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Comparison of the Molecular Structure and Spectra of Benzene and Borazine

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Ab initio SCF MO and CI calculations for two different gaussian basis sets are carried out for the isoelectronic molecules benzene C_6H_6 and borazine $B_3N_3H_6$ in order to investigate the effect of increasing the flexibility in the representation of their respective π systems. In the process it is found from comparison of orbital charge density contour diagrams and inner shell orbital energies of borazine with analogous data for other systems that the BN bonds of this compound are considerably less polar (B^+N^-) than that of ammonia borane BNH_6 (B^-N^+). CI calculations employing the larger basis set produce generally better agreement with the experimental transition energies of benzene than do those using the smaller basis. In both treatments ${}^1E_{2g}$ is predicted to lie lower than ${}^1E_{1u}$, in contrast to single excitation results; an analogous inversion in the calculated order of states is not observed in the study of borazine but the effect of double and triple excitation configurations is also found to be quite important for this system. For both benzene and borazine the CI calculations suggest in addition that transitions to $\sigma \rightarrow \pi^*$ states occur at relatively low energy, perhaps within 0.5 eV of the strongest $\pi \rightarrow \pi^*$ absorption in each case.

Es wurden *ab initio* SCF-MO- und CI-Berechnungen für die isoelektrischen Moleküle Benzol C_6H_6 und Borazin $B_3N_3H_6$ durchgeführt; dabei werden zwei verschiedene Gaußfunktions-Basissätze von unterschiedlicher Güte hinsichtlich der Darstellung der entsprechenden π-Systeme der Moleküle verwendet, und ihr Einfluß wird diskutiert. Beim Vergleich von Orbital-Elektronendichtediagrammen sowie den Orbitalenergien der inneren Schalen von Borazin mit entsprechenden Daten von anderen Systemen stellt sich heraus, daß die BN-Bindungen in $B_3N_3H_6$ bedeutend weniger polar (B^+N^-) sind als die entsprechende Bindung (B^-N^+) in BNH_6. Die CI-Rechnungen liefern bei Zugrundelegung der flexibleren AO-Basis Werte für die Übergangsenergien in Benzol, welche im allgemeinen in besserer Übereinstimmung mit den experimentellen Daten sind als bei Verwendung der kleineren Basis. In beiden Verfahren liegt der ${}^1E_{2g}$-Zustand niedriger als der ${}^1E_{1u}$, im Gegensatz zu den Ergebnissen, welche lediglich mit einer einfach angeregten Konfiguration erhalten werden; eine ähnliche Inversion in der berechneten Reihenfolge der Borazin-Zustände wird nicht gefunden, aber der Einfluß von zwei- und dreifach angeregten Konfigurationen stellt sich bei diesem Molekül ebenfalls als sehr wesentlich heraus. Die CI-Rechnungen legen weiterhin nahe, daß in den beiden Molekülen Benzol und Borazin $\sigma \rightarrow \pi^*$-Übergänge bei verhältnismäßig niedrigen Energien vorkommen, ungefähr 0,5 eV von der stärksten $\pi \rightarrow \pi^*$-Absorption entfernt.

Calculs *ab-initio* dans deux bases de gaussiennes, SCF-MO et I.C., pour les molécules isoléletroniques de benzène C_6H_6 et de borazole $B_3N_3H_6$, aux fins d'étude de la flexibilité de représentation de leurs systèmes π. De la comparaison des diagrammes de contour de densité de charge orbitale et des énergies des orbitales des couches internes du borazole avec des données analogues pour d'autres systèmes on déduit que les liaisons B-N de ce composé sont considérablement moins polaires (B^+N^-) que celles du borure d'ammonium BNH_6 (B^-N^+). Des calculs d'I.C. utilisant la plus grande base donnent généralement de meilleures énergies de transition pour le benzène que ceux utilisant la plus petite base. Dans les deux cas $^1E_{2g}$ est trouvée en dessous de $^1E_{1u}$ contrairement à ce que donne l'approximation monoparticulaire; une inversion analogue de l'ordre des états calculés n'est pas observée dans l'étude du borazole mais l'effet des configurations di- et tri-excitées est aussi assez important pour ce système. Pour le benzène comme pour le borazole les calculs d'I.C. suggèrent d'autre part que les transitions $\sigma \rightarrow \pi^*$ se produisent à des énergies relativement basses, à 0,5 eV peut être de la plus forte absorption $\pi \rightarrow \pi^*$ dans chaque cas.

1. Introduction

The spectrum of benzene and its BN analog borazine $B_3N_3H_6$ have been compared by means of theoretical (semi-empirical) calculations earlier by Roothaan and Mulliken [1]. These authors have pointed out from essentially group theoretical arguments that a close relationship between the spectra of these two systems should exist; contemporary experimental investigations by Platt and Schaeffer *et al.* [2–4] were interpreted quite plausibly in terms of this theory. More recently advances in the method of calculating the electronic spectra of general polyatomics coupled with more sophisticated experimental investigations of this subject (particularly the benzene electronic spectrum) have made a reevaluation of the existing theory desirable. In particular the feasibility of carrying out *ab initio* SCF and CI calculations to study the electronic structure of benzene and borazine forms the basis for the work to be discussed herein.

A previous *ab initio* CI treatment of benzene [5] leads to several conclusions which appear worthy of further consideration. First of all, it has been found that doubly and more highly excited electronic configurations (relative to the SCF ground state function) have a pronounced effect on the calculated results, in agreement with the findings of Bloor *et al.* [6] obtained from a semi-empirical treatment. Secondly, the SCF orbital energies obtained from the *ab initio* calculation indicate that at least one of the σ orbitals of benzene is more stable than the lowest π species, thereby suggesting the possible importance of $\sigma \rightarrow \pi^*$ transitions in the benzene spectrum. Again earlier semi-empirical work suggests a similar interpretation, in this instance with regard to the borazine spectrum, since Hoffmann [7] has calculated the highest occupied MO of this system to be of σ type. In all this, however, it should be pointed out that the basis set employed in the previous *ab initio* calculation suffers from the fact that its π orbitals are completely determined by symmetry and thus it would seem necessary to test the above conclusions by employing a more flexible basis set capable of allowing for optimization of the π MO's by the SCF procedure.

In addition to enabling a detailed comparison of the spectra of benzene and borazine such calculations also allow for a continuation of the comparative study of the molecular structure of isoelectronic BN and carbon analogs by *ab initio* techniques begun with calculations for ammonia borane (borazane) BNH_6 and ethane [8]. The mode of charge transfer in borazine is expected to be considerably different from that observed for ammonia borane and the question of relative magnitude of the effective electronic charges of the boron and nitrogen atoms in these two systems will also be investigated.

2. Details and Results of the SCF Calculations

Calculations are reported for the experimental nuclear geometries of benzene and borazine respectively; the BN distance of borazine has thus been chosen as 2.72 bohrs (approximately 1.44 Å) and the NH and BH distances have been assumed to be 1.90 and 2.25 bohrs respectively. A basis set of approximate Hartree-Fock AO's expanded in terms of gaussian lobe functions is employed for both systems; details concerning these bases haves been given earlier [5, 8]. A total of 42 group functions, three *s* and one *p* on each of the heavy atoms and one *s* on each hydrogen is utilized; these groups include ten *s* and five *p* primitive gaussians for B, C, and N and five *s* for H (180 functions total for each molecule).

The benzene calculation of this type has been discussed previously and, as mentioned in the Introduction, one of its major drawbacks is the fact that its π type MO's are completely determined by symmetry. In addition then a second more flexible treatment has been carried out for both systems in which the $p\pi$ groups (but not $p\sigma$) are decomposed into a four-component short range part and a one-component long range part (smallest exponent), thereby increasing the number of free coefficients in the SCF procedure to 48 in this treatment. Total, orbital and kinetic energies for each of these four calculations are contained in Tables 1 and 2 for benzene and borazine respectively.

For both systems the lowering in energy effected by increasing the flexibility of the $p\pi$ representation is relatively small. The σ MO's, not surprisingly, are very similar for both treatments. In spite of the rather small total energy lowerings observed, the composition of the π orbitals is greatly altered by allowing the short and long range $p\pi$ groups to assume optimum relative weighting. In benzene the ratio between long and short range expansion coefficients (occupied MO's) is found to be from 15 to 20 times smaller in the second treatment than in the first, in which case the relative weights are those found to be optimum for the carbon atom. Similar results are observed for borazine; in both systems the ratio between long and short range expansion coefficients increases with the energy of the π orbitals, but in all cases (including the three lowest lying virtual MO's) it is much smaller than in the approximate Hartree-Fock AO expansions. Thus in summary the π MO's of these systems prefer much more contracted electronic distributions than in the atoms, although this tendency is less pronounced in the unoccupied species.

Experimental ionization potentials for benzene and borazine are compared with the present theoretical values calculated via Koopmans' theorem in Tables 3a–b respectively. The agreement between experiment and present calculation worsens with increasing stability of the orbitals (at least for benzene); in each case the SCF results overestimate the experimental quantities. The minimum I.P. is calculated to be from 0.7 to 1.0 eV higher than the experimental values reported. For borazine the agreement is somewhat worse for the minimum I.P.; semi-empirical calculations [9] have been reported which underestimate the experimental quantity by only 0.35 eV and which overestimate it by 2.8 eV. The *ab initio* results find the highest occupied MO of borazine to be of π type, in disagreement with the earlier EHT calculations of

Table 1. *Total energy E_t, kinetic energy E_k and orbital energies for the ground state of benzene, obtained from two different* SCF *calculations. (In this paper all energies are given in hartrees, unless otherwise specified)*

	Fixed group basis	Extended basis
$1a_{1g}$	−11.3545	−11.3443
$1e_{1u}$	−11.3541	−11.3438
$1e_{2g}$	−11.3531	−11.3427
$1b_{1u}$	−11.3524	−11.3422
$2a_{1g}$	− 1.1735	− 1.1687
$2e_{1u}$	− 1.0428	− 1.0381
$2e_{2g}$	− 0.8484	− 0.8431
$3a_{1g}$	− 0.7406	− 0.7349
$2b_{1u}$	− 0.6737	− 0.6697
$1b_{2u}$	− 0.6600	− 0.6423
$3e_{1u}$	− 0.6263	− 0.6216
$1a_{2u}(\pi)$	− 0.5380	− 0.5429
$3e_{2g}(\sigma)$	− 0.5256	− 0.5187
$1e_{1g}(e)$	− 0.3788	− 0.3781
$1e_{2u}(e^*)$	0.1392	0.0968
$1b_{2g}(\pi^*)$	0.3723	0.3018
$2a_{2u}$	—	0.4975
$2e_{1g}$	—	0.5578
$4e_{2g}$	0.5871	0.5972
E_t	−230.3745	−230.3934
$-E_k/E_t$	0.9919	0.9926

Table 2. *Total energy E_t, kinetic energy E_k and orbital energies for the ground state of borazine, obtained from two different* SCF *calculations*

	Fixed group basis	Extended basis
$1a'_1$	−15.5448	−15.5731
$1e'$	−15.5448	−15.5731
$2a'_1$	− 7.7270	− 7.7291
$2e'$	− 7.7270	− 7.7291
$3a'_1$	− 1.2077	− 1.2129
$3e'$	− 1.1369	− 1.1430
$4a'_1$	− 0.7633	− 0.7672
$4e'$	− 0.7509	− 0.7538
$5e'$	− 0.6299	− 0.6349
$1a'_2$	− 0.6166	− 0.6220
$5a'_1$	− 0.5794	− 0.5800
$1a''_2(\pi)$	− 0.5379	− 0.5431
$6e'(\sigma)$	− 0.4815	− 0.4849
$1e''(e)$	− 0.4295	− 0.4360
$2e''(e^*)$	0.1615	0.1221
$2a''_2(\pi^*)$	0.3004	0.1880
$3e''$	—	0.3745
$3a''_2$	—	0.4108
$7e'$	0.4896	0.4874
E_t	−240.8636	−240.8970
$-E_k/E_t$	0.9988	0.9968

Table 3. *Ionization potentials* (eV) *of benzene* (a) *and borazine* (b) *obtained from different calculations via Koopmanns' theorem*

		Fixed group basis	Extended basis	Experiment
(a)	$2a_{1g}$	31.94	31.81	≈30.0[a]
	$2e_{1u}$	28.38	28.25	≈26.0
	$2e_{2g}$	23.09	22.95	19.2
	$3a_{1g}$	20.16	20.00	16.9
	$2b_{1u}$	18.33	18.23	15.4
	$1b_{2u}$	17.96	17.48	14.7
	$3e_{1u}$	17.04	16.92	13.8
	$1a_{2u}(\pi)$	14.64	14.78	12.1
	$3e_{2g}(\sigma)$	14.30	14.12	11.4
	$1e_{1g}(e)$	10.31	10.29	9.3
	$1e_{2u}(e^*)$	−3.79	−2.63	
	$1b_{2g}(\pi^*)$	−10.13	−8.21	
(b)	$3a'_1$	32.87	33.01	
	$3e'$	30.94	31.11	
	$4a'_1$	20.77	20.88	
	$4e'$	20.44	20.51	
	$5e'$	17.14	17.28	
	$1a'_2$	16.78	16.93	
	$5a'_1$	15.77	15.79	
	$1a''_2$	14.64	14.78	
	$6e'$	13.10	13.20	
	$1e''$	11.69	11.87	10.3[b]
	$2e''$	−4.39	−3.32	
	$2a''_2$	−8.18	−5.12	

[a] All experimental values for C_6H_6 are from B.-Oe. Jonsson and E. Lindholm, Arkiv f. Fysik, 0, 1 (1968).

[b] Brown, D. A., McCormack, C. G.: Theoret. chim. Acta (Berl.) **6**, 350 (1966).

Hoffmann [7], which find an orbital of e' symmetry to be 0.7 eV less stable than the highest occupied π MO.

The ordering and relative spacing of the calculated energy levels is interesting in itself. In both systems at both levels of treatment, for example, it is found that the highest occupied σ MO($3e_{2g}$ in C_6H_6 and $6e'$ in $B_3N_3H_6$) is less stable than the most bonding π MO($1a_{2u}$ and $1a''_2$ respectively). For benzene the experimental data [10] also indicate this relationship to hold; indeed the present calculated energy level ordering agrees completely with experiment (Table 3a). This situation would seem to be quite important with reference to the electronic spectra of these compounds, suggesting quite clearly that excitations of the $\sigma \rightarrow \pi^*$ type may also occur at relatively low energy in both benzene and borazine.

Finally in this connection it is worth noting that the energy spacings between π levels of borazine are significantly smaller than between the corresponding benzene species. This result is a consequence of the fact that the occupied π MO's of borazine are largely constructed from the nitrogen AO's while the virtual orbitals possess mostly boron character; since no two nitrogen atoms or boron atoms are adjacent to one another there is less interaction within their respective π AO sets and thus less widely spaced energy levels than in benzene, where adjacent carbon π AO's are required by symmetry to interact. The energy gap between occupied and virtual MO's is greater in borazine than in benzene, however, but this fact is in obvious agreement with the foregoing analysis. Nevertheless it is still somewhat surprising that the energy difference between lowest occupied and highest unoccupied π MO is smaller for the BN analog than for benzene itself. Apparently the decrease in antibonding character in the highest occupied MO of $B_3N_3H_6$ relative to benzene outweighs the effect of the lower stability of the boron AO's.

Although SCF binding energies are generally unreliable on an absolute scale there is reason to expect that they show the proper ordering. In the present case it is found that benzene is more bound than borazine by 0.14 hartree (84 kcal/mole); a somewhat larger difference is calculated between ethane and borazane (0.16 hartree, 96 kcal/mole). Recalling that there are three times as many BN pairs in borazine it is clear that this system possesses much stronger BN bonds than does ammonia borane, as indeed one would expect from valence bond theory, which ascribes strong covalent σ bonds (albeit weak dative π bonds) to the ringed system but only a weak dative σ bond to the other.

3. Comparison of the Charge Distributions

A. Composition of Orbitals

In the previous study of ammonia borane [8] it has been found that the MO's of this system are well separated with respect to B and N character. Thus one B 1*s* and two BH orbitals are clearly identifiable even in the MO framework as are three NH and one N 1*s* species. There is some interaction between the remaining BH and N→B $p\sigma$ dative bonds respectively, but overall the relatively great separation of boron and nitrogen character in the MO's of this system allows for an easy interpretation of its electronic structure.

Unfortunately the situation is not so clear in borazine but at least this type of model is a good starting point from which to begin analysis of the electronic structure of this system. The description of borazine in terms of valence bond units analysed from the standpoint of group theory (Table 4) is also helpful in this connection. The inner shell orbitals as usual are found to be well separated with respect to B and N character and thus $1a_1'$ and $1e'$ MO's are clearly associated with the N 1*s* AO's while the $2a_1'$ and $2e'$ are constructed solely

Table 4. *Symmetry of occupied molecular orbitals of borazine derived from a group theoretical analysis of the valence bond structure of the molecule*

VB-Description	Occupied MO's
6 × 1*s*(3B, 3N) AO's	a_1', a_1', e', e'
6 × BN bonds	a_1', a_2', e', e'
3 × BH bonds	a_1', e'
3 × NH bonds	a_1', e'
3 × π bonds	a_2'', e''
	$5 \times a_1', 1 \times a_2', 6 \times e', 1 \times a_2'', 1 \times e''$

from the corresponding boron species. It has been pointed out previously [11] that the charge distributions arising from such inner shell orbitals for a given heavy atom do not vary from one system to another and subsequently advantage will be taken of this invariance to allow for direct observation of the local environment of the boron and nitrogen nuclei.

The expansion coefficients for the π MO's of borazine indicate that the nitrogen AO's make by far the greater contribution to the occupied π ($1a_2''$ and $1e''$) species. (The nitrogen AO's are actually somewhat more dominant in the less stable $1e''$ species.) A simple population analysis indicates that only 0.20 e is located on each boron atom; each of the BN bonds is also calculated to have 0.40 e, however, so that the total $N \rightarrow B$ π charge transfer is still quite substantial. These findings are in fair agreement with earlier semi-empirical findings [7, 9]. It is of course to be expected that the lateral $N \rightarrow B$ charge transfer through the π MO's in borazine is considerably weaker than the corresponding $N \rightarrow B$ $p\sigma$ electron transfer in ammonia borane (see Fig. 11 of Ref. [8]).

In terms of valence bond entities (Table 4) the next least stable classes of MO's are those corresponding to the BH and NH bonds respectively; these can be associated quite unambiguously with the $6e'$ and $5a_1'$ orbitals in the case of the BH species, $5e'$ and $4a_1'$ for NH. From expansion coefficients and charge density contour diagrams it is apparent that the nitrogen AO's are much more dominant in their corresponding hydrogen bonds than are their boron counterparts in the BH species; in other words, the hydrogens appear to receive a greater share of the electronic charge in the BH MO's while the opposite is true for the NH orbitals. In addition nitrogen AO's are much more prominent in the BH orbitals than are boron AO's in those of NH type; these observations are certainly consistent with the electronegativity ordering $N > H \geq B$. Comparison with the upper valence MO's of benzene (Fig. 5a of Ref. [12], $3e_{2g}$ MO), points up a fundamental difference between the two isoelectronic molecules; apparently CH and CC bonding are of sufficiently equal importance energetically to appear in almost equal admixture in benzene orbitals whereas in borazine the corresponding bonding types are much more separated.

The remaining four MO's ($3a_1'$, $3e'$, $4e'$ and $1a_2'$) then must correspond by process of elimination (Table 4) in the main to BN bonding orbitals. The least stable of this set, the $1a_2'$, consists of six essentially equivalent lobes, with nodal planes through each B and N atom and thus fits this description quite well. Each of these lobes, however, has its maximum nearer to its respective nitrogen nucleus than to that of boron. The other three MO's of this BN-bonding type show an increasing proportion of nitrogen character with decreasing orbital energy; the most stable of these, the $3a_1'$, which is expanded almost exclusively in terms of the $2s$ AO's of both heavy atoms, is calculated to have a nitrogen-to-boron ratio of SCF coefficients of almost 5 to 1. In other words, the orbitals which correspond to the BN σ framework of borazine appear to be heavily nitrogen in character; therefore, the $N \rightarrow B$ π charge transfer would seem to be greatly outweighed by the $B \rightarrow N$ charge transfer in the σ MO's.

The overall effect is that each boron atom is donating electronic charge to its adjacent hydrogen and nitrogen atoms while each nitrogen is accepting charge from all of its adjacent atoms.

B. Analysis of Inner Shell Orbital Energies

The extent to which these various electronic charge transfers affect the environment of the B and N nuclei in borazine relative to that in related systems can be evaluated in a systematic manner by taking advantage of the experimental fact that the inner shell orbitals of like atoms have almost exactly the same charge distribution [11] (usually to within one part in 10^6) regardless of their extranuclear environment; consequently variations in the orbital energies of these species from one system to another are caused almost exclusively by differences in potential surrounding their respective nuclei. A lower inner shell orbital energy indicates a more positive valence charge distribution, a higher value a more negative distribution.

Application of this general relationship to the case of borazine is aided by Table 5, in which inner shell orbital energies for boron and nitrogen in various systems at several levels of SCF treatment are compared. In considering these data it is necessary to distinguish between effects caused by adjacent hydrogen atoms and those caused by neighbouring heavy atoms. It has been noted previously [13], for example, that the 1*s* energies of C_2 hydrocarbons increase monotonically with increasing number of hydrogen atoms (see Fig. 3 of Ref. [13]). At the same time it is important to point out that these quantities, at least in molecular calculations, are quite sensitive to differences in treatment, as can be seen by comparing BH_3 and NH_3 results for the fixed group and a less restrictively group basis set. In these cases it seems clear, that where large differences exist, the values corresponding to the least restrictive basis set are to be preferred; the effects of grouping are much less significant in atomic calculations. Thus one also concludes from Table 5 that bonding with hydrogen effectively adds electronic charge to the extranuclear environment, because the

Table 5. *Inner shell* N *and* B *orbital energies for several molecules and the atoms, obtained from different* SCF *treatments*

Fixed group basis			Extended basis	
	N	B	N	B
$B_3N_3H_6$	−15.5448	−7.7270	−15.5731	−7.7291[a]
BNH_6	−15.6324	−7.5518	−15.6265	−7.5266
BH_3	—	−7.7249	—	−7.6173
NH_3	−15.4779	—	−15.5312	—

Hartree-Fock results[b]

	N	B
Atoms	−15.62892 (^4S)	−7.69528 (^2P)
Negative Ions	−15.24207 (^3P)	−7.42470 (^3P)
Positive Ions	−16.28437 (^3P)	−8.18587 (^1S)

[a] Decomposition of $p\pi$ AO's only.

[b] Values taken from Clementi, E.: Tables of atomic functions, Supplement to IBM Journal of Research and Development **9**, 2 (1965). Atomic values calculated using the present gaussian basis set differ by less than 0.001 a.u. in each case from the corresponding Hartree-Fock result.

extended basis set treatment yields higher B and N inner shell orbital energies in BH_3 and NH_3 respectively than in the corresponding atomic cases.

Similarly comparison of the ammonia and borane inner shell orbital energies with those of borazane BNH_6 leads readily to an interpretation of this system as an $N \rightarrow B$ donor complex; the nitrogen 1*s* energy in BNH_6 decreases relative to that of NH_3 while the boron counterpart increases relative to that of BH_3. The net result is apparently that the nitrogen atom in BNH_6 is only a little more negative than when it is isolated, while the boron in this system is much more negative than the free atom; the boron is quite negative in borazane, the nitrogen almost neutral with the six hydrogens sharing the residual positive charge, those attached to nitrogen possessing the greater share of it.

When comparing inner shell orbital energies of borazine with those of BNH_6, one must also be mindful of the differences in the level of SCF treatment since only $p\pi$ groups are decomposed for the larger system while all p groups and the 2*s* are decomposed in the borazane calculation. Nevertheless it seems clear from the data of Table 5 that the boron atoms of borazine are much more positive than that of BNH_6, as a consequence of the overall $B \rightarrow N$ charge transfer in the ringed system and also of the decrease in the number of attached hydrogen atoms. More surprisingly, however, the calculations seem to indicate that the borons of $B_3N_3H_6$ are no more than *slightly* more positive than a free atom; such a result is in major disagreement with conclusions based on relative magnitudes of nitrogen and boron AO SCF coefficients discussed previously. Because the inner shell orbital energies can be classified as quantum mechanical observables (since identification with ionization potentials via Koopmans' theorem is valid) it seems clear furthermore than conclusions based on these quantities are more reliable than those resulting from a comparison of SCF coefficients (population analysis).

Similarly the inner shell orbital energies of nitrogen imply that this atom possesses only a *weakly* negative environment in borazine $B_3N_3H_6$, despite the appearance of the SCF coefficients. Apparently nitrogen is still somewhat more positive in ammonia borane BNH_6, in spite of the greater number of attached hydrogen atoms in the small system; the polarity of the BN bonds is thus opposite in borazine (B^+N^-) than in BNH_6, but the magnitude of this charge separation is considerably smaller in the ringed compound (of course, the total dipole moment of borazine must vanish by virtue of its D_{3h} nuclear symmetry).

4. Electronic Spectrum of Benzene

A. Calculations

A CI calculation of the electronic spectrum of benzene has been reported previously [5] in which all $\pi \rightarrow \pi^*$ excitations are taken into account; the basis set for this calculation consists of the SCF MO's of the more restrictive of the two treatments discussed in Sect. 2. A systematic study of the effects of adding double and higher excitation species (Fig. 1a) to the CI calculation has shown that such configurations significantly alter the calculated benzene spectrum relative to that predicted solely on the basis of a single excitation treatment. The same

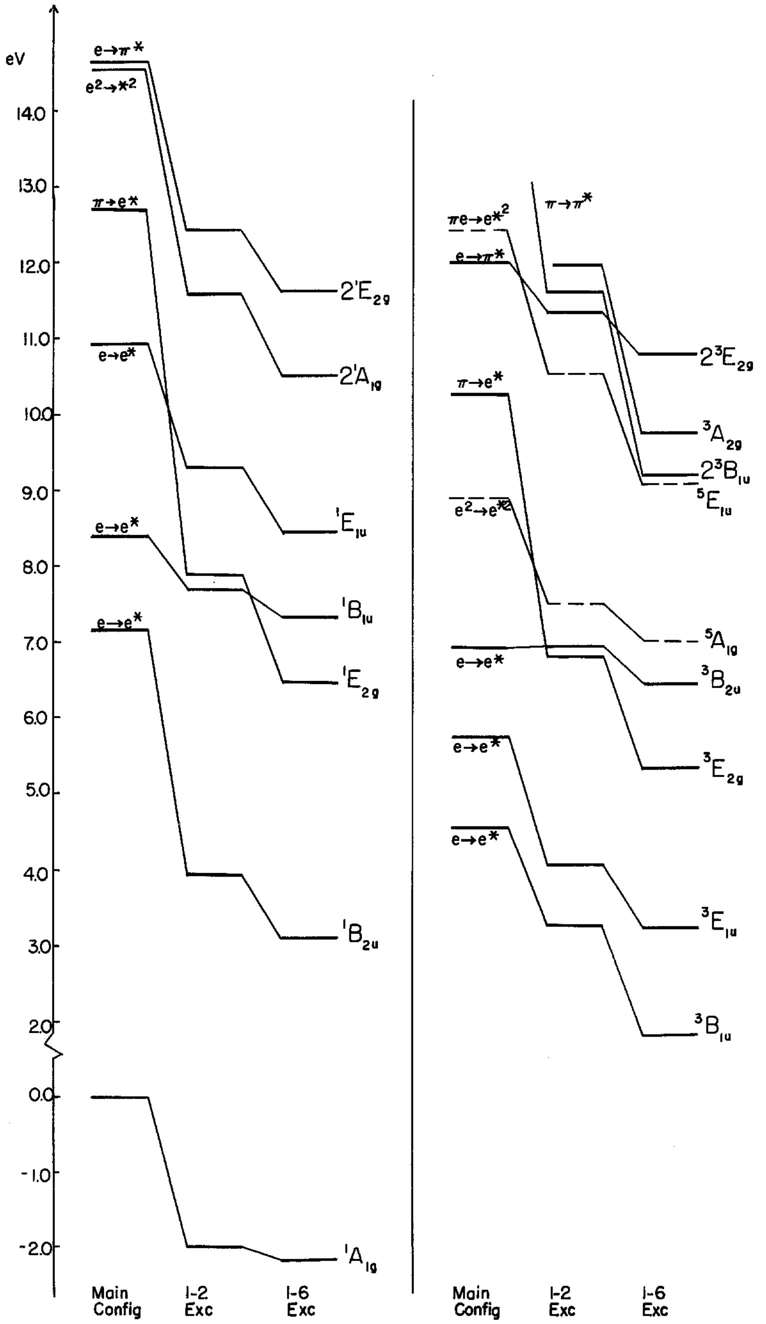

Fig. 1a

Fig. 1a and b. Energy levels of benzene for ground and excited states from (a) the fixed group CI(6π) and (b) various CI treatments based on the extended SCF MO basis set. (Note that in the latter diagram $\pi \rightarrow \pi^*$ energy levels for the CI(6π) and the CI($6\pi, 2\sigma$) calculations are essentially equal.) Main configuration notation in the figures specifies σ for $3e_{2g}$, π for $1a_{2u}$, e for $1e_{1g}$, e^* for $1e_{2u}$ and π^* for $1b_{2g}$

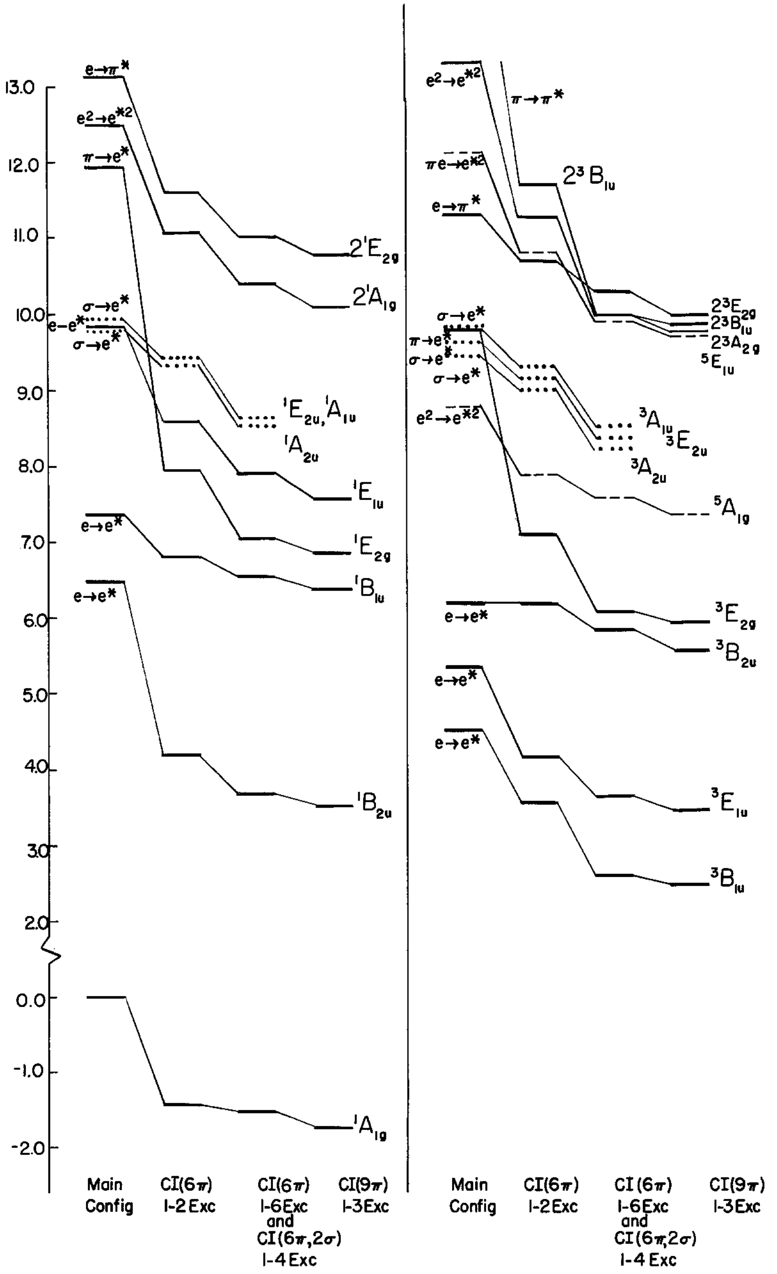

Fig. 1b

conclusion has been reached earlier by Bloor *et al.* [6] on the basis of semi-empirical investigations, but a survey of several other treatments of this genre [14] has emphasized that the effect of higher excitations species varies rather broadly with the method of parametrization chosen. This experience with

Table 6. *Number of configurations in each irreducible representation and multiplicity that are considered in the* CI *calculations for benzene:* (a) $\pi \rightarrow \pi^*$ *species and* (b) $\sigma \rightarrow \pi^*$ *species*

	CI(6π) (1–6 Exc)	CI(9π) (1–3 Exc)	CI(6π, 2σ) (1–4 Exc)		CI(6π, 2σ) (1–4 Exc)
$^1A_{1g}$	22	61	56	$^1B_{1g}$	38
$^3A_{1g}$	12	61	42	$^3B_{1g}$	53
$^5A_{1g}$	4	21	18	$^5B_{1g}$	16
$^7A_{1g}$	—	2	1	$^7B_{1g}$	1
$^1E_{2g}$	30	94	81	$^1E_{1g}$	70
$^3E_{2g}$	30	115	90	$^3E_{1g}$	97
$^5E_{2g}$	6	31	26	$^5E_{1g}$	29
$^7E_{2g}$	—	1	2	$^7E_{1g}$	2
$^1A_{2g}$	10	43	32	$^1B_{2g}$	38
$^3A_{2g}$	18	69	57	$^3B_{2g}$	53
$^5A_{2g}$	2	18	12	$^5B_{2g}$	16
(a) $^7A_{2g}$	—	1	2	(b) $^7B_{2g}$	1
$^1B_{1u}$	16	44	37	$^1A_{1u}$	34
$^3B_{1u}$	18	55	47	$^3A_{1u}$	47
$^5B_{1u}$	3	12	12	$^5A_{1u}$	14
$^7B_{1u}$	1	1	2	$^7A_{1u}$	1
$^1E_{1u}$	27	94	75	$^1E_{2u}$	73
$^3E_{1u}$	33	126	100	$^3E_{2u}$	103
$^5E_{1u}$	6	34	27	$^5E_{2u}$	32
$^7E_{1u}$	—	2	2	$^7E_{2u}$	2
$^1B_{2u}$	13	41	34	$^1A_{2u}$	34
$^3B_{2u}$	15	53	44	$^3A_{2u}$	47
$^5B_{2u}$	2	12	10	$^5A_{2u}$	14
$^7B_{2u}$	—	—	—	$^7A_{2u}$	1

semi-empirical formulations thus suggests the advisability of testing what effect the level of treatment chosen for the *ab initio* calculation has upon the benzene spectrum.

To this end a series of CI calculations has been carried out using the SCF MO's of the less restrictive SCF calculation of Sect. 2 in which two $p\pi$ AO's per atom are employed and the resulting π and π^* MO's are no longer completely determined by symmetry. Again only excitations involving the first six π MO's are considered, at least in the initial calculation (hereafter referred to as CI(6π) calculation); the configurations implied by this definition are categorized according to symmetry in Table 6. Just as with the previous set of SCF MO's, a study of the effect of adding double and higher excitation electronic configurations is made and the resulting calculated energy levels are given in Fig. 1b. Comparison of this figure with that preceding shows some significant differences in the two sets of calculations; in general the second set of energy levels is seen to vary less sharply upon successive addition of higher excitation configurations.

Transition energies to the excited states of benzene are found to be generally lower than in the first (fixed group) calculation but not uniformally so; a comparison of these two sets of transition energies is given in Table 7 along with those of several other CI treatments to be discussed subsequently. The $^1B_{1u}$ species is

Table 7. *Theoretical spectrum of benzene (values in eV) obtained from different levels of treatment*

	Fixed group basis	Extended basis			
	CI(6π) 1–6 Exc	CI(6π) 1–6 Exc	CI(9π) 1–3 Exc	CI(6π, 2σ) 1–4 Exc	Exp.[a]
$^1A_{1g}$	0.0	0.0	0.0	0.0	0.0
$^1B_{2u}$	5.26	5.20	5.27	5.21	4.674–5.0
$^1B_{1u}$	9.48	8.08	8.09	8.09	5.96 –6.20
$^1E_{2g}$	8.62	8.56	8.60	8.57	
$^1E_{1u}$	10.61	9.41	9.30	9.42	6.72 –6.96
$^1A_{1g}$	12.67	11.89	11.82	11.89	7.24 –8.20
$^1E_{2g}$	13.78	12.54	12.52	12.54	8.36 –8.89
$^1A_{2u}$	—	—	—	10.06	
$^1E_{2u}$	—	—	—	10.16	
$^1A_{1u}$	—	—	—	10.17	
2 $^1A_{1g}$	13.13	12.58	12.62	12.58	
$^5A_{1g}$	9.17	9.09	9.06	9.09	
$^5E_{1u}$	11.25	11.40	11.42	11.40	
$^3B_{1u}$	3.98	4.12	4.21	4.13	3.65 –3.95
$^3E_{1u}$	5.39	5.20	5.21	5.20	4.58 –4.75
$^3B_{2u}$	8.61	7.35	7.28	7.35	5.40 –5.76
$^3E_{2g}$	7.48	7.59	7.65	7.60	5.96 –6.55
$^3B_{1u}$	11.34	11.48	11.56	11.51	8.84
$^3A_{2g}$	11.91	11.47	11.49	11.47	
$^3E_{2g}$	12.96	11.80	11.70	11.81	
$^3A_{2u}$	—	—	—	9.72	
$^3E_{2u}$	—	—	—	9.87	
$^3A_{1u}$	—	—	—	10.02	

[a] Ref. [17–22].

found to be relatively more stable in the second calculation, lying somewhat below the $^1E_{2g}$, in contrast to the first case; the $^1E_{1u}$, to which transitions from the $^1A_{1g}$ ground state are fully allowed, is predicted to lie above both, however, in disagreement with single excitation treatments [15].

An interesting fact about the preceding two sets of calculations is that the ground state $^1A_{1g}$ energy is found to be slightly lower in the first CI treatment (−230.4543 vs. −230.4494 hartree in the second case), even though the corresponding SCF wavefunction is the worse of the two being considered. This result does not violate the variation principle, of course, and is not even so surprising when one considers that the CI(6π) level accounts for all $\pi \rightarrow \pi^*$ excitations in the first calculation with only one $p\pi$ AO per carbon, but only for a rather small (albeit significant) number of the total in the other (since six other virtual π MO's have been ignored in this case). This fact suggests that employment of the less restrictively grouped π AO basis set requires that excitations among a larger class of π MO's must be considered in order to achieve the full benefit of this flexibility.

Thus another CI calculation has been caried out based on the decomposed $p\pi$ group SCF MO's in which excitations from the occupied π orbitals to the first six virtual π^* species ($1e_{2u}$, $1b_{2g}$, $2a_{2u}$ and $2e_{1g}$) are considered; because of the relatively small interaction observed for quadruple and higher excitation configurations in CI(6π), however, only triple and lower excitations are included in this CI(9π) calculation. The numbers of configurations of each symmetry thereby included in this treatment are also given in Table 6. Symmetrized multi-determinantal functions are obtained for this calculation according to a method discussed earlier by the authors [16].

The resulting energy levels are plotted in Fig. 1b and appear to lie uniformally lower (by approximately 0.2–0.3 eV) than those calculated in the CI(6π) treatment for the same set of MO's. The ground state energy (-230.4570 hartrees) in this case is somewhat below that obtained from the former fixed group CI calculation; at the same time the transition energies are not greatly different from those obtained from the CI(6π) treatment employing the same set of SCF MO's (Table 7). Since attainment of reliable transition energies is the main goal in the present investigation further expansion of the class of $\pi \rightarrow \pi^*$ configurations has not been carried through.

Instead attention is turned to the implications of the relatively unstable σ type MO($3e_{2g}$) calculated for benzene. Since excitation from $1a_{2u}$ to $1e_{2u}$ gives one of the main components of the ${}^1E_{2g}$ state (which turns out to be one of the lowest lying excited species once higher excitation configurations are included in the calculation) it certainly seems possible that the $3e_{2g} \rightarrow 1e_{2u}$ transition might also lead to relatively low energy (Table 1). In order to investigate this possibility a CI calcultaion (using the decomposed p group basis again) which considers excitations from the $1a_{2u}$, $3e_{2g}$ and $1e_{1g}$ MO's into the $1e_{2u}$ and $1b_{2g}$ is carried out. In this CI($6\pi, 2\sigma$) treatment no configurations which correspond to greater than quadruple excitations from the SCF ground state function are included; Table 6 contains a breakdown of these configurations according to symmetry.

The results of this treatment are, not surprisingly, very similar to those of the CI(6π) calculation for the $\pi \rightarrow \pi^*$ transitions, as can be seen from Table 7. The A_{1u}, A_{2u} and E_{2u} states have their origin in the $\sigma \rightarrow \pi^*$ excitations, however, and the calculations find a singlet and triplet of each type within the energy range of 9.7–10.2 eV. These energies are relatively high from an experimental point of view but when it is recognized that a) the lowest $\sigma \rightarrow \pi^*$ singlet ${}^1A_{2u}$ is calculated to lie only 0.6 eV above the important ${}^1E_{1u}$, b) transitions to this state from the ${}^1A_{1g}$ ground state are fully allowed according to group theoretical selection rules and c) most importantly, the CI treatment undertaken would seem to be biased in favour of the $\pi \rightarrow \pi^*$ species since only one σ MO is allowed to participate in the excitations, it seems quite plausible that $\sigma \rightarrow \pi^*$ transitions may be observable in the benzene electronic spectrum in roughly the same region heretofore attributed only to the $\pi \rightarrow \pi^*$ excitations.

B. Comparison with Experimental Data

The electronic spectrum of benzene has been the subject of numerous experimental studies, which have led to a variety of predictions for the location of the energy levels of this system and assignments thereof [17–22]. These data are summarized in Table 7. The calculated transition energies already discussed should be upper limits to the true values since the treatments considered all employ ground state SCF MO's as basis; thus the excited states in the benzene transitions are less satisfactorially represented than is the ground state itself. The fact that the decomposed $p\pi$ group SCF calculation allows for a greater selectivity in the construction of the π^* MO's tends to oppose this effect in general by preferentially improving the excited state representation; the data of Table 7 seem to be consistent with this line of reasoning.

All the present CI calculations agree with experiment that the first three excited states of benzene are ${}^3B_{1u}$, ${}^3E_{1u}$ and ${}^1B_{2u}$; the calculated transition energies resulting from the extended basis set treatments for these three states are from 0.3 to 0.6 eV higher than the corresponding experimental values. This agreement is obtained only after inclusion of double and higher excitation configurations in the CI treatment, as has been noted previously [5] in connection with the fixed group calculations; single excitation CI invariably finds ${}^3B_{2u}$ more stable than ${}^1B_{2u}$ (Fig. 1a–b).

The overestimation of transition energies apparently increases for the more highly excited states to a range of about 2.0–2.5 eV. Transitions to the ${}^1E_{1u}$ from the ground state are fully allowed and it is fairly certain that this species is the upper state in the strong 6.72–6.96 eV absorption [4]. Assuming this assignment to be correct, the question still remains as to the number and identity of the singlet-singlet transitions occurring at lower energy. The calculations predict both ${}^1B_{1u}$ and ${}^1E_{2g}$ to be lower than ${}^1E_{1u}$ but experimentally the indication is that only one of these states is actually more stable, this generally believed [18, 22] to be ${}^1B_{1u}$. Recently an interpretation of a flash photolysis experiment [19] has suggested that the ${}^1E_{2g}$ state lies somewhat above ${}^1E_{1u}$. Nevertheless the low transition probability expected for both ${}^1B_{1u}$ and ${}^1E_{2g}$ makes none of these experimental assignments positive and the fact is that the ordering ${}^1B_{1u} < {}^1E_{1u} < {}^1E_{2g}$ is no longer that predicted theoretically once the effect of higher excitation configurations is taken into account. The calculated order of triplets is altered upon the employment of the more flexible AO basis set, thereby coming into complete agreement with that assigned experimentally; the energy differences between calculation and experiment for the third and fourth triplet fall in the range of 1.0–1.7 eV.

The next three triplet-singlet pairs of states are found to be of the $\sigma \to \pi^*$ variety. These states have never been predicted from absorption or electron impact studies but it has been suggested [23] that the polarizibility tensor of benzene derived from molecular collision studies can best be explained by the existence of relatively low lying species of this type. More extensive investigations, both experimental and theoretical, would therefore seem desirable in order to establish the true location of these out-of-plane transitions.

Deficiencies in the present theoretical treatment could be at least partially removed by carrying out open shell SCF calculations on the excited states of benzene and then following these with a CI for each state based on its own set of SCF MO's. Such a technique has worked well for formaldehyde and it would almost certainly lead to significant lowerings in the transition energies of benzene since it provides a more direct calculation of the excited states than is obtained from the CI based exclusively on the SCF MO's of the ground state. Calculations of this type are presently being carried out by the authors.

5. Electronic Spectrum of Borazine

The spectrum of borazine has received much less attention than that of benzene but there is reason to expect the same general features in both. Thus calculations which are equivalent to those discussed in the preceding section for C_6H_6 are carried our for borazine. Because of the lower symmetry of this system, however, it is not possible to partition the resultant secular equations as thoroughly as in the case of benzene. A correlation table for the irreducible representations of the two point groups involved, D_{6h} and D_{3h}, and the information of Table 6 will give the orders of the pertinent secular equations which are to be solved for borazine. The results of these various calculations are given in Figs. 2a–b and Table 8 (no calculation with more than six π MO's in the valence set has been carried out).

The effect of double and higher excitation configurations is also quite significant for borazine but it is not as important as in the case of benzene. The energy lowering produced by the CI for the ground state ${}^1A_1'$ is also smaller for borazine, so that the general conclusion is that CI is more effective for C_6H_6; the relatively small intereaction among the configurations of $B_3N_3H_6$ has previously been equated with its smaller resonance energy [3][1].

Table 8. *Theoretical spectrum of borazine (values in eV) obtained from different levels of treatment*

	Fixed group basis	Extended basis		
	CI(6π)	CI(6π)	CI($6\pi, 2\sigma$)	Exp.[a]
${}^1A_1'$	0.0	0.0	0.0	0.0
${}^1A_2'$	6.97	7.88	7.88	6.2–6.5
${}^1A_1'$	8.75	9.01	9.02	6.7–6.9
${}^1E'$	9.57	9.59	9.59	7.7
$2\,{}^1E'$	10.86	11.34	11.34	
$3\,{}^1E'$	13.03	11.66	11.67	
${}^1A_2''$	—	—	9.86	
${}^1E''$	—	—	10.40	
${}^1A_1''$	—	—	10.92	
${}^3A_1'$	6.46	7.93	7.93	
${}^3E'$	7.30	8.05	8.05	
${}^3A_2'$	8.52	8.33	8.33	
$2\,{}^3E'$	8.92	9.89	9.89	
$3\,{}^3E'$	11.81	11.69	11.69	
${}^3A_2''$	—	—	9.42	
${}^3E''$	—	—	10.05	
${}^3A_1''$	—	—	10.85	

[a] Ref. [1, 4].

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[1] For borazine the CI based on the fixed group SCF MO's appears to be considerably more effective than that based on the extended set. This difference would doubtless become less significant if more π virtual MO's were included in the valence set of the extended treatment.

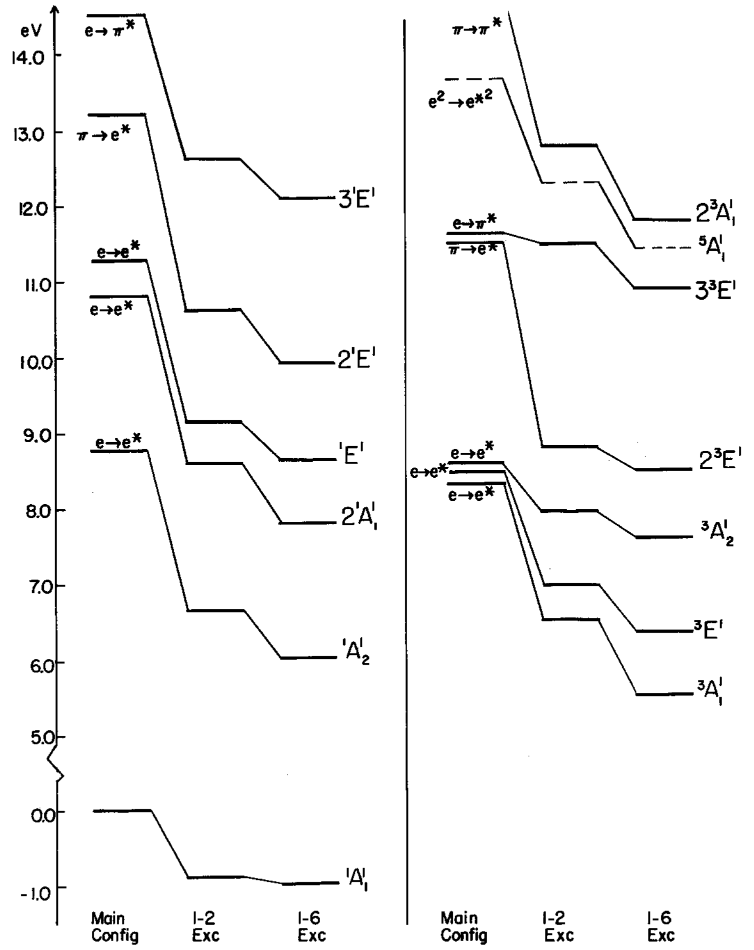

Fig. 2a

Fig. 2a and b. Energy levels of borazine for ground and excited states from (a) the fixed group CI(6π) and (b) various CI treatments based on the extended SCF MO basis set. (Note that in the latter diagram corresponding $\pi \rightarrow \pi^*$ energy levels for the CI(6π) and the CI($6\pi, 2\sigma$) calculations are essentially equal.) Main configuration notation in the figures specifies σ for $6e'$, π for $1a''_2$, e for $1e''$, e^* for $2e''$ and π^* for $2a''_2$

The lowest three excited states calculated for $B_3N_3H_6$ are $^3A'_1$, $^1A'_2$ and $^3E'$, which correspond by symmetry to the lowest three of benzene; the energy separations are much smaller, however, particularly in the treatment employing the extended set of SCF MO's. Of these the singlet state is found to be relatively more stable compared to the two triplets in the case of borazine than for C_6H_6. An interesting point is the fact that the calculated order of the first three triplets in the single (main) configuration treatment of borazine is opposite for the two different sets of MO's employed; on the other hand, after the CI has been carried out, the calculated triplet order is the same for both basis sets.

One consequence of the decrease in symmetry is that the E_{2g} and E_{1u} states of benzene correspond to the same irreducible representation in borazine, E'. A re-

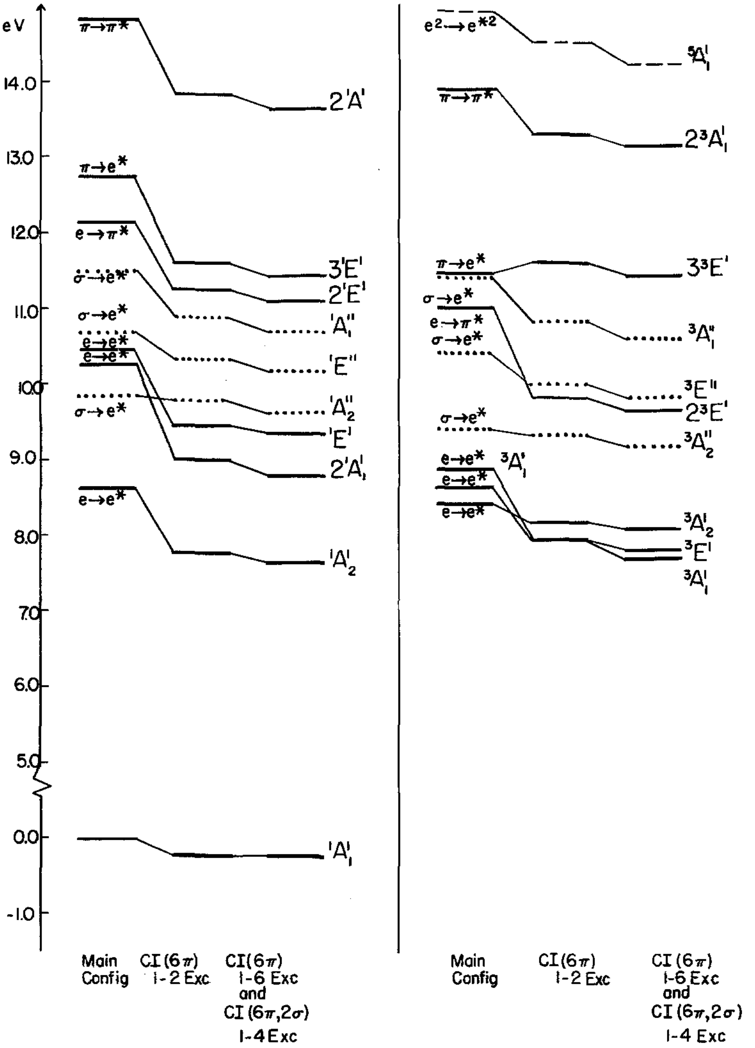

Fig. 2b

curring feature of the benzene calculations has been the inversion in the order of the $1\,^1E_{1u}$ and $1\,^1E_{2g}$ states of this system after the CI has been carried out. The analogous result is not found for borazine; instead the most stable $^1E'$ state is calculated to consist mainly of the $1e'' \rightarrow 2e''$ configuration (E_{1u} type) both before and after the CI.

The second excited singlet predicted from the calculations for $B_3N_3H_6$ is $2\,^1A_1'$, which corresponds to $^1B_{1u}$ in benzene; transitions to this state and to $^1A_2'$ from the $^1A_1'$ ground state are forbidden but all those involving $^1E'$ upper states are allowed. The experimental ordering [1, 4] agrees with that calculated but again the experimentally observed transition energies are everywhere smaller (by from 1.3–2.1 eV), as can be seen from Table 8. No experimental investigation of the triplets of borazine has yet been reported; the calculated order of these states corresponds exactly to that obtained for benzene ($2\,^3E'$ correlates with $^3E_{2g}$).

A major difference found to exist between the two systems under discussion is that in borazine there are only three $\pi \rightarrow \pi^*$ excited singlets calculated to be more stable than the lowest three $\sigma \rightarrow \pi^*$ states of this multiplicity, whereas in benzene there are four $\pi \rightarrow \pi^*$ singlets which are more stable; in both systems there are four $\pi \rightarrow \pi^*$ triplets preceding the lowest three $\sigma \rightarrow \pi^*$ triplets. The energy separation between the $^1E'$ and $^1A_2''$, to both of which transitions are fully allowed, is only 0.3 eV in borazine, less than half the difference between corresponding transition energies ($^1E_{1u}$ and $^1A_{2u}$ states) in benzene. Thus it appears that a similarly good case for the existence of low lying $\sigma \rightarrow \pi^*$ transitions can be made for $B_3N_3H_6$. The use of open shell SCF techniques to further investigate the spectrum of this system should also be effective.

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