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

X *. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE TETRAMERS $(HAlN\text{-}i\text{-}Pr)_4$ AND $(MeAlN\text{-}i\text{-}Pr)_4$

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Summary

The crystal and molecular structures of the tetramer $(HAlN\text{-}i\text{-}Pr)_4$ (I) and its methylated derivative $(MeAlN\text{-}i\text{-}Pr)_4$ (II) have been determined from single-crystal, three-dimensional X-ray diffraction data obtained on a diffractometer. A block-matrix least-squares refinement converged to a conventional R factor of 8.4% for I and 7.0% for II. Both molecular structures are built up of a cubic cage $(AlN)_4$. Main average bond lengths are: Al—N 1.913(2) in I and 1.923(1) in II; N—C 1.509(6) in I and 1.485(9) in II; Al—H 1.50(5) and Al—C 1.946(11) Å. Crystal data: I, orthorhombic, space group *Pccn*, cell constants a 21.965(7), b 20.006(9), c 19.833(12) Å, $Z = 16$; II, triclinic, space group $P\bar{1}$, cell constants a 16.924(11), b 8.864(5), c 9.471(7) Å, α 109.5(1), β 110.9(1), γ 90.2(1)°, $Z = 2$.

Introduction

As a part of a research program on the stereochemistry of poly(*N*-alkyliminoalanes), we have determined the structures of the tetramer $(HAlN\text{-}i\text{-}Pr)_4$, and its methylated analogue $(MeAlN\text{-}i\text{-}Pr)_4$, referred to as PIA-Tet and Tet-ME, respectively. Single crystals of PIA-Tet were obtained by reaction of $LiAlH_4$ with iso-$C_3H_7NH_2$ [1]; those of Tet-ME were obtained by a reaction of $Al(CH_3)_3$ with i-$C_3H_7NH_2$, as will be discussed in a future paper [2].

Experimental

Single crystals of PIA-Tet (dimensions 1.05 × 1.05 × 1.35 mm) and of Tet-ME (dimensions 0.63 × 0.19 × 1.05 mm), colourless and prismatic, were sealed in a

* For part IX see ref. 16.

TABLE 1

CRYSTAL DATA FOR $(HAlN\text{-}i\text{-}Pr)_4$ AND $(MeAlN\text{-}i\text{-}Pr)_4$

Molecular formula	$(HAlN\text{-}i\text{-}C_3H_7)_4$	$(CH_3AlN\text{-}i\text{-}C_3H_7)_4$
Molecular weight	340.4	396.5
Space group	*Pccn* (No. 56)	*P*1 (No. 2)
Molecules/unit cell	16	2
Cell constants	*a* 21.965(7), *b* 20.006(9), *c* 19.833(12) Å	*a* 16.924(11), *b* 8.864(5), *c* 9.471(7) Å
(Mo-K_α radiation, γ 0.71069)		α 109.5(1), β 110.9(1), γ 90.2(1)°
Cell volume	8715.3 $Å^3$	1238.7 $Å^3$
Calculated density	1.037 g cm^{-3}	1.063 g cm^{-3}
Linear absorbtion coefficient	2.24 cm^{-1}	2.06 cm^{-1}

thin-walled glass capillary under dry nitrogen. From rotation and Weissenberg photographs, the cell dimensions and space groups were determined. The cell dimensions were later refined by a least-squares fit of the angular parameters of 22 reflections for PIA-Tet and 32 reflections for Tet-ME, carefully centered on the diffractometer. For the former compound space group *Pccn* was determined from the systematic extinctions of $hk0$ with $h + k$ odd and $h0l$ and $0kl$ with l odd; for the latter a triclinic symmetry was deduced and the $P\bar{1}$ space group assumed and subsequently confirmed by successful refinement.

Intensities were measured by a conventional $\theta - 2\theta$ scan with Zr-filtered Mo-K_α radiation on a single-crystal Siemens AED automated diffractometer.

Other experimental details were identical with those described previously [3—7].

For PIA-Tet a unique data set was gathered in the range $\theta < 26°$, yielding 4045 independent reflections of which 2311 with $I > 3.5\sigma(I)$ were used in the structure determination and refinement. The decay in the intensity of the standard reflection reached 10% at the end of the run; therefore a correction factor varying continuously from 1.0 and 1.11 was applied to the measured intensities.

For Tet-ME 3434 independent reflections were collected within a hemishpere up to θ 26° and 2528 of these with $I > 3.0\sigma(I)$ were utlized throughout. Maximum decay in intensity was 5%; a correction of the intensities similar to that mentioned above was applied. In both cases no correction for absorption was found necessary.

A summary of the crystal data is given in Table 1.

Structure determination and refinement

The structure of PIA-Tet was solved by direct methods using the computer program MULTAN by Main et al. [8] and refined by block-matrix least-squares with anisotropic thermal parameters. The strongest 300 reflections with $|E| > 1.74$ and the weakest 50 reflections were used as input data. Of the 16 calculated set of phases, that having the best "figures of merit" (ABSFOM = 1.40, PSIZERO = 1584, RESID = 28.8) allowed the solution of the structure. From the corresponding *E*-map the positions of the aluminum and nitrogen atoms were deduced. A Fourier map revealed the positions of the carbon atoms. Hydridic hydrogen atoms were all located in a difference Fourier map and isotropically

TABLE 2

FINAL ATOMIC FRACTIONAL COORDINATES (× 10^4) AND THERMAL PARAMETERS (× 10^2 A^2) FOR (HAlN-i-Pr)$_4$. STANDARD DEVIATIONS IN PARENTHESES . IN THIS AND FOLLOWING TABLES, REFER TO THE LAST DIGIT

Molecule 1

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al(1)	3253(1)	4785(1)	3826(1)	519(14)	509(14)	595(14)	28(12)	10(12)	0(12)
Al(2)	2953(1)	5330(1)	5027(1)	569(14)	686(16)	454(12)	-13(13)	-10(12)	38(12)
Al(3)	2071(1)	4816(1)	4222(1)	520(13)	495(13)	641(14)	-76(12)	44(12)	14(12)
Al(4)	2639(1)	5955(1)	3870(1)	516(13)	440(12)	519(12)	3(11)	33(11)	45(11)
N(1)	2811(3)	4484(3)	4601(4)	749(43)	321(32)	681(39)	-3(31)	85(35)	164(30)
N(2)	3387(3)	5633(3)	4254(3)	413(32)	492(36)	596(36)	-168(28)	20(30)	-2(31)
N(3)	2506(3)	5107(3)	3439(3)	459(32)	594(37)	450(31)	35(32)	29(30)	-40(30)
N(4)	2213(3)	5652(3)	4656(3)	455(34)	563(37)	502(33)	47(29)	80(29)	-65(31)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
C(1)	2889(5)	3807(6)	4921(6)	971(32)	C(9)	2745(5)	5348(5)	2243(6)	845(28)
C(2)	2467(8)	3693(8)	5457(8)	1456(49)	C(10)	1729(4)	6076(5)	4995(4)	611(21)
C(3)	3507(8)	3747(9)	5145(9)	1574(53)	C(11)	1984(6)	6714(7)	5267(7)	1111(36)
C(4)	3983(4)	5996(5)	4257(5)	621(21)	C(12)	1421(5)	5685(6)	5555(5)	883(29)
C(5)	4472(5)	5603(6)	4599(6)	893(30)	H(Al1)	3751(36)	4272(42)	3446(40)	758(232)
C(6)	3915(5)	6672(6)	4594(6)	985(32)	H(Al2)	3056(36)	5393(39)	5675(41)	1097(237)
C(7)	2305(4)	5026(4)	2729(4)	608(22)	H(Al3)	1432(36)	4434(40)	4268(41)	884(232)
C(8)	2227(5)	4295(6)	2555(5)	868(29)	H(Al4)	2627(40)	6604(40)	3550(39)	893(223)
H(C1)	2791	3430	4549	900	H(C7)	1871	5263	2650	900
H'(C2)	2533	3247	5713	900	H'(C8)	2101	4213	2036	900
H''(C2)	2004	3791	5331	900	H''(C8)	1906	4057	2884	900
H'''(C2)	2572	4114	5868	900	H'''(C8)	2675	4029	2630	900
H'(C3)	3657	3283	5424	900	H'(C9)	2608	5287	1729	900
H''(C3)	3672	4156	5551	900	H''(C9)	3200	5119	2304	900
H'''(C3)	3896	3818	4769	900	H'''(C9)	2792	5876	2357	900
H(C4)	4114	6101	3753	900	H(C10)	1381	6206	4618	900
H'(C5)	4914	5859	4615	900	H'(C11)	1653	7003	5557	900
H''(C5)	4554	5120	4340	900	H''(C11)	2227	7011	4935	900
H'''(C5)	4363	5470	5128	900	H'''(C11)	2340	6566	5693	900
H'(C6)	4323	6944	4619	900	H'(C12)	1071	5999	5791	900
H''(C6)	3740	6601	5123	900	H''(C12)	1760	5573	5945	900
H'''(C6)	3561	6969	4340	900	H'''(C12)	1220	5233	5384	900

Molecule 2

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al(1)	4978(1)	3530(1)	3027(1)	733(17)	611(15)	552(14)	-66(15)	-61(13)	48(12)
Al(2)	4355(1)	3849(1)	1904(1)	485(13)	464(13)	675(15)	30(11)	-45(12)	29(12)
Al(3)	4953(1)	2672(1)	1962(1)	587(14)	383(13)	742(15)	3(12)	-88(13)	4(12)
Al(4)	5581(1)	3829(1)	1871(1)	476(12)	461(13)	565(14)	-9(11)	-49(11)	-9(11)
N(1)	4350(3)	3108(3)	2502(3)	489(36)	482(38)	706(41)	-128(31)	62(30)	61(32)
N(2)	4984(3)	4268(3)	2418(3)	635(38)	370(34)	632(37)	-58(31)	0(32)	-50(28)
N(3)	5576(3)	3084(3)	2486(4)	513(37)	502(40)	728(43)	107(31)	-200(32)	52(33)
N(4)	4952(3)	3418(3)	1355(3)	521(35)	503(36)	438(31)	-1(31)	-42(29)	-20(28)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
C(1)	3779(5)	2791(5)	2773(5)	806(26)	C(9)	6549(6)	3189(7)	3137(7)	1097(36)
C(2)	3409(6)	2508(7)	2216(6)	1073(34)	C(10)	4941(4)	3397(5)	599(5)	712(24)
C(3)	3924(6)	2257(7)	3276(7)	1103(38)	C(11)	4882(5)	4073(6)	293(5)	823(27)
C(4)	4991(5)	5010(5)	2616(5)	673(22)	C(12)	4444(6)	2929(6)	348(6)	1018(34)
C(5)	5537(5)	5154(5)	3059(5)	803(26)	H(Al1)	4979(35)	3588(42)	3772(41)	826(239)
C(6)	4984(5)	5448(7)	1985(6)	1045(36)	H(Al2)	3842(36)	4176(42)	1627(41)	963(231)
C(7)	6162(5)	2725(6)	2691(6)	998(32)	H(Al3)	4948(35)	1947(44)	1819(41)	358(242)
C(8)	6080(6)	2085(7)	3009(7)	1318(37)	H(Al4)	6159(36)	4134(42)	1474(40)	850(231)
H(C1)	3488	3189	3046	900	H(C7)	6400	2651	2237	900
H'(C2)	2990	2259	2390	900	H'(C8)	6523	1861	3143	900
H''(C2)	3688	2088	1986	900	H''(C8)	5854	1723	2672	900
H'''(C2)	3307	2849	1831	900	H'''(C8)	5810	2102	3473	900
H'(C3)	3506	2043	3516	900	H'(C9)	6956	2933	3272	900
H''(C3)	4200	2446	3703	900	H''(C9)	6300	3343	3573	900
H'''(C3)	4164	1857	3043	900	H'''(C9)	6667	3634	2839	900
H(C4)	4579	5107	2909	900	H(C10)	5368	3163	411	900
H'(C5)	5529	5684	3195	900	H'(C11)	4903	4035	-267	900
H''(C5)	5946	5050	2784	900	H''(C11)	5274	4383	439	900
H'''(C5)	5517	4860	3510	900	H'''(C11)	4475	4304	435	900
H'(C6)	4983	6004	2114	900	H'(C12)	4373	2922	-178	900
H''(C6)	4577	5389	1663	900	H''(C12)	3976	3181	549	900
H'''(C6)	5380	5387	1655	900	H'''(C12)	4437	2460	576	900

TABLE 3

FINAL ATOMIC FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^2$ Å^2) FOR (MeAlN-i-Pr)$_4$

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al(1)	1911(1)	2840(2)	2682(2)	510(7)	740(8)	359(6)	-107(6)	87(5)	234(6)
Al(2)	3326(1)	5068(1)	4193(1)	430(5)	397(5)	317(5)	80(4)	156(4)	175(4)
Al(3)	3178(1)	2741(1)	5375(1)	573(6)	418(6)	339(5)	18(5)	158(5)	181(4)
Al(4)	2254(1)	5146(2)	5607(2)	450(6)	792(8)	406(6)	169(6)	210(5)	301(6)
N(1)	3391(2)	5067(4)	6256(3)	430(15)	433(15)	295(13)	92(12)	152(12)	167(12)
N(2)	1971(2)	2829(5)	4752(4)	518(19)	809(24)	439(17)	-95(16)	165(15)	299(17)
N(3)	2123(2)	5170(5)	3538(4)	432(16)	697(21)	406(16)	154(14)	139(13)	311(15)
N(4)	3118(2)	2747(4)	3315(4)	582(18)	409(15)	314(14)	32(13)	179(13)	140(12)
C(1)	4052(3)	6015(5)	7846(5)	486(20)	480(20)	300(16)	62(16)	147(15)	106(15)
C(2)	3899(3)	5676(6)	9235(6)	758(29)	722(28)	386(21)	51(23)	180(21)	220(20)
C(3)	4111(4)	7802(6)	8147(6)	829(32)	519(25)	500(24)	41(22)	233(23)	76(20)
C(4)	1382(4)	1680(10)	4918(8)	635(33)	1786(63)	830(37)	-126(35)	255(29)	750(41)
C(5)	1629(5)	1983(12)	6730(9)	1028(51)	2338(84)	914(46)	-461(52)	191(39)	951(53)
C(6)	551(6)	1744(15)	4143(13)	965(56)	2720(108)	1437(77)	-40(60)	508(54)	1239(76)
C(7)	1670(4)	6293(8)	2785(7)	677(29)	1020(38)	621(27)	363(26)	226(23)	501(27)
C(8)	1771(4)	6064(9)	1186(8)	887(39)	1348(49)	769(35)	303(34)	291(30)	733(36)
C(9)	741(5)	6147(11)	2514(9)	825(40)	1970(72)	951(44)	696(44)	347(35)	884(48)
C(10)	3553(3)	1718(6)	2305(5)	844(30)	536(24)	387(20)	103(21)	285(21)	116(18)
C(11)	3366(4)	2023(7)	753(6)	1001(37)	755(31)	499(25)	123(26)	421(26)	176(23)
C(12)	3355(7)	-31(8)	1964(9)	2353(82)	581(33)	856(41)	487(41)	917(50)	253(30)
C(13)	1035(4)	1492(10)	575(8)	818(38)	1278(51)	575(32)	-261(35)	41(28)	248(32)
C(14)	4137(3)	6351(5)	3883(5)	614(24)	470(21)	499(21)	25(18)	254(19)	225(17)
C(15)	3818(4)	1340(6)	6422(6)	970(34)	569(26)	539(25)	197(23)	285(24)	302(21)
C(16)	1643(4)	6556(9)	6922(8)	820(37)	1414(50)	729(35)	510(35)	462(31)	473(34)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
H(C1)	4565	5871	7860	900	H'''(C9)	424	6760	1810	900
H'(C2)	3479	5789	9105	900	H(C10)	4092	2142	2798	900
H''(C2)	3733	4533	8846	900	H'(C11)	2825	1760	362	900
H'''(C2)	4337	6175	10353	900	H''(C11)	3479	3245	960	900
H'(C3)	3652	7990	8039	900	H'''(C11)	3646	1423	65	900
H''(C3)	4316	8013	7575	900	H'(C12)	2836	-199	1514	900
H'''(C3)	4497	8431	9321	900	H''(C12)	3279	-313	3126	900
H(C4)	1485	439	4396	900	H'''(C12)	3611	-890	1315	900
H'(C5)	1405	2798	6910	900	H'(C13)	724	2144	723	900
H''(C5)	1011	1082	6116	900	H''(C13)	1255	879	524	900
H'''(C5)	2184	1890	7525	900	H'''(C13)	1151	868	-893	900
H'(C6)	459	2853	4802	900	H'(C14)	4189	7497	4345	900
H''(C6)	280	2034	2882	900	H''(C14)	3954	6344	2702	900
H'''(C6)	93	989	4087	900	H'''(C14)	4724	5999	4219	900
H(C7)	1885	7326	3334	900	H'(C15)	4243	1134	6349	900
H'(C8)	1541	5160	714	900	H''(C15)	3953	1794	7606	900
H''(C8)	1382	6963	536	900	H'''(C15)	3464	235	5954	900
H'''(C8)	2388	6094	1278	900	H'(C16)	1839	7440	7179	900
H'(C9)	556	5331	2125	900	H''(C16)	1028	6509	6365	900
H''(C9)	664	6582	3573	900	H'''(C16)	1774	6401	7984	900

refined; not all hydrogens bonded to carbon atoms were in this way located, thus for some of them the positional parameters were computed following the usual carbon geometry. These atoms were included in the refinement as invariant with isotropic B 9.0 Å^2. Refinement converged to a conventional R factor of 0.084. The structure of Tet-ME was solved by usual Patterson procedures. All the hydrogen atoms were revealed by a difference Fourier synthesis, but their positional parameters were not included in the refinement and their thermal parameters were fixed isotropically at B 9.0 Å^2. For all other atoms the refinement was carried out by block-matrix least-squares using anisotropic thermal parameters. The final R factor was 0.07. The function minimized was $\Sigma w(F_o - F_c)^2$ using Cruickshank's weighting scheme [9]. Scattering factors for neutral atoms were those of Cromer and Man [10] for Al, N, C, and of Stewart et al. [11] for H.

TABLE 4

SELECTED GEOMETRICAL PARAMETERS FOR $(HAlN\text{-}i\text{-}Pr)_4$ AND $(MeAlN\text{-}i\text{-}Pr)_4$

$(H\ Al\ N\text{-}i\text{-}Pr)_4$			$(Me\ Al\ N\text{-}i\text{-}Pr)_4$	
	Molecule 1	Molecule 2		
Al(1)-N(1)	1.915(8)	1.923(7)	Al(1)-N(2)	1.930(6)
Al(1)-N(2)	1.920(7)	1.908(7)	Al(1)-N(3)	1.930(4)
Al(1)-N(3)	1.923(7)	1.916(7)	Al(1)-N(4)	1.923(4)
Al(2)-N(1)	1.917(7)	1.899(7)	Al(2)-N(1)	1.918(4)
Al(2)-N(2)	1.904(7)	1.911(7)	Al(2)-N(3)	1.917(4)
Al(2)-N(4)	1.897(7)	1.910(7)	Al(2)-N(4)	1.922(3)
Al(3)-N(1)	1.910(7)	1.914(7)	Al(3)-N(1)	1.927(3)
Al(3)-N(3)	1.914(7)	1.906(7)	Al(3)-N(2)	1.923(5)
Al(3)-N(4)	1.907(7)	1.913(7)	Al(3)-N(4)	1.919(5)
Al(4)-N(2)	1.922(7)	1.915(7)	Al(4)-N(1)	1.920(4)
Al(4)-N(3)	1.922(7)	1.926(7)	Al(4)-N(2)	1.919(4)
Al(4)-N(4)	1.917(7)	1.906(7)	Al(4)-N(3)	1.932(5)
Mean Al-N	1.914(2)	1.912(2)	Mean Al-N	1.923(1)
Overall mean	1.913(2)			
N(1)-C(1)	1.506(14)	1.505(12)	N(1)-C(1)	1.474(7)
N(2)-C(4)	1.497(11)	1.536(12)	N(2)-C(4)	1.506(9)
N(3)-C(7)	1.485(11)	1.529(14)	N(3)-C(7)	1.474(9)
N(4)-C(10)	1.517(11)	1.500(11)	N(4)-C(10)	1.488(6)
Mean N-C	1.501(8)	1.517(10)	Mean N-C	1.485(9)
Overall mean	1.509(6)			
Al(1)-H(Al1)	1.68(8)	1.48(8)	Al(1)-C(13)	1.974(9)
Al(2)-H(Al2)	1.31(8)	1.41(8)	Al(2)-C(14)	1.941(5)
Al(3)-H(Al3)	1.60(8)	1.48(9)	Al(3)-C(15)	1.939(7)
Al(4)-H(Al4)	1.45(8)	1.61(8)	Al(4)-C(16)	1.932(7)
Mean Al-H	1.51(9)	1.50(5)	Mean Al-C	1.946(11)
Overall mean	1.50(5)			
Mean C-C	1.488(13)	1.501(12)	Mean C-C	1.49(2)
Overall mean	1.494(9)			
Mean Al-N-Al	89.9(2)	89.9(1)	Mean Al-N-Al	89.6(1)
Overall mean	89.9(1)			
Mean N-Al-N	90.1(2)	90.1(2)	Mean N-Al-N	90.4(1)
Overall mean	90.1(1)			
Mean Al-N-C	125.3(5)	125.3(7)	Mean Al-N-C	125.5(7)
Overall mean	125.3(4)			
Mean $N\text{-}C\text{-}CH_3$	110.4(11)	111.3(7)	Mean $N\text{-}C\text{-}CH_3$	111.7(5)
Overall mean	110.8(6)			
Mean C-C-C	110.4(5)	110.9(5)	Mean C-C-C	111.0(9)
Overall mean	110.7(3)			
Mean N-Al-H	125.1(13)	125.1(10)	Mean $N\text{-}Al\text{-}CH_3$	124.9(2)
Overall mean	125.1(7)			

Final atomic fractional coordinates and thermal parameters for PIA-Tet and Tet-Me are given in Tables 2 and 3. A table of observed and calculated structure factors is available from the authors on request.

With the exception of MULTAN and ORTEP [12], all other computer programs were those of Immirzi [13].

Results and discussion

The molecular structure of both compounds is essentially built up of an $(AlN)_4$ "cubane" skeleton, identical with that recently observed for the fully substituted phenyl analogue, $Al_4N_4(C_6H_5)_8$ [14]. Perspective views of the two molecules with labelling schemes are given in Fig. 1 and 2, while selected bond distances and mean values of other geometrical parameters are reported in Tab. 4.

In the solid state, PIA-Tet exists as two conformers (1 : 1 ratio), related by rotation of the isopropyl groups about the N—C bonds. The unsymmetrical conformer is represented in Fig. 1; the other one, formed by a 60° rotation of each of two alkyl groups, adopts a tetrahedral symmetry. The methylated derivative, Tet-Me, shows an intermediate symmetry, with only a binary axis present in the molecule.

It is of interest to observe that two rotational conformers have also been found in the crystal structure of the corresponding hexamer, PIA-Hex, i.e. $(HAlN\text{-}i\text{-}Pr)_6$: this is probably due to the greater rotational freedom of isopropyl groups in aluminum hydride derivatives than in the more hindered methylated or chlorinated analogues. The presence of two rotational conformers may relieve any packing effect: in the two cases mentioned it appears negligible.

As in PIA-Hex, the geometry of the two independent molecules of PIA-Tet, in particular of the cages, are practically coincident; therefore the overall means of the parameters have been used for comparison with the corresponding values of other compounds.

The mean Al—N bond length, 1.913(2) Å, in PIA-Tet is not significantly dif-

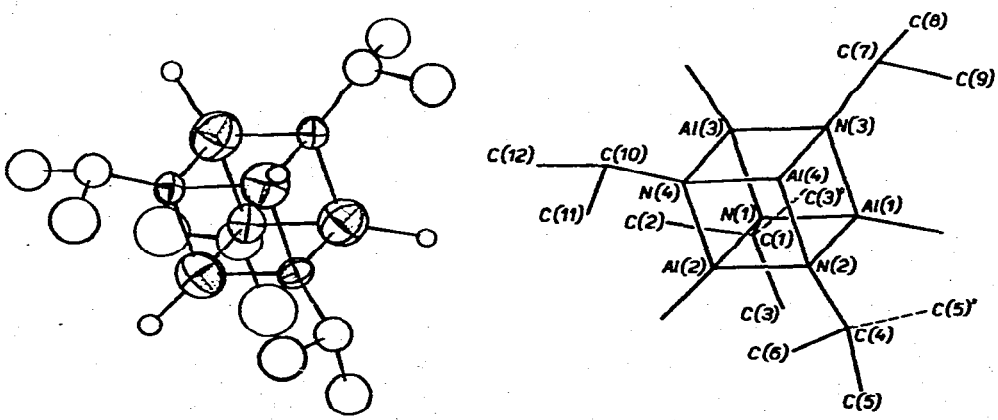

Fig. 1. A perspective view of a cage molecule of $(HAlN\text{-}i\text{-}Pr)_4$ with a labelling scheme. The unsymmetrical conformer is shown. Dotted lines refer to the C(3) and C(5) positions in the tetrahedral conformer.

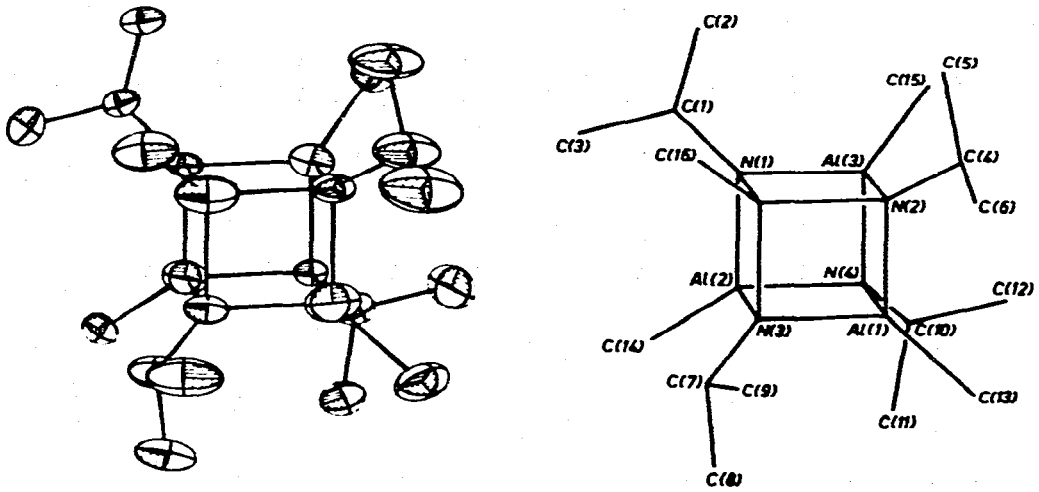

Fig. 2. Perspective view and labelling scheme for the molecule of $(MeAlN\text{-}i\text{-}Pr)_4$.

ferent from that of 1.917(3) Å observed in PIA-Hex, and that of 1.914(5) Å calculated for $Al_4N_4(C_6H_5)_8$. However, for Tet-Me, the mean value of the Al—N bond is 1.923(5) Å. A similar small increase in mean Al—N bond distance has also been observed for the methylated derivative of PIA-Hex [15], as would be expected when a hydridic hydrogen is replaced by an electron-donating substituent. The other mean Al—H, N—C and C—C distances do not differ significantly from those of many other compounds of this series [3—7]. The mean Al—C bond distance in Tet-ME, 1.946(11) appears slightly shorter than the corresponding bond in the methylated hexamer, 1.977(3) Å. However, the relatively large standard deviation of the former value casts some doubt on the comparison. In both compounds four-membered rings $(Al—N)_2$ are strictly planar. As in all the structures of the series previously reported, the trend of the Al—N—Al bond angle to be slightly smaller than the N—Al—N bond angle is followed (see Tab. 4) even though the differences are very small. Neither PIA-Tet nor Tet-ME present any critical intermolecular contact, since the closest C···C distances are greater than 3.80 and 3.88 Å respectively.

Acknowledgments

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References

1 S. Cucinella, G. Dozzi, A. Mazzei and T. Salvatori, J. Organometal. Chem., 90 (1976) 257.
2 S. Cucinella, T. Salvatori, C. Busetto and M. Cesari, to be published.
3 S. Cucinella, T. Salvatori, C. Busetto, G. Perego and A. Mazzei, J. Organometal. Chem., 78 (1974) 185.
4 M. Cesari, G. Perego, G. Del Piero, S. Cucinella and E. Cernia, J. Organometal. Chem., 78 (1974) 203.
5 G. Perego, M. Cesari, G. Del Piero, A. Balducci and E. Cernia, J. Organometal. Chem., 87 (1975) 33.
6 M. Cesari, G. Perego, G. Del Piero, M. Corbellini and A. Immirzi, J. Organometal. Chem., 87 (1975) 43.
7 G. Perego, G. Del Piero, M. Cesari, A. Zazzetta and G. Dozzi, J. Organometal. Chem., 87 (1975) 53.

8 P. Main, H.H. Woolfson and G. Germain, Computer Program MULTAN, 1971; G. Germain, P. Main and H.H. Woolfson, Acta Crystallogr., 16 (1963) 1169.
9 D.W.J. Cruickshank, in J.S. Rollet (ed.), Computing Methods in Crystallography, Pergamon, London, 1965, p. 114.
10 D.T. Cromer and B. Man, Acta Crystallogr. Sect. A, 24 (1968) 321.
11 R.F. Stewart, E.R. Davidson and W.R. Simpson, J. Chem. Phys., 42 (1965) 3175.
12 C.K. Johnson (1965), ORTEP, Oak Ridge National Laboratory report ORNL-3794, Oak Ridge, Tennessee.
13 A. Immirzi, Ric. Sci., 37 (1967) 847; ibid., 850; J. Appl. Crystallogr., 6 (1973) 246.
14 T.R.R. McDonald and W.S. McDonald, Acta Crystallogr. Sect. B, 28 (1972) 1619.
15 G. Del Piero, G. Perego, S. Cucinella and A. Mazzei, to be published.
16 S. Cucineila, T. Salvatori, C. Bursetto and M. Cesari, J. Organometal. Chem., 121 (1976) 137.