Journal of Organometallic Chemistry, 132 (1977) 339—350

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

XII *. ^{1}H-NMR FEATURES

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(Received November 11th, 1976)

Summary

This paper discusses the results of ^{1}H-NMR studies of poly(*N*-alkyliminoalanes) prepared from various amines, in particular, the relationship between the NMR parameters and molecular structure is examined Also, the effects of polar solvents and of partial or complete replacement of hydridic hydrogens by chlorine atoms and alkyl groups on characteristic features of the spectra are reported

Introduction

For many years derivatives of aluminum hydride have been studied in these laboratories because of their application in the polymerization of olefins and diolefins [1]. Particular attention has been paid to the synthesis and structural characterization of poly(*N*-alkyliminoalanes), (PIA), which display a high catalytic activity [2] These products derive from replacement of the hydridic hydrogens of AlH_3 by imino radicals of primary amines [3] Recent research demonstrated that they are characterized by 'cage" molecular structures, with a skeleton formed by 4 or 6 membered rings, $(Al—N)_2$ or $(Al—N)_3$ (Figs 1, 2) Various PIA of general composition $(HAlNR)_n$, with n ranging from 4 to 10, have been prepared. The structure of the products is affected by several factors the nature of the amine, the reaction conditions, and the preparation methods [4a,5] In addition to the basic compounds of formula $(HAlNR)_n$, other compounds containing imino and amino radicals have been prepared

In general, PIA consist of a larger class of compounds corresponding to

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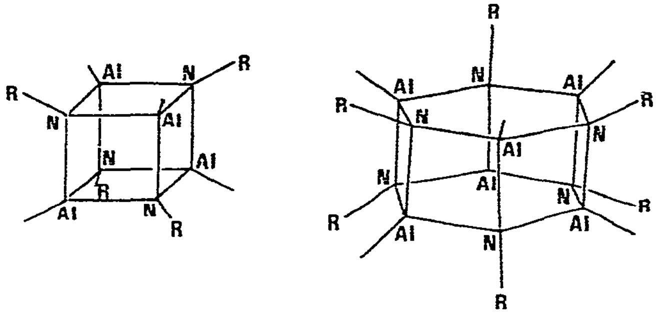
* For Part XI see ref 15



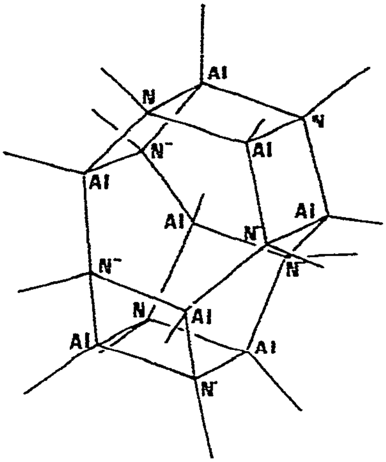


Fig 1 A perspective view of cage molecules with skeletons fromed by 4 or 6 member rings

Fig 2 Molecular structure of $(HAlN\text{—}n\text{-}C_3H_7)_8$

$Al_n(H_{act} + NR)_{2n+i}$ $(0 \leqslant i \leqslant 3)$. The molecular structures corresponding to several different compositions [4b,6,7] have been determined, generally by X-ray structural methods

Further classes of compounds retaining the typical cage structure derive from partial or complete substitution of hydridic hydrogens of PIA by chlorine atoms or alkyl groups [2b,8,9]. This paper deals with the ^{1}H-NMR characterization of most of these compounds Considerable ^{1}H-NMR data previously published [4a,5b,8,9] are reported here for purposes of comparison and discussion The spectral parameters have been related to different molecular arrangements, and, in some cases, also to the thermal stability and to the geometric parameters deduced from X-ray studies

Results and discussion

Regular closed cages

In Table I the values of the chemical shifts of several PIA of composition $(HAlNR)_n$ are reported, these compounds form regular closed cages. In the cases where the crystal and molecular structures were not solved by X-ray diffraction techniques, the compounds were characterized by mass spectrometry and by molecular weight determination via the ebullioscopic method [4a,5]. All these compounds exhibited only one resonance due to the alkyl group linked to the nitrogen atom, over the range of temperature from —60°C to 90°C In Fig 3 the ^{1}H-NMR spectrum of hexameric PIA from isopropylamine is reported Thus, the alkyl environments in each compound are all equivalent. This is consistent with the geometric equivalence shown for tetrameric and hexameric PIA by X-ray determination [4b,14] (Fig 1). For the octamer $(HAlN\text{-}n\text{-}C_3H_7)_8$ the crystalline structure [15], shows two types of environments for the nitrogen atoms· i e , one nitrogen, N′, is shared by two four-membered rings, $(Al\text{—}N)_2$, and by one six-membered ring, $(Al\text{—}N)_3$, while the other, N″, belongs to one four-membered ring and two six-membered rings (Fig 2)

TABLE 1

^{1}H-NMR SPECTRAL PARAMETERS OF CLOSED CAGES OF POLY(*N*-ALKYLIMINOALANES) IN BENZENE

Sample	Compound	τ (ppm)	Multiplicity	Relative area	Assignment groups
i Pr—PIA-Hex	$(HAlN\text{-}i\text{-}C_3H_7)_6$	8.49	doublet	6.0	CH_3
		6.29	septet	1.0	CH
		5.43 [a]	singlet	1.0	Al—H
i Pr—PIA-Tet	$(HAlN\text{-}i\text{-}C_3H_7)_4$	8.68	doublet	6.0	CH_3
		6.70	septet	1.0	CH
s-Bu—PIA-Hex	$(HAlN\text{-}s\text{-}C_4H_9)_6$	9.04	triplet	3.0	nitrogen γ-CH_3
		8.40	doublet	3.0	nitrogen β-CH_3
		8.06	multiplet	2.0	CH_2
		6.54	multiplet	1.0	CH
s-Bu—PIA-Tet	$(HAlN\text{-}s\text{-}C_4H_9)_4$	9.04	triplet	3.0	nitrogen γ CH_3
		8.63	doublet	3.0	nitrogen β-CH_3
		8.27	multiplet	2.0	CH_2
		6.88	multiplet	1.0	CH
n-Pr—PIA-Oct	$(HAlN\text{-}n\text{-}C_3H_7)_8$	9.07	triplet	3.0	CH_3
		7.96	multiplet	2.0	nitrogen β-CH_2
		6.74	triplet	2.0	nitrogen α-CH_2
n-Pr-PIA-Hex	$(HAlN\text{-}n\text{-}C_3H_7)_6$	9.07	triplet	3.0	CH_3
		8.23	multiplet	2.0	nitrogen β-CH_2
		6.83	triplet	2.0	nitrogen α-CH_2
i Bu—PIA-Hex	$(HAlN\text{-}i\text{-}C_4H_9)_6$	8.92	doublet	6.0	CH_3
		7.96	multiplet	1.0	CH
		6.80	doublet	2.0	CH_2
t-Bu—PIA-Tet	$(HAlN\text{-}t\text{-}C_4H_9)_4$	8.56	singlet		CH_3
Ph—Et—PIA-Tet	$(HAlN\text{-}CH(CH_3)C_6H_5)_4$	8.41 [b]	doublet	3.0	CH_3
		5.63 [c]	quartet	1.0	CH

[a] Measured at −70°C [b] Measured at 70°C [c] The signals relative to aromatic protons are obscured by the solvent

As a consequence the mean value of the three Al—N′—Al bond angles (99.45°) is lower than the mean value of the Al—N″—Al bond angles (110.11°). Furthermore differences in C—N—Al bond angles are also observed. These factors correspond to changes in the sp^3 hybridisation of the different nitrogen atoms, due to a higher *s* character in the N′—C bond than in the N″—C. So different magnetic resonances for alkyl groups N′—R and N″—R should be seen. However, only one signal was observed for all the R groups (Fig. 4). To explain this unexpected equivalence, it may be observed that the mean length of the three Al—N bonds of nitrogen atom N′ or N″ are practically identical, with an overall mean bond length of 1.916 Å, (see Table 2), and that a similar identity also occurs for the N′—C and N″—C bond lengths (1.507(4) and 1.526(5) Å). Therefore, in spite of the difference in *sp* character of the three individual Al—N bonds, the average charge distributions along the N—C bonds may be rather similar, and the N—R groups thus magnetically equivalent. The data in Table 2 show that average Al—N bond lengths in tetrameric, hexameric and octameric cage molecules are very similar; it is our opinion that Al—N and N—C bonds are made practically equal by some kind of internal compensation of the charge distribution along the Al—N bonds. Measurements of thermal stability seem to support our hypothesis: the hexamer and the tetramer from isopropylamine decompose at

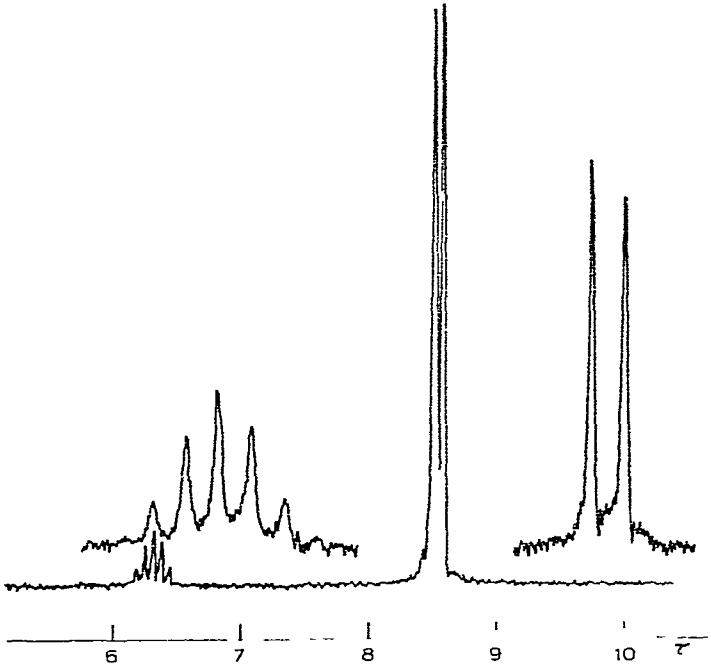


Fig 3 ¹H NMR spectrum of $(HAlN{-}i\text{-}C_3H_7)_6$ in benzene

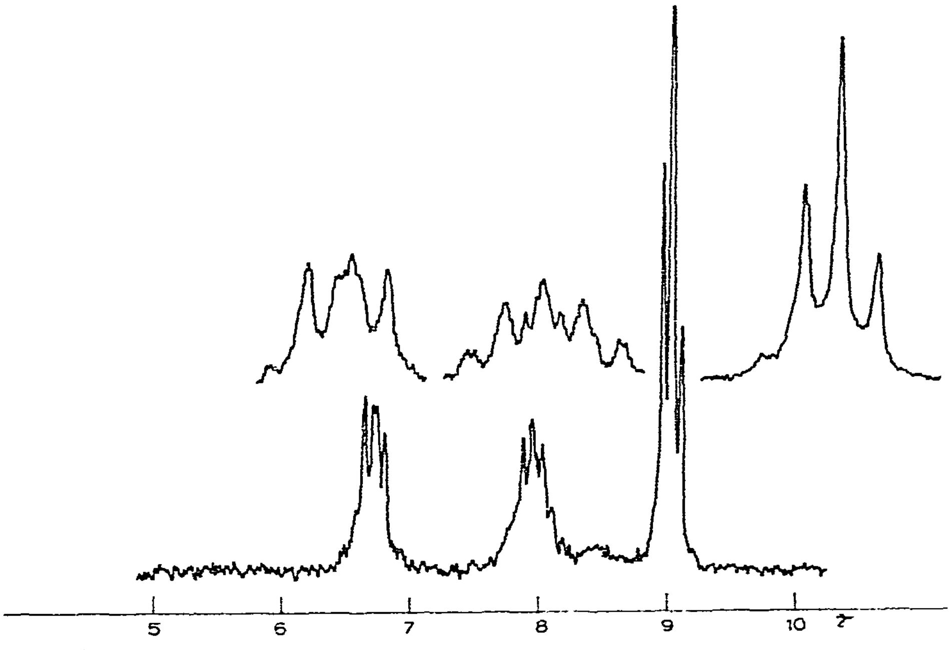


Fig. 4 ¹H NMR spectrum of $(HAlN{-}n\text{-}C_3H_7)_8$ in benzene

TABLE 2

AVERAGE Al—N BOND LENGTHS FOR CLOSED POLY(N ALKYLIMINOALANES)

Sample	Compound	Nitrogen type	Bond lengths (Å)	Mean length of the Al—N bonds
n-Pr—PIA-Oct	$(HAlN—n\text{-}C_3H_7)_8$	N	in six memb rings 1 882(3) 1 925(3) in transverse bonds 1 943(3)	1 916
		N	in six memb rings 1 897(4) 1 908(6) in transverse bonds 1 941(2)	1 916
i Pr—PIA-Hex	$(HAlN\text{-}i\text{-}C_3H_7)_6$		in six memb rings 1 898(2) in transverse bonds 1 956(2)	1 917
i Pr—PIA-Tet	$(HAlN\text{-}i\ C_3H_7)_4$		in four memb rings 1 913(7)	1 913

nearly the same temperature, 241 and 245°C respectively [10]

So, because of the quite similar electronic charge distribution along the frameworks of the various cages, PIA obtained from the same amine should show the same chemical shift independent of the cage type Therefore the observed differences must be attributed to differing spatial arrangements of the alkyl substituents in the various cages. In fact, the X-ray structure [4b,15] of the hexameric cage of n-propylamine shows the two hydrogens of the α-carbons facing two four-membered rings $(Al—N)_2$, while in the octameric cage they face one four and one six-membered ring, $(Al—N)_3$. This implies that in solution we can expect these conformers, arising by rotation of alkyl groups about the N—C bonds, to predominate. On this basis, in the octamer of n-propylamine the two C—H bonds would exchange in solution between the two possible situations in which they face, a four and a six-membered ring, respectively In this way the observed chemical shift arises from an intermediate conformation in which the magnetic sites at N′ and N″ are equivalent * Furthermore the variation of NMR signals with temperature supports the hypothesis that the freedom of rotation about N—C bonds is clearly lower in an octamer with respect to a tetramer: in fact the broadness of the proton signals on decreasing the temperature follows the sequence octamer > hexamer for n-Pr—PIA, hexamer > tetramer for i-Pr—PIA In the case of hexameric and tetrameric structures from isopropylamine, the resonance of the hydridic hydrogen is displayed at low temperature At —60°C a very broad signal appears at 5 3 τ with a relative intensity of 1 0. The extensive broadening of this signal is certainly due to the relatively large electric quadrupole effects associated with the ^{27}Al nucleus The chemical shifts for the tetrameric 1-phenylethylamine derivatives $(HAlNCH(CH_3)C_6H_5)_4$, [11] were measured at 70°C At room temperature both the CH and the CH_3 signals are broadened due to hindered rotation around the N—C bond because of the bulky phenyl groups (Fig. 5).

The effect of polar solvents like diethylether, triethylamine, and THF on the

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* While we were completing this work we learned of the paper of Noth and Wolfgardt [13] In contrast with our NMR results on $(HAlN—n\text{-}C_3H_7)_8$ these workers found two series of signals for alkyl groups of $(HAlNC_2H_5)_8$

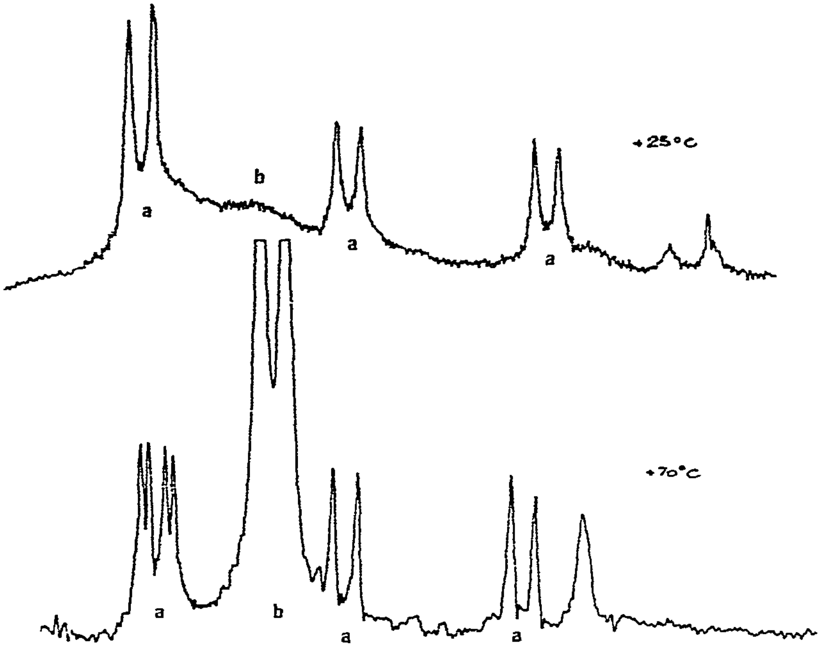

Fig 5 The temperature effect on the CH_3 signals of the spectrum of regular closed (b) and open (a) cages of PIA from 1-phenylethylamine in toluene

spectra of PIA from isopropylamine was studied With respect to the spectra in benzene, the only change in the position of the signals depended on the electron-donor effect of the solvent coordinated to the aluminum atom (Table 3), the interaction with the polar solvent does not modify the equivalence of the alkyl group It is noteworthy that in most cases the proton-proton coupling constants in the alkyl group bonded to the nitrogen atom are practically the same as in the corresponding free amine

Irregular open cages

The spectra of several products or mixtures of products obtained from several amines with "irregular" cage structures were also studied Generally these

TABLE 3

CHEMICAL SHIFT OF THE METHYL GROUP DOUBLETS OF POLY(N ISOPROPYLIMINOALANES) IN POLAR SOLVENTS

Sample	Compound	Solvent	τ (ppm)
i Pr—PIA-Hex	$(HAlN\text{-}i\ C_3H_7)_6$	benzene	8 49
		diethyl ether	8 63
		THF	8 71
		triethylamine	8 60
i Pr-PIA-Tet	$(HAlN\text{-}i\ C_3H_7)_4$	benzene	8 68
		diethyl ether	8 80
		THF	8 81

products, with separate $>AlH_2$ and $>NHR$ groups instead of imino—HAl—NR— units (open cages), give rise to a multiplicity of signals in the alkyl range Thus signal overlap sometimes precluded an unambiguous assignment Nevertheless, for tetrameric derivatives from t-butylamine and 1-phenylethylamine the resonances of the open cage structures were measured; the values of the chemical shifts are reported in Table 4 Clearly the opening of an Al—N bond destroys the magnetic equivalence of the alkyl radical bonded to the nitrogen atoms (Fig 6) For both compounds signals with relative intensity 2 0 were attributed to radicals R′ linked to nitrogen atoms located between one AlH_2 and two AlH groups. Since the AlH_2 group is linked to only two NR groups in this open cage structure, it should be a stronger Lewis acid than in a closed structure Consequently, more electronic charge should be released by the NR groups toward the AlH_2 group, thus deshielding the protons of the R groups An analogous, opposite effect is observed for the protons of radicals bonded to the NH group Therefore the signal at 8 57 τ for the t-butylamine derivative, and that at 8 62 τ for the methyl protons of the 1-phenylethylamine derivative, must be assigned to R groups on the nitrogen atoms which are bonded to three AlH groups It is important to note that, in the case of the 1-phenylethylamine derivative, the different steric situation in the open and closed cage structure greatly influences the resolution of the signals The open-cage form gives well resolved signals at room temperature, while a large broad signal is observed for the corresponding closed-cage form (Fig. 5) It is quite reasonable that in an open cage there is nearly free rotation of the alkyl groups about the N—C bonds Furthermore, at 70°C we observed that the methyl doublet of the R radicals linked to the nitrogen located between one AlH_2 and two AlH groups, split into two 1 . 1 doublets, and even the $J(CH—CH_3)$ coupling constant increases with the temperature (Table 5) A detailed examination of a probable model of the open cage suggests that the rotation of the R groups about the C—N bonds could be greatly hindered by the phenyl group, which at this temperature could begin to rotate However, a full rotation of the phenyl group would cause a severe interaction between the *ortho* hydrogen of the phenyl ring and one hydrogen atom of the adjacent AlH_2 group; consequently the hindered rotation about the N—C bond would lock the 1-phenylethyl group into two position corresponding to a "*trans*" and a "*gauche*" conformation, as sketched in Fig 7 This steric model also explains the variation of the coupling constants $J(CH—CH_3)$ (Table 5), in fact, in the stable "*trans*" and "*gauche*" conformations the rotational equilibria of CH_3 groups could also change

Another effect observed for both compounds is the approach of the chemical

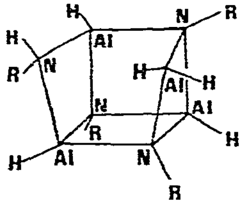

Fig 6 A perspective view of an open tetrameric cage

TABLE 4

^{1}H NMR SPECTRAL PARAMETERS OF IRREGULAR OPEN CAGES OF POLY(*N*-ALKYLIMINOALANES) IN BENZENE

	Sample	Compound	τ (ppm)	Multiplicity	Relative area	Assignment
open	t-Bu–PIA Tet	$t\text{-}C_4H_9NH–(HAlN–t\text{-}C_4H_9)_3–AlH_2$	8.40	Singlet	2.0	t-Bu groups on nitrogen linked to two Al–H and to one AlH$_2$ groups
			8.57	Singlet	1.0	t-Bu groups on nitrogen linked to three AlH groups
			8.63	Singlet	1.0	t-Bu groups on NH
open	Ph–Et–PIA Tet	$CH_3(C_6H_5)CH–NH–(HAlN–CH(CH_3)C_6H_5)_3–AlH_2$				
			8.05	Doublet	6.0	CH$_3$ } of 1-phenylethyl on nitrogen linked to two Al–H and to one AlH$_2$ groups
			5.30	Quartet	2.0	CH
			8.62	Doublet	3.0	CH$_3$ } of 1-phenylethyl on nitrogen linked to three AlH groups
			6.84	Quartet	1.0	CH
			9.16	Doublet	3.0	CH$_3$ } of 1-phenylethyl on NH
			7.31	Quartet	1.0	CH

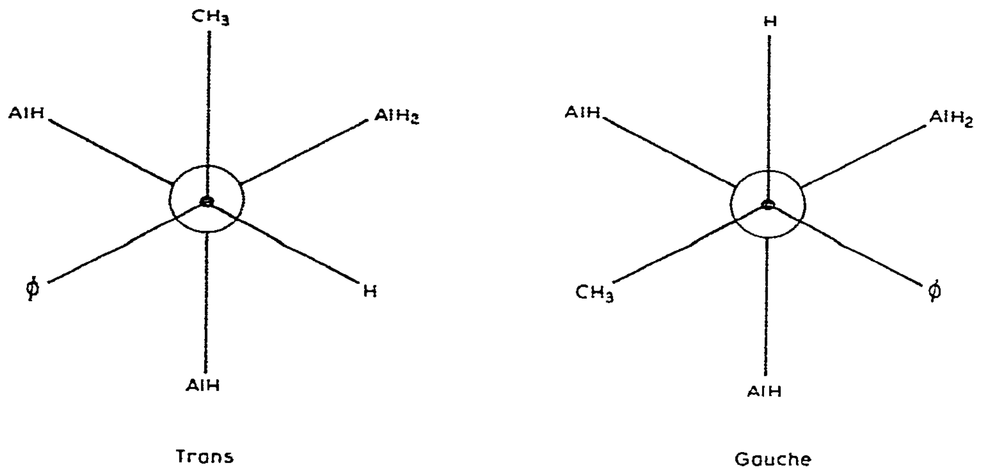

Fig. 7 "*trans*" and "*gauche*" conformations of PIA from 1-phenylethylamine about the N—C bond

shifts towards the values of the corresponding closed cage molecules with increase in temperature (Table 5), while the signals of the closed form remain unaffected. This general effect could be ascribed to a trend of conformational equilibria of the open cages approaching those of the closed cages, in particular this would lead to more close contacts between nitrogen and aluminum atoms of NHR and AlH_2 groups

Chloro-poly(N-alkylaminoalanes)

These compounds derive from partial or complete substitution of hydridic hydrogens by chlorine atoms in some species of PIA previously described [8] Table 6 lists the spectral parameters for the compounds characterised Conclu-

TABLE 5

CH_3-^1H NMR SPECTRAL PARAMETERS OF IRREGULAR OPEN CAGES

Sample		Temp (°C)	Radicals on nitrogen linked to two AlH and to one AlH_2		Radicals on nitrogen linked to three AlH		Radicals on NH	
			τ (ppm)	J (Hz)	τ (ppm)	J (Hz)	τ (ppm)	J (Hz)
open	t-Bu—PIA-Tet	—20	8 38		8 59		8 66	
		0	8 39		8 58		8 65	
		25	8 40		8 57		8 63	
		55	8 40		8 57		8 62	
		70	8 40		8 56		8 59	
		90	8 40		[a]		8 58	
open	Ph—Et—PIA-Tet [b]	0	8 03	6 4	8 62	6 4	9 20	6 4
		25	8 05	6 7	8 61	6 7	9 16	6 7
		70	8 06 8 08	7 2	8 59	6 7	9 07	6 7

[a] The signal is obscured by the signal of the closed tetrameric cage [b] $J(CH_3—CH) = 6\ 4$ Hz (for free amine)

TABLE 6

^{1}H NMR SPECTRAL PARAMETERS OF CHLORO-POLY(N-ALKYLIMINOALANES) IN BENZENE

Sample	Compound	τ (ppm)	Multiplicity	Relative area	Assignment
Cl_1—t-Bu—PIA-Tet	$(HAlN{-}t\text{-}C_4H_9)_3{-}(ClAlN{-}t\text{-}C_4H_9)$	8.54	singlet	3.0	t-Bu groups on nitrogen linked to two AlH and to one AlCl
		8.63	singlet	1.0	t-Bu groups on nitrogen linked to three AlH
Cl_2—t-Bu—PIA-Tet	$(HAlN{-}t\text{-}C_4H_9)_2{-}(ClAlN{-}t\text{-}C_4H_9)_2$	8.50	singlet	1.0	t-Bu groups on nitrogen linked to two AlCl and to one AlH
		8.61	singlet	1.0	t-Bu groups on nitrogen linked to one AlCl and to two AlH
Cl_4—t-Bu—PIA-Tet	$(ClAlN\text{-}t\text{-}C_4H_9)_4$	8.49	singlet		t-Bu groups
Cl_4—i-Pr—PIA-Tet	$(ClAlN\text{-}i\text{-}C_3H_7)_4$	8.64	doublet	6.0	CH_3 groups
		6.63	septet	1.0	CH groups

sive considerations are as yet possible only for the tetrameric derivatives, because of both the high complexity of the spectra of mixtures of partially chlorinated hexameric PIA as well as their poor solubility. The substitution of the hydrogen by a chlorine atom in t-butyl tetramer splits the alkyl radical signals into two, one at 8.54 τ, with relative intensity 3, due to the three radicals on the nitrogen atom adjacent to the chlorinated aluminum atom, the other one at 8.63 τ, with intensity 1, due to the last radical. The difference in electronegativity between the chlorine and the hydrogen atom is probably not the dominant cause of this splitting, an important p_π—d_π back-bonding opposes the inductive effect of the chlorine atom [12]. The Al—Cl bond distance of 2.12 Å (deduced by X-ray studies in hexachloro PIA from isopropylamine [7] is shorter than the sum of the covalent radii [12], and so should favor the back-bonding.

Probably two opposite effects on the chemical shift occur: *(a)* a different charge distribution in the Al—N bonds (surely longer than in the corresponding hydrogenated compound) causes a shielding effect, *(b)* on the other hand, the chlorine atom, which is located close to the hydrogens of the three nearest radicals, probably induces a long-range deshielding effect.

The substitution by chlorine of a second hydrogen atom splits the four alkyl radicals on the nitrogen atoms into two magnetically different pairs of signals (8.50 and 8.61 τ). The signals at 8.50 τ were attributed to radicals on the nitrogen atoms linked to two chlorinated aluminum atoms.

Finally the derivatives formed by complete substitution of hydridic hydrogens by chlorine in $(HAlN{-}t\text{-}C_4H_9)_4$ gives rise to single signal at 8.49 τ; this is in agreement with the view that only the complete chlorination of the cage causes a prevailing deshielding effect of the chlorine atom.

Alkyl-poly(N-alkyliminoalanes)

Hydridic hydrogen atoms of PIA can also be substituted by alkyl groups without the destruction of the cage molecular structure: products derived by a complete or partial substitution by methyl and ethyl groups have recently been obtained (Table 7) [9].

The proton NMR spectra of fully substituted tetramers from *i*-$C_3H_7NH_2$ show two distinct signals, one due to the R groups bonded to the nitrogen atoms, the other one to the R′ (ethyl or methyl) group on the aluminum atoms. A complete substitution preserves the symmetry of the original cage structure and consequently the magnetic equivalence of the positions of the nitrogen and aluminum atoms.

In the case of the fully alkylated tetramers from *iso*-propylamine, the isopropyl protons resonate at higher field than those of the corresponding hydridic compound. As expected, this effect is exactly opposite to that observed for chlorinated derivatives, and depends on the donor-acceptor properties of the substituent of the aluminum atom. Accordingly, the alkyl substitution increases the electronic density along the Al—N bonds. Therefore the R alkyl groups linked to the nitrogen atoms are more shielded.

The values of the corresponding chemical shifts suggest that the shielding

TABLE 7

^{1}H NMR SPECTRAL PARAMETERS OF ALKYL-POLY(N-ALKYLIMINOALANES) IN BENZENE

Sample	Compound	τ (ppm)	Multiplicity	Relative area	Assignment
Me_1—t-Bu—PIA-Tet	$(HAlN{-}t\text{-}C_4H_9)_3{-}$ $(MeAlN{-}t\text{-}C_4H_9)$	8.53	Singlet	3.0	t-Bu groups on nitrogen linked to three AlH
		8.60	Singlet	9.0	t-Bu groups on nitrogen linked to two AlH and to one AlMe
		10.02	Singlet	1.0	Al—CH_3 groups
Me_2—t-Bu—PIA-Tet	$(HAlN{-}t\text{-}C_4H_9)_2{-}$ $(MeAlN{-}t\text{-}C_4H_9)_2$	8.58	Singlet	3.0	t-Bu groups on nitrogen linked to one AlMe and to two AlH
		8.63	Singlet	3.0	t-Bu groups on nitrogen linked to two AlMe and to one AlH
		10.00	Singlet	1.0	Al—CH_3 groups
Me_4—i-Pr—PIA-Tet	$(MeAlN{-}i\text{-}C_3H_7)_4$	8.77	Doublet	6.0	CH_3 groups of imino radicals
		6.73	Septet	1.0	CH groups of imino radicals
		10.13	Singlet	3.0	Al—CH_3 groups
Et_4—i-Pr—PIA-Tet	$(EtAlN{-}i\text{-}C_3H_7)_4$	8.74	Doublet	6.0	CH_3 groups of imino radicals
		6.60	Septet	1.0	CH groups of imino radicals
		9.47	Quartet	2.0	CH_2—Al groups
		8.54	Triplet	3.0	CH_3 on Al—CH_2 groups

effect is greater for the methyl than for the ethyl group.

The partial alkyl substitution destroys the magnetic equivalence of the groups linked to the nitrogen atoms. The ^{1}H-NMR spectra of partially substituted products generally show a multiplicity of signals, which must be ascribed to both magnetically non equivalent positions in the same cage at the nitrogen atoms, and to the presence of a mixture of products with differing degrees of alkylation. In this case therefore a complete assignment of the signals was successful only for the derivatives from t-butylamine Because of the absence of a long-range deshielding effect noted for the halogen derivatives, the only effect of the monoalkylation is a relative increase of electronic density along the three Al—N bonds converging to the substituted aluminum, therefore the alkyl groups bonded to these three nitrogen atoms resonate at higher field than those in the corresponding hydrogenated compounds. Conversely the resonance of the fourth group shows a downfield shift

The substitution of two hydridic hydrogens with alkyl groups in the tetramer of t-butylamine leads to two types of t-butyl groups, the NMR spectrum exhibits two distinct signals of equal intensity at 8.58 and 8 63 τ The signal at higher field has been assigned to the t-butyl groups which are mainly screened by $\mathrm{Al{-}CH_3}$ groups these two t-butyl groups are linked to the nitrogen atoms belonging to the four membered ring, $\mathrm{(Al{-}N)_2}$, defined by the presence of two alkylated aluminum atoms The lower field signal is due to the two other t-butyl groups, which are each influenced by the shielding effect of the adjacent $\mathrm{Al{-}CH_3}$ methyl group and by the deshielding effect of the methyl group at the aluminum atom in the opposite corner of the cubo-type cage

Experimental

The compounds examined were prepared by published methods [3a,4a,5,8,9]. ^{1}H-NMR spectra were recorded on a Varian HA-100 spectrometer The products were generally examined in anhydrous benzene solution, THF, diethylether and triethylamine were also used in studies of the solvent effect The temperature effects were examined on toluene solutions

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