Crystal Structure and Molecular Geometry of 7,8-μ-Dimethylalumina-1,2-dicarba-*nido*-undecaborane(13), $B_9C_2H_{12}AlMe_2$, at −100 °C

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The title compound, has been subjected to a low-temperature (−100 °C) *X*-ray diffraction study. The compound crystallizes in the non-centrosymmetric triclinic space group *P*1 (C_1^1, No. 1) with *a* = 7·460(6), *b* = 6·462(7), *c* = 6·985(4) Å, α = 115·37(5), β = 97·02(11), γ = 87·61(10)°, *Z* = 1. The structure was solved from photographic data by Fourier methods and refined by least-squares techniques to *R* 13·5% for 875 non-zero reflections. All non-hydrogen atoms were located. The $B_9C_2H_{12}$ moiety is present as an icosahedral fragment with the $AlMe_2$ group lying outside the cage and interacting with only two boron atoms.

SEVERAL alumina-carborane species have been reported, including $B_9C_2H_{11}AlEt,2thf$ (ref. 1) (thf = tetrahydrofuran), $B_9C_2H_{11}AlR$ (ref. 2), and $B_9C_2H_{12}AlR_2$ (ref. 2) (R = Me or Et). We have shown [2,3] that in $B_9C_2H_{11}$-AlEt the aluminium atom is bonded symmetrically to the open pentagonal B_3C_2 face of a 1,2-dicarbollyl ligand. We now report details of a low-temperature (−100 °C) *X*-ray diffraction study of the compound $B_9C_2H_{12}AlMe_2$; a preliminary account of this structure has appeared previously.[4]

EXPERIMENTAL

Crystal Data.—$C_4H_{18}AlB_9$, *M* = 190·54, Triclinic, *a* = 7·460(6), *b* = 6·462(7), *c* = 6·985(4) Å, α = 115·37(5), β = 97·02(11), γ = 87·61(10)°, *U* = 301·9 Å^3, D_c = 1·05, *Z* = 1, *F*(000) = 100. [D_m not measured, owing to the great air- and moisture-sensitivity.] Space group *P*1 (C_1^1, No. 1). Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 10·1 cm^{-1}.

Data Collection and Reduction.—Single crystals of the compound were sealed into Lindemann glass capillary tubes. Since preliminary studies had showed that the crystals decomposed in an *X*-ray beam in <1 h at room temperature, it was decided that data should be collected at −100 °C at which temperature the crystals had a longer lifetime. However, the quality of diffraction data was so poor (diffuse spots having a large mosaicity, with reflections being at least 4° across) that data were collected photographically [5] rather than with our diffractometer; equi-inclination Weissenberg geometry was used. Two crystals were used for data collection: crystal (A) for the levels 0—6*kl* was mounted about *a*, and crystal (B) for *h*0—2*l* mounted about *b*. Intensities were measured visually by use of a calibrated strip.

All data were corrected for Lorentz, polarization, and absorption effects.[6] Transmission factors ranged from 0·53 to 0·69 for data from crystal (A) and 0·55—0·69 for crystal (B). All 'Friedel pairs' were averaged and data were merged to a common scale using a least-squares method which minimizes a sum of residuals linear in the logarithms of the scale factors for the individual levels.[7] A Wilson plot [8] was then used to determine the approximate absolute scale-factor and the overall isotropic thermal parameter $\bar{B}$ (0·26 Å^2).

Solution and Refinement of the Structure.—A Howells–Phillips–Rogers plot [9] of the distribution of *X*-ray intensities as a function of sin θ indicated that the crystals belonged to the non-centrosymmetric triclinic space group *P*1 (rather than to the more common centrosymmetric alternative, $P\bar{1}$). The aluminium atom position was defined as ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$). A Fourier synthesis, phased only by the aluminium contribution (*R* 48·0%) led to the location of the remaining thirteen non-hydrogen atoms. Full-matrix least-squares refinement of positional and thermal parameters for all non-hydrogen atoms (with Al restrained to its origin-defining value of $\frac{1}{2},\frac{1}{2},\frac{1}{2}$) along with an overall scale-factor, led to convergence at *R* 13·5% for the 875 independent non-zero reflections. A final difference–Fourier synthesis failed to indicate the positions of any hydrogen atoms and showed no other significant features, thus confirming the correctness of the refined structure.

While a final *R* of 13·5% is higher than normally expected for contemporary structural analyses, we emphasize the chemical significance of the results obtained. The high *R* results particularly from a combination of the following effects: (i) poor quality of diffraction data; (ii) significant decomposition of crystals, even at −100 °C; and (iii) insufficiently precise temperature control, from one Weissenberg layer to the next, using our home-built cooling system.

Anisotropic thermal parameter refinement was thought to be unwise and was not attempted.

During the least-squares refinement process, the function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized. The weighting scheme used was that of Hughes [10a] with $4F_{\text{min.}} = 4$ (*i.e.*, $F \geqslant 4$, $w = |F_o|^{-2}$; $F < 4$, $w = [4|F_o|^{\frac{1}{2}}]^{-2}$). Scattering factors for neutral aluminium, carbon, and boron were used throughout the analysis.[10b]

Unless otherwise stated, crystallographic calculations were performed on the Harvard University IBM 360/65 computer by use of the CRYM system (an integrated sequence of crystallographic routines written under the direction of Dr. R. E. Marsh at the California Institute of Technology).

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20294 (3 pp.,

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1 microfiche).* Atomic co-ordinates and isotropic thermal parameters are listed in Table 1.

TABLE 1

Atomic co-ordinates and isotropic thermal parameters for $B_9C_2H_{12}AlMe_2$ at −100 °C, with estimated standard deviations in parentheses

Atom	x	y	z	$B/Å^2$
Al	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0·103(65)
C(1)	0·0867(19)	0·2225(23)	−0·0494(20)	0·92(21)
C(2)	0·0676(17)	0·2935(20)	0·1859(19)	0·83(19)
B(4)	0·2621(21)	0·3633(25)	−0·0682(21)	0·79(23)
B(5)	0·0337(22)	0·4447(26)	−0·1211(23)	0·98(24)
B(6)	−0·0970(23)	0·3799(28)	0·0458(24)	1·18(26)
B(7)	0·1970(24)	0·4872(30)	0·3614(25)	1·52(27)
B(8)	0·3538(21)	0·5568(25)	0·2174(20)	0·93(23)
B(9)	0·1996(20)	0·6587(21)	0·0479(18)	0·65(20)
B(10)	−0·0286(20)	0·6800(31)	0·1141(21)	1·31(22)
B(11)	−0·0219(22)	0·5657(25)	0·3118(21)	0·77(24)
B(12)	0·1522(24)	0·7395(26)	0·3225(24)	1·11(24)
Me(1)	0·5976(20)	0·1910(25)	0·4061(22)	1·26(23)
Me(2)	0·5747(19)	0·7892(24)	0·7440(21)	1·30(23)

RESULTS AND DISCUSSION

Crystal Structure.—The crystal consists of discrete molecular units of $B_9C_2H_{12}AlMe_2$, which are mutually separated by normal van der Waals' distances. Figure 1 shows the packing of molecules within the crystal.

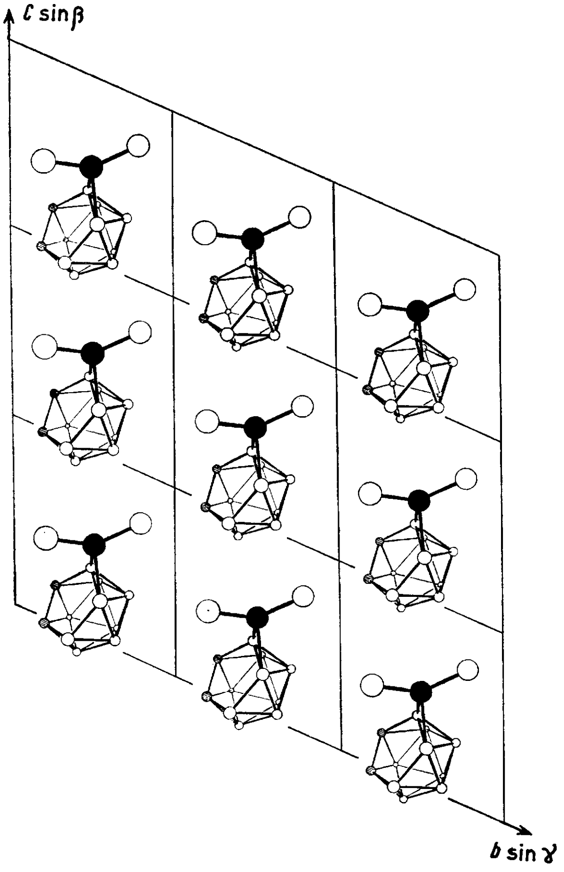

FIGURE 1 Packing of $B_9C_2H_{12}AlMe_2$ molecules in the unit cell, viewed down *a*

Molecular Structure.—Bond distances and important intramolecular contacts, with estimated standard deviations, are shown in Table 2 and bond angles in Table 3. The geometric arrangement of aluminium, carbon, and boron atoms is illustrated in Figure 2 which also shows the crystallographic numbering system used. [Hydrogen atoms were not located, *vide supra*. The two carbon atoms were differentiated from boron atoms by the following properties: (i) they appeared as the two strongest peaks among the cage atoms on all electron-density maps; (ii) when treated as boron atoms their isotropic

TABLE 2

Distances (Å) within the $B_9C_2H_{12}AlMe_2$ molecule

(*a*) Distances from aluminium atom

Al ··· B(7)	2·338(18)	Al–Me(1)	1·954(15)
Al ··· B(8)	2·298(15)	Al–Me(2)	1·958(14)
Al ··· B(4)	3·90(2)		
Al ··· C(1)	4·36(2)		
Al ··· C(2)	3·65(2)		

(*b*) Distances within carborane ligand

C(1)–C(2)	1·528(19)		
C(1)–B(4)	1·673(20)	C(2)–B(6)	1·701(21)
C(1)–B(5)	1·728(21)	C(2)–B(7)	1·581(22)
C(1)–B(6)	1·696(22)	C(2)–B(11)	1·742(20)
B(4)–B(5)	1·803(22)	B(7)–B(11)	1·728(24)
B(4)–B(8)	1·900(21)	B(7)–B(12)	1·776(24)
B(4)–B(9)	1·791(20)	B(8)–B(9)	1·852(20)
B(5)–B(6)	1·792(23)	B(8)–B(12)	1·889(22)
B(5)–B(9)	1·796(21)	B(9)–B(10)	1·802(21)
B(5)–B(10)	1·793(23)	B(9)–B(12)	1·835(21)
B(6)–B(10)	1·865(23)	B(10)–B(11)	1·818(22)
B(6)–B(11)	1·761(23)	B(10)–B(12)	1·780(23)
B(7)–B(8)	1·817(23)	B(11)–B(12)	1·726(23)

TABLE 3

Interatomic angles (°) for $B_9C_2H_{12}AlMe_2$

(*a*) Angles around aluminium atom *

Me(1)–Al–Me(2)	131·9(0·6)	Me(2)–Al ··· B(7)	114·1(0·6)
Me(1)–Al ··· B(7)	110·5(0·6)	Me(2)–Al ··· B(8)	112·1(0·6)
Me(1)–Al ··· B(8)	111·2(0·6)	B(7) ··· Al ··· B(8)	46·1(0·6)

(*b*) Angles around triangular faces

Atoms	No. of angles	Range *	Mean
C–B–C	1		53·4(0·8) *
C–C–B	2	63·1(0·9)—63·4(0·9)	63·3(0·2) †
B–C–B	4	61·5(0·9)—64·0(0·9)	62·8(1·0) †
C–B–B	8	56·5(0·8)—63·4(0·9)	58·6(2·8) †
B–B–B	30	57·0(0·8)—63·4(0·9)	60·0(1·8) †
	Total 45		

(*c*) Angles around pentagonal rings

C–C–B	4	109·3(0·8)—118·9(1·0)	113·3(4·1) †
B–C–B	2	116·4(1·0)—116·8(1·0)	116·6(0·3) †
C–B–B	12	100·8(0·8)—106·6(0·8)	104·1(1·8) †
B–B–B	27	101·9(0·8)—112·6(0·9)	107·3(3·1) †
	Total 45		

* Estimated standard deviations for individual angles are obtained *via* the least-squares calculation. † Estimated standard deviations for 'equivalent' bond angles are calculated from the equation:

$$\sigma = \left\{\left[\sum_{i=1}^{i=N}(\chi_i - \bar{\chi})^2\right]\Big/(N-1)\right\}^{\frac{1}{2}}$$

where χ_i is the *i*th bond angle and $\bar{\chi}$ is the mean of N equivalent bond angles.

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* See note concerning Supplementary Publications in Notice to Authors No. 7, *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

thermal parameters refined to negative values, whereas when refined as carbon atoms their final isotropic thermal parameters (0·92 and 0·83 Å^2) are comparable to those of the remaining nine boron atoms of the carborane ligand (B 0·65—1·52 Å^2); and (iii) in common with all previously reported carborane and metallo–carborane structures, the observed carbon–carbon bond distance of 1·528(19) Å is shorter than the mean carbon–boron distance (1·687 Å) which, in turn, is shorter than the mean boron–boron distance (1·897 Å).]

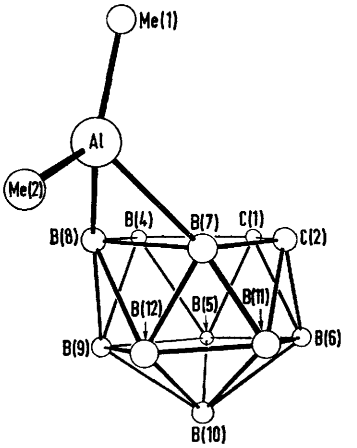

FIGURE 2 Molecular structure of the $B_9C_2H_{12}AlMe_2$ molecule, showing the numbering system used

The Aluminium Atom.—The values of the two aluminium–methyl bonds [Al–Me(1) 1·954(15) and Al–Me(2) 1·958(14) Å] are comparable to those found for the analogous terminal bonds in hexamethyldialuminium [1·956(2) and 1·949(2) Å] [11] and to the Al–Et bond of 1·930(6) Å in $B_9C_2H_{11}AlEt$.[2,3]

Distances of the aluminium atom from the five atoms in the open pentagonal face are (in order of increasing distance): Al · · · B(8) 2·298(15), Al · · · B(7) 2·338(18), Al · · · C(2) 3·65(2), Al · · · B(4) 3·90(2), and Al · · · C(1) 4·36(2) Å. Clearly the aluminium atom is involved in some form of bonding only to B(7) and B(8).

Angles around the aluminium atom are: Me(1)–Al–Me(2) 131·9(0·6), B(7) · · · Al · · · B(8) 46·1(0·6), Me(1)–Al · · · B(7) 110·5(0·6), Me(1)–Al · · · B(8) 111·2(0·6), Me(2)–Al · · · B(7) 114·1(0·6), and Me(2)–Al · · · B(8) 112·1(0·6)°. The immediate co-ordination environment of the aluminium thus has approximate C_s symmetry.

The aluminium atom clearly lies outside the rim of the $B_9C_2H_{12}$ ' nest ', as is evidenced by the dihedral angle of 130·3° between the planes defined by B(7), Al, B(8), and B(7), B(8), B(4), C(1), C(2) (see Table 4).

The $B_9C_2H_{12}$ *Ligand.*—The two carbon and nine boron atoms define eleven of the twelve apices of a (slightly irregular) icosahedron. Boron–boron distances range from 1·726(23) to 1·900(21) Å, mean 1·807(48) Å.‡

TABLE 4

Equations of least-squares planes * within the $B_9C_2H_{12}AlMe_2$ molecule and in (square brackets) deviations (Å) of atoms from the planes

Plane (A): Open face of carborane ligand	$-0{\cdot}5890X + 0{\cdot}7825Y - 0{\cdot}2921Z = 0{\cdot}825$	[C(1) 0·014, C(2) −0·041, B(4) 0·015, B(7) 0·046, B(8) −0·034]
Plane (B): Lower pentagonal belt of carborane ligand	$-0{\cdot}6204X + 0{\cdot}7566Y - 0{\cdot}2944Z = 2{\cdot}208$	[B(5) 0·006, B(6) 0·016, B(9) −0·026, B(11) −0·032, B(12) 0·036]
Plane (C): Pentagon attached to Al	$0{\cdot}1079X + 0{\cdot}6915Y + 0{\cdot}3399Z = 3{\cdot}239$	[B(7) −0·026, B(8) 0·029, B(9) −0·024, B(10) 0·010, B(11) 0·010, Al 0·584 †]
Plane (D): Al, B(7), B(8)	$-0{\cdot}1531X + 0{\cdot}7884Y + 0{\cdot}5957Z = 2{\cdot}843$	

* Cartesian co-ordinates (X, Y, Z) are related to triclinic fractional cell co-ordinates (x, y, z) by the transformations

$$X = xa\,.\,\sin\gamma + zc\,(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma,$$
$$Y = yb + xa\,.\,\cos\gamma + zc\,.\,\cos\alpha,$$
$$Z = zc\,[(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)/\sin^2\gamma]^{\frac{1}{2}}.$$

† This atom was given zero weight in calculating the least-squares plane. All other atoms were given a weight of unity.

While these boron–boron vectors are not all chemically equivalent, there seems to be no clear correlation between position (relative, for example, to the open pentagonal face) and bond distance. Thus, mean B–B distances are 1·859(59) in plane (A) (Table 4), 1·807(57) between planes (A) and (B), 1·782(41) within plane (B), and 1·812(33) Å between plane (B) and B(10). However the boron–carbon distances in the open face, *i.e.*, C(2)–B(7) 1·581(22) and C(1)–B(4) 1·673(20) Å, do appear to be shorter than those within the body of the icosahedron [*viz.*, 1·696(22)—1·742(20), mean 1·717(22) Å].

The carbon–carbon distance [C(1)–C(2) 1·528(19) Å] is significantly shorter than normally found in *pentahapto* [12]-1,2-dicarbollyl complexes {*e.g.*, 1·636(13) in (3,4′)-$(Me_2B_9C_2H_9)_2Ni^{IV}$,[13] 1·616(17) and 1·636(16) in $[(B_9C_2H_{10})_2S_2CH]Co^{III}$,[14,15] and 1·60 Å (mean) in $[(B_9C_2H_{11}{\cdot}Co{\cdot}B_8C_2H_{10})_2Co^{3-}]$ [16]} but is comparable to distances found between the non-co-ordinated carbon atoms in the ' slipped ' bis(*trihapto*-1,2-dicarbollyl)-metal species of d^8 and d^9 electronic configuration {[*cf.* 1·53(1) in $[(B_9C_2H_{11})_2Cu^{II\,2-}]$ [17] and 1·49(3) Å in $[(B_9C_2H_{11})_2Cu^{III-}]$ [18]}.

Hydrogen-atom Positions.—Thus far we have studiously avoided mention of the twelve hydrogen atoms associated with the $B_9C_2H_{12}$ moiety, since we have no direct crystallographic information concerning their location. We now make the following observations.

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‡ Estimated standard deviations on mean distances and angles are calculated as shown in the footnote to Table 3.

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(i) In keeping with other information on carborane systems we can immediately assign single terminal hydrogen atoms to B(10) and to the five boron atoms of plane (B) [*i.e.*, B(5), B(6), B(11), B(12), B(9); Table 4]. There are thus six hydrogen atoms associated, in some way, with the open pentagonal face C(1)–C(2)–B(7)–B(8)–B(4).

(ii) We can clearly assign terminal hydrogens to the atoms C(1), C(2), and B(4). We have now to consider the probable locations of the remaining three protons.

(iii) The long Al · · · B(7) and Al · · · B(8) vectors [2·338(18) and 2·298(15) Å], the unusually small B(7) · · · Al · · · B(8) angle of 46·1(0·6)°, and the fact that the aluminium atom lies outside the rim of the open face near the position normally occupied by terminal boron protons, leads us to conclude that, in the solid state at least, the aluminium atom is most probably linked to the cage by two hydride bridges, B(7)–H–Al and B(8)–H–Al.

(iv) Finally we postulate that the remaining hydrogen atom occupies a bridging position between B(4) and B(8), *vide infra* [the B(4)–B(8) distance of 1·900(21) Å is the longest boron–boron distance in the molecule].

Hawthorne and his co-workers [4,19] have obtained high-resolution n.m.r. spectra of the $B_9C_2H_{12}AlMe_2$ molecule. One bridging hydride is observed (τ 13·6 in the ^1H spectrum), having the characteristics of a B–H–B system, thus confirming our postulated position for the final hydride ligand. [Resonances for the bridging protons attached directly to aluminium have not been assigned, perhaps owing to quadrupole broadening by ^{27}Al ($I = 5/2$). While methyl and C–H protons give distinct peaks, the remainder of the B–H protons provide an undecipherable pattern.]

The ^{11}B spectrum is temperature-dependent, with equilibration of the pairs B(4) and B(7), B(5) and B(11), and B(9) and B(12) at room temperature; resonances for B(6), B(8), and B(10) are not strongly temperature-dependent. Hawthorne [4,19] has suggested an intramolecular rearrangement mechanism whereby the Me_2Al bridge swings from B(7) to B(4) [maintaining B(8) as the pivot] accompanied by formation of a B(8)–H–B(7) bridge, with concomitant rearrangement of the facial hydride ligands.

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[1/1717 *Received, 20th September,* 1971]

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