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

XI *. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE HEXAMER $(HAlN\text{-}n\text{-}Pr)_6$ AND THE OCTAMER $(HAlN\text{-}n\text{-}Pr)_8$

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Summary

The crystal and molecular structures of the hexamer, $(HAlN\text{-}n\text{-}Pr)_6$ (I) and octamer $(HAlN\text{-}n\text{-}Pr)_8$ (II) have been determined by the Patterson procedure and by direct methods, respectively, using tridimensional X-ray diffraction data collected by counter methods. The block-matrix least-squares refinement led to a final R value of 5.7% for I and 5.8% for II. The molecular framework of I, $(AlN)_6$, is shaped as a hexagonal prism, while that of II, $(AlN)_8$, may be derived from a combination of such a hexameric cage with a square ring of a dimer. The main average bond lengths (Å) are: Al—N, 1.913(11) for I and 1.916(2) for II; N—C, 1.508(5) and 1.516(4); Al—H, 1.53(2) and 1.50(2), respectively. Crystal data: I, trigonal space group $P\bar{3}$; a 16.801(2), c 9.647(2) Å; $Z = 3$; II, triclinic space group $P\bar{1}$, a 21.99(1), b 10.58(1), c 9.75(1) Å, α 97.7(5), β 91.9(5), γ 100.3(5)°; $Z = 2$.

Introduction

Structural investigations on poly(*N*-alkyliminoalanes), (PIA), have previously centered on *N*-isopropylimino derivatives [1—4]. In this paper, we report the crystal structure of two *N*-n-propyliminoalanes, i.e. the hexamer $(HAlN\text{-}n\text{-}Pr)_6$, referred to as Hex-ANP and the octamer $(HAlN\text{-}n\text{-}Pr)_8$ (Oct-ANP).

The principal interest in the former compound stems from the possible differences in the cage structure due to the different alkyl substituent at nitrogen; the major importance of the second compound resides in the possiblity of

* For Part X see ref. 11.

elucidating a novel octameric cage structure of the $(AlN)_8$ type.

Single crystals of Hex-ANP were obtained from a fraction of a mixture of oligomers as described in a previous paper [9] of this series. Single crystals of the Oct-ANP were obtained by a direct synthesis of poly(*N*-alkyliminoalanes) recently reported by Cucinella et al. [10].

Experimental

Crystals of both compounds, colourless and fairly sensitive to moisture, were sealed in thin-walled capillaries under dry nitrogen. Preliminary crystal data were obtained from rotation and Weissenberg photographs. Cell dimensions were subsequently refined by application of the least-squares method to the setting angles measured for 20 reflections on the diffractometer. The successful structure refinements confirmed the choice of the space groups. Intensity data were collected on a Siemens single crystal diffractometer, using Zr-filtered Mo-K_α radiation; other experimental conditions were identical to those described in previous papers of this series [1,4].

A crystal of Hex-ANP, with approximate dimensions 0.39 × 0.45 × 0.72 mm was chosen and a total of 5041 reflections were collected within a quadrant up to θ 26°; the intensities of 3017 independent reflections were averaged with their equivalent reflections; 1593 of these, having $I > 2.5\sigma(I)$, were used for the structure determination.

For Oct-ANP a total of 8576 reflections were collected within a hemisphere up to θ 26°, from a crystal of dimensions 0.52 × 0.60 × 0.82 mm; 5765 reflections, with $I > 3.0\sigma(I)$ were used. Correction was applied for intensity decay, which at the end of the run was of 7% for Hex-ANP and 9% for Oct-ANP. No correction for absorption was applied in view of the low transmission factor ($\mu R < 0.2$ for both crystals).

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

Structure determination and refinement

The structure of Hex-ANP has been solved by standard Patterson methods which allowed the location of the aluminum and the nitrogen atoms. From a Fourier map, phased with these atoms, the position of the carbon atoms was

(continued on p. 296)

TABLE 1

CRYSTAL DATA FOR $(HAlN\text{-}n\text{-}Pr)_6$ AND $(HAlN\text{-}n\text{-}Pr)_8$

Molecular formula	$(HAlN\text{-}n\text{-}C_3H_7)_6$	$(HAlN\text{-}n\text{-}C_3H_7)_8$
Molecular weight	510.6	680.7
Space group	$P\bar{3}$ (No. 147)	$P\bar{1}$ (No. 2)
Molecules/unit cell	3	2
Cell constants (Mo-K_α radiation, λ 0.71069)	a 16.801(2), c 9.647(2) Å	a 21.99(1), b 10.58(1), c 9.75(1) Å α 97.7(1), β 91.9(1), γ 100.3(1)°
Cell volume	2358.3 Å^3	2207.6 Å^3
Calculated density	1.078 g cm^{-3}	1.024 g cm^{-3}
Linear absorption coefficient μ	2.33 cm^{-1}	2.21 cm^{-1}

TABLE 2. ATOMIC FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^2$ Å^2) FOR $(HAlN\text{-}\underline{n}\text{-}Pr)_6$ (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)	1219(1)	1066(1)	972(1)	263(4)	273(5)	243(4)	125(4)	-21(4)	-7(4)
N(1)	1019(2)	-146(2)	1070(3)	286(13)	346(14)	200(12)	160(12)	5(10)	47(10)
C(1)	1697(3)	-245(3)	1950(4)	296(16)	418(18)	305(18)	204(15)	-24(13)	67(14)
C(2)	1533(3)	-227(3)	3472(4)	497(23)	464(22)	336(21)	245(19)	-28(17)	26(16)
C(3)	2205(4)	-350(4)	4373(6)	640(30)	702(30)	432(25)	392(26)	-135(22)	-7(22)

Molecule 2

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al(1)	7949(1)	4269(1)	6776(1)	285(5)	301(5)	234(5)	138(4)	-20(4)	-11(4)
Al(2)	7602(1)	2988(1)	4837(1)	280(5)	297(5)	250(5)	157(4)	28(4)	2(4)
N(1)	7556(2)	3000(2)	6859(3)	317(14)	313(14)	226(13)	172(11)	-63(10)	-47(10)
N(2)	7892(2)	4226(2)	4753(3)	276(13)	288(13)	231(13)	102(11)	12(10)	-6(10)
C(1)	8145(3)	2760(3)	7768(4)	376(18)	381(18)	323(18)	238(16)	-58(14)	0(14)
C(2)	8043(3)	2892(3)	9293(5)	463(21)	553(24)	310(20)	311(20)	10(16)	54(16)
C(3)	8578(3)	2602(4)	10204(5)	558(25)	693(29)	350(22)	383(24)	-38(19)	68(20)
C(4)	8699(2)	4827(3)	3832(4)	202(14)	380(18)	279(17)	99(13)	39(12)	31(13)
C(5)	8454(3)	4679(3)	2333(4)	300(17)	441(20)	305(19)	150(15)	89(14)	81(15)
C(6)	9252(3)	5319(4)	1411(5)	465(24)	660(28)	364(22)	217(21)	99(17)	103(19)

Molecule 1

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
H(Al1)	2052(24)	1814(25)	1674(38)	372(85)	H''(C1)	7880(26)	2122(26)	7548(41)	440(88)
H'(C1)	2268(25)	267(25)	1770(37)	318(79)	H'(C2)	7431(29)	2493(29)	9479(43)	633(99)
H''(C1)	1573(29)	-883(30)	1814(46)	680(103)	H''(C2)	8219(25)	3517(25)	9352(39)	412(85)
H'(C2)	1036(27)	-750(28)	3618(41)	498(92)	H'(C3)	8342(26)	1974(26)	10127(40)	423(86)
H''(C2)	1636(27)	327(27)	3665(42)	546(95)	H''(C3)	9079(29)	2778(29)	9986(42)	581(97)
H'(C3)	2042(27)	-956(29)	4238(43)	647(98)	H'''(C3)	8513(27)	2758(27)	10989(43)	456(93)
H''(C3)	2654(28)	-124(27)	4050(41)	548(93)	H'(C4)	8882(26)	5411(26)	3939(39)	356(85)
H'''(C3)	2291(28)	-13(28)	4999(43)	562(95)	H''(C4)	9193(23)	4703(24)	3985(35)	255(76)
Molecule 2					H'(C5)	8287(25)	4076(25)	2121(37)	311(81)
					H''(C5)	7995(27)	4816(27)	2161(41)	485(93)
H(Al1)	8890(24)	4960(23)	7357(37)	249(77)	H'(C6)	9753(27)	5168(26)	1568(42)	476(91)
H(Al2)	8249(26)	2722(27)	4046(42)	474(92)	H''(C6)	9400(26)	5927(27)	1562(42)	475(91)
H'(C1)	8769(27)	3188(26)	7516(38)	402(86)	H'''(C6)	9051(28)	5188(29)	489(45)	662(100)

TABLE 3. ATOMIC FRACTIONAL COORDINATES (X 10^4) AND THERMAL PARAMETERS (X 10^2 $Å^2$) FOR $(HAlN\text{-}\underline{n}\text{-}Pr)_8$

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al(1)	1411(1)	2856(1)	8691(1)	285(5)	411(5)	404(5)	133(4)	20(4)	98(4)
Al(2)	1997(1)	3568(1)	11196(1)	332(5)	426(5)	346(5)	140(4)	63(4)	93(4)
Al(3)	2728(1)	4896(1)	9490(1)	347(5)	316(5)	350(5)	119(4)	48(4)	62(4)
Al(4)	2002(1)	883(1)	9021(1)	286(4)	337(5)	388(5)	73(4)	-4(4)	98(4)
Al(5)	3756(1)	3534(1)	7749(1)	290(4)	352(5)	356(5)	89(4)	30(4)	63(4)
Al(6)	3466(1)	1082(1)	8252(1)	312(5)	332(5)	334(5)	124(4)	-1(4)	40(4)
Al(7)	3313(1)	2534(1)	10686(1)	312(5)	334(5)	318(5)	110(4)	-15(4)	55(4)
Al(8)	2584(1)	2690(1)	6641(1)	303(5)	366(5)	314(5)	99(4)	5(4)	82(4)
N(1)	1855(1)	4457(3)	9634(3)	353(14)	381(14)	413(15)	181(12)	54(11)	101(12)
N(2)	1578(1)	1951(3)	10225(3)	318(14)	424(15)	406(15)	107(12)	60(11)	123(12)
N(3)	2873(1)	3904(3)	10968(3)	353(14)	320(13)	307(13)	98(11)	14(10)	42(10)
N(4)	1898(1)	1869(3)	7509(3)	296(13)	366(14)	355(14)	95(11)	-14(10)	75(11)
N(5)	3908(1)	2697(3)	9296(3)	270(13)	363(14)	374(14)	95(10)	-19(10)	41(11)
N(6)	3303(1)	1923(3)	6722(3)	330(13)	369(14)	293(13)	123(11)	26(10)	32(10)
N(7)	2838(1)	985(3)	9585(3)	324(13)	317(13)	330(13)	122(10)	14(10)	77(10)
N(8)	3014(1)	4261(3)	7780(3)	318(13)	335(13)	341(13)	101(10)	44(10)	87(11)
C(1)	1524(2)	5587(4)	9608(4)	493(17)	472(16)	510(17)	277(14)	60(14)	92(13)
C(2)	1068(2)	5701(5)	10684(5)	614(23)	672(23)	798(27)	377(19)	241(20)	157(20)
C(3)	744(2)	6847(5)	10616(6)	648(25)	706(26)	948(32)	407(22)	224(23)	141(23)
C(4)	1123(2)	1222(4)	11099(4)	407(16)	513(17)	539(18)	116(13)	134(13)	190(14)
C(5)	517(2)	1721(5)	11204(5)	427(18)	717(24)	742(25)	163(17)	185(17)	231(20)
C(6)	84(2)	971(6)	12125(6)	522(22)	970(32)	928(33)	182(22)	303(22)	344(27)
C(7)	3168(2)	4828(3)	12254(3)	423(15)	411(14)	357(14)	107(12)	15(11)	-19(11)
C(8)	3849(2)	5399(4)	12150(4)	430(17)	554(19)	475(17)	37(14)	-3(13)	-11(14)
C(9)	4116(2)	6371(6)	13405(6)	603(25)	872(32)	807(30)	-53(22)	-48(22)	-272(25)
C(10)	1450(1)	1030(3)	6388(4)	353(14)	465(16)	428(15)	65(12)	-47(11)	84(12)
C(11)	1713(2)	-41(4)	5541(4)	529(19)	503(18)	497(18)	101(15)	-50(15)	-44(14)
C(12)	1223(2)	-898(5)	4514(5)	702(26)	667(25)	618(24)	-14(20)	-42(20)	-77(19)
C(13)	4577(1)	2957(4)	9803(4)	287(13)	515(17)	566(18)	102(12)	-76(12)	61(14)
C(14)	4825(2)	1839(4)	10084(7)	426(20)	548(22)	1517(47)	110(16)	-303(24)	228(26)
C(15)	5492(2)	2157(6)	10670(7)	481(22)	827(30)	1402(45)	198(21)	-295(25)	304(30)
C(16)	3482(2)	1236(3)	5381(3)	409(15)	522(17)	330(14)	154(13)	26(11)	0(12)
C(17)	4178(2)	1447(4)	5242(4)	469(18)	751(24)	464(18)	210(17)	98(14)	8(16)
C(18)	4363(2)	640(5)	3984(5)	672(24)	995(32)	504(20)	457(24)	127(18)	73(21)
C(19)	2892(2)	-176(3)	10332(3)	437(15)	340(13)	395(14)	137(11)	-1(11)	83(11)
C(20)	2524(2)	-255(3)	11612(4)	511(17)	407(15)	405(15)	121(13)	43(13)	143(12)
C(21)	2650(2)	-1365(4)	12366(4)	731(23)	448(17)	448(17)	177(16)	51(16)	159(13)
C(22)	3095(2)	5355(3)	6892(3)	426(15)	367(13)	403(14)	96(11)	56(12)	128(11)
C(23)	2502(2)	5850(4)	6614(4)	551(20)	505(18)	573(19)	217(16)	54(15)	217(15)
C(24)	2597(3)	6926(5)	5720(5)	955(32)	662(24)	681(25)	407(23)	147(23)	322(21)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
H(Al1)	745(16)	2843(32)	8089(35)	447(75)	H''(C11)	1886(16)	-603(31)	6193(36)	442(79)
H(Al2)	1799(15)	3876(32)	12615(34)	396(74)	H'(C12)	1141(27)	-567(54)	4025(59)	1038(157)
H(Al3)	2970(18)	6323(36)	9863(38)	531(86)	H''(C12)	881(25)	-1238(51)	5057(55)	988(144)
H(Al4)	1689(19)	-384(40)	8860(43)	673(102)	H'''(C12)	1352(20)	-1778(42)	3972(46)	772(113)
H(Al5)	4336(19)	4457(38)	7274(42)	589(94)	H'(C13)	4579(27)	3503(55)	10513(59)	1129(159)
H(Al6)	3752(16)	-100(33)	7961(35)	450(77)	H''(C13)	4838(24)	3449(49)	9111(52)	896(133)
H(Al7)	3535(18)	2215(36)	12044(40)	575(89)	H'(C14)	4534(26)	1270(55)	10596(59)	1067(159)
H(Al8)	2350(19)	2876(39)	5165(42)	633(100)	H''(C14)	4831(27)	1280(56)	8989(61)	1060(157)
H'(C1)	1843(18)	6560(36)	9681(39)	575(90)	H'(C15)	5625(23)	1853(48)	9845(52)	975(135)
H''(C1)	1320(18)	5515(37)	8864(40)	612(92)	H''(C15)	5454(18)	2463(37)	11426(39)	588(91)
H'(C2)	1285(25)	5786(49)	11431(54)	1039(142)	H'''(C15)	5562(29)	1350(59)	10844(63)	1218(173)
H''(C2)	755(23)	4887(47)	10285(51)	994(131)	H'(C16)	3286(19)	1509(39)	4546(42)	617(100)
H'(C3)	532(23)	6748(47)	9711(50)	944(130)	H''(C16)	3351(18)	276(36)	5381(40)	525(89)
H''(C3)	484(20)	6840(41)	11339(44)	734(109)	H'(C17)	4340(19)	2386(40)	5097(43)	661(101)
H'''(C3)	1018(22)	7475(45)	10531(49)	845(122)	H''(C17)	4369(18)	1254(38)	6039(41)	609(94)
H'(C4)	951(19)	269(38)	10657(42)	699(98)	H'(C18)	4790(25)	904(50)	3772(56)	980(139)
H''(C4)	1336(18)	1427(37)	12122(40)	658(93)	H''(C18)	4218(24)	854(49)	3158(53)	963(138)
H'(C5)	618(21)	2713(43)	11593(46)	796(116)	H'''(C18)	4290(28)	-136(57)	4019(62)	1239(169)
H''(C5)	300(25)	1363(53)	10131(57)	1214(158)	H'(C19)	2759(17)	-922(34)	9708(37)	463(81)
H'(C6)	223(18)	1065(36)	12997(38)	568(88)	H''(C19)	3305(17)	-192(35)	10608(38)	490(84)
H''(C6)	71(23)	41(47)	11883(50)	900(127)	H'(C20)	2590(21)	639(43)	12410(46)	643(113)
H'''(C6)	-216(22)	1231(45)	12007(50)	844(121)	H''(C20)	2058(17)	-425(35)	11290(38)	492(83)
H'(C7)	3076(13)	4370(27)	13122(30)	314(61)	H'(C21)	3058(22)	-1402(44)	12470(47)	777(117)
H''(C7)	2959(16)	5563(33)	12398(35)	449(76)	H''(C21)	2491(19)	-2248(39)	11850(41)	634(97)
H'(C8)	4075(19)	4713(39)	12100(42)	630(97)	H'''(C21)	2359(23)	-1501(46)	13212(51)	870(129)
H''(C8)	3919(16)	5772(33)	11278(36)	478(79)	H'(C22)	3218(17)	5016(35)	5974(38)	496(86)
H'(C9)	4204(26)	5776(53)	14032(58)	1110(152)	H''(C22)	3358(17)	5992(34)	7332(36)	513(80)
H''(C9)	3854(26)	7013(51)	13562(57)	1077(152)	H'(C23)	2356(19)	6219(39)	7426(43)	683(98)
H'''(C9)	4576(26)	6880(53)	13366(58)	1104(155)	H''(C23)	2253(17)	5204(35)	6246(38)	530(84)
H'(C10)	1364(17)	1576(36)	5698(39)	546(86)	H'(C24)	2828(21)	7558(43)	6187(47)	778(111)
H''(C10)	1052(18)	669(37)	6870(41)	597(93)	H''(C24)	2832(25)	6690(51)	4822(54)	1104(149)
H'(C11)	2037(19)	432(39)	4987(43)	709(102)	H'''(C24)	2212(21)	7229(41)	5564(45)	698(109)

TABLE 4

SELECTED GEOMETRICAL PARAMETERS FOR $(HAlN\text{-}\underline{n}\text{-}Pr)_6$ AND $(HAlN\text{-}\underline{n}\text{-}Pr)_8$

$(H\ Al\ N\text{-}n\text{-}Pr)_6$		$(H\ Al\ N\text{-}n\text{-}Pr)_8$			
Al(1)-N(1)[a]	1.893(4)	Al(1)-N(1)	1.897(4)	Al(5)-N(5)	1.898(3)
Al(1)-N(1)'[a]	1.894(4)	Al(1)-N(2)	1.940(4)	Al(5)-N(6)	1.942(3)
Al(1)-N(1)''[a]	1.972(3)	Al(1)-N(4)	1.930(3)	Al(5)-N(8)	1.924(3)
Al(1)-N(1)	1.892(4)	Al(2)-N(1)	1.939(3)	Al(6)-N(5)	1.943(4)
Al(1)-N(1)'	1.884(4)	Al(2)-N(2)	1.902(4)	Al(6)-N(6)	1.892(3)
Al(1)-N(2)	1.953(3)	Al(2)-N(3)	1.921(3)	Al(6)-N(7)	1.926(3)
Al(2)-N(2)	1.886(4)	Al(3)-N(1)	1.907(4)	Al(7)-N(3)	1.878(3)
Al(2)-N(2)'	1.892(4)	Al(3)-N(3)	1.943(3)	Al(7)-N(5)	1.917(3)
Al(2)-N(1)	1.953(3)	Al(3)-N(8)	1.883(3)	Al(7)-N(7)	1.942(3)
Mean Al-N[b]	1.913(11)	Al(4)-N(4)	1.947(3)	Al(8)-N(4)	1.886(3)
(in six-memb. rings)	1.890(4)	Al(4)-N(2)	1.902(4)	Al(8)-N(6)	1.906(3)
(in transverse bonds)	1.959(8)	Al(4)-N(7)	1.882(3)	Al(8)-N(8)	1.940(3)
		Mean Al-N	1.916(5)		
N(1)-C(1)[a]	1.495(5)	N(1)-C(1)	1.510(6)	N(5)-C(13)	1.502(5)
N(1)-C(1)	1.520(6)	N(2)-C(4)	1.509(6)	N(6)-C(16)	1.508(5)
N(2)-C(4)	1.509(6)	N(3)-C(7)	1.530(5)	N(7)-C(19)	1.530(5)
		N(4)-C(10)	1.520(5)	N(8)-C(22)	1.525(5)
Mean N-C	1.508(5)	Mean N-C	1.516(4)		
Mean C-C	1.506(5)	Mean C-C	1.512(5)		
Mean Al-H	1.53(3)	Mean Al-H	1.50(2)		

Mean N-Al-N		Mean N-Al-N	
(in six-memb. rings)	115.2(2)		114.1(3)
(in four memb. rings)	91.2(2)		91.1(2)
Mean Al-N-Al		Mean Al-N-Al	
(in six-memb. rings)	124.3(2)		120.8(3)
(in four memb. rings)	88.6(2)		88.8(2)
Mean Al-N-C		Mean Al-N-C	
(type Al(1)-N(1)-C(1))	113.4(7)	(involving N(1),N(2),N(5),N(6))	118.45(7)
(type Al(2)-N(1)-C(1))	122.7(7)	(involving N(3),N(4),N(7),N(8))	107.97(5)

Deviation of the atoms from the least-squares planes ($\mathring{A}$) for six-membered rings in $(H\ Al\ N\text{-}n\text{-}Pr)_8$

Al(1)	N(1)	Al(3)	N(4)	Al(8)	N(8)	Al(3)	N(3)	Al(7)	N(8)	Al(5)	N(5)
0.11	0.18	-0.29	-0.30	0.18	0.12	0.19	0.12	-0.29	-0.32	0.12	0.18
Al(2)	N(2)	Al(4)	N(3)	Al(7)	N(7)	Al(4)	N(4)	Al(8)	N(7)	Al(6)	N(6)
0.11	0.19	-0.29	-0.31	0.19	0.11	0.19	0.11	-0.28	-0.31	0.12	0.17

[a] Bond belonging to molecule 1. [b] In this and in all papers of this series the standard deviation of the means s has been calculated as $s^2 = \Sigma_i^n (x_i - \bar{x})^2/(n-1)n$, where $\bar{x}$ is the mean of the x_i values, n their number.

determined. Hydrogen atoms were all located in a difference map and refined with isotropic parameters. For all the other atoms the refinement was performed by block-matrix least-squares with anisotropic thermal parameters. The R factor converged to the final value of 0.057.

The structure of Oct-ANP was solved by direct methods by means of the computer program MULTAN written by Main et al. [5]. From the intensities put in approximate absolute scale by Wilson's method, the $|E|$ values were computed; 300 reflections with $|E| > 2.08$ and 50 with $|E| < 0.5$ were used as input data. Of 64 phase sets of $|E|$, that corresponding to the "figures of merit" (ABSFOM = 1.06, PSIZERO = 3344 and RESID = 17.2) allowed the solution of the structure. From the corresponding E-map all the aluminum and nitrogen atoms were located, and from the next Fourier map the position of all the 36 carbon atoms was deduced (R = 0.20). The refinement and the locations of the hydrogen atoms progressed in a way similar to that described above for Hex-ANP, and the final R value of 0.058 was calculated. Atomic structure factors for the neutral atom were those of Cromer and Man [6] for Al, N and C, and of Stewart et al. [7] for H. Computer programs written by Immirzi [8] were used throughout.

The final values of positional and thermal parameters are reported in Tab. 2 for Hex-ANP and in Tab. 3 for Oct-ANP. The lists of structure factors are obtainable from the authors on request.

Results and discussion

The molecular structure of Hex-ANP contains a cage framework, $(AlN)_6$, quite similar to that of its iso-propyl analogue, (PIA-Hex): i.e. a hexagonal prism formed by two flat six-membered rings, $(AlN)_3$, linked together by six transverse Al—N bonds. A view of the molecule, with a labelling scheme, is given in Fig. 1. The unit cell contains three molecules but the number of independent atomic

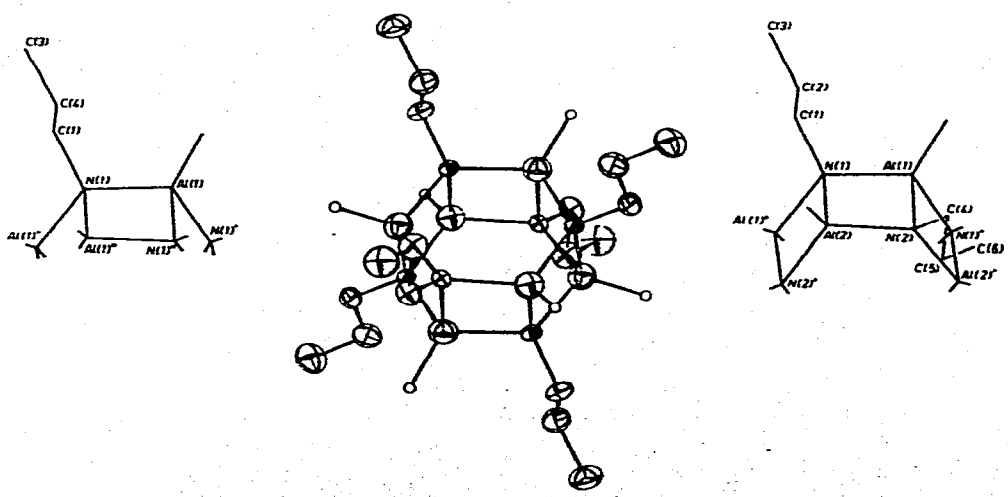

Fig. 1. A perspective view and labelling scheme for the molecule of (HAlN-n-Pr)$_6$.

parameters is correspondingly highly reduced. A molecule, indicated "1", lies on $\bar{3}$ axis, hence 1/6 of it is independent. The other two molecules are located on ternary axes and related by a symmetry centre: of these molecules a part corresponding to 1/3 of a molecule (and indicated as molecule "2") is independent. It should be noticed that even these last molecules preserve a symmetry very close to that required in the molecule "1" by a $\bar{3}$ axis.

The main geometrical parameters of the molecules of Hex-ANP are reported in Tab. 4. There are no significant differences between the mean bond lengths and angles of this compound and the corresponding values for PIA-Hex [1]. The spatial arrangement of the n-propyl groups is quite similar in the three independent cases according to the molecular symmetry mentioned above. The Al—N—C—C rotation angles, where Al—N is a transverse bond, are close to 180°, indicating a *trans* conformation: as a consequence, the two α-hydrogen atoms point toward the centres of two contiguous square rings $(AlN)_2$. More complex is the cage structure of Oct-ANP, whose perspective view is shown in Fig. 2. The cage may be formally derived by addition of two cubic-shaped tetrameric cages, each one with two open bonds on a face, or conversely by combining a hexameric cage with the square ring of a dimer, $(AlN)_2$. The octameric cage is thus composed of four six-membered rings, $(AlN)_3$, and of six four-membered rings, $(AlN)_2$. This configuration constrains the hexagonal rings to assume a "boat" conformation, as may be noted from the deviation of the atoms from their least-squares planes (see Tab. 4, the minus sign indicates a displacement toward the centre of the cage). The mean values of the torsion angles are ±4.6(3)° and ±31.2(7)°, indicating that the rings are flatter than a "boat" form of the cyclohexane molecule (where the corresponding angles are 0° and 60°): this is mainly due to the large values (considerably greater than 110°) of the bond angles on Al

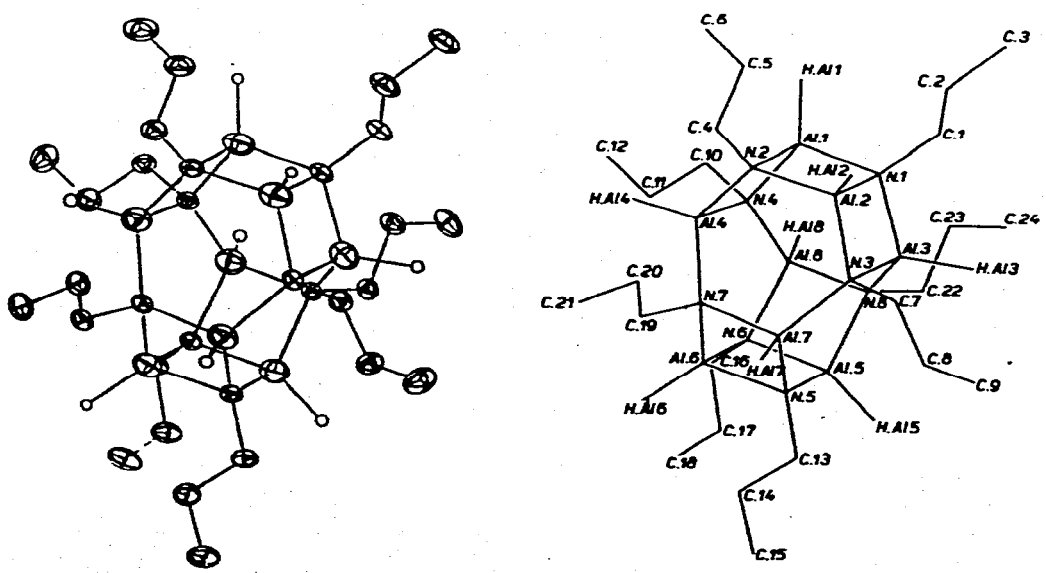

Fig. 2. A perspective view and labelling scheme for the molecule of (HAlN-n-Pr)$_8$.

and N atoms. Considerable flatness is shown by the four-membered rings, $(AlN)_2$.

While in both cited hexamers the Al—N bonds are shorter in hexagonal rings and longer in transverse bonds, this clearly is not the case for Oct-ANP, where more complex configurations arise from the arrangement of six- and four-membered rings. Thus, if the longest Al—N bonds are those common to the two square rings, an alternation of shorter and longer bonds is observed along the hexagonal rings, depending on whether the bond is shared by two hexagonal or by one hexagonal and one square ring. It may also be noted that the nitrogen (or aluminum) atoms do not display an equivalent geometry with respect to bond angles: this is because half of the atoms (i.e. N(1), N(2), N(5) and N(6)) are common to one hexagonal and two square rings, while the other half to one square and two hexagonal rings. In spite of the scattering of Al—N bond lengths (Tab. 4), it must be pointed out that the overall mean of this bond, 1.916(2) Å, does not differ significantly from the corresponding distance in the aforementioned hexamers. Moreover, in all these molecules the overall mean is exactly equal to every average of three bonds converging to the same nitrogen (or aluminum): this fact is particularly remarkable for the octamer because of the previously discussed non equivalence of the nitrogen atoms. However, this mean does not represent the true value of a specific Al—N bond; it indicates that in equivalent coordinative configurations, as in these cage molecules, there is a sort of electronic compensative effect on the three bonds to each N or Al atom. The Al—H and C—C mean bond distances are also consistent with those observed in the other structures of the series. The alkyl substituents are arranged apart from some differences in Al—N—C bond angles, in such a way that one α-hydrogen points toward the centre of a hexagonal ring, $(AlN)_3$, and the other one toward the centre of a square ring, $(AlN)_2$. In both compounds the packing is consistent with Van der Waals interactions.

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