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

XVI *. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE COMPOUND $[HAlNCH(CH_3)C_6H_5]_6 \cdot \frac{1}{3} C_6H_{14}$

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Summary

The crystal structure of $[HAlNCH(CH_3)C_6H_5]_6 \cdot \frac{1}{3} C_6H_{14}$ has been determined by single crystal three-dimensional X-ray analysis. Block-matrix least-squares refinement led to conventional *R* factor of 0.08. The molecule is built up of a prismatic hexagonal framework, $(AlN)_6$. Average Al—N distances are 1.893(6) and 1.981(7) Å in the six-membered rings and in transverse bonds, respectively. Crystal data: hexagonal, space group $P6_3$, *a* 22.296(5), *c* 18.144(4) Å, *V* 7811.2 Å^3, $Z = 6$, D_c 1.16 g cm^{-3}.

Introduction

In a previous paper [4] we reported the characterization by ^{1}H NMR spectrometry of poly(*N*-alkyliminoalanes) (PIA) from 1-phenylethylamine. The reaction of $AlH_3 \cdot N(CH_3)_3$ with (+)- or (—)-1-phenylethylamine was found to give mixtures of PIA having closed hexameric (I), closed (II) and open (III) tetrameric cage structures. The analogies with PIA from various amines [5] allowed the assignment of the several NMR signals to the hydrocarbon radicals bonded to the nitrogen atoms of the different structures, and these assignments are substantially supported by the full characterization of the crystalline hexakis-(*N*-phenethyliminoalane), hereafter denoted by PIA—PH. This paper concerns the X-ray molecular structural determination with a single crystal of this compound crystallized from n-hexane solution. It is noteworthy that only the hexamer is crystalline independent of the solvent (diethyl ether, toluene or n-hexane) from which it separates, and the X-ray powder patterns of the com-

* For parts I—XV see refs. 1, 2 and 3.

TABLE 1

CRYSTALLOGRAPHIC DATA OF $[HAlNCH(CH_3)C_6H_5]_6 \cdot \frac{1}{3}C_6H_{14}$

Molecular formula	$(HAlNCH(CH_3)C_6H_5)_6 \cdot \frac{1}{3}C_6H_{14}$
Molecular weight	911.7
Space group	$P6_3$ (No. 173)
Molecules/unit cell	6
Cell constants	a 22.296(5), c 18.154(4) Å
Cell volume	7811.2 Å^3
Calculated density	1.162 g cm^{-3}
Linear absorption coefficient (Mo-K_α radiation, λ 0.71069 Å)	1.75 cm^{-1}

pletely solvent-free products are the same and very similar to that of the powder obtained from the crystal herein described. In contrast both the closed and the open tetrameric compounds are amorphous, and attempts to crystallize them have been unsuccessful.

Experimental

A crystal 0.5 × 0.5 × 0.25 mm was used. Unit cell calibration was carried out by a least-squares fit of the angular parameters of 20 reflections. A unique data set in the range $2\vartheta < 40°$ was gathered, following $\vartheta - 2\vartheta$ scan, using a Siemens AED diffractometer with Zr-filtered Mo—$K_{\bar{\alpha}}$ radiation. Of the yielded 5082 independent reflections, 1595 with $I > \sigma(I)$ were used in the structure solution and refinement. A summary of the crystal data is given in Tab. 1. No correction for absorption was found necessary. The structure was solved by direct methods and refined by block-matrix least-squares with anisotropic thermal parameters. Hydrogen atoms, including the hydridic ones, and the carbon atoms of n-hexane molecules, which were poorly resolved in a difference Fourier map, were included as invariants (B = 9.0 Å^{-2}). Refinement converged to R = 0.08. Lists of structure amplitudes and of hydrogen parameters are obtainable from the authors on request.

Scattering factors used for neutral atoms are those of Stewart et al. [9] for the hydrogen atoms and those of Cromer and Man [8] for the other atoms.

Computation was carried out using the MULTAN program [7], and the crystallographic computer system of Immirzi [10].

Results and discussion

The molecular structure of PIA—PH is similar to those observed for other hexameric poly(*N*-alkyliminoalanes), for example $(HAlN\text{-}i\text{-}Pr)_6$ (I) [1], $(HAlN\text{-}n\text{-}Pr)_6$ (II) [2] and $(ClAlN\text{-}i\text{-}Pr)_6$ (III) [3]. The structure of all these compounds consists essentially of a prismatic hexagonal skeleton $(AlN)_6$, which is built up from two six-membered $(AlN)_3$ rings joined together by six transverse Al—N bonds, giving rise to six four-membered rings, $(AlN)_2$. The six-membered rings are a little puckered and show a distorted chair shape; the deviations of Al and N atoms from their mean-planes are shown in Table 3.

The phenyl groups of the N-bonded $CH(CH_3)C_6H_5$ substituents point in the

TABLE 2

FINAL ATOMIC FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^2$ Å^2) FOR NON-HYDROGEN ATOMS OF [HAIN-CH(CH_3)C_6H_5]$_6 \cdot \frac{1}{3}C_6H_{14}$

Standard deviations in parentheses, in this and in the following tables, refer to last digit.

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al(1)	6943(3)	6643(3)	5282(4)	227(23)	282(25)	242(26)	185(41)	-53(48)	21(49)
Al(2)	7260(3)	7546(3)	3724(4)	219(22)	210(22)	293(28)	224(41)	36(48)	47(50)
Al(3)	7256(3)	6049(3)	3737(4)	244(23)	316(24)	252(27)	389(43)	35(48)	16(47)
Al(4)	6396(3)	6365(3)	2982(3)	239(23)	303(25)	179(24)	313(45)	-133(46)	-103(49)
Al(5)	6082(3)	5470(3)	4555(4)	215(23)	242(22)	244(26)	222(38)	-5(48)	79(48)
Al(6)	6092(3)	6971(3)	4541(4)	227(23)	272(24)	239(28)	277(40)	-37(49)	19(47)
N(1)	7098(6)	7444(7)	4752(8)	92(58)	246(63)	160(80)	39(100)	-90(107)	-164(114)
N(2)	7382(6)	6859(7)	3253(8)	109(56)	288(68)	119(70)	45(104)	1(98)	18(89)
N(3)	7095(7)	5996(7)	4780(9)	189(64)	310(71)	307(92)	298(113)	-6(123)	137(131)
N(4)	6255(6)	5579(7)	3508(8)	142(59)	220(62)	314(92)	130(100)	-336(118)	-284(117)
N(5)	5966(6)	6173(7)	4995(8)	101(60)	398(71)	203(76)	224(109)	-111(107)	-186(126)
N(6)	6244(6)	7014(7)	3509(8)	160(61)	359(70)	99(82)	328(113)	-69(108)	-109(120)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
C(1)	7426(9)	8073(9)	5242(12)	327(39)	C(25)	5920(11)	4868(11)	3172(13)	419(47)
C(2)	7296(10)	8636(10)	4993(13)	381(45)	C(26)	6220(12)	4920(11)	2403(14)	476(54)
C(3)	8174(9)	8327(9)	5418(11)	301(39)	C(27)	5135(9)	4520(9)	3096(11)	267(36)
C(4)	8396(12)	8301(12)	6126(15)	531(55)	C(28)	4782(11)	3810(11)	3020(14)	511(51)
C(5)	9083(13)	8548(13)	6309(16)	610(60)	C(29)	4078(13)	3466(13)	2921(17)	647(61)
C(6)	9548(12)	8820(12)	5735(15)	552(57)	C(30)	3720(12)	3818(11)	2969(15)	532(50)
C(7)	9385(13)	8846(13)	5026(17)	674(66)	C(31)	4051(11)	4500(11)	3080(14)	474(51)
C(8)	8678(11)	8598(11)	4898(14)	462(50)	C(32)	4781(10)	4840(11)	3141(13)	438(48)
C(9)	7908(10)	7194(10)	2624(12)	329(41)	C(33)	5432(8)	5958(8)	5650(10)	200(33)
C(10)	7889(11)	6675(11)	2078(13)	443(49)	C(34)	5442(12)	5409(12)	6150(15)	526(56)
C(11)	8649(9)	7658(9)	2903(11)	262(37)	C(35)	4718(8)	5731(8)	5411(11)	225(34)
C(12)	8974(11)	7411(11)	3334(13)	392(46)	C(36)	4347(11)	5147(11)	5022(14)	437(49)
C(13)	9658(12)	7828(13)	3569(15)	555(57)	C(37)	3646(14)	4881(14)	4868(16)	623(65)
C(14)	10010(13)	8502(13)	3363(16)	623(61)	C(38)	3329(13)	5250(13)	5085(15)	591(59)
C(15)	9684(12)	8764(12)	2979(15)	587(55)	C(39)	3691(13)	5825(13)	5460(16)	624(63)
C(16)	8993(12)	8316(12)	2722(14)	522(55)	C(40)	4389(11)	6084(10)	5633(13)	417(46)
C(17)	7425(9)	5629(10)	5114(12)	327(41)	C(41)	5962(9)	7344(9)	2977(11)	236(35)
C(18)	7114(11)	5363(11)	5883(14)	461(51)	C(42)	6022(11)	8019(11)	3277(13)	436(48)
C(19)	8204(10)	6044(9)	5188(12)	340(41)	C(43)	5206(9)	6841(9)	2795(12)	299(40)
C(20)	8593(13)	5760(13)	4933(15)	602(58)	C(44)	4995(10)	6623(10)	2099(13)	378(45)
C(21)	9305(14)	6103(14)	5000(18)	726(68)	C(45)	4304(13)	6206(13)	1930(15)	583(59)
C(22)	9625(12)	6713(12)	5333(15)	588(54)	C(46)	3821(13)	5997(13)	2427(16)	632(63)
C(23)	9289(15)	7031(15)	5565(18)	823(75)	C(47)	3967(11)	6151(11)	3157(14)	448(51)
C(24)	8541(12)	6668(12)	5505(15)	570(58)	C(48)	4703(11)	6618(11)	3360(14)	405(47)
C(49)	6647	2960	2780	900	C(55)	6279	2960	2780	900
C(50)	7023	3713	3069	900	C(56)	7028	3341	3069	900
C(51)	7023	3713	3918	900	C(57)	7028	3341	3918	900
C(52)	6297	3341	4207	900	C(58)	6660	3713	4207	900
C(53)	6297	3341	5056	900	C(59)	6660	3713	5056	900
C(54)	6647	2960	5345	900	C(60)	6279	2960	5345	900

n-Hexane atoms C(49)···C(60) have a site occupation factor of 0.1666666.

TABLE 3

SELECTED GEOMETRICAL PARAMETERS FOR $[HAlN\text{-}CH(CH_3)C_6H_5]_6 \cdot \frac{1}{3}C_6H_{14}$

(six-membered rings)		(six-membered rings)		(transverse bonds)	
Al(1) - N(1)	1.90(2)	Al(1) - N(3)	1.87(2)	Al(1) - N(5)	1.96(2)
Al(2) - N(1)	1.89(2)	Al(2) - N(2)	1.89(2)	Al(2) - N(6)	2.00(2)
Al(3) - N(2)	1.90(2)	Al(3) - N(3)	1.92(2)	Al(3) - N(4)	1.98(2)
Al(4) - N(4)	1.88(2)	Al(4) - N(6)	1.90(2)	Al(4) - N(2)	1.97(2)
Al(5) - N(4)	1.93(2)	Al(5) - N(5)	1.89(2)	Al(5) - N(3)	2.00(2)
Al(6) - N(5)	1.85(2)	Al(6) - N(6)	1.90(2)	Al(6) - N(1)	1.98(2)
Mean Al-N (six-memb. rings)	1.893(6)			Mean Al-N	1.981(7)
N(1) - C(1)	1.51(3)	N(2) - C(9)	1.54(3)	N(3) - C(17)	1.48(3)
N(4) - C(25)	1.50(3)	N(5) - C(33)	1.58(2)	N(6) - C(41)	1.53(2)
Mean N-C	1.52(1)				
Mean C-C (non-phenyl)	1.516(6)				
Mean C-C (phenyl)	1.369(7)				
N(1)-Al(1)-N(3)	117.3(5)	N(1)-Al(2)-N(2)	116.4(4)	N(2)-Al(3)-N(3)	116.7(5)
N(4)-Al(4)-N(6)	116.4(5)	N(4)-Al(5)-N(5)	114.4(4)	N(5)-Al(6)-N(6)	115.2(4)
Mean N-Al-N (six-membered rings)	116.1(4)				
N(1)-Al(1)-N(5)	90.0(4)	N(1)-Al(2)-N(6)	91.7(3)	N(1)-Al(6)-N(5)	90.7(4)
N(1)-Al(6)-N(6)	92.2(4)	N(2)-Al(2)-N(6)	90.6(3)	N(2)-Al(3)-N(4)	89.9(3)
N(2)-Al(4)-N(4)	90.8(4)	N(2)-Al(4)-N(6)	91.3(4)	N(3)-Al(1)-N(5)	92.3(4)
N(3)-Al(3)-N(4)	92.7(3)	N(3)-Al(5)-N(4)	91.8(4)	N(3)-Al(5)-N(5)	90.6(4)
Mean N-Al-N (four-membered rings)	91.2(3)				
Al(1)-N(1)-Al(2)	123.1(4)	Al(1)-N(3)-Al(3)	122.1(4)	Al(2)-N(2)-Al(3)	123.3(3)
Al(4)-N(4)-Al(5)	123.2(3)	Al(4)-N(6)-Al(6)	123.6(4)	Al(5)-N(5)-Al(6)	126.3(4)
Mean Al-N-Al (six-membered rings)	123.6(6)				
Al(1)-N(1)-Al(6)	88.4(4)	Al(1)-N(3)-Al(5)	88.0(4)	Al(1)-N(5)-Al(5)	88.8(4)
Al(1)-N(5)-Al(6)	90.6(4)	Al(2)-N(2)-Al(4)	89.6(4)	Al(2)-N(1)-Al(6)	88.3(3)
Al(2)-N(6)-Al(4)	88.2(4)	Al(2)-N(6)-Al(6)	87.6(4)	Al(3)-N(2)-Al(4)	89.5(4)
Al(3)-N(3)-Al(5)	87.5(4)	Al(3)-N(4)-Al(4)	89.7(4)	Al(3)-N(4)-Al(5)	87.8(4)
Mean Al-N-Al (four-membered rings)	88.7(3)				
Mean Al-N-C (type Al(1)-N(1)-C(1))	109.2(5)				
Mean Al-N-C (type Al(2)-N(1)-C(1))	121.3(9)				
Mean Al-N-C (type Al(6)-N(1)-C(1))	117.9(7)				

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

18.8991 x + 0.0224 y + 3.6676 z -13.152 = 0	18.8995 x + 0.0056 y + 3.7038 z - 15.135 = 0
Al(4) 0.044 ; Al(5) 0.025 ; Al(6) 0.042 Å	Al(1) -0.053 ; Al(2) -0.030 ; Al(3) -0.034 Å
N(4) -0.032 ; N(5) -0.031 ; N(6) -0.049 Å	N(1) 0.044 ; N(2) 0.025 ; N(3) 0.048 Å

same direction, giving the molecule a somewhat elongated shape, as shown in Fig. 1. The whole molecule possesses a very rough D_3 point symmetry, the larger deviations from the ideal symmetry being those of the C(27) · · · C(32) phenyl group.

The main geometrical parameters of PIA—PH are reported in Table 3. Mean bond lengths and angles in six-membered rings are quite similar to those found

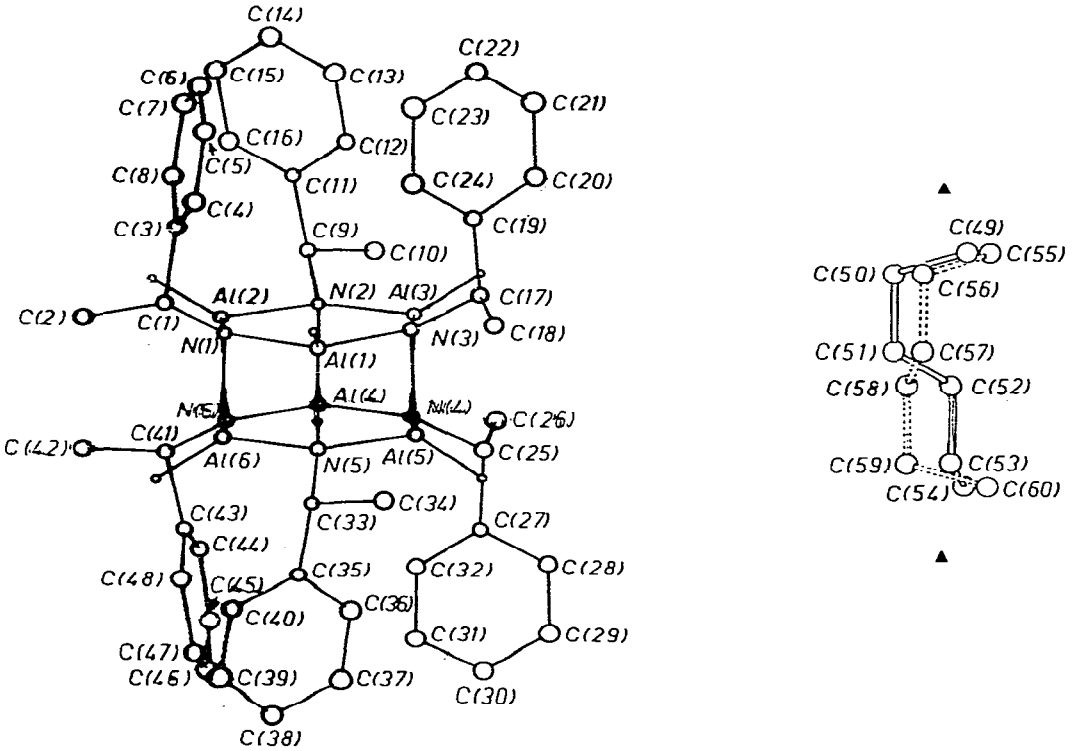

Fig. 1. Perspective view and labelling of the molecule of $[HAlNCH(CH_3)C_6H_5]_6 \cdot \frac{1}{3} C_6H_{14}$.

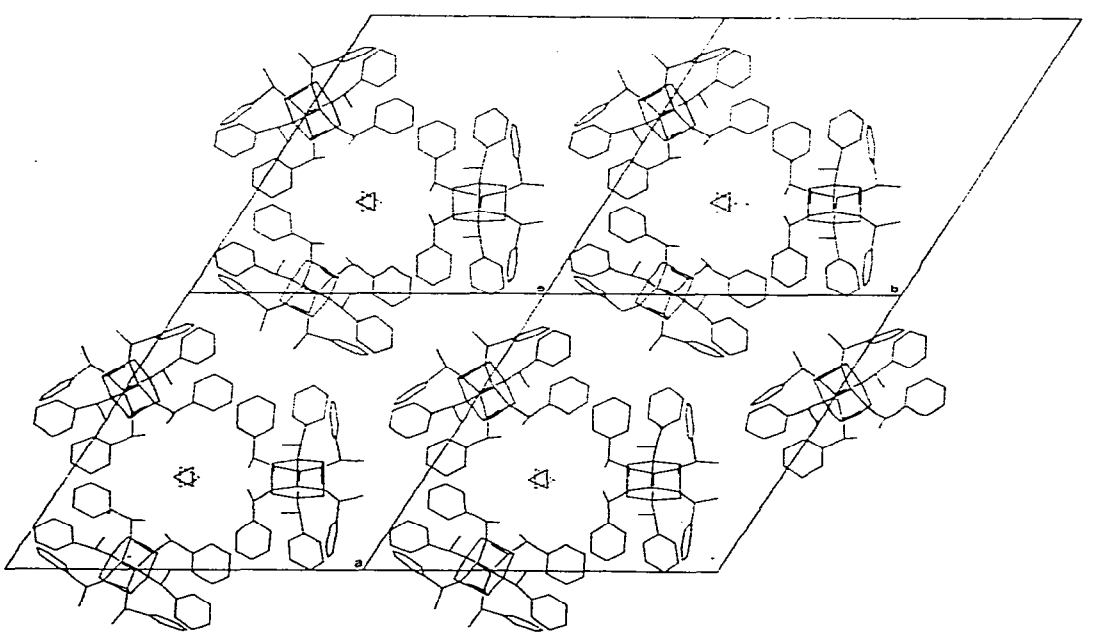

Fig. 2. A representation of the packing of $[HAlNCH(CH_3)C_6H_5]_6 \cdot \frac{1}{3} C_6H_{14}$. Projection along the c axis.

for the parent compounds I, II and III. In contrast, the mean Al—N transverse bond length (1.981(7) Å) is significantly longer than the corresponding values 1.956(2), 1.959(8) and 1.955(3) Å, found in I, II and III, respectively. Moreover in PIA—PH the transverse Al—N bond lengths show a regular alternation of shorter (1.96 Å), middle (1.98 Å) and longer (2.00 Å) values. This accounts for some distortions in the prismatic hexagonal skeleton $(AlN)_6$, which is rather regular in the other poly(*N*-alkyliminoalanes) hexamers I, II and III.

From one point of view the packing may be regarded as consisting essentially of layers of PIA—PH molecules, disposed perpendicularly to the direction of the *c* axis. One of these layers is shown in Fig. 2. The molecules are arranged in the layer in such a way as to give rise to holes around the crystallographic threefold axis; in these holes the clathrate molecules of n-hexane are located, one per hole, in statistically disordered positions.

Intermolecular distances show no critically short values. It is noteworthy that the completely solvent-free parent compound is presumably isostructural with PIA—PH, as is indicated by the close similarity of the corresponding X-ray powder patterns.

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