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The Crystal Structure of $Al_4N_4(C_6H_5)_8$

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The compound $Al_4N_4(C_6H_5)_8$ is shown to have a cubical Al_4N_4 skeleton with Al and N atoms at alternate vertices of a cube of edge 1·91 Å, and one phenyl group attached to each atom of the cube. There is some disorder in the crystal, and 15 % of the molecules are in an orientation which interchanges Al and N positions. The structural relationship to the apparently isomorphous octaphenylcyclooctatetraene is discussed.

Introduction

A series of compounds of general formula $[C_6H_5AlNAr]_4$, obtained by reaction of triphenylaluminum and a primary aromatic amine, were reported by Jones & McDonald (1962). To establish the molecular structures of these compounds we have carried out a crystal structure determination of the compound $[C_6H_5AlNC_6H_5]_4$. Our preliminary work on this compound has already been reported (McDonald & McDonald, 1963).

Crystal data

$Al_4N_4C_{48}H_{40}$, $M=780·8$. Tetragonal, $a=19·93 \pm 0·05$, $c=10·82 \pm 0·03$ Å, $U=4298$ Å^3, $D_m=1·20$, $Z=4$, $D_c=1·206$. Space group $I4_1/a$, Molecular symmetry $\bar{4}$.

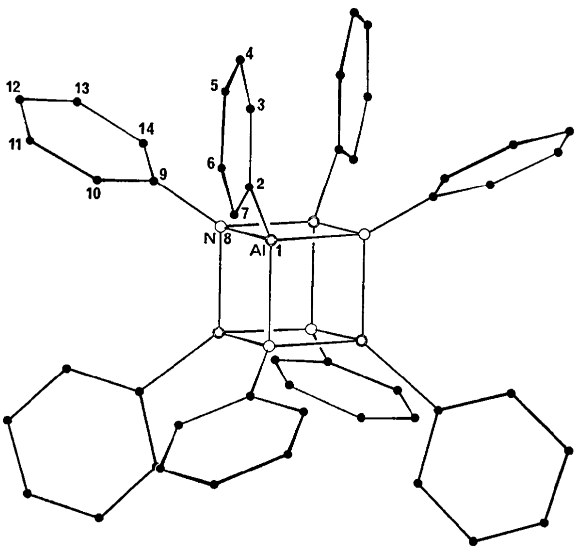

Fig. 1. The molecular structure of $Al_4N_4(C_6H_5)_8$.

Structure determination

The compound was prepared by addition of the stoichiometric amount of aniline to a refluxing solution of triphenylaluminum in dry benzene. After concentration and slow cooling of the solution crystals of $Al_4N_4(C_6H_5)_8$ were obtained as colourless tetragonal bipyramids. The compound reacts rapidly with oxygen or water, and the preparation and subsequent manipulation were carried out in an atmosphere of dry nitrogen. Crystals for X-ray work were sealed in soft glass capillaries.

The space group was uniquely determined from systematic absences and cell dimensions were measured from an *h*0*l* Weissenberg photograph. Intensities were measured visually from equi-inclination Weissenberg photographs of reciprocal lattice layers *h*0*l* to *h*13*l*, taken with Cu *Kα* radiation. After application of Lorentz and polarization factors the data were placed on a single scale by means of the symmetry-equivalent reflexions in different layers, to give 732 independent structure amplitudes. No absorption corrections were applied.

On examination of the three-dimensional Patterson synthesis it was evident that the four aluminum and four nitrogen atoms of each molecule were at the vertices of a cube of edge about 1·9 Å, the expected Al–N bonded distance. The space group requires that the molecule has $\bar{4}$ symmetry and the cube shape means that the Al and N atoms are related by a non-crystallographic fourfold axis. As a result each Al–Al vector coincides with an N–N vector, except for the single-weight intermolecular vectors produced by the centre of symmetry. These vectors were so poorly resolved that their peak heights did not permit a determination of which position was Al and which was N. The Al–N vectors provide no information on this since they would obviously be unaffected by interchange of Al

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and N. Trial coordinates for the carbon atoms C(2), C(5), (C9) and C(12) were obtained by assuming that the Al–C and N–C bonds were collinear with the body-diagonals of the cube and that they were equal in length to their expected mean. Structure factor calculations using both possible assignments of Al and N sites gave R values of 49·2 and 50·2%. The phases from the set of the lower R value were used to compute an electron density synthesis, from which the remaining eight carbon atoms were located, reducing the R value to 28·7%. Positions from a further Fourier synthesis reduced R to 24·5%.

Block-diagonal least-squares refinement was then carried out using the *DEUCE* program of J.S. Rollett. $\sum w||F_o|-|F_c||^2$ was minimized, with $w^{1/2}=1$ for $F_o \leq 80$, $w^{1/2}=80/F_o$ for $F_o>80$. The R value was reduced to 12·0% at convergence.

This refinement produced temperature factors for the nitrogen atom much lower than those for the aluminum. The nitrogen had $U_{11}=0{\cdot}025$, $U_{22}=0{\cdot}026$, $U_{33}=0{\cdot}025$ and for aluminum they were $U_{11}=0{\cdot}058$, $U_{22}=0{\cdot}053$, $U_{33}=0{\cdot}053$, both with relatively small off-diagonal components. These values are physically unreasonable, since Al and N occupy geometrically equivalent positions in a rather rigid molecular skeleton, and should therefore have very similar temperature factors. We consider the above U_{ii} values to arise from partial disorder in the orientation of the molecules so that the aluminum site is partially occupied by nitrogen and *vice versa*. The nitrogen atom would then acquire lower temperature factors in order to simulate the greater scattering power due to partial occupancy by aluminum; conversely the aluminum would acquire a higher temperature factor. The expected equality of temperature factors for Al and N was made the basis for estimation of the amount of disorder. For an initial calculation the scattering factors for Al and N (*International Tables for X-ray Crystallography*, 1962) were replaced by 0·9 Al + 0·1 N and 0·9 N + 0·1 Al respectively, and isotropic temperature factors of $U=0{\cdot}046$ were used for both atoms. Two cycles of least squares produced shifts in the direction of the original U_{ij} values, and suggested that 15% interchange was more appropriate. Similar refinement with 0·85 + 0·15 scattering factors produced only very small shifts of the temperature factors, in the opposite direction to those obtained previously. We conclude, therefore, that a 15% interchange of Al and N (*i.e.* 30% disorder) is close to the actual value in our crystal. The substantial difference between the Al–C and N–C distances (see Discussion) is not consistent with greater disorder. The final R value was 11·3%.

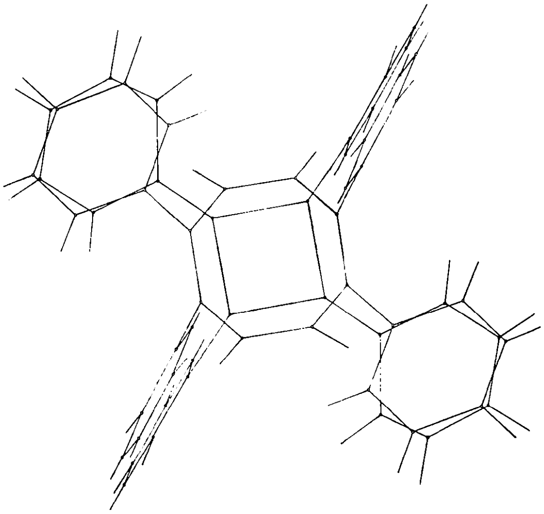


Fig. 2. The structures of $Al_4N_4(C_6H_5)_8$ (solid circles) and $C_8(C_6H_5)_8$ (open circles) superimposed.

The final coordinates, vibration tensor components, and their e.s.d.'s are given in Table 1, and the observed and calculated structure factors are listed in Table 2.

Discussion

The bond lengths and angles with their e.s.d.'s are given in Table 3. Fig. 1 shows the molecular structure, with the atom numbering indicated.

Table 1. *Final fractional coordinates* (× 10^4), *vibration tensor components* (Å^2) (× 10^3) *and their e.s.d.'s.*

The temperature factor expression is $\exp [-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Al(1)	583 (2)	2158 (3)	2137 (4)	45 (2)	50 (2)	45 (2)	2 (3)	−8 (3)	2 (3)
C(2)	1211 (7)	1787 (7)	3208 (13)	74 (6)	65 (6)	68 (6)	8 (11)	−19 (11)	−19 (11)
C(3)	1053 (9)	1825 (9)	4465 (15)	110 (8)	99 (8)	86 (8)	33 (14)	2 (15)	−23 (14)
C(4)	1510 (10)	1601 (11)	5376 (18)	134 (11)	150 (11)	108 (9)	69 (18)	49 (18)	28 (18)
C(5)	2104 (9)	1323 (9)	5015 (16)	141 (9)	108 (8)	81 (8)	66 (14)	−30 (15)	−88 (15)
C(6)	2296 (9)	1257 (10)	3794 (18)	91 (8)	137 (10)	126 (10)	75 (19)	−12 (17)	−12 (16)
C(7)	1822 (8)	1505 (9)	2873 (16)	62 (7)	119 (9)	102 (8)	13 (16)	−17 (14)	19 (13)
N(8)	−341 (4)	1917 (4)	2148 (8)	48 (3)	49 (3)	45 (3)	−2 (6)	9 (6)	−17 (6)
C(9)	−648 (6)	1362 (6)	2841 (12)	58 (5)	62 (6)	53 (5)	−60 (9)	−17 (10)	−19 (9)
C(10)	−297 (8)	752 (7)	2949 (15)	103 (8)	42 (6)	107 (8)	−10 (12)	−9 (15)	−16 (11)
C(11)	−574 (9)	199 (9)	3543 (16)	110 (9)	97 (8)	105 (9)	8 (16)	−52 (15)	−23 (14)
C(12)	−1238 (9)	262 (8)	4062 (13)	153 (10)	85 (7)	57 (7)	−34 (12)	−19 (14)	−50 (14)
C(13)	−1591 (9)	873 (8)	3932 (15)	124 (9)	81 (7)	88 (8)	−59 (13)	14 (15)	−50 (13)
C(14)	−1287 (7)	1421 (8)	3318 (12)	67 (6)	97 (7)	57 (6)	−18 (11)	−5 (10)	−64 (11)

The Al_4N_4 cube shows no significant departures from regularity, and the Al–N bond lengths are probably not affected by the disorder since the regular cube shape of the molecule permits interchange of the Al and N atoms without change in their coordinates. The mean Al–N distance is 1·914 (5) Å. In aluminum nitride (Jeffrey, Parry & Mozzi, 1956) the mean Al–N distance is 1·893 Å. In $(Me_2AlNHMe)_3$ (Gosling, McLaughlin, Sim & Smith, 1970) the mean Al–N distance is 1·953 (5), and in Me_3AlNMe_3 (Anderson, Forgaard & Haaland, 1971) Al–N is 2·10 (1) Å. These lengths suggest a progressive increase in the series: AlN, RAlNR, R_2AlNR_2, R_3AlNR_3, in all of which both Al and N are 4-coordinate.

All other bond lengths involve the coordinates of carbon atoms, which are affected by positional disorder because of the difference in Al–C and N–C bond lengths. The Al–C and N–C distances of 1·86 (2) and 1·47 (2) Å should be shorter and longer respectively than their true values because of the disorder.

The dimensions of the phenyl groups are normal. The equations of their mean planes, referred to unit (Å) axes are:

$$\text{C(2) to C(7)} \quad 0{\cdot}426X+0{\cdot}904Y+0{\cdot}037Z=4{\cdot}370$$
$$\text{C(9) to C(14)} \quad 0{\cdot}388X+0{\cdot}313Y+0{\cdot}867Z=3{\cdot}009$$

Table 2. *Observed and calculated structure factors*

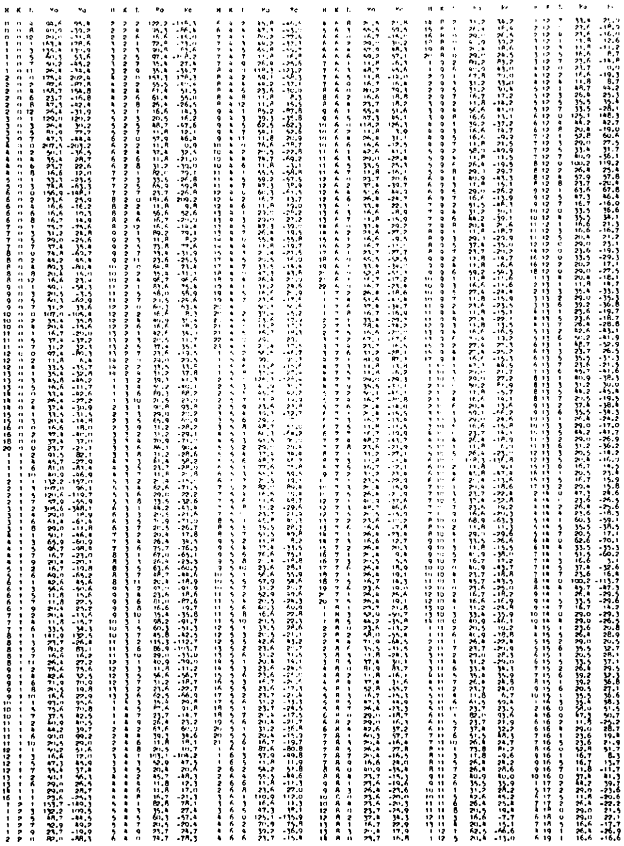


Table 3. *Bond lengths and bond angles with their e.s.d.'s*

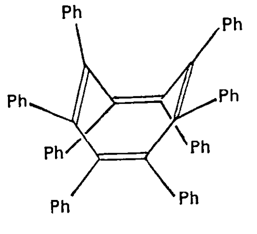
Bond	Length
Al(1)–N(8)	1·90 (1) Å
Al(1)–N(8′)	1·91 (1)
Al(1)–N(8″)	1·93 (1)
Al(1)–C(2)	1·86 (2)
N(8)—C(9)	1·47 (2)
C(2)—C(3)	1·40 (2)
C(3)—C(4)	1·42 (3)
C(4)—C(5)	1·36 (3)
C(5)—C(6)	1·38 (3)
C(6)—C(7)	1·46 (3)
C(7)—C(2)	1·39 (2)
C(9)—C(10)	1·41 (2)
C(10)-C(11)	1·39 (2)
C(11)-C(12)	1·44 (3)
C(12)-C(13)	1·41 (2)
C(13)-C(14)	1·42 (2)
C(14)—C(9)	1·38 (2)

Angle	Value
Al(1)—N(8)—Al(1′)	90·0 (0·4)°
Al(1)—N(8)—Al(1″)	89·7 (0·4)
Al(1′)–N(8)—Al(1″)	89·6 (0·4)
N(8)—Al(1)–N(8′)	90·0 (0·4)
N(8)—Al(1)–N(8″)	90·3 (0·4)
N(8′)—Al(1)–N(8″)	90·4 (0·4)
N(8)—Al(1)–C(2)	123·4 (0·5)
N(8′)—Al(1)–C(2)	123·2 (0·5)
N(8″)–Al(1)–C(2)	128·6 (0·5)
Al(1)—N(8)—C(9)	127 (1)
Al(1′)–N(8)—C(9)	129 (1)
Al(1″)-N(8)—C(9)	121 (1)
Al(1)—C(2)—C(3)	116 (1)
Al(1)—C(2)—C(7)	126 (1)
N(8)—C(9)—C(10)	119 (1)
N(8)—C(9)—C(14)	121 (1)
C(2)—C(3)—C(4)	121 (2)
C(3)—C(4)—C(5)	119 (2)
C(4)—C(5)—C(6)	124 (2)
C(5)—C(6)—C(7)	116 (2)
C(6)—C(7)—C(2)	122 (2)
C(7)—C(2)—C(3)	118 (2)
C(9)—C(10)-C(11)	122 (2)
C(10)—C(11)-C(12)	118 (2)
C(11)—C(12)-C(13)	120 (2)
C(12)—C(13)-C(14)	120 (2)
C(13)—C(14)-C(9)	120 (2)
C(14)--C(9)—C(10)	120 (1)

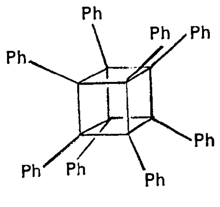
The plane C(2) to C(7) makes an angle of 2° ($\sin^{-1}$ 0·037) with a plane containing the $\bar{4}$ axis of the molecule.

Relationship to octaphenylcyclooctatetraene

Freedman & Petersen (1962) gave the unit cell and space group of a compound which they believed to be octaphenylcubane, $C_8(C_6H_5)_8$. The space group is $I4_1/a$, as in the present compound, and their cell dimensions ($a=19{\cdot}49$, $c=10{\cdot}65$ Å) are similar to ours. Our preliminary results demonstrating that $Al_4N_4(C_6H_5)_8$ contains an Al_4N_4 'cubane' skeleton provided a strong indication that $C_8(C_6H_5)_8$ also has the cubane structure, since the two compounds seem to be isomorphous. However, Wheatley (1965) carried out a crystal structure determination on $C_8(C_6H_5)_8$ and showed that it is actually octaphenylcyclooctatetraene (I) rather than the cubane (II).



(I)



(II)

Table 4. *Comparison of atomic coordinates* (Å) *of* $C_8(C_6H_5)_8$ (*Wheatley*, 1965) *and of* $Al_4N_4(C_6H_5)_8$

	$C_8(C_6H_5)_8$				$Al_4N_4(C_6H_5)_8$		
	X	*Y*	*Z*		*X*	*Y*	*Z*
C(1)	0·92	−1·23	0·56	Al(1)	1·16	−0·68	0·96
C(2)	1·84	−1·63	1·69	C(2)	2·41	−1·42	2·12
C(3)	1·42	−1·36	3·01	C(3)	2·10	−1·35	3·48
C(4)	2·32	−1·65	4·04	C(4)	3·01	−1·79	4·46
C(5)	3·57	−2·20	3·83	C(5)	4·19	−2·35	4·07
C(6)	3·97	−2·48	2·52	C(6)	4·58	−2·48	2·75
C(7)	3·11	−2·19	1·43	C(7)	3·63	−1·98	1·76
C(8)	−0·39	−1·53	0·51	N(8)	−0·68	−1·16	0·97
C(9)	−1·07	−2·45	1·45	C(9)	−1·29	−2·27	1·72
C(10)	−0·50	−3·72	1·73	C(10)	−0·59	−3·48	1·84
C(11)	−1·18	−4·59	2·60	C(11)	−1·14	−4·59	2·48
C(12)	−2·43	−4·23	3·14	C(12)	−2·47	−4·46	3·04
C(13)	−3·00	−2·99	2·86	C(13)	−3·17	−3·24	2·90
C(14)	−2·30	−2·09	1·99	C(14)	−2·57	−2·15	2·24

Another analysis of $C_8(C_6H_5)_8$ by Pawley & Lipscomb (1964) used our coordinates for $Al_4N_4(C_6H_5)_8$ as starting point for a least-squares refinement which led to a final structure essentially identical with that of Wheatley (1965). Thus although $Al_4N_4(C_6H_5)_8$ and $C_8(C_6H_5)_8$ have different molecular skeletons, corresponding atoms in the two structures have similar coordinates. The two sets of coordinates, expressed in Å relative to the molecular centre at $\bar{4}$, are compared in Table 4. The distances between corresponding atoms vary from 0·1 to 0·8 Å. The close correspondence, particularly in the outer parts of the molecule can be seen in Fig. 2, which shows the two structures superimposed. The apparent isomorphism clearly arises from a similarity in the outer parts of the two molecules giving very similar molecular packing for the two crystals.

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