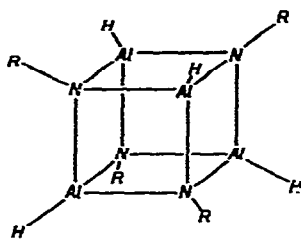
Compound	Amine	Fraction	Sample ^b	%	X-ray analysis ^c	Chemical composition ^d Found (calcd.)				$\nu(\text{Al-H})^e$ (cm^{-1})	Physicochemical data, suggest:
						Al (%)	N (%)	Hact,	Hact/Al atomic ratio		
EtPIA	$\text{C}_2\text{H}_5\text{NH}_2$		EtPIA-P	60	XX	36.58	19.01	15.37	1.13	1795; 1830 and 1850	A mixture of heptamer and octamer
			EtPIA-R	40	XX	32.48 (37.97)	16.96 (19.71)	12.40 (14.07)	1.03	1820 and 1850	A mixture of hexamer, heptamer, octamer, nonamer
n-BuPIA	n-C ₄ H ₉ NH ₂		n-BuPIA-C	30	A	24.88	12.36	10.97	1.19	1810 to 1850	A mixture of hexamer, heptamer, octamer and higher molecular weight compounds
			n-BuPIA-R	70	XX	26.28 (27.22)	13.17 (14.13)	11.39 (10.09)	1.17	1810 to 1850	
s-BuPIA	sec-C ₄ H ₉ NH ₂		s-BuPIA-C	25	XX	26.38	13.25	12.89	1.32	1845	Predominantly hexamer
			s-BuPIA-R	75	n.d.	25.57 (27.22)	13.56 (14.13)	11.08 (10.09)	1.17	1850	Hexamer
t-BuPIA	iso-C ₄ H ₉ NH ₂		t-BuPIA-C	65	XX	26.58	13.94	10.24	1.04	1850	Hexamer
			t-BuPIA-R	35	XX	25.55 (27.22)	13.49 (14.13)	9.66 (10.09)	1.02	1850	Predominantly hexamer
t-BuPIA	tert-C ₄ H ₉ NH ₂		t-BuPIA-C	50	XX	25.94	14.10	11.24	1.17	1850	Tetramer
			t-BuPIA-R	50	XX	26.39 (27.08)	13.39 (14.06)	12.42 (12.55)	1.27	1850 to 1860	Tetramer
			t-BuPIA-H ^h	50	XX	26.78 (27.22)	13.55 (14.13)	10.21 (10.09)	1.03		Tetramer
c-HexPIA	$\text{C}_6\text{H}_{11}\text{NH}_2$		c-HexPIA-P	65	XX	21.03	11.36	7.86	1.01	1835; 1845 and 1880	Predominantly hexamer
			c-HexPIA-C	15	XX	21.33	10.95	8.29	1.05	1835; 1845 and 1875	Predominantly hexamer
			c-HexPIA-R	20	A	18.09 (21.56)	8.29 (11.19)	9.59 (7.99)	1.43		

^a By reaction of $\text{AlH}_3 \cdot \text{NMe}_3$ with RNH_2 . ^b p = insoluble fraction in diethyl ether at room temperature; C = precipitated fraction at -50°C from the ethereal solution; R = residue to the separation of C. ^c As evidenced by the X-ray powder pattern; XX = crystalline; A = amorphous. ^d Hact. = hydride hydrogen content indicated as meq/g. ^e In nujol mull. ^f Calc. values are referred to the general formula $(\text{HAINR})_n$. ^g Calc. values for $[\text{HAINR}]_3(\text{H}_2\text{AINHR})$. ^h Obtained by ageing t-BuPIA-R in toluene solution for 17 h at $70-80^\circ\text{C}$.

the two groups on nitrogen atoms linked to two AlH and one AlH₂ groups. Finally the τ 8.63 signal would correspond to a unique NHR group. These results suggest that from reaction 1 a structure such as VIII is formed, which changes to IX on heating.



(VIII)



(IX)

Typical X-ray powder patterns for different PIA are collected in Table 10.

Conclusions

These results allow us to draw some general conclusions:

(a) the formation of three dimensional oligomers by association of —HAL—NR— units via four or six membered rings can be inferred as a characteristic

TABLE 10

X-RAY POWDER DATA OF POLY(N-CYCLOHEXYLIMINOALANE) AND POLY(N-tert-BUTYL-IMINOALANE)

c-HexPIA—P ^a		t-BuPIA—H ^a	
I	d (Å)	I	d (Å)
s	10.46	s	8.63
ms	8.42	vs	7.69
ms	7.86	vs	7.00
m	5.72	vs	4.97
s	5.29	mw	4.58
m	4.73	ms	4.30
mw	4.44	mw	4.06
w	4.24	w	3.76
mw	4.07	mw	3.66
mw	3.88	m	3.20
vw	3.69	mw	3.04
vw	3.49	m	2.950
m	3.16	m	2.840
vw	2.862	m	2.797
vw	2.767	w	2.574
mw	2.648	w	2.485
w	2.505	mw	2.430
m	2.436	m	2.350
m	2.377	vw	2.196
m	2.321	m	2.149
w	2.212	m	2.074
mw	1.929	vw	2.027
		w	1.963
		m	1.855

^aReference is made to Table 9.

feature of PIA. On the basis of X-ray investigations on a variety of single crystals of PIA [7,9], our opinion is that the formation of cage structures is extremely favourable;

(b) the PIA structure can depend on the synthetic method. This has been shown to be so particularly for PIA obtained from isopropylamine. The different synthetic methods 1 and 2 provide somewhat different products;

(c) the nature of the amine influences the structure of the corresponding PIA. By using the same preparative method 1 we have obtained (i) tetramers from an amine having a tertiary carbon in the α -position with respect to the nitrogen atom; (ii) hexamers from amines having a secondary carbon in the α - or β -position; (iii) oligomer mixtures from amines having a primary carbon atom in the α - and β -positions.

Experimental

Reagents and solvents

LiAlH_4 was prepared from LiH (Degussa) and aluminum trichloride (Kulmann) in diethyl ether using the method of Finholt et al. [10] $\text{AlH}_3 \cdot \text{NMe}_3$ was synthesized from LiAlH_4 and $\text{NMe}_3 \cdot \text{HCl}$ following the method of Ruff and Hawthorne [11]. Pure amines and propionitrile were dried and purified by distillation from Na or from KOH . All solvents were purified and dried by the known methods and all syntheses were carried out under an atmosphere of nitrogen.

Chemical analyses and physicochemical measurements

Chemical analyses were carried out on solutions obtained by decomposition of weighed samples with dilute aqueous acid. The aluminum content was evaluated by the $\text{EDTA}-\text{ZnSO}_4$ method. The Kjeldahl method was generally used for nitrogen analyses. The hydridic hydrogen content was determined by the measurement of hydrogen liberated by decomposition of a weighed sample with small amounts of *n*-octylalcohol and then with aqueous 50% H_2SO_4 in a flask directly connected to the gas volumetric apparatus. The lithium content was determined by atomic absorption.

IR spectra were recorded on a Perkin-Elmer model 225 spectrometer. Low resolution mass spectra ($\text{RP} = 1000$) were measured with a LKB 9000 Mass Spectrometer. High resolution ($\text{RP} = 10,000$) spectra were measured with an AEI MS 902 S Mass Spectrometer attached to an AEI DS 10 Data System. Both low and high resolution mass spectra were obtained by direct probe insertion at 70 eV and with a source temperature of 240–270°. X-ray powder patterns were collected by a Debye-Scherrer camera (diameter 114.6 mm). ^1H NMR spectra were recorded with a Varian HA-100.

Synthesis of poly(N-alkyliminoalanes)

Typical preparations are reported for each synthesis route.

Poly(N-isopropyliminolan). (a) A solution of isopropylamine (133 mmol) in diethyl ether (40 ml) was added dropwise to a stirred solution of $\text{AlH}_3 \cdot \text{N}(\text{CH}_3)_3$ (133 mmol) in diethyl ether (100 ml) at room temperature. Hydrogen evolution took place immediately. The reaction mixture was stirred at room temperature for 2 h and left overnight.

The solvent and $N(\text{CH}_3)_3$ were then removed by evaporation in vacuo. The white solid residue was dissolved in diethyl ether (ca. 100 ml) and the solution was filtered to remove small traces of an insoluble material and cooled to -50° . A precipitate was formed which was separated by filtration at -50° , dried (10 h, room temperature, 10^{-3} mm Hg) and analyzed. (Found: Al, 30.67; N, 16.24; $H_{\text{active}}/\text{Al}$, 1.01. $(\text{HAlNC}_3\text{H}_7)_n$ calcd.: Al, 31.71; N, 16.46; $H_{\text{active}}/\text{Al}$, 1.) The remaining solution was evaporated in vacuo and the residue was dried (10 h, room temperature, 10^{-3} mm Hg) and analyzed. (Found: Al, 28.55; N, 15.97; $H_{\text{active}}/\text{Al}$, 0.99. $(\text{HAlNC}_3\text{H}_7)_n$ calcd.: Al, 31.71; N, 16.46; $H_{\text{active}}/\text{Al}$, 1.) Further information is reported in Table 1.

Similar results were achieved when the reaction mixture was directly cooled to -50° , after the removal of a part (ca. 40%) of the solvent in vacuo.

(b) $\text{iso-C}_3\text{H}_7\text{NH}_2 \cdot \text{HCl}$ (156 mmol) was added slowly to a stirred solution of LiAlH_4 (156 mmol) in diethyl ether (200 ml) at room temperature. Hydrogen evolution took place immediately. The mixture was stirred for 2 h at room temperature and left overnight. The solution was then filtered to remove LiCl , concentrated in vacuo to ca. 60% of the initial volume and cooled to -50° . A precipitate was formed which was separated by filtration, dried (10 h, room temperature, 10^{-3} mm Hg) and analyzed. (Found: Al, 28.94; N, 14.80; $H_{\text{active}}/\text{Al}$, 1.25. $(\text{HAlNC}_3\text{H}_7)_n$ calcd.: Al, 31.71; N, 16.46; $H_{\text{active}}/\text{Al}$, 1.)

The remaining solution was evaporated in vacuo to give a white solid which was dried (10 h, room temperature, 10^{-3} mm Hg) and analyzed. (Found: Al, 29.77; N, 15.93; $H_{\text{active}}/\text{Al}$, 1.38. $(\text{HAlNC}_3\text{H}_7)_n$ calcd.: Al, 31.71; N, 16.46; $H_{\text{active}}/\text{Al}$, 1.) Further information is reported in Table 1.

Poly(N-n-propyliminoalanes). (a) A solution of n-propylamine (153 mmol) in diethyl ether (50 ml) was added slowly to a stirred solution of $\text{AlH}_3 \cdot N(\text{CH}_3)_3$ (153 mmol) in diethyl ether (180 ml) at room temperature. The reaction mixture was stirred at room temperature for 2 h.

Besides hydrogen evolution, the formation of a precipitate was observed. After standing overnight, the precipitate was filtered, dried (10 h, room temperature, 10^{-3} mm Hg) and analyzed. (Found: Al, 28.82; N, 16.01; $H_{\text{active}}/\text{Al}$, 1.07. $(\text{HAlNC}_3\text{H}_7)_n$ calcd.: Al, 31.71; N, 16.46; $H_{\text{active}}/\text{Al}$, 1.)

The solution was concentrated in vacuo to ca. 60% of the initial volume and cooled to -50° . A precipitate was formed which was separated by filtration, dried (10 h, 10^{-3} mm Hg, room temperature) and analyzed. (Found: Al, 29.77; N, 16.03; $H_{\text{active}}/\text{Al}$, 1.07. $(\text{HAlNC}_3\text{H}_7)_n$ calcd.: Al, 31.71; N, 16.46; $H_{\text{active}}/\text{Al}$, 1.)

Finally the remaining solution was evaporated in vacuo and the residue was dried (10 h, 10^{-3} mm Hg, room temperature) and analyzed. (Found: Al, 30.08; N, 15.81; $H_{\text{active}}/\text{Al}$, 1.22. $(\text{HAlNC}_3\text{H}_7)_n$ calcd.: Al, 31.71; N, 16.46; $H_{\text{active}}/\text{Al}$, 1.)

(b) A solution of propionitrile (150 mmol) in diethyl ether (50 ml) was added dropwise to a solution of $\text{AlH}_3 \cdot N(\text{CH}_3)_3$ (150 mmol) in diethyl ether (120 ml). The formation of a precipitate occurred. The reaction mixture was stirred for 2 h at room temperature and left to stand overnight. The precipitate was separated by filtration, dried (10 h, 10^{-3} mm Hg, room temperature) and analyzed. (Found: Al, 27.44; N, 15.04; $H_{\text{active}}/\text{Al}$, 0.98. $(\text{HAlNC}_3\text{H}_7)_n$ calcd.: Al, 31.71; N, 16.46; $H_{\text{active}}/\text{Al}$, 1.)

The remaining solution was concentrated in vacuo to ca. 60% of the initial volume and cooled to -78° but did not give a precipitate.

The solvent was then completely removed in vacuo and the residue was dried (10 h, 10^{-3} mm Hg, room temperature) and analyzed. (Found: Al, 27.50; N, 16.23; $H_{\text{active}}/\text{Al}$, 0.97. $(\text{HAlNC}_3\text{H}_7)_n$ calcd.: Al, 31.71; N, 16.46; $H_{\text{active}}/\text{Al}$, 1.) Further information is given in Table 7.

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