in C_{2v} and C_2 and vibronically-allowed along z in C_{4v}. The $d_{x^2-y^2} \rightarrow d_{xy}$ transition is allowed along z in C_2 symmetry and can only occur through vibronic coupling in C_{2v} and C_{4v}. Thus, if the $d_{x^2-y^2} \rightarrow d_{z^2}$ transition accounts for the 27,000 cm.$^{-1}$ band, the 11,000 cm.$^{-1}$ band can be assigned as the $d_{x^2-y^2} \rightarrow d_{xy}$ transition. If the 27,000 cm.$^{-1}$ band (which does seem high for a copper d–d transition) does not correspond to $d_{x^2-y^2} \rightarrow d_{z^2}$, then the 11,000 cm.$^{-1}$ band may correspond to either or both the $d_{x^2-y^2} \rightarrow d_{x^2}$ and the $d_{x^2-y^2} \rightarrow d_{xy}$ transitions.

Hansen and Ballhausen[9] have recently reviewed the theoretical aspects of this problem and have proposed a new interpretation of the electronic spectrum of copper(II) acetate monohydrate. References to previous theoretical work may be found in their paper.

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[9] A. E. Hansen and C. J. Ballhausen, to be published.

Contribution from Boeing Scientific Research
Laboratories, Seattle, Washington

An Extended Hückel Theory Investigation of the Electronic Structure of 2,4-Diiododecaborane(12), $B_{10}H_{12}I_2$

By Emmett B. Moore, Jr.

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We have carried out an extended Hückel theory (EHT) molecular orbital (MO) investigation[1] of the electronic structure of $B_{10}H_{12}I_2$ in order to predict some of its physical properties, as has been done for $B_{10}H_{14}$ in similar studies,[2-4] and specifically to determine theoretically the polarizations of the first allowed electronic transitions in order to compare them with the experimental polarizations observed by Smallwood and Eberhardt.[5] For this purpose we have used Hoffmann's IBM 7094 EHT program.[4,6] This program computes molecular orbital coefficients and energies for up to 68 atomic orbitals given the atomic positions of up to 20 hydrogen atoms and up to 17 atoms of principal quantum number 2. The basis atomic orbitals are 1s Slater orbitals for hydrogen and 2s, $2p_x$, $2p_y$, and $2p_z$ Slater orbitals for the other atoms. The program computes all ss, sσ, $\sigma\sigma$, and $\pi\pi$ type overlap integrals and resolves them into appropriate integrals between basis orbitals. The program also allows one to use whatever values for the Slater exponents and Coulomb integrals one wishes and allows several choices for resonance integrals. We report here results for two alternate choices of the resonance integral: $H_{ij} = KS_{ij}$ with a value of -18.0 e.v. for K and $H_{ij} = 0.5K'(H_{ii} + H_{jj})S_{ij}$ with a value[7] of 1.75 for K'. The program also computes the population matrix and charge distribution in the molecule.

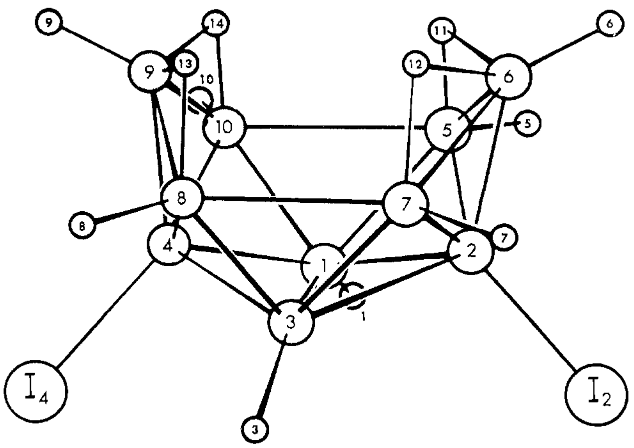

Figure 1.—$B_{10}H_{12}I_2$. The boron and hydrogen atoms are numbered conventionally and each iodine atom takes the number of its nearest neighbor boron atom. The twofold (z) axis is perpendicular to the line B-1–B-3.

To obtain the positions of the atoms in $B_{10}H_{12}I_2$ we synthesized the $B_{10}H_{12}I_2$ results of Schaeffer[8] and the $B_{10}H_{14}$ results of Moore, Dickerson, and Lipscomb.[9] Synthesis is necessary because Schaeffer's X-ray work located only the iodine atoms with respect to the boron framework and not the boron atoms individually in the $B_{10}H_{12}I_2$ crystal. We forced the atomic positions into C_{2v} symmetry because the molecules have nearly this symmetry in the crystal, even though the space groups[8,10] require only C_2 symmetry. The structure of $B_{10}H_{12}I_2$ is derived from $B_{10}H_{14}$ by replacing hydrogen atoms 2 and 4 by iodine atoms (Figure 1).

For the hydrogen 1s, boron 2s and 2p, and iodine 5p Coulomb integrals we chose Mulliken's values[11] of the valence state ionization energies, which are -13.60, -15.36, -8.63, and -11.16 e.v., respectively. For the iodine 5s Coulomb integral we chose -21.09 e.v., which is consistent with Mulliken's other values. For the hydrogen and boron Slater exponents we used 1.0 and 1.3, respectively. Since the presently available EHT program does not handle atoms of principal quantum number 5, we varied the iodine Slater exponent and found that 1.3 gave values for the overlap integrals involving iodine orbitals which are good approximations to, but somewhat less than, the correct values.

Results

Our results are summarized in Table I for both $B_{10}H_{14}$ and $B_{10}H_{12}I_2$. Both molecules have stable, closed-

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[1] For a more complete discussion, see E. B. Moore, Jr., "The Electronic Structure of $B_{10}H_{12}I_2$," Boeing Scientific Research Laboratories Document D1-82-0352, March 1964.

[2] E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

[3] E. B. Moore, Jr., *ibid.*, **37**, 675 (1962).

[4] R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962).

[5] E. Smallwood and W. H. Eberhardt, private communication.

[6] R. Hoffmann's extended Hückel theory computer program is available from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind.

[7] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[8] R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2726 (1957).

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[10] J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

[11] R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).

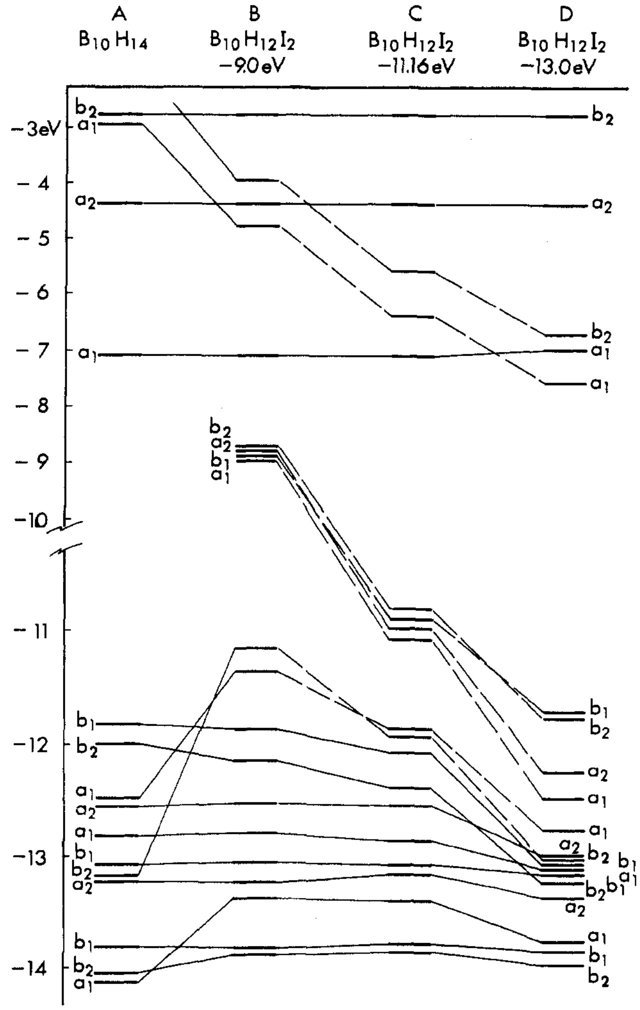

Figure 2.—Comparison of energy levels in $B_{10}H_{14}$ and $B_{10}H_{12}I_2$ for $K = -18.0$ e.v. As the iodine 5p Coulomb integral is made more negative (values at the top of the graph), the iodine and boron–hydrogen framework levels mix and the correlation becomes less clear-cut, which explains the apparent violation of the noncrossing rule between columns C and D. Note the change in scale at -10 e.v. and that other energy levels lie outside the range of the graph. The energy level diagram for $K' = 1.75$ is qualitatively the same.

TABLE I

RESULTS FOR TWO CHOICES OF THE RESONANCE INTEGRAL[a]

		$B_{10}H_{14}$		$B_{10}H_{12}I_2$	
K, e.v.		-18.0		-18.0	
Ionization energy, e.v.		11.87		10.80	
First four electronic transitions, e.v.		4.83	$B_1\,x$	3.73	$B_2\,y$
		4.94	$B_1\,y$	3.86	$B_1\,x$
		5.36	$A_1\,z$	3.91	A_2
		5.41	A_2	4.02	$A_1\,z$
Dipole moment, D.		3.85		4.58	
Charge distribution, e	H-1	-0.22		-0.22	
	H-2	-0.24			
	H-5	-0.26		-0.26	
	H-6	-0.25		-0.25	
	H-11	-0.03		-0.03	
	B-1	0.22		0.23	
	B-2	0.13		0.06	
	B-5	0.26		0.26	
	B-6	0.41		0.41	
	I–2			-0.18	
K'		1.75		1.75	
Ionization energy, e.v.		10.85		10.38	
First four electronic transtions, e.v.		3.69	$B_1\,x$	3.23	$B_2\,y$
		3.76	$B_2\,y$	3.37	$B_1\,x$
		4.10	$A_1\,z$	3.53	A_2
		4.15	A_2	3.80	$A_1\,z$
Dipole moment, D.		6.60		10.44	
Charge distribution, e	H-1	-0.18		-0.18	
	H-2	-0.20			
	H-5	-0.21		-0.20	
	H-6	-0.20		-0.20	
	H-11	0.03		0.03	
	B-1	0.09		0.08	
	B-2	0.05		0.26	
	B-5	0.21		0.21	
	B-6	0.37		0.36	
	I-2			-0.39	

[a] The ionization energies are assumed to be the energies of the highest filled MO's, and the dipole moments are calculated on the basis of the charge being centered on the atom in question.

shell electronic configurations. The introduction of two iodine atoms has virtually no effect on the $B_{10}H_{14}$ charge distribution except for boron atoms 2 and 4. This can also be seen in the energy level correlation diagram (Figure 2) which we arrived at by careful inspection of the MO coefficients. The 14 available electrons carried by the two iodine atoms go into two iodine 5s inner-shell MO's (at -21 e.v., not shown), into two bonding boron–iodine MO's, and into four nonbonding iodine 5p MO's. The electrons added to the structure do not appreciably disturb the original $B_{10}H_{14}$ energy levels with the exception of the boron–iodine bonding and antibonding levels. This fact presumably correlates with the fact that the iodine atoms disturb only the charges on boron atoms 2 and 4.

No value of the ionization energy of $B_{10}H_{12}I_2$ has yet been published. However our calculated values are less than the calculated values of the ionization energy of $B_{10}H_{14}$, so we feel confident in predicting that the ionization energy of $B_{10}H_{12}I_2$, when it is measured, will be found to be 0.5 to 1.0 e.v. lower than the ionization energy of $B_{10}H_{14}$. Our calculated values of the ionization energy of $B_{10}H_{14}$, 11.9 and 10.9 e.v., may be compared with the experimental[12–14] values of 11.0, 10.7, and 10.26 e.v.

In each of the $B_{10}H_{14}$ calculations the order of the boron atom charges is the same as the now well-known experimental order[15]: negative B_2, $B_4 < B_1$, $B_3 < B_5$, B_7, B_8, $B_{10} < B_6$, B_9 positive. This order is not changed in $B_{10}H_{12}I_2$ with the exception of borons 2 and 4, as already discussed. The bridge hydrogen atoms are all more positively charged than the terminal hydrogens in both $B_{10}H_{14}$ and $B_{10}H_{12}I_2$. This is in apparent agree-

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(12) J. L. Margrave, *J. Chem. Phys.*, **32**, 1889 (1960).

(13) R. M. Reese, private communication in ref. 12.

(14) J. J. Kaufman, W. S. Koski, L. J. Kuhns, and R. W. Law, *J. Am. Chem. Soc.*, **84**, 4198 (1962).

(15) I. Dunstan, R. L. Williams, and N. J. Blay, *J. Chem. Soc.*, 5012 (1960).

ment with the fact[16] that it is the bridge hydrogen atoms which are the acidic hydrogens in $B_{10}H_{14}$, although an elucidation of the exact nature of the $B_{10}H_{13}^-$ anion may show that the abstracted bridge hydrogen atom does not necessarily carry a positive charge in neutral $B_{10}H_{14}$. The calculated order of hydrogen charges is not in agreement with the fact that in B_2H_6 the bridge hydrogens are found both theoretically[17] and experimentally[18] to be more negatively charged than the terminal hydrogens.

No value of the dipole moment of $B_{10}H_{12}I_2$ has yet been published, however our calculated value of 3.85 D. for $B_{10}H_{14}$ ($K = -18.00$ e.v.) is just outside the experimental[19] range of 3.17 to 3.62 D. In each of the calculations the dipole moment of $B_{10}H_{12}I_2$ is larger than the corresponding $B_{10}H_{14}$ dipole moment. Thus we predict that the dipole moment of $B_{10}H_{12}I_2$, when it is measured, will be found to be larger than that of $B_{10}H_{14}$, possibly around 4.6 D.

The difference in magnitude between the corresponding charges and dipole moments of the two sets of results serve to warn us that the calculation of these quantities by EHT is not yet well understood and deserves further attention. It is apparent, however, that the use of the equation for the resonance integral involving K' rather than K tends to pile up negative charge on atoms which have the more negative Coulomb integrals.

In Table I we give in order the energy of excitation (which is to be regarded as strictly qualitative), the symmetry of the excited total wave function, and the polarization, if allowed, of the first four electronic transitions for each calculation. The symmetry of the excited state is the direct product of the symmetry of the energy level from which the electron is excited and the symmetry of the energy level to which the electron is excited. Both molecules have the totally symmetric A_1 ground state. In each $B_{10}H_{14}$ calculation the first two allowed transitions are polarized perpendicular to the twofold axis of the molecule and the third is polarized parallel to the twofold axis, which is in agreement with the experimental results of Haaland and Eberhardt.[20]

In $B_{10}H_{12}I_2$ the four transitions of lowest energy are from nonbonding iodine MO's to the boron framework a_1 MO. Again the first two allowed transitions are polarized perpendicular to the twofold axis of the molecule and the third is polarized parallel to the twofold axis. These theoretical polarizations are in agreement with the experimental observations of Smallwood and Eberhardt.[5]

Discussion

We also carried out the same calculations on models of $B_{10}H_{14}$ and $B_{10}H_{12}I_2$ from which all hydrogen atoms were omitted.[1] The neglect of hydrogen atoms does not materially affect the results, and in either case all of the interesting effects appear to be occurring at, or because of, the iodine–boron bond.

Finally we varied the iodine 5p Coulomb integral to see what effect this would have on the results. Making this integral more negative has the effects of increasing the molecular ionization energy, of increasing the negative charge on the iodines, at the expense of the adjacent boron atoms, of increasing the dipole moment, and of lowering the iodine energy levels rather sharply (Figure 2) and of lowering the original $B_{10}H_{14}$ energy levels somewhat less.

Acknowledgments.—We wish to thank Professor William H. Eberhardt for suggesting this problem, for his continued interest, and for his discussion of his own results. We are grateful to Professor M. F. Hawthorne for his discussion of the charge distribution in $B_{10}H_{14}$ and to Dr. Roald Hoffmann for making his extended Hückel theory program available to the Quantum Chemistry Program Exchange. We also wish to acknowledge the use of The Boeing Company's IBM 1620 and 7094 computers and the computing help of Dale Speakes, Gordon Thomas, Fran Brown, and William Cook.

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[16] See the following and the references therein for a discussion of the acidic nature of the bridge hydrogens: M. F. Hawthorne, *Advan. Inorg. Chem. Radiochem.*, **5**, 307 (1963).

[17] W. C. Hamilton, *Proc. Roy. Soc.* (London), **A235**, 395 (1956).

[18] R. A. Ogg, *J. Chem. Phys.*, **22**, 1933 (1954).

[19] R. Bottei and A. W. Laubengayer, *J. Phys. Chem.*, **66**, 1449 (1962).

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Volumes of Activation of Some Electron-Transfer Reactions

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The question of whether electron transfer proceeds through an inner or outer-sphere mechanism has constituted a central theme in recent studies of electron-transfer reactions of metal ions.[1–3] In a number of favorable cases, direct determination of the mechanism is possible, examples being the reduction of various pentaamminecobalt(III) complexes, $Co(NH_3)_5X^{2+}$ (X = Br, Cl, N_3, etc.) by Cr^{2+}(aq)[4] or by $Co(CN)_5{}^{3-}$,[2] which yield the substitution-inert products $Cr(H_2O)_5X^{2+}$ and $Co(CN)_5X^{3-}$, respectively, on oxidation, thereby providing proof of an inner-sphere mechanism. Frequently, however (*e.g.*, in the corresponding reactions involving Eu^{2+}, V^{2+}, or Fe^{2+} as reductants,[1,5,6] which yield substitution-labile products on oxidation), the necessary conditions of substitution inertness of reac-

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[1] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

[2] J. P. Candlin, J. Halpern, and S. Nakamura, *ibid.*, **85**, 2517 (1963).

[3] J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964).

[4] H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

[5] A. Haim, *ibid.*, **85**, 1016 (1963); *ibid.*, **86**, 2352 (1964).

[6] J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).