least-motion dimerization of RNO. Or, again, molecule **10** possesses 12 π electrons, whereas **11** has only 10 such. A level crossing occurs in the simple closure.

The difficulties with the planar transition state are easily bypassed by rotating one nitroso group in **11** or **12** 90° out of planarity. This conformation is then prepared for a bonding interaction involving the oxygen lone pair and the low-lying nitroso group π^* level (see Figure 10). The analogy with the nitroso compound dimerization is clear.

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Ab Initio Studies of the Electronic Structures of BH_3, BH_2F, BHF_2, and BF_3[1a]

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Abstract: The electronic structures of the molecules BH_3, BH_2F, BHF_2, and BF_3 have been studied by the *ab initio* self-consistent field molecular orbital method. Of especial interest are changes of certain quantities through the series from no fluorination (BH_3) to complete fluorination (BF_3). These include essentially constant atomic charges for H and F atoms, linearly increasing total positive charge of the central B atom, increase of the 2pπ-type population on B, increasing BF overlap—consisting of a balance between decreasing π overlap and increasing σ overlap, and linear increase of the orbital energy of the lowest unoccupied molecular orbital. Excluding the B 2pπ from bonding yields directly a π energy of 27 kcal for BH_2F, and an estimated value of 59 kcal for BF_3, based on the π overlap populations. The first ionization potential is examined for the series, and an explanation based on splitting of the degeneracy of the highest filled molecular orbital in BH_3 accounts for the decrease in the ionization potential upon initial fluorination. Consideration of calculated and experimental ionization potentials for BH_3 and BF_3 leads to an estimate of 11.8 and 13.6 eV for the first ionization potentials of BH_2F and BHF_2. Comparisons of both inner-shell and valence-shell ionization potentials have also been made with the analogous series CH_4 to CHF_3, based on *ab initio* calculations of Ha and Allen. The 1s binding energies of B and C correlate linearly with the Mulliken charge on the atom, and for multiple fluorination the changes in 1s binding energy are multiples of the change for a single fluorination.

The electronic structures of trigonally bonded boron compounds have been of interest for many years. In the simplest picture sp^2 hybrids of B are used for bonding with atoms (ligands) attached to B, and the empty 2pπ atomic orbital of the B atom can accept electrons from the π orbitals (if there are any) of the attached atoms, with a corresponding increase in the strength of chemical bonding. Such concepts have been discussed both in the valence-bond[2] and the molecular orbital (MO) pictures.[3] A general discussion of this family of molecules and the coordination compounds they form has been presented by Coyle and Stone.[4] Several semiempirical calculations have been published about such systems recently,[5–9] but nonempirical studies exist only for BH_3[10,11] and for BHF_2.[12]

We chose to study the entire series BH_3, BH_2F, BHF_2, and BF_3 for obvious reasons. The successive substitution of F for H, with the corresponding changes in electronic structure, presented an interesting opportunity to study a *series* of well-related molecules. Since many chemical phenomena are of a relative nature, it is especially worthwhile to examine such a series.

This paper will first describe and summarize the calculations done. Then the valence-shell electronic structure will be analyzed. Finally, the changes in both the first (smallest) ionization potential and the binding energy of the B 1s electron through the series are considered. A comparison will be made of these results for the latter quantities with similar quantities for the series CH_4 to CHF_3, as well as with available experimental results.

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(1) (a) Supported in part by the National Science Foundation, the Air Force Office of Scientific Research, and the Petroleum Research Fund administered by the American Chemical Society; (b) address correspondence to this author at the University of Notre Dame.

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The Calculations

The wave functions are determined through the all-electron self-consistent field molecular orbital (SCF MO) method in the linear combination of atomic orbitals (LCAO) formulation.[13] MO's were expanded in terms of the groups of gaussian lobe functions determined by Whitten[14] for the first row atoms. These functions constitute accurate atomic orbitals of approximately "double ζ" quality.[14] For the H 1s function the five-term gaussian expansion of ref 11 has been used. All calculations were done with the MOLE Quantum Chemistry System.[15]

Although BH_3 is known from chemical experiments,[16,17] its geometrical structure has not been determined experimentally. Therefore a D_{3h} geometry has been used, with R (B–H) = 2.31 au (1.22 Å) as found by calculation.[18] The scale factor of the H 1s function was optimized at $\sqrt{1.8}$. These values of R (B–H) and scale factor were used subsequently for all systems considered. This B–H distance is close to the experimental value[19] of 1.19 Å for the terminal B–H in diborane. The experimental value[19] of R (B–F) = 1.295 Å (2.4472284 au) for $D_{3h}BF_3$ was used for all systems. All bond angles in BH_2F and BHF_2 were fixed at 120°. During the course of this work the structure of BHF_2 from microwave spectroscopy was published[20] as planar, with R (B–H) = 1.19 Å, R (B–F) = 1.31 Å, and θ (FBF) = 118°. These are so close to the assumed geometry that it did not seen worthwhile to do a calculation at this experimental geometry. It also suggests that the assumed geometry for the (as yet undetected[16]) molecule BH_2F is reasonably accurate.

The energy quantities from the LCAO SCF MO wave functions are summarized in Tables I–IV. Unless explicitly stated to the contrary, all energy quantities will be in atomic units (1 au = 627.5 kcal/mol = 27.21 eV). In addition to the usual orbital energies ϵ_i, to be associated with ionization potentials *via* Koopmans' theorem,[21] these results include the "partitioned energy" e_i defined for the ith MO ϕ_i as

$$e_i = \langle \phi_i(1)/h(1)/\phi_i(1) \rangle + \epsilon_i$$

where $h(1)$ is the operator associated with a single electron in the field of the bare nuclei. This quantity has the property[13a] that

$$\Sigma_i e_i = E_{el'}$$

the total electronic energy (no nuclear repulsion), the sum being taken over the doubly occupied space orbitals. The interesting point about these e_i is that the order of the e_i and the ϵ_i is not always the same—that is (*cf.* Tables II, III, IV), an orbital whose ϵ_i is more positive than the ϵ_i of another orbital may in fact have a more negative e_i than the other orbital, and hence a larger contribution to the (negative) energy. These e_i and ϵ_i quantities form a useful check on the numerical accuracy of the calculations: the sum of the e_i, already mentioned, must equal the electronic energy; also, the sum $\Sigma_i 2\epsilon_i$ should give the electronic energy plus the electron repulsion energy V_{ee}. Both procedures applied to Tables I–IV give essentially perfect checks.

Table I. Energy Results for BH_3[a]

$E = -26.3546$ $V_{ee} = 14.7074$
$T = 26.0697$ $V_{nn} = 7.2433$
$V_{ne} = -74.3750$ $-V/2T = 1.0055$

MO	ϵ	e
$1a_1'$	−7.7036	−21.4377
$2a_1'$	−0.7229	−4.4138
$1e_1'$	−0.5094	−3.8732
$1a_2''$	+0.0659	

[a] E = total energy, T = electronic kinetic energy, V_{ne} = electron–nuclear attraction energy, V_{ee} = electron repulsion energy, V_{nn} = nuclear repulsion energy, $V = V_{ne} + V_{ee} + V_{nn}$ = total potential energy.

Table II. Energy Results for BH_2F

$E = -125.2032$ $V_{ee} = 74.5525$
$T = 125.6101$ $V_{nn} = 27.3355$
$V_{ne} = -352.7014$ $-V/2T = 0.9984$

MO	ϵ	e
$1a_1$	−26.2283	−69.1669
$2a_1$	−7.8263	−24.8056
$3a_1$	−1.6305	−13.0267
$4a_1$	−0.7908	−9.8016
$1b_2$	−0.7133	−10.1858
$1b_1$	−0.6636	−10.7010
$5a_1$	−0.6465	−7.7528
$2b_2$	−0.4940	−7.0984
$2b_1$	+0.0874	

Table III. Energy Results for BHF_2

$E = -224.0573$ $V_{ee} = 149.1038$
$T = 225.2115$ $V_{nn} = 62.4188$
$V_{ne} = -660.7915$ $-V/2T = 0.9974$

MO	ϵ	e
$1a_1$	−26.2413	−76.0606
$1b_2$	−26.2413	−76.0606
$2a_1$	−7.9507	−28.1750
$3a_1$	−1.6765	−15.0395
$2b_2$	−1.6345	−15.0252
$4a_1$	−0.8283	−12.4950
$5a_1$	−0.7665	−11.7850
$3b_2$	−0.7510	−12.9502
$1b_1$	−0.7245	−12.3867
$4b_2$	−0.6540	−13.1899
$1a_2$	−0.6498	−13.0439
$6a_1$	−0.5677	−10.2647
$2b_1$	−0.1077	

Several aspects of the orbital energies are easy to spot by recalling atomic orbital energies.[14] Orbitals of energy about −7.7 to −8.0 clearly correspond to B 1s, those at about −26 correspond to F 1s, and those at −1.63 to −1.73 correspond to F 2s; these are all

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(18) These are the same geometry and scale factor as ref 11. The calculated results shown in Table I differ from those of ref 11. Upon laborious searching of the original computer output, it was found that those workers had used a four term expansion of B 2p instead of the five-term expansion used here. We therefore explored both the scale factor and R (B–H) and found the same optimum values for our basis.

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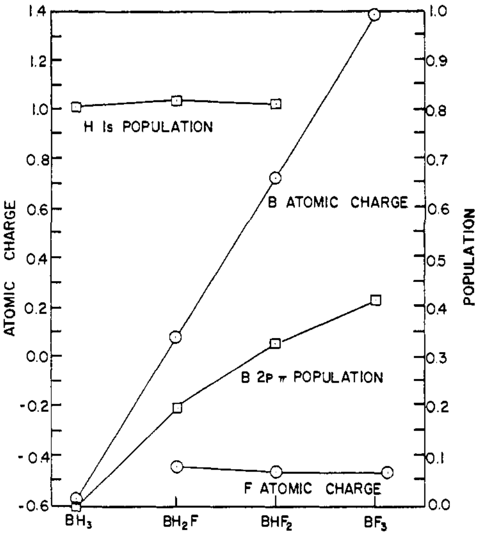

Figure 1. Gross atomic populations and atomic charges.

essentially nonbonding orbitals. The lowest empty MO, with slightly positive ϵ, corresponds to the perturbed B $2p\pi$ orbital—empty in the B atom and in BH_3. We shall say more about these energies later.

Table IV. Energy Results for BF_3

$E = -322.9018$	$V_{ee} = 238.1147$
$T = 324.7455$	$V_{nn} = 112.4930$
$V_{ne} = -998.2550$	$-V/2T = 0.9972$

MO	ϵ	e
$1a_1'$	−26.2695	−72.9693
$1e'$	−26.2695	−72.9693
$2a_1'$	−8.0793	−31.5480
$3a_1'$	−1.7291	−17.0821
$2e'$	−1.6678	−17.0424
$4a_1'$	−0.8630	−14.8577
$3e'$	−0.8114	−14.7892
$1a_2''$	−0.7860	−14.2334
$4e'$	−0.6925	−15.1058
$1e''$	−0.6826	−14.9228
$1a_2'$	−0.6659	−15.0452
$2a_2''$	+0.1273	

The wave functions have been analyzed by the population analysis of Mulliken.[22] These populations are summarized in Tables V and VI, and related graphical representations of interest appear in Figures 1 and 2. σ refers to orbitals symmetric with respect to the molecular plane, and π to those antisymmetric (*i.e.*, composed of the $2p\pi$ atomic functions).

Table V. Gross Atomic Populations at Each Atom

	B			H	F		
Molecule	Total	σ	π	Total (σ)	Total	σ	π
BH_3	5.569	5.569	0.000	0.810			
BH_2F	4.918	4.720	0.198	0.821	9.439	7.637	1.802
BHF_2	4.274	3.948	0.326	0.813	9.457	7.620	1.837
BF_3	3.612	3.197	0.415		9.463	7.601	1.862

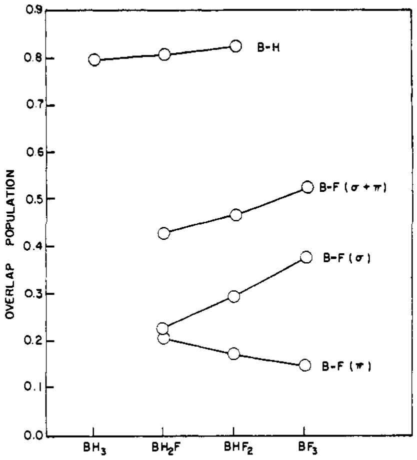

Figure 2. Overlap populations between bonded pairs of atoms.

It is not particularly useful to make explicit comparisons of our results with those of previous workers, since the previous studies were either for only one molecule at a time or else they were semiempirical calculations.

Table VI. Overlap Population between Bonded Pairs of Atoms

	B–H	B–F		
Molecule	Total (σ)	Total	σ	π
BH_3	0.794			
BH_2F	0.806	0.426	0.223	0.204
BHF_2	0.825	0.465	0.294	0.171
BF_3		0.525	0.378	0.147

It is worth noting, however, that our accurate atomic basis set has produced lower molecular energies than those from the relevant previous *ab initio* calculations on BH_3 and BHF_2. A population analysis comparison has also been omitted since these may be sensitive to the basis set, which varied for the previous calculations.

Analysis of the Valence Shell Electronic Structure

There are several rather striking features of the population analysis. The total electronic population at B decreases linearly with F substitution, but the H and F total populations remain essentially constant. But closer examination of Table V and Figure 1 shows that while the total and σ population of B decrease, the $2p\pi$ population increases with increasing fluorination. This clearly shows the competition between "inductive" and "conjugative" effects, with the former winning out overall. More specifically, in the series BH_2F, BHF_2, and BF_3, the net gains in σ population for each F are respectively 0.637, 0.620, and 0.601, while the corresponding π population losses are 0.198, 0.163, and 0.138. At F these variations along the series effectively cancel one another, and the total population of each F is almost constant. But at B the replacement of one H by one F effectively means a net loss by B of about 0.65 electron.

The electron distribution changes are also reflected by the overlap populations (Table VI and Figure 2). The π overlap for each B–F bond decreases through the series, presumably because the increasing number of F atoms (and, hence, of π electrons) slightly increases the π population at B and thence reduces the π acceptor

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[22] R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841, 2338, 2343 (1955).

power of B. Concomitantly, the increased π population at each F seems to reduce its effective σ withdrawing power, so that the B–F σ overlap is larger.

The energy of the lowest empty orbital of trigonal B molecules has been of some interest, since it is supposedly a measure of part of the ability of the molecule to accept a pair of electrons from a donor molecule.[4,6] Strictly, by Koopmans' analysis[21] this is the energy change associated with the addition of one electron to the system without any change in the MO's.

It is natural to expect the energy of this lowest unoccupied orbital to increase in the series BH_3 to BF_3. In the first member, this orbital is just the empty $2p\pi$ on B, while in the subsequent members the $2p\pi$ is increasingly used for some occupied orbitals (*i.e.*, the $2p\pi$ on B is partially filled). Thus, the orthogonality requirement for the lowest empty orbital with all the occupied ones will increase the nodes, and hence the energy, of this empty orbital. Figure 3 shows this energy behavior. There have been many studies of the relative acceptor abilities of trigonal B compounds.[4] The authors just remark briefly that the two commonly mentioned opposing effects are quite apparent in these calculations: increasing positive charge at B with fluorination (supposedly a good thing for acceptors) competes with increasing total B–F π bonding and higher energy of the lowest empty orbital (supposedly a bad thing). It is the opinion of the authors that acceptor abilities can only be seriously examined by an actual examination of the changes occurring as the acceptor molecule distorts *and* the donor molecule approaches to donate electrons.

The so-called "π energy" of molecules such as these has been commented upon frequently, and a separate *ab initio* calculation has been done to consider this effect. Since the π energy is thought of as the increased bonding energy due to π bonding, the π energy is defined as the energy difference between and LCAO SCF MO wave function which does not include π basis functions on B, and one which does include the π basis functions on B. For the simplest π bonding system here, BH_2F, a calculation was done without the B $2p\pi$ basis function, and an energy 0.0435 au = 1.18 eV = 27 kcal/mol higher than the result which included B $2p\pi$ was found. Such explicit calculations have not been done for BHF_2 and BF_3, but if the π energy is assumed to be proportional to total B–F π overlap,[22] 47 kcal for BHF_2 and 59 kcal for BF_3 are calculated. This BHF_2 value is larger than 36 kcal found by Armstrong[12] with his modest-sized gaussian basis calculation. But the BF_3 result is remarkably similar to the estimates of 48–57 kcal given by Cotton and Leto[23] in their early study. Armstrong and Perkins[6] obtained values from their π-only semiempirical calculations ranging from about 56 to 124 kcal, depending on what empirical parameters were used.

Ionization Energies, Both Valence and Inner Shell

In this section Koopmans' theorem[21] will be employed to discuss ionization potentials (IP). That is, the negative or orbital energies, $-\epsilon_i$, are taken as a measure of the IP's. Though this procedure neglects both reorganization and correlation energy changes, it is expected to be useful to discuss the *relative* IP values of the series of molecules studied. For BH_3 and BH_2F the authors have explicitly calculated the IP's of both the outermost valence electron (first IP) and the inner-shell corresponding to B 1s, by direct open-shell[24] SCF calculations on the ions as well as SCF calculations of the ground state. For both of the IP's the changes between BH_3 and BH_2F are essentially the same, whether based on the orbital energies or based on the direct calculations. There are two anchor points with the measured first IP's of 12.32 eV for BH_3,[25] and 15.95 eV (from a σ level[7]) for BF_3. The highest orbital energies from this calculation yield IP's of 13.8 and 18.1 eV for BH_3 and BF_3, respectively, the errors being +1.48 and +2.15 eV. Thus the estimate of the BH_3 to BF_3 *shift* in IP of +4.3 eV differs from the experimental result of 3.63 eV by just +0.67 eV.

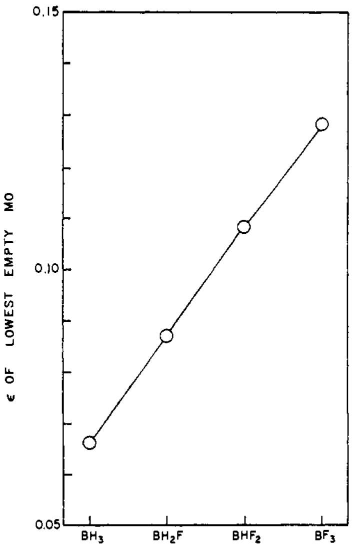

Figure 3. Energies of the lowest empty molecular orbitals.

Based on semiempirical calculations,[7] the first IP of BF_3 has been assigned to an e′ MO (*i.e.*, a doubly degenerate σ orbital) and Davies' CNDO calculations do likewise,[8] whereas the highest MO of this treatment is σ, but of nondegenerate a_2' symmetry. (This is the normalized symmetric sum of the F 2p orbitals tangential to the BF lines.) Since the spread in the values of both the experimental[7] and calculated[7,8] first three IP's of BF_3 is so small, this matter is obviously not settled. It is worth noting, however, that these *ab initio* calculations and the two semiempirical calculations[7,8] all place a σ level above the highest π level in energy. (Armstrong and Perkins[6] calculated a "reasonable" IP, but it was for a π electron!)

Let us now consider the first IP's through the series BH_3 to BF_3. The calculated values are 13.8, 13.4, 15.4, and 18.1 eV from the highest occupied orbital energies of Tables I–IV. These are all from σ orbitals. Note that the first IP actually decreases slightly from BH_3 to BH_2F. This result is somewhat surprising at first glance, but there is a straightforward explanation. In BH_3 the highest orbital is the doubly degenerate e′,

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(23) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

(24) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

(25) From ref 16. In a personal communication to M. E. S., Fehlner says an instrument miscalibration renders the value from ref 17 unreliable; he suggests the ref 16 value.

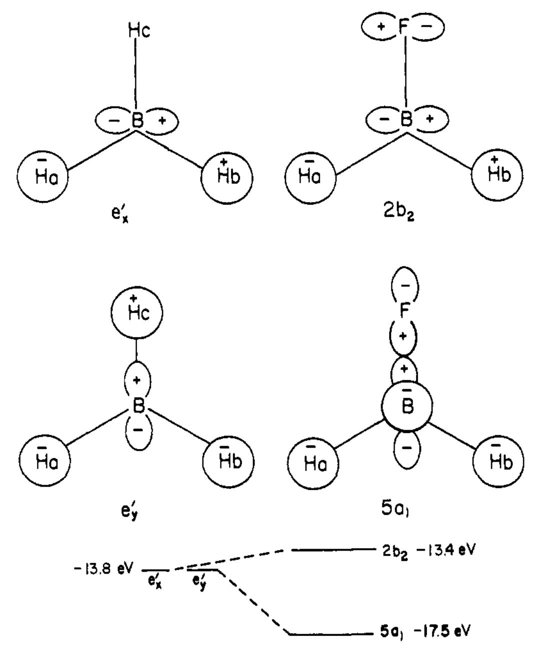

Figure 4. Schematic representation of the rise of the highest orbital energy from BH_3 to BH_2F.

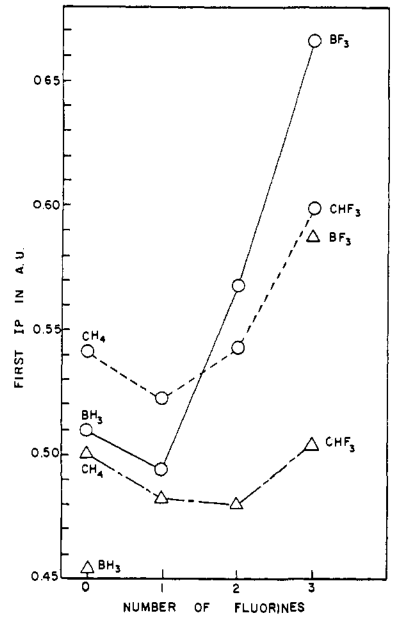

Figure 5. First ionization potentials. The circles denote calculated values; the triangles, experimental ones. See text.

whose two components are roughly

$$e_z' = 0.62\text{B}2px + 0.35(\text{H}_b1s - \text{H}_a1s)$$

$$e_y' = 0.62\text{B}2py + 0.40\text{H}_c1s - 0.20(\text{H}_a1s + \text{H}_b1s)$$

In BH_2F, H_c is replaced by F, and the e′ orbital of BH_3 splits into the $5a_1$ and $2b_2$ orbitals of BH_2F, which are roughly

$$5a_1 = -0.44\text{BS}_3 + 0.39\text{B}2py - 0.25(\text{H}_a1s + \text{H}_b1s) - 0.56\text{F}2py - 0.10\text{FS}_3$$

$$2b_2 = 0.53\text{B}2px + 0.36(\text{H}_b1s - \text{H}_a1s) - 0.53\text{F}2px$$

Here S_3 refers to those group functions[14] on B and F which largely compose the atomic 2s orbitals. These changes are schematically represented in Figure 4. From the nodal structure it is seen that the e′ orbitals in BH_3 are B–H bonding. In BH_2F the $5a_1$ orbital is both B–H and B–F bonding, and its energy is considerably lowered from the parent e_y' orbital of BH_3. But the $2b_2$ orbital in BH_2F is B–H bonding, and B–F antibonding, so its energy is a little higher than the parent e_z' orbital of BH_3. Hence the first IP decreases.

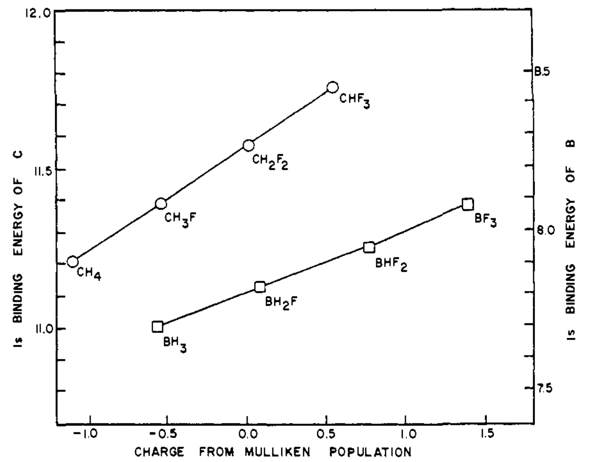

Figure 6. Calculated relative binding energies *vs.* Mulliken atomic charge for B and C 1s electrons.

Other cases have been found in the literature of such a phenomenon. The IP's of CH_4[26] and the fluorinated molecules[8] CH_3F, CH_2F_2, and CHF_3 are especially interesting in connection with the present results, since there is degeneracy in the highest occupied CH_4 orbital which is split by F substitution. Both semiempirical[8] and *ab initio*[27] calculations are also available for the series. In Figure 5 are displayed the experimental and calculated *ab initio* IP values for BH_3 to BF_3 and CH_4 to CHF_3. Though the trend is quantitatively exaggerated by the theoretical calculations on the latter series, it is qualitatively well represented. By assuming that the results are high by about 1.6 eV for BH_2F and 1.8 eV for BHF_2, it is predicted that the experimental IP's will be about 11.8 and 13.6 eV, respectively. The IP's for these two molecules have not yet been measured.

The developing techniques of electron spectroscopy for chemical analysis (ESCA)[28] offer new tools for probing electronic structure. In particular, it is now possible to measure the binding energies of inner-shell electrons accurately enough to detect relatively small changes in these quantities for an atom in different molecular environments. A most interesting correlation has emerged: there is an essentially linear relation of measured inner-shell binding energies with the charge, which is estimated to be associated with the atom under study. This is known for S 2p (ref 29 and 30) and N 1s (ref 31) levels. This has been discussed in a recent paper.[32]

(26) K. Hamrin, *et al.*, *Chem. Phys. Lett.*, **1**, 613 (1968).

(27) T. K. Ha and L. C. Allen, *Int. J. Quantum Chem.*, *IS.*, 199 (1967), and unpublished calculations.

(28) K. Siegbahn, *et al.*, "ESCA-Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Booksellers, Stockholm, Sweden, 1967; *Nova Acta Regiae Soc. Sci. Upsal.*, *Ser. IV*, **19** (4) (1967).

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The present results for BH_3 to BF_3 and the results of Ha and Allen[27] for CH_4 to CHF_3 show the changes of both B and C 1s levels in the changing environment of successive fluorination. The orbital energies and atomic charges calculated on the basis of the population analyses are plotted in Figure 6. There is indeed a good linear correlation of binding energy *vs.* this definition of charge. Note that in both series the 1s binding energies of the multiply fluorinated molecules are shifted from the nonfluorinated molecule by amounts almost precisely a multiple of the shift for a single fluorination. It is interesting that the binding energy of B 1s should correlate linearly with overall B charge, since we have seen that the partitioning of atomic populations into σ and π contributions changes through the series. However, the N and S experimental results are for a very wide variety of molecules, and the overall energy *vs.* charge correlation seems still to hold reasonably well, even though the charges are difficult to define unambiguously.[32]

There are no experimental results for direct comparison with these calculated ones. We look forward to the experimental measurements on the systems we have studied.[33]

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(32) M. E. Schwartz, C. A. Coulson, and L. C. Allen, *J. Amer. Chem. Soc.*, in press.

(33) NOTE ADDED IN PROOF. Recent experimental studies[34] of the halomethanes and recent theoretical studies[35] of C 1s in several molecules have both shown that 1s energy shifts may be overestimated by MO wave functions expanded in terms of these accurate *atomic* functions. More flexibility as a *molecular* basis is required for satisfactory calculations of inner-shell shifts. M. E. S. will report on such studies relevant to the boron compounds later. The trends of linearity and additivity do seem to be valid, however.[32,34,35]

(34) T. D. Thomas, *J. Amer. Chem. Soc.*, in press.

(35) M. E. Schwartz, submitted for publication.

Kinetics of the Cycloaddition of Photoexcited Benzene to 2-Butene in the Gas Phase[1a]

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Abstract: Cycloaddition of the photoexcited benzene to *cis*- and *trans*-2-butene in the gas phase has been studied at 25°. Different adducts are formed from the two geometric isomers of 2-butene. Nmr analyses of the addition products show that the two main adducts from *trans*-2-butene are two stereoisomers (*endo,exo* and *exo,endo*) of the major adduct from *cis*-2-butene (6,7-dimethyltricyclo[3.3.0.0^{2,8}]oct-3-ene). The cycloadditions to both *cis*- and *trans*-2-butene take place with retention of configuration of the butene moiety. This, together with the effects of small additions of oxygen and biacetyl, indicates that the excited singlet of benzene, and not the triplet $^3B_{1u}$, is involved in the photoaddition. The kinetics of the photoaddition has been studied and is discussed.

Photoaddition of benzene to *cis*-2-butene in the uv spectral region at 2370–2530 Å has been observed both in the gas phase[2a] and in the liquid phase.[2b] These and other photoaddition and photoisomerization reactions of the benzene ring have been recently reviewed by Bryce-Smith.[3a] An excited form of benzene, a singlet biradical, has been suggested by Bryce-Smith and Longuet-Higgins[3b] as the common precursor for benzene addition to olefins and for its isomerization to benzvalene and fulvene. However, some questions have been raised in connection with this postulate. Kaplan and Wilzbach[2a] have found that the yields of benzvalene and of the adduct to *cis*-2-butene have opposite dependences on the wavelength of the exciting radiation and concluded that, if there is a common intermediate, the ratio of products must vary with its energy content.

The present work is an extension of our recent study[4] of the quenching of benzene fluorescence by hydrocarbons at relatively high pressures, in which it has been found that monoolefins of molecular weight greater than 2-butene show very small but measurable quenching efficiences. This result suggests the possibility that the fluorescence quenching and adduct formation are related processes, both involving the excited singlet benzene, $^1B_{2u}$. We have, therefore, investigated the kinetics and the stereochemistry of adduct formation between benzene and *cis*- and *trans*-2-butene in order to obtain further information about the photoaddition process.

Experimental Section

A U-shaped quartz tube, 8-mm i.d., 65 mm high, and with the two arms 30 mm apart, was used as the reactor. Its total volume was 8 ml. The lower half of the reactor was irradiated by a Hanovia 673A 10 medium-pressure mercury arc through two filters, a Corning 9-54 glass filter and a 50-mm long quartz cell containing mercury vapor and 50 Torr hydrogen.

2-Butene isomers were analyzed on a propylene carbonate on fire brick column at 0°. The products of photoaddition were analyzed on a 20% silicone rubber, SE-30, on Anakrom AW (Analytical Engineering Laboratories) column, at 125°. Helium carrier gas and thermal conductivity detectors were used. Mass spectrometer (Atlas CH-4)–gas chromatography combination and nmr spectroscopy (Varian Associates HA-100D) were used to determine the mass and the structure of the products.

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(1) (a) Issued as NRC No. 11245; (b) National Research Council postdoctoral fellow.

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