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# *Ab initio* Studies of the Low-Lying π-States of Borazine*

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Self-consistent-field and configuration-interaction studies were performed on borazine, using a double-zeta basis set augmented by six diffuse $\pi$-functions. Low-lying singlet and triplet states of the $A_1'$, $A_2'$, and $E'$ species were calculated, corresponding to $\pi \rightarrow \pi^*$ excited valence and Rydberg states. A selection out of singly and doubly excited configurations relative to a set of reference configurations was made for each species. Calculated vertical excitation energies (in eV) are 7.12 for $^1A_2'(V)$, 8.45 for $^1E'$ $(3p\pi\text{-}R)$, 8.57 for $^1A_1'(V)$, ~8.9 for $^1E'(V\text{-}R)$, ~9.55 for $^1E'(3d\pi\text{-}R)$, 6.98 for $^3A_1'(V)$, 7.27 for $^3E'(V)$, 7.82 for $^3A_2'(V)$, ~8.30 for $^3E'(3p\pi\text{-}R)$, and ~9.5 for $^3E'(3d\pi\text{-}R)$, where $V$ and $R$ refer to valence or Rydberg character. The results are compared with experimental excitation energies, previous *ab initio* studies of borazine, and with recent *ab initio* studies of benzene.

**Key words:** Borazine, excited $\pi$-states of – Borazine, *ab initio* configuration interaction studies of ~

## 1. Introduction

A new theoretical *ab initio* study of the $\pi$-electronic spectrum of borazine $B_3N_3H_6$ was necessitated by various considerations: 1) there is still considerable disagreement between experimental and theoretical singlet excitation energies; 2) the triplet spectrum of borazine has been the subject of some controversy, and new attempts have been made to establish good experimental values; 3) recent improved theoretical studies on the $\pi$-spectrum of benzene will allow for interesting comparisons between benzene and borazine; 4) theoretical methods have much improved since

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* Dedicated to Professor Dr. H. Hartmann on the occasion of his 65th birthday.

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the last reported borazine calculations, and therefore allow for a new study with a much wider scope, e.g. the inclusion of diffuse functions in the basis set, and better accuracy.

The most recent *ab initio* configuration interaction (CI) study on the $\pi$-spectrum of borazine has been performed by Peyerimhoff and Buenker (PB) [1]. A slightly extended minimal basis set of contracted Gaussian functions ($3s$, $1p$ for each B and N, $1s$ for H) was employed (total of 42 functions), which was later relaxed to allow for a splitting of the six $p\pi$ functions into two sets (total of 48 functions). No diffuse orbitals were used. For the CI treatment, a limited number (about 100) of excited configurations was generated, with restrictions imposed by the maximum size of matrix that could be diagonalized. Two CI calculations were performed, one allowing for excitations among the $\pi$-orbitals only, the other one including also two $\sigma$-orbitals in the excitations. The PB results will be given in the discussion section. In comparison with the experimental transition energies for the three lowest singlet $\pi \rightarrow \pi^*$ states, they are too high by 1.6 to 2.5 eV, a result which is actually quite good in the light of recent experience with CI calculations.

No other *ab initio* CI study on the borazine spectrum is known to us. However, a number of semiempirical calculations were performed [2–9], with results in general agreement with the *ab initio* results.

The experimental singlet spectrum of borazine is well established for the low-lying $\pi \rightarrow \pi^*$ transitions [10–14]. Using the $D_{3h}$ symmetry group for borazine, the lowest $\pi \rightarrow \pi^*$ transition corresponds to $e'' \rightarrow e''$, and gives rise to $A_2'$, $A_1'$, and $E'$ states. They correlate with the $B_{2u}$, $B_{1u}$, and $E_{1u}$ states for $D_{6h}$ symmetry, arising from the excitation $e_{1g} \rightarrow e_{2u}$. From a group theoretical point of view, transitions to ${}^1A_1'$ and ${}^1A_2'$ are electric dipole forbidden, whereas transition to ${}^1E'$ is electric dipole allowed. Transitions to ${}^1A_1'$ may be observed due to vibronic interactions with $e'$ or $a_2''$ vibrations, and to ${}^1A_2'$ due to $e'$ vibrations. Kaldor [12] located the ${}^1A_2'$ system at 6.28, ${}^1A_1'$ at 6.56 and the allowed ${}^1E'$ system at 7.55 eV, by determining and analyzing the absorption spectrum of vapor-phase and matrix-isolated borazine. Kroner *et al.* [14] measured somewhat higher transition energies, 6.4–6.5 for ${}^1A_2'$, 7.1–7.2 for ${}^1A_1'$, and 7.6–7.7 eV for ${}^1E'$. Without implying a quality judgement, Kaldor's values will be used for comparison with the theoretical results. The question of $A_2'$ or $A_1'$ being lower has generally been settled in favor of $A_2'$. Other experimentally observed singlet states of borazine have not been reported.

An early photochemical attempt [7] to locate the triplet state of borazine by studying the triplet quantum yield of benzene upon addition of borazine resulted in the conclusion that the triplet state of borazine should be no higher than 4.86 eV, in contrast to theoretical calculations which place it not lower than 5.5 eV. A recent attempt to locate the triplet states of borazine by trapped electron spectroscopy was made by Doiron *et al.* [15]. A peak was observed at 7.9 eV, which is thought to represent a composite of the lowest ${}^3A_2'$ and ${}^3E'$ transitions. The transition to ${}^3A_1'$ is believed to be hidden below the onset of the peak at 6.5 eV.

In this work, double zeta basis sets will be used with additional $p\pi$ diffuse orbitals, such that in addition to the valence states low-lying $\pi$-Rydberg states are included.

For the CI treatment, all singly and doubly excited configurations relative to a set of reference configurations will be generated, and the most important ones selected for final matrix diagonalization. Only $\pi$-excited states of $A_1'$, $A_2'$, and $E'$ symmetry will be calculated according to various orbital excitation schemes, allowing for $\pi \rightarrow \pi^*$ as well as additional $\sigma \rightarrow \sigma^*$ excitations subject to the overall symmetry restrictions.

The scope of this treatment is similar to that of Hay and Shavitt [16] for benzene, $C_6H_6$, which has a structure very similar to that of borazine, with C atoms replacing the alternating B–N atoms, and interesting parallels will be drawn with their work. Therefore, a brief review of their method may be appropriate. Their basis set is similar to ours, double-zeta with diffuse $p\pi$-functions. In their CI procedure, however, they first obtained the natural orbitals (NO) from a CI including all $\pi$-type single and double excitations relative to the ground-state SCF wavefunction, then used the $\pi$-NO's to build a CI including also triple excitations, with the restriction that the less important NO's (17 out of 23) be doubly occupied at the most. The $\sigma$-electrons were held frozen. The final number of configurations was in the order of 1000 to 2700. Hay and Shavitt's results will be given in the discussion section.

## 2. SCF and CI Procedures

Basis set I is Dunning's [17] ($9s$, $5p/4s$, $2p$) on B and N, and Duijneveldt's [18] ($4s/1s$) on H. The total number of contracted functions is therefore 66. The geometry used with this basis set corresponds to a simplified model of planar borazine with all bond angles equal to 120°, the B–N distance being 1.44 Å, the N–H distance 0.995 Å, and the B–H distance 1.19 Å ($D_{3h}$). For basis set II, six diffuse $p\pi$ Gaussian functions were added to the previous basis set, all being located in the centers of the B–N bonds, with exponents 0.02. The number of contracted functions is now 72. With this second basis set, the experimental geometry of Harshbarger *et al.* [19] was used. They determined from electron diffraction studies a B–N bond length of 1.435 ± 0.002 Å, a B–H bond length of 1.258 ± 0.014 Å, and a N–H bond length of 1.050 ± 0.012 Å, with bond angles NBN of 117.7 ± 1.2°, and BNB of 121.1 ± 1.2°. A planar $D_{3h}$ and non-planar $C_{3v}$ and $C_2$ models were fitted to these data. Since borazine does not have a dipole moment, the $C_{3v}$ model should not apply. However, no definite choice between $D_{3h}$ and $C_2$ could be made by these authors. For the purpose of this paper, we used their $D_{3h}$ coordinates, which correspond to a planar borazine with ring bond angles of 117.2° (NBN) and 122.8° (BNB), and B–N, N–H, and B–H distances of 1.434, 1.046, and 1.244 Å, respectively.

SCF calculations were performed on the ground state of borazine, using the BIGGMOLI program [20]. The electronic ground state configuration is $\ldots 1a_2'^2 5a_1'^2 1a_2''^2 6e'^4 1e''^4$. Some orbital energies and characteristics for basis set II are given in Table 1. Orbitals of $a_2''$ and $e''$ type are $\pi$-orbitals. Due to substantial orbital mixing a clear distinction between valence and Rydberg character is not possible for all orbitals, in particular for the ones labeled as $V_R$ or $R_V$. The SCF ground state energies are $-241.04356$ and $-241.04215$ hartree for basis sets I and II, respec-

**Table 1.** Orbital energies and characteristics for basis set II[a]

| $D_{3h}$ | $C_{2v}$ | $\varepsilon$ (hartree) | Char.[b] |
|---|---|---|---|
| $3a_1'$ | $5a_1$ | −1.2129 | $V$ |
| $4a_1'$ | $8a_1$ | −0.7431 | $V$ |
| $5a_1'$ | $10a_1$ | −0.5503 | $V$ |
| $6a_1'$ | $15a_1$ | 0.2688 | $V$ |
| $3e'$ | $6a_1 + 3b_1$ | −1.1379 | $V$ |
| $4e'$ | $7a_1 + 4b_1$ | −0.7445 | $V$ |
| $5e'$ | $9a_1 + 6b_1$ | −0.6078 | $V$ |
| $6e'$ | $11a_1 + 7b_1$ | −0.4726 | $V$ |
| $7e'$ | $12a_1 + 8b_1$ | 0.1729 | $V$ |
| $8e'$ | $13a_1 + 9b_1$ | 0.2241 | $V$ |
| $9e'$ | $14a_1 + 10b_1$ | 0.2321 | $V$ |
| $10e'$ | $16a_1 + 11b_1$ | 0.4669 | $V$ |
| $1a_2'$ | $5b_1$ | −0.6279 | $V$ |
| $1a_2''$ | $1b_2$ | −0.5337 | $V$ |
| $2a_2''$ | $3b_2$ | 0.0500 | $R_V(3p\pi)$ |
| $3a_2''$ | $7b_2$ | 0.2224 | $V_R$ |
| $4a_2''$ | $9b_2$ | 0.4488 | $V$ |
| $5a_2''$ | $11b_2$ | 0.8929 | $V$ |
| $1e''$ | $1a_2 + 2b_2$ | −0.4276 | $V$ |
| $2e''$ | $2a_2 + 4b_2$ | 0.0655 | $R(3d\pi)$ |
| $3e''$ | $3a_2 + 5b_2$ | 0.0841 | $R_V$ |
| $4e''$ | $4a_2$[c] $+ 6b_2$ | 0.1490 | $V_R$ |
| $5e''$ | $5a_2 + 8b_2$ | 0.4101 | $V_R$ |
| $6e''$ | $6a_2 + 10b_2$ | 0.8245 | $V_R$ |

[a] In $C_{2v}$ notation, basis set II contains $32a_1, 22b_1, 7a_2$, and $11b_2$ orbitals. The highest occupied orbitals are $11a_1$, $7b_1$, $1a_2$, and $2b_2$.

[b] Orbital characteristics. $V$: valence, $R$: Rydberg. Strongly mixed orbitals are indicated as $V_R$ or $R_V$.

[c] The original $4a_2$ orbital was dropped due to "overdiffuseness".

tively. It should be noticed that the experimental geometry leads to a higher energy, despite an improved basis set. An optimized geometry for borazine is published elsewhere [21]. Unequal ring bond angles do in fact lead to a lower energy than 120° angles.

For the CI calculations, a set of reference configurations was determined for each symmetry species in such a way that all configuration functions (CF) in the final CI with coefficients in excess of $|0.10|$ were among the reference CF's. Then all single and double excitations were produced relative to the reference CF's, with a specified number of MO's frozen. Finally, the most important CF's were selected, using a threshold energy criterion $\delta$, and the corresponding matrices diagonalized. The procedures followed are described by Buenker and Peyerimhoff [22]. In all CI calculations, the Abelian subgroup $C_{2v}$ of the $D_{3h}$ symmetry group was used. Since

Table 2. Orbital participation in various CI options

| Orbital type | Basis set I[a] | | | Basis set II | |
|---|---|---|---|---|---|
| | $A(12\pi)$ | $B(12\pi + 8\sigma)$ | $C(12\pi + 26\sigma)$ | $D(17\pi)$ | $E(15\pi + 26\sigma)$ |
| $a_1(\sigma)$ | — | $11a_1$–$14a_1$ | $9a_1$–$23a_1$ | — | $9a_1$–$23a_1$ |
| $b_1(\sigma)$ | — | $7b_1$–$10b_1$ | $5b_1$–$15b_1$ | — | $5b_1$–$15b_1$ |
| $a_2(\pi)$ | $1a_2$–$4a_2$ | $1a_2$–$4a_2$ | $1a_2$–$4a_2$ | $1a_2$–$6a_2$ | $1a_2$–$6a_2$ |
| $b_2(\pi)$ | $1b_2$–$8b_2$ | $1b_2$–$8b_2$ | $1b_2$–$8b_2$ | $1b_2$–$11b_2$ | $1b_2$–$9b_2$ |

[a] Basis set I contains $32a_1$, $22b_1$, $4a_2$, and $8b_2$ orbitals. The highest occupied orbitals are $11a_1$, $7b_1$, $1a_2$, and $2b_2$.

attention was focused on the $\pi$-electron spectrum of borazine, only excited states of symmetries $A_1'$, $A_2'$, and $E'$ ($a_2'' \times a_2'' = A_1'$, $a_2'' \times e'' = E'$, and $e'' \times e'' = A_1' + A_2' + E'$) were considered. The correlation between the $D_{3h}$ and $C_{2v}$ groups is $A_1' \rightarrow A_1$, $A_2' \rightarrow B_1$, and $E' \rightarrow A_1 + B_1$. As will be outlined later, in some of the CI sets $\sigma \rightarrow \sigma^*$ CF's are added to the $\pi \rightarrow \pi^*$ CF's, always staying within the symmetry restrictions (for example, single excitations among the $\sigma$ orbitals lead to $a_1' \times a_1' = A_1'$, $a_1' \times e' = E'$, and $e' \times e' = A_1' + A_2' + E'$). However, single excitations of the types $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ were not included. Correlation of the important MO's is given in Table 1. At the end, the $D_{3h}$ symmetry was recovered by grouping excited states according to degenerate energies, using the appropriate correlation. Data on orbital participation in the CI, and number of configurations generated and selected, refer to the $C_{2v}$ symmetry group (Tables 2 and 3).

In the following, the choice of orbitals will be outlined for the various CI runs. Options $A$ to $C$ go with basis set I, $D$, and $E$ with basis set II. In Table 2 the orbital participation in the CI is summarized. In CI sets $A$ to $C$, all $\pi$ MO's participate fully in the excitations. The various sets differ in $\sigma$-orbital participation, ranging

Table 3. CI information. For particular state, first line gives number of configurations generated/selected, second line the number of reference configurations ($RC$)/number of roots ($R$)/ energy criterion in microhartree. At bottom, ground state CI energies are given in hartree

| State | $A(12\pi)$ | $B(12\pi + 8\sigma)$ | $C(12\pi + 26\sigma)$ | $D(17\pi)$ | $E(15\pi + 26\sigma)$ |
|---|---|---|---|---|---|
| $^1A_1$ | 1428/1428 | 8462/604 | 100463/3859 | 3314/907 | 160691/1972 |
| | $10RC/3R/0$ μh | $9RC/3R/10$ μh | $5RC/3R/20$ μh | $8RC/4R/20$ μh | $9RC/3R/40$ μh |
| $^1B_1$ | 1378/1378 | 7226/563 | 85779/2325 | 3894/980 | 140417/1379 |
| | $8RC/2R/0$ μh | $7RC/2R/10$ μh | $5RC/2R/20$ μh | $10RC/4R/20$ μh | $7RC/2R/40$ μh |
| $^3A_1$ | 2051/2051 | 17425/742 | 275396/2142 | 4885/1212 | 322800/2232 |
| | $9RC/2R/0$ μh | $9RC/2R/10$ μh | $8RC/2R/20$ μh | $7RC/4R/20$ μh | $10RC/2R/40$ μh |
| $^3B_1$ | 1893/1893 | 13301/719 | 147670/2169 | 5487/1180 | 239763/1081 |
| | $6RC/2R/0$ μh | $6RC/2R/10$ μh | $5RC/2R/20$ μh | $10RC/4R/20$ μh | $7RC/2R/40$ μh |
| $E(X^1A_1)$ | −241.09004 | −241.09232 | −241.20124 | −241.08816 | −241.16244 |

from no such participation in set $A$ to 26 $\sigma$-orbitals participating in set $C$. Using $C_{2v}$ notation, the ground state SCF configuration is $\cdots 11a_1^2 7b_1^2 1a_2^2 2b_2^2$. All orbital notations in Table 2 refer to the ground state SCF wavefunction. In CI set $C$, for example, the 3 highest occupied $a_1$ orbitals and the 12 lowest vacant $a_1$ orbitals participate in the excitations, out of a total of $32a_1$ orbitals. Since $11a_1$ is the highest occupied $a_1$ orbital, $9a_1$ to $23a_1$ are "unfrozen". Information on the number of generated and selected CF's, as well as the number of reference configurations ($RC$), roots ($R$) calculated and energy threshold used, is given in Table 3. Set $E$ is the most extensive CI, involving $15\pi$ and 26 $\sigma$-orbitals. Due to the enormous size of the CF space, a cutoff criterion of 40 $\mu$hartree was employed, and fewer roots were calculated. All CI energies were extrapolated, following Ref. [22]. Excitation energies, as given later, were obtained by comparing the excited state with the ground state energy obtained for the same CI set. The ground state CI energies for each set are included in Table 3.

## 3. Results and Discussion

Calculated vertical excitation energies, principal excitations as obtained for CI set $D$, and character of state are given in Table 4.

The largest number of states was obtained for CI set $D$, which uses the diffuse orbital extended basis set, and excitations within the complete $\pi$-orbital space. For set $E$, two unimportant $\pi$-orbitals were omitted, but 26 $\sigma$-orbitals added for excitations. However, for reasons indicated earlier, only the three lowest excited states were calculated, rather than the five lowest as for set $D$.

Looking at basis set I results (CI sets $A$, $B$, $C$), it is seen that the inclusion of 8 $\sigma$-orbitals ($B$) does not improve the energy, whereas 26 $\sigma$-orbitals ($C$) move $2^1E'$ and

**Table 4.** Calculated vertical excitation energies for borazine in eV

| | Basis set I | | | Basis set II | | | Leading CF[b] |
|---|---|---|---|---|---|---|---|
| State | $A(12\pi)$ | $B(12\pi+8\sigma)$ | $C(12\pi+26\sigma)$ | $D(17\sigma)$ | $E(15\pi+26\sigma)$ | $V/R$[a] | $1e''\rightarrow$ |
| $1^1A_2'$ | 7.34 | 7.37 | 7.37 | 7.38 | 7.12 | $V$ | $4e''$ |
| $1^1E'$ | — | — | — | 8.73 | 8.45 | $R$ | $2a_2''$ |
| $1^1A_1'$ | 8.61 | 8.65 | 8.62 | 8.73 | 8.57 | $V$ | $4e''$ |
| $2^1E'$ | 9.16 | 9.17 | 8.87 | 9.12 | — | $V$ | $4e''$, $2e''$ |
| $3^1E'$ | — | — | — | 9.76 | — | $R$ | $2e''$ |
| $1^3A_1'$ | 7.22 | 7.21 | 6.85 | 7.32 | 6.98 | $V$ | $4e''$ |
| $1^3E'$ | 7.62 | 7.61 | 7.19 | 7.67 | 7.27 | $V$ | $4e''$ |
| $1^3A_2'$ | 8.16 | 8.10 | 7.60 | 8.12 | 7.82 | $V$ | $4e''$ |
| $2^3E'$ | — | — | — | 8.50 | — | $R$ | $2a_2''$ |
| $3^3E'$ | — | — | — | 9.69 | — | $R$ | $2e''$ |

[a] Valence ($V$) or Rydberg ($R$) character of state.

[b] Leading configuration, for $D$-set.

all three triplet states to significantly lower energies. Obviously, some of the important $\sigma$-orbitals were missing in set $B$. A similar, however more general energy drop, is experienced with set $E$ relative to $D$. The valence states obtained from set $D$, with the expanded basis set, differ in energy hardly from the set $A$ states. However, the Rydberg states $1^1E'$, $3^1E'$, $2^3E'$, and $3^3E'$ are now added. The slight difference in geometry used for basis sets I and II has no apparent effect on the results.

The set $E$ results are by far the best in terms of low excitation energies. The energy drop relative to set $D$ is 0.2 to 0.4 eV.

Since many of the virtual orbitals are not pure valence or Rydberg orbitals, and since the configuration mixing enhances the mixing of valence and Rydberg character, the best criterion for characterization of states is not so much the CI wavefunction but the absence of calculated states in basis set I results. The leading configurations of set $D$, as shown in Table 4, agree with this characterization.

In the following, the calculated energies will be compared with the PB and with experimental results (Table 5). For consistency, the set $E$ results will be used, and missing set $E$ excitation energies will be estimated to be the set $D$ results minus 0.2 eV. Since only higher $E$ states are missing, and since the $E$–$D$ energy differences are increasing with higher roots, the correction by 0.2 eV is certainly justifiable.

PB observe that their smaller basis set gives lower excitation energies for some states, especially the low-lying states. We observe similarly that some of the excitation energies from basis I are lower than the corresponding ones from basis II.

**Table 5.** Vertical excitation energies (in eV) of borazine, and comparison with benzene

| | Borazine | | | | Benzene | | |
|---|---|---|---|---|---|---|---|
| Char. of state | State | *PB*[a] | This work[b] | Exptl[c] | State | Theor[d] | Exptl[e] |
| $V$ | $1^1A_2'$ | 7.88 | 7.12 | 6.28 | $1^1B_{2u}$ | 5.0 | 4.9 |
| $3p\pi$-$R$ | $1^1E'$ | — | 8.45 | — | $1^1E_{1u}$ | 7.26 | 7.4 |
| $V$ | $1^1A_1'$ | 9.02 | 8.57 | 6.56 | $1^1B_{1u}$ | 7.64 | 6.2 |
| $V_R$ | $2^1E'$ | 9.59 | ~8.90 | 7.55 | $2^1E_{1u}$ | 8.34 | 6.98 |
| $3d\pi$-$R$ | $3^1E'$ | — | ~9.55 | — | $1^1E_{2g}$ | 7.90 | 7.98 |
| $V$ | $?^1E'$ | — | — | — | $2^1E_{2g}$ | 8.33 | 7.3 |
| $V$ | $1^3A_1'$ | 7.93 | 6.98 | ~6.5 | $1^3B_{1u}$ | 3.83 | 3.9 |
| $V$ | $1^3E'$ | 8.05 | 7.27 | ~7.9 | $1^3E_{1u}$ | 4.98 | 4.7 |
| $V$ | $1^3A_2'$ | 8.33 | 7.82 | | $1^3B_{2u}$ | 7.00 | 5.6 |
| $3p\pi$-$R$ | $2^3E'$ | — | ~8.30 | — | $2^3E_{1u}$ | 7.24 | — |
| $V$ | $?^3E'$ | — | — | — | $1^3E_{2g}$ | 7.28 | 6.55 |
| $3d\pi$-$R$ | $3^3E'$ | — | ~9.50 | — | $2^3E_{2g}$ | 7.90 | — |

[a] Ref. [1]. Results of extended basis set, with CI ($6\pi$, $2\sigma$). Higher excited states omitted.
[b] Result of set $E$ whenever possible, otherwise adjusted set $D$ results.
[c] Ref. [14] for singlet states, Ref. [15] for triplet states.
[d] Ref. [16]. Results of (1 + 2 + 3)-CI. Higher excited states omitted.
[e] Experimental values according to Ref. [16].

Table 5 shows that our results are 0.25 to 1 eV lower than PB's, but still significantly higher (0.8 to 2 eV) than the experimental results for the singlet states, and in reasonable agreement with the suggested triplet energies (Ref. [15]), which will be discussed later. All experimentally observed singlet states are believed to be valence-like, and the observed $^1E'$ at 7.55 eV is therefore associated with our second $^1E'$ state. Again, the calculations place the $^1A_2'$ state clearly below the $^1A_1'$ state, quite independent of the basis set or the type of CI used. As will be indicated later, $^1A_1'$ is more difficult to calculate than $^1A_2'$, as is reflected in the larger discrepancy with the experimental result; however, a reversal of the ordering can hardly be expected even when more sophisticated methods are applied.

Of great interest is the comparison with the theoretical results obtained by Hay and Shavitt [16] for benzene. Table 5 compares the benzene states with the corresponding borazine states, using the appropriate correlation between the symmetry groups $D_{6h}$ and $D_{3h}$, and the type of principal excitation as guide. Higher excited states calculated for benzene are omitted from this table. The significant impression of this comparison is that the order of the borazine states is very similar to the order of the benzene states, which also includes Rydberg states in relation to valence states. For example, the second lowest excited singlet state for both benzene and borazine is the $3p\pi$ Rydberg state, and the order of the singlet states arising out of the lowest energy $e'' \to e''$ excitation is the same for both molecules. Whereas the lowest $^1B_{2u}$ for benzene is calculated to be very close to the experimental value, the corresponding $^1A_2'$ state of borazine is about 0.9 eV too high. However, other calculated singlet valence states of borazine are too high by similar amounts as the corresponding states of benzene. Although some of the experimental values are not yet established beyond doubt, it can be said that the overall accuracy of the calculated excited states is similar to that of the benzene states. In the past, there has been a persistent impression that borazine is much more difficult to treat than benzene, which fortunately cannot be confirmed. In both cases, the degenerate state resulting from the lowest energy electron excitation is a mixed valence-Rydberg state. For borazine, the extent of diffuse character cannot be easily assessed. One leading configuration is $1e'' \to 4e''$, the other is $1e'' \to 2e''$. $4e''$ is a mixed valence-Rydberg orbital (see Table 1), whereas $2e''$ is almost purely Rydberg.

The calculated singlet Rydberg states are $3p\pi$ ($2a''$) and $3d\pi$ ($2e''$). The excitation $1e'' \to 2e''$ leads to $A_1'$, $A_2'$, and $E'$, of which only the $E'$ component was calculated. Both $A_1'$ and $A_2'$ would appear as higher roots of the secular equations. For borazine, the $3d\pi$ Rydberg state is calculated to be higher than the $^1E'$ mixed valence state, whereas the opposite is true for benzene. However, experimental benzene values, included in Table 5, show the $3d\pi$ state to be higher than the $E$-valence state. Hay and Shavitt obtain another valence state, $2^1E_{2g}$, in close proximity to $2^1E_{1u}$. This state contains a significant double excitation component. For borazine, a similar valence state was not found. It is possible that this state was missed because of the choice of reference configurations in the CI, and in particular the absence of the $1e''^2 \to 4e''^2$ configuration.

The order of calculated triplet states for borazine resembles that for benzene except for a valence-like $^3E_{2g}$ state which was calculated for benzene to be below the $3d\pi$ Rydberg state, but not obtained for borazine, parallel to the singlet situation. Here, the Rydberg states are above the group of valence states which result from the lowest $e'' \rightarrow e''$ excitation. For benzene, the two lowest valence triplets are calculated in good agreement with experimental values. This could indicate that the 7.9 eV peak found for the borazine triplets by Doiron *et al.* is $^3A_2'$, and that both $^3E'$ and $^3A_1'$ are actually below the onset of the peak, ~6.5 eV, or for some reason completely absent. It is noteworthy that the three borazine valence triplets arising from $1e'' \rightarrow 4e''$ are very close in energy, within less than 1 eV, whereas the corresponding benzene values spread over 3.2 eV (experimentally only 1.7 eV).

In Figs. 1 and 2 the calculated results are compared with the experimental results, and the borazine states are correlated with the corresponding benzene states. Figure 1 is for singlet, Fig. 2 for triplet states. Some points previously discussed become quite obvious from these figures. For example, the singlet states of borazine and benzene, although always higher for borazine, have the same ordering except for the calculated $E$–$3d\pi$ states crossing with the $2^1E$–$2^1E_{1u}$ states, whereas the ordering is the same for all triplet states. Roothaan and Mulliken [23] assigned the borazine spectrum in 1948 on the basis of the expected similarity with the benzene spectrum. In relation to the corresponding benzene states, the borazine triplet states are higher in energy than the borazine singlet states. The only benzene states for which no analogous borazine states were obtained are the valence $^1E_{2g}$ and $^3E_{2g}$ states, as outlined previously.

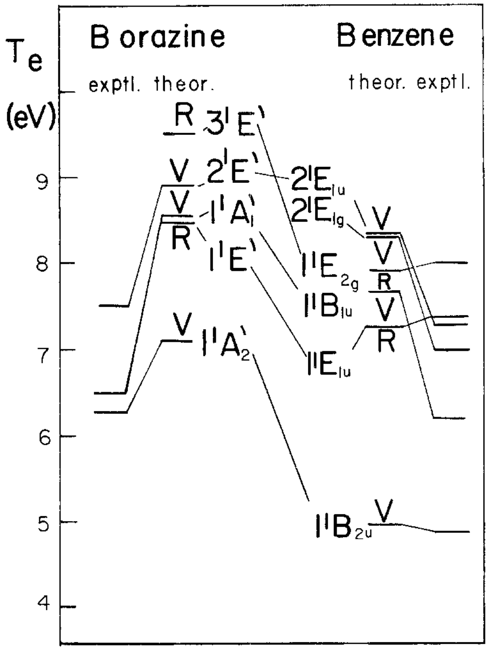

Fig. 1. Experimental and theoretical vertical excitation energies to π-electronic singlet states of borazine and benzene

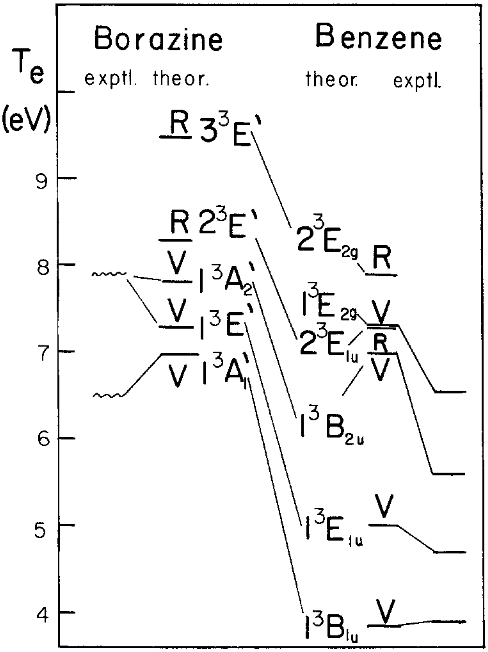

Fig. 2. Experimental and theoretical vertical excitation energies to $\pi$-electronic triplet states of borazine and benzene

Hay and Shavitt point out that calculated excitation energies for benzene are too high for such states which result from ionic valence bond structures, in particular for ${}^1B_{1u}$, ${}^1E_{1u}$, and ${}^3B_{2u}$. It is interesting that the corresponding borazine states are also calculated much too high (2 eV for ${}^1A_1'$, 1.35 eV for ${}^1E'$). Due to the lack of sufficient experimental data for borazine, such conclusions are not necessarily valid, but are nevertheless quite interesting.

## 4. Conclusion

The above presented CI results on borazine constitute a significant improvement over previous *ab initio* results, and include for the first time low-lying Rydberg states of borazine. In comparison with the few available experimental excitation energies, the theoretical results are too high by 0.8–2 eV, with the largest deviation obtained for states which correspond to ionic valence structures. Comparisons with studies of the benzene spectrum, performed at a similar level, confirm the remarkable similarity of the benzene and borazine spectra. The above studies refer to $\pi \rightarrow \pi^*$ states only, and need to be extended to include also other types of excited states, such as $\sigma \rightarrow \pi^*$.

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