Weak-field matrix elements

Γ_1 representation

$(9|8) = (\sqrt{2}/5)(-2Q_2 + Q_1 + Q_0)$
$(8|3) = (-\sqrt{210}/5)\alpha$
$(9|4) = (2\sqrt{6})\alpha$

Γ_4 representation

$(6|5) = (\sqrt{14}/70)(2Q_2 - 2Q_0 + 10B_{2-2})$

Γ_5 representation

$(3|1) = (-\sqrt{42}/7)B_{2-2}$

Strong-field matrix elements

Γ_1 representation

$(9|8) = -2\alpha - 3F_2 + 15F_4$
$(5|4) = 2i\alpha$
$(7|4) = \sqrt{6}\alpha$

$(8|4) = -\sqrt{2}\alpha$
$(9|4) = \sqrt{2}\alpha$

Γ_4 representation

$(3|1) = \sqrt{2}\alpha$
$(4|2) = -\sqrt{2}\alpha$

Γ_5 representation

$(10|9) = 6F_2 - 30F_4$

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Comments on the Inductive Rule in Carboranes. Charge Distributions in $B_8C_2H_{10}$ Isomers

Sir:

All known positions of halogen substitution[1] on *o*-$B_{10}C_2H_{12}$ follow a simple inductive rule[2] relating to ground-state charge distribution in this carborane: substitution occurs first on those B atoms which are furthest from C. More sophisticated molecular orbital studies[1,3] of *o*-$B_{10}C_2H_{12}$ give the same predictions, if ambiguities in total charges are resolved by favoring the more polarizable charges. Thus, this apparent domination of the transition state by the ground-state charge distribution of the parent carborane may be useful as a starting point for studies of more complex reactions, where steric, multiple-step kinetic and other effects may also be important. Here, we wish to record (Table I) both molecular orbital charge distributions and a simple development of the inductive rule for the various isomers (Figure 1) of $B_8C_2H_{10}$, in view of the earlier success with *o*-$B_{10}C_2H_{12}$ and of the recent preparation in quantity of two isomers[4] of this formerly mass spectroscopic[5] species.

Calculations by the nonempirical molecular orbital method,[6] based upon self-consistent field (minimum basis set) molecular parameters from B_2H_6 and C_2H_6, confirm the order of charges B-9 (−0.25), B-4 (−0.03), B-5 (−0.02), and B-2 (0.15) predicted earlier in Hückel calculations on *m*-$B_{10}C_2H_{12}$. Application of the simple inductive rule shows that in *m*-$B_{10}C_2H_{12}$ only atoms 9 and 10 are bonded to no C atoms, while atoms 2 and 3 are bonded to two C atoms. Atoms of types 4 and 5 are each bonded to one C atom, but 4 is slightly closer than 5 to the other C atom; however, this simple rule may neglect an undiscovered *trans* effect of C-7 on B-5, for which no evidence presently exists. It is to be noted that MO theory gives four most negative B atoms in *o*-$B_{10}C_2H_{12}$, but only two (9 and 10) in *m*-$B_{10}C_2H_{12}$.

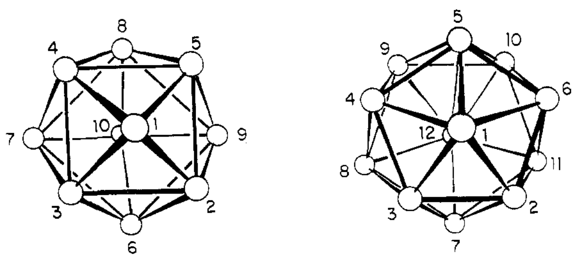

Figure 1.—Numbering convention for the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ polyhedra.

TABLE I

FRAMEWORK (BH UNIT) CHARGES FOR $B_8C_2H_{10}$ ISOMERS[a,e]

NEMO[c]	EH[d]	I[a]	NEMO	EH	I
1,2[b] Isomer			1,6 Isomer		
3 (0.18)	3 (0.14)	3	2 (0.14)	2 (0.17)	2
4 (−0.12)	4 (0.04)	4	4 (0.00)	7 (0.04)	4
6 (−0.03)	6 (0.03)	6	7 (−0.04)	4 (0.03)	7
7 (−0.21)	7 (−0.11)	7	10 (−0.16)	10 (0.02)	10
10 (−0.38)	10 (−0.14)	10	8 (−0.24)	8 (−0.11)	8
2,3 Isomer			2,4 Isomer		
6 (0.12)	6 (0.14)	6	3 (0.12)	3 (0.16)	3
1 (0.03)	1 (0.11)	1	1 (−0.01)	1 (0.14)	1
7 (−0.03)	4 (0.04)	4	6 (−0.04)	6 (0.02)	6
4 (−0.06)	7 (0.02)	7	10 (−0.41)	10 (−0.20)	10
8 (−0.20)	8 (−0.10)	8			
10 (−0.43)	10 (−0.19)	10			
2,6 Isomer			2,7 Isomer		
3 (0.12)	3 (0.13)	3	3 (0.11)	3 (0.16)	3
5 (−0.03)	5 (0.04)	5	5 (−0.04)	5 (0.02)	5
1 (−0.17)	1 (−0.03)	1	4 (−0.07)	4 (0.01)	1
4 (−0.23)	4 (−0.12)	4	1 (−0.18)	1 (−0.03)	4

[a] Total charges are given in parentheses. The inductive order *I* probably favors the higher energy, more polarizable molecular orbitals. The criteria are that B's bonded to two C's are most positive, those bonded to no C's are most negative, and, where these factors are equal, the apex B is more negative than equatorial B. Differences in charges less than about 0.05 are not regarded as significant. [b] Positions of C atoms identify the isomers. [c] Nonempirical molecular orbital method.[6] [d] Extended Hückel method.[3] [e] All calculations here are based upon the geometry of the $B_{10}H_{10}^{2-}$ ion. Similar NEMO calculations for all puckered geometries in which C–C distances and B–C distances are appropriately shorter than B–B distances indicate no change in the order of atom types, except for interchange of B-1 and B-6 of the 2,4 isomer.

Predictions for the $B_8C_2H_{10}$ isomers (Table I) are somewhat more risky than for the icosahedral carboranes, because of the important difference in polyhedral coordination of the two types of positions (Figure 1). For example, in the $B_{10}H_{10}^{2-}$ ion[7] the B_5 units of C_{4v} symmetry have a B (apex)–B (basal) distance of

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(1) J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, *J. Am. Chem. Soc.*, **88**, 628 (1966).

(2) W. N. Lipscomb, American Chemical Society Western Regional Meeting, Nov 18–20, 1965, Los Angeles, Calif. See also H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

(3) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962); **37**, 520 (1962). In the present calculations, H atoms are included explicitly; see *ibid.*, **37**, 2872 (1962).

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

(5) I. Shapiro, *Talanta*, **11**, 211 (1964).

(6) M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **53**, 1089 (1965); also M. D. Newton, F. P. Boer, and W. N. Lipscomb, to be published.

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

1.76 A, but the B (basal)–B (basal) distance of 1.86 A and the interatomic contacts of 1.81 A between B_5 units may impose smaller steric restrictions on groups entering in equatorial regions, as compared with the apical regions. Moreover, the two apex B atoms in $B_{10}H_{10}^{2-}$ are more negative than are the other B atoms. With these qualifications and differences in mind, we then place the B atoms in order of increasing charge as those bonded to (a) no C atoms, (b) one C atom, or (c) two C atoms, but, where these factors are the same, the apical position is taken as more negative than the equatorial position. Only in one not very significant instance (positions 1 and 4 of the 2,7 isomer) does this rule change the order of charges assigned by MO methods.

Finally, we suggest that the ^{11}B nuclear magnetic resonance spectra of these isomers may follow the order found[6] for o-$B_{10}C_2H_{12}$, but suitably modified by the low-field position of the apical B atoms relative to that of the equatorial atoms. The only available experimental evidence, which can be interpreted as a probable 1:5:2 distribution of peaks for the one known unsymmetrical isomer of $B_8C_2H_{10}$, is compatible with either the 1,2 or the 1,6 assignment for C atom positions.

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