acteristic of B_5H_9, especially at 892 (s), 1010 (m), 1385 (s), 1595 (m), and 1800 (m) cm^{-1}, in addition to absorptions attributable to B–H stretch and alkyl groups, at 2950 (vs), 2900 (s), 2860 (s), 2590 (vs), 1445 (s), 1165 (w), 1070 (w), 940 (w), 838 (w), 785 (m), 685 (w), and 630 (w) cm^{-1}. The single sharp spike at 2590 cm^{-1} eliminates BH_2 groups, and alkyl substituents other than butyl (*e.g.*, diethyl, ethyldimethyl) are precluded by the absence of bands in the 1280–1350-cm^{-1} range characteristic of B–CH_3 and B–C_2H_5 deformation. *sec*-Butyl and *n*-butyl ligands are not distinguishable by these data, but the *sec*-butyl structure is much more probable in view of the facile preparation from dimethylacetylene and the reported synthesis of 2-*sec*-butyl pentaborane(9) from B_5H_9 and 2-butene.[20]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

Molecular and Crystal Structure of 1,7-Dimethyl-1,7-dicarbaclovooctaborane(8)

BY HASKELL HART AND WILLIAM N. LIPSCOMB

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The molecular structure of 1,7-dimethyl-1,7-dicarbaclovooctaborane(8), $B_6H_6C_2(CH_3)_2$, has C_2 symmetry. The B_2C_2 unit is nearly, but distorted from, the idealized D_{2d} geometry found earlier for B_8Cl_8 and recently for $B_8H_8^{2-}$. Molecular orbital calculations suggest that outermost electrons are most available on BH units 2 and 8 (connected to one C and three other B), next on BH units 5 and 6 (connected to one C and four other B), and least on BH units 3 and 4 (connected to two C and three other B) in the ground state. The crystal structure at −50° has the space group C2/c, four molecules in a unit cell having parameters a = 15.243, b = 5.89, c = 12.740 Å, and β = 131.39°, a calculated density of 0.968 g/cm³, and a final value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.11$ for 491 X-ray reflections.

The gas-phase reaction[1] of B_6H_{10} and dimethylacetylene and the pyrolysis[2] of $B_7C_2H_{11}(CH_3)_2$ in diphenyl ether yield $B_6H_6C_2(CH_3)_2$ along with other carboranes. Prior to our preliminary report,[3] the structure of $B_6H_6C_2(CH_3)_2$ was uncertain. The earlier interpretation[1] of the 12.8-Mc ^{11}B nuclear magnetic resonance (nmr) spectrum was based upon a chemically reasonable distortion of the polyhedron which was established earlier[4] in B_8Cl_8 and recently[5] in $B_8H_8^{2-}$ to have idealized symmetry D_{2d}. However, this interpretation requires that two different types of boron atoms have coincident ^{11}B nmr resonances. Confirmation of this coincidence at 19.3 Mc led[2] to some favoritism for a structure based, when idealized, upon an Archimedian antiprism of D_{4d} symmetry for an equal-atom structure. On the other hand, the theoretical treatment by Hoffmann and Lipscomb[6] of B_8H_8 of D_{2d} symmetry indicated an unfilled singly degenerate level immediately above the filled levels, thus providing a reasonable basis for prediction of a $B_8H_8^{2-}$ structure of D_{2d} symmetry. The possibilities of distortions, an intermediate structure, or a dynamical fluctuating structure (unlikely at room temperature) between the two idealized extremes based upon equal-atom D_{2d} and D_{4d} structures have all been discussed[6] as part of the structural ambiguities of this B_6C_2 polyhedron. We show here that small distortions do indeed occur toward such an intermediate structure. Also, the attachment of methyl groups to the C atoms allows us to establish with certainty the positions of the C atom in the B_6C_2 molecule.

Structure Determination

Single crystals about 0.5 × 0.5 × 1 mm were grown from the neat liquid (mp −39 to −40°) which had been sealed into glass capillaries. The crystal was maintained at approximately −50° by means of a stream of cold gaseous nitrogen.[7] Extinction of $h0l$, when h or l is odd, and of hkl, when $h + k$ is odd, are consistent with space groups Cc or C2/c. Monoclinic unit cell parameters, calibrated by least squares from a superimposed powder diffraction pattern of Al (a = 4.0493 Å) are $a = 15.243 \pm 0.003$ Å, $c = 12.740 \pm 0.002$ Å, and $\beta = 131.39 \pm 0.03°$, as determined from a Weissenberg $h0l$ zone taken with the aid of Cu Kα radiation (λ 1.54178 Å). The two estimates of b = 5.88 and 5.90 Å (average 5.89 Å) were made[8] from a precession photograph of the $hk0$ zone taken with the aid of MoKα radiation (λ 0.71069 Å). This separate determination of $b = 5.89 \pm 0.01$ Å was necessary because the crystals grew so that the b axis was consistently along the capillary axis.

Weissenberg multiple films were taken of hkl data for $0 \leqslant k \leqslant 4$ with Ni-filtered Cu Kα radiation, and

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(1) R. E. Williams and F. J. Gerhart, *J. Am. Chem. Soc.*, **87**, 3513 (1965).

(2) F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *ibid.*, **88**, 609 (1966).

(3) H. V. Hart and W. N. Lipscomb, *ibid.*, **89**, 4220 (1967).

(4) (a) R. A. Jacobson and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 605 (1959); (b) R. A. Jacobson and W. N. Lipscomb, *J. Am. Chem. Soc.*, **80**, 5571 (1958); (c) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin Co., New York, N. Y., 1963, p 23; (d) G. S. Pawley, *Acta Cryst.*, **20**, 631 (1966).

(5) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).

(6) W. N. Lipscomb, *Science*, **153**, 373 (1966). The unpublished molecular orbital studies of B_8H_8 (D_{2d}) and $B_8H_8^{2-}$ (D_{2d}) referred to here were carried out by R. Hoffmann.

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

(8) M. M. Qurashi and W. H. Barnes, *Am. Mineralogist*, **38**, 552 (1953).

precession films were taken of *hkl* data for $0 \leqslant l \leqslant 3$ from a second crystal with Zr-filtered Mo Kα radiation. A timed exposure scale was used for measurement of Weissenberg data, while precession data were read with the aid of a Joyce-Loebl Model E12 MK III microdensitometer. Symmetry-equivalent precession data were averaged, and integrated intensities were taken as proportional to peak height in view of the large size of collimator and crystal (~1 mm). Where, on the Weissenberg photographs, the Kα_1 and Kα_2 reflections were separated, the intensity was taken as three-halves that of Kα_1, and weights of half of the usual values were assigned in the least-squares refinements. After the usual Lorentz-polarization corrections were made, the data were scaled and correlated. A single logarithmic average film factor (corrected for inclination angle) was calculated for all Weissenberg photographs in the same pack. Separate logarithmic average film factors were calculated for all precession photographs. No absorption corrections were applied. Their values are all less than 4% of the intensities, because the crystals were about 1 mm in largest dimension and the absorption coefficient is 3.0 for Cu Kα and 0.5 for Mo Kα radiation. Some indication of the quality of the 885 observations of 757 unique reflections is shown by the value of the correlation factor R_c

$$R_c = \frac{\sum_h (I_{hb} - I_{hc})}{\sum_h (I_{hb} + I_{hc})} = 0.075$$

for all reflections (designated as h) in levels about either the b axis or the c axis. This result was obtained from a least-squares procedure which minimizes

$$R = \sum_h w_{hbc}(\ln I_{hb} - \ln I_{hc})^2$$

where the weights

$$w_{hbc} = 1/[\sigma^2(I_{hb}) + \sigma^2(I_{hc})]$$

are expressed in terms of standard deviations[9] σ of the appropriate intensities. Of these 757 unique reflections, 282 were below the limit on the films. In the least-squares refinements below these, 475 observed reflections have been augmented by only those several unobserved reflections for which the calculated intensities exceed the observational lower limit.

A plot[10] of the intensity distribution suggested that the space group was centrosymmetric, but the presence of extra molecular symmetry is known[11] to distort significantly this kind of analysis. Nevertheless, this result was taken as tentative evidence that the space group is C2/c, and not Cc. Reasonable molecular volumes or densities for similar molecules indicate that 4 is the only possible even number of molecules per unit cell and thus lead to a calculated density of 0.968 g/cm³ at −50°. In the space group C2/c, the molecule is then required to have a twofold axis or a center of symmetry, but neither symmetry element was assumed at this stage. The structure was solved by Sayre's method[12] with the aid of our modified version of the multiple-solution computer program of Long, REL.[13] Details of this method have been discussed elsewhere.[14] The signs of those 216 normalized structure factors E, scaled from the Wilson plot, having values greater than unity were established. The interpretable electron density was found from those signs having the second highest consistency index

$$C = \langle |E_h \sum_k E_k E_{h-k}| \rangle / \langle |E_h| \sum_k |E_k| |E_{h-k}| \rangle = 0.77$$

which required nine cycles, three more than the uninterpretable solution having $C = 0.83$. All B and C atoms were located in this density function, computed from these largest 216 E values as coefficients. The value of

$$R = \Sigma \, ||F_o| - |F_c|| / \Sigma |F_o|$$

was 0.33 at this stage, but six cycles of three-dimensional least-squares refinements in which individual isotropic thermal parameters were assigned to B and C reduced R to 0.19. The H atoms bound to B were then introduced at chemically reasonable positions and were refined assuming isotropic thermal parameters, along with anisotropic thermal parameters for B and C, to a value of $R = 0.12$. Subtraction of B and C atoms from the electron density revealed that the H atoms of CH_3 were almost completely disordered, but their introduction at chemically reasonable positions into the greatest density and subsequent refinement led, finally, to $R = 0.11$. Values of

$$R_w = \Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^4 = 0.02$$

and

$$G = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(m - s)]^{1/2} = 2.53$$

were obtained, where the ideal value of the "goodness of fit" G is unity for the most appropriate weighting factors (properly scaled) if the errors are truly statistical in a system having m observations and s parameters. The function minimized in the least-squares refinements was

$$\Sigma w \, (|F_o|^2 - |F_c|^2)^2$$

where $w = 1/\sigma^2(|F_o|^2)$. Of the reflections which were below the observational limit in value, those 16 which had values of $|F_c|^2$ greater than the minimum observable $|F_o|^2$ were included in these final least-squares refinements, making a total of 491 observations.

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(9) For our particular data set $\sigma(I) = [3.66 + 0.056I + 0.1I^2 (I_{\max} - I)^{-2}] \times \{1 + 0.25 \exp[-50(0.5 - \sin^2 \theta)^2]\}$. This function is designed specially for visual estimates of intensities by the use of a standard intensity scale. The first term ($I_{\min}/3$) raises the error for readings which are low on the intensity scale, the second term dominates for readings in the intermediate region of the scale, and the third term raises the error again for readings near the high end of the scale. The exponential raises the error for readings affected by α_1,α_2 splitting.

(10) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

(11) J. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959).

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

(13) R. E. Long, Ph.D. Thesis, Part III, University of California at Los Angeles, 1965.

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

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (F_{000} = 264)[a]

H 0 0		
4	65	-77
6	100	-98
8	167	-171
10	94	92
12	113	113
14	28	32
H 0 2		
2	291	306
4	271	283
-4	64	-69
6	140	139
-6	50	49
8	69	69
10	111	-109
-10	38	45
12	75	-76
-12	59	-54
-14	-27	15
-16	-16	-8
H 0 4		
0	20	4
2	334	-358
-2	90	-71
4	216	-210
-4	171	-185
6	78	-83
-6	118	109
8	-27	-14
-8	288	-294
10	61	53
-10	46	-51
-12	29	28
-14	74	-80
-16	27	-11
H 0 6		
0	23	27
2	124	122
-2	142	131
4	-28	18
-4	302	320
6	-27	-13
-6	78	-84
8	-22	-5
-8	103	113
-10	81	-86
-12	139	-154
-14	49	63
-16	-27	11
-18	17	11
H 0 8		
0	119	109
2	79	73
-2	-25	10
4	87	80
-4	198	-192
6	-19	27
-6	-22	23
-8	-23	-13
-10	89	98
-12	219	240
-14	-28	15
-16	-27	16
-18	18	17
H 0 10		
0	150	-134
2	93	-82
-2	89	-89
-4	99	73
-6	31	26
-8	-26	5
-10	29	-36
-12	150	-165
-14	-27	2
-16	-27	-2
-18	23	-33
H 0 12		
0	64	38
-2	55	36
-4	60	-46
-6	60	-63
-8	55	-59
-10	46	-35
-12	55	56
-14	65	-68
-16	68	-73
-18	-23	0
H 0 14		
-4	35	35
-6	34	35
-8	21	23
-10	-27	11
-12	46	-43
-14	42	40
-16	77	85
-18	22	26
H 0 16		
-12	69	66
-14	15	20
H 1 0		
3	178	184
5	39	42
7	184	185
9	95	92
11	51	-46
13	-33	1
H 1 1		
1	417	460
3	210	203
-3	436	436
5	99	-99
-5	129	-127
7	-30	3
-7	68	-70
9	89	87
-9	36	30
11	78	76
-11	50	47
13	47	48
-13	62	63
-15	-22	19
H 1 2		
1	279	274
-1	514	614
3	217	-207
-3	176	-153
5	104	-92
-5	233	228
7	128	-119
-7	126	-91
9	-34	-28
-9	103	-104
11	68	53
-11	61	67
13	-9	21
-13	-34	-31
-15	26	-24
H 1 3		
1	101	101
-1	24	-25
3	140	139
-3	225	-214
5	154	156
-5	313	276
7	-34	12
-7	263	268
9	45	-40
-9	90	95
11	-28	-17
-13	-34	-14
-15	-33	-12
H 1 4		
1	52	-27
-1	215	-215
3	145	120
-3	336	357
5	37	30
-5	73	-69
7	55	48
-7	44	-51
9	-34	-14
-9	-28	21
11	-14	-19
-11	143	-145
-13	-35	17
-15	68	65
-17	-21	15
H 1 5		
1	159	-155
-1	145	-160
3	105	-107
-3	76	79
5	76	-73
-5	66	-64
7	-35	-6
-7	202	-173
9	-28	-4
-9	74	-84
-11	109	-103
-13	-34	-16
-15	-35	13
-17	24	-10
H 1 6		
1	34	30
-1	107	108
3	-34	-8
-3	247	-265
5	-34	18
-5	224	-229
7	-33	-12
-7	28	-27
9	-13	11
-9	-28	18
-11	258	253
-13	77	72
-15	55	-56
-17	-31	-19
H 1 7		
1	-33	8
-1	71	61
3	-34	-13
-3	-27	-13
5	-35	-6
-5	38	-35
7	-25	-7
-7	37	-42
9	-24	6
-9	93	-79
-11	-32	28
-13	-34	7
-15	-34	-26
-17	-33	1
H 1 8		
1	85	-81
-1	124	-114
3	37	-41
-3	99	96
5	-30	-13
-5	190	200
7	-20	14
-7	109	115
-9	90	93
-11	218	-211
-13	142	-135
-15	-34	11
-17	-34	-14
H 1 9		
1	75	67
-1	-34	41
3	63	53
-3	-33	43
-5	-32	34
-7	73	71
-9	169	160
-11	82	73
-13	-34	26
-15	-34	19
-17	-34	-13
-19	-20	19
H 1 10		
1	63	57
-1	132	104
3	-24	11
-3	-35	-1
-5	97	-93
-7	81	-86
-9	139	-137
-11	51	64
-13	85	82
-15	-34	-19
-17	-34	39
-19	-22	-14
H 1 11		
1	49	-33
-1	-34	-17
-3	-34	1
-5	40	28
-7	-34	22
-9	69	-60
-11	52	-44
-13	-34	-8
-15	-34	4
-17	47	43
-19	-22	9
1 12		
-1	74	-49
-3	33	-28
-5	-34	12
-7	-34	8
-9	73	61
-11	-34	-7
-13	-34	-24
-15	61	60
-17	-32	-11
H 1 13		
-3	32	-33
-5	64	-61
-7	81	-71
-9	-34	-21
-11	-34	-3
-13	-35	-15
-15	-34	-18
-17	49	-48
H 1 14		
-5	-26	-2
-7	36	24
-9	-34	15
-11	-34	28
-13	-34	17
-15	70	-67
-17	23	-28
H 1 15		
-7	41	34
-9	-27	12
-11	-30	-9
-13	-30	-10
-15	-27	-7
H 1 16		
-13	37	-36
H 2 0		
0	200	257
2	179	-206
4	152	-152
6	109	-108
8	181	-188
10	77	-75
12	-42	-31
H 2 1		
0	128	123
2	204	-216
-2	47	-49
4	-27	-19
-4	-22	12
6	95	91
-6	134	119
8	-40	-25
-8	65	-69
10	-42	6
-10	-40	-18
12	-38	-3
-12	-43	2
-14	-34	-12
H 2 2		
0	250	-294
2	76	66
-2	-16	17
4	82	71
-4	-21	16
6	95	93
-6	91	-114
8	130	120
-8	-34	31
10	-43	12
-10	-39	-22
12	32	-14
-12	-41	6
-14	55	49
H 2 3		
0	72	61
2	176	182
-2	38	46
4	-34	-15
-4	117	-114
6	75	-54
-6	247	-221
8	-41	3
-8	80	77
10	-39	-10
-10	55	58
-12	-41	10
-14	-43	14
-16	31	-29
H 2 4		
0	233	234
2	62	66
-2	80	73
4	-38	41
-4	26	39
6	-41	3
-6	173	197
8	-43	-5
-8	117	110
10	71	42
-10	202	192
-12	105	109
-14	50	-46
-16	36	-23
H 2 5		
0	50	-36
2	98	-90
-2	44	-36
4	-40	21
-4	101	106
6	70	47
-6	274	286
8	-38	18
-8	-32	-12
-10	70	-59
-12	-40	-19
-14	46	-41
-16	43	39
H 2 6		
0	153	-142
2	57	-66
-2	-32	-3
4	42	-46
-4	203	222
6	-42	-14
-6	43	33
8	-26	-10
-8	-32	12
-10	183	-177
-12	183	-194
-14	-41	12
-16	48	35
H 2 7		
0	72	71
2	74	74
-2	62	62
4	41	-19
-4	-33	-14
6	58	-35
-6	184	-196
-8	-34	9
-10	91	89
-12	-40	28
-14	74	67
-16	-42	-20
-18	32	-33
H 2 8		
0	91	73
2	-42	13
-2	-39	-8
4	-40	-7
-4	226	-228
6	-14	-23
-6	201	-208
-8	189	-190
-10	-38	-12
-12	144	149
-14	-41	18
-16	-42	-13
-18	41	-30
H 2 9		
0	55	-52
2	-42	-25
-2	56	-56
4	44	22
-4	38	-22
-6	118	121
-8	40	39
-10	72	-63
-12	-41	-24
-14	64	-59
-16	-42	13
-18	40	38
H 2 10		
0	54	-17
2	-32	14
-2	60	-38
-4	72	75
-6	133	123
-8	174	165
-10	116	107
-12	54	-56
-14	-42	-11
-16	-42	-13
-18	-31	-12
H 2 11		
0	-35	9
-2	-43	15
-4	-42	13
-6	61	-55
-8	-41	-39
-10	-41	18
-12	-40	1
-14	39	41
-16	-42	-7
-18	41	-39
H 2 12		
-2	91	55
-4	49	41
-6	50	35
-8	-42	-1
-10	45	-29
-12	-42	32
-14	-43	-7
-16	-40	4
-18	41	36
H 2 13		
-4	-34	4
-6	33	25
-8	-43	7
-10	-43	-25
-12	-43	4
-14	-42	-17
-16	-36	3
-18	31	32
H 2 14		
-6	74	-48
-8	84	-58
-10	44	-38
-12	41	-39
-14	36	18
-16	43	34
H 2 15		
-10	34	26
-12	-31	11
-14	-29	7
H 3 0		
1	258	-308
3	-17	-3
5	82	86
7	151	155
9	74	76
11	38	-24
13	25	-22
H 3 1		
1	44	-50
-1	97	-97
3	27	31
-3	34	-22
5	147	-155
-5	217	-219
7	78	-78
-7	52	-55
9	33	-33
-9	29	24
11	39	-33
-11	30	-34
-13	-27	9
H 3 2		
1	63	72
-1	236	280
3	151	-153
-3	117	90
5	145	-149
-5	67	61
7	97	-92
-7	77	-86
9	-34	10
-9	80	-92
11	72	49
-11	-32	-11
-13	-31	-6
-15	-13	4
H 3 3		
1	134	-154
-1	74	-74
3	138	-136
-3	121	-109
5	63	56
-5	181	175
7	31	26
-7	-23	22
9	-30	2
-9	163	-152
-11	51	-39
-13	61	-41
-15	-22	-6
H 3 4		
1	78	86
-1	85	-86
3	140	121
-3	100	-76
5	35	33
-5	157	-146
7	-34	-21
-7	54	-49
9	74	-47
-9	-27	11
-11	-30	-29
-13	-34	9
-15	-26	17
H 3 5		
1	182	175
-1	108	120
3	113	117
-3	137	135
5	40	-21
-5	121	-115
7	-30	-1
-7	82	-77
-9	166	155
-11	84	79
-13	83	69
-15	-29	13
H 3 6		
1	66	-59
-1	62	-58
3	-32	-3
-3	87	-81
5	58	47
-5	32	15
7	48	36
-7	75	66
-9	37	23
-11	60	66
-13	-33	13
-15	-31	-14
-17	-17	-3
H 3 7		
1	93	-91
-1	55	-56
3	-34	-12
-3	41	-31
5	85	46
-5	144	147
-7	179	164
-9	56	-44
-11	-30	-23
-13	47	-45
-15	-32	-11
-17	73	64
H 3 8		
1	-34	-18
-1	-30	25
3	59	-37
-3	126	117
5	-16	-27
-5	129	114
-7	-28	27
-9	-29	13
-11	60	-56
-13	-33	-26
-15	-32	9
-17	-23	-8
H 3 9		
1	-31	-1
-1	-33	1
3	52	-38
-3	-30	-4
-5	123	-122
-7	190	-172
-9	-29	-17
-11	-30	-16
-13	-33	16
-15	-32	18
-17	79	-66
H 3 10		
1	68	39
-1	51	39
-3	-34	-17
-5	77	-61
-7	43	-40
-9	39	-35
-11	32	25
-13	-34	24
-15	-32	-8
-17	-23	16
H 3 11		
-1	-25	0
-3	-32	-14
-5	-34	24
-7	79	67
-9	31	-18
-11	-33	-15
-13	-34	-19
-15	50	-38
-17	43	38
H 3 12		
-1	-12	-31
-3	34	-20
-5	-30	-1
-7	-33	-2
-9	-34	12
-11	-34	-1
-13	-32	1
-15	42	29
-17	-20	0
H 3 13		
-5	-23	12
-7	-28	2
-9	74	53
-11	59	51
-13	32	25
-15	47	33
H 3 14		
-9	-24	19
-11	-25	20
-13	-24	4
-15	42	-34
H 4 0		
0	208	220
2	138	151
4	69	69
6	-34	-18
8	-45	-26
10	-42	6
12	32	21
H 4 1		
0	90	-103
2	97	-109
-2	154	-172
4	111	115
-4	45	45
6	170	167
-6	210	210
8	-45	1
-8	-41	45
10	42	-30
-10	-44	-6
12	-59	-35
-12	77	-41
H 4 2		
0	88	-89
2	-28	18
-2	115	-114
4	76	67
-4	98	-98
6	54	48
-6	-31	-26
8	-43	-4
-8	38	37
10	53	-31
-10	42	39
-12	34	25
H 4 3		
0	49	58
2	46	44
-2	165	155
4	95	-93
-4	48	41
6	82	-67
-6	167	-159
8	45	30
-8	-36	-36
-10	-45	-10
-12	40	23
-14	90	52
H 4 4		
0	112	-128
2	150	-146
-2	58	-57
4	98	-85
-4	-27	-8
6	-42	-16
-6	-30	18
8	-30	13
-8	-35	-23
-10	46	-39
-12	62	-40
-14	60	-35
H 4 5		
0	-34	-24
2	-42	-36
-2	97	-87
4	42	27
-4	81	-58
6	-37	6
-6	119	96
8	-18	-23
-8	-35	-14
-10	-43	-9
-12	-44	6
-14	57	-45
H 4 6		
0	112	111
2	54	50
-2	114	112
4	-40	-6
-4	81	72
6	-27	-18
-6	-33	-10
-8	37	-32
-10	37	-25
-12	-45	-9
-14	-38	2
H 4 7		
0	-46	-5
2	36	26
-2	-41	-2
4	-33	-8
-4	-37	-3
-6	112	-103
-8	-39	9
-10	-43	33
-12	51	-25
-14	-39	20
-16	43	-24
H 4 8		
0	-43	30
2	76	54
-2	-46	-9
-4	37	-33
-6	-41	-2
-8	51	47
-10	87	67
-12	78	55
-14	54	36
-16	43	24
H 4 9		
0	-38	-9
2	44	-23
-2	37	20
-4	37	28
-6	99	87
-8	-45	-7
-10	93	-62
-12	-44	3
-14	-39	-16
-16	59	30
H 4 10		
0	89	-53
-2	54	-43
-4	-43	-15
-6	-44	7
-8	-45	10
-10	-44	-1
-12	-42	-19
-14	-37	-19
-16	34	-20
H 4 11		
-2	-28	0
-4	-37	-18
-6	75	-51
-8	-42	9
-10	116	74
-12	38	28
-14	38	23
-16	35	-24
H 4 12		
-2	-24	12
-6	-34	-2
-8	30	-19
-10	52	-38
-12	54	-36
-14	51	-27
H 4 13		
-8	-29	4
-10	92	-53
-12	54	-33
-14	38	-23
H 5 1		
1	93	97
-1	90	105
3	76	55
-3	91	86
5	64	-56
-5	77	-75
7	-59	3
-7	-58	-34
9	-60	39
-9	-59	32
H 5 3		
1	-73	-22
3	-75	-5
5	-78	53
-5	124	107
-7	105	85

[a] Under each heading is (from left to right) the value of h, $10F_o$, and $10F_c$. A minus sign before F_o indicates a "less than" observation. Atomic scattering factors are from the "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, p 202.

Residual peaks which remained in the final difference electron density map were within the limits 0.36 and -0.33 e$^-$/Å^3. When only B and C were subtracted, the three H atoms bonded to B atoms in the asymmetric unit had peak heights of 0.37, 0.51, and 0.56 e$^-$/Å^3. The ring of electron density associated with disordered or rotating methyl H atoms was reexamined by calculation of a difference map in the plane of disorder, but no preferred positions could be assigned within this ring. High thermal parameters for methyl hydrogens also suggested disorder, but the quality of the data did not seem to us to justify further refinement with a hindered rotation model for these hydrogens. Reasonable temperature factor ellipsoids were found by Waser's method[15] for B and C atoms. The shortest intermolecular H–H contacts are 2.80, 2.93, 2.97, and 2.98 Å. An analysis of the list of observed and calculated structure factors (Table I) revealed no systematic anomalies. Final coordinates and thermal parameters are given in Table II.

Geometric Results

The crystal structure (Figure 1) has the molecular C_2 axis coincident with the crystallographic C_2 axis of the space group C2/c and is composed of equal numbers of enantiomorphic molecules. The molecular structure (Figure 2) has the bond distances and angles given in Table III. The structure confirms the proposal of Williams and Gerhart[1] and differs by distortions of the order of 0.5 Å from the Archimedean antiprism,[2] but there are some indications of a tendency toward an intermediate structure. The C atoms of the B_6C_2 framework are separated from one another and are in the positions expected for greatest stability in the interaction of their atomic cores with the molecular orbitals. This B_6C_2 polyhedron, if idealized to equal atoms and therefore symmetry-equivalent interactions, is quite comparable with the idealized polyhedron of D_{2d} symmetry found for[4] B_8Cl_8 and for[5] $B_8H_8^{2-}$. For example, the 1–2 and 7–8 distances (Figure 2), which pass through the molecular $\bar{4}$ axis in B_8Cl_8 and $B_8H_8^{2-}$, are the shortest in all three of these molecules. Similarly the longest distances in these molecules are between adjacent pairs of the 3,4,5,6 atoms.

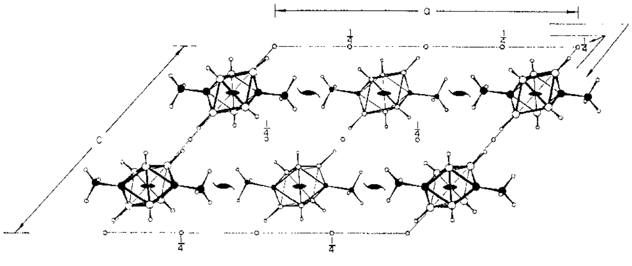

Figure 1.—Crystal structure of $B_6H_6C_2(CH_3)_2$ as seen in the $h0l$ projection.

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(15) J. Waser, *Acta Cryst.*, **8**, 731 (1955).

TABLE II

FINAL ATOMIC PARAMETERS[a]

Atomic Positions in Fractions of a Unit Cell Edge

Atom	x	y	z
C(1)	0.0842 (3)	0.5608 (6)	0.2481 (4)
C(1′)	0.1826 (3)	0.4401 (9)	0.2680 (7)
B(2)	−0.0052 (3)	0.7405 (10)	0.3584 (5)
B(3)	0.0596 (4)	0.5010 (8)	0.3488 (5)
B(5)	0.0827 (3)	0.7961 (8)	0.3237 (5)
H(2′)	−0.0078 (23)	0.8295 (58)	0.4378 (37)
H(3′)	0.1045 (21)	0.3688 (53)	0.4256 (35)
H(5′)	0.1521 (27)	0.9068 (62)	0.3784 (35)
Methyl H(1)[d]	0.1789 (62)	0.2402 (224)	0.2824 (83)
Methyl H(1′)[d]	0.1596 (61)	0.4857 (126)	0.1729 (108)
Methyl H(1″)[d]	0.2530 (46)	0.5048 (74)	0.3370 (64)

Temperature Factors[b] (Anisotropic, ×10⁴)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	90 (3)	216 (16)	116 (5)	13 (11)	149 (6)	33 (14)
C(1′)	94 (3)	440 (22)	195 (8)	36 (15)	217 (8)	57 (25)
B(2)	92 (3)	311 (22)	96 (7)	−2 (14)	109 (9)	−46 (18)
B(3)	80 (3)	267 (18)	99 (5)	45 (12)	116 (6)	60 (18)
B(5)	78 (2)	253 (20)	139 (8)	−44 (12)	110 (8)	−77 (19)

Temperature Factors[c] (Isotropic)

Atom	B
H(2′)	1.9 (0.8)
H(3′)	1.2 (0.6)
H(5′)	2.7 (0.6)
Methyl H(1)[d]	18.7 (2.8)
Methyl H(1′)[d]	14.1 (3.1)
Methyl H(1″)[d]	7.1 (1.4)

[a] Standard deviations are indicated in parentheses, *e.g.*, 0.0842 (3) = 0.0842 ± 0.0003. [b] Anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. [c] The isotropic thermal parameter is of the form $\exp[-B(\sin^2\theta)/\lambda^2]$. [d] Disordered.

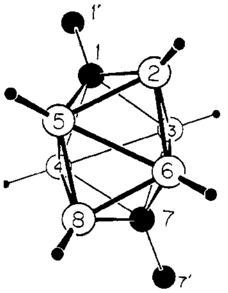

Figure 2.—Molecular structure of $B_6H_6C_2(CH_3)_2$. Boron atoms are indicated by open circles, carbon atoms by large black circles, and hydrogen atoms by small black circles (methyl hydrogens not shown). Atom pairs related by the molecular C_2 axis are C(1)–C(7), C(1′)–C(7′), B(2)–B(8), B(3)–B(4), and B(5)–B(6).

TABLE III

DISTANCES AND ANGLES[a–c]

Bond	Distance, Å	Atoms	Angle, deg
C(1)–C(1′)	1.521 (9)	B(6)–B(3)–C(7)	58.6 (3)
C(1)–B(2)	1.500 (7)	C(1)–B(3)–B(4)	52.4 (3)
C(1)–B(3)	1.695 (8)	C(1)–B(5)–B(2)	50.6 (3)
C(1)–B(4)	1.595 (8)	C(1)–B(5)–B(4)	53.4 (3)
C(1)–B(5)	1.697 (6)	B(2)–B(5)–B(6)	54.4 (3)
B(2)–B(3)	1.772 (8)	B(6)–B(5)–B(8)	59.9 (3)
B(2)–B(5)	1.806 (7)	B(4)–B(5)–B(8)	59.9 (3)
B(2)–B(6)	1.696 (9)	H(1)–C(1′)–H(1′)	114 (6)
B(3)–B(4)	1.894 (7)	H(1)–C(1′)–H(1″)	114 (5)
B(3)–B(6)	1.842 (7)	H(1′)–C(1′)–H(1″)	107 (8)
B(5)–B(6)	1.902 (7)	H(1)–C(1′)–C(1)	110 (6)
C(1′)–H(1)	1.20 (13)	H(1′)–C(1′)–C(1)	99 (6)
C(1′)–H(1′)	1.05 (11)	H(1″)–C(1′)–C(1)	112 (5)
C(1′)–H(1″)	0.91 (7)	C(1′)–C(1)–B(2)	126.4 (5)
B(2)–H(2′)	1.16 (4)	C(1′)–C(1)–B(3)	133.0 (4)
B(3)–H(3′)	1.07 (3)	C(1′)-C(1)–B(4)	119.5 (4)
B(5)–H(5′)	1.03 (4)	C(1′)–C(1)–B(5)	132.0 (4)
		H(2′)–B(2)–C(1)	130 (2)
Atoms	**Angle, deg**		
B(2)–C(1)–B(5)	68.5 (3)	H(2′)–B(2)–B(3)	139 (2)
B(2)–C(1)–B(3)	67.0 (3)	H(2′)–B(2)–B(5)	119 (2)
B(3)–C(1)–B(4)	70.2 (4)	H(2′)–B(2)–B(6)	129 (2)
B(4)–C(1)–B(5)	68.0 (3)	H(3′)–B(3)–B(1)	124 (2)
C(1)–B(2)–B(3)	61.7 (3)	H(3′)–B(3)–B(2)	124 (2)
C(1)–B(2)–B(5)	60.9 (3)	H(3′)–B(3)–B(4)	133 (2)
B(3)–B(2)–B(6)	64.1 (3)	H(3′)–B(3)–B(6)	140 (2)
B(5)–B(2)–B(6)	65.7 (3)	H(3′)–B(3)–C(7)	123 (2)
B(2)–B(3)–B(6)	55.9 (3)	H(5′)–B(5)–C(1)	121 (3)
C(1)–B(3)–C(7)	104.3 (3)	H(5′)–B(5)–B(2)	119 (2)
B(1)–B(3)–B(2)	51.2 (3)	H(5′)–B(5)–B(4)	135 (2)
		H(5′)–B(5)–B(6)	140 (2)
		H(5′)–B(5)–B(8)	126 (3)

[a] Standard deviations are indicated in parentheses, *e.g.*, 114 (6) = 114 ± 6, and were estimated from the errors in x, y, and z for the atoms involved. [b] H(1), H(1′), and H(1″) are methyl hydrogens (not shown in Figure 2). Other hydrogens have the same number (with a prime added) as the boron to which they are bonded. [c] Other bond distances and angles are related by the molecular C_2 axis.

Now, with attention to details of the distances in $B_6H_6C_2(CH_3)_2$ we note that the rather long distance B_3–B_4 of 1.89 ± 0.01 Å is the same as the distances of 1.89 ± 0.04 Å in *m*-$B_{10}H_8Br_2C_2H_2$[16] and 1.89 ± 0.06 Å in *m*-$B_{10}Cl_{10}C_2H_2$[17] for bonds between two B atoms each of which is bonded to two C atoms. The temptation to regard this as a general phenomenon in carboranes must be resisted, however, because a recent study of the $B_7H_7C_2(CH_3)_2$ structure[14] yields a distance of only 1.76 ± 0.03 Å for this same situation. Finally, we note that there appears to be some tendency for the $C_1B_3B_4C_7$ unit and the $B_2B_5B_6B_8$ unit to deviate slightly toward the square shape: the B_3–B_4 and B_5–B_6 distances of 1.89 and 1.90 Å, respectively, are more than 5 standard deviations longer than the 1.84 Å distance for both B_3–B_6 and B_4–B_5. Also, the ratios $(C_1$–$C_7)/(B_3$–$B_4)$ = 1.37 and $(B_2$–$B_8)/(B_5$–$B_6)$ = 1.51 are substantially less than the idealized value of 1.62 which is present in such an idealized polyhedron as an icosahedron.

Molecular Orbital (MO) Studies

Previous studies[18] by molecular orbital methods of the various $B_{10}C_2H_{12}$ and $B_8C_2H_{10}$ isomers led to a simple inductive rule as an aid in predicting positions of electrophilic or nucleophilic substitution on these polyhedral species. Appropriately qualified,[19] the rule is that B atoms in order of increasing positive charge are those bonded to (a) no C atoms, (b) one C atom, and (c) two C atoms, and for a given category (a), (b), or (c) a BH unit bonded to four other BH or CH units is more negative than when it is bonded to five other such units. As applied to $B_6H_6C_2H_2$, this simple rule gives increasing charge in the order B_2 (B_8), B_5 (B_6), and B_3 (B_4), the

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[16] H. A. Beall and W. N. Lipscomb, *Inorg. Chem.*, **6**, 874 (1967).

[17] J. A. Potenza and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1917 (1966).

[18] J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **5**, 1301 (1966).

[19] J. A. Potenza and W. N. Lipscomb, *ibid.*, **5**, 1471 (1966).

TABLE IV

ORTHOGONALIZED ATOMIC COORDINATES IN ÅNGSTRÖMS FOR MO CALCULATIONS

Atom	*x*	*y*	*z*
	$B_6H_6C_2(CH_3)_2$		
C(1)	0.8069	3.3030	2.3714
C(1′)	0.5245	2.5923	2.5619
B(2)	−3.0982	4.3614	3.4254
B(3)	−2.0291	2.9511	3.3335
B(5)	−1.4671	4.6893	3.0939
H(2′)	−3.8348	4.9073	4.2151
H(3′)	−1.9862	2.0423	4.1908
H(5′)	−0.7389	5.4824	3.7299
Methyl H(1)	0.3355	1.5669	2.9018
Methyl H(1′)	1.0670	2.5725	1.6109
Methyl H(1″)	1.1194	3.1262	3.3103
C(7)	−3.4047	3.3030	2.4074
C(7′)	−4.7362	2.5923	2.2170
B(8)	−1.1135	4.3614	1.3535
B(4)	−2.1825	2.9511	1.4453
B(6)	−2.7445	4.6893	1.6849
H(8′)	0.3769	4.9073	0.5638
H(4′)	−2.2254	2.0423	0.5880
H(6′)	−3.4718	5.4824	1.0489
Methyl H(7)	−4.5566	1.5669	1.8776
Methyl H(7′)	−5.2781	2.5725	3.1685
Methyl H(7″)	−5.3305	3.1262	1.4691
	$B_6H_6C_2H_2$[a]		
H(1′)	0.1514	2.7914	2.5085
H(7′)	−4.3630	2.7914	2.2702

[a] The B_6C_2 cage and the B-bonded hydrogens have the same coordinates as in $B_6H_6C_2(CH_3)_2$.

TABLE V

PARAMETERS

A. α's and Exponents

B_4H_4			C_2H_6		
Orbital	Exponent	α	Orbital	Exponent	α
B 1s	4.700	−7.696	C 1s	5.700	−11.277
B 2s	1.300	−1.084	C 2s	1.625	−1.449
B 2p	1.300	−0.323	C 2p	1.625	−0.365
H 1s	1.200	−0.465	H 1s	1.200	−0.501

B. Mulliken Approximation Coefficients[a]

One-center	
K_{1s-2s}	0.6535

Two-center	
K_{1s-1s}	1.000
K_{1s-2s}	0.8094
K_{1s-2p}	0.8227
K_{1s-H}	0.8116

Two-center	
K_{2s-2s}	1.0917
K_{2s-2p}	1.1998
K_{2s-H}	1.0202
$K_{2p\sigma-2p\sigma}$	1.1350
$K_{2p\pi-2p\pi}$	1.0444
K_{2p-H}	1.0047
K_{H-H}	0.9115

C. Zero-Overlap Coefficient

K^{ZO} 0.229

[a] Taken from SCF calculation of B_4H_4 (see ref 14).

TABLE VI

TOTAL FRAMEWORK CHARGES[a]

	B(3)–H(3′)	B(5)–H(5′)	B(2)–H(2′)
$B_6H_6C_2(CH_3)_2$			
Extended Hückel	0.36	0.11	0.06
NEMO I (K^{ZO} = 0)	0.07	−0.16	−0.04
NEMO I (K^{ZO} = 0.229)	0.09	−0.20	−0.07
NEMO II	−0.30	−0.30	−0.25
$B_6H_6C_2H_2$			
Extended Hückel	0.38	0.12	0.09
NEMO I (K^{ZO} = 0)	0.10	−0.12	0.02
NEMO I (K^{ZO} = 0.229)	0.13	−0.14	−0.01
NEMO II	−0.22	−0.22	−0.06

[a] In units of +1 electron.

TABLE VII

CUMULATIVE FRAMEWORK POPULATIONS[a,b]

$B_6H_6C_2(CH_3)_2$				$B_6H_6C_2H_2$			
ε, au	B(3)–H(3′)	B(5)–H(5′)	B(2)–H(2′)	ε, au	B(3)–H(3′)	B(5)–H(5′)	B(2)–H(2′)
Extended Hückel (HFMO)							
−0.40	0.04	0.26	0.41	−0.41	0.05	0.29	0.42
−0.41	0.37	0.57	0.74	−0.42	0.37	0.61	0.76
−0.44	0.38	1.04	0.96	−0.44	0.37	1.13	1.01
−0.44	0.56	1.13	1.10	−0.45	0.55	1.22	1.15
−0.46	0.76	1.24	1.23	−0.47	0.75	1.37	1.28
Extended Hückel (LEMO)							
−0.27	0.13	0.06	0.52	−0.27	0.13	0.07	0.54
−0.13	0.37	0.50	0.72	−0.13	0.38	0.51	0.75
−0.12	0.74	0.80	0.83	−0.12	0.77	0.81	0.86
−0.06	0.87	1.00	1.22	−0.05	0.93	1.00	1.25
−0.02	1.32	1.33	1.37	−0.02	1.36	1.35	1.42
NEMO I (K^{ZO} = 0) (HFMO)							
−0.30	0.06	0.18	0.32	−0.35	0.08	0.28	0.37
−0.38	0.26	0.28	0.53	−0.40	0.16	0.67	0.63
−0.38	0.30	0.69	0.76	−0.42	0.40	0.78	1.05
−0.40	0.48	0.75	1.04	−0.43	0.83	1.11	1.17
−0.42	0.91	1.05	1.12	−0.44	1.25	1.39	1.24
NEMO I (K^{ZO} = 0) (LEMO)							
−0.07	0.11	0.08	0.44	−0.08	0.11	0.09	0.51
0.20	0.40	0.46	0.58	0.20	0.44	0.47	0.65
0.23	0.67	0.84	0.74	0.24	0.75	0.86	0.83
0.38	0.80	0.98	1.03	0.39	1.08	1.16	0.98
0.43	1.21	1.22	1.20	0.45	1.27	1.24	1.39
NEMO I (K^{ZO} = 0.229) (HFMO)							
−0.31	0.07	0.20	0.31	−0.36	0.11	0.29	0.36
−0.39	0.27	0.30	0.56	−0.41	0.24	0.55	0.63
−0.39	0.31	0.65	0.80	−0.42	0.35	0.68	1.08
−0.41	0.46	0.79	1.10	−0.44	0.48	1.25	1.30
−0.44	0.90	1.13	1.15	−0.44	1.08	1.53	1.38
NEMO I (K^{ZO} = 0.229) (LEMO)							
−0.07	0.12	0.07	0.45	−0.08	0.12	0.08	0.51
0.20	0.42	0.44	0.62	0.21	0.46	0.44	0.67
0.24	0.67	0.82	0.79	0.25	0.76	0.83	0.87
0.38	0.83	1.00	1.02	0.38	1.15	1.18	0.98
0.42	1.22	1.22	1.24	0.45	1.35	1.26	1.41
NEMO II (HFMO)							
−0.15	0.07	0.11	0.42	−0.20	0.04	0.09	0.31
−0.32	0.34	0.32	0.62	−0.33	0.29	0.41	0.66
−0.32	0.45	0.68	0.96	−0.35	0.57	0.62	0.84
−0.33	0.76	0.78	1.24	−0.37	0.74	0.93	1.07
−0.36	1.04	1.15	1.28	−0.40	1.02	1.17	1.19
NEMO II (LEMO)							
0.18	0.02	0.04	0.28	0.11	0.02	0.16	0.27
0.18	0.07	0.12	0.64	0.15	0.12	0.23	0.86
0.18	0.10	0.18	1.02	0.16	0.15	0.29	1.18
0.29	0.19	0.31	1.04	0.44	0.38	0.46	1.24
0.35	0.32	0.51	1.08	0.45	0.49	0.59	1.33

[a] Abbreviations: HFMO, highest filled molecular orbital; LEMO, lowest empty molecular orbital; ε, one-electron energy in au; NEMO, nonempirical molecular orbital method I[22] or II;[23] K^{ZO}, zero-overlap constant.[22] Under the heading for each molecule are listed the cumulative framework (B–H unit) populations (CFP) and eigenvalues (in au) for the three methods of calculation. Cumulative framework populations (in au) are listed beginning with the HFMO and going down in energy and beginning with the LEMO and going up in energy. [b] The CFP are sums over MO's of subtotal gross atomic populations. For terminology see R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

last most positive. In correlation[18] of these simple rules with molecular orbital theories, our earlier studies[19] have suggested that the cumulative charges in the highest filled molecular orbitals (HFMO) and the lowest empty molecular orbitals (LEMO) are more relevant to reactivity in simple reactions than are the total atomic charges.

Molecular orbital calculations were made on $B_6H_6C_2(CH_3)_2$ and $B_6H_6C_2H_2$ by three methods. Experimental values of this X-ray study were employed for the B_6C_2 cage, and idealized parameters [B(apex)–H = 1.21 Å, B(equatorial)–H = 1.25 Å, C–H = 1.095 Å, ∠HCH = 109.5°] were taken for H atoms. Atomic coordinates (Table IV) are given in an orthogonal system. The first MO method is the extended Hückel approach of Hoffmann and Lipscomb,[20] in which 1s electrons are taken as part of a nonpolarizable core. Diagonal matrix elements are negatives of the valence-state ionization potentials (15.36 eV for B 2s, 8.63 eV for B 2p, 21.40 eV for C 2s, 11.40 eV for C 2p, and 13.61 eV for H 1s), and the value of $K = 1.75$ was assumed for the constant in the Wolfsberg–Helmholz approximation for off-diagonal elements.[21] The second MO method[22] is nonempirical (NEMO) in the sense that matrix elements (Table V) are taken from self-consistent field (SCF) calculations on small related molecules (B_4H_4[23] and C_2H_6[24]). The 1s electrons are included specifically, and overlap and kinetic energy integrals are calculated exactly. In the NEMO I method, the off-diagonal potential energy elements are calculated from an approximation by Mulliken suitably modified by a factor K which is determined[22] from the SCF results on model compounds (Table V). The value of K^{ZO} in the equation for the one-center 2s–2p matrix elements was taken as 0.229 au (from B_4H_4) in one calculation, and as zero in a second calculation in order to test the sensitivity to assumptions concerning zero-overlap elements. The third method[25] (NEMO II) is similar to NEMO I, except that all (both zero- and nonzero-overlap) matrix elements are computed from

$$H_{pq} = T_{pq} + C_{pq}\sum_r S_{pr}S_{qr}(\alpha_r - T_{rr})$$

where T is kinetic energy, the α_r are diagonal SCF elements from the model compounds, the C_{pq} also are obtained from model compounds, and the sum extends over all basis functions. All of these methods are rotationally invariant in the senses described in the original papers.

Framework charges (Table VI) are sums over both B and H for each type of BH unit. The considerable variation among the three theories suggests that further development in the directions of adjustments of parameters for charge transfer and of calibration from SCF results on more closely related molecules would be reasonable lines for further study. The cumulative charges in the most polarizable filled and lowest unfilled molecular orbitals show a far greater internal consistency (Table VII) among these different molecular orbital methods. The trend (most negative) B_2 (B_8), B_5 (B_6), and B_3 (B_4) (most positive) for the filled orbitals is consistent as one adds electrons from lower energies for at least the first several orbitals, and we suggest that the order of electrophilic attack might be found to correspond to these predictions when experimental studies of substituted carboranes of this type become available.

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[20] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).

[21] (a) R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962); (b) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

[22] F. P. Boer, M. D. Newton, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2361 (1966); see also ref 16.

[23] W. E. Palke and W. N. Lipscomb, *J. Chem. Phys.*, **45**, 3945 (1966).

[24] W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2384 (1966).

[25] D. B. Boyd and W. N. Lipscomb, to be submitted for publication.