

spectively, for the sake of simplicity. From eq 16, it can be predicted that when  $Z_{i_1}C_{ir_1}^0C_{jr_1}^0$  has the same sign as that of  $Z_{i_2}C_{ir_2}^0C_{jr_2}^0$ , the absolute value of  $d_{ij}$  increases in magnitude by the four-center interaction, in comparison with that by a two-center interaction, to lead to a larger change in chemical reactivity. On the other hand, when two terms have different signs, the reverse is true to lead to a smaller change in chemical reactivity. Similar features are expected for multicenter interactions for dynamic orbital mixing as well as combinations of static and dynamic orbital mixings. Consequently, catalytic activity for multicenter interactions should depend upon the symmetry of molecular orbitals, which is in harmony with the Woodward-Hoffmann rule<sup>6-8</sup> of chemical reactivity already proven to be very useful for the prediction of catalytic activities.<sup>13</sup> However, it should be worthwhile to note that our general rules can also be applied to the system lacking molecular symmetry. This conclusion has led us to the probability that catalytic action of enzymatic reaction can be illustrated by orbital mixings from signs of molecular orbitals concerned, since multicenter interactions are usually found in many enzymatic reactions. Studies on applications of orbital mixing to enzymatic reactions are now in progress and will be reported in the near future.

**Acknowledgment.** We would like to acknowledge the continuing encouragement and stimulating discussions of Professors C. Nagata and T. Tsuruta.

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## Substituent Effects on Subjacent Orbital Control

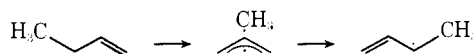
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**Abstract:** One electron MO theory indicates that subjacent orbital control is important in nonpolar 1,3 sigmatropic shifts but not in highly polar 1,3 shifts. This conclusion is supported by Mulliken-Wolfsberg-Helmholz, SCF-MO-INDO, and ab initio (STO-4G) calculations.

The Woodward-Hoffmann theory<sup>2a</sup> of sigmatropic reactions has been the first systematic attempt to rationalize and predict the stereochemical outcome of these migrations. Recently, the limitations of one-determinant MO theory were pointed out and new guidelines for the prediction of the stereochemistry of pericyclic reactions in which the two interacting molecules or fragments bear substituents of varying electronic nature were proposed on the basis of a qualitative configuration interaction (CI) treatment.<sup>2b-d</sup> In another recent development, Berson and Salem discussed "subjacent orbital control" as an important electronic factor which determines the stereochemistry of sigmatropic shifts.<sup>3</sup> This treatment was carried out within the confines of one-determinant MO theory and the model reaction examined was the 1,3 sigmatropic shift of a methyl group

across an allyl framework, e.g., a nonpolar sigmatropic shift.

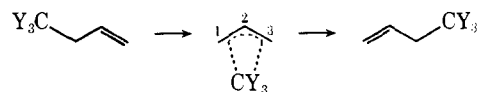


In our laboratories we have been interested in the effect of substituents upon the rates, stereoselectivity, and regioselectivity of pericyclic reactions. Thus, it became of interest to study the effect of substituents upon "subjacent orbital control" in 1,3 sigmatropic shifts, the reactions examined by Berson and Salem in their original publication. In this work we provide a general theoretical argument supported by Mulliken-Wolfsberg-Helmholtz (MWH) empirical,<sup>4</sup> SCF-INDO semiempirical,<sup>5</sup> and ab initio (STO-4G basis set)<sup>6</sup> calculations which show that "subjacent orbital con-

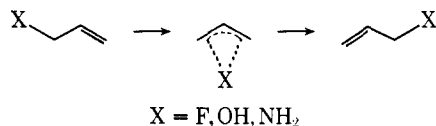
trol" is indeed present in nonpolar systems, as argued by Berson and Salem, but absent in highly polar systems.

### Theory

The transition state of a 1,3 sigmatropic shift involves the interaction between the migrating group, formally represented by the trisubstituted carbon radical  $Y_3C\cdot$ , and the migration framework, which can be formally represented by the allyl radical. The transition state of the reaction can be



conveniently designated as polar or nonpolar depending upon the relative ionization potential of the two interacting groups. A nonpolar transition state obtains when both the migrating group and the migration framework have comparable ionization potentials. This occurs when the allyl migration framework is unsubstituted and the migrating group is a simple alkyl or when *both* the migrating group and the migration framework are substituted by electron donating or electron accepting groups. A typical 1,3 polar sigmatropic shift occurs when the allyl migration framework is substituted by electron donor groups, e.g., has a low ionization potential, and the migrating group is substituted by electron acceptors, e.g., has a high ionization potential. Other typical polar 1,3 sigmatropic shifts obtain when the migration framework is an unsubstituted allyl radical and the migrating group or atom is of high electronegativity.



We first examine the case of a typical nonpolar 1,3 sigmatropic shift, e.g., the migration of a methyl group across the allyl migration framework. Figure 1 shows the interaction diagram for the suprafacial methyl migration with retention. In Hückel MO (HMO) theory the energies of the singly occupied NBMO's of methyl and allyl radicals are equal to  $\alpha$ , the coulomb integral of the carbon atom, and the energies of the  $\psi_1$  and  $\psi_3$  MO's of the allyl system are equally spaced above and below the energies of the allyl NBMO,  $\psi_2$ . As a result, the  $p_z$  AO of carbon interacts appreciably with both  $\psi_1$  and  $\psi_3$ . This results in a net two-electron stabilization and bonding along the union sites since the lowest state configuration of the suprafacial transition state involves placing two electrons in a pair of degenerate NBMO's and two electrons in a BMO of the transition state complex, e.g., the transition state of a nonpolar suprafacial shift involves pericyclic bonding. The same conclusions are reached if instead of HMO energies one uses SCF-MO energies or ionization potential data. However, in these latter instances, the  $\psi_1$ - $p_z$  interaction turns out to be greater than the  $\psi_3$ - $p_z$  interaction, and, as a result, the energy ordering of the various MO's of the total system depicted in Figure 1 changes to  $\epsilon(\omega_4) > \epsilon(\omega_3) > \epsilon(\omega_2) > \epsilon(\omega_1)$ .

Let us now turn to the case of a highly polar 1,3 shift. A representative example is that of the 1,3 migration of fluorine. The interaction diagram for this situation is qualitatively depicted in Figure 2. It can be seen that the dominant orbital interaction is between the  $p_z$  AO of fluorine and the  $\psi_1$  of the allyl molecular orbitals and results in zero net pericyclic bonding, since a BMO and an ABMO of the transition state complex are both doubly occupied. Clearly, "subjacent orbital control" is not a factor, as it was in the nonpolar case, in stabilizing the transition state of a 1,3 highly polar sigmatropic shift.

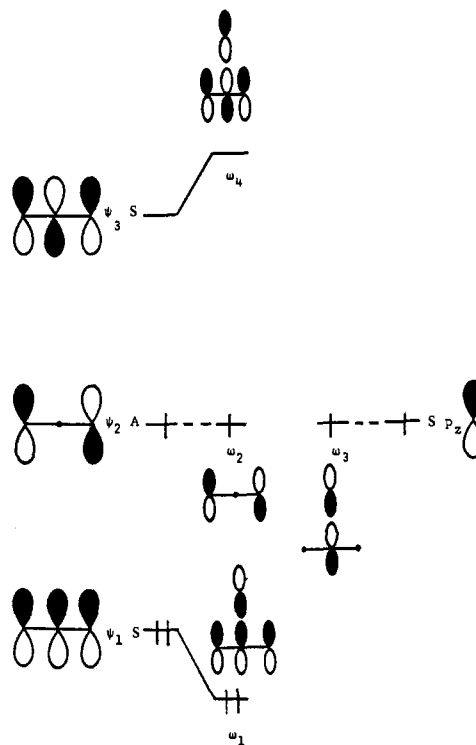


Figure 1. Interaction diagram for a *nonpolar* suprafacial 1,3 sigmatropic shift with retention.

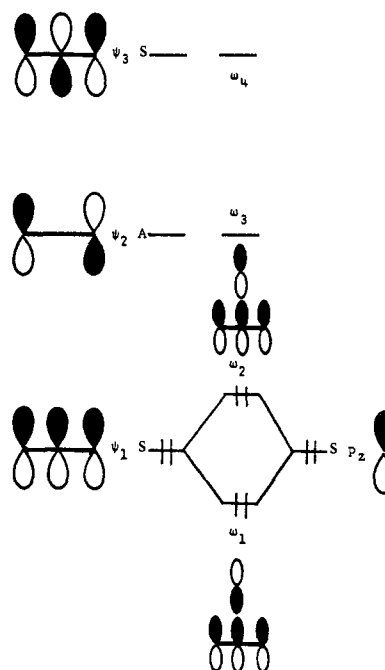


Figure 2. Interaction diagram for a *polar* suprafacial 1,3 sigmatropic shift with retention.

The theoretical analysis presented above neglects overlap but, as we shall see, explicit inclusion of overlap will not alter qualitatively our conclusions.

### Results

In order to test the validity of the predictions obtained from one-electron perturbation theory, we have used molecular orbital calculations at three levels of sophistication. The model transition state consisted of an unsubstituted allyl migration framework with the migrating group placed above the midpoint of the distance between  $C_1$  and  $C_3$  of the allyl rad-

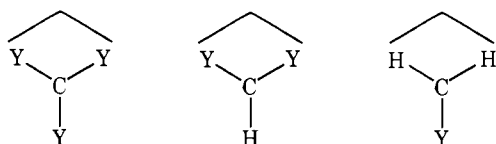
Table I. Overlap Populations for a 1,3 Suprafacial Sigmatropic Shift from a Mulliken–Wolfsberg–Helmholtz (MWH) Calculation

Migrating group	Ionization potential of migrating group, eV	$d^a$	$C_1(p_z)-X(p_z)$ $p\sigma$ overlap population	$C_2(p_z)-X(p_z)$ $p\sigma$ overlap population
CH <sub>3</sub>	10.0500	1.90	0.03137	0.10981
OH	11.4437	1.90	0.01506	0.04172
F	18.8313	1.90	-0.00446	-0.00560
CH <sub>2</sub> (CN)	11.0996	1.90	0.02909	0.10465
CH(CN) <sub>2</sub>	11.7608	1.90	0.02359	0.10169
C(CN) <sub>3</sub>	12.2351	1.90	0.02055	0.09611

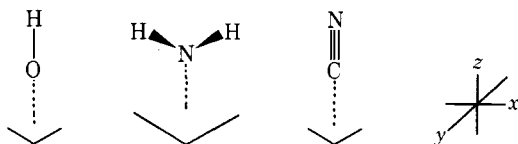
<sup>a</sup> Distance (in ångströms) of migrating group above allyl radical framework.



ical. The assumed geometries for the migration of  $\cdot CY_3$ ,  $\cdot CHY_2$ , and  $\cdot CH_2Y$  groups across the allyl migration frame-

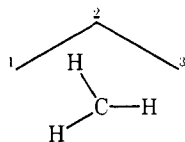


work are shown below. In all cases the formal radicals  $\cdot CY_3$ ,  $\cdot CHY_2$ , and  $\cdot CH_2Y$  as well as the formal allyl radical were assumed to be planar and standard bond lengths and bond angles were utilized in the calculations. The assumed geometries for the migrations of electronegative groups such as  $\cdot OH$ ,  $\cdot NH_2$ , and  $\cdot CN$  are shown below. The  $\angle HNH$



bond angle was taken to be the standard tetrahedral angle and standard bond lengths were utilized in the calculations.

The MWH and the SCF-INDO calculations were carried out for the geometries discussed above utilizing standard bond angles and bond lengths. On the other hand, the ab initio calculations utilizing an STO-4G basis set were performed after optimizing the geometry of the allyl framework and assuming a planar formal methyl radical. For the purpose of obtaining rapid convergence, an unsymmetrical geometry for the migration of the methyl group was chosen and it is shown below.



The results of the MWH calculations are shown in Table I.<sup>7</sup> The distance, in ångströms, of the migrating group above the allyl radical framework was taken to be a 20% extension of a covalent carbon-carbon single bond. It is useful, for comparative purposes, to group the migrating radicals into two types. The first category of migrating groups is characterized by a  $p_z$  AO coefficient of unity, or near unity (e.g.,  $\cdot OH$ ), in its NBMO and is represented by the first three migrating groups in Table I. As can be seen, the  $C_1(p_z)-X(p_z)$   $p\sigma$  overlap population decreases as the ionization potential of the migrating group<sup>8</sup> increases as predicted by the theoretical model. An extremely polar 1,3 sigmatropic shift ( $X = F$ ) is calculated to involve no pericyclic

bonding as shown by the negative  $C_1(p_z)-X(p_z)$  and  $C_2(p_z)-X(p_z)$  overlap populations. This arises because the MWH calculations include overlap explicitly and upon inclusion of overlap the ABMO in Figure 2 becomes more antibonding than the BMO is bonding and, therefore, the bond orders  $C_1(p_z)-X(p_z)$  and  $C_2(p_z)-X(p_z)$  are expected to be negative.

Migrating groups of the type  $\cdot CY_3$ , where Y is an electron withdrawing group, constitute the second section of Table I. As the migrating group is substituted by an increasing number of electron acceptor groups, pericyclic bonding progressively decreases. This is primarily a result of two factors. The first factor is the increase in the ionization potential of the migrating group, as shown in Table I. The second factor is the progressive decrease of the magnitude of the eigenvector of the carbon  $2p_z$  AO of the non-bonding MO of the migrating group down the series. Since the total energy of a system in any Hückel-type calculation equals the sum of the occupied one-electron spin orbitals, one can calculate the stabilization energy due to the interaction of the  $\pi$  MO's of the allyl framework and the  $\pi$  MO's of the migrating group. This stabilization energy will be denoted as  $SE^\pi$  and can be defined as follows

$$SE^\pi = E^\pi(\text{allyl} + M) - E^\pi(\text{allyl}\cdot) - E^\pi(M\cdot) \quad (1)$$

$$SE^{\pi'} = E^\pi(\text{allyl} + M) - E^\pi(\text{allyl}^+) - E^\pi(M^-) \quad (2)$$

if  $\epsilon_{\text{HOMO}}(\text{allyl}\cdot) < \epsilon_{\text{HOMO}}(M\cdot)$

$$SE^{\pi'} = E^\pi(\text{allyl} + M) - E^\pi(\text{allyl}^-) - E^\pi(M^+) \quad (2')$$

if  $\epsilon_{\text{HOMO}}(\text{allyl}\cdot) > \epsilon_{\text{HOMO}}(M\cdot)$ . According to eq 1, one compares the total system to the isolated formal radicals, while, according to eq 2 and 2', one compares the total system to the isolated ions. In terms of Figures 1 and 2,  $E^\pi(\text{allyl} + M)$  is the sum of the energies of the occupied  $\omega_n$  spin MO's,  $E^\pi(\text{allyl}\cdot)$  is the sum of the energy of the occupied  $\psi_n$  spin MO's,  $E^\pi(M\cdot)$  is the sum of the energy of the occupied  $\pi$  spin MO's of M, and  $\epsilon_{\text{HOMO}}$  denotes the energy of the highest occupied MO. An ambiguity exists as to which of the three equations one should use in order to calculate the stabilization energies. However, this problem is easily resolved by selecting the electronic configurations of the isolated allyl and isolated M which yield the lowest possible energy. For example, for the case of methyl migration, we have

$$E^\pi(\text{allyl}\cdot) + E^\pi(\text{CH}_3\cdot) = -45.8439 \text{ eV} \quad (3)$$

$$E^\pi(\text{allyl}^\oplus) + E^\pi(\text{CH}_3^\ominus) = -36.1787 \text{ eV} \quad (4)$$

As a result,  $SE$  should be calculated by reference to eq 3. The calculated stabilization energies for representative systems are shown in Table IV. The results clearly support the view that the greater the "pericyclicity" of the reaction, as revealed by the appropriate overlap populations, the greater the stabilization of the migration. Thus, it appears that the validity of the general theoretical argument is well secured.

SCF-INDO calculations of a variety of model transition states are displayed in Table II. Again we divide the table into comparable groups as was done in the MWH calculation. The distance of the migrating group above the allyl radical framework in the first section of Table I is equal to a 30% extension of the standard C-X bond while a 20% extension of the standard carbon-carbon single bond was assumed in other cases. As was the case in the MWH calculation, we observe a decrease in pericyclic bonding as the ionization potential of the migrating group increases. For the extremely polar case of  $X = F$ , we find that the  $C_1(p_z)-X(p_z)$   $p\sigma$  overlap population is negative but the  $C_2(p_z)-X(p_z)$   $p\sigma$  overlap population is positive. This occurs because, although overlap is not included in the INDO calculations, which are done within the zero differential overlap

Table II. Overlap Populations for a 1,3 Suprafacial Sigmatropic Shift from an INDO Calculation

Migrating group	$d^a$	$C_1(p_z) - X(p_z)$	$C_2(p_z) - X(p_z)$
		$p\sigma$ overlap population	$p\sigma$ overlap population
CH <sub>3</sub>	2.03	0.03955	0.09739
CN	1.93	0.03049	0.08369
NH <sub>2</sub>	1.94	0.02961	0.08136
OH	1.89	0.00100	0.01508
F	1.80	-0.00313	0.06078
CH <sub>2</sub> (CHO)	1.90	0.03529	0.10253
C(CHO) <sub>3</sub>	1.90	0.03422	0.08756
CH <sub>2</sub> CN	1.90	0.05543	0.07647
C(CN) <sub>3</sub>	1.90	0.05150	0.06760

<sup>a</sup> Distance (in ångströms) of migrating group above allyl radical framework.

(ZDO) approximation, there is unsymmetrical mixing between the  $F(p_z)$ AO and the BMO of the allyl system which results in an overall bonding  $p\sigma$  overlap population rather than a zero overlap population. Substituent effects resulting in a decrease in pericyclic bonding when the migrating group is of the  $\cdot CY_n$  type can be attributed to the same reasons as the ones previously discussed. In general, the INDO calculations, which are carried out within the zero differential overlap (ZDO) approximation, are able to reproduce the trends in the bonding between migrating groups of varied electronic natures and an allyl migration framework but overemphasize the bonding between the two interacting fragments because of the neglect of overlap. This point becomes clear by comparison of the data in Tables I, II, and III.

Ab initio calculations using a STO-4G basis set also show that highly polar 1,3 sigmatropic shifts are unaffected by subjacent orbital stabilization. Representative nonpolar and polar transition states were calculated and the results, shown in Table III, emphasize again the conclusion that pericyclic bonding exists only in nonpolar 1,3 shifts and not in the case of a highly polar 1,3 sigmatropic migration. Calculations of  $SE^\pi$  and  $SE^{\pi'}$  cannot be carried out in the case of SCF-INDO and SCF ab initio calculations because in SCF theory the total energy of a system is not a simple sum of one-electron orbital energies. Thus, in these calculations we have restricted our attention to overlap populations.

### Conclusion

We are now prepared to contrast the conclusions of the CI approach and the "subjacent orbital control" treatment with regard to the stereochemistry of 1,3 sigmatropic shifts.

Two-electron CI stabilization of a suprafacial migration with retention relative to a suprafacial migration with inversion can be important in both polar and nonpolar 1,3 shifts.<sup>9</sup> Furthermore, two-electron CI stabilization is relatively unimportant in either polar or nonpolar suprafacial 1,3 shifts occurring with inversion. On the other hand, one-electron PMO theory predicts that the stabilization of suprafacial migration with inversion relative to suprafacial migration with retention is greater in nonpolar than polar 1,3 shifts. Hence, two-electron CI would tend to reverse the Woodward-Hoffmann stereoselectivity in polar 1,3 shifts more than in nonpolar 1,3 shifts. Here, we note that "subjacent orbital control" was already implicit in our discussions of the effect of CI in nonpolar 1,3 shifts;<sup>10</sup> e.g., one cannot separate the relative importance of the one-determinantal subjacent orbital control and CI mixing using delocalized functions.

The Salem-Berson analysis showed that orbital interactions could stabilize a suprafacial nonpolar 1,3 shift proceeding with retention. In this work, we have found that the

Table III. Overlap Populations for a 1,3 Suprafacial Sigmatropic Shift from a STO-4G ab Initio Calculation

Migrating group	$p\sigma$ overlap population		
	$C_1(p_z) - X(p_z)$	$C_2(p_z) - X(p_z)$	$C_3(p_z) - X(p_z)$
CH <sub>3</sub>	0.02904	0.08837	0.03541
F	-0.0061	-0.0033	-0.0061

Table IV. Stabilization Energies for a 1,3 Suprafacial Sigmatropic Shift for a MWH Calculation

Migrating group	$SE^\pi$ , eV <sup>a</sup>
CH <sub>3</sub>	-10.1945
OH	-0.2366
F	4.2066
CH <sub>2</sub> CN	-5.1661
CH(CN) <sub>2</sub>	0.8677
C(CN) <sub>3</sub>	14.5096

<sup>a</sup> A minus sign signifies stabilization and vice versa.

reversal of Woodward-Hoffman stereoselectivity of nonpolar as well as moderately polar 1,3 sigmatropic shifts can be effected by means of "subjacent orbital control". On the other hand, in extremely polar 1,3 shifts "subjacent orbital control" vanishes and CI becomes the best candidate for explaining a reversal of Woodward-Hoffmann stereoselectivity.

We summarize the most important conclusions of this work. (a) The Berson-Salem analysis is supported by semiempirical and ab initio calculations. It is to be noted that the analysis of these workers utilized Hückel wave functions where the NBMO's of the allyl and methyl radical fragments have equal energies, while it is known that the ionization potentials of methyl and allyl radicals are significantly different, e.g., 9.84 eV for methyl and 8.16 eV for allyl.<sup>11</sup> Furthermore, overlap was neglected. Our calculations show that these approximations were completely justified.

(b) As the ionization potential of the migrating group is progressively raised, a point is reached where subjacent orbital control is obliterated. This trend is revealed by the simple one-electron MO analysis and is also confirmed by the calculations. On the other hand, the exact minimum ionization potential of a migrating group requisite for the annihilation of subjacent orbital control cannot be assessed without the calculation of complete potential surfaces for the 1,3 sigmatropic shift of typical groups across an allyl framework.

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### References and Notes

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a diexcited configuration and, on the basis of this definition, CI was stated to be unimportant in nonpolar and important in polar 1,3 shifts. In terms of the more general definition of CI, e.g., a total wave function written as a linear combination of more than one Slater determinant, it can be said that CI is important in both nonpolar and polar 1,3 shifts. For this clarification see footnote 6 in ref 2c.

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## Localized Molecular Orbitals for Polyatomic Molecules. II. Structural Relationships and Charge Distributions for Open Boron Hydrides and Ions

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**Abstract:** Wave functions calculated in the partial retention of diatomic differential overlap (PRDDO) approximation are presented for  $B_8H_{12}$ ,  $B_8H_{14}$ ,  $B_8H_{13}^-$ ,  $B_9H_{15}$ ,  $B_9H_{14}^-$ ,  $B_{10}H_{14}$ ,  $B_{10}H_{14}^{2-}$ ,  $B_{10}H_{13}^-$ ,  $B_{11}H_{13}^{2-}$ ,  $C_2B_7H_{13}$ ,  $C_2B_9H_{12}^-$ , and  $C_2B_{10}H_{13}^-$ . The wave functions are analyzed in terms of the ground state charge distribution. Mulliken overlap populations, atomic and group charges, dipole moments, and ionization potentials are presented for these molecules. We compare reactivity predictions for electrophilic and nucleophilic attack at boron based on three different criteria: inner shell eigenvalues, group charges, and population sums over the highest occupied molecular orbitals. Localized molecular orbitals (LMO's) obtained using the Boys criterion are reported. The molecules are grouped into three families based on common structural features with  $B_8H_{12}$ ,  $B_{10}H_{14}$ , and  $B_{11}H_{13}^{2-}$  serving as parent molecules. Within each family, differences in LMO structure are correlated with differences in the geometrical structure and charge distribution.

We compared, in paper I,<sup>1</sup> the Edmiston-Ruedenberg (ER)<sup>2</sup> and Boys<sup>3</sup> localization criteria for a group of boranes and carboranes which ranged from  $B_2H_6$  to 2,4- $C_2B_5H_7$  in size.<sup>4</sup> The two methods yielded identical localized bond models in nearly all cases, even though computationally the Boys procedure was found to be approximately 100 times faster for these molecules. The single difference occurred in 1,2- $C_2B_4H_6$ , for which the ER criterion yielded a pair of open<sup>5</sup> three-center B-C-B bonds while the Boys structure displayed only central three-center bonds.<sup>1</sup>

We here apply the computationally efficient Boys method to a series of structurally related nido boranes and carboranes which contain from 8 to 12 boron and carbon atoms. The molecules and ions considered here fall into three main families for which  $B_8H_{12}$ ,  $B_{10}H_{14}$ , and  $B_{11}H_{13}^{2-}$  can serve as parent structures (Figure 1). With the aid of the localized orbitals, we examine the relationship of bonding patterns within the families. In addition, since the chemical behavior of these systems toward electrophiles and nucleophiles has not yet been extensively explored experimentally, we offer predictions, based on the ground state charge distributions, for relative reactivity in electrophilic and nucleophilic processes. The principal indicators employed for this purpose are Mulliken atomic<sup>6</sup> and group charges (see below) and inner-shell eigenvalues.<sup>7</sup> The self-consistent-field calculations upon which these predictions are based are minimum-basis-set Slater orbital calculations carried out in the recently introduced approximation of partial retention of diatomic differential overlap (PRDDO).<sup>8</sup>

**Molecular Geometries.** The geometries of  $B_8H_{12}$ ,  $B_8H_{13}^-$ ,  $B_9H_{15}$ ,  $B_9H_{14}^-$ ,  $B_{10}H_{14}^{2-}$ ,  $B_{10}H_{13}^-$ ,  $B_{11}H_{13}^{2-}$ ,  $C_2B_7H_{13}$ ,  $C_2B_9H_{12}^-$ , and  $C_2B_{10}H_{13}^-$  were taken from, or extrapolated from, X-ray crystal structures,<sup>9-18</sup> and the geometry of  $B_{10}H_{14}$  was taken from the neutron diffraction

study.<sup>19</sup> Each set of crystallographic coordinates was idealized to the presumed molecular symmetry, and appropriate B-H<sub>i</sub> distances (1.19 Å) were imposed to correct the systematic X-ray shortenings.<sup>20</sup> However, the facial proton in  $C_2B_9H_{12}^-$  was left at its crystal structure B-H<sub>i</sub> distance of 1.33 Å. Since the structure of  $B_8H_{14}$  is uncertain the geometries employed for  $B_8H_{14}$  are hypothetical and utilize B-H-B and B-B distances from  $B_8H_{12}$  and  $B_8H_{13}^-$  (see below) together with B-H<sub>i</sub> distances of 1.19 Å. The numbering schemes used throughout this paper are given in Figures 3-16. For clarity, one terminal hydrogen is omitted from each heavy atom. In order to compare more easily molecules within each family (Figure 1), each molecule has been numbered in accordance with the parent molecule for that family (thus, except for the parent molecules we have used a nonstandard numbering).<sup>21</sup>

**SCF Calculations.** As details of the PRDDO method are described elsewhere,<sup>8</sup> we give here only a brief account. The PRDDO method uses a Slater basis set and explicitly treats all electrons. No experimental parameters are employed, but certain contributions to the two-electron matrix are parameterized to reproduce ab initio matrix elements for a variety of small molecules.<sup>8</sup> Thus, PRDDO is a *nonempirical* molecular orbital method. For molecules of the size considered here, computing times are roughly 100 times smaller than those for the reference ab initio SCF calculations. Extensive comparisons<sup>8c,22</sup> of PRDDO results with those given by other methods have established that PRDDO is greatly superior to CNDO and INDO<sup>23</sup> and is comparable to STO-3G<sup>24</sup> in reproducing energy differences, charge distributions, dipole moments, and eigenvalues from reference ab initio minimum Slater basis set calculations. For this study, exponents for boron and attached hydrogens have been taken from optimized values for  $B_2H_6$ <sup>25a</sup> while exponents