steric effects involving *all* reactants. The ^{1}H nmr spectrum of $H[(CH_3)_2N]_2B_3N_3H_2CH_3$ indicates the product to be 55% of the ortho,para isomer and 45% of the ortho,ortho isomer. These data might indicate that the dichloro derivative can be formed by more than one reaction path.
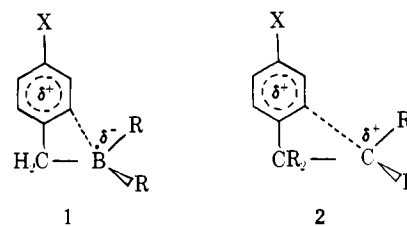
Charge-Transfer Transitions in Para-Substituted Tribenzylboranes

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Abstract: The ultraviolet spectra of XC_6H_5-substituted tribenzylboranes (X is *p*-H, -F, and -CH$_3$, and CH$_3$O and 2,4,6-Me$_3$) in addition to the benzenoid ^1L_b transition maxima exhibit a medium intensity absorption maximum in the region 240–285 nm which is assigned to intramolecular charge transfer from aryl group to the boron vacant 2p orbital. This assignment is supported by a linear correlation of transition energy with XC_6H_5 ionization potential and by semiempirical molecular orbital calculations. A similar absorption maxima in the spectra of tribenzylamine and tribenzylphosphine may also be assigned to intramolecular charge transfer, from N or P lone-pair to antibonding vacant benzene π^* orbitals. A large red shift of the benzene ^1L_a transition of $(C_6H_5CH_2)_3B:NH_3$ is attributed to boron–carbon hyperconjugation.

Intramolecular charge transfer (CT) transition energies are well approximated by eq 1 in which I_p is the donor ionization potential, E_a is the acceptor electron affinity, and r is the distance between positive and negative charge. A linear dependence of electronic transition energy on donor group ionization potential is a generally accepted[2] criterion for assignment of an observed transition in a series of similar molecules to a charge-transfer transition. In a preliminary communication[3] we pointed out that the difference in r between triphenylboron and tribenzylboron, if applied in eq 1 to the observed CT transitions of triarylboranes near 300 nm, predicted a similar but less intense CT transition below 200 nm in tribenzylboranes. Indeed, tribenzylamine[4] and tribenzylphosphine[5] spectra have transitions near 247 and 248 nm which we have assigned[3] to charge-transfer transitions from nitrogen or phosphorus to the vacant π^* orbitals of benzene, *i.e.*, the reverse of the transition in tribenzylborane. The close analogy between the valence bond description of the CT excited state of a benzylborane **1** and the π complex intermediate or transition states such as **2** which have been suggested[6] in the solvolysis of some β-arylalkyl tosylates, etc., is readily apparent and provided a further cause for the study of these transitions. The success of this analogy is explored in a companion paper.

$$E_{CT} = I_p - E_a - e^2/r \qquad (1)$$

Results and Discussion

Because the two highest π orbitals of a para-disubstituted benzene are relatively close in energy there should in fact be two low-energy charge-transfer transitions in a monobenzylborane (six in the case of tribenzylborane). These orbitals are identified below as A' or A'', which are their symmetry representations under the C_s point group. This point group has as a single symmetry element a plane perpendicular through the substituted ring carbons, the CH_2, and the boron. By virtue of charge distribution[7] in the excited state, the lowest energy CT transition, CT_1, is from π orbital a' to the boron vacant 2p orbital which is also a'; that is, A' → A'. The second charge-transfer transition, CT_2, (orbitals a'' → a'), should be slightly higher in energy and has the state notation A' → A''. Both a point-charge approximation from (e^2/r), eq 1, and semiempirical molecular orbital calculations discussed later, however, predict that the difference between the CT_1 and CT_2 transition energies will be only a few tenths (~0.3) electron volt and therefore smaller than the differences, 0.6–0.9 eV, calculated for the analogous transitions in arylboranes, -amines, or -arsenes.[7]

(1) Address correspondence to this author at San Francisco State College.

(2) J. N. Murrell, *Quart. Rev., Chem. Soc.*, **15**, 191 (1961).

(3) B. G. Ramsey and N. K. Das, *J. Amer. Chem. Soc.*, **91**, 6192 (1969).

(4) R. Shula and S. T. Zenchelsky, *ibid.*, **82**, 4138 (1960).

(5) H. Schindlbauer, *Monatsh. Chem.*, **94**, 99 (1963).

(6) (a) H. C. Brown and C. J. Kim, *J. Amer. Chem. Soc.*, **90**, 2082 (1968); (b) M. D. Bentley and M. J. S. Dewar, *ibid.*, **92**, 3996 (1970).
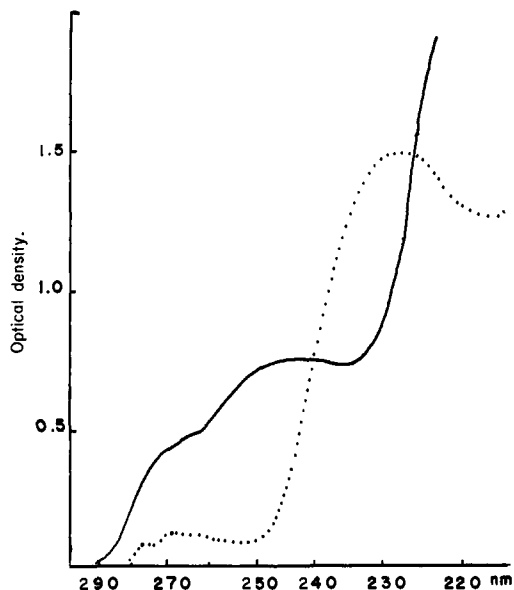
(7) M. Godfrey and J. N. Murrell, *Proc. Roy. Soc., Ser. A*, **278**, 57, 64 (1964).

Figure 1. The ultraviolet spectrum of $(C_6H_5CH_2)_3B$ (———) and $(C_6H_5CH_2)_3B:NH_3$ (······) in hexane and CH_3CN, respectively.

Because of poor spatial overlap between the benzene orbital of A'', which has a node at the substituted carbon, and the vacant boron 2p, at least in a monobenzylborane, the CT_2 transition should be substantially weaker than CT_1. Some caution is necessary in extending this argument to the tribenzylboranes, however, since symmetry effects here may alter the transition intensities somewhat, particularly if the more symmetrical geometry with a threefold axis of symmetry is assumed; this, however, is the least likely geometry for the tribenzylborane.


A'   A''
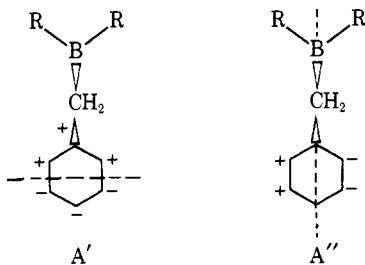
Before proceeding further, a brief preliminary outline of the experimental methods will be given here. The tribenzylboranes (p-$XC_6H_4CH_2)_3B$ (X is H, F, CH₃, and CH₃O) and $[2,4,6-(CH_3)_3C_6H_2CH_2]_3B$ were prepared by Grignard reaction of benzyl halides with boron trifluoride etherate and purified by distillation and/or fractional crystallization under nitrogen until no changes in infrared or ultraviolet spectra of the samples could be observed. In particular, infrared spectra were free of the very strong 7.4-μ (1350 cm⁻¹) band very characteristic of boron–oxygen bonds in general and found also in spectra of the benzylboranes after exposure to air.

Samples for spectra were prepared and cells were loaded in a nitrogen-filled glovebox whose atmosphere was tested by exposure to tri-n-butylborane and absence of its oxidation. Solvents used were degassed by high vacuum line techniques. We recite these precautions at this point to allay reasonable fears that the medium intensity electronic transitions reported might

represent absorption due to oxidation products of tribenzylboranes.

The ultraviolet spectra of tribenzylborane and its ammonia adduct are given in Figure 1. The broad absorption maximum at 242.7 nm in the spectrum of tribenzylborane clearly lacks the intensity required to assign it to a ^1L_a transition of benzene; furthermore, the maximum disappears in the spectrum of the ammonia complex, which demonstrates the requirement of the vacant boron 2p orbital for the appearance of the 242.7-nm absorption maximum in the spectrum of the free benzylborane. We could on the above arguments alone then assign the transition to intramolecular charge transfer. Since the transition obeys Beer's law within experimental error over a 100-fold concentration change, it is unlikely the transition is *inter*molecular. The usual benzenoid ^1L_b transition, apparent in the ammonia complex spectrum at 264 (sh), 268, and 275 nm, must be buried under the long-wavelength edge of the CT transition, but is probably revealed by the inflection points in the tribenzylborane spectrum at 264 and 270 nm. The benzene ^1L_a transitions are found at 205.0 nm, in the spectrum of tribenzylborane.

To satisfy ourselves still further that the 243-nm maximum was not the result of *in situ* oxidation, the cyclohexane solution of tribenzylborane was shaken with a small amount of acidified and degassed water which would normally result in the immediate hydrolysis of any boron–oxygen bonds. There was no change in the tribenzylborane spectrum of the solution. The spectrum of tribenzylborane regenerated from the ammonia complex with hydrogen chloride gas was also identical with that obtained previously. Finally, if the tribenzylborane–cyclohexane solutions are exposed to air, pronounced changes in the spectra do take place, and although we did not extensively investigate the air oxidation products, the spectra in general of the substituted tribenzylboranes in cyclohexane after exposure to air corresponded closely to that expected of a mixture of p-XC_6H_4CHO, and what is probably bibenzyl, a previously[8] observed oxidation product. A reasonable mechanism for benzaldehyde formation is eq 2 since

$$(C_6H_4CH_2)_2 - B - O - OCHC_6H_5 \longrightarrow$$

$$RH + C_6H_4CHO + (C_6H_4CH_2)_2BO\cdot \quad (2)$$
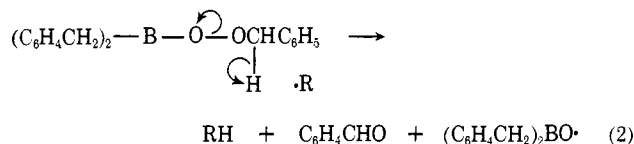
alkylboranes oxidize[9] by a free-radical mechanism.

If we look next at the spectrum of (p-CH_3OC_6-$H_4CH_2)_3B$ in cyclohexane (Figure 2), we find that the charge-transfer transition is strongly red shifted to 281 nm in keeping with the lower ionization potential of anisole as compared with benzene (see eq 1).

In the spectrum of $(2,4,6-(CH_3)_3C_6H_2CH_2)_3B$ (Figure 3) the charge-transfer transition appears to be superimposed on top of the benzenoid ^1L_b transition, and we place the CT absorption maximum near 270 nm. The uv spectrum of $(2,4,6-(CH_3)_3C_6H_2CH_2)_3B$ in the region between 240 and 200 nm is quite similar to that reported[10] for other highly substituted and crowded rings such as $1,2,4,6-(CH_3)_4C_6H_2$ and $1,2,3-(CH_3)_3C_6H_3$.

(8) (a) R. Koster, private communication to N. K. Das; (b) N. V. Kruglova, *Izv. Akad. Nauk SSR, Ser. Khim.*, 1163 (1967).
(9) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 311 (1969).
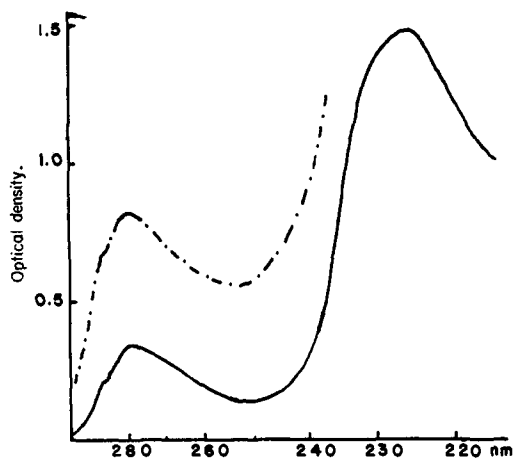(10) L. C. Jones and L. W. Taylor, *Anal. Chem.*, 27, 228 (1955).

Figure 2. The ultraviolet spectrum of (p-CH$_3$OC$_6$H$_4$CH$_2$)$_3$B in hexane.

Figure 4. The ultraviolet spectrum of (p-FC$_6$H$_4$CH$_2$)$_3$B in hexane (————) and (p-FC$_6$H$_4$CH$_2$)$_3$B:NH$_3$ in CH$_3$CN (· · · ·).

Figure 3. The ultraviolet spectrum of (2,4,6-(CH$_3$)$_3$C$_6$H$_2$CH$_2$)$_3$B in hexane.
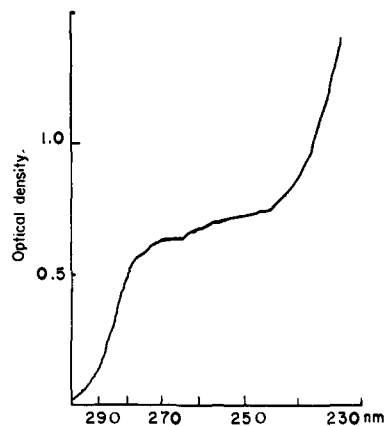
Figure 5. The ultraviolet spectrum of (p-CH$_3$C$_6$H$_4$CH$_2$)$_3$B in hexane.

Qualitatively we find [2,4,6-(CH$_3$)$_3$C$_6$H$_2$CH$_2$]$_3$B to be much less sensitive to air oxidation than the other benzylboranes. Models show the molecule to be sterically crowded in such a way as to reduce maximum overlap between the rings and the vacant boron 2p atomic orbital. This probably accounts for the lower intensity of the CT transition. A similar effect on CT transition intensity is observed[11] in the spectra of triarylboranes in the case of trimesitylborane and is a general characteristic of intramolecular charge-transfer transitions.

As may be seen from the spectra of (p-FC$_6$H$_4$CH$_2$)$_3$B, (p-FC$_6$H$_4$CH$_2$)$_3$B:NH$_3$, and (p-CH$_3$C$_6$H$_4$CH$_2$)$_3$B in cyclohexane (Figures 4 and 5), it is more difficult to fix the exact position of the charge-transfer transition in the spectra of these molecules. Nevertheless, if one assumes the benzenoid ^{1}L$_b$ transition of (p-FC$_6$H$_4$-CH$_2$)$_3$B to be approximated by that of the ammonia complex, and that of (p-CH$_3$C$_6$H$_4$CH$_2$)$_3$B by the tribenzylborane–ammonia complex, a crude hand gaussian resolution (which seems all that is justified) of the spectra can be used to estimate a CT transition near

243 nm for (p-FC$_6$H$_4$CH$_2$)$_3$B and 254 nm for (p-CH$_3$-C$_6$H$_4$CH$_2$)$_3$B.

Absorption maxima and molar extinction coefficients for the spectra of the tribenzylboranes are summarized in Table I. Maxima assigned to CT are in italics.

Provided our assignments of the intramolecular charge-transfer transition energies in the substituted tribenzylboranes are correct, according to eq 1 we should observe a linear dependence of CT transition energy on the ionization potential of the aryl group, similar to that previously observed[11] for the CT transition energies of triarylboranes. A plot (Figure 6) of ionization potentials of p-XC$_6$H$_5$ (X is H, F, or CH$_3$-CH$_3$O) and 2,4,6-(CH$_3$)$_3$C$_6$H$_3$ as a function of charge-transfer transition energies does in fact provide an excellent correlation of I_p[12] with E_{CT}.

Even if we are slightly off in our assignment of the CT transitions where X is F or CH$_3$, the correlation of Figure 6 should remain satisfactory. We believe, therefore, that on the basis of the experimental criteria the 242.7 nm maximum in the spectrum of tribenzylborane and similar maxima in the spectra of other tri-

(11) B. G. Ramsey, *J. Phys. Chem.*, 70, 611 (1966).

(12) K. Watanabe, *J. Chem. Phys.*, 26, 542 (1957).

Table I. Ultraviolet Absorption Maxima of Tribenzylboranes in Hexane[a]

Compound	$\lambda_1$max, Å	$\epsilon_1$max, × 10⁻³	$\lambda_2$max, Å	$\epsilon_2$max, × 10⁻³	$\lambda_3$max, Å	$\epsilon_3$max, × 10⁻³	$\lambda_4$max, Å	$\epsilon_4$max, × 10⁻³	$\lambda_5$max, Å	$\epsilon_5$max, × 10⁻³
$(C_6H_5CH_2)_3B$	2720 (4.6 eV)	2.63	2427 (5.1 eV)	4.72	2050 (6.05 eV)	40.0				
$(FC_6H_4CH_2)_3B$	2775	4.06	2700	5.74	2634	5.40	(2430)	3.68		
$(MeC_6H_4CH_2)_3B$	2696	4.74	(2544)	4.23						
$(MeOC_6H_4CH_2)_3B$	2800	7.04	2260	3.08	1940	110				
$(2,4,6\text{-}Me_3C_6H_2CH_2)_3B$	2790	1.09	2700	1.28	2310	18.7	2254	22.0	2200	24.4
$(FC_6H_4CH_2)_3B:NH_3$	2680	2.22	2230	18.0						
$(C_6H_4CH_2)_3B:NH_3$	2680	1.53	2275	19.0						

[a] Maxima in italics are wavelengths assigned to charge-transfer transitions; parentheses indicate estimated position of maximum; ϵ is the molar extinction coefficient; spectra of ammonia complexes in acetonitrile.

benzylboranes may be assigned to three nearly degenerate intramolecular charge-transfer transitions, derived from what may be regarded as $^1A' \rightarrow {}^1A'$ locally excited states and which are here designated as a group, CT_1. The assumption in this latter statement is that although the CT states of tribenzylborane may be expressed as linear combinations of three locally excited states, the perturbations between states will be small. Thus, the spectrum of tribenzylborane and substituent effects on tribenzylborane CT transitions will be satisfactorily close to the spectra and substituent effects expected in monobenzyldialkylboranes. Molecular orbital calculations, as will be shown next, seem to bear this assumption out.
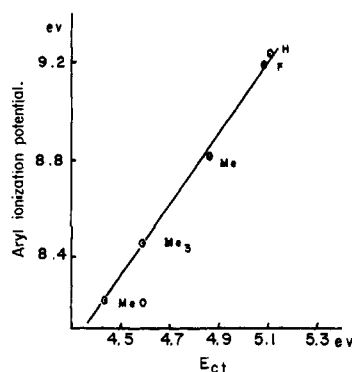

Figure 6. CT transition energies of X-phenyl-substituted tribenzylboranes vs. X-phenyl ionization potentials.

At this time the location of the CT_2 transitions $(A' \rightarrow A'')$, of which there are three, cannot be identified, and we must assume that they are buried somewhere in the region between 230 and 235 nm. This may in fact account for the rather broad and flat character of the CT band envelope in the p-methyl- and -fluorotribenzylborane derivatives. The CT_2 transition energies should be relatively insensitive to para substitution, however.

The spectra of the ammonia complexes of tribenzylborane and $(p\text{-}FC_6H_5CH_2)_3B$ are also, in their own right, interesting in view of the large red shift of ^1L_a transitions which appear at 225 and 223 nm, respectively. They should be compared, for example, with those for toluene at 206 nm and 1-methyl-4-ethylbenzene at 213 nm.[13] The ^1L_a transition energies of the benzylborane-ammonia complexes are in fact much

more comparable to those observed[14] for benzyl derivatives of group IV metalloids such as $C_6H_5CH_2Si(CH_3)_3$ (^1L_a λ_{max} 227 nm) or $C_6H_5CH_2Ge(CH_3)_3$ (^1L_a λ_{max} 225 nm). This red shift of the ^1L_a transition in the benzyl group IV metalloids and similar red shifts of the $\pi \rightarrow \pi^*$ transition energies in the spectra of homoconjugated olefins[15] ($R_3MCH_2CH=CH_2$) and acetylenes[16] ($R_3MCH_2C\equiv CH_2$) have been the subject in recent years of considerable attention.[17] Explanations[18] have invoked either a special role in $d\pi$-$p\pi^*$ bonding for low-lying vacant metalloid d orbitals, a hyperconjugation mechanism as indicated by **3**, which raises the energy of the highest filled benzene π orbital, or a combination of both d orbital and hyperconjugation effects. Unlike the group IV metalloids, tetracoordinate boron has no low-lying d orbitals which might interact with the benzene π^* orbitals, and the observed red shift in the ^1L_a transition energy of tribenzylborane-ammonia complex can only be ascribed to boron-carbon hyperconjugation of type **4**. By inference, this provides further support for the absence of a major role for the influence of d-p π bonding on the ^1L_a transition energies of $C_6H_5CH_2Si(CH_3)_3$, $CH_2=CH-CH_2Si(CH_3)_3$, etc., and indicates instead important hyperconjugation. We believe this is the first published experimental evidence of boron-carbon hyperconjugation.
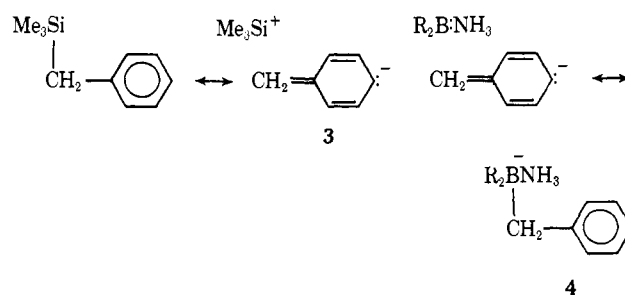
Semiempirical Molecular Orbital Calculations

Preliminary Pariser–Parr–Pople self-consistent field calculations have been carried out including complete configuration interaction (CI) on a monobenzylborane

(13) Taken as average of wavelength range for absorption maximum given in ref 10.

(14) J. Nagy, J. Reffy, A. Kuszmann-Borbely, and K. P. Becker, J. Organometal. Chem., 7, 393 (1967).

(15) V. A. Petukhov, V. F. Mironov, and P. P. Shorygin, Izv. Akad. Nauk SSR, Ser. Khim., 2203 (1964).

(16) H. Bock and H. Seidl, J. Chem. Soc., 1158 (1968).

(17) For a recent extensive review of this question see B. G. Ramsey, "Electronic Transitions in Organometalloids," Academic Press, New York, N. Y., 1969.

(18) (a) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960; (b) W. Hanstein, H. J. Berwin, and T. G. Traylor, J. Amer. Chem. Soc., 92, 7476 (1970); (c) ref 14–17.

Table II. Energy and Atomic Orbital Mixing Coefficients for SCF Orbitals of a Benzylborane[a]

E, eV	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7
−14.75	0.008	0.407	0.408	0.409	0.409	0.409	0.409
−9.97	−0.016	−0.578	−0.289	0.288	0.576	0.288	−0.289
−9.97	0.000	0.000	−0.500	−0.500	−0.000	0.500	0.500
−1.06	0.993	0.060	−0.046	−0.026	0.065	−0.026	−0.046
−0.42	0.000	0.000	0.500	−0.500	0.000	0.500	−0.500
−0.41	0.112	−0.575	0.287	0.287	−0.573	0.287	0.287
1.91	−0.014	0.407	−0.407	0.409	−0.409	0.409	−0.407

[a] β(B–C) is −0.144 eV, B(VSIP) is 1.06 eV.

Table III. Calculated Transition Energies[a] of Benzylboranes below 7.0 eV

Monobenzylboranes				Tribenzylborane			
Assignment	Without[b] CI	With CI	% CT[c]	Assignment	Without CI[b]	With CI	% CT[c]
^1L_b; A''	6.00	4.93	1.2	^1L_b	6.43	5.30	2.8
					6.57	5.31	2.2
					6.50	5.34	2.8
CT_1; A'	6.19	6.13	85	CT_1	6.19	6.16	87
					6.19	6.16	87
^1L_a; A'	6.64	6.26	13		6.19	6.18	87
				CT_2	6.30	6.33	92
CT_2; A''	6.30	6.32	97		6.31	6.33	92
					6.31	6.35	92
^1B_a; A'	6.66	7.06	0.0	^1L_a	6.65	6.40	6.5
					6.64	6.45	6.5
					6.64	6.46	6.5
^1B_b; A'	6.01	7.06	0.0	^1B_b	6.71	6.94	0
					7.05	6.96	0
					7.08	7.08	0
				^1B_a	7.09	7.08	0
					6.99	7.12	0
					6.94	7.13	0

[a] Energies in electron volts. [b] CI is configuration interaction. [c] Per cent charge-transfer character after CI.

($C_6H_5CH_2BR_2$) and limited CI on tribenzylborane using a modified version of the Bloor and Gilson[19] QCPE program 71.2. Since boron is in effect a non-adjacent atom, the program was modified to include all nonadjacent core resonance integrals (β_{ij}) according to the method of Flurry and Bell,[20] except that in the case of tribenzylborane, resonance integrals for atoms not in the same ring were neglected. To accommodate non-coplanarity, the Flurry–Bell expression for the overlap integral S_{ij} was multiplied by D, eq 3, where θ_{ij} is the dihedral twist angle between the p orbitals of atoms i and j and φ_i is the acute angle which the p orbital of atom i makes with a line joining the nuclei of atoms i and j. Two-centered repulsion integrals, γ_{ij}, were calculated by the Mataga formula of the program, and one-centered integrals, γ_{ii}, used were carbon (11.13 eV) and boron[21a] (5.97 eV). In the calculations reported here, a boron vacant 2p orbital valence-state ionization potential of 1.06 eV was adopted since it had been widely used by others,[21] and appeared to meet the *minimum* requirement[22] for an arylborane low-energy charge-transfer transition in that this value placed the initial boron vacant 2p orbital lower in energy than the lowest vacant benzene π* orbitals at −0.428 eV

when calculated by this procedure. Pertinent results of these calculations are summarized in Tables II and III.

$$D = (\cos \theta_{ij})(\sin \phi_i)(\sin \phi_j) \qquad (3)$$

Structures 5 and 6 define the numbering system and geometries for the benzyl- and tribenzylboranes. The unsymmetrical structure 6 (C_s symmetry), rather than a more symmetrical one with a threefold axis of rotation, is assumed simply on the basis of statistical preference. Some calculations have in fact been carried out for the C_3 point group geometry also, but no significant differences in results were obtained.

5   6
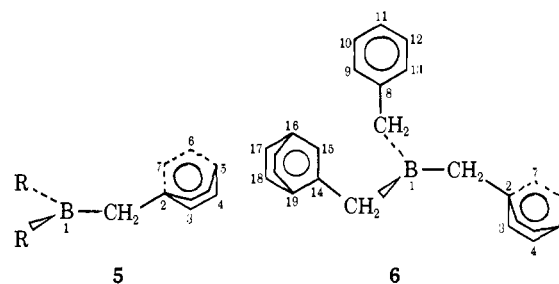
A correlation diagram for calculated SCF orbital energies for benzene, benzylborane, and tribenzylborane is given in Figure 7. The calculated boron–carbon nearest neighbor resonance integral (β) is only −0.144 eV and perturbation of the benzene orbitals by boron is therefore very small, Table I. Thus, it is no surprise that the calculated transition energies of benzylborane (Table III), even after complete configura-

(19) Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(20) R. L. Flurry, Jr., and J. J. Bell, *J. Amer. Chem. Soc.*, **89**, 525 (1967).

(21) (a) D. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, **8**, 138 (1967), and leading references; (b) N. C. Baird and M. A. Whitehead, *Can. J. Chem.*, **45**, 2059 (1967); (c) D. W. Davis, *Trans. Faraday Soc.*, **56**, 1713 (1960).

(22) B. G. Ramsey and H. Ito, *Theor. Chim. Acta*, **17**, 188 (1970).

-0.428 -0.409 A' -0.389 16 0.413
-0.424 A'' 0.423 12,13 0.424 11 14,15

-1.06 -1.06 A' -1.07 10

-1.97 -1.97 A' -1.98 -1.97 -1.97
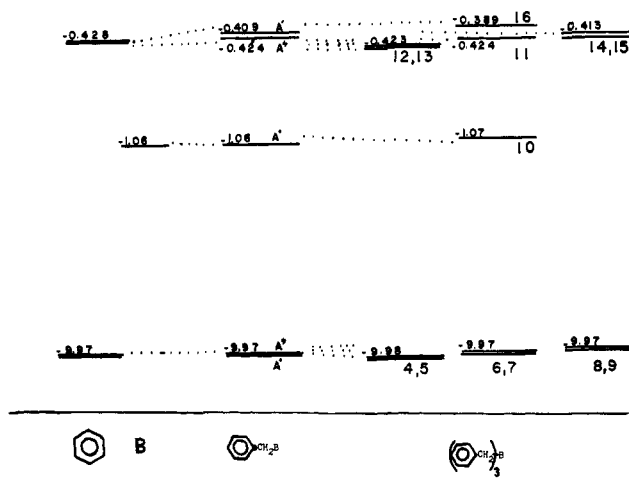A'' 4,5 6,7 8,9

B CH₂B CH₂B

Figure 7. Correlation diagram of benzene, benzylborane, and tribenzylborane SCF molecular orbital energies.

tion interaction, remain virtually the same as those of benzene (4.93, 6.23, 7.06, and 7.06 eV) except for the addition of two charge-transfer transitions at 6.13 (CT₁) and 6.32 (CT₂) eV. Further, from Table III it is seen that configuration interaction has almost no effect on the calculated energy of the charge-transfer transitions. The results appear to carry over into the calculations on tribenzylborane, where before configuration interaction the charge-transfer configurations are found at the same energy as in monobenzylborane. Up to this time, on tribenzylborane, configuration interaction calculations have been limited to transitions between the six lowest vacant and six highest filled orbitals, since Armstrong and Perkins[21a] in a PPP-SCF calculation on triphenylborane had reported earlier that inclusion of higher energy vacant orbitals led to an overall state improvement of only 0.5%. The limited CI interaction treatment of tribenzylborane is less satisfactory in that the transitions derived from localized benzene ¹L_b, ¹L_a, and transitions are 0.4 and 0.2 eV higher in energy than expected as a result of excluding transitions to the seventh highest orbital (number 16 in Figure 7). Unlike triphenylboron, the seventh vacant orbital (14 in Figure 7) in tribenzylborane is not sufficiently higher in energy to justify its exclusion and more complete CI calculations are in progress. Nevertheless, several important conclusions may be reached. Since introduction of the additional configurations corresponding to transitions to orbital 16 will alter only slightly the CT transition energies, the calculated charge-transfer transitions of tribenzylborane will remain nearly triply degenerate, at the same energies (within 0.05 eV) of those of monobenzylborane. Secondly, there is little splitting in the locally derived benzene ¹L_a, ¹L_b, and ¹B states. With *complete* configuration interaction, the remaining tribenzylborane transition energies therefore also should lie within a few hundreths of an electron volt of those calculated for the monobenzylborane.

The observed tribenzylborane absorption maxima (4.6 ¹L_b, 5.1 CT, and 6.05 ¹L_a eV) are in qualitative agreement with those calculated for a monobenzylborane in that the second uv maximum is predicted to be a composite of charge-transfer transitions derived from those local benzene π orbitals nonnodal at the

BCH₂ carbon. Agreement between calculated and observed transition energies can be improved either by increasing the B–C resonance integral (since the ratio of β_{C-C} to β_{B-C} is only about one-half the ratio found in other calculations) or by increasing the B vacant 2p valence-state ionization potential (*i.e.*, increasing its electron affinity). We have begun exploring these two possibilities. Briefly we find that if β_{B-C} is increased to −0.25 eV, calculated transition energies for the benzylborane are 4.5 and 5.8 (CT₁) and 6.0 and 6.14 eV (CT₂), which, although it provides agreement with the ¹L_b and ¹L_a transitions, agreement with the first CT transition is, however, still not acceptable. The increase in β does not improve the calculated energy *difference* between the ¹L_b and CT₁ transitions either. The first three calculated CT transitions of tribenzylborane are also found at 5.78, 5.79, and 5.81 eV, so that an increase in β_{B-C} also does not increase the splitting between the local CT₁ states. As mentioned previously, a choice of 1.06 eV was utilized in these initial calculations. In an earlier paper, however, we demonstrated[22] that agreement between PPP–SCF calculations (not including nonnearest neighbor β) and variable electronegativity–PPP–SCF calculations required a boron VSIP of some 2.0 eV or greater in the traditional PPP–SCF method. *We do find that the disagreement between calculated and observed first CT transition energy may be removed by a choice of 2.0 ± 0.1 eV as the boron VSIP*, with little change in calculated ¹L_b and ¹L_a energies. And currently we are exploring not only the effect of simultaneously varying both the β_{B-C} resonance integral and the boron VSIP, but also the effect of low-lying $\sigma \rightarrow \pi^*$ transitions or a hyperconjugation effect on the CT₁ transition energy similar to that already suggested in the tribenzylborane–ammonia complexes. These results will be published elsewhere.

It is very unlikely, however, that any refinement of calculations will change the basic conclusion that the broad medium intensity absorption band between 240 and 285 nm in the spectra of tribenzylboranes should be assigned to charge-transfer transitions which may be essentially described as locally excited states (¹A' → ¹A'). To the extent that there must be some perturbation between the locally excited states for the (C_s) symmetry of structure **6**, the three degenerate ¹A' CT₁ states are split into one A'' and two A' states, whereas the CT₂ states are split into one A' and two A''.

The observation of a charge-transfer transition across an intervening CH₂ group in tribenzylborane supports the previous assignment[11] of charge-transfer transitions in triarylboranes which has been questioned[21a] on the basis of PPP–SCF–MO calculations, makes reasonable the observation of similar reverse CT transitions in tribenzylamine and -phosphine, and suggests that similar transitions might be observed in the uv spectra of ions such as $C_6H_5CR_2CR_2^+$.

Experimental Section

As a matter of general procedure, all reactions were carried out under nitrogen or argon using solvents previously distilled under nitrogen from lithium aluminum hydride.

Tribenzylborane was prepared by the Grignard reaction under nitrogen of benzylmagnesium chloride in ether with 1 equiv of boron trifluoride etherate which was added to the reaction in ether dropwise under nitrogen. After self-reflux was complete, the reaction mixture was allowed to stand overnight and hydrolyzed

with oxygen free water. With all operations carried out under nitrogen, the ether layer was separated and the product obtained and purified by vacuum fractional distillation under nitrogen in a one-piece Claisen distillation apparatus. The yield of $(C_6H_5CH_2)_3B$ (bp 159–160° (0.25 mm)) was 53%: nmr chemical shifts of neat liquid relative to internal TMS, δ 2.61 (s, CH_2), 7.2 (m,C_6H_5); principal ir bands 3.29, 3.31, 3.45, 3.55, 6.25, 6.70, 6.90, 7.88, 9.2, 9.4, 13.2, 14.1, and 19.9 μ.

Tris(p-fluorobenzyl)borane was prepared from p-$FC_6H_4CH_2Cl$ by the same procedure used for tribenzylborane (bp 181–183° (0.7 mm)): yield 44%; nmr chemical shifts (neat), δ 2.50 (s, CH_2), 6.8 (m, FC_6H_4); principal infrared bands 3.10, 3.25, 7.49, 6.26, 6.67, 7.86, 8.25, 8.65, 9.15, 9.80, 12.0, 13.2, 18.8, 20.5, and 25.8 μ.

Tris(p-methylbenzyl)boranes are prepared as above from p-$CH_3C_6H_4CH_2Br$ with a yield of 32.4% (bp 195–197° (0.15 mm)); nmr chemical shifts (neat), δ 2.60 (s, CH_2), 2.16 (s, CH_3), 6.85 (C_6H_4, m); principal infrared bands 3.17, 3.28, 3.35, 6.57, 6.90, 7.84, 9.0, 9.55, 9.75, 12.35, 17.8, 18.9, and 20.6 μ.

Tris(2,4,6-trimethylbenzyl)borane was not prepared in the usual manner due to unusually large amounts of benzyl coupling product from the reaction of 2,4,6-trimethylbenzyl chloride with magnesium. This difficulty was overcome by adding the benzyl chloride slowly to magnesium turnings in an ether solution already containing the boron trifluoride etherate under nitrogen so that the Grignard reagent was generated in the presence of the BF_3. The reaction was initiated with ethylene bromide. Work-up under nitrogen, after removal of the solvent, gave a waxy white solid which could be recrystallized from n-hexane to give large transparent crystals (34% yield): mp 179–180° (sealed capillary); nmr chemical shifts (CCl_4) were δ 2.10 (o-CH_3), 2.19 (p-CH_3), 2.32 (CH_2), and 6.75 (C_6H_2).

Anal. Calcd for $C_{30}H_{39}B$: C, 87.78; H, 9.58; B, 2.64. Found: C, 87.59; H, 9.75; B, 2.72.

Tris(p-methoxybenzyl)borane was prepared by the Grignard reaction of p-$CH_3OC_6H_4CH_2MgCl$ with boron trifluoride etherate in tetrahydrofuran (THF) under nitrogen. After the reaction was complete the reaction was hydrolyzed with NH_4Cl in deoxygenated water, and the ether layer separated and dried under argon. A large amount of coupling product ((p-$CH_3OC_6H_4CH_2)_2$) made purification difficult. After removal of the solvent, the crude product, a yellow viscous liquid, was allowed to stand for 1 week

during which time p,p'-dimethoxybibenzyl separated as a sticky white solid. The remaining liquid fraction was partially distilled at 18 mm of pressure to give a fraction boiling between 65 and 71°. The major portion of the product, however, was left in the pot and redissolved in diethyl ether. Cooling of this diethyl ether solution to −30° resulted in further precipitation of bibenzyl which was again filtered off. Finally the ether was removed and the (p-CH_3-$OC_6H_4CH_2)_3B$ was distilled at 0.05 mm of pressure (bp 210–212°) in an overall yield of 14%. Nmr chemical shifts in CCl_4 relative to internal tetramethylsilane were δ 2.51 (s, CH_2), 3.63 (s, CH_3O), and 6.6 (s, C_6H_4); principal infrared bands 3.33, 3.40, 3.51, 6.19, 6.31, 6.61, 6.82, 6.93, 7.89, 7.70, 7.85, 8.02, 8.5, 9.1, 9.6, 12.1, 13.1, and 19.1 μ.

Ammonia complexes of tribenzylborane and tris(tri-p-fluorobenzyl)borane were prepared under nitrogen by passing anhydrous ammonia gas into ether solutions of the borane, filtering off the white precipitate, washing with ether, and drying under a vacuum. Anhydrous HCl gas may be used to regenerate the borane.

Spectra. The tribenzylboranes used for ultraviolet spectra were further purified by fractional distillation in a single unit all-glass apparatus until no changes in spectral properties were observed. Spectrograde hexane previously degassed on a high-vacuum line were used to prepare solutions of the tribenzylboranes in a nitrogen-filled glovebox. The uv cells (0.1, 1.0, and 1.0 cm path lengths) were also loaded in the drybox and spectra were run on a Perkin-Elmer Model 451 spectrophotometer. Infrared spectra were recorded in 0.015-mm path-length KBr cells as neat liquids on a Perkin-Elmer Infracord, between 2.5 and 25 μ. Prior to use, the atmosphere of the box was tested by the exposure of tri-n-butylborane. Proton nmr spectra were obtain on a Varian Model A-60 and are reported as parts per million downfield from internal tetramethylsilane. After uv and ir spectra were obtained, the cells were briefly exposed to air which resulted in oxidation of the borane and alteration of the spectra. This provided assurance that oxidation had not previously occurred while benzylborane spectra were being recorded or in preparation of the solutions.

Semiempirical molecular orbital calculations were carried out on the Stanford University IBM 360-67 computer. The program was tested by complete CI, all β calculations on benzene, and found to give results in complete agreement with those reported by Flurry and Bell.[20]

A Charge-Transfer Model for β-Arylalkyl Carbonium Ions in Solvolysis

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Abstract: Solvolysis rates of β-(p-X-phenyl)alkyl tosylates, brosylates, halides, etc., are shown to be correlated by ionization potentials of XC_6H_5 from the highest filled π orbital which does not have a perpendicular nodal plane through X. This is equivalent to a correlation of solvolysis rate with para-substituted tribenzylborane CT transition energies. On this basis it is suggested that the solvolysis of β-arylalkyl derivatives with a primary carbon leaving group proceeds through a CT (π complex) transition state. A π-bridged β-arylalkyl intimate ion pair is suggested for reactions in which a secondary or possibly tertiary cation is formed. Formation of this intimate ion pair is suggested as rate limiting.

In a companion paper[2] we have established the presence of an intramolecular charge-transfer transition in the ultraviolet spectra of aryl-substituted tribenzylboranes such as $(C_6H_5CH_2)_3B$. If the electronic

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(2) B. G. Ramsey and N. K. Das, *J. Amer. Chem. Soc.*, 94, 4227 (1972).

transition is written as in eq 1, then the similarity of the *excited state* of the benzylboranes to possible π-complex transition states or intermediates of β-arylalkyl tosylate, chloride, etc., solvolysis reactions is apparent. The π-complex carbonium ions 4 have been often suggested[3] as alternative intermediates or tran-

(3) (a) H. C. Brown and C. J. Kim, *ibid.*, 90, 2082 (1968); (b) M. D.