borane was removed under vacuum. Benzene was removed at room temperature to leave white solid tetraadduct (96%) which was handled under nitrogen because of its extreme sensitivity to moisture and air. Identification was based on infrared spectrum, preparative stoichiometry (3.48 mmol of hexamine to 13.38 mmol of $BH_3$ consumed, corresponding to a 1:3.85 ratio), and analysis.

*Anal.* Calcd for $(CH_2)_6N_4 \cdot 4BH_3$: C, 36.9; H, 12.4; N, 28.7; B, 22.1. Found: C, 38.3, 38.9; H, 11.8, 11.0; N, 29.6, 29.0; B, 21.4.

The tetraadduct slowly decomposes to the triadduct and diborane even at room temperature in sealed ampoules, which fact accounts for the high CH and low B values.

**Borane Removal with Pyridine.** A white viscous mixture of 10 ml of pyridine and 900 mg (4.58 mmol) of tetraadduct was stirred overnight at room temperature. The solid was filtered, washed with pyridine, and identified as monoadduct, 656 mg, 90%. The filtrate was freed of pyridine by heating at 50° under high vacuum for 2 hr to leave 889 mg of pyridine–borane, 94% yield based on boron charged.

**$H_2BP(CH_3)_3N_4(CH_2)_6{}^+$ Salts.** A 3.62-mmol sample of hexamine-borane was monoiodinated in 10 ml of chloroform by slow addition, with stirring, of 408 mg (1.61 mmol) of iodine in 20 ml of chloroform. A 10% excess of trimethylphosphine was condensed into the flask under vacuum, and the resulting mixture was stirred 3 hr at room temperature. Solvent was removed under vacuum and the remaining (iodide salt) solid was dissolved in 5 ml of warm water and treated with excess $NH_4{}^+PF_6{}^-$ solution. The white precipitate was collected and recrystallized from 50° water to give 143 mg of $(CH_2)_6$-$N_4BH_2P(CH_3)_3{}^+PF_6{}^-$.

*Anal.* Calcd for $(CH_2)_6N_4BH_2P(CH_3)_3{}^+PF_6{}^-$: C, 28.9; H, 6.2; N, 15.0; B, 2.9. Found: C, 27.9; H, 5.9; N, 13.0; B, 2.5.

**$H_2BpyN_4(CH_2)_6{}^+$ Salts.** A combination of hexamine–$BH_2I$ solution in chloroform or benzene (prepared as described) with pyridine gave no isolable cation salt. The reverse combination of excess hexamine with 257 mmol of py–$BH_2I$ (prepared from 2.57 mmol of py–$BH_3$ and 163.1 mg of iodine) in benzene resulted in a slow deposition of white solid product which was separated by filtration. This product was dissolved in hot water and treated with ammonium hexafluorophosphate solution, whereupon the slightly soluble hexafluorophosphate salt precipitated. It was collected by filtration quickly to minimize decomposition.

*Anal.* Calcd for $BH_2pyN_4(CH_2)_6{}^+PF_6{}^-$: C, 35.0; H, 5.1; N, 18.6. Found: C, 34.8; H, 4.3; N, 16.6.

**Pyrolysis of Tetraadduct.** A 3.5-mmol sample of tetraadduct was prepared in a 50-ml flask attached to a vacuum line. Benzene solvent was removed under vacuum and the flask sealed off at a constriction and placed in an oil bath behind safety shielding. Pyrolysis was carried out by heating at 110° for 10 hr, 130° for 24 hr, and 140° for 2 hr. A clear liquid and white and yellow solids were present at this time. After cooling to room temperature the flask was opened and 6.77 mmol of noncondensable gas ($H_2$ ?) was separated from condensable material fractionated through −40°, −78°, and −196° traps. Trimethylamine (0.349 mmol) collected in the −196° trap, and $[(CH_3)_2N]_2BH$ as a clear liquid and $[(CH_3)_2NBH_2]_2$ as a white solid collected in the −78 and −40° traps, respectively. Identification was made by gas density molecular weight measurements and infrared data. The measured molecular weight of the liquid was 97 (17.13 mg, 19.74 mm, 167.1 ml, 24.8°) compared with the theoretical 99.8, and the measured molecular weight of the solid was 117 (8.70 mg, 8.29 mm, 166.8 ml, 24.2°) compared with the theoretical 113.6. Infrared spectra were similar to those reported for these compounds.[15] These borane compounds accounted for 47% of the boron charged. Treatment of the nonvolatile residue with warm methanol gave some insoluble monoborane hexamine adduct and a solution containing material which could not be characterized.

**Acknowledgment.** Support of this research by a grant from the National Science Foundation is gratefully acknowledged.

**Registry No.** $(CH_2)_6N_4 \cdot BH_3$, 14547-02-5; $(CH_2)_6N_4 \cdot 2BH_3$, 42976-00-1; $(CH_2)_6N_4 \cdot 3BH_3$, 42976-01-2; $(CH_2)_6N_4 \cdot 4BH_3$, 42976-02-3; $(CH_2)_6N_4$, 100-97-0; $B_2H_6$, 19287-45-7; $(CH_2)_6N_4BH_2P(CH_3)_3$-$PF_6{}^-$, 42934-44-1; $BH_2pyN_4(CH_2)_6{}^+PF_6{}^-$, 42934-45-2.

[15] E. P. Schram and R. E. Hall, *Inorg. Chem.*, 8, 270 (1969).

---

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

# *Ab Initio* Self-Consistent-Field Study of Boron Halides: $B_4F_4$ and $B_4Cl_4$

JOHN H. HALL, Jr., and WILLIAM N. LIPSCOMB*

*Received August 1, 1973*

The molecules $B_4F_4$ and $B_4Cl_4$ have been studied by *ab initio* self-consistent-field (SCF) methods employing a minimum basis set of Slater orbitals. Mulliken overlap populations, atomic charges, midpoint densities, atomization energies, orbital populations, and ionization potentials are reported, and some quantities are compared to earlier results on $B_4H_4$. The MO's for $B_4F_4$ and $B_4Cl_4$ consist of E, $T_1$, and $T_2$ bonding orbitals composed mainly of fluorine 2p and chlorine 3p orbitals. Thus, both molecules are stabilized by back donation of ligand p orbitals into the $B_4$ tetrahedron. The antibonding E*, $T_1$*, and $T_2$* MO's are composed mostly of boron 2p orbitals. The amount of ligand $\pi$ back-donation into the $B_4$ tetrahedron is greater for $B_4F_4$ than for $B_4Cl_4$. Localized molecular orbitals for $B_4F_4$ and $B_4H_4$ are obtained by using Boys' method of maximizing the sum of the squares of the distances between the orbital centroids, and the results for $B_4H_4$ are compared to our earlier Edmiston–Ruedenberg localization results for $B_4H_4$.

## I. Introduction

The electronic structures of certain boron halides have been of interest for many years. In particular, the molecules studied most extensively by experimental and both semiempirical and *ab initio* theoretical methods have been the trigonally bonded boron halides $BX_3$ (X = F, Cl, Br, or I).[1-6] Also, there have been several approximate self-consistent-field (SCF) and extended Huckel (EH) studies of $B_2Cl_4$[1] and $B_4Cl_4$.[6,7] The bonding in these molecules is of particular interest because of the possibility of back-coordination from the halides to vacant p orbitals on the borons.[8,9] For in-

[1] H. Kato, K. Yamaguchi, T. Yonezawa, and K. Fubui, *Bull. Chem. Soc. Jap.*, 38, 2144 (1965).

[2] M. Lappert, M. Litzow, J. Pedley, P. Riley, and A. Tweedale, *J. Chem. Soc. A*, 3105 (1968).

[3] D. Armstrong and P. Perkins, *Theor. Chim. Acta*, 15, 413 (1969).

[4] M. Schwartz and L. C. Allen, *J. Amer. Chem. Soc.*, 92, 1466 (1970).

[5] D. Armstrong, P. Perkins, and J. Stewart, *J. Chem. Soc. A*, 3674 (1971).

[6] D. Gautier and L. Burnelle, *Chem. Phys. Lett.*, 18, 460 (1972).

[7] A. G. Massey and D. S. Urch, *J. Chem. Soc.*, 6180 (1965).

[8] H. C. Longuet-Higgins, *Quart. Rev., Chem. Soc.*, 11, 121 (1957).

stance, various semiempirical methods applied to the series $BF_3$, $BCl_3$, $BBr_3$, and $BI_3$ have indicated that $\pi$ back-donation decreases in the series $BI > BBr \approx BCl \gg BF$.[2] This trend, however, is in direct opposition to the expected behavior based on the relative Lewis acidities of the molecules.[10] The back-coordination in the only known tetraboron tetrahalide,[11] $B_4Cl_4$, is thought not only to relieve the electron deficiency but also to stabilize the molecule over, for example, the still unknown molecules[7,8] $B_4H_4$ and $B_4F_4$. Obviously, the possibility of back-bonding does not exist for $B_4H_4$; and it has been argued[7] that the large electronegativity of fluorine would cause the E orbitals in $B_4F_4$ to retain so much ligand character that the electrons in these orbitals could not stabilize the molecule. Thus, $B_4F_4$ should be unstable as well, as is $B_4H_4$. Also of interest is the decomposition of $B_4Cl_4$ into BCl fragments under flash photolysis upon the absorption of 245-mμ radiation,[12] which has been supposed[7] to excite an electron into a vacant E* orbital, thus weakening the boron cage bonding.

To date there are only a few accurate *ab initio* SCF studies of boron halides.[4-6] These were studies[5,6] of $BF_3$ and/or $BCl_3$ and the series[4] $BH_3$, $BH_2F$, $BHF_2$, and $BF_3$. All previous theoretical work on the larger boron halides has been at the semiempirical level. Therefore, there is clearly a need for *ab initio* SCF studies of large boron halides. In this paper we present partially optimized, minimum basis set *ab initio* wave functions for $B_4F_4$ and $B_4Cl_4$. We compare these wave functions with the $B_4H_4$ calculation by Hall, Epstein, and Lipscomb[13] in order to gain more insight into the role that back-coordination, where it exists, plays in the relative stabilities of these molecules.

## II. Procedures

All SCF calculations were performed on an IBM 360/195 computer with a modified version of Stevens' polyatomic SCF program.[14] The $B_4Cl_4$ calculation is the largest *ab initio* SCF calculation employing a Slater basis set ever attempted on a molecule containing second row atoms. The SCF program previously available[14] did not calculate the appropriate two-electron integrals in the atomic orbital basis involving both 3s and 3p orbitals. The program described in ref 14 has been modified by Stevens to include more quadrature points and use a finer grid for the numerical integration of the two-electron integrals and was subsequently successful in evaluating all the required integrals. Total computing times for $B_4F_4$ and $B_4Cl_4$ were 8 and 40 min, respectively. The geometries of both molecules were assumed to be regular tetrahedral; however, both calculations were done in the point group $C_{3v}$ for computational convenience. The $C_3$ axis was taken as the $z$ axis. All B–B distances were 1.70 Å.[11] The B–Cl and B–F distances were 1.70[11] and 1.26 Å,[15] respectively. Boron exponents for the minimum basis set were taken from ref 13. Chlorine and fluorine exponents were obtained by optimizing the Cl and F exponents in the diatomic systems BCl and BF, in which we used the internuclear distances and B exponents appropriate for the polyatomic calculations. Basis sets are summarized in Table I.

## III. Energetics

Total energies, components of the total energies, virial ratios, ionization potentials, and dissociation energies for $B_4F_4$ and $B_4Cl_4$ are listed in Table II. The virial ratios $(-E/T)$ are quite close to unity. Massey and Urch,[16] in an attempt to observe positive ions of boron chlorides by mass spectrometry, observed the first appearance of $B_4Cl_4^+$ at 9 eV. The actual appearance potential or ionization potential was not determined,[16] but the true ionization potential should be slightly less than 9 eV. The calculated ionization potential from Koopmans' theorem is 9.6 eV. Therefore, our calculated ionization potential is probably close to the true value even though we have neglected reorganization energy, correlation, and vibrational effects.

## IV. Population Analysis and Electron Density

The overlap populations, bond midpoint densities, and atomic charges are listed in Table III. The values for $B_4H_4$ from ref 13 are also listed for reasons of comparison. The invalidity of comparing bond overlap populations between different basis sets has been stressed before.[17] Therefore, one should not compare the overlap populations of the B–F, B–Cl, or B–H bonds. Nor should the B–B overlap populations be compared, unless one is interested in the differences in bonding in the boron cage for the various ligands.

However, the total densities are more nearly comparable since the *total* density is invariant to any partitioning scheme. Thus, the B–B midpoint densities (Table III) for $B_4F_4$, $B_4Cl_4$, and $B_4H_4$ are essentially the same. However, it can be seen from these midpoint densities that the B–F bond contains a much greater concentration of electronic charge than do the B–Cl or the B–H bonds. We note that the midpoint densities do not correlate with B–X distance (where X is H, F, or Cl); *i.e.*, correlation is to be expected only between bonds composed of the same atoms. Note that in our examples, the most electronegative ligand has the highest concentration of electronic density in its boron–ligand bond, a trend noted earlier.[4] The influence of electronegativity on the boron cage can be seen in Figure 1, where we plot the total density along a line which connects the center of a B–B–B triangle with the midpoint of a B–B bond. There is a *higher* concentration of electronic density on the face of a tetrahedron for $B_4H_4$ than for either $B_4F_4$ or $B_4Cl_4$. Also, the ordering of the magnitudes of the density at the center of a triangle is $B_4H_4 > B_4Cl_4 > B_4F_4$. These trends are again in order of the relative electronegativities; the molecule containing the most electronegative ligand has the lowest electronic density at the center of each triangle of the $B_4$ tetrahedron.

We see then that the cage bonding is fairly similar for all three molecules. The electronic density is less at the center of each face of the regular tetrahedron than along the edges of the tetrahedron. This bonding tendency was predicted by Massey and Urch[7] and occurs in semiempirical calculations on $B_4Cl_4$ by Armstrong, Perkins, and Stewart[5] and in *ab initio* localized molecular orbital studies of $B_4H_4$ by Hall, Epstein, and Lipscomb.[13]

## V. Discussion of SCF Results

The relative amounts of $\pi$ back-donation of the ligands into the $B_4$ tetrahedron for $B_4F_4$ and $B_4Cl_4$ are clearly of interest.

---

(9) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(10) (a) T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, 1, 104 (1964); (b) G. Urry, "The Chemistry of Boron and its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 333.

(11) M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, 21, 172 (1953); *Acta Crystallogr.*, 6, 547 (1953).

(12) A. G. Massey and J. J. Zwolenik, *J. Chem. Soc.*, 5354 (1963).

(13) J. H. Hall, Jr., I. R. Epstein, and W. N. Lipscomb, *Inorg. Chem.*, 12, 915 (1973).

(14) R. M. Stevens, *J. Chem. Phys.*, 52, 1397 (1970).

(15) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1967.

(16) A. G. Massey and D. S. Urch, *Chem. Ind. (London)*, 607 (1965).

(17) For instance, see D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 94, 8692 (1972).

**Table I.** Basis Sets for $B_4F_4$ and $B_4Cl_4$

| | | | | | |
|---|---|---|---|---|---|
| B (1s) | 4.686 | F (1s) | 8.653 | Cl (1s) | 16.525 |
| B (2s) | 1.386 | F (2s) | 2.574 | Cl (2s) | 5.709 |
| B (2p) | 1.389 | F (2p) | 2.576 | Cl (2p) | 6.499 |
| | | | | Cl (3s) | 2.372 |
| | | | | Cl (3p) | 2.069 |

**Table II.** Energetics for $B_4F_4$ and $B_4Cl_4$ [a]

| Energies | $B_4F_4$ | $B_4Cl_4$ |
|---|---|---|
| Nuclear repulsion | 291.119 | 522.888 |
| Nuclear attraction | −1764.471 | −5649.327 |
| Kinetic energy | 495.193 | 1932.920 |
| Total energy | −494.640 | −1932.858 |
| $-E/T$ | 0.9989 | 0.9999 |
| Ionization potential | 0.319 | 0.353 |
| Atomization energy[b] | | |
| Best-atom exponents[c] | 0.880 | 0.767 |
| Molecular exponents[d] | 0.989 | 0.883 |

[a] All quantities in au. [b] Best-atom atomization energies were calculated using exponents from E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 38, 2686 (1963). [c] $E$(B) = −24.498, $E$(F) = −98.942, and $E$(Cl) = −458.524. [d] $E$(B) = −24.473, $E$(F) = −98.940, and $E$(Cl) = −458.521.

**Table III.** Overlap Populations, Midpoint Densities, and Atomic Charges

| | | Overlap pop | Midpoint densities, e/au$^3$ | Bond dis, Å |
|---|---|---|---|---|
| $B_4F_4$ | B-B | 0.342 | 0.125 | 1.70 |
| | B-F | 0.614 | 0.344 | 1.26 |
| $B_4Cl_4$ | B-B | 0.458 | 0.124 | 1.70 |
| | B-Cl | 0.760 | 0.184 | 1.70 |
| $B_4H_4$ | B-B | 0.492 | 0.125 | 1.70 |
| | B-H | 0.824 | 0.167 | 1.19 |

B +0.130 B +0.039 B +0.0046
F −0.130 Cl −0.039 H −0.0046

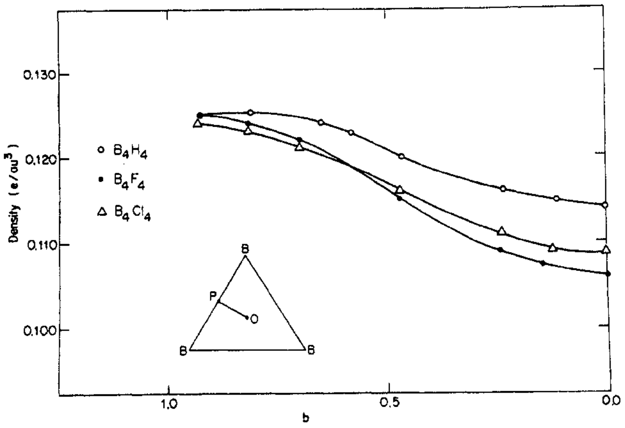

**Figure 1.** Total density along the line which connects the center of a B-B-B triangle with the midpoint of an edge of the triangle. The quantity *b* gives the distances from the point P to the point O, along the line segment PO.

The electronegativity of fluorine does not severely curtail the back-donation by the fluorine ligand into the vacant orbitals of the boron cage. In fact, our calculations suggest that there is even more back-donation in $B_4F_4$ than in $B_4Cl_4$, as follows. First, examination of the $\sigma$ and $\pi$ populations for the valence E MO's indicate that $B_4F_4$ has a higher boron $\pi$ population, suggesting that back-donation is greater (Table IV). Second, there is more favorable overlap between the BF $\pi$ orbitals (0.07 for BF and 0.03 for BCl). Third, the energy difference between the MO's involved in back-coordination and the lowest unoccupied MO's also suggests that back-coordination is greater for $B_4F_4$. The differences between the valence E MO's and the lowest unoccupied E* MO's for $B_4F_4$ and $B_4Cl_4$ are 0.470 and 0.405 au, respectively, and the differences between the highest occupied orbitals (in both cases a $T_2$ orbital) and the E* MO's are 0.732 and 0.524 au, respectively (see Table V).

**Table IV.** $\sigma$ and $\pi$ Populations for the Valence E Molecular Orbitals in $B_4F_4$ and $B_4Cl_4$ [a]

| $B_4F_4$ | | $B_4Cl_4$ | |
|---|---|---|---|
| B ($\pi$) | 0.255 | B ($\pi$) | 0.203 |
| B ($\sigma$) | 0.085 | B ($\sigma$) | 0.038 |
| F ($\pi$) | 1.151 | Cl (2$p_\pi$) | 0.018 |
| F ($\sigma$) | 0.506 | Cl (2$p_\sigma$) | 0.003 |
| | | Cl (3$p_\pi$) | 1.280 |
| | | Cl (3$p_\sigma$) | 0.427 |

[a] The $\sigma$ and $\pi$ refer to local axes of the B-X bond.

**Table V.** Eigenvalues for $B_4F_4$ and $B_4Cl_4$

| $B_4F_4$ | | $B_4Cl_4$ | |
|---|---|---|---|
| Eigenvalue | Symmetry | Eigenvalue | Symmetry |
| −26.3213 | $A_1$ | −104.7580 | $A_1$ |
| −26.3213 | $T_2$ | −104.7580 | $T_2$ |
| −7.6123 | $A_1$ | −10.3509 | $A_1$ |
| −7.6177 | $T_2$ | −10.3509 | $T_2$ |
| −1.5699 | $A_1$ | −7.8277 | $T_2$ |
| −1.5672 | $T_2$ | −7.8275 | $A_1$ |
| −0.8953 | $A_1$ | −7.8237 | $T_1$ |
| −0.6616 | $T_2$ | −7.8236 | $T_2$ |
| −0.6382 | $A_1$ | −7.8235 | E |
| −0.6006 | $T_2$ | −7.6761 | $A_1$ |
| −0.5802 | E | −7.6754 | $T_2$ |
| −0.5584 | $T_1$ | −1.0990 | $A_1$ |
| −0.3186 | $T_2$ | −1.0814 | $T_2$ |
| +0.1520 | E | −0.9351 | $A_1$ |
| | | −0.5971 | $T_2$ |
| | | −0.5588 | $A_1$ |
| | | −0.5042 | $T_2$ |
| | | −0.4711 | E |
| | | −0.4475 | $T_1$ |
| | | −0.3529 | $T_2$ |
| | | +0.0531 | E |

These energy differences can be related to the relative amounts of boron and ligand character in the molecular orbitals. The form of the E molecular orbitals (Table VI) implies that the energy difference between the E and E* MO's should increase with increasing boron character in the occupied E molecular orbitals. Similarly, the energy difference between the $T_2$ and E* MO's also should increase with increasing boron character in the $T_2$ molecular orbitals. The above energy differences then imply that the bonding E and $T_2$ orbitals for $B_4F_4$ contain more boron character than do the E and $T_2$ orbitals for $B_4Cl_4$. Therefore, at the minimum basis set level of approximation, the fluorine ligands donate more $\pi$ electrons into the boron cage than do the chlorine ligands.

We must investigate the possibility that the B-F bond length used in the calculations may alter our conclusions regarding the $2p_\pi$ back-donation in $B_4F_4$, since this bond length was not optimized beforehand. If the B-F distance was too short, exaggerated overlap and orbital populations could be obtained. After the *ab initio* calculations were performed, the new method of partial retention of diatomic differential overlap (PRDDO) became available.[18] This method has been shown to give a charge distribution for small, first-row polyatomics [18] and for large boron hydrides[19] closely approaching

---

(18) T. A. Halgren and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, 69, 652 (1972); T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.*, 58, 1569 (1973).

(19) D. S. Marynick, J. H. Hall, Jr., and W. N. Lipscomb, to be submitted for publication.

**Table VI.** Expressions for the Occupied E Molecular Orbitals[a]

| $B_4F_4$ | $E_1$ | $E_2$ |
|---|---|---|
| $B_1$ | $-0.055\ 2p_x$<br>$-0.155\ 2p_z$ | $0.165\ 2p_y$ |
| $B_2$ | $0.110\ 2p_x$<br>$0.095\ 2p_y$<br>$0.078\ 2p_z$ | $0.095\ 2p_x$<br>$-0.135\ 2p_z$ |
| $B_3$ | $0.110\ 2p_x$<br>$-0.095\ 2p_y$<br>$0.078\ 2p_z$ | $-0.095\ 2p_x$<br>$0.135\ 2p_z$ |
| $B_4$ | $-0.165\ 2p_x$ | $-0.165\ 2p_y$ |
| $F_1$ | $-0.146\ 2p_x$<br>$-0.415\ 2p_z$ | $0.440\ 2p_y$ |
| $F_2$ | $0.293\ 2p_x$<br>$0.254\ 2p_y$<br>$0.207\ 2p_z$ | $0.254\ 2p_x$<br>$-0.359\ 2p_z$ |
| $F_3$ | $0.293\ 2p_x$<br>$-0.254\ 2p_y$<br>$0.207\ 2p_z$ | $-0.254\ 2p_x$<br>$0.359\ 2p_z$ |
| $F_4$ | $-0.440\ 2p_x$ | $-0.440\ 2p_y$ |

| $B_4Cl_4$ | $E_1$ | | $E_2$ | |
|---|---|---|---|---|
| $B_1$ | $-0.047\ 2p_x$<br>$-0.132\ 2p_z$ | | $0.140\ 2p_y$ | |
| $B_2$ | $0.093\ 2p_x$<br>$0.081\ 2p_y$<br>$0.066\ 2p_z$ | | $0.081\ 2p_x$<br>$0.114\ 2p_z$ | |
| $B_3$ | $0.093\ 2p_x$<br>$0.066\ 2p_y$<br>$-0.081\ 2p_z$ | | $0.081\ 2p_x$<br>$0.114\ 2p_z$ | |
| $B_4$ | $-0.140\ 2p_x$ | | $-0.140\ 2p_y$ | |
| $Cl_1$ | $0.039\ 2p_x$<br>$0.111\ 2p_z$ | $-0.153\ 3p_x$<br>$-0.433\ 3p_z$ | $0.117\ 2p_y$ | $0.459\ 3p_y$ |
| $Cl_2$ | $-0.078\ 2p_x$<br>$-0.068\ 2p_y$<br>$-0.055\ 2p_z$ | $0.306\ 3p_x$<br>$0.265\ 3p_y$<br>$0.217\ 3p_z$ | $-0.067\ 2p_x$<br>$0.096\ 2p_z$ | $0.265\ 3p_x$<br>$-0.375\ 3p_z$ |
| $Cl_3$ | $-0.078\ 2p_x$<br>$0.068\ 2p_y$<br>$-0.055\ 2p_z$ | $0.306\ 3p_x$<br>$-0.256\ 3p_y$<br>$0.217\ 3p_z$ | $0.067\ 2p_x$<br>$-0.096\ 2p_z$ | $-0.265\ 3p_x$<br>$0.375\ 3p_z$ |
| $Cl_4$ | $0.177\ 2p_x$ | $-0.459\ 3p_x$ | $-0.117\ 2p_y$ | $-0.459\ 3p_y$ |

[a] The numbers listed are coefficients for the atomic orbital and atom indicated. The E molecular orbitals are direct linear combinations of these atomic orbitals. Atom $B_1$ is in the *xz* plane. $B_4$ is on the $C_3$ axis (*i.e.*, the *z* axis). $B_2$ and $B_3$ are related to $B_1$ by 120° rotations about the *z* axis. $E_1$ and $E_2$ are the two components of the pair of E orbitals. These E orbitals are absent in a minimum basis set for $B_4H_4$ and are here composed of electrons of $\pi$ symmetry with respect to each of the B–X bonds.

direct *ab initio* methods in accuracy. Using the PRDDO method, we optimized the B–F distance in $B_4F_4$ and obtained a bond length of 1.301 Å. However, there was no appreciable change in either the boron–fluorine $\pi$ overlap or the orbital populations; typical changes were about 0.003 au for the former and 0.02 electron for the latter. Geometry optimizations in BF and $BF_3$ yielded B–F bond lengths of 1.26 and 1.33 Å. These values are to be compared with the experimental and theoretical values of 1.26 and 1.30 Å, respectively. Therefore, the B–F distance for $B_4F_4$ optimized by the PRDDO method may be slightly larger than the actual value. In any case, our conclusions regarding the relative amounts of back-coordination in $B_4F_4$ and $B_4Cl_4$ remain unchanged.

A previous semiempirical study of trigonal boron halides[2] has suggested that the order of $\pi$ back-donation in these molecules is $BI_3 > BBr_3 > BCl_3 > BF_3$. In other words, the back-donation decreases with increasing electronegativity. *Ab initio* calculations[6] on $BF_3$ and $BCl_3$ indicate, however, a slightly smaller gross atomic population in B ($2p_z$) (perpendicular to the molecular plane) in $BF_3$ (0.36) than in $BCl_3$ (0.41). However, three halogens compete for the $2p_z$ orbital of B in these molecules, as compared with one halogen in $B_4F_4$ and $B_4Cl_4$. Experimental values[10] of acidities suggest that $BCl_3$ is a stronger Lewis acid than is $BF_3$. However, other factors involving repulsions and transition states may be of dominant importance in these experiments.

The inclusion of 3d orbitals on chlorine in the $B_4Cl_4$ calculation may be of some importance in studying the problem of $\pi$ donation in these molecules. The omission of 3d orbitals may possibly lead to an underestimation of the $\pi$ donation from chlorine to boron and an overestimation of the 3p contribution to the $\pi$ donation.

It is interesting that the condensation of BCl in the presence of $BCl_3$ at −196° yields appreciable amounts of $B_4Cl_4$, while condensation of BF in the presence of $BF_3$ at the same temperature yields $B_2F_2$ and $(BF_2)_2BF$.[20] Generally, there are quite a number of polyhedral boron chlorides, some of which are quite stable, while boron fluorides tend to form boron hydride analogs with $BF_2$ groups acting as terminal and bridging groups as in $B(BF_2)_3$, $B_2(BF_2)_6$, and $B_5(BF_2)_9$.[20] Also, $BHF_2$ exists while $BH_2F$ has not been synthesized. These experimental results would indicate that fluorine prefers to form, with boron, open boron fluorides with $B-BF_2$ bonds rather than BF bonds, while chlorine tends to form polyhedral boron chlorides with terminal B–Cl bonds.[21] It is generally thought that this behavior is a direct consequence of large electronegativity of fluorine, such that the fluorine electrons may not be able to participate in back-coordination to the extent of the chlorine electrons. However, our calculations suggest that more extensive experimental and theoretical studies of the boron halides would be profitable.

Our results for $B_4Cl_4$ indicate the existence of a low-lying E* orbital which can readily accept an electron excited from an occupied $T_2$ MO. This orbital is analogous to the unoccupied nonbonding E orbital of $B_4H_4$.[22] The possibility that $B_4Cl_4$ has an E* orbital with almost a zero eigenvalue has been assumed by Massey and Urich[7] to explain the decomposition of $B_4Cl_4$ into BCl fragments under absorption of 245-mμ radiation.[12] The MO for this E* orbital consists mainly of boron character, and an electron in this MO (excited from the $T_2$ orbital) would weaken the boron cage bonding consistent with dissociation into BCl fragments.

**Localized Molecular Orbitals.** Localized molecular orbitals (LMO's) have been employed in the study of a large number of boron hydrides and carboranes and have led to some interesting interpretations of the valence structures for these molecules.[23] These calculations have, so far, always employed the Edmiston–Ruedenberg (ER) method of maximizing the intraorbital self-repulsion energy

$$J = \sum_i \int \phi_i(1)\phi_i(1)(1/r_{12})\phi_i(2)\phi_i(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \qquad (1)$$

to obtain the LMO's. However, the ER method is an $n^5$ ($n$ = number of MO's being localized) iterative process, requiring a prohibitively large quantity of computer time for a number of large ($n \gtrsim 30$) molecules. An ER calculation on $B_4F_4$, which has only 28 occupied orbitals, would be a formidable calculation for two reasons. First, the ER method requires a calculation of all the two-electron integrals over MO's. This computation involves a time-consuming transformation of the two-electron integrals from the symmetry orbital basis to the MO basis, requiring approximately $n^5$ operations. Second, since the ER method is also an $n^5$ itera-

---

(20) P. L. Timms, *Accounts Chem. Res.*, 6, 118 (1973).

(21) G. F. Lanthier, T. Kane, and A. G. Massey, *J. Inorg. Nucl. Chem.*, 33, 1569 (1971).

(22) B. Crawford, W. H. Eberhardt, and W. N. Lipscomb, *J. Chem. Phys.*, 22, 989 (1954).

(23) W. N. Lipscomb, *Accounts Chem. Res.*, 6, 257 (1973).

tive process, some four to five ER iterations for $B_4F_4$ would require approximately 1 hr of IBM 360/195 computer time. Therefore, the localization calculation would dwarf the actual SCF calculation.

Boys[24] has introduced an alternate method for obtaining LMO's consisting of *minimizing* the orbital self-extension

$$I = \sum_i \int \phi_i(1)\phi_i(1) r_{12}^2 \phi_i(2)\phi_i(2) \mathrm{d}\tau_1 \mathrm{d}\tau_2 \qquad (2)$$

The minimization of $I$ in eq 2 was shown by Boys[24c] to be equivalent to maximizing the sum of the squares of the distances of the orbital centroids from some arbitrarily defined gauge of the molecular coordinate systems[24c]

$$D = \sum_i \langle\phi_i|r|\phi_i\rangle\cdot\langle\phi_i|r|\phi_i\rangle \qquad (3)$$

Therefore, the Boys method only requires a knowledge of the dipole moment matrix and is approximately an $n^3$ iterative process, requiring much less computer time than the ER method.[25]

The localized orbitals for $B_4H_4$ and $B_4F_4$[26] are obtained by performing successive two-orbital transformations on an orbital pair $(\phi_i,\phi_j)$ in order to maximize eq 3. The canonical molecular orbitals (CMO's) were obtained from the PRDDO calculations on $B_4H_4$ and $B_4F_4$ and were subjected to an initial random unitary transformation. At the conclusion of each calculation, a *partial* second derivative test, which excluded inner shells, was performed. A detailed description of the 2 × 2 transformation, the partial second derivative test, and an extensive comparison of the ER and Boys method applied to boron hydrides and carboranes is now in preparation and will be published shortly.[27]

The Boys LMO's for $B_4H_4$ and $B_4F_4$ reflect the relative amounts of $\pi$ back-donation in these molecules. In the case of $B_4H_4$, there can be no $\pi$ back-donation because there are no occupied p orbitals on hydrogen, and $B_4H_4$ localizes (Table VII) to four inner shells, four central three-center bonds, and four single B-H bonds. The B-B-B bonds for $B_4H_4$ are equivalent and *symmetric* with typical values for the delocalization index. The B-H bonds are also equivalent and quite well localized ($d$ = 6.34%). The molecule $B_4F_4$ localizes beautifully to eight inner shells, four lone pairs, each centered on a fluorine, four equivalent, central three-center B-B-B bonds, and twelve B-F $\tau$ bonds (three per B-F interaction). The B-F LMO's are very polar, with most of the electronic population centered on fluorine (Table VII). The three-center B-B-B bonds in $B_4F_4$, located on each face of the regular tetrahedron, consist of equivalent contributions from each boron. The four largest eigenvalues from the second derivative test are −0.0492, −0.0625, −0.0630, and −0.0640. The eigenvalues indicate that the localization is insensitive, to second order, to certain couplings between the B-F LMO's.

**Table VII.** Localized Orbitals for $B_4H_4$ and $B_4F_4$

| | | A | A′ | A″ | $d^a$ |
|---|---|---|---|---|---|
| $B_4H_4$ | B (inner shell) | 2.01 | | | 2.84 |
| | B-H | 1.02 | 0.99 | | 6.34 |
| | B-B-B | 0.68 | 0.68 | 0.68 | 20.11 |
| $B_4F_4$ | B (inner shell) | 2.01 | | | 2.70 |
| | F (inner shell) | 2.00 | | | 0.83 |
| | F (lone pair) | 1.98 | | | 19.06 |
| | B-F[b] | 0.29 | 1.71 | | 8.20 |
| | B-B-B | 0.66 | 0.66 | 0.66 | 31.10 |

[a] The per cent delocalization ($d$) is defined as $d = [1/2\int(\phi_i^{\mathrm{L}} - \phi_i^{\mathrm{T}})\mathrm{d}t]^{1/2}(100\%)$, where $\phi^{\mathrm{L}}$ is a localized orbital and $\phi^{\mathrm{T}}$ is $\phi^{\mathrm{L}}$ modified by setting all nonlocal contributions equal to zero. [b] We term the B-F bonds as "$\tau$ like" because there are three "bonds" per B-F interaction and they are all equivalent; however, these bonds *do not* constitute a triple bond in the conventional sense of the definition. The population on boron is quite small, and the total populations on boron and fluorine are 0.87 and 5.13 and, therefore, the total populations are more representative of single-bond populations.

We have found[27] that PRDDO wave functions localized by Boys' procedure give the same localized valence structures as does the ER procedure except for cases where there is a difference between a $\sigma$-$\pi$ as opposed to equivalent bond descriptions. The Boys procedure appears to prefer the equivalent orbital description. An apparent exception is the great difference between the results described here for $B_4H_4$ of $T_d$ symmetry and the earlier results[13] for the ER localization of this hypothetical molecule. Suspecting an error in the generation of some non-Hartree-Fock two-electron integrals for the E representation of the $C_{3v}$ point group, we have now repeated the calculation in $C_s$ symmetry. The ER results have now converged to the same basic valence structure as that found by the Boys method. Moreover, the self-repulsion energy for the correct structure is 16.345 au as opposed to the value of 14.972 au in ref 13.

The Boys localization method, coupled with the PRDDO SCF method, promises to be a powerful tool for studying the valence structure of large molecules. It is an *ab initio* method, much easier to implement than the ER method, and, as presently implemented, reduces the required computation time for a localization calculation by almost a factor of 100, when compared with the ER method.

In conclusion, a minimum basis set approximation to the wave functions for $B_4F_4$ and $B_4Cl_4$ indicates more $\pi$ back-donation for $B_4F_4$ than for $B_4Cl_4$. However, we must qualify our results by suggesting than an expanded basis set calculation may be necessary before further conclusions can be made regarding the bonding in these molecules.

**Acknowledgments.** We wish to thank IBM Research at San Jose, Calif., and E. Clementi for supplying computer time for the $B_4F_4$ and $B_4Cl_4$ calculations. We also thank the Office of Naval Research for supporting part of this work and D. S. Marynick for several interesting comments.

**Registry No.** $B_4F_4$, 49567-49-9; $B_4Cl_4$, 17156-85-3.

---

(24) (a) S. F. Boys, *Rev. Mod. Phys.*, 32, 296 (1960); (b) J. M. Foster and S. F. Boys, *ibid.*, 32, 300 (1960); (c) S. F. Boys, "Quantum Theory of Atoms, Molecules, and the Solid State," Per-Olov Lowdin, Ed., Academic Press, New York, N. Y., 1966, p 253.

(25) If we convert computer times for our (unpublished) Boys localization of 2,4-$C_2B_5H_7$ on the IBM 360/91 and the ER localization of 2,4-$C_2B_5H_7$ (see ref 23) on the IBM 360/65 to the model 195, we obtain 720 and 9 sec, respectively, for a complete calculation, including a second derivative test. Thus, for this molecule and the present programs, the Boys method is approximately 80 times faster than the Edmiston-Ruedenberg method.

(26) The dipole moment routines, at present, will only evaluate integrals over 1s, 2s, and 2p atomic orbitals, and therefore we cannot, as yet, calculate the LMO's for $B_4Cl_4$.

(27) T. A. Halgren, D. A. Kleier, J. H. Hall, Jr., and W. N. Lipscomb, to be submitted for publication.