Crystal Structure and Molecular Geometry of 3-Ethyl-3-alumina-1,2-dicarba-*closo*-dodecaborane (12), 1,2-$B_9C_2H_{11}AlEt$

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The title compound crystallizes in the orthorhombic space-group *Pnma* (D_{2h}^{16}; No. 62) with a = 16·304(15), b = 7·533(7), c = 9·398(6) Å, and Z = 4. A three-dimensional single-crystal *X*-ray structural analysis based on counter data has led to the location of all atoms save ethyl hydrogens. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to R 8·49% for 499 independent non-zero reflections. The crystal consists of discrete, well separated, molecular units of 1,2-$B_9C_2H_{11}AlEt$ in which the aluminium atom is σ-bonded to an ethyl group and is linked symmetrically to the open B_3C_2 face of a dicarba-*nido*-undecaborane ligand.

THE dicarba-*nido*-undecaborane dianion, (3)-1,2-$B_9C_2H_{11}^{2-}$ [hereafter referred to by its trivial name, the dicarbollyl ligand], has been shown to form complexes with a wide variety of transition metals.[1,2] There are, however, few examples in which the dicarbollyl ligand is bonded to a main-group element. The 1,2-$B_9C_2H_{11}AlEt$ molecule is prepared [3] by a two-stage reaction [equations (1) and (2)]. We have previously [4,5] reported the structure of $B_9C_2H_{12}AlMe_2$ (which is, of course, closely related to $B_9C_2H_{12}AlEt_2$†) and now report details of a crystallographic study on 1,2-$B_9C_2H_{11}AlEt$.

$$\text{(3)-1,2-}B_9C_2H_{13} + Et_3Al \xrightarrow{50°/1\text{ h}} \text{1,2-}B_9C_2H_{12}AlEt_2 \quad (1)$$

$$\text{1,2-}B_9C_2H_{12}AlEt_2 \xrightarrow{77°/25\text{ h}} \text{1,2-}B_9C_2H_{11}AlEt \quad (2)$$

EXPERIMENTAL

Crystal Data.—$C_4H_{16}AlB_9$, M = 188·45, Orthorhombic, a = 16·304(15), b = 7·533(7), c = 9·398(6) Å, U = 1154·2 Å^3, D_c = 1·084, Z = 4, F(000) = 392. Space-group *Pnma* (D_{2h}^{16}, No. 62) or $Pn2_1a$ (C_{2v}^{9}, No. 33) from the systematic absences: $0kl$ for $k + l = 2n + 1$ and $hk0$ for $h = 2n + 1$. Cu-K_α radiation (graphite monochromator d = 3·3539 Å), λ = 1·5418 Å; μ(Cu-K_α) = 10·83 cm^{-1}. (D_m

† $B_9C_2H_{12}AlEt_2$ is even more sensitive to irradiation by *X*-rays than is $B_9C_2H_{12}AlMe_2$ (see refs. 4, 5). We have been unable to collect intensity data on this molecule.

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[2] L. J. Todd, *Adv. Organometallic Chem.*, 1970, **8**, 87.

[3] D. A. T. Young, G. R. Willey, M. F. Hawthorne, M. R. Churchill, and A. H. Reis, *J. Amer. Chem. Soc.*, 1970, **92**, 6663.

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[5] M. R. Churchill and A. H. Reis, preceding paper.

was not obtained because of the extreme sensitivity of the compound towards air and moisture.) Unit-cell dimensions were obtained from calibrated [$Pb(NO_3)_2$, $a = 7{\cdot}857$ Å] precession photographs taken at 25 °C.

Collection and Reduction of Data.—Two crystals, each sealed into a Lindemann glass capillary, were used for data collection. Crystal (B) ($0{\cdot}70 \times 0{\cdot}44 \times 0{\cdot}22$ mm) was mounted along its *b* axis, and crystal (C) ($0{\cdot}38 \times 0{\cdot}48 \times 0{\cdot}24$ mm) was aligned along *c*.

Diffraction data were collected with a PAILRED diffractometer, scanning at a rate of 2·5° min^{-1}, and by use of a stationary-background–ω-scan–stationary-background sequence over a 5° scan range. Initial and final backgrounds (B_1 and B_2) were each counted for 20 s. Equi-inclination Weissenberg data for the levels $h0$—$5l$ were collected from crystal (B) and for $hk0$—3 from crystal (C). Reflections not significantly (3σ) above background or with grossly asymmetric backgrounds ($B_1 > 3B_2$ or $B_2 > 3B_1$) were rejected; of the 915 independent reflections collected, 499 were used in the subsequent analysis. All data were correctly adjusted for Lorentz, double polarization (by monochromator and sample), and absorption effects and were merged to a common scale by a least-squares analysis of common reflections[6] [transmission coefficients ranged 0·64—0·80 for crystal (B) and 0·62—0·73 for crystal (C)]. A Wilson plot[7] was used to determine the approximate absolute scale-factor and the overall isotropic thermal parameter.

Solution and Refinement of Structure.—All calculations were performed on the IBM 7094 computer of Harvard University using the CRYRM system of Dr. R. E. Marsh. Scattering factors for neutral aluminium, boron, carbon, and hydrogen were taken from ref. 8. The function minimized during least-squares refinement was $\Sigma w(|F_o|^2 - (1/k^2)|F_c|^2)^2$, where k is the overall scale-factor. The weighting scheme was based on that of Hughes[9] with $4F_{\text{min.}} = 4$ [*i.e.*, $F_o \geqslant 4$, $w = |F_o|^{-4}$; $F_o < 4$, $w = (4|F_o|)^{-2}$].

The position of the aluminium atom ($x = -0{\cdot}06$, $z = 0{\cdot}10$) was determined from a three-dimensional Patterson map. The y co-ordinate is indeterminate for space-group $Pn2_1a$ or (assuming no gross disorder) is precisely $\frac{1}{4}$ for space-group *Pnma*; it was therefore assigned the value $\frac{1}{4}$. A three-dimensional Fourier synthesis phased only by the aluminium atom (R 50·7%) revealed a set of peaks consistent with the molecule having a mirror plane, but with disorder of the terminal methyl group of the ethyl ligand. Subsequent calculations were therefore carried out under the assumption (later justified) that the true space-group was *Pnma*. Refinement of individual atomic positional and isotropic thermal parameters led to a reduction in R from 31·7 to 20·3%. Continued refinement, using anisotropic thermal parameters for all non-hydrogen atoms, led to convergence at R 10·8%. A difference–Fourier synthesis now revealed the positions of all eleven hydrogen atoms of the dicarbollyl cage, but no indications of hydrogen atoms of the (partially disordered) ethyl ligand. Full-matrix least-squares refinement, now including hydrogen atoms, led (in four cycles) to convergence [$(\Delta/\sigma)_{\text{max.}}$ 0·05] at R 8·4%, at which stage refinement was judged to be complete. During the final four cycles, positional parameters for hydrogen atoms were refined; their isotropic thermal parameters were, however, each maintained at a value of B 1·4 Å^2.

A final difference-Fourier map showed no significant features, thereby providing an independent verification of the correctness of the structure. All bond distances, bond angles, and thermal parameters are reasonable, thus militating against assignment of the crystal to the alternative non-centrosymmetric space-group $Pn2_1a$.

Final observed and calculated structure-factor amplitudes are listed in Supplementary Publication No. SUP 20296 (7 pp., 1 microfiche).*

Atomic co-ordinates are listed in Table 1; anisotropic thermal parameters are shown in Table 2.

TABLE 1

Atomic co-ordinates,* with estimated standard deviations

Atom	x	y	z
Al	−0·06206(21)	$\frac{1}{4}$	0·09715(27)
C(1)	−0·1856(4)	0·1464(10)	0·0717(6)
B(4)	−0·1166(5)	0·0619(12)	−0·0445(9)
B(5)	−0·2232(5)	0·0613(10)	−0·0832(9)
B(6)	−0·2679(7)	$\frac{1}{4}$	−0·0010(12)
B(8)	−0·0704(7)	$\frac{1}{4}$	−0·1298(11)
B(9)	−0·1523(5)	0·1314(12)	−0·2135(8)
B(10)	−0·2451(7)	$\frac{1}{4}$	−0·1875(13)
C(3)	−0·0111(8)	$\frac{1}{4}$	0·2826(11)
C(4)	−0·0500(11)	0·1592(29)	0·3944(15)
H(1)	−0·199(4)	0·105(12)	0·146(10)
H(4)	−0·089(4)	−0·088(10)	−0·030(8)
H(5)	−0·259(5)	−0·080(11)	−0·061(8)
H(6)	−0·332(6)	$\frac{1}{4}$	0·055(11)
H(8)	−0·005(6)	$\frac{1}{4}$	−0·215(12)
H(9)	−0·114(4)	0·055(10)	−0·312(7)
H(10)	−0·297(6)	$\frac{1}{4}$	−0·283(11)

* All atoms lying at $y = \frac{1}{4}$ and also C(4) were entered into the structure-factor calculation with occupancy factors of $\frac{1}{2}$.

TABLE 2

Anisotropic thermal parameters * ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	29·8 (1·4)	132·8 (6·3)	30·0 (3·0)	0	−25·1 (3·4)	0
C(1)	28(3)	88(14)	27(5)	−12(11)	4(7)	−26(26)
B(4)	24(4)	90(14)	49(8)	9(12)	−10(8)	−25(37)
B(5)	22(3)	42(12)	68(9)	−6(11)	−15(10)	19(35)
B(6)	21(5)	74(19)	56(12)	0	25(14)	0
B(8)	23(5)	76(20)	31(10)	0	−7(12)	0
B(9)	19(3)	109(16)	47(7)	45(14)	−5(7)	−1(32)
B(10)	15(4)	110(23)	74(15)	0	−15(13)	0
C(3)	36(6)	314(43)	40(12)	0	−44(12)	0
C(4)	63(9)	319(53)	68(15)	−104(10)	−18(19)	52(73)

* In the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

RESULTS AND DISCUSSION

Crystal Structure.—The 1,2-$B_9C_2H_{11}AlEt$ molecules are separated by normal van der Waals' distances and there are no abnormally short intermolecular contacts. The packing of molecules within the unit cell (as viewed down *c*) is shown in Figure 1.

Molecular Structure.—Interatomic distances, with their estimated standard deviations, are listed in Table 3. Individual angles about the aluminium atom, and mean

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

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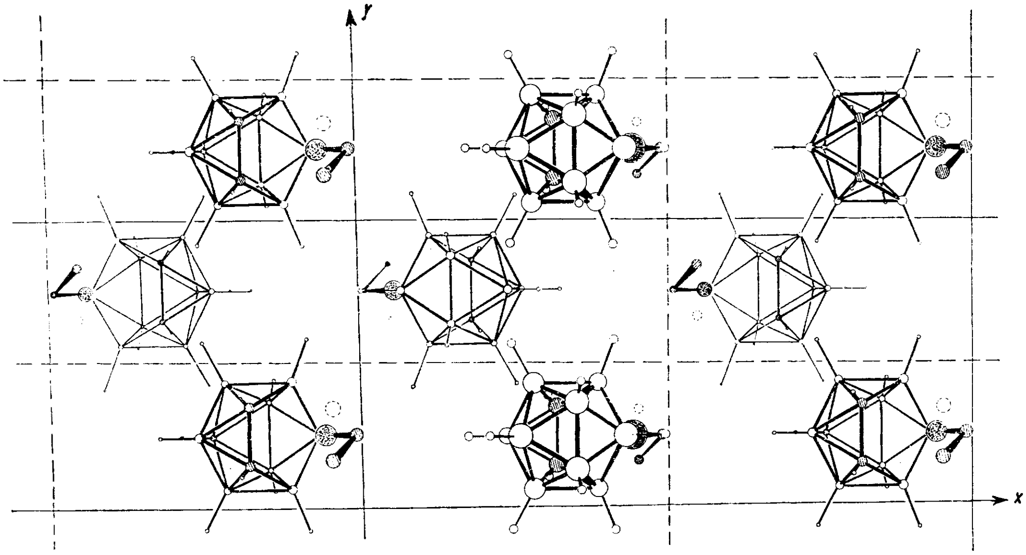

FIGURE 1 Packing of 1,2-$B_9C_2H_{11}$AlEt molecules within the unit cell, viewed down *c*

angles involving only ' light atoms ' of the cage, are collected in Table 4. (It was thought inadvisable to report the 90 individual angles within the B_9C_2 system. However, the extreme ranges of individual values are shown.) Important least-squares planes, along with deviations of individual atoms from these planes, are presented in Table 5.

TABLE 3

Interatomic distances (Å)

(*a*) Distances from aluminium atom

Al–C(1)	2·173(7)	Al–B(4)	2·138(8)
Al–C(3)	1·930(4)	Al–B(8)	2·136(9)
		Mean (Al–B)	2·137(1) *

(*b*) Distances within dicarbollyl ligand

C(1)–C(2)	1·561(9)		
C(1)–B(4)	1·691(10)		
C(1)–B(5)	1·705(10)	C(1)–B(6)	1·696(11)
		Mean (C–B)	1·697(7) *
B(4)–B(5)	1·776(11)	B(5)–B(10)	1·762(12)
B(4)–B(8)	1·793(12)	B(6)–B(10)	1·790(12)
B(4)–B(9)	1·770(11)	B(8)–B(9)	1·777(12)
B(5)–B(6)	1·774(12)	B(9)–B(10)	1·774(12)
B(5)–B(9)	1·764(11)	B(9)–B(12)	1·787(11)
		Mean (B–B)	1·777(11) *
C(1)–H(1)	0·79(9)		
B(4)–H(4)	1·22(8)	B(8)–H(8)	1·33(9)
B(5)–H(5)	1·23(8)	B(9)–H(9)	1·09(7)
B(6)–H(6)	1·17(8)	B(10)–H(10)	1·23(8)
		Mean (B–H)	1·21(8) *

(*c*) Distances involving ethyl group

C(3)–C(4)	1·405(20)	C(4) · · · C(1)	3·754(17)
		C(4) · · · B(4)	4·328(17)

* Estimated standard deviations for mean bond lengths are calculated from the expression:

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

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

The overall geometry of the 1,2-$B_9C_2H_{11}$AlEt molecule and the numbering scheme used are shown in Figure 2.

TABLE 4

Bond angles (°)

(*a*) Angles around aluminium atom

C(1)–Al–C(2)	42·1(0·3)	C(1)–Al–B(7)	77·5(0·3)
C(1)–Al–B(4)	46·2(0·3)	C(1)–Al–B(8)	80·3(0·3)
B(4)–Al–B(8)	49·6(0·3)	B(4)–Al–B(7)	83·0(0·3)
C(1)–Al–C(3)	119·9(0·4)	Al–C(3)–C(4)	118·7(1·0)
B(4)–Al–C(3)	137·8(0·4)		
B(8)–Al–C(3)	158·1(0·5)		

(*b*) Mean angles in triangular faces of dicarbollyl ligand

Atoms	No. of angles	Range	Mean
C–B–C	1	54·8(0·5)	54·8
C–C–B	2	62·6(0·4)	62·6
B–C–B	4	62·9(0·5)—63·1(0·4)	63·0(0·1) *
C–B–B	8	58·3(0·4)—58·8(0·4)	58·5(0·3) *
B–B–B	30	59·2(0·4)—60·9(0·6)	60·0(0·5) *
	Total 45		

(*c*) Mean angles in pentagonal rings of dicarbollyl ligand

Atoms	No. of angles	Range	Mean
C–C–B	4	112·1(0·5)	112·1
B–C–B	2	116·1(0·6)	116·1
C–B–B	12	102·6(0·7)—105·7(0·6)	104·1(1·0) *
B–B–B	27	104·3(0·7)—109·5(0·6)	107·7(1·3) *
	Total 45		

* See footnote to Table 3.

The aluminium atom lies symmetrically below (*i.e.*, is ' π-bonded ' to) the five atoms of the dicarbollyl ligand. The aluminium–carbon distances are each 2·173(7) Å while aluminium–boron distances range from 2·136(9) to 2·138(8), mean 2·137(1) Å.†

The aluminium–ethyl bond length of 1·930(6) Å is in excellent agreement with aluminium–methyl σ-bond

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† Estimated standard deviations for mean dimensions are calculated using the expression shown as a footnote to Table 3.

lengths of 1·954(15) and 1·958(14) Å in $B_9C_2H_{12}AlMe_2$ [4,5] and 1·949(2) and 1·956(2) Å in hexamethyldialuminium.[10]

The nine boron and two carbon atoms define the expected icosahedral dicarbollyl cage. The equatorial pentagonal rings have root-mean-square deviations from planarity of only 0·015 Å [plane (A): C(1), C(2), B(4), B(7), B(8)] and 0·003 Å [plane (B): B(5), B(6), B(9), B(11), B(12)]. The aluminium atom lies 1·586 Å below plane (A).

TABLE 5

Important least-squares planes * within the $B_9C_2H_{11}AlEt$ molecule and (in square brackets) deviations (Å) of atoms for the planes

Plane (A): $0·7066X + 0·0000Y + 0·7077Z = 1·655$

[C(1) 0·006, C(2) 0·006, B(4) −0·015, B(7) −0·015, B(8) 0·018, Al † 1·586]

Plane (B): $0·7270X + 0·0000Y + 0·6866Z = -3·183$

[B(5) 0·003, B(6) −0·004, B(9) −0·001, B(11) 0·003, B(12) −0·001]

* Cartesian co-ordinates (*X, Y, Z*) are related to the fractional cell co-ordinates (*x, y, z*) by the transformation: [*X, Y, Z*] = [*xa, yb, zc*]. † This atom was given zero weight in the plane calculation. All other atoms were assigned unit weight.

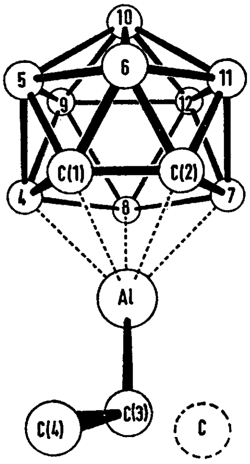

FIGURE 2 The geometry of the 1,2-$B_9C_2H_{11}AlEt$ molecule and the numbering system used. Atom C(4) is disordered; one position is drawn bonded to C(3), the other is shown as a broken circle. Because of the molecular mirror plane there is the equivalence C(1), B(4), B(5), B(9) ≡ C(2), B(7), B(11), B(12)

Mean distances within the dicarbollyl cage are: B–B 1·777(11), B–C 1·697(7), and C(1)–C(2) 1·561(9) Å. While the first two of these values are consistent with distances obtained from structural studies on other species containing *pentahapto*-dicarbollyl ligands (see Table 6),[11-19] the carbon–carbon bond seems shorter than usual.

TABLE 6

Distances within *pentahapto*-dicarbollyl ligands for selected molecules

	⟨B–B⟩	⟨B–C⟩	⟨C–C⟩
$(B_9C_2H_{11})Fe(C_5H_5)$ [a]	1·75	1·68	1·58
$[Cs^+][(B_9C_2H_{11})Re(CO)_3^-]$ [b]	1·78(2)	1·72(2)	1·61(2)
$[NMe_4^+][(B_9C_2H_8Br_3)_2Co^-]$ [c]	1·786(7)	1·725(13)	1·654(17)
$[Cs^+]_2[(B_9C_2H_{11}Co)_2B_8C_2H_{10}^{2-}]$ [d]	1·78(2)	1·71(2)	1·613(8)
$(B_9C_2H_{11})_2Ni$ [e]	1·784	1·700	1·605(7)
$(B_9C_2H_9Me_2)_2Ni$ [f]	1·749	1·669	1·636(13)
$\{(B_9C_2H_{10})_2S_2CH\}Co$ [g]	1·788(25)	1·710(31)	1·625(16)
$[NEt_4^+]_3[(B_9C_2H_{11}CoB_8C_2H_{10})_2Co^{3-}]$ [h]	1·83	1·75	1·601
$B_9C_2H_{11}AlEt$ [i]	1·777(11)	1·697(7)	1·561(9)

[a] Ref. 11. [b] Ref. 12. [c] Ref. 14. [d] Ref. 15. [e] Ref. 16. Ref. 17. [g] Ref. 18. [h] Ref. 19. [i] This work.

The refined hydrogen-atom positions give rise to boron–hydrogen bonds of 1·09(7)—1·33(9) Å, mean 1·20(8) Å. The (icosahedral carbon)–hydrogen linkage is 0·80(8) Å. The accepted values for these linkages are: B–H 1·19(1) and C–H (for trisubstituted carbon) 1·070(7) Å.[20] However, *X*-ray diffraction studies customarily give rise to X–H bond lengths which are systematically reduced from the true internuclear distance by *ca.* 10%. This is the result of the centroid of electron density surrounding the hydrogen atom being displaced into the X–H bond and not coinciding with the nuclear position.

The ethyl group is partially disordered; the angle Al–C(3)–C(4) is 118·7(1·0) and the C(3)–C(4) bond distance is 1·405(20) Å.

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