

Sequential Substitution Reactions on B₁₀H₁₀-2 and B₁₂H₁₂-2

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In the electric-dipole transition calculation matrix elements enter as the product

$$(f^x\psi || C^{[1]} || \psi_1)(\psi_1 || C^{[k]} || f^x\psi'). \quad (\text{II-5})$$

Therefore, these matrix elements, expressed in the form of equation (II-4), enter into the calculation to form reduced matrix elements of $U^{[l]}$ between the almost closed shell f^{14-x} states. With the aid of the relationship

for reduced matrix elements of $U^{[l]}$ (l even)

$$(f^x\psi || U^{[l]} || f^x\psi') = -(f^{14-x}\psi || U^{[l]} || f^{14-x}\psi'),$$

and inspecting the phase of Eq. (II-4) according to the product of expression (II-5), we find that the angular part from the nd^94f^{x+1} interaction is of the same form and phase as that from the $4f^{x-1}nd$ interaction.

Sequential Substitution Reactions on $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$

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Predictions are made of the order of sequential electrophilic substitution on the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ polyhedral ions. Simple LCAO—MO calculations are used and resonance and inductive effects are treated separately.

IN comparison with boron hydrides and their ions the closed polyhedral $B_{10}H_{10}^{-2}$ of D_{4d} symmetry^{1,2} and $B_{12}H_{12}^{-2}$ of icosahedral symmetry³ are so extraordinarily stable that they can be regarded as pseudoaromatic in character. They have also been reported⁴ to form a very interesting series of substitution derivatives, as yet incompletely identified, of the type $B_{10}H_{10-n}X_n^{-2}$ where $0 \leq n \leq 10$, and $X = F, Cl, Br, \text{ or } I$. This indication that a large number of sequentially substituted derivatives can be prepared has led us to make predictions of reactivities of the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ ions in an effort to include resonance and inductive effects in unsubstituted and substituted polyhedral ions as formulated by an extension of our LCAO—MO descriptions⁵ of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$. We are encouraged by the initial prediction, verified by experiment^{2,4} that apparent electrophilic attack by D^+ appears to produce preferential exchange in $B_{10}H_{10}^{-2}$ at the two apices, which are more negatively charged than the eight other B atoms.

Formulated in terms of a specific example, the question investigated here is the following: Suppose that attack by a halogen is electrophilic and that successive

TABLE I. Atom-atom polarizabilities in 10^{-3} units of electronic charge/eV.

$B_{12}H_{12}^{-2}$ in											
-52	0	0	11	11	0	0	11	11	0	11	0
0	-52	11	0	0	11	11	0	0	11	0	11
0	11	-52	0	0	11	11	0	11	0	11	0
11	0	0	-52	11	0	0	11	0	11	0	11
11	0	0	11	-52	0	11	0	0	11	11	0
0	11	11	0	0	-52	0	11	11	0	0	11
0	11	11	0	11	0	-52	0	0	11	11	0
11	0	0	11	0	11	0	-52	11	0	0	11
11	0	11	0	0	11	0	11	-52	0	11	0
0	11	0	11	11	0	11	0	0	-52	0	11
11	0	11	0	11	0	11	0	11	0	-52	0
0	11	0	11	0	11	0	11	0	11	0	-52

$B_{10}H_{10}^{-2}$ surface										
-179	24	40	40	40	40	4	4	4	4	4
24	-179	4	4	4	4	40	40	40	40	40
35	4	-121	17	3	17	20	20	0	0	0
35	4	17	-121	17	3	20	0	0	0	20
35	4	3	17	-121	17	0	0	20	20	0
35	4	17	3	17	-121	0	20	20	0	0
4	35	20	20	0	0	-121	17	3	17	3
4	35	20	0	0	0	20	17	-121	17	3
4	35	0	0	20	20	3	17	-121	17	17
4	35	0	20	20	0	17	3	17	-121	17

$B_{10}H_{10}^{-2}$ in										
-87	0	12	12	12	0	0	0	0	0	0
0	-87	0	0	0	0	12	12	12	12	12
21	1	-80	15	-1	15	19	19	0	0	0
21	1	15	-80	15	-1	19	0	0	0	19
21	1	-1	15	-80	15	0	0	0	19	19
21	1	15	-1	15	-80	0	19	19	0	0
1	21	19	19	0	0	-80	15	-1	15	15
1	21	19	0	0	19	15	-80	15	-1	15
1	21	0	0	19	19	-1	15	-80	15	15
1	21	0	19	19	0	15	-1	15	-80	15

¹ W. N. Lipscomb, M. F. Hawthorne, and A. R. Pitochelli, *J. Am. Chem. Soc.* **81**, 5833 (1959).

² A. Kaczmarczyk, R. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci.* **48**, 729 (1962).

³ J. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.* **82**, 4427 (1960).

⁴ W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muettterties, *J. Am. Chem. Soc.* **84**, 1056 (1962).

⁵ R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.* (to be published).

TABLE II. Pathways for electrophilic substitution on $B_{12}H_{12}^{-2}$, $B_{10}H_{10}^{-2}$.

Pathway												Multiplicity	Weight
$B_{12}H_{12}^{-2}$													
1	3	10	6	7	12	4	9	5	2	8	11	133 $\frac{1}{3}$	aaa
1	3	10	6	7	4	11	8	2	5	9	12	133 $\frac{1}{3}$	aaba
1	3	10	6	7	4	8	11	2	5	9	12	133 $\frac{1}{3}$	aabb
1	3	10	6	4	7	11	8	2	5	9	12	100	aba
1	3	10	6	4	7	8	11	2	5	9	12	100	abb
1	2	3	5	8	10	11	9	12	7	4	6	48	baa
1	2	3	5	8	10	6	11	4	7	9	12	48	bab
1	2	3	4	5	8	9	12	7	6	10	11	4	bbaaa
1	2	3	4	5	8	9	7	12	6	10	11	8	bbaab
1	2	3	4	5	8	6	10	11	7	9	12	4	bbaba
1	2	3	4	5	8	6	7	9	12	10	11	1	bbabba
1	2	3	4	5	8	6	7	9	10	11	12	1	bbabbb
1	2	3	4	5	6	7	9	12	8	10	11	4	bbba
1	2	3	4	5	6	7	8	9	12	10	11	1	bbbba
1	2	3	4	5	6	7	8	9	10	11	12	1	bbbb
												720	
$B_{10}H_{10}^{-2}$													
	1	2	3	5	7	9	4	6	8	10		1	aa
	1	2	3	5	7	9	4	8	6	10		1	ab
	1	2	3	9	4	5	8	7	6	10		2	ba
	1	2	3	9	4	8	5	7	6	10		2	bb
												6	

halogen atoms attack sequentially; what can be said theoretically about the positions that successive halogen atoms substitute on the boron framework? In order to answer this question we first perform an LCAO-MO calculation of the $3N$ type on the B_N framework, choosing the three hybrids as one, mostly s , pointing *in* and two, pure p , directed along the polyhedron surface. As a result of a Mulliken population analysis we then obtain a charge distribution for the molecule. We then assume that electrophilic attack will be most likely to take place at the most negative site of the polyhedron, this being an apex in $B_{10}H_{10}^{-2}$ [Q (apex) = -0.535 , Q (equatorial) = -0.116],⁶ or any position in $B_{12}H_{12}^{-2}$. Once the substituent is one we inquire about the new charge distribution. A more complex calculation is then avoided by simulating the effect on the substituted boron. For this purpose the required atom-atom polarizabilities, i.e., changes in charge with respect to variation of an *in* or *surface* α have been

computed. These polarizabilities are given in Table I, except for $\partial q/\partial \alpha_{\text{surface}}$ for $B_{12}H_{12}^{-2}$ which have already been written down elsewhere.⁵

We now make the following association with aromatic reaction theory. We presume we have substituents which act as sources or sinks of electronic charge by either a resonance R or an inductive I mechanism. The resonance interaction is probably predominant, stabilizing structures in which substituents have π orbitals which are available for extension of polyhedral delocalization. We simulate a resonance effect by a change in the *surface* Coulomb integral of the substituted site, an inductive effect by a change in the corresponding *in* Coulomb integral. For $+R$, $+I$ the substituent is a source of electrons; this effect is approximated by making the substituted site positive, i.e., $\Delta\alpha > 0$. For $-R$, $-I$ the substituent is a sink and we therefore make the substituted site negative by setting $\Delta\alpha < 0$.

The first clear result is that in apex substituted $B_{10}H_9X^{-2}$ electrophilic substitution should proceed at the other apex regardless of the nature of the substituent. Subsequently there will be eight equivalent sites left. From this point on we consider each molecule separately.

⁶ The parameters used in the calculation were $\alpha(2s) = -15.36$ eV, $\alpha(2p) = -8.63$ eV, $K = -23$ eV for $B_{12}H_{12}^{-2}$, $K = -20$ eV for $B_{10}H_{10}^{-2}$. The reaction pathways are insensitive to small changes in K .

TABLE III. Isomer ratios in $B_{12}X_nH_{12-x}^{-2}$ and $B_{10}X_nH_{10-x}^{-2}$.

n	$B_{12}X_nH_{12-x}^{-2}$	
	isomer type	relative frequency
2	1, 3	$600a$
	1, 2	$120b$
3	1, 3, 10	$600a$
	1, 2, 3	$120b$
4	1, 3, 10, 6	$600a$
	1, 2, 3, 5	$96ba$
	1, 2, 3, 4	$24b^2$
5	1, 3, 10, 6, 7	$400a^2$
	1, 3, 10, 6, 4	$296ab$
	1, 2, 3, 4, 5	$24b^2$
6	1, 3, 10, 6, 7, 12	$133\frac{1}{3}a^2$
	1, 3, 10, 6, 7, 4	$266 \cdot a^2b + 296ab$
	1, 2, 3, 4, 5, 8	$18b^2a$
	1, 2, 3, 4, 5, 6	$6b^2$
7	1, 3, 10, 6, 7, 12, 4	$133\frac{1}{3}(a^3 + a^3b) + 148ba^2$
	1, 3, 10, 6, 7, 4, 8	$133\frac{1}{3}a^2b^2 + 148ab^2$
	1, 2, 3, 4, 5, 8, 9	$12b^2a^2$
	1, 2, 3, 4, 5, 6, 7	$6(b^3a + b^3)$
8	1, 3, 4, 6, 7, 9, 10, 12	$133\frac{1}{3}(a^3 + a^3b + a^3b^2) + 148ab^2 + 100a^2b$
	1, 2, 3, 5, 8, 9, 10, 11	$48a^2b + 4b^2a^3$
	1, 2, 3, 4, 5, 7, 8, 9	$12b^3a^2 + 4b^3a$
	1, 2, 3, 4, 5, 6, 7, 8	$2(b^4a + b^4)$
9	1, 3, 4, 5, 6, 7, 9, 10, 12	$133\frac{1}{3}(a^3 + a^3b + a^3b^2) + 148(a^2b + b^2a) + 12b^3a^2 + 4(b^2a^3 + b^3a)$
	1, 2, 3, 4, 5, 6, 7, 8, 9	$2(b^4a + b^4)$
10	1, 2, 3, 4, 5, 6, 7, 9, 10, 12	$133\frac{1}{3}(a^3 + a^3b + a^3b^2) + 148(a^2b + b^2a) + 4(b^2a^3 + b^3a) + 12b^3a^2 + b^4a^2 + b^4a$
	1, 2, 3, 4, 5, 6, 7, 8, 9, 10	$b^5 + b^5a$
$B_{10}X_nH_{10-x}^{-2}$		
4	1, 2, 3, 4	$2a$
	1, 2, 3, 8	$4b$
5	1, 2, 3, 5, 7	$2a$
	1, 2, 3, 9, 4	$4b$
6	1, 2, 3, 5, 7, 9	$2a$
	1, 2, 3, 9, 4, 5	$2ba$
	1, 2, 3, 9, 4, 8	$2b^2$
7	1, 2, 3, 5, 7, 9, 4	$2a$
	1, 2, 3, 9, 4, 5, 8	$2(ba + b^2)$
8	1, 2, 3, 4, 5, 6, 7, 9	a^2
	1, 2, 3, 4, 5, 7, 8, 9	$3ab + 2b^2$

Case I. $+R, +I; \Delta\alpha_i > 0$ $B_{12}H_{12}^{-2}$ (Fig. 1)

Neighboring atoms become most negative and substitution propagates around first substituted site. If site 1 is attacked first, the next substituent should go on

at position 4, 5, 8, 9, or 11. If it goes at 4, positions 8, 10, 11 succumb next, etc. The notation we will use to indicate the process is a sequence of 12 numbers which give, in order from left to right, one symmetry equivalent pathway for sequential attack at the enumerated sites. Thus for the case discussed above, the sequence is 1, 4, 5, 8, 9, 11, 3, 6, 7, 2, 10, 12.

 $B_{10}H_{10}^{-2}$ (Fig. 1)

As stated above, the sequence is apex 1, apex 2, followed by 3, 7, 4, 8, 6, 9, 5, 10.

Case II. $-R, -I; \Delta\alpha_i < 0$ $B_{12}H_{12}^{-2}$

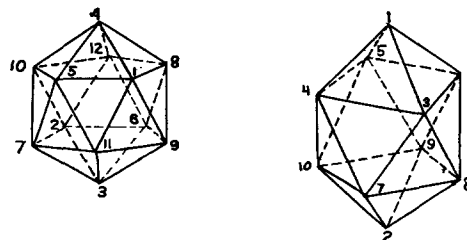
Here there are 15 symmetry nonequivalent pathways to fill the polyhedron, listed in Table II; relative multiplicities of the paths are also given. Enantiomeric pathways are not distinguished. For the $-R$ the matter is complicated by the presence often of two possible pathways of similar but unequal probabilities. The source of the difficulty is that for $-R$ if, say, $\Delta\alpha_1 < 0$ then the most negative sites are 3, 6, 7, 10, 12 (a), but site 2 (b) is almost as negative and may react also. The final column of Table II gives a sequence of a 's and b 's which indicate how many "decisions" of this type are confronted in following a given path. To find the multiplicity of a given route being traveled, the geometric multiplicity must be multiplied by an appropriate weighting factor $a^n b^m$ where $a/2$ is the probability of choosing a when confronted with one a and one b ; $b = 2 - a$, $1 \leq a \leq 2$. For $-I$, $a = b = 1$, and the criterion of distinguishability of pathways is purely geometrical.

 $B_{10}H_{10}^{-2}$

For $-R$ one sequence is predominant; apex 1, apex 2, followed by 3, 9, 4, 8, 5, 10, 6, 7. For $-I$ an ambiguity similar to the one for $-R$ $B_{12}H_{12}^{-2}$ arises. There are four alternate pathways, which are listed, along with their multiplicities and weights in Table II.

From the above considerations we may thus attempt to make a prediction of the distribution of geometrical isomers for a given n in $B_N H_{N-n} X_n^{-2}$.

In criticism of the above treatment there are factors related to the validity of our basic assumptions which

FIG. 1. Numbering convention for $B_{12}H_{12}^{-2}$ and $B_{10}H_{10}^{-2}$.

may require an extension of this relatively simple theory, if experimental results so demand: (a) an assumption, such as sequential instead of coordinated attack by halogen, may have to be modified, or, (b) there may be competing rearrangements of the framework, such as those discussed by Kaczmarczyk, Dobrott, and Lipscomb² for $B_{10}H_{10}^{-2}$. For example, a motion of only about 0.35 Å of B atoms will convert an icosahedron into a cube octahedron. Two such consecutive transformations may lead to isomerization of 1,4- $B_{12}X_2H_{10}^{-2}$ to 1,10- $B_{12}X_2H_{10}^{-2}$. If the physical conditions, e.g., high temperature, favor such motions of the framework, complete randomization may result, but there is some evidence^{2,4} that these isomerization reactions may be relatively slow, at least for $B_{10}H_{10}^{-2}$.

Nevertheless, we think it worthwhile to compute expected isomer ratios for $B_NX_nH_{N-n}^{-2}$. For $+R$, $+I$ only one sequence is predicted for both $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$, thus no direct isomerism. For $-R$ there is also one predominant sequence for $B_{10}H_{10}^{-2}$ but a variety of pathways for $B_{12}H_{12}^{-2}$. Expected ratios are 1,3- $B_{12}X_2H_{10}^{-2}/1,2-B_{10}X_2H_{10}^{-2}=5 a/b$. Other ratios are

given in Table III. For $+I$, the $B_{12}H_{12}^{-2}$ ratios are the same as for $-R$, but with $a=b=1$. The $B_{10}H_{10}^{-2}-I$ ratios are also given in Table III. Presumably in the reaction with halogens the $+R$ effect is most important; however, the most interesting results should arise from $-R$ and $-I$ substituents.

It is, in our opinion, too early to extend these results into a more generally valid substituent theory of these polyhedral molecules in a way comparable with the present theory of aromatic molecules. However, such an extension is clearly possible, and will be made if these preliminary theoretical findings are closely verified by experiment. The preliminary comparisons on $B_{10}H_{10}^{-2}$ are at least encouraging, and hence the area of polyhedral molecules may form an ideal test for LCAO-MO theories of reactivity.

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Microwave Spectrum of Methyl difluoroarsine*

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The spectrum of CH_3AsF_2 was investigated over the range 10–33 kMc/sec. Three Q branches ($K_c=5\rightarrow4$, $6\rightarrow5$, $7\rightarrow6$) and two R transitions ($J=2\rightarrow3$, $K_c=2\rightarrow3$; $J=3\rightarrow4$, $K_c=3\rightarrow4$) were fitted by a Hamiltonian which included terms for over-all rotation, internal rotation, nuclear quadrupole coupling, and centrifugal distortion. The internal rotation perturbation calculations were carried in some cases to the fifth order. The reciprocal moments of inertia are $A=5414.49\pm0.15$ Mc/sec, $B=5381.28\pm0.15$ Mc/sec, and $C=3871.88\pm0.15$ Mc/sec. The b axis is perpendicular to the plane of symmetry. The height of the internal rotation barrier (assumed to be sinusoidal) is 463 ± 6 cm⁻¹. The quadrupole coupling constants for As⁷⁵ are $eQq_{cc}=-220\pm4$ Mc/sec and $\eta_0=(q_{bb}-q_{aa})/q_{cc}=-1.20\pm0.05$. The structure, barrier height, and quadrupole coupling constants are discussed briefly.

INTRODUCTION

BARRIERS restricting internal rotation about single bonds are not well understood.^{1,2} The accumulation of pertinent data for various series of mole-

cules might assist in the identification of variables which determine barrier parameters. When the present work was started, no barrier data for rotation about As-C bonds were available, and since that time, the only example in this category reported has been the study of $As(CH_3)_3$ by Lide.³

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¹ E. B. Wilson, Jr., "The Problem of Barriers to Internal Rotation in Molecules," in *Advances in Chemical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. II.

² C. C. Lin and J. D. Swalen, *Revs. Modern Phys.* **31**, 841 (1959).

³ D. R. Lide, Jr., *Spectrochim. Acta.* **473** (1959).