tion(16) of oxygen on carbon yielded the tabulated value of 1.217 (4) Å which appears to be a normal carbonyl length. Similar calculations for other skeletal bonds gave only insignificant corrections in length.

The bridging carbon atoms and the oxygen atoms lie ±0.013 (5) and ±0.032 (4) Å, respectively, from the plane defined by the four carbon atoms in the polyhedra [C(1), C(1′), C(2), and C(2′)]. Thus the six cabon atom ring is not strictly planar but has a very slight "chair" conformation.

The polyhderal bond angles are summarized in Table VI. Although the listed angles approximate those of 60.0 and 108.0° for a regular icosahedron, a distortion which might be described as a compression of the carbon atoms along the twofold axis of the *o*-carborane moiety is evident. The latter distortion is also apparent in the relative shortness of the polyhedral bond lengths involving carbon (Table V).

Disorder as is commonly found in the icosahedral positions of carboranes[13,15] is not possible in the present *doubly* connected bis *o*-carborane. More subtly, however, the carbonyl groups might be tilted above and below the C(1)–C(2)–C(1′)–C(2′) plane so as to give the six carbon atom ring a chair-like configuration. The latter disorder could average to give the observed planar carbon atom ring without destroying the crystallographically demanded molecular inversion center. However, all the atom positions were well defined, the thermal ellipsoid diagram (Figure 3) showed no irregularities, and the difference Fourier map showed no residual electron density in the carbonyl vicinity. Therefore, we exclude the possibility of disorder.

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Molecular and Crystal Structure of Dimethyl-1,6-dicarba-*closo*-decaborane(10)

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A three-dimensional single-crystal X-ray diffraction study at −20 to −35° shows the molecule of dimethyl-1,6-dicarba-*closo*-decaborane(10), $B_8H_8C_2(CH_3)_2$, to have essentially C_s symmetry. The B_8C_2 unit is a bicapped square antiprism only slightly distorted from full D_{4d} symmetry. The charges on the B atoms, determined by LCAO–MO methods, become more positive in the order B8 (attached to no C atoms) < B10, B7, B9, B3, B4 (attached to one C) < B2, B5 (attached to two C atoms). The compound crystallizes in the orthorhombic space group Pbca with eight molecules in a cell of dimensions $a = 11.36 \pm 0.01$, $b = 11.81 \pm 0.01$, and $c = 14.74 \pm 0.01$ Å. A density of 0.997 g/cm³ was calculated from these cell dimensions. The 1615 X-ray reflections observed on film were refined to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.084$.

Introduction

The 1,6 isomer of $B_8H_8C_2(CH_3)_2$ is produced,[1] along with $B_6H_6C_2(CH_3)_2$ and $B_7H_7C_2(CH_3)_2$, when $B_7C_2H_{11}(CH_3)_2$ is pyrolyzed near 200° in the presence of diphenyl ether. The ^{11}B nuclear magnetic resonance spectrum[1] of this molecule at 19.3 Mc shows two peaks: a doublet of area 1 at low field and a complex peak of area 7 at high field. The doublet at low field was assigned[1] to an apical BH position, like that previously assigned[2] for $B_{10}H_{10}^{2-}$, and all others were assigned to equatorial positions on a bicapped square-antiprism cage. Our X-ray study, as described below, proves that the C atoms are in the nonadjacent 1 and 6 positions, not in the adjacent 1 and 2 positions which would also be consistent with the ^{11}B nmr spectrum. Thus, the 1 and 6 assignment for C atoms, considered more plausible on chemical grounds, has been confirmed by our study. In addition a detailed molecular geometry which is suitable for theoretical study is established below.

Experimental Section

Liquid 1,6-$B_8H_8C_2(CH_3)_2$ (mp 1.0–1.6°) was sealed into Pyrex capillaries having uniform wall thickness and inside diameter about 0.7 mm. The sample size was regulated to yield crystals, grown in a cold stream of N_2,[3] which were roughly equal in all dimensions. X-Ray data were collected between −20 and −35°. Crystals were stable for periods of up to 4 months when maintained in this temperature range, and all necessary data were collected from two crystals. Reciprocal lattice symmetry D_{2h} and systematic absences of $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd indicated that the space group is Pbca. Unit cell parameters of $a = 11.36 \pm 0.01$, $b = 11.81 \pm 0.01$, and $c = 14.74 \pm 0.01$ Å were obtained from Weissenberg photographs calibrated by the superposition of a powder diffraction pattern of Al, using 4.04916 Å for the Al cell constant and λ 1.54178 Å for Cu Kα. The cell dimensions were refined by a previously described least-squares procedure[4] using as data 2θ values for 50 reflections. Assuming eight molecules in the unit cell, a reason-

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(1) F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **88**, 609 (1966).

(2) W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *ibid.*, **81**, 5833 (1959).

(3) W. N. Lipscomb, *Norelco Rep.*, **4**, 54 (1957).

(4) T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1076 (1968).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 1,6-$B_8H_8C_2(CH_3)_2$[a,b]

[illegible]

[a] The three columns contain, from left to right, values of K, F_o, and F_c. Reflections designated by an asterisk were assigned zero weight in the refinements. A minus sign before F_o indicates a reflection that was too weak to be observed. [b] Multiply by 0.25 to place on an absolute scale with $F_{000} = 624$.

able density of 0.997 g/cm^3 was calculated. No attempt was made to measure the density experimentally, but the related compound $B_7C_2H_{11}(CH_3)_2$ has a density[5] of 0.92 g/cm^3. Thus, there is one molecule in the asymmetric unit, and all atoms are expected to be in general positions.

Data were taken on an equiinclination Weissenberg camera using Ni-filtered Cu Kα radiation and multiple films. Some 1615 reflections (Table I) were indexed on levels hKl for $0 \leq K \leq 9$ and Hkl for $0 \leq H \leq 3$. Of these, 647 were below the observational limits. Intensities were estimated by comparison with an intensity scale prepared from the same substance. Corrections were applied for Lorentz and polarization factors and for oblique incidence of X-rays on the upper level films. A standard deviation was assigned to each intensity reading using the function

$$\sigma(I) = \left[\frac{I_{\min}}{3} + bI + \frac{0.1I^2}{(I_{\max} - I)^2}\right] \times \{1 + 0.25\exp[-50(0.5 - \sin^2\theta)^2]\}$$

where $I_{\min}$ and $I_{\max}$ are the maximum and minimum values on the intensity scale. The fractional parameter b was determined during film-to-film scaling by an analysis of the consistency of intensities for reflections read on more than one film. Actual values of b were 0.091 for the a-axis data and 0.096 for the b-axis data. The use of this error function, which attempts to reproduce the uncertainties in estimating intensities visually, has been described.[6,7]

The intensities were placed upon a common scale by a least-squares procedure minimizing

$$\sum_{\substack{hij \\ i \neq j}} w_{hij}(\ln(s_iI_{hi}) - \ln(s_jI_{hj}))^2$$

where s_i is the scale factor for the ith set, I_{hi} is the measurement of reflection h on set i, and $1/w_{hij} = \sigma^2(I_{hi})/I_{hi}^2 + \sigma^2(I_{hj})/I_{hj}^2$. Weights were assigned to the final scaled intensities based upon the input deviations which were propagated through the scaling calculations. These weights were used in all subsequent refinements. Zero weight was assigned to eleven reflections for which the two intensity readings taken from different sets disagreed by more than 30%.

No attempt was made to introduce an absorption correction. The magnitude of absorption effects was estimated at less than 3% from the calculated value of $\mu = 2.91$ cm^{-1} for Cu Kα radiation and the radius of our crystals (0.035 cm).

Structure Determination and Refinement

The structure was solved by application of the symbolic addition procedure of Karle and Karle.[8] Initially,

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(5) D. Voet and W. N. Lipscomb, *Inorg. Chem.*, **6**, 113 (1967).

(6) D. J. Duchamp and R. E. Marsh, *Acta Crystallogr., Sect. B*, **25**, 5 (1969).

(7) H. Hart and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1070 (1968).

(8) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

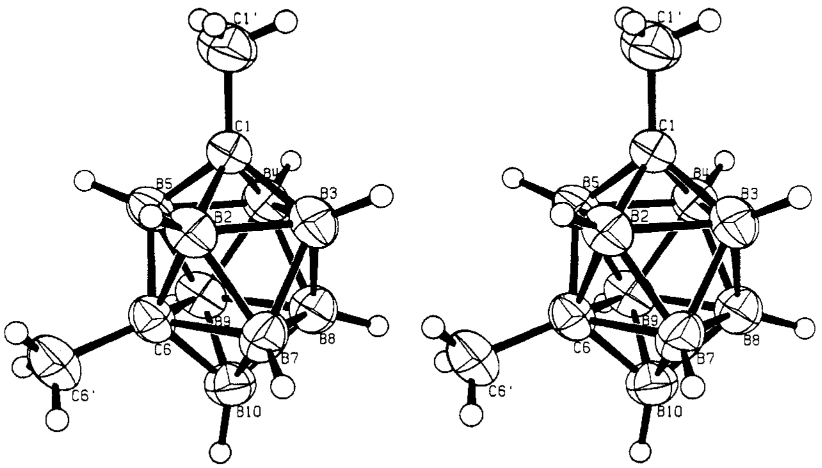

Figure 1.—Stereodrawing showing the molecule and numbering scheme for 1,6-$B_8H_8C_2(CH_3)_2$.

signs were arbitrarily chosen for three reflections in order to fix the origin. Introduction of unknown symbols as the signs of four other reflections and application by hand of the Σ_2 formula[8] led to determination of signs for 49 of the 55 reflections having normalized structure factors[9] $|E| \geq 2.2$ and $\rho = (\sin^2 \theta)/\lambda^2 \leq 0.34$. During this procedure it became possible to introduce definite signs for the four unknown symbols. Using a program for the IBM 7094 computer written in this laboratory[10,11] the 49 signs determined by symbolic addition were extended with Sayre's equation[12] to yield signs for the 302 reflections having $|E| \geq 1.3$, all of which ultimately proved correct in the final refinement. An E map made from these reflections readily showed the locations of the twelve B and C atoms, and a structure factor calculation based upon the unrefined model gave a value of $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.205$. The eight cage H atoms were next located from a difference map, and two cycles of least-squares refinement were carried out[13] varying position and isotropic thermal parameters[14] for B and C atoms. The quantity minimized in these refinements was $\Sigma w^2(k^2|F_o|^2 - |F_c|^2)^2$, where $w = 1/\sigma(F_o^2)$. Unobserved reflections were omitted from the least squares unless $I_c > I_{\min}$, where $I_{\min}$ is the minimum observable intensity estimated for the reflection in question. At this stage the agreement had improved such that $R_F = 0.136$. Large reflections did not appear to be significantly underestimated, so no attempt was made to correct for extinction. In order to locate methyl H atoms, a new difference map was computed, and sections normal to the two C–C bonds were plotted. Five of the six methyl H atoms were fairly well resolved in these sections, and the sixth was fitted to the others. Introduction of anisotropic temperature factors for the heavy atoms and two further cycles of full matrix least-squares refinement gave $R_F = 0.084$. In the last cycle no parameter shifted by more than 0.4σ, and the average shift in all parameters was less than 0.1σ, for nonhydrogen atoms.[15] Attempts to refine isotropic temperature factors for the cage H atoms gave unrealistically low values, so in the final refinement these thermal parameters for all H atoms were set equal to 4.2, the average obtained for the heavy atoms in the earlier refinement. Coordinates were refined only for cage H atoms; the methyl H atoms were kept fixed. A final difference map showed no peaks greater than 0.29 e/Å^3.

Geometrical Results

The molecule, which is shown with thermal ellipsoids[16] in Figure 1, has the two C atoms with attached methyl groups located in the 1 and 6 positions as previously suggested.[1] The thermal motion appears to be quite isotropic. Tables II and III give atomic coordinates and thermal parameters which in turn yield the bond distances and angles of Tables IV and V. Figure 2 displays[17] the packing of the eight molecules within one unit cell. A calculation of intermolecular contacts showed the closest approaches to be 2.71 Å (methyl H to cage H) and 2.77 Å (methyl H to methyl H). These distances are longer than normal van der Waals contacts because the experimental C–H and B–H bond lengths in the molecule are anomalously short, as is commonly the case for bond distances involving H determined by X-ray methods.

The molecular structure of 1,6-$B_8H_8C_2(CH_3)_2$ shows only slight distortions of the bicapped square antiprism cage from the full D_{4d} symmetry reported for the isoelectronic $B_{10}H_{10}^{2-}$ unit in $Cu_2B_{10}H_{10}$.[18] Atoms B2, B3,

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(9) $E_{hkl}^2 = F_{hkl}^2[\epsilon\Sigma_i f_i^2(hkl)]^{-1}$ where F_{hkl}^2 has been corrected for thermal attenuation; $\epsilon = 2$ for $0kl$, $h0l$, and $hk0$; $\epsilon = 4$ for $h00$, $0k0$, $00l$; and $\epsilon = 1$ for all other reflections in the space group Pbca. The summation is over all 208 atoms in the unit cell, and atomic scattering factors f_i were taken from "The International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 202.

(10) G. N. Reeke, Jr., R. L. Vincent, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **90**, 1663 (1968).

(11) G. N. Reeke, Jr., Ph.D. Thesis, Harvard University, 1969.

(12) D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952).

(13) The CRYRM crystallographic computing system was used to perform film-to-film scaling, to calculate Fourier maps, and to carry out least-squares refinements. See D. J. Duchamp, Program and Abstracts, American Crystallographic Association Meeting, Bozeman, Mont., 1964, paper B-14, p 29.

(14) Isotropic temperature factors are given by $\exp[-B(\sin^2 \theta)/\lambda^2]$.

(15) The maximum and average shifts in the coordinates of cage H atoms were 0.8σ and 0.2σ, respectively.

(16) Thermal ellipsoids were calculated according to the method outlined by J. Waser, *Acta Crystallogr.*, **8**, 731 (1955).

(17) C. K. Johnson, "ORTEP, a Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration," Oak Ridge Technical Manual 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., June 1965.

(18) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).

TABLE II

COORDINATES AND ANISOTROPIC THERMAL PARAMETERS[a] ($\times 10^4$) FOR NONHYDROGEN ATOMS

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C1	0.3234 (3)	0.1528 (3)	0.0257 (2)	75 (4)	62 (4)	37 (2)	−3 (6)	−11 (5)	1 (5)
B2	0.2654 (4)	0.1644 (4)	0.1239 (3)	67 (5)	83 (5)	42 (2)	−3 (8)	2 (6)	8 (6)
B3	0.3001 (4)	0.2819 (5)	0.0499 (3)	73 (5)	82 (6)	44 (3)	2 (8)	−13 (6)	18 (6)
B4	0.4456 (5)	0.2221 (4)	0.0261 (3)	73 (5)	81 (5)	40 (2)	−2 (8)	9 (6)	7 (5)
B5	0.4126 (4)	0.1025 (5)	0.0992 (3)	76 (5)	81 (5)	33 (2)	6 (8)	8 (5)	2 (6)
C6	0.3828 (3)	0.1747 (3)	0.2004 (2)	70 (4)	75 (4)	37 (2)	12 (7)	9 (5)	10 (5)
B7	0.3037 (5)	0.2991 (4)	0.1712 (3)	84 (5)	59 (5)	53 (3)	14 (8)	8 (6)	−4 (5)
B8	0.4311 (4)	0.3421 (5)	0.1035 (3)	80 (5)	75 (5)	48 (3)	−20 (8)	1 (6)	5 (6)
B9	0.5102 (4)	0.2115 (4)	0.1369 (3)	57 (4)	102 (6)	42 (2)	−11 (8)	6 (6)	5 (6)
B10	0.4435 (5)	0.2992 (4)	0.2118 (3)	94 (6)	78 (5)	46 (3)	−25 (9)	4 (7)	−15 (6)
C1′	0.2726 (4)	0.0883 (4)	−0.0532 (3)	113 (6)	103 (5)	51 (2)	15 (7)	−47 (6)	−15 (6)
C6′	0.3749 (4)	0.1013 (4)	0.2855 (3)	119 (5)	108 (5)	41 (2)	−1 (8)	11 (6)	28 (5)

[a] Anisotropic temperature parameters are calculated by the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

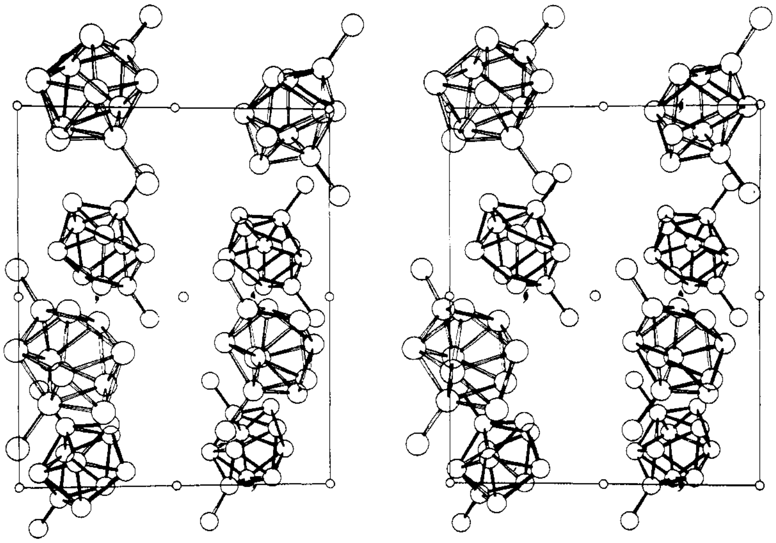

Figure 2.—Stereoview of the unit cell in the 0kl Projection. The origin is at the lower left with $\vec{c}$ pointing up and $\vec{b}$ across.

TABLE III

COORDINATES OF HYDROGEN ATOMS

Atom	x	y	z
H2	0.183 (4)	0.120 (3)	0.144 (3)
H3	0.239 (4)	0.331 (4)	0.009 (2)
H4	0.502 (4)	0.223 (3)	−0.039 (3)
H5	0.441 (4)	0.011 (4)	0.103 (3)
H7	0.232 (4)	0.341 (4)	0.212 (3)
H8	0.458 (4)	0.427 (4)	0.080 (3)
H9	0.600 (4)	0.184 (4)	0.150 (3)
H10	0.475 (4)	0.332 (4)	0.275 (3)
$H1_a'$	0.307	0.040	−0.073
$H1_b'$	0.203	0.067	−0.047
$H1_c'$	0.246	0.133	−0.097
$H6_a'$	0.437	0.068	0.300
$H6_b'$	0.318	0.050	0.282
$H6_c'$	0.341	0.141	0.334

B4, and B5 are very nearly planar, as are C6, B7, B8, and B9. In both cases, the least-squares plane passes within 0.004 Å of all four atoms. The B–C bonds in the molecule are between 0.05 and 0.10 Å shorter than B–B bonds of equivalent type, while the standard deviation in B–B and B–C bond lengths is approximately 0.007 Å. Among the six bonds between equatorial B atoms, the smallest differs from the largest by only 0.041 Å. The three types of B–B bonds in $Cu_2B_{10}H_{10}$ have average distances 1.73 ± 0.02 (apical), 1.815 ± 0.015 (equatorial), and 1.86 ± 0.03 Å (basal). These agree fairly well with the corresponding average distances for 1,6-$B_8H_8C_2(CH_3)_2$, which are 1.69, 1.805, and 1.83 Å, respectively. It is worth noting that bond B2–B5, between B atoms bonded to both C's, is the longest bond in the molecule. The distance of 1.861 ± 0.007 Å compares well with 1.89 ± 0.01 Å in the related compound $B_6H_6C_2(CH_3)_2$,[7] 1.89 ± 0.04 Å in m-$B_{10}Br_2H_8C_2H_2$,[19] and 1.89 ± 0.06 Å in m-$B_{10}Cl_{10}C_2H_2$[20] for the same type of distance. However, no abnormal lengthening of this bond was observed for $B_7H_7C_2(CH_3)_2$,[4] where the distance is 1.76 ± 0.03 Å.

Molecular Orbital Studies

Molecular orbital (MO) calculations were carried out using both the extended-Hückel[21,22] and nonempirical molecular orbital (NEMO) methods.[23,24] To simplify matters somewhat, the calculations were performed for

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[20] (a) J. A. Potenza and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, **56**, 1917 (1966); (b) J. A. Potenza, Ph.D. Thesis, Harvard University, 1966.

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TABLE IV
COMPLETE BOND DISTANCES[a]

	Bond	Bond length, Å	Bond	Bond length, Å
		B–C, Apical C		
Type I	C1–B2	1.596 (6)	C1–B5	1.598 (6)
Type II	C1–B3	1.588 (7)	C1–B4	1.611 (6)
		B–B at Base of C Apex		
Type I	B2–B5	1.861 (7)		
Type II	B2–B3	1.808 (7)	B4–B5	1.815 (7)
Type III	B3–B4	1.831 (7)		
		Equatorial B–C		
	B2–C6	1.750 (6)	B5–C6	1.752 (6)
		Equatorial B–B		
Type I	B2–B7	1.790 (7)	B5–B9	1.787 (7)
Type II	B3–B7	1.800 (6)	B4–B9	1.795 (7)
Type III	B3–B8	1.828 (7)	B4–B8	1.827 (7)
		B–C at Base of B Apex		
	C6–B7	1.774 (7)	C6–B9	1.777 (6)
		B–B at Base of B Apex		
	B7–B8	1.830 (7)	B8–B9	1.851 (7)
		B–C, Apical B		
	C6–B10	1.632 (7)		
		B–B, Apical B		
Type I	B7–B10	1.696 (8)	B9–B10	1.692 (7)
Type II	B8–B10	1.681 (7)		
		C–C		
Type I	C1–C1′	1.505 (6)		
Type II	C6–C6′	1.527 (6)		
		Apical B–H		
	B10–H	1.08 (4)		
		Equatorial B–H		
Type I	B2–H	1.11 (4)	B5–H	1.13 (5)
Type II	B3–H	1.09 (4)	B4–H	1.15 (4)
Type III	B7–H	1.13 (4)	B9–H	1.08 (4)
Type IV	B8–H	1.10 (5)		
		C–H		
	$C1'–H1_a'$	0.74		
	$C1'–H1_b'$	0.83		
	$C1'–H1_c'$	0.89		
	$C6'–H6_a'$	0.83		
	$C6'–H6_b'$	0.89		
	$C6'–H6_c'$	0.93		

[a] Assumption of C_s symmetry leads to three pairs of equivalent B atoms: B2 and B5, B3 and B4, B7 and B9.

TABLE V
COMPLETE BOND ANGLES

	Angle	Degrees	Angle	Degrees
		Around Apical C		
Type I	B2–C1–B3	69.2 (3)	B4–C1–B5	68.9 (3)
Type II	B2–C1–B5	71.3 (3)		
Type III	B3–C1–B4	69.8 (3)		
		B–B–B Angles at Base of C Apex		
Type I	B3–B2–B5	89.3 (3)	B2–B5–B4	89.8 (3)
Type II	B2–B3–B4	90.9 (3)	B3–B4–B5	90.0 (3)
		C–B–B Angles at Base of C Apex		
Type I	C1–B2–B3	55.2 (3)	C1–B5–B4	55.9 (3)
Type II	C1–B2–B5	54.4 (2)	C1–B5–B2	54.3 (2)
Type III	C1–B3–B2	55.6 (3)	C1–B4–B5	55.2 (2)
Type IV	C1–B3–B4	55.7 (3)	C1–B4–B3	54.5 (3)
		Equatorial B–B–B		
Type I	B3–B2–B7	60.0 (3)	B4–B5–B9	59.8 (3)
Type II	B2–B3–B7	59.5 (3)	B5–B4–B9	59.3 (3)
Type III	B7–B3–B8	60.6 (3)	B8–B4–B9	61.5 (3)
Type IV	B4–B3–B8	59.9 (3)	B3–B4–B8	60.0 (3)
Type V	B2–B7–B3	60.5 (3)	B4–B9–B5	60.9 (3)
Type VI	B3–B7–B8	60.5 (3)	B4–B9–B8	60.1 (3)
Type VII	B3–B8–B7	59.0 (3)	B4–B8–B9	58.4 (3)
Type VIII	B3–B8–B4	60.1 (3)		
		Equatorial C–B–B		
Type I	C6–B2–B5	57.9 (2)	C6–B5–B2	57.9 (2)
Type II	C6–B2–B7	60.1 (3)	C6–B5–B9	60.3 (3)
Type III	C6–B7–B2	58.8 (3)	C6–B9–B5	58.9 (2)
		Equatorial B–C–B		
Type I	B2–C6–B5	64.2 (3)		
Type II	B2–C6–B7	61.0 (3)	B5–C6–B9	60.8 (3)
		B–B–B at Base of B Apex		
Type I	B7–B8–B9	90.4 (3)		
Type II	B7–B8–B10	57.6 (3)	B9–B8–B10	57.0 (3)
Type III	B8–B7–B10	56.8 (3)	B8–B9–B10	56.4 (3)
		C–B–B at Base of B Apex		
Type I	C6–B7–B8	87.8 (3)	C6–B9–B8	87.1 (3)
Type II	C6–B7–B10	56.0 (3)	C6–B9–B10	56.0 (3)
		B–C–B at Base of B Apex		
Type I	B7–C6–B9	94.7 (3)		
Type II	B7–C6–B10	59.6 (3)	B9–C6–B10	59.3 (3)
		Around Apical B		
Type I	C6–B10–B7	64.4 (3)	C6–B10–B9	64.6 (3)
Type II	B7–B10–B8	65.6 (3)	B8–B10–B9	66.6 (3)
		Angles Including Apical Methyl C		
Type I	C1′–C1–B2	125.9 (4)	C1′–C1–B5	125.4 (4)
Type II	C1′–C1–B3	126.6 (3)	C1′–C1–B4	126.1 (3)
		Angles Including Equatorial Methyl C		
Type I	C6′–C6–B2	116.4 (3)	C6′–C6–B5	115.8 (3)
Type II	C6′–C6–B7	129.7 (3)	C6′–C6–B9	128.3 (4)
Type III	C6′–C6–B10	116.8 (3)		

1,6-$B_8C_2H_{10}$, where the CH_3 groups are replaced by H atoms. Otherwise, the geometry was taken directly from the X-ray study with slight adjustments in the somewhat uncertain H positions. The B–H distance was fixed at 1.196 Å, the terminal B–H distance in B_2H_6 as determined by gas-phase electron diffraction.[25] The H atoms attached to C were positioned to give a C–H distance of 1.102 Å, the value calculated from infrared and Raman spectra of C_2H_6.[26] The complete adjusted coordinates are given in Table VI.

Previous MO studies of various $B_8C_2H_{10}$ and $B_{10}C_2H_{12}$ isomers led[27] to a simple rule for predicting the relative charges of different B atoms in these systems. The rule gives in order of increasing positive charge those B atoms bonded to (a) no C atoms, (b) one C atom, and (c) two C atoms. Within a given category a four-coordinated apical B is predicted to be more negative than a five-coordinated equatorial B atom. The net Mulliken atomic charges[28] for 1,6-$B_8C_2H_{10}$ are given in Table VII for each of the six MO calculations. In the extended Hückel results, the relative order is that predicted by the rule given above, B8 < B10 < B7, B9,

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TABLE VI
ORTHOGONAL COORDINATES (Å) FOR $B_8C_2H_{10}$[a]

Atom	x	y	z
C1	3.673	1.804	0.379
B2	3.014	1.941	1.826
B3	3.408	3.329	0.736
B4	5.061	2.622	0.384
B5	4.686	1.210	1.462
C6	4.347	2.063	2.954
B7	3.449	3.532	2.524
B8	4.896	4.039	1.525
B9	5.794	2.497	2.018
B10	5.037	3.533	3.121
H1	3.251	1.246	−0.473
H2	2.007	1.379	2.141
H3	2.644	3.964	0.072
H4	5.721	2.637	−0.613
H5	5.024	0.064	1.514
H6	4.283	1.438	3.859
H7	2.589	4.060	3.166
H8	5.230	5.126	1.154
H9	6.917	2.143	2.225
H10	5.432	3.969	4.162

[a] As adjusted to give an idealized model for the purposes of MO calculations.

B3, B4 < B2, B5, also in agreement with the earlier calculations[27] which were based on the geometry of the $B_{10}H_{10}^{2-}$ ion. The same order holds for the charges calculated by the NEMO method (Table VIII), except that the apical B atom, B10, is very slightly more positive than B7 and B9. The net framework charges (Table IX) follow the same general order as the atomic charges. Dipole moments have been calculated from the NEMO wave functions using Ruedenberg's invariant method of partitioning[29] and are included in Table VII along with point charge dipoles calculated from the net Mulliken charges alone. The direction of the dipole makes the side of the molecule containing the C atoms positive.

Earlier NEMO calculations on $B_6H_6C_2(CH_3)_2$[7] and $B_7H_7C_2(CH_3)_2$[4] were based upon self-consistent field (SCF) results for B_4H_4[30] and C_2H_6,[31] and used Slater exponents except for H_{1s} which was assigned an exponent of 1.2. Results were obtained with the one-center 2s–2p zero-overlap constant[24] set equal to $K^{ZO} = 0.229$, the value from B_4H_4, and again with $K^{ZO} = 0$.

TABLE VII
ATOMIC CHARGES AND DIPOLE MOMENTS[a]

Atom	Net Mulliken charge I	II	III	IV	V	VI
C6 (equatorial)	−0.53	−0.48	0.50	0.31	0.10	−0.06
C1 (apical)	−0.63	−0.61	0.48	0.29	0.05	−0.07
B2, B5 (bonded to both C's)	0.57	0.57	0.25	−0.05	0.39	0.15
B3, B4 (bonded to one C, equatorial)	0.34	0.35	0.17	−0.12	0.24	0.03
B7, B9 (bonded to one C, equatorial)	0.31	0.32	0.10	−0.17	0.15	−0.04
B10 (bonded to one C, apical)	0.25	0.23	0.12	−0.15	0.17	−0.01
B8 (bonded to no C's)	0.14	0.13	−0.02	−0.24	−0.03	−0.16
(C)H	0.05	0.04	−0.14	−0.01	−0.03	−0.06
(B)H	−0.22	−0.23	−0.23	0.06	−0.22	−0.02
			Dipole moments, D			
Total dipole moment[b]			5.88	5.89	5.96	5.98
Point charge dipole moment			5.30	4.29	4.54	3.55

[a] (I) Extended Hückel; α's (eV): B_{2s}, −15.02; B_{2p}, −8.55; C_{2s}, −20.78; C_{2p}, −11.31; H_{1s}, −13.60; optimized exponents from Table VIII. (II) Extended Hückel; α's (eV): B_{2s}, −15.36; B_{2p}, −8.63; C_{2s}, −21.4; C_{2p}, −11.4; H_{1s}, −13.61; Slater exponents except 1.2 for H_{1s}. (III) NEMO with parameters from Table VIII and $K^{ZO} = 0.3902$. (IV) NEMO with parameters from Table VIII and $K^{ZO} = 0.0$. (V) NEMO with parameters from ref 7 and $K^{ZO} = 0.229$. (VI) NEMO with parameters from ref 7 and $K^{ZO} = 0.0$.
[b] Calculated as $\int \psi^2 r d\tau$.

TABLE VIII
NEMO PARAMETERS
A. α's and Exponents

B_5H_9 Orbital	Exponent	α, au	C_2H_6 Orbital	Exponent	α, au
B_{1s}	4.680	−7.4988	C_{1s}	5.680	−11.2078
B_{2s}	1.443	−1.1748	C_{2s}	1.730	−1.5312
B_{2p}	1.477	−0.2770	C_{2p}	1.760	−0.2957
H_{1s}	1.147	−0.4183	H_{1s}	1.160	−0.5239

B. Mulliken Approximation Coefficients

One-center

$K_{1s-2s} = 0.6599$

Two-center

$K_{1s-1s} = 1.0000$
$K_{1s-1s} = 0.7939$
$K_{1s-2p} = 0.8050$
$K_{1s-H} = 0.8118$

Two-center

$K_{2s-2s} = 1.0603$
$K_{2s-2p} = 1.1071$
$K_{2s-H} = 1.0167$
$K_{2p\sigma-2p\sigma} = 1.1249$
$K_{2p\pi-2p\pi} = 1.0085$
$K_{2p-H} = 0.8792$
$K_{H-H} = 0.8643$

C. Zero-Overlap Coefficient
$K^{ZO} = 0.3902$

For purposes of comparison, calculations were performed in the same manner for 1,6-$B_8C_2H_{10}$. Two additional calculations used parameters (Table VIII) derived from SCF results for B_5H_9,[32] with optimized exponents for B and C taken from B_2H_6[33] and C_2H_6,[34] respectively.

In each of our six MO calculations B7(B9) are more negative than B3(B4), even though these four equatorial B atoms bonded to one C should be equivalent according to the simple rule. We await electrophilic substitutions on the molecule to determine if these positions are, in fact, chemically distinguishable.

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TABLE IX

FRAMEWORK CHARGES[a]

Type	I	II	III	IV	V	VI
C–H equatorial (C6)	−0.48	−0.44	0.38	0.30	0.08	0.02
C–H apical (C1)	−0.58	−0.57	0.32	0.28	0.01	0.00
B–H bonded to both C's (B2, B5)	0.35	0.34	0.01	0.01	0.15	0.13
B–H bonded to 1 C (B3, B4)	0.12	0.11	−0.07	−0.07	0.00	−0.01
B–H bonded to 1 C (B7, B9)	0.10	0.10	−0.10	−0.09	−0.05	−0.02
B–H bonded to 1 C, apical (B10)	0.03	0.02	−0.13	−0.08	−0.05	−0.01
B–H bonded to no C's (B8)	−0.09	−0.10	−0.23	−0.19	−0.25	−0.19

[a] Defined as the sum of the atomic charges for a B–H or C–H unit.

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The Chlorination of 2,4-Dicarba-*closo*-heptaborane(7)

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The *closo*-carborane, $C_2B_5H_7$, reacts rapidly with Cl_2 in the presence of $AlCl_3$ to form HCl and 5-$ClC_2B_5H_6$. The reaction without $AlCl_3$ is accelerated by light forming, in addition to the 5 isomer, 1-$ClC_2B_5H_6$ and 3-$ClC_2B_5H_6$. The identity and structure of the new compounds are indicated by their mass spectra and ^{11}B nmr spectra. A trans effect is observed in the ^{11}B nmr of the 1-chloro derivative and reciprocal effects are observed in all compounds.

Introduction

Recent studies have shown that chlorine and bromine can be substituted for boron-bonded hydrogen on $C_2B_4H_8$[1] and B_5H_9[2] by treating the compound with molecular halogen. In the case of B_5H_9, both apex and base substitutions occur when no aluminum halide catalyst is used. If aluminum halide is present, substitution takes place at only the apex position. In $C_2B_4H_8$ substitution occurs at the base position adjacent to a carbon atom. In both compounds, the aluminum halide catalyzed substitutions are directed toward the boron atom with the most negative or least positive charge.

The charge distribution of 2,4-dicarba-*closo*-heptaborane(7)[3] has also been calculated[4] and the 5,6-boron atoms have the highest negative charge: −0.179 *vs.* 0.031 and 0.334 for the 3 and 1,7 positions, respectively. Therefore, it is expected that electrophilic substitution will occur at the 5 position in the presence of aluminum halide. This investigation reports the synthesis and properties of 5-$ClC_2B_5H_6$ by such a reaction. In addition, the other two boron-substituted isomers are also produced from a similar reaction in which no $AlCl_3$ is added.

Experimental Section

Standard high-vacuum equipment was used for the manipulation of all volatile components. 2,4-Dicarba-*closo*-heptaborane(7), $C_2B_5H_7$, was synthesized by the pyrolysis of $C_2H_4H_8$.[5] It was purified by glpc. *Chlorine* was distilled to remove hydrogen chloride and water; it was measured as a gas using a mercury manometer which was protected by silicone oil.

Gas chromatography equipment (glpc) consisted of a 20-ft glass coil, of $^5/_{16}$-in. inside diameter, packed with 20% Apiezon L on Chromosorb P. This column packing proved to be much better for separating the compounds involved here than the Kel-F on firebrick used in previous studies. Infrared spectra were recorded from 2 to 15 μ by a Perkin-Elmer 137 or Beckman IR-5 instrument. Gas-phase spectra at 10–20 Torr were obtained in 10-cm cells. The nmr spectra were run on Varian instruments at 220 and 100 MHz for ^1H and 32.1 MHz for ^{11}B. External tetramethylsilane and boron trifluoride diethyl etherate were used for respective standards. Mass spectra were obtained from West Coast Technical Service, San Gabriel, Calif.

Chlorine and $C_2B_5H_7$ in the Presence of Aluminum Chloride.—About 0.3 g of $AlCl_3$ was introduced into a 1 l. bulb which was then evacuated. The $AlCl_3$ was sublimed onto the walls of the flask by flaming gently. Chlorine gas, 1.5 mmol, and $C_2B_5H_7$, 3.0 mmol, were condensed into the bulb at −196° which was

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