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^{1}H NMR Features of Poly(N-1-phenyl ethyliminoalanes)

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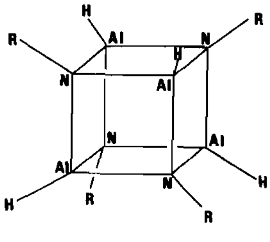
Some of us have reported on the activity of poly(N-alkyliminoalanes) derived from 1-phenylethylamine, Ph-Et-PIA, in the asymmetric reduction [1, 2].

For these compounds they have not found univocal results of molecular weight. Cryoscopic measurements were in favour of formation of hexamer $(HAlNR)_6$, whereas mass spectrometry evidenced the presence of tetramer $(HAlNR)_4$. This discrepancy prompted us to investigate the molecular features of these products. Then the products of many preparations carried out according to the reaction (1)

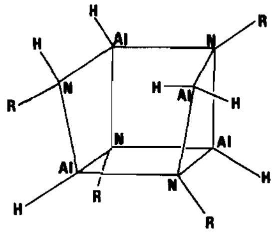
$$AlN_3{\cdot}NMe_3 + RNH_2 \xrightarrow{Et_2O} \frac{1}{n}(HAlNR)_n + 2H_2 + NMe_3 \qquad (1)$$

have been investigated by ^{1}H NMR spectrometry. This has evidenced the formation of mixtures of different species.

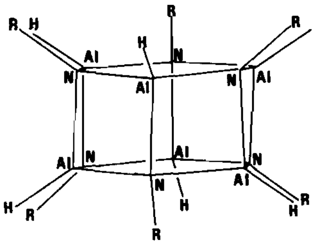
Previously [3] we have described the spectrum of a product which agreed well with the formation of a closed tetrameric cage structure (I) beside the corresponding open tetramer(II) (Table I).



I



II



III

A similar situation has been found for poly(N-alkyliminoalanes) from t-butylamine [4]. In other preparations, in addition to the signals attributed to (I) and (II) the ^{1}H NMR spectrum in benzene has shown one doublet at τ 8.15 and one quartet at τ 5.33 attributable to the protons CH_3 and CH respectively of an unknown closed cage structure. Contrary to the products containing essentially tetrameric

TABLE I. ^{1}H NMR Spectral Parameters of Poly(N-1-Phenylethyliminoalanes) in Benzene[a].

Sample	Compound	τ	Multiplicity	Relative Area	Assignment
Closed Ph-Et-PIA-Hex	$(HAlN{-}CH(CH_3)C_6H_5)_6$	8.15	doublet	3.0	CH_3 protons
		5.33	quartet	1.0	CH protons
Closed Ph-Et-PIA-Tet	$(HAlN{-}CH(CH_3)C_6H_5)_4$[b]	8.41	doublet	3.0	CH_3 protons
		5.63	quartet	1.0	CH protons
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-phenyl-ethyl on nitrogen linked to two AlH and to one AlH_2 groups
		5.30	quartet	2.0	CH
		8.62	doublet	3.0	CH_3 } of 1-phenyl-ethyl on nitrogen linked to three AlH groups
		6.84	quartet	1.0	CH
		9.16	doublet	3.0	CH_3 } of 1-phenyl-ethyl on NH
		7.31	quartet	1.0	CH

[a] The signals relative to aromatic protons are covered by solvent. [b] Measured at 70 °C.

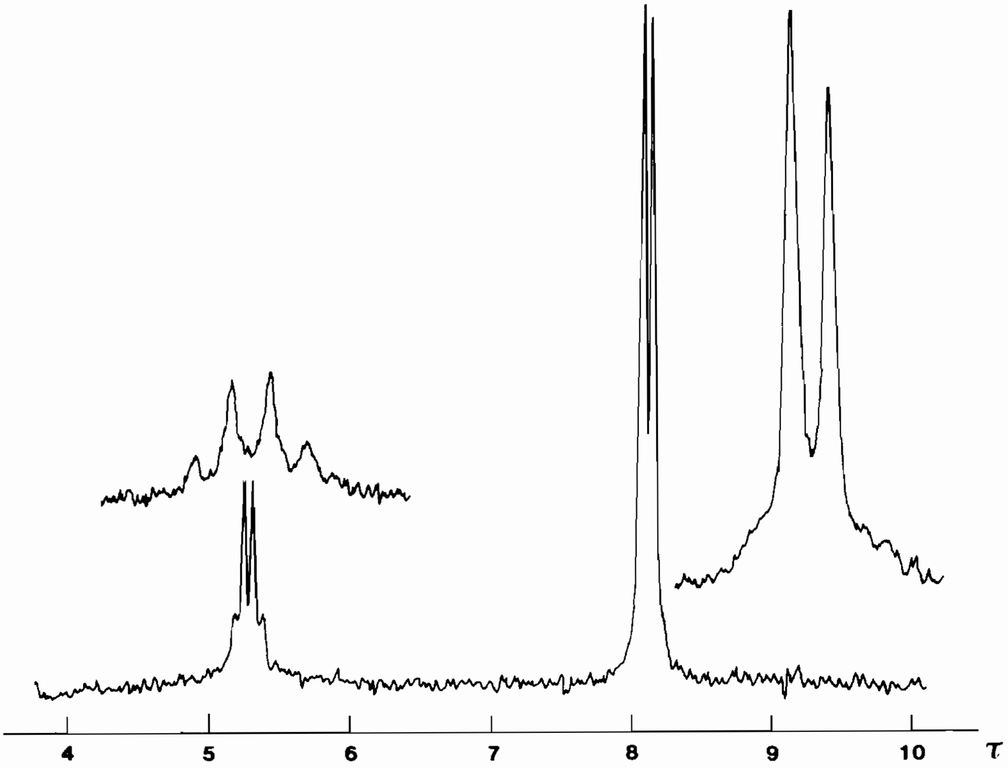


Figure 1. ^{1}H NMR spectrum in benzene of Ph-Et-PIA-Hex.

species, which were amorphous, the products of these preparations were found to be crystalline by X-ray analysis. In one case we have been successful in isolating single crystals. Then the full characterisation of the molecular structure of this new compound by X-ray diffractometry has been possible [5]. It consists of an hexameric cage structure (III) similar to that found for PIA from isopropylamine [6].

In Fig. 1 the corresponding ^{1}H NMR spectrum of this compound, perfectly dried from the crystallization solvent under vacuum, is shown. It allows us to assign the aforementioned signals. It can be concluded that the reaction (1) yields a mixture of well definite tetrameric and hexameric species and that they can be singly individualised by ^{1}H NMR spectra. The correlation of the chemical shift of closed tetramer and hexamer species confirms the observation reported for analogous species from isopropylamine and sec-butylamine [3]. The electronic shielding on radicals bonded to nitrogen increases with increasing oligomerisation degree and this is responsible for the shift of signals to lower fields.

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