

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 87, NUMBER 3

FEBRUARY 5, 1965

Physical and Inorganic Chemistry

LCAO-MO Calculations on Boron Compounds. I. LCAO-MO-SCF Calculations on Borazines

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MO calculations for borazines using an LCAO technique have been performed in the framework of the following three different approximations: (1) Hückel, (2) Pariser-Parr (without iteration), and (3) Pople (iterated to self-consistency) utilizing the Pariser-Parr approximations for the integrals. Several different theoretical models for choice of input parameters have been utilized. Modified values for boron electron-repulsion integrals, which take into account electron correlation effects, have been calculated for each different choice of theoretical model. Comparison of the calculated LCAO-MO-SCF results for molecular energy levels against known experimental data and examination of the magnitude of the terms of the final SCF Hamiltonian matrix to be diagonalized indicated a reasonable choice for a calculational model.

Introduction

Theoretical Background of the Calculational Methods. For conjugated molecules with a planar nuclear framework, it is possible to separate the atomic orbitals into noncombining classes, π and σ , according to whether or not they have a node in the nuclear plane.

One of the methods extensively used in the quantum mechanical study of the π -electrons of conjugated molecules is the semiempirical molecular orbital theory developed by Hückel. According to this theory, the mobile electrons can be treated as occupying a set of delocalized molecular orbitals, these orbitals being eigenfunctions of a one-electron Hamiltonian repre-

senting the kinetic energy, the field of the nuclei, and the smoothed-out distribution of the other electrons. By approximating the orbitals as linear combinations of atomic orbitals centered on the various atoms and estimating certain integrals empirically, the theory has been developed in a simple form enabling it to be applied to a wide range of molecules.²

However, although it has the merit of great simplicity, the Hückel procedure has serious defects—connected with the difficulty of giving a precise definition of the one-electron Hamiltonian. Strictly speaking, the problem should be formulated in terms of the complete many-electron Hamiltonian in which the interelectronic repulsions are included explicitly.^{3,4}

The Pariser-Parr and Pople theories start from this π -electron approximation in which the π -electrons are treated separately from the rest, and it is supposed that the effect of the σ -electrons on the π -structure can be represented by a "core" in whose potential the π -electrons move.^{4,5} The potential of an atom contributing to the "core" represents that due to the nuclear charge and to all the σ -electrons associated with the atom.

The molecular orbital equations rigorously derived from the correct many-electron Hamiltonian are simplified by a series of systematic approximations and reduce to equations comparable with those used in

(2) (a) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, p. 52; (b) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 33.

(3) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(4) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(5) (a) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953); (b) *ibid.*, **21**, 767 (1953).

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the semiempirical method based on an incompletely defined one-electron Hamiltonian, but the Pariser–Parr and Pople equations differ in that they include certain important terms representing electronic interaction. In the Pople method, these systematic integral approximations are applied to the self-consistent equations of Roothaan.⁶

Recent studies of heterocyclic systems by the Roothaan SCF technique have provided a justification for the Hückel method and at the same time indicated suitable values for, and demonstrated origins of, the various parameters arising in the Hückel method.⁷ One example is that the SCF analog of the familiar Hückel Coulomb integral, α , is identified with the diagonal element of the final SCF Hamiltonian to be diagonalized. This analogy will be shown to be of considerable usefulness in the present studies.

Borazine. Borazine (formerly called borazole) has been called “inorganic benzene” because of its similarity in both structure and physical properties to benzene with which it is isoelectronic. Many of the properties of borazine are believed to arise from the “ π ”-system of this molecule.

Mulliken had postulated that on theoretical grounds a one-to-one correspondence and close resemblance between the electron configuration and over-all states of borazine and benzene are to be expected.^{8,9} Mulliken and Roothaan performed a semiempirical Hückel-type calculation of borazine and compared the results with the observed ultraviolet spectrum.¹⁰ By taking a reasonable value for the difference in electronegativity of boron and nitrogen, they obtained a value of β in fair agreement with theoretical expectations.

In the intervening years since Mulliken’s Hückel calculation on borazine, the Pariser–Parr and Pople methods for calculations of the electronic structures of π -systems based on the correct many-electron Hamiltonian have been used successfully for calculations on many organic π -systems.

At the Centre de Mécanique Ondulatoire Appliquée, there is a general research program on the applicability and validity of the Pariser–Parr and Pople calculations for various types of molecules including alternant and nonalternant hydrocarbons and heterocyclics. It was of interest to treat borazine by these methods in order to develop a theoretical calculational model for B–N bonds in π -systems.

Details of the Calculations

MO calculations for borazines using an LCAO technique have been performed in the framework of the following three different approximations: (1) Hückel, (2) Pariser–Parr, and (3) Pople-SCF. These calculations were carried out on the IBM 7090 in Paris and the IBM 7094 at the Martin Co. Computing Center in Baltimore with the aid of an entirely automatic program written by Dr. Bessis of the Centre de Mécanique Ondulatoire Appliquée.

(6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 61 (1951).

(7) R. D. Brown, B. A. W. Collier, and M. L. Heffernan, *Tetrahedron*, **18**, 343 (1962).

(8) Quoted in L. E. Jacobs, J. R. Platt, and G. W. Schaeffer, *J. Chem. Phys.*, **16**, 116 (1948).

(9) Quoted in J. R. Platt, H. B. Klevens, and G. W. Schaeffer, *ibid.*, **15**, 598 (1947).

(10) C. C. J. Roothaan and R. S. Mulliken, *ibid.*, **16**, 118 (1948).

Results and Discussion

Borazine. The most difficult part of the borazine calculation was the choice of a theoretical model from which to evaluate the necessary input parameters for the Pariser–Parr and Pople calculations.

Model I. Description. It seemed preferable to try to treat borazine as the other heteroatomic compounds had been treated (without imposing a preconceived notion of what one imagined the bonding in borazine should be). After inspecting the results of the preliminary calculations, it would then be possible to modify the σ -core, if necessary, for agreement with experimental observations.

In view of the fair success of Mulliken’s Hückel calculation and the relationship of Hückel to SCF calculations, a model for the Pariser–Parr and Pople calculations was chosen which was an analog of the original Mulliken model. The physical implications of this model with respect to bonding in the σ - and π -frameworks of borazine will be discussed later, after the results of the calculation are presented.

The Mulliken model required uniquely that the π -electron would see a potential on the boron or the nitrogen atom approximately equivalent to that which a π -electron in a free *neutral* boron or nitrogen atom would see. (That this model I is contradictory to the formerly popular notion that borazine is composed of B[−] and N⁺ atoms is obvious. B[−] atom denotes the original valence state of the boron atom from which the borazine is considered to be formed; namely, B[−] has three electrons in its σ -frame and a fourth extra electron which it donates to the π -system. N⁺ denotes the original valence state in which N has only three electrons in its σ -framework and a fourth which it donates to the π -system. However, as will be shown, this model I is surprisingly close to what appears to be a fairly accurate representation of the true molecular binding, both σ and π , of borazine.)

The basic parameters necessary for the calculations are the valence state ionization potentials of the boron and nitrogen, modified values for the one-center two-electron repulsion integrals which include a correction for electron correlation and correspondingly scaled values for the two-center two-electron repulsion integrals. For these modified one-center two-electron repulsion integrals ($pp|pp$), simple expressions had been derived by Pariser and Parr for carbon and nitrogen

$$(pp|pp) = I - A$$

where I = the valence state ionization potential and A = the valence state electron affinity. These expressions were later shown to be the leading term of a more exact expression which could be derived from spectroscopic term values.¹¹ However, because boron originally has less than a half-filled shell, the above expression was shown not to be valid for the ($pp|pp$) of boron, and the modified value for the one-center two-electron repulsion integral of boron, 7.094 e.v., was derived exactly from the complete expansion in spectroscopic term values.¹² The two-center two-electron

(11) A. Julg, *J. chim. phys.*, **55**, 413 (1958).

(12) J. J. Kaufman and G. Berthier, Technical Report No. 7 on Office of Naval Research Contract Nonr 3471(00) Task No. 356-433, Dec. 1962 (also RIAS Technical Report TR 62-21).

repulsion integrals were then scaled by the usual Pariser–Parr procedure.^{5a}

The two-center electronic repulsion integrals ($pp|qq$) were determined for $r \geq 2.80$ Å. from the uniformly charged sphere model formula

$$(pp|qq) = \left(\frac{7.1975}{r}\right) \left\{ 1 + \left(\frac{1}{2r}\right)^2 (R_p - R_q)^2 \right\}^{-1/2} + \left\{ 1 + \left(\frac{1}{2r}\right)^2 (R_p + R_q)^2 \right\}^{-1/2} \text{ e.v.} \quad (1)$$

in which $R_p = (4.597/Z_p) \times 10^{-8}$ cm., where Z_p is Slater's effective nuclear charge; for $r \leq 2.80$ Å., the integrals ($pp|qq$) were determined by extrapolation down to $r = 0$ by use of an equation of the form

$$ar + br^2 = \left(\frac{1}{2}\right)[(pp|pp) + (qq|qq)] - (pp|qq) \quad (2)$$

in which the constants a and b were obtained by fitting values calculated from eq. 1 for $r = 2.80$ and 3.70 Å.

In calculations of this type, β is usually treated as an empirical parameter. To pick a reasonable value of β_{BN} for the preliminary calculations, the suggestion of Kubo that $\beta_{BN}/\beta_{CC} = S_{BN}/S_{CC}$ was followed (where S is the magnitude of the overlap integral).¹³ It would also have been possible to have evaluated β_{BN} from the observed ultraviolet spectrum of borazine and the energy formulas Pariser and Parr give for s -triazine which has the same symmetry. From the experimentally measured value of the ${}^1A_2'$ borazine transition (6.5 e.v.) and the formula $E({}^1A_2') - E_N = -2\beta_{12} + \frac{1}{6}(11\ 22) - \frac{3}{2}(11\ 33) - \frac{3}{2}(22\ 44) + 2(11\ 44)$, the values calculated for β_{BN} ranged only from -2.52 e.v. for model I to -2.21 e.v. for models II and III (these models will be described in the succeeding sections). Therefore the values used in this article, $\beta_{BN} = -2.31$ or -2.39 e.v. are good compromise values (see Table I).

Table I. Basic Parameters Used in the Calculations

	Model I	Model II	Model III
Z_B	2.60	2.25	2.25
Z_N	3.90	4.25	4.25
α_B	-8.33	-1.06	-1.06
α_N	-14.63	-28.16	-28.16
n_B^a	1	1	0
n_N^a	1	1	2
β_{BN}	-2.31	-2.31	-2.39
(11 11) _B	6.91	4.74	4.74
(22 22) _N	12.27	15.91	15.91
(11 22)	6.88106	7.04534	7.04534
(11 33)	5.06018	4.87906	4.87906
(11 44)	4.71103	4.66173	4.66173
(22 44)	5.46201	5.62276	5.62276

^a n is the number of π -electrons donated.

Calculational Results. *A.* There are several points at which SCF calculations of benzene and borazine must bear a definite predetermined relationship to each other in order to reproduce the observed experimental similarities of the two molecules.

1. Ionization Potentials. The ionization potential of borazine has been measured by electron impact as 10.3 ± 0.2 e.v.; in the same study, the ionization

potential of benzene was measured as 9.6 ± 0.2 e.v.¹⁴ The ionization potential of benzene is known to be due to removal of a π -electron. It seems probable that the ionization potential of borazine is also due to removal of an electron from its π -system, since to remove an electron from a B–H or N–H bond is known to require more energy¹⁵ (at least 12.4 e.v. is necessary to remove an electron from a B–H bond, and an estimated 17 e.v. is necessary to remove an electron from an N–H bond), and to remove an electron from the B–N σ -framework can be reasonably be postulated to require more energy because to remove an electron from a σ -bond is known to require 1.14 e.v. more than to remove an electron from a π -bond between the same two types of atoms.

The ionization potential of an electron from a π -system is proportional to the energy of the highest occupied molecular orbital (HOMO), plus a correction factor. For hydrocarbons, the SCF calculated energy of the highest molecular orbital plus 2 e.v. is equivalent to the measured electron impact ionization potential. Therefore, the SCF calculated energy of the HOMO of benzene should be about -11.6 ± 0.2 e.v., and that of borazine, -12.3 ± 0.2 e.v. The SCF calculational result for the HOMO of benzene was -11.58 e.v. and for borazine, -11.84 e.v. These results are in reasonably good agreement with expectation.

To verify the absolute magnitudes of the calculated energy levels, ionization potentials are of more value than ultraviolet spectra, which can only give differences between energy levels.

2. Comparison of the Diagonal Terms in the Final SCF Hamiltonian. As mentioned previously, the analog of the Hückel Coulomb integral α is the diagonal term in the final SCF matrix. The entire final SCF Hamiltonians for both benzene and borazine were calculated. The diagonal term for benzene, -5.96 e.v., is equivalent to α_C in a Hückel calculation. The corresponding terms in borazine for boron and nitrogen, -2.32 and -9.23 e.v., are equivalent to α_B and α_N in the Hückel calculations. To fulfill the condition that this SCF calculation for borazine is really a good approximation to Mulliken's calculation, α_B should be about the same amount greater than α_C that α_N is less than α_C . It is apparent that this condition is moderately satisfied. More important is that these differences also be close to the $\beta_{Hückel}$ to satisfy the following conditions: $\alpha_B = \alpha_C - \beta_{CC}$ and $\alpha_N = \alpha_C + \beta_{CC}$. The value of $\beta_{Hückel}$ to be used in comparisons of this type is -4.8 e.v. Therefore, these SCF calculations seem to indicate that model I is a reasonably good approximation for a theoretical calculational model of borazine.

B. Ultraviolet Spectrum. The ultraviolet spectrum of borazole has been measured and several of the observed transitions have been assigned¹⁶: ${}^1A_1'$, 6.86 e.v.; ${}^1A_2'$, 6.50 e.v.; and ${}^1E_1'$, 7.70 e.v. The lowest excitations are achieved by exciting either one of the ground-state $1e''$ MO's to either one of the (excited) $2e''$ MO's—excitation from a degenerate MO to a degenerate MO. Linear combinations of wave func-

(14) E. D. Loughran and C. L. Mader, Los Alamos Scientific Laboratory Report LA-2368, Jan. 14, 1960.

(15) W. S. Koski, J. J. Kaufman, C. F. Pachucki, and F. J. Shipko, *J. Am. Chem. Soc.*, **80**, 3202 (1958).

(16) See Platt, Kleven, and Schaeffer, ref. 9.

(13) H. Watanabe, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 3294 (1960).

tions representing all the possible excitations are necessary to form irreducible representations of the excited states. The energy levels of the states are found by evaluating the integrals over the correct linear combinations of antisymmetrized product functions. (The procedure followed for calculation of the borazine ultraviolet spectrum is identical with that of Roothaan for calculation of the benzene spectrum.¹⁷)

$${}^1A_1' = \epsilon_4 - \epsilon_2 - J_{24} + 2K_{24} - M_{23,45} + 2M_{24,35}$$

$${}^1A_2' = \epsilon_4 - \epsilon_2 - J_{25} + 2K_{25} + M_{23,45} - 2M_{25,34}$$

$${}^1E_1' = \epsilon_4 - \epsilon_2 - J_{24} + 2K_{24} + M_{23,45} - 2M_{24,35}$$

$${}^3A_1' = \epsilon_4 - \epsilon_2 - J_{24} - M_{23,45}$$

$${}^3A_2' = \epsilon_4 - \epsilon_2 - J_{25} - M_{23,45}$$

$${}^3E_1' = \epsilon_4 - \epsilon_2 - J_{24} + M_{23,45}$$

where

$$J_{ij} = e^2 \int \frac{\psi_i^*(\mu)\psi_j^*(\nu)\psi_i(\mu)\psi_j(\nu)}{r_{\mu\nu}} d\nu_\mu d\nu_\nu$$

$$K_{ij} = e^2 \int \frac{\psi_i^*(\mu)\psi_j^*(\nu)\psi_j(\mu)\psi_i(\nu)}{r_{\mu\nu}} d\nu_\mu d\nu_\nu$$

$$M_{ijkl} = e^2 \int \frac{\psi_i^*(\mu)\psi_k^*(\nu)\psi_j(\mu)\psi_l(\nu)}{r_{\mu\nu}} d\nu_\mu d\nu_\nu$$

The calculated values (e.v.)

${}^1A_1'$	5.741	${}^3A_1'$	5.740
${}^1A_2'$	6.509	${}^3A_2'$	5.822
${}^1E_1'$	7.145	${}^3E_1'$	5.781

are in fairly good agreement with those which have been observed.

Physical Implications of This Model. This model for the π -system of borazine implies certain definite conclusions about the σ -framework of borazine since the effective potential of an atom in the "core" is due to both its nuclear charge and its σ -electrons.

At first thought, to have a π -electron in borazine see a potential as if it were in a neutral boron or nitrogen atom might be construed to suggest that there is no σ -framework connecting the boron and nitrogen. However, this is not the case at all. Rather, it has been reported very recently that in cases where a covalent-type bond exists between boron and nitrogen, such as in $X_3B:NY_3$ compounds, experimental dipole moments show that even in these compounds there is virtually no charge transfer from nitrogen to boron.¹⁸ Similarly, in a true covalent B-N bond, the greater electronegativity of the nitrogen would be expected to lead to the result that the most of the electron density in a B-N σ -bond will be on the nitrogen atom.

The final calculated π -electron density shows π -electron charges of 0.478 on boron and 1.522 on nitrogen. This is concomitant with σ -electron densities in which σ -electron charge has been transferred from the boron to the nitrogen. This is in good agreement with experimental results on quadrupole coupling constants in graphitic boron nitride which suggest 0.45 electron is donated to the boron if the boron electrons

form three planar trigonal bonds to the neighboring nitrogen atoms.¹⁹

It is gratifying that this model, which was originally chosen solely on the basis of the properties required to satisfy the conditions for calculations on the π -system of borazine, reproduces quite well the behavior to be anticipated for both the σ - and π -systems of this molecule (see Table II).

Table II. Borazine. Model I (Pople-SCF)

MO	AO Symmetry			
	a_2'' ϕ_1	e'' ϕ_2	e'' ϕ_3	e'' ϕ_4
χ_1	0.329641	-0.001436	0.361225	0.731649
χ_1	0.473994	0.632681	0.368640	-0.167860
χ_2	0.329641	0.313549	-0.179369	-0.391381
χ_4	0.473993	0.002912	-0.732238	0.360935
χ_5	0.329641	-0.312112	-0.181857	-0.340267
χ_8	0.473994	-0.635592	0.363597	-0.193075
	e'' ϕ_5	a_2'' ϕ_6		
χ_1	0.029510	0.473993		
χ_2	-0.319858	-0.329641		
χ_3	0.618871	0.473994		
χ_4	0.014558	-0.329641		
χ_5	-0.648381	0.473994		
χ_8	0.305300	-0.329641		

Model II. Description. As a check on the sensitivity of the calculations to the choice of a theoretical model, it was desirable to have an SCF calculation for borazine based on the "fashionable" B^-N^+ model.

One previous SCF calculation of this type had been attempted by Davies.²⁰ However, he carried out this calculation in terms of $\Delta\omega$, differences in diagonal elements of the final SCF Hamiltonian, and ΔG , differences in repulsion integrals, *without* committing himself to the absolute values of these.

In order to have a valid comparison of an SCF calculation of this model II with that of model I, a complete SCF calculation was performed for a B^-N^+ model of borazine. The effective Slater nuclear charges used corresponded to B^- and N^+ , and the electron repulsion integrals were those calculated rigorously for the atoms B^- and N^+ .

The evaluation of the necessary input parameters for this model was more difficult than that for model I for the following reason. In order to evaluate the modified value of the one-center two-electron repulsion integral of B^- ($pp|pp$)_B (which physically resembles ($pp|pp$)_C in a π -system since both the B^- and the C have three electrons in a σ -framework and donate one electron to the π -system), it is necessary to have the valence-state electron affinities of B^- to form B^{2-} in at least two different valence states. The electron affinity of B^- to form B^{2-} even in the ground state had never been measured experimentally. This ground-state electron affinity of B^- can be estimated from the rigorous extrapolation procedure of Edlen.²¹ However, it is not possible to evaluate subsequently the necessary valence-state promotional energies of B^{2-} .

(17) C. C. J. Roothaan, "New Developments in Molecular Orbital Theory. Second Installment," University of Chicago, 1950.

(18) Discussions at International Symposium on Boron-Nitrogen Chemistry, Duke University, April 22-25, 1963.

(19) A. H. Silver and P. J. Bray, *J. Chem. Phys.*, **32**, 288 (1960).

(20) D. W. Davies, *Trans. Faraday Soc.*, **56**, 1713 (1960).

(21) B. Edlen, *J. Chem. Phys.*, **33**, 98 (1960).

This difficulty was circumvented by extrapolating directly the different valence-state electron affinities of B^- .²² The values for the one-center two-electron repulsion integral of B^- calculated by two independent methods, spectroscopic expansion and estimation by the Pariser-Parr expression, 4.74 and 4.02 e.v., agreed quite well.²² This was gratifying in view of the fact that each calculation depends on extrapolated values for the electron affinities of B^- in different valence states.

Calculational Results. A. Applying the same criteria for the relationships which must be satisfied between the SCF calculations of benzene and borazine, it can be seen that this model II for borazine, B^- and N^+ , leads to completely unreasonable calculational results.

1. *Ionization Potentials.* From measured ionization potentials of benzene and borazine and comparison with the SCF calculated HOMO of benzene, the SCF calculated energy of the HOMO of borazine should be of the order of -12.3 ± 0.2 e.v. The SCF calculated energy for the HOMO of model II is -20.17 e.v., about 8 e.v. too high.

2. *Comparison of the Diagonal Terms in the Final SCF Hamiltonian.* The diagonal terms in the final SCF Hamiltonian for boron (+7.64 e.v.) and nitrogen (-19.78 e.v.) show much too large a difference from that of carbon in benzene (-5.96 e.v.).

B. *Ultraviolet Spectrum.* The values (e.v.) for the ultraviolet transitions calculated from model II

$^1A_1'$	22.610	$^3A_1'$	21.539
$^1A_2'$	22.649	$^3A_2'$	22.055
$^1E_1'$	22.877	$^3E_1'$	21.797

are not at all in agreement with those measured experimentally.

Physical Implications of This Model. The calculated π -electron charge distribution from this model II is 0.045 on boron and 1.955 on nitrogen. This would imply that there is virtually no π -electron donation from nitrogen to boron. This is contrary to the experimental results on quadrupole coupling constants in graphitic boron nitride which suggest 0.45 electron is donated to the boron if the boron electrons form three planar trigonal bonds to the neighboring nitrogen atoms.

On all bases, this model of B^-N^+ does not appear to be a reasonable physical model for borazine (see Table III).

Model III. Description. The calculations were performed for still another model of borazine—one in which the borons are presumed to contribute no electrons and each nitrogen two electrons to the π -system.

Calculational Results. A. A comparison of the relationships between the SCF calculations of benzene and borazine indicates that while model III is not in quite as good agreement as model I, it is still not too unreasonable a model judged on this basis.

1. *Ionization Potentials.* The SCF calculated energy of the HOMO of borazine was -14.63 e.v. compared to a desired value of -12.3 e.v.

(22) O. Chalvet and J. J. Kaufman, Technical Report No. 8 on Office of Naval Research Contract Nonr 3471(00) Task No. 356-433, Dec. 1962 (also RIAS Technical Report TR 62-22).

Table III. Borazine. Model II (Pople-SCF)

MO	AO Symmetry			
	a_2'' ϕ_1	e'' ϕ_2	e'' ϕ_3	e'' ϕ_4
χ_1	0.120262	-0.001052	0.089282	0.805158
χ_2	0.564690	0.698034	0.414051	-0.034567
χ_3	0.120260	0.077848	-0.043731	-0.490962
χ_4	0.564678	0.009567	-0.811549	0.088580
χ_5	0.120260	-0.076795	-0.045554	-0.314194
χ_6	0.564691	-0.707600	0.397481	-0.054014
	e'' ϕ_5	a_2'' ϕ_6		
χ_1	0.102058	0.564685		
χ_2	-0.082327	-0.120261		
χ_3	0.646258	0.564687		
χ_4	0.011228	-0.120261		
χ_5	-0.748315	0.564687		
χ_6	0.071099	-0.120261		

2. *Comparison of Diagonal Terms in the Final SCF Hamiltonian.* The diagonal terms of

$$\alpha_B = -3.62 \text{ e.v.} = \alpha_C^{\text{SCF}} - 0.49\beta$$

$$\alpha_N = -12.42 \text{ e.v.} = \alpha_C^{\text{SCF}} + 1.35\beta$$

no longer have the symmetry of the Mulliken model; however, the values seem reasonable.

B. *Ultraviolet Spectrum.* The calculated values (e.v.) for the ultraviolet transitions

$^1A_1'$	6.288	$^3A_1'$	6.871
$^1A_2'$	6.765	$^3A_2'$	6.644
$^1E_1'$	8.017	$^3E_1'$	6.760

are in moderate agreement with the observed values.

Physical Implications of This Model. The calculated π -electron densities of 0.387 on B and 1.613 on N are in fairly good agreement with the results of the quadrupole coupling experiments. Model III is not too unreasonable a model for borazine, but seems less preferable than model I (see Table IV).

Table IV. Borazine. Model III (Pople-SCF)

MO	AO Symmetry			
	a_2'' ϕ_1	e'' ϕ_2	e'' ϕ_3	e'' ϕ_4
χ_1	0.307214	-0.290675	-0.120235	0.753176
χ_2	0.488828	-0.597543	0.457877	-0.149599
χ_3	0.307214	0.041211	0.311850	-0.394839
χ_4	0.488828	0.696258	0.287999	0.314438
χ_5	0.307214	0.249464	-0.191615	-0.358336
χ_6	0.488828	-0.098714	-0.746976	-0.164839
	e'' ϕ_5	a_2'' ϕ_6		
χ_1	0.021075	0.488828		
χ_2	-0.276711	-0.307214		
χ_3	0.641732	0.488828		
χ_4	0.008798	-0.307214		
χ_5	-0.662807	0.488828		
χ_6	0.267912	-0.307214		

Naphthalene and Diphenyl Analogs of Borazine. The complete SCF calculations for the naphthalene and diphenyl analogs of borazine were carried out for

models I, II, and III. Again the calculations for model I gave results which were consistently close to those of corresponding calculations for the hydrocarbons, model II gave results which were quite unreasonable, and model III gave reasonably good results but did not seem as preferable as model I.

Conclusion

LACO-MO-SCF calculations for borazine have been performed for three different theoretical models for borazine. The results of the calculations for model I when compared with experimental and theoretical criteria indicate that this model is a promising one for future calculations on B-N pairs in π -systems of the borazine type. The results of the calculations for model II, B-N⁺, are always less reasonable for borazines when judged by the same criteria. Model III gives calculational results which are not too unreasonable for the borazine family; however, this model seems less preferable than model I.

Calculational results for energy levels, total energies (Table V), and coefficients of atomic orbitals in all molecular orbitals for borazine by the Hückel (Table VI) and Pople-SCF (Tables II-IV) methods are listed. The calculational results by the Pariser-Parr method, which are very similar to those by the Pople-SCF method as well as the analogous results for the naphthalene and diphenyl analogs of borazine are available upon request (to J. J. K.).

Acknowledgment. This research was supported in part by the Chemistry Branch, Office of Naval Research, by the Air Force Office of Scientific Research of the Office of Aerospace Research, under Contract No. AF49(638)-1220, and by the Ordnance Materials Research Office. J. J. K. wishes to thank the Soroptimist Federation of the Americas for a study grant. We also wish to thank Mr. Sol James, Chief of Auto-

Table V. Orbital and Total Energies of Borazine

MO	Hückel (in β)	Pople-SCF (in e.v.)		
		Model I	Model II	Model III
ϕ_1	2.0069	-14.3780	-20.9492	-17.0457
ϕ_2	1.3255	-11.8405	-20.1712	-14.6312
ϕ_3	1.3255	-11.8405	-20.1712	-14.6312
ϕ_4	-1.3255	0.2704	8.0253	-1.4457
ϕ_5	-1.3255	0.2704	8.0253	-1.4457
ϕ_6	-2.0069	2.8603	8.8267	1.0689
E_{total}	9.3157	-86.0552	-148.9653	-131.4841

Table VI. Borazine. Models I, II, and III (Hückel)

MO	AO			
	Symmetry			
	a_2'' ϕ_1	e'' ϕ_2	e'' ϕ_3	e'' ϕ_4
χ_1	0.2891701	0.2194785	-0.1835251	-0.2260988
χ_2	0.4997138	0.7181638	0.2627832	0.2789853
χ_3	0.2891701	0.0491981	0.2818365	-0.5196197
χ_4	0.4997139	-0.5866588	0.4905565	-0.0845872
χ_5	0.2891701	-0.2686767	-0.0983114	0.7457185
χ_6	0.4997139	-0.1315050	-0.7533397	-0.1943981
	e'' ϕ_5	a_2'' ϕ_6		
χ_1	-0.7305434	-0.4997139		
χ_2	0.0633994	0.2891701		
χ_3	0.5610790	-0.4997138		
χ_4	-0.2733081	0.2891701		
χ_5	0.1694644	-0.4997138		
χ_6	0.2099087	0.2891701		

matic Computations, Martin Company Computing Center, for arranging to have some of the calculations run at the Martin Company Computing Center; and Mr. Jon Hamann of RIAS for assistance with some of the calculations of model III.

Rare Gas Ion Reactions with Pentaborane-9¹

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The reactions between He⁺, Ne⁺, Ar⁺, Kr⁺, and Xe⁺ ions and pentaborane-9 have been studied using a two-stage mass spectrometer in which the ionic products of collisions between positive ions with kinetic energies ranging from 2 to 200 e.v. and neutral molecules can be detected. The fragmentation of the pentaborane varied markedly as a function of the recombination energy of the rare gas ion. With xenon ions, only B₅H₇⁺ and B₅H₈⁺ were produced in significant amounts, while helium ion bombardment resulted in a variety of B₅H_n⁺, B₄H_n⁺, and B₃H_n⁺ ions. The kinetic energy of the bombarding ion in many cases had a significant effect on the relative abundances of the products. By plotting

the relative abundances of the products as a function of the excitation energy of the rare gas ions, breakdown curves for pentaborane-9 were constructed. The mass spectrum obtained by integrating the breakdown curves is in reasonably good agreement with the 70-v. electron impact spectrum. The possible role of the pentaborane-9 fragment ions in the proposed mechanism of the rare gas sensitized radiolysis is discussed.

Introduction

Recent studies³⁻⁵ of radiolysis of the boron hydrides have reported the formation of higher hydrides as a

(1) This work was done under the auspices of the United States Atomic Energy Commission.

(2) Lever Brothers Foundation Fellow.

(3) H. Schmied and W. S. Koski, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959, p. 38M.