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Semiempirical Molecular Orbital Calculations on Boranes

I. The Relation between Transitions in Arylboronic Acids and Arylboranes

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Traditional Pariser-Parr-Pople and variable electronegativity calculations have been carried out on $C_6H_5B(OR)_2$ and p-$CH_3OC_6H_4B(OR)_2$, and the results compared with calculations for $C_6H_5BR_2$. It is concluded that the VE-SCF method offers a real advantage over the simple PPP method for predicting percent charge transfer and transition intensity in cases where excited states possess substantial C.T. character. The restriction that empirically chosen parameters fit the observed transition energies and intensities of both triarylboranes and $ArB(OR)_2$ requires the choice of a boron VSIP greater than 2.0 eV in the fixed parameter procedure of the usual PPP-SCF-CI method for these molecules. Observed transitions in $C_6H_5B(OR)_2$ correlate with ^1L_b, ^1L_a, ^1B_b, whereas the first absorption maximum of $(C_6H_5)_3B$ is assigned to C.T. ($^1A_1 \rightarrow {}^1A_1$) local C_{2v} symmetry.

PPP- und VE SCF-Rechnungen wurden für $C_6H_5B(OR)_2$ und p-$CH_3OC_6H_4(OR)_2$ durchgeführt, und die Ergebnisse wurden mit denjenigen für $C_6H_5BR_2$ verglichen. Es kann der Schluß gezogen werden, daß die VE SCF-Methode einen Vorteil gegenüber der einfachen PPP-Methode bietet, um den prozentualen Charge Transfer und Übergangsintensitäten in Fällen zu bestimmen, in denen die angeregten Zustände einen wesentlichen C.T.-Charakter besitzen. Die Bedingung, daß die empirisch gewählten Parameter den beobachteten Übergangsenergien und -intensitäten von sowohl Triarylboranen als auch $ArB(OR)_2$ angepaßt sein sollen, erfordert die Wahl eines Bor-VSIP größer als 2,0 eV im Rahmen der üblichen Parametrisierung der PPP-SCF-CI-Methode. Beobachtete Übergänge in $C_6H_5B(OR)_2$ korrelieren mit ^1L_b, ^1L_a, ^1B_b, wogegen das erste Absorptionsmaximum des $(C_6H_5)_3B$ einem C.T.-Übergang ($^1A_1 \rightarrow {}^1A_1$) lokaler C_{2v}-Symmetrie zugeordnet wird.

Des calculs traditionnels Pariser-Parr-Pople et des calculs d'électronégativité variable ont été effectués sur $C_6H_5B(OR)_2$ et p-$CH_3OC_6H_4B(OR)_2$ avec comparison aux résultats obtenus pour $C_6H_5BR_2$. La conclusion est que la méthode VE-SCF offre un réel avantage sur la méthode PPP simple en ce qui concerne la prédiction du transfert de charge et de l'intensité de transition pour les états excités possèdant un net caractère de transfert de charge. La restriction selon laquelle les paramètres empiriques doivent permettre de reproduire les énergies de transition et les intensités des deux triarylboranes et de $ArB(OR)_2$, nécessite le choix d'un potential d'ionisation de l'état de valence du bore supérieur de 2 eV à celui employé dans les méthodes ordinaires. Les transitions observées dans $C_6H_5B(OR)_2$ sont reliées à ^1L_b, ^1L_a, ^1B_b, tandis que la première absorption de $(C_6H_5)_3B$ est attribuée à un transfert de charge ($^1A_1 \rightarrow {}^1A_1$) de symétrie locale C_{2v}.

Numerous traditional Pariser-Parr-Pople self consistent field calculations including configuration interaction (PPP-SCF-CI) of the electronic transition energies of a variety of aryl and vinyl boranes including phenyl and *para* tolylboronic acid [1α] (esters) have been carried out previously by Armstrong and Perkins [1] with good success in predicting observed transition energies.

However when these same parameters such as valence state ionization potentials (VSIP) and one center repulsion integrals for boron were used to calculate the transition energies of triphenylboron, in the words of Armstrong and Perkins [2], a marked disagreement was found between experimental results and the calculations on $(C_6H_5)_3B$, and the observed and calculated spectra of other phenylboranes. There is substantial disagreement between this author [3] and other [4] who, on the basis of experimental data and simple molecular orbital calculations, assign the lowest energy $(C_6H_5)_3B$ transition at 280 nm to a charge transfer (C.T.) transition, and Armstrong and Perkins whose calculations [2] assign this transition to essentially the locally excited ^1L_b benzene transition with little C.T. character.

In order to resolve the conflicts outlined above, as a preliminary move, we carried out simple Hückel molecular orbital calculations on BO_2 and $C_6H_5BO_2$ using for carbon and oxygen parameters recommended by Streitwieser [5] and for boron a coulomb integral $(\alpha^\circ - 0.9\beta^\circ)$, previously [3] found to satisfactorily predict the charge transfer character observed in the first transition of the triarylboranes. The results are summarized in the correlation diagram Fig. 1, where numbers to the left of the bar are energies in units of β and parenthetical numbers to the right are boron orbital mixing coefficients in the Hückel molecular orbital. The results show that the first transitions to the lowest vacant phenylboronic acid molecular orbital is *not* charge transfer, although it is predicted to have about 25% C.T. character, because the lowest vacant molecular orbital of BO_2 is *higher* in energy than the vacant degenerate benzene orbitals. We now wish to show that the results of these naive molecular orbital calculations which accommodate the observed spectra of both the arylboronic

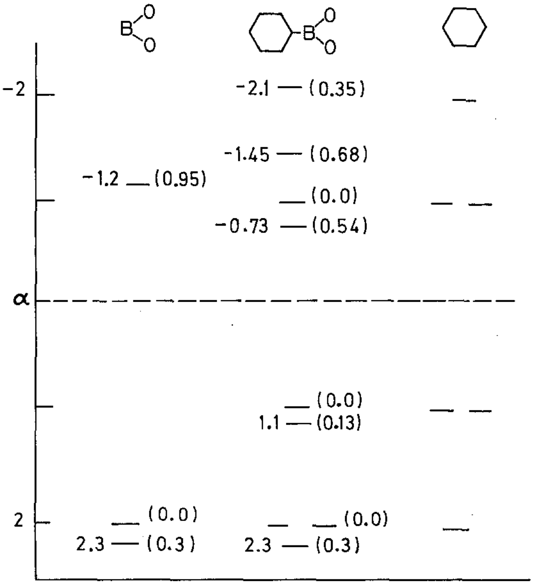


Fig. 1. Energies and boron atomic orbital mixing coefficients of simple Hückel molecular orbitals for BO_2, $C_6H_5BO_2$ and C_6H_6. Energy units are the Hückel β

acids and the triarylboranes can be preserved in the more sophisticated Pariser-Parr-Pople SCF calculations including configuration interaction.

In addition the Variable Electronegativity (VE-SCF) method of Brown and Heffernan [6] was used to calculate transition energies for $C_6H_5B(OR)_2$ and p-$CH_3OC_6H_4(OR)_2$. The use of Hückel rather than SCF orbitals was also examined and found to give virtually the same transition energies as obtained from SCF orbitals.

Comparison with calculations for $C_6H_5BR_2$ demonstrate a reasonable choice for boron VSIP which allows a consistent interpretation of the spectra of arylboranes including triarylboranes such as triphenylboron.

Experimental

Spectra. Phenylboronic acid and p-methoxyphenyl boronic acid were prepared by the appropriate grignard reaction with methyl borate. The boronic acids were recrystallized first from benzene and then from water. The observed absorption maxima (nm) and molar extinction coefficients ($\varepsilon \times 10^{-3}$) were; for $C_6H_5B(OH)_2$ 216 (7.1), 265 (0.401) nm in water, and for p-$CH_3OC_6H_4B(OH)_2$ 199 nm (30), 266.5 (12), 264 sh, 272 (1.0), 280 (0.83) nm in acetonitrile.

Method of Calculation

The computation of orbital energies and excitation energies by the traditional PPP-SCF-CI method is so widely known that numerous textbooks now outline the methods and even provide sample calculations [7]. We will therefore simply indicate the equations and assumptions used in this paper for the integrals necessary to solve the Roothaan [8] equations:

$$\sum_q C_{iq}(F_{pq} - S_{pq}E) = 0 . \tag{1}$$

The diagonal elements (α_p) of the core Hamiltonian matrix are given from the Goeppert-Mayer Sklar method [9], neglecting penetration integrals, as (2) where n is the number of π-electrons contributed to the system and I_p the valence state ionization potential.

$$\alpha_p = -I_p - [n_p(n_p - 1)(pp|pp)/2(3 - n_p)] - \sum_{q \neq p} n_q(qq|pp) . \tag{2}$$

For the purposes of calculation we have chosen a model where boron contributes no electrons to the π-system, i.e. $n_B = 0$. This model has been found to give good agreement [10] with observed transition energies of borazene. Thus the diagonal element of the Hamiltonian matrix for boron is approximately the vacant boron $2p$ electron affinity. Bond angles and distances used were $\sphericalangle CCC = \sphericalangle OBO = 120°$; C–C = 1.397 Å; B–C = 1.550 Å; B–O = 1.204 Å.

The required one and two centered Coulomb repulsion integrals, $(pp|pp)$ and $(pp|qq)$ are taken after Pariser [11], and Mataga and Nishimoto [12] as:

$$(pp|pp) = I_p - (EA) , \tag{3}$$

$$(pp|qq) = \frac{14.3986}{r_{pq} + 28.7972[(pp|pp) + (qq|qq)]^{-1}} . \tag{4}$$

The off diagonal elements β_{pq} of the core matrix are computed as

$$\beta_{pq} = \frac{-1.75}{4} S_{pq}[(I_p) + (I_q)] \,. \tag{5}$$

To facilitate comparison of our results with those of Armstrong and Perkins we have used for boron the same value of $(pp|pp)$, derived in unpublished results by J. J. Kaufman [10], and used by Armstrong and Perkins [1].

In the Brown and Heffernan VE-SCF calculation, one center integrals determined by Matsuoka and I'Haya [13] were used. Required valence state ionization potentials and electron affinities for $B^-(t_1t_2t_3)$ and $O(S^2x^2yz)$ were determined [13] by least squares extrapolation from the isoelectronic series $C^0(t_1t_2t_3\pi)$, N^+, O^{+2}, F^{+3} and F^+, Ne^{+2}, Na^{+3}. Eqs. (6) and (7) are derived for B^- and O respectively.

$$I_p = 3.3897\,Z^2 - 7.8986\,Z + 1.1567 \,, \tag{6a}$$

$$(EA) = 3.8223\,Z^2 - 17.0631\,Z + 15.6843 \,, \tag{6b}$$

$$I_p = 3.9928\,Z^2 - 19.1465\,Z + 22.0388 \,, \tag{7a}$$

$$(EA) = 3.8431\,Z^2 - 23.1416\,Z + 28.3563 \,. \tag{7b}$$

In the VE-SCF method the effective nuclear charge Z_r for first row elements is taken as a function of π electron density P_{rr} at atom r, according to Eq. (8) where N_r is atomic number of r and σ_r is the number of atom $r\sigma$ electrons.

$$Z_r = N_r - 1.35 - 0.35(\sigma_r + P_{rr}) \,. \tag{8}$$

In this fashion all integrals in the Hamiltonian matrix become dependent on charge density.

Since we are interested in focusing attention on the percent charge transfer character in each excited state after including configuration interaction, the percent charge transfer character (% C.T.) was calculated by the expression (9) where $B_{i\to j}$ are eigenvectors of the CI matrix.

$$\%\,\text{C.T.} = 100 \times \sum_{ij}^{\text{CI}} B^2_{i\to j} \times \sum_{p}^{\text{PhH}} C^2_{ip} \times \sum_{p}^{\text{B(OR)}_2} C_{jp} \,. \tag{9}$$

Table 1

Method	VSIP			Integrals[c]					
	C[b]	B[a]	O	(CC|CC)[b]	(BB|BB)	(OO|OO)	β_{CC}[b]	β_{BC}	β_{B-O}
Armstrong and Perkins	11.16	1.06	15.30	9.76	5.97	11.83	−2.33		
R + H PPP-SCF-CI	11.16	—	15.30	9.76	5.97	11.83	−2.39	−1.35	−2.00
VE-SCF-CI	11.3	2.76	18.13	10.6	5.81	15.13	−2.4	−1.56	−2.57
PPP-HMO-CI	11.30	2.75	18.09	10.60	5.80	15.12	−2.43	−1.55	−2.57

[a] VSIP of boron varied from 1.06 to 2.80 eV.

[b] Dependent on position of carbon in VE-SCF calc.

[c] For p-$CH_3OC_6H_4B(OR)_2$ $\beta_{C-O} = -2.063$ eV, $(OO|OO)_{OCH_3} = 15.01$ eV.

As a matter of curiosity the PPP-CI calculations were also performed using Hückel molecular orbitals, rather than SCF orbitals, from parameters $\alpha_B = \alpha_C^\circ - 0.9\,\beta^\circ$, $\beta_{B-C} = 0.7\,\beta^\circ$; $\alpha_O = \alpha_C^\circ + 2.00\,\beta_{CC}$; $\beta_{BO} = 0.7\,\beta_{CC}$.

Values of other parameters used in each set of calculations are given in Table 1. Calculations were carried out on an IBM 360-44 computer using a suitably modified version of a previously tested program [14].

Results and Discussion

The 12 lowest energy singlet and triplet excited state transition energies, their intensities and charge transfer character were calculated by the PPP-SCF-CI method boron VSIP of 1.06, 1.60, 1.80, 2.00 and 2.80. Only results for the PPP-SCF-CI calculation with a boron VSIP of 2.00 eV (Table 2) and 2.80 eV (Table 4) are given here since differences in results were small. Transition energies and percent charge transfer character calculated by the VE-SCF-CI and PPP-HMO-CI method are given in Tables 3 and 4 respectively.

Using the same boron valence state ionization potential and one centered repulsion integral, calculations are in satisfactory agreement with those of Armstrong and Perkins [1a], whose calculated [1a] energies are some 0.1 to 0.3 eV lower chiefly because of a lower value (2.33 eV) for the integral β_{C-C} and a small correction applied to boron ionization potential and repulsion integrals for the σ inductive effect of oxygen.

To account both for the absence of a low energy C.T. transition in arylboronic acids or esters and the substantial C.T. character in the long wavelength transition of the triarylboranes, a Hückel α for boron of $\alpha_B = \alpha_C^\circ - 0.9\,\beta^\circ$ is required in simple molecular orbital calculations, although others [15] have suggested $\alpha_B = \alpha^\circ - 1.0\,\beta^\circ$, or greater.

The value of the Hückel α is a guide to the boron VSIP required for SCF calculations. From Eq. (10) below [16], assuming the values appropriate to benzene (CC/CC) of 11.35 eV, carbon I_p of 11.2 eV, and $h_B = -0.9$, evaluation of β equals -3.0 eV from the spectrum of ethylene, or $\beta = -2.37$ eV from the spectrum of benzene, places the required boron VSIP in the range 2.5–3.1 eV.

$$h_r = -\delta I_p + \tfrac{1}{2}(n_\pi - (\mathrm{CC/CC})) \qquad (10)$$

where n_π is number of π electrons contributed by atom r.

Alternatively one may substitute the value of $\alpha = -40.39$ eV required [17] to fit the observed and calculated benzene ionization potential into the expression for the PPP calculated difference in energy between $C_6H_6^-$ and C_6H_6 $(\alpha + 42.06)$ and add to it 0.1 β (0.24 eV) to estimate a boron VSIP of 1.89 eV.

Based on the above considerations, the PPP-SCF-CI calculations for phenylboronic acid were examined over the range 1.06 to 2.8 eV boron VSIP. The most striking result was a very small decrease (0.1 eV) of the first $^1B_2$ energy with an increase in boron VSIP from 1.06 to 2.8 eV. Over the same range the two lowest $^1A_1$ and second lowest $^1B_2$ transition energies were only a little more sensitive, decreasing in energy by 0.22 and 0.36 eV respectively. A change of boron VSIP from 1.06 to 2.00 eV did not, however, change *any* of the four lowest transition energies by more than 0.15 eV. *A unique choice of a 1.06 eV valence* *state ionization potential for boron obviously is not required to obtain satisfactory agreement between observed and calculated transition energies of phenylboronic acids.* Rather, the first $^1A_1$ transition, which is the most sensitive of the observable transitions to the choice of boron I_p, requires a boron VSIP between 2.00 and 2.80 to give the best agreement between observed and calculated transition energy.

Molar extinction coefficients of the first three observed [18] transitions of $C_6H_5B(OC_4H_9)_2$ are in the ratio 1:17:75, compared with calculated oscillator strength ratios as the boron VSIP is changed of 1.06 (1:19:700), 2.0 (1:20:240), 2.8 (1:20:100), where the sum of the second $^1A_1$ and $^1B_2$ oscillator strengths are used. If the observed 190–200 nm absorption represents a single transition, calculated oscillator strength ratios are (1:19:350); (1:20:120); (1:20:50). With increasing boron VSIP, calculated percent charge transfer of the two lowest $^1A_1$ and $^1B_2$ transitions increases, as oscillator strengths, but the ratio of lowest $^1A_1$:$^1B_2$ intensity remains virtually the same. Agreement between calculation and experiment again seems to require the choice of a boron VSIP between 2.0 and 2.8 eV. This difference between 1.06 and the >2.0 boron VSIP may, of course, be regarded as a correction for σ inductive effects, $\sigma\pi$ repulsion integrals, and similar terms normally neglected.

The VE-SCF calculation for $PhB(OR)_2$ begins with a boron VSIP of 0.53 eV derived by Eq. (6) but arrives at an SCF VSIP of 2.76 eV. The agreement between calculated and observed transition energies especially those of di-*n*-butyl phenylboronate are excellent. It should also be noticed that the VE-SCF calculation results in 10% greater C.T. character in the lowest $^1A_1$ excited state than did the PPP calculation with a comparable boron VSIP. Further, where the use of boron VSIP 1.06 eV assigns the third lowest excited state to $^1A_1$ (see above or Ref. [1]) the VE-SCF calculation assigns the third lowest excited state to $^1B_2$. This is a prediction which offers some hope of experimental verification. The VE-SCF procedure has been criticized [16] as not giving results very different from those obtained by the more straightforward PPP approach. However, VE-SCF calculations seem to possess an advantage over the traditional PPP calculations on arylboranes and other molecules such as aniline or phenylphosphine where substantial C.T. character may be present in low energy excited states.

VE-SCF calculations were also carried out on p-$CH_3OC_6H_4B(OR)_2$ and good agreement was obtained with the observed transition energies of 4.6, 5.2

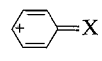
Table 2. *Transition energies* (eV), *oscillator strengths and percent charge transfer for* $C_6H_5B(OR)_2$ *by* PPP-SCF-CI-*method, boron* VSIP 2.00 eV

$^1A_1$	f_z	% C.T.	$^3A_1$	$^1B_2$	f_x	% C.T.	$^3B_2$
5.63	0.145	23	2.93	4.79	0.007	18	4.05
6.42	0.901	8.5	4.10	6.48	0.828	14	4.82
7.46	0.172	56	5.71	7.48	0.259	57	5.70
8.15	0.000	27	7.09	8.50	0.007	2.6	7.53
8.96	0.000	11	8.29	8.90	0.001	6.7	8.56
10.3	0.019	37	9.81	9.37	0.206	0.1	8.79

Table 3. *Calculated transition energies* (eV) *and percent charge transfer by* VE-SCF-*method*

$^1A_1$	% C.T.	$^3A_1$	$^1B_2$	% C.T.	$^3B_2$
$C_6H_5B(OR)_2$					
5.46	48	2.68	4.77	33	3.92
6.53	7.9	4.03	6.36	28	4.84
7.47	35	5.52	7.36	32	5.56
8.14	47	6.51	8.69	1.8	7.09
9.21	8.4	8.29	9.21	3.1	8.71
10.1	41	9.76	12.6	0.0	10.7
p-$CH_3OC_6H_4B(OR)_2$					
5.33	49	2.67	4.75	32	3.94
6.50	8.5	3.99	6.28	29	4.68
7.34	31	5.47	7.35	31	5.60
8.03	47	6.39	8.61	1.3	7.05
9.05	7.9	8.15	9.18	3.4	8.67
9.90	38	9.65	11.6	0.0	10.7

and 5.9–6.2 eV. These results are given in Table 3. The result that the calculated C.T. character in the first $^1A_1$ transition of *p*-$CH_3OC_6H_4B(OR)_2$ is not significantly greater than that for $C_6H_5B(OR)_2$ contradicts the common assumption that a strong electron donor in the para position of C_6H_5X will greatly increase the importance of valence bond structures such as I in the ^1L_a excited state. Structures I and II appear appropriate to a valence bond description of the ^1L_a state, but not III.



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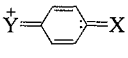
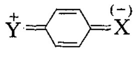


II



III

The C.T. character depends primarily on the relative energies of the vacant benzene and boron π orbitals, whereas the CH_3O substitution effect for the most part only filled orbital energy levels of benzene.

Calculated π bond orders and charge densities are indicated in structures II, III, IV and V. The calculated charge density on boron, and boronoxygen π bond order are a little lower than reported by Armstrong and Perkins [1] as 0.335 charge densities and 0.497 bond order respectively. Our results seem to us to that extent more satisfactory in view, for example, of a 1350 cm^{-1} B–O stretching frequency when compared with C–O stretching frequencies of 1560 cm^{-1} stretch in $CH_3CO_2^-$ or 1390 cm^{-1} in $CH_3C^+(OCH_3)_2$ which are estimated to have ~0.5 and 0.3 π bond orders respectively [19]; it seems unreasonable that the B–O π bond order should be very nearly 0.5. We should further point out that introduction of a para CH_3O group does not significantly change the electron density on boron in the ground state.

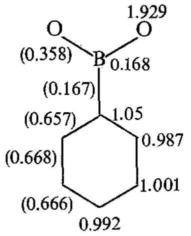
In order to relate the $C_6H_5B(OR)_2$ calculations to triphenylborane in a preliminary fashion, we carried out the PPP-SCF calculations for $C_6H_5BR_2$ where R does not interact with the π-system. For a boron VSIP of 2.00 eV and a planar molecule the six lowest calculated singlet transition energies eV (% C.T.) are $^1B_2$ 4.68 (34); $^1A_1$ 5.30 (46); $^1B_2$ 6.16 (26); $^1A_1$ 6.27 (8); $^1B_2$ 6.91 (33);

Table 4

Method	Sym	E_t (eV)	f	% C.T.	E_t (eV)	f	% C.T.	E_t (eV)	f	% C.T.
Ramsey and Ito										
PPP-SCF-CI	$^1A_1$	5.42	0.247	38	6.32	0.673	8.3	7.28	0.313	43
BVSIP 2.80	$^1B_2$	4.72	0.012	28	6.30	0.570	21	7.23	0.493	42
Armstrong	$^1A_1$	5.53	0.131	(11)[a]	6.33	0.946	(6.2)[a]	7.39	0.124	(64)
and Perkins	$^1B_2$	4.67	0.005	(17)[a]	6.36	0.811	(8.2)[a]	7.40	0.213	(61)
VE-SCF-CI	$^1A_1$	5.46	—	48	6.53	—	7.9	7.47	—	35
	$^1B_2$	4.77	—	33	6.36	—	28	7.36	—	32
PPP-HMO-Cl	$^1A_1$	5.45	—	13	6.54	—	2.4	7.44	—	22
	$^1B_2$	4.78	—	21	6.40	—	22	7.39	—	32
Observed [18] for	$^1A_1$	5.45	(10,500)		6.39	(47,000)				
$C_6H_5B(OC_4H_9)_2$	$^1B_2$	4.78	(622)		6.39					
$C_6H_5B(OH)_2$	$^1A_1$	5.59	(7,000)							
	$^1B_2$	4.55	(401)							

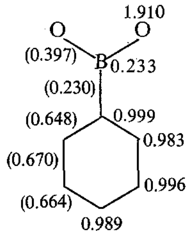
[a] C.T. character calculated by Ramsey and Ito using BVSIP 1.06 eV.

$^1A_1$ 7.18 (36). Triphenylboron is however propeller shaped nonplanar and belongs to the D_3 point group with the plane of the phenyl rings some 30–40° out the plane of the boron sp^2 bonds [3]. The calculated transition energies (% C.T.) after rotating the phenyl ring of $C_6H_5BR_2$ 45° out of plane are $^1B_2$ 4.85 (29); $^1A_1$ 5.69 (51); $^1A_1$ 6.26 (20); $^1B_2$ 6.34 (44); $^1B_2$ 6.91 (24); $^1A_1$ 6.92 (26). Clearly then the choice of a VSIP for boron greater than 2.00 eV enables us to characterize the lowest energy transition of $^1A_1$ local symmetry (C_{2v}) in triphenylboron as an intramolecular charge transfer transition. (The VE-SCF method applied to $C_6H_5BR_2$ predicts a lowest $^1A_1$ transition energy of 4.6 eV with 60% C.T. character.)



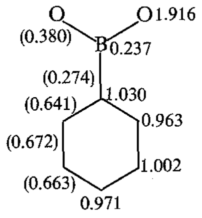
II

PPP-SCF-CI
boron VSIP 1.06



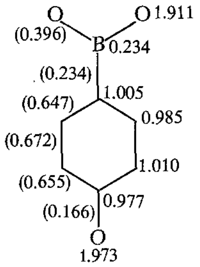
III

VE-SCF-CI



IV

PPP-HMO-CI



V

VE-SCF-CI

The spectral relationship between $C_6H_5BR_2$ and $(C_6H_5)_3B$ is exactly analogous to that between $C_6H_5NH_2$ and $(C_6H_5)_3N$. In aniline the ^1L_b transition is found at 280 nm and the ^1L_a at 230 nm ($\varepsilon = 8.6 \times 10^3$), but in triphenylamine there is strong configuration interaction between the locally excited $^1A_1$ states which shifts the ^1L_a derived transition to 297 mμ ($\varepsilon = 23 \times 10^3$), completely burying the less intense ^1L_b states. Thus, whereas in $C_6H_5BR_2$ we would expect the $^1A_1 \rightarrow {}^1A_1$ charge transfer transition near 230 nm and the ^1L_b near 265 nm it may be confidently expected that in $(C_6H_5)_3B$, as in $(C_6H_5)_3N$, the charge transfer transition will be substantially red shifted and may bury the ^1L_b states for which configuration interaction terms are smaller.

This seems to be the case, for in the spectrum [3] triphenyl boron itself we find a broad intense double maximum absorption band 4.3 to 4.5 eV ($\varepsilon = 3.9 - 3.5 \times 10^4$) which is assigned to the charge transfer transition. Further in the spectrum of trimesitylboron [3] where the C.T. transition is found at 331 nm, the ^1L_b transition may be discerned as a pronounced shoulder at 282 nm ($\varepsilon = 3 \times 10^4$).

After completing our work we found that Bloor and coworkers [20] had carried out an identical series of calculations (that is, fixed parameter Pariser-Parr-Pople, variation of substituent VSIP, and VE-SCF) on aniline with results and conclusions very similar about the relative merits of the procedures.

Conclusions

We believe the following conclusions are justified. One, in the traditional PPP-SCF-CI calculation for monosubstituted benzenes, C. T. character and oscillator strength is a significantly more sensitive function than transition energy of the choice of a substituent VSIP, if the VSIP is within an electron volt of the energy of the benzene degenerate orbitals. The VE-SCF method will probably provide better results than the PPP-SCF method where low-lying excited states of monosubstituted benzene possess substantial C.T. character.

Secondly the first broad intense absorption band near 300 nm in the spectra triarylboranes should be assigned to a C.T. transition derived from locally excited $^1A_1$ states *not* $^1B_2(^1L_b)$ states. By contrast the first four observed transitions of phenylboronic acids (esters) correlate with the benzene ^1L_b, ^1L_a and $^1B_{ab}$ transitions.

Previous calculations on boranes by Armstrong and Perkins (Refs. [1, 2] and leading references) should be reexamined in light of the above results.

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