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

XIII *. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE HEXAMERS $(ClAlN\text{-}i\text{-}Pr)_6$ AND $(Me_{0.83}H_{0.17}AlN\text{-}i\text{-}Pr)_6(MeAlN\text{-}i\text{-}Pr)_6$

G. DEL PIERO, G. PEREGO, S. CUCINELLA, M. CESARI * and A. MAZZEI
Snamprogetti S.p.A., Direzione Ricerca e Sviluppo, 20097 San Donato Milanese, Milano (Italy)

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Summary

The crystal and molecular structures of $(ClAlN\text{-}i\text{-}Pr)_6$ (I), and of $(Me_{0.83}H_{0.17}AlN\text{-}i\text{-}Pr)_6(MeAlN\text{-}i\text{-}Pr)_6$ have been determined by single crystal three-dimensional X-ray analysis. Block-matrix least-squares refinements led to conventional R factor of 0.039 for I and 0.037 for II. The compounds are isostructural, as the cage molecules consist of a prismatic hexagonal framework, $(AlN)_6$, similar to that observed for the parent hydrogenated analogue $(HAlN\text{-}i\text{-}Pr)_6$. Some differences in bond distances and angles are discussed, in connection with the different Al-bonded substituents. Crystal data: I, trigonal space group $R\bar{3}$; $a = 17.083(2)$, $c = 9.652(1)$; $Z = 3$; D_c 1.46 g cm^{-3}; II, trigonal space group $R\bar{3}$, $a = 17.378(3)$, $c = 9.706(3)$ Å; $Z = 3$; D_c 1.15 g cm^{-3}.

Introduction

In the course of an extensive study of the synthesis, reactions and structure of poly(*N*-alkyliminoalanes), (PIA), various derivatives have been prepared by complete or partial substitution of the hydridic hydrogens by various substituents [1,2]. In this paper we report the crystal structure of $(ClAlN\text{-}i\text{-}Pr)_6$ and $(Me_{0.83}H_{0.17}AlN\text{-}i\text{-}Pr)_6(MeAlN\text{-}i\text{-}Pr)_6$, referred to below as HEXCL and HEXME respectively. Both compounds are derived from the precursor, $(HAlN\text{-}i\text{-}Pr)_6$, (PIAHEX), the structure of which has been previously reported [3].

Single crystals of HEXCL were obtained by reaction of PIAHEX with a stoichiometric quantity of $TiCl_4$ in n-heptane [1]. The methyl derivatives were obtained with different ratio Me/H_{active} by reaction of PIAHEX with $Al(CH_3)_3$;

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* For parts I—XII see refs. 1—6, 12, 13.

these preparations will be reported later [2]. Mass spectral analysis of single crystals of HEXME (from one of these syntheses) showed that they consist of half $(Me_{0.83}H_{0.17}AlN\text{-i-}Pr)_6$ and half $(MeAlN\text{-i-}Pr)_6$. In other words, in one half of the molecules of PIAHEX, all the hydridic hydrogens were substituted by methyl groups while in the other half only five hydrogens were replaced.

Experimental

From Weissenberg photographs taken with Cu-$K_{\bar{\alpha}}$ radiation both crystals were assigned to the trigonal system with rombohedral lattice. The observed systematic absences (hkl for $-h + k + l \neq 3n$) were consistent with the space group $R\bar{3}$. A summary of the crystal data for both compounds is given in Table 1. Cell dimensions were refined by a least-squares fit of the angular parameters of 24 reflections for HEXCL and 21 reflections for HEXME.

Data collection was carried out with Zr-filtered Mo-K_α radiation, on a Siemens AED automated diffractometer. The experimental details were as described in previous papers in this series [3—6].

For HEXCL a single crystal of approximate dimensions 0.33 × 0.24 × 0.90 mm was used, and 1066 independent reflections were measured ($\theta_{max} = 26°$); 977 of these, having intensities greater than 2.5 $\sigma(I)$, were used in the structure determination. The decay of the standard reflection was about 3%: a correction based on a linear interpolation was applied to the intensities. The dimensions of the crystal of HEXME were 0.25 × 0.25 × 0.72 mm. A total of 1284 independent reflections were collected ($\theta_{max} = 27°$) and 1058 with intensities greater than 2.5 $\sigma(I)$ were used for the structure determination. The standard reflection showed no significant decay.

No correction for absorption was necessary in either case.

Structure determination and refinement

The crystal structures were solved by usual Patterson and Fourier procedures.

For HEXCL, after a few cycles of block-matrix least-squares refinement, a difference Fourier map revealed the positions of all the hydrogen atoms. The next few cyclces, with anisotropic temperature factors for Cl, Al, N and C, and isotropic for H, converged to a final R factor of 0.039.

For HEXME the X-ray analysis did not permit distinction between a fully

TABLE 1

CRYSTAL DATA FOR $(ClAlN\text{-i-}Pr)_6$ AND $(Me_{0.83}H_{0.17}AlN\text{-i-}Pr)_6(MeAlN\text{-i-}Pr)_6$

Molecular formula:	$(ClAlN\text{-i-}C_3H_7)_6$	$((CH_3)_{0.92}H_{0.08}AlN\text{-i-}C_3H_7)_6$
Molecular weight:	717.2	587.7
Space group:	$R\bar{3}$ (No. 148)	$R\bar{3}$ (No. 148)
Cell constants:	a 17.083(2), c 9.652(1) Å	a 17.378(3), c 9.706(3) Å
Molecules/unit cell:	3	3
Cell volume:	2439.4 $Å^3$	2538.5 $Å^3$
Calculated density:	1.464 g cm^{-3}	1.153 g cm^{-3}
Linear absor. coeff. μ: (Mo-K_α radiation, λ = 0.71069)	7.30 cm^{-1}	2.25 cm^{-1}

and a partially methylated molecule; therefore the structure determination was carried out in the basis of a molecule having a statistical occupancy of the sites at the aluminum atoms by 11/12 of methyl groups, corresponding to an occupancy factor of 0.9167, and 1/12 of hydrogen atoms. All the hydrogens bonded to carbon atoms were revealed by a difference Fourier synthesis, and their positional parameters and isotropic thermal factors were included in the refinement. Attempts to locate the residual hydridic hydrogen atoms statistically bonded to the aluminum atoms were unsuccessful, and in view of their negligible contribution to the scattering they were disregarded.

Refinement was carried out by block-matrix least-squares using anisotropic thermal parameters for non hydrogen atoms. Final conventional *R* factor was 0.037. The function minimized was $w(F_o - F_c)$ using Cruickshank's weighting scheme [7]. Scattering factors for neutral atoms used throughout were those of Cromer and Man [8] for Al, N and C in HEXME, those of Moore [9] for Cl, Al, N and C in HEXCL and of Stewart et al. [10] for H. All computer programs were those of Immirzi [11].

A list of the structure factors may be obtained from the authors on request.

Results and discussion

As expected, HEXCL and HEXME are isostructural with their hydrogenated precursor PIAHEX [3]. Perspective views of the molecules of HEXCL and HEXME with labelling schemes are shown in Fig. 1 and 2 respectively, and the main geometrical parameters are listed in Tab. 2.

As more bulky substituents replace the hydridic hydrogen atoms, the spherical shape of the molecules increases; but clearly the rotation of the alkyl groups about the N—C bonds is also affected. In both these derivatives, only a single conformer is found in the solid state, with strict $\bar{3}$ symmetry, while in PIAHEX two rotational conformers are observed [3]. The same behaviour was found for the corresponding series of tetramers from isopropylamine [12], with enhanced

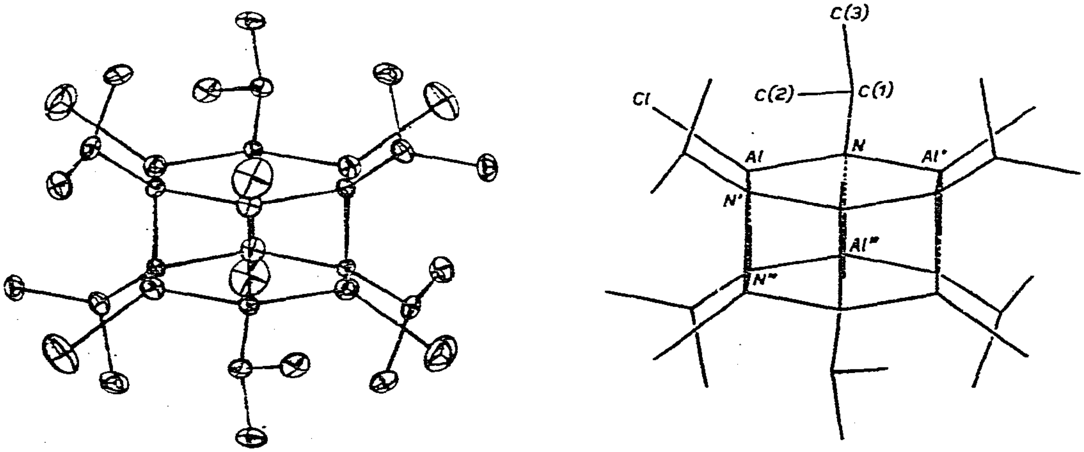

Fig. 1. Perspective view and labelling scheme for the molecule of $(ClAlN\text{-}i\text{-}Pr)_6$.

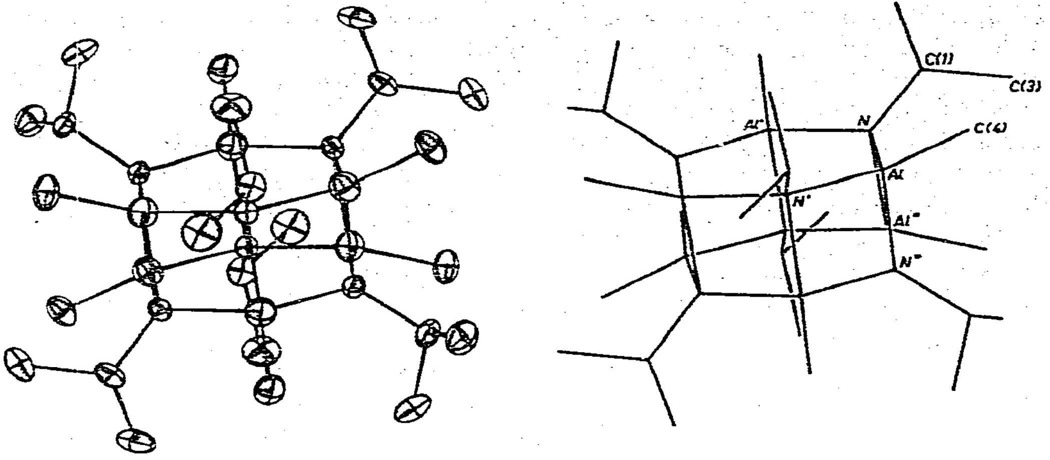

Fig. 2. Perspective view and labelling scheme for the molecule of $(Me_{0.83}H_{0.17}AlN\text{-}i\text{-}Pr)_6(MeAlN\text{-}i\text{-}Pr)_6$.

freedom of rotation of the isopropyl groups in the hydride derivative compared to the more hindered methylated or chlorinated omologues. The $(AlN)_6$ framework of HEXME and HEXCL shows a few differences from that of PIAHEX.

TABLE 2

FINAL ATOMIC FRACTIONAL COORDINATES (× 10^4) AND THERMAL PARAMETERS (× 10^2 Å^2) FOR $(ClAlN\text{-}i\text{-}Pr)_6$ AND FOR $(Me_{0.83}H_{0.17}AlN\text{-}i\text{-}Pr)_6(MeAlN\text{-}i\text{-}Pr)_6$. STANDARD DEVIATIONS IN PARENTHESES REFER TO THE LAST DIGIT

$(Cl\ Al\ N\text{-}i\text{-}Pr)_6$

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	-312(1)	-2350(1)	2041(1)	304(3)	189(3)	368(3)	116(2)	-36(2)	87(2)
Al	-129(1)	-1185(1)	970(1)	153(3)	136(3)	175(3)	72(2)	-5(2)	11(2)
N	-1162(1)	-1030(1)	1055(2)	153(8)	157(8)	180(8)	75(7)	23(6)	27(6)
C(1)	-1878(2)	-1741(2)	2007(3)	213(11)	174(10)	269(11)	71(9)	76(9)	62(8)
C(2)	-2843(2)	-1989(2)	1618(4)	171(11)	307(15)	408(17)	59(10)	41(10)	0(12)
C(3)	-1669(3)	-1437(3)	3514(3)	378(16)	363(15)	233(13)	159(13)	79(11)	86(11)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
H(C1)	-1760(31)	-2284(31)	1772(45)	643(102)	H'(C3)	-1057(26)	-1305(24)	3797(39)	278(75)
H'(C2)	-2931(25)	-2138(25)	688(44)	305(79)	H''(C3)	-1705(30)	-812(30)	3777(43)	483(90)
H''(C2)	-2846(22)	-1443(24)	1477(33)	227(63)	H'''(C3)	-2095(25)	-1912(26)	4009(40)	259(72)
H'''(C2)	-3293(32)	-2486(31)	2151(46)	459(96)					

$(Me_{0.83}\ H_{0.17}\ Al\ N\text{-}i\text{-}Pr)_6(Me\ Al\ N\text{-}i\text{-}Pr)_6$

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al	1179(1)	1060(1)	967(1)	205(2)	221(2)	260(2)	99(1)	-20(1)	-24(1)
N	121(1)	1134(1)	1055(1)	234(5)	211(5)	276(5)	118(4)	-4(4)	-32(4)
C(1)	125(1)	1835(1)	1987(2)	388(9)	317(8)	385(9)	220(7)	-33(7)	-112(6)
C(2)	187(2)	1625(2)	3484(3)	660(16)	581(14)	341(10)	315(13)	15(9)	-159(9)
C(3)	815(2)	2781(2)	1639(3)	603(15)	303(9)	659(16)	205(10)	-85(11)	-126(9)
C(4)[a]	2258(2)	1984(2)	1903(3)	294(9)	372(10)	543(13)	136(8)	-109(8)	-163(9)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
H(C1)	-442(17)	1840(16)	1834(25)	414(55)	H''(C3)	726(25)	2912(25)	683(41)	992(96)
H'(C2)	755(22)	1674(20)	3620(29)	579(71)	H'''(C3)	704(25)	3146(25)	2269(36)	838(90)
H''(C2)	-305(22)	1046(22)	3699(31)	668(73)	H'(C4)	2187(23)	2012(23)	2822(41)	798(89)
H'''(C2)	148(23)	2024(23)	4064(36)	743(81)	H''(C4)	2421(29)	2570(28)	1592(38)	1058(116)
H'(C3)	1403(22)	2871(19)	1748(29)	604(70)	H'''(C4)	2696(24)	1831(23)	1881(35)	835(87)

The average Al—N bond distance is longer in the methylated derivative, 1.932(16) Å, than in the chlorinated one, 1.922(17) Å, which in turn is slightly longer than that of the hydrogenated compound, 1.917(3) Å. Such an effect has been observed also for the tetramers [12]. Moreover the Al—N bond distances in the six membrered ring $(Al—N)_3$ show an alternance of shorter and longer values, a feature which is not apparent in PIAHEX. However, the average deviation of Al and N atoms from the least-squares planes of their hexagonal rings is the same (±0.04 Å) for the three compounds. The bond angles of the cages also require a brief comment. As in PIAHEX, the N—Al—N bond angles in six-membered rings of both derivatives are systematically smaller than the corresponding Al—N—Al bond angles. The mean values are: 117.7(1)° and 122.0(1)° for

TABLE 3

GEOMETRICAL PARAMETERS FOR $(ClAlN\text{-}i\text{-}Pr)_6$ AND FOR $(Me_{0.83}H_{0.17}AlN\text{-}i\text{-}Pr)_6(MeAln\text{-}i\text{-}Pr)_6$. STANDARD DEVIATIONS IN PARENTHESES REFER TO THE LAST DIGIT

$(Cl\ Al\ N\text{-}i\text{-}Pr)_6$		$(Me_{0.83}\ H_{0.17}\ Al\ N\text{-}i\text{-}Pr)_6(Me\ Al\ N\text{-}i\text{-}Pr)_6$	
Bond lengths (Å)			
Al-Cl	2.122(1)	Al-C(4)	1.977(3)
Al-N	1.914(3)	Al-N	1.908(2)
Al-N'	1.898(3)	Al-N'	1.926(2)
Al-N''	1.955(3)	Al-N''	1.964(2)
N-C(1)	1.527(4)	N-C(1)	1.514(3)
C(1)-C(2)	1.529(5)	C(1)-C(2)	1.515(3)
C(1)-C(3)	1.526(5)	C(1)-C(3)	1.511(4)
Bond angles (°)			
Cl-Al-N	113.3(1)	C(4)-Al-N	118.6(1)
Cl-Al-N'	117.5(1)	C(4)-Al-N'	114.9(1)
Cl-Al-N''	120.3(1)	C(4)-Al-N''	119.7(1)
N-Al-N'	117.7(1)	N-Al-N'	115.7(1)
N-Al-N''	91.6(1)	N-Al-N''	91.6(1)
N'-Al-N''	92.1(1)	N'-Al-N''	91.1(1)
Al-N-Al'	122.0(1)	Al-N-Al'	123.9(1)
Al-N-Al''	87.9(1)	Al-N-Al''	88.8(1)
Al'-N-Al''	88.3(1)	Al'-N-Al''	88.3(1)
Al-N-C(1)	110.0(1)	Al-N-C(1)	117.6(1)
Al'-N-C(1)	118.5(1)	Al'-N-C(1)	109.7(1)
Al''-N-C(1)	125.8(1)	Al''-N-C(1)	124.3(1)
N-C(1)-C(2)	113.4(1)	N-C(1)-C(2)	110.6(1)
N-C(1)-C(3)	110.1(1)	N-C(1)-C(3)	115.1(1)
C(2)-C(1)-C(3)	111.4(1)	C(2)-C(1)-C(3)	111.3(1)

Equation of the least-squares planes for six-membered rings and deviation of the atoms from it.

$z-0.9773=0$	$z-0.9813=0$
Al -0.041 ; N +0.041 Å	Al -0.043 ; N +0.043 Å

HEXCL; 115.7(1)° and 123.9(1)° for HEXME; 116.4(2)° and 123.2(2)° for PIAHEX. There is thus a well defined trend: i.e. the difference of the angles is largest in the methylated derivative, followed by the hydrogenated one, and then the chlorinated compound. It is clear therefore that the difference decreases with the electron donating ability of the substituent. No particular trend was remarked for the same angles in the four-membered rings, where the situation is the opposite, i.e. the N—Al—N bond angles are greater than the corresponding Al—N—Al bond angles; values are: average N—Al—N 91.8(3)°, 91.3(4)° and 91.4(5)°, average Al—N—Al 88.1(3)°, 88.5(4)° and 88.5(4)° for HEXCL, HEXME and PIAHEX respectively.

Average N—C and C—C bond lengths are comparable for HEXME and PIAHEX, while for HEXCL they are slightly larger. The Al—C bond length in the methylated derivative and the Al—Cl in the chlorinated one are in good agreement with literature values.

No critical intermolecular contacts were observed in either compound, the closest C···C distances being more than 3.85 and 3.98 Å for HEXCL and HEXME respectively.

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