Reaction of $B_{10}H_{10}^{-2}$ with Aryldiazonium Salts[1]

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A coupling reaction between salts of $B_{10}H_{10}^{-2}$ and salts of aryldiazonium ions in acetonitrile has produced a series of apically substituted $B_{10}H_{10}^{-2}$ derivatives related to the azobenzenes. Nitrogen-protonated conjugate acids of these materials have also been isolated. The pK_a values associated with the acid–base equilibrium have been determined for eight pairs of compounds and are a linear function of Hammett's σ-values with a ρ-value of 1.7. The effects of substituent and solvent on the charge-transfer band found in the ultraviolet visible spectra of the dyes and their conjugate acids were investigated. The new dyes have been cleaved to apically substituted $B_{10}H_9NH_3^-$ and $RC_6H_4NH_2$ using a variety of reducing agents. $B_{10}H_9NH_3^-$ may be coupled with a second mole of diazonium ion to give an azo dye and its conjugate acid carrying an $-NH_3^+$ group on the B_{10} polyhedron. Reduction of this latter material afforded $1,10\text{-}(NH_3)_2B_{10}H_8$. The p-methoxybenzenediazonium ion did not kinetically distinguish between $B_{10}H_{10}^{-2}$ and $B_{10}D_{10}^{-2}$ in a competition experiment. In water, $B_{10}H_{10}^{-2}$ and diazonium ions combine to form insoluble and explosive salts.

Salts of $B_{10}H_{10}^{-2}$, when treated with aryldiazonium tetrafluoroborates or hexafluorophosphates in acetonitrile solution, give rise to intense absorptions in the 515-mμ region of the visible spectrum. While the origin of this absorption had not been investigated, it was previously employed as a precise quantitative measure of $B_{10}H_{10}^{-2}$ concentration.[3] The purpose of the work reported here was to examine the interaction of $B_{10}H_{10}^{-2}$ with aryldiazonium ions.

Results and Discussion

The stoichiometry of the over-all interaction was investigated with the aid of a spectrophotometric titration. The absorption at 515 mμ of a standard solution of $(Et_3NH)_2B_{10}H_{10}$ in acetonitrile containing varying concentrations of p-methoxybenzenediazonium hexafluorophosphate was measured and plotted against the concentration of aryldiazonium ion added. A linear increase in optical density resulted from addition of up to 0.94 molar equivalent of diazonium ion. Thereafter, no further increase in optical density accompanied the addition of up to 4 molar equivalents. The stoichiometry of the reaction was thereby established as 1:1.

The stability of the 1:1 products was illustrated by their isolation. When equivalent quantities of various aryldiazonium tetrafluoroborates were mixed with $K_2B_{10}H_{10}$ in acetonitrile, 1 equiv. of KBF_4 precipitated and highly colored potassium salts remained after removal of the solvent. When these salts were dis-

solved in acidic aqueous solution and aqueous tetramethylammonium chloride was added, a series of salts (I) precipitated. If tetramethylammonium chloride was added to basic aqueous solutions of the colored salts, the tetramethylammonium salts of a second series of materials (II) precipitated.[4] The electronic, ^{1}H n.m.r. and ^{11}B n.m.r. spectra of the I series showed this series of salts to contain the same anions as were present in the crude potassium salts isolated from acetonitrile.

The conversion of I to the corresponding II was accomplished by addition of base and the conversion of II to the corresponding I by the addition of acid. In the case of the tetramethylammonium salts of p-CH₃O-I and p-CH₃O-II, the ratios of tetramethylammonium protons to p-CH₃O protons were readily obtained by integration of ^{1}H n.m.r. spectra. These ratios were 4:1 and 8:1 for p-CH₃O-I and -II, respectively. Series I and II therefore corresponded to mono- and dinegative anions, respectively, and constituted acid–base pairs. A similar conclusion resulted from consideration of Figure 1 which presents a typical titration curve for a sample of p-Br-II which had been passed through an acid ion-exchange column and then titrated with standard sodium hydroxide solution. Two breaks which corresponded to the neutralization of the hydronium ion salt of p-Br-I and the conversion of p-Br-I to p-Br-II resulted and required equal quantities of base. Similar equivalent weight data were obtained for other members of the I and II series.

Structural and stoichiometric relationships required that $K_2B_{10}H_{10}$ and aryldiazonium ions react in equal molar quantities to form I whose elemental analyses and equivalent weights required a $B_{10}H_{10}$ cage, a substituted phenyl ring with its two nitrogen atoms, and an over-all ionic charge of -1. The empirical formulas of the I anions are therefore $B_{10}H_{10}\cdot RC_6H_4N_2^-$. The composition of the II series differs from that of the I series by a proton, and II must therefore be $B_{10}H_9\cdot RC_6H_4N_2^{-2}$. Table I presents relevant analytical data (also see Experimental).

The proton n.m.r. spectra of the II series and azobenzene exhibited marked similarities. For example, the spectrum of p,p'-dimethoxyazobenzene consisted of a singlet at 4.59 p.p.m. and two doublets centered at 7.12 ($J = 9$ c.p.s.) and 7.90 p.p.m. ($J = 9$ c.p.s.) while p-CH₃O-II showed a singlet at 4.22 p.p.m. and two doublets at 7.08 ($J = 9$ c.p.s.) and 7.73 p.p.m. ($J = 10$ c.p.s.). The structures of the II series must therefore incorporate the azo linkage between the phenyl ring and the $B_{10}H_9^{-2}$ fragment.

The ^{11}B n.m.r. spectra of the II series were consistent with this structure and proved the site of attachment of

(1) Reported in part: M. F. Hawthorne and F. P. Olsen, *J. Am. Chem Soc.*, **86**, 4219 (1964).
(2) Alfred P. Sloan Research Fellow.
(3) M. F. Hawthorne, R. L. Pilling, and R. Grimes, *J. Am. Chem. Soc.*, **86**, 5338 (1964).

(4) The terms I and II will be used to refer to the two general classes of compounds isolated from acidic and basic solutions, respectively. When specific compounds are implied, the substituent will be designated, as for example, p-CH₃O-II.

Table I. Analytical Data for Tetramethylammonium Salts of Azo Dyes Prepared

| | I series | | | | II series | | | |
| | Found | | Calcd. | | Found | | Calcd. | |
Substit-uent	Equiv. wt.	% B	Equiv. wt.	% B	Equiv. wt.	% B	Equiv. wt.	% B
p-CH_3	306	34.2	311	34.8	382	27.7	381	28.3
p-CH_3O	312	34.7	327	33.0	403	28.4	397	27.2
p-H	296	35.5	297	36.4	363		367	29.4
m-CH_3O	327	32.3	327	33.0	Not obtained crystalline			
p-Br	370	28.6	376	28.7	446	23.9	450	24.1
m-CF_3	367	31.0	365	29.6	418	25.1	435	24.8
m-NO_2			a		345[b]	25.5	345	26.1

[a] This compound, along with the acid and base forms of p-NO_2, was prone to violent decomposition when dry and was handled only in solution. Their ultraviolet–visible, infrared, [11]B, and ^{1}H spectra proved them to be authentic members of the I and II series as assigned.
[b] Analysis and equiv. wt. is for K^+ rather than tetramethylammonium salt.

the azo linkage to be at an apical position of the B_{10} polyhedron. The spectrum of unsubstituted II (Figure 2) consisted of a singlet at -16.1 and doublets at $+8.2$ and $+27.3$ p.p.m. with relative areas of 1:1:8. The high-field resonance of $B_{10}H_{10}^{-2}$ (Figure 2), assigned to the eight equatorial boron atoms, remained essentially intact in II. The low-field doublet of $B_{10}H_{10}^{-2}$ assigned to the two apical boron atoms was halved in area and a new singlet of area 1 appeared at lower field. The low-field doublet now represents a single unsubstituted apical boron atom while the new singlet in the apical region serves to identify the point of attachment of the azo nitrogen atoms to the boron cage.[5] The structure of II is therefore apical $B_{10}H_9$-$N{=}NAr.^{-2}$
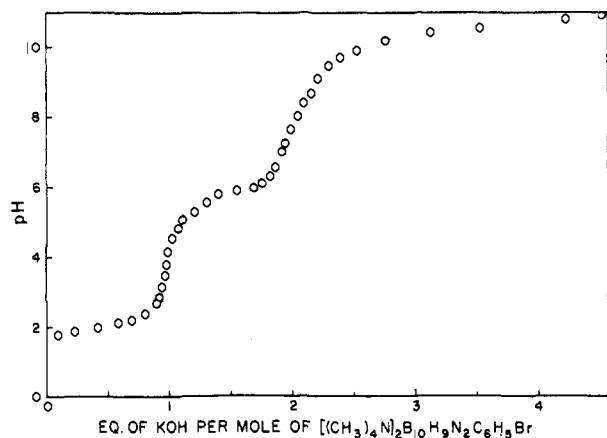

Figure 1. Potentiometric titration of $(H_3{}^+O)\cdot p$-Br-I with aqueous KOH solution.

Both the ^{1}H and [11]B n.m.r. spectra of the I series were similar to those of the II series with the only difference being the locations of the various resonances. Upon protonation of p-CH_3O-II, the singlet attributed to the p-methoxy protons in the [1]H n.m.r. spectrum was shifted 0.22 p.p.m. downfield to 4.00 p.p.m. while the two doublets assignable to the aromatic protons were shifted 0.19 and 0.34 p.p.m. downfield to 7.27 ($J = 9$ c.p.s.) and 8.07 p.p.m. ($J = 10$ c.p.s.), respectively. Such shifts are consistent with increased charge in the aryl portion of the ion. No resonance associated with the added proton was observed. The

[11]B n.m.r. spectrum of unsubstituted I is shown in Figure 2. The high-field doublet, while representing a total of eight boron atoms, is seen to be an unsymmetrical 1:2:1 triplet formed by the overlap of two

Figure 2. The [11]B n.m.r. spectrum of $B_{10}H_{10}^{-2}$, unsubstituted I, and unsubstituted II at 19.3 Mc./sec.

doublets of area 4. These two doublets represent the two boron atoms present in equal numbers[6] in I. Thus, in the I series the two equatorial bands of boron atoms appeared to differ to a greater extent than in the II series. The low-field resonance of I collapsed to a single pattern consisting of a low-field shoulder whose

(5) It should be noted that a few per cent of an equatorially substituted product could easily go unnoticed in view of the broad line widths encountered in [11]B n.m.r. spectra.

(6) At 60 Mc./sec. the high-field resonance resolves into four peaks of equal size. We are indebted to Mr. Eugene Pier of the Varian Corp. for these spectra.
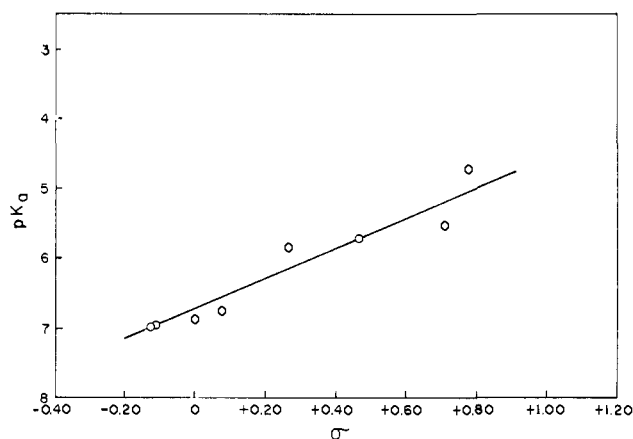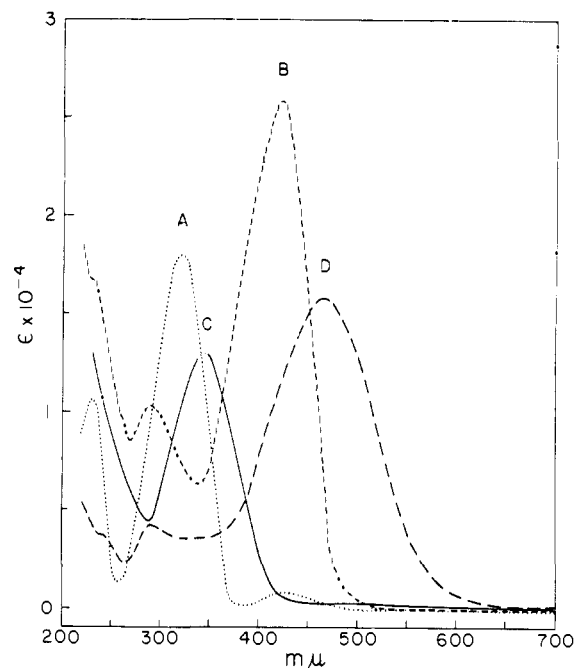
Figure 3. Hammett plot of pK_a values of the I series.

Figure 4. Ultraviolet and visible spectrum of azobenzene. A; protonated azobenzene. B; unsubstituted II, C; and unsubstituted I, D.

area represented 0.5 boron atom and an area composed of 1.5 boron atoms at slightly higher field. The only reasonable assignment for this array is the coincidental overlap of a singlet and a doublet (areas 1:1). The similarities seen in the two types of spectra demonstrated the conversion of II to I to be a simple proton transfer uncomplicated by possible structural rearrangements.

On an *a priori* basis, the site of protonation could be any of the following: (a) on the aryl ring, (b) on nitrogen, (c) at the apical boron atom which bears the nitrogen, (d) elsewhere on the B_{10} polyhedron. The proton n.m.r. spectra eliminated possibility a, while the ^{11}B n.m.r. spectra of the I series eliminated possibility c owing to the fact that this boron atom appeared as a singlet in both the I and II series. Possibility d is not so readily eliminated. Protonation at the apical boron atom opposite the site of substitution was ruled out since this would require a low-field triplet in the ^{11}B n.m.r. spectra of the I series which was not observed. Consistent with the observation of two sets of equivalent equatorial boron atoms, the only remaining position on the polyhedron available for protonation would be a B–B edge, with the added requirement that the proton move around the polyhedron with such rapidity that only an averaged ^{11}B signal is observed. While such a structure is not aesthetically pleasing and has no analogy in $B_{10}H_{10}^{-2}$ chemistry, it cannot be excluded unequivocally by any of the foregoing data. The remaining possibility—protonation on nitrogen—appeared to be much more plausible and was strongly preferred when the basicities of the substituted dyes and their spectroscopic properties were compared with similar properties of the azobenzenes.

Basicity of II. Table II lists the pK_a values determined for eight pairs of anions. These data were correlated with Hammett's σ-values as shown in Figure 3 and produced a ρ-value of $+1.7$. Correlation was obtained with σ rather than σ^+ or σ^-. The azo linkage of azobenzene is known to undergo protonation with a pK_a (for dissociation) of about -1. Azobenzene is therefore about 8 pK units less basic than II. The greater basicity of II may be attributed to the enhanced electron donor properties of the B_{10} cage compared to an aryl group and/or to the difference in charge type. An analogy exists in the greater basicity[7]

of $B_{10}H_9N(CH_3)_2^{-2}$ compared to that of N,N-dimethylaniline.[8] While the pK_a of $B_{10}H_9N(CH_3)_2^{-2}$ has not been reported, it may be estimated to be at least 6 pK units more basic than N,N-dimethylaniline. In the azobenzene series, the ρ-value obtained by varying substituents in one ring depends somewhat upon the identity of the substituents in the other ring.[9] For

Table II. pK_a and Spectroscopic Data for Azo Dyes

Substit-uent	pK_a	—CH_3CN, $Å_{,max}{}^a$—		σ
		Acid	Base	
p-CH$_3$	6.98	5165	3461	-0.129
p-CH$_3$O	6.96	5152	3534	-0.111
p-H	6.88	5149	3570	0.000
m-CH$_3$O	6.77	5240	3603	$+0.076$
p-Br	5.85	5430	3695	$+0.265$
m-CF$_3$	5.74	5324	3715	$+0.467$
m-NO$_2$	5.56	$\sim$5400^a	3727	$+0.710$
p-NO$_2$	4.74	5626	4425	$+0.778$
10-NH$_3{}^+$	6.20	4675	3320	...

^{a} Unstable in solution.

p'-H and m'-NO$_2$ the ρ-values are $+2.20$ and $+2.75$, respectively, and σ^+ is required to correlate the data. For p'-CH$_3$, p'-OCH$_3$, and p'-OH, on the other hand, σ suffices with ρ-values of $+1.83$, $+1.80$, and 1.61, respectively.

Since the $B_{10}H_9^{-2}$ polyhedron is electron releasing, the II series should be compared with the latter three compounds. The correlation with σ and the similar magnitude of ρ in the two systems is consistent with the proposal that protonation of II occurs on nitrogen.

Electronic Spectra. Figure 4 presents the electronic spectra of azobenzene, its conjugate acid, unsubstituted II, and its conjugate acid, unsubstituted I.

(7) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

(8) N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932).
(9) S. J. Yeh and H. H. Jaffé, *ibid.*, **81**, 3279 (1959).

Unsubstituted II and azobenzene exhibit similar spectra. The major absorption band of azobenzene near 320 mμ, assigned to a $\pi \rightarrow \pi_1{}^*$ transition,[10] occurs near 345 mμ in unsubstituted II. The weaker n $\rightarrow \pi_1{}^*$ band near 420 mμ in azobenzene and barely visible near 460 mμ in unsubstituted II is similarly shifted toward the red. Whereas azobenzene shows a distinct absorption maximum near 230 mμ assigned[10] to a $\phi \rightarrow \phi^*$ or possible $\phi \rightarrow \pi_2{}^*$ transition, unsubstituted II shows only end absorption. When II bears *para* substituents, however, distinct peaks appear in this region.

Protonation of azobenzene shifts the $\pi \rightarrow \pi_1{}^*$ transition 104 mμ toward the red, while the similar transition in unsubstituted II is shifted 112 mμ toward the red in unsubstituted I. The n $\rightarrow \pi_1{}^*$ transition occurs at 300 mμ in protonated azobenzene, shifted toward the blue by 120 mμ, while the similar transition in I occurs at 289 mμ shifted toward the blue by about 170 mμ. The $\phi \rightarrow \phi^*$ transition at about 230 mμ in protonated azobenzene (relatively unchanged from that of azobenzene) occurs as a shoulder at about 225 mμ in unsubstituted I and is apparently unchanged from II. These similarities very strongly suggest that the protonation of the II series occurs in the same position as the protonation of azobenzene, that is, at nitrogen.

The energies of the $\pi \rightarrow \pi_1{}^*$ transitions in I and II (expressed as E_t) are listed as a function of substituent in Table II and were plotted against Hammett's σ-values. A line (not shown) of decreasing E_t with increasing σ resulted. This is consistent with the proposed electronic transition which employs the aromatic ring as the acceptor. Compounds of the I series appeared less sensitive to substituent than did compounds of the II series. Since the transitions are not purely $\pi \rightarrow \pi_1{}^*$,[10] both plots were far from precise.

The effect of solvent composition upon the $\pi \rightarrow \pi_1{}^*$ transition for p-CH$_3$O-I and p-CH$_3$O-II was determined in aqueous acetone solutions and is presented in Table III. When these data were correlated with the

Table III. Effect of Solvent on $\mathring{A}_{,max}$ of p-CH$_3$O Azo Dyes

Solvent, vol. % acetone in H$_2$O	$\mathring{A}_{,max}$		Kosower Z value
	Acid	Base	
0.0	4640	3473	94.6
57.8	5060	3530	86.0
66.3	5100	3550	84.0
75.0	5165	3544	82.0
81.7	5200	3536	80.0
86.7	5230	3573	78.0
90.8	5273	3568	76.0
93.8	5315	3568	74.0
96.2	5352	3591	72.0
98.0	5375	3595	70.0
99.0	5393	3602	68.0
100.0	5400	3624	65.7

proper Kosower[11] "Z" values, both the I and the II ions gave plots (not shown) of E_t vs. Z whose slopes were positive, the I ion being more sensitive than the base to changes in solvent. Such behavior is con-

(10) H. H. Jaffé, S. J. Yeh, and R. W. Gardner, *J. Mol. Spectry.*, 2, 120 (1958).
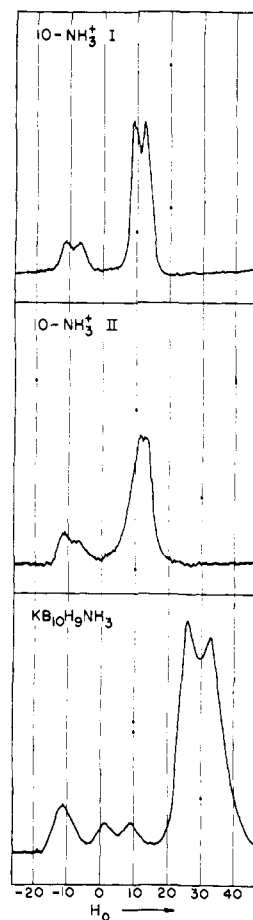(11) E. M. Kosower, *J. Am. Chem. Soc.*, 80, 3253 (1958).

Figure 5. The [11]B n.m.r. spectrum of B$_{10}$H$_9$NH$_3^-$, 10-NH$_3^+$-I, and 10-NH$_3^+$-II at 19.3 Mc./sec.

sistent with that obtained for other $\pi \rightarrow \pi^*$ transitions. The plot for the I ion was slightly concave.

$B_{10}H_9NH_3^-$. The presence of a B–N bond in both the I and II series was conclusively demonstrated by their reduction to B$_{10}$H$_9$NH$_3^-$ and the corresponding aniline. Reduction was accomplished with basic zinc dust, basic hydrosulfite, or tin in acidic methanol. The latter method gave amines directly, while a compound presumed to be the hydrazine could also be isolated from reactions which employed basic conditions. Consistent with the observed[7] basicity of equatorial B$_{10}$H$_9$N(CH$_3$)$_2^{-2}$, apical B$_{10}$H$_9$NH$_2^{-2}$ was isolated from either acidic or basic solution as its N-protonated derivative. The [11]B n.m.r. spectrum of B$_{10}$H$_9$NH$_3^-$ shown in Figure 5 consisted of a low-field singlet of area 1, a low-field doublet of area 1, and a high-field doublet of area 8. The singlet represented the point of attachment of the –NH$_3^+$ group to the B$_{10}$ cage which again corresponded to an apical boron.

10-$NH_3B_{10}H_8N_2C_6H_5^-$. Reaction of B$_{10}$H$_9$NH$_3^-$ with benzenediazonium ion led to coupling and the formation of an azo dye containing the –NH$_3^+$ group as a substituent on the B$_{10}$ polyhedron. This dye could be isolated as an ether-soluble solid protonated both on the azo linkage and on the amino group, or as a mono-anion in which the N=N linkage was not protonated. The reaction of aryldiazonium ions with B$_{10}$H$_9$NH$_3^-$ was substantially slower than their reaction with B$_{10}$H$_{10}^{-2}$. The [11]B n.m.r. spectra of the acid and base forms of the dye prepared from benzenediazonium ion

and $B_{10}H_9NH_3^-$ are shown in Figure 5. Assuming that the 10-NH_3^+ group remains at an apical position during the coupling reaction, both of these spectra strongly suggested that the material was 1,10-disubstituted. The apparent low-field doublet must arise from two singlets.

The pK_a associated with the acid–base equilibrium of the 10-NH_3^+ substituted dye was determined to be 6.20. Addition of the $-NH_3^+$ group at the opposite apex on the B_{10} cage has therefore lowered the pK_a of the protonated azo linkage by 0.68 pK_a unit. A decrease of about 1.5 pK_a units would be anticipated for addition of an $N(CH_3)_3^+$ group at the *para* position of the benzene ring. The somewhat smaller decrease for the 10-ammonio group is taken to imply that the B_{10} cage is more effective in insulating the positive charge from the site of protonation than is the phenyl ring.

1,10-$(NH_3)_2B_{10}H_8$. Conclusive proof of 1,10-disubstitution in the above materials was obtained by their reduction to the previously reported[12] 1,10-diamino derivative of $B_{10}H_{10}^{-2}$. Positive identification of the 1,10-diamino derivative provided firm support for the assignment of apical substitution on the B_{10} cage throughout the above sequence of reactions.

Reaction in H_2O. Yellow materials are rapidly precipitated when aryldiazonium salts are treated with $B_{10}H_{10}^{-2}$ salts in aqueous solution. These materials detonated with considerable brisance after drying. When added to acetone or acetonitrile they dissolved to generate the characteristic color of I, which could be isolated as its tetramethylammonium salt in the usual manner. Conventional elemental analyses of the yellow products could not be made, but equivalent weight values for the phenyldiazonium product were obtained by treatment with an acid ion-exchange resin followed by potentiometric titration with base. The observed value (153) was in good agreement with the theoretical value (164) required for a simple $B_{10}H_{10}^{-2}$ salt which contained two aryldiazonium cations. This view is further strengthened by the presence of a band at 2220 cm.$^{-1}$ in the infrared spectra of the yellow products. Such a band is observed in authentic aryldiazonium salts. The characteristic yellow color of these salts may be due to a charge-transfer interaction of the component ions.

Mechanism of Formation of II. The formation of II formally corresponds to an electrophilic substitution of $RC_6H_4N_2^+$ for H^+ in $B_{10}H_{10}^{-2}$. Such a process is mechanistically attractive in view of the great susceptibility of $B_{10}H_{10}^{-2}$ to electrophilic substitution and the recognized electrophilic properties of aryldiazonium cations. The site of substitution (apical boron) is in agreement with a prediction of relative reactivities toward electrophilic attack[13] based upon ground-state charge distributions. Preferential apical substitution has been observed in other electrophilic substitution reactions.[7,12,14] Certain substitution reactions which are apparently electrophilic in nature have, however, been

reported to give equatorial products,[14a,15] and it has been pointed out that ground-state charge distribution need not strongly influence transition state stability.[15] Until more mechanistic information regarding the reactions of $B_{10}H_{10}^{-2}$ with electrophiles is available, we do not feel free to speculate on the validity of the above prediction.

In the present case, *p*-methoxybenzenediazonium ion did not distinguish between $B_{10}H_{10}^{-2}$ and $B_{10}D_{10}^{-2}$ in a competition experiment which employed an excess of a 1:1 mixture of the latter two materials. This is consistent with (1) a single-step process in which B–H bond breaking in the transition state has not progressed to a degree sufficient to give a detectable isotope effect, or (2) a multistep process in which a step prior to that in which the B–H bond is broken is rate determining.

A transient yellow color is observed upon mixing $B_{10}H_{10}^{-2}$ and aryldiazonium ions in acetonitrile solution, and it is tempting to propose that this color is due to the formation of the same species isolated from water. To obtain information concerning this point, a sample of the water-insoluble material from *p*-methoxybenzenediazonium ion was dissolved in acetonitrile containing a fivefold excess of $B_{10}D_{10}^{-2}$ at $-35°$. After stirring at $-35°$ for 0.5 hr. the solution was allowed to warm slowly to room temperature and the *p*-CH_3O-I isolated as its triethylammonium salt. The infrared spectrum of this salt revealed extensive (essentially statistical) incorporation of deuterium. This observation is in agreement with the rapid and reversible formation of a charge-transfer stabilized salt of ArN_2^+ and $B_{10}H_{10}^{-2}$ prior to the irreversible formation of II.

Experimental

Preparation and Purification of Starting Materials. Commercially available substituted anilines were recrystallized or sublimed. They were then diazotized with sodium nitrite in aqueous hydrochloric acid and the resulting aryldiazonium salts precipitated as their tetrafluoroborates[16] or hexafluorophosphates.[17] The triethylammonium salt[18] of $B_{10}H_{10}^{-2}$ was prepared from $B_{10}H_{14}$ and triethylamine in toluene at the reflux temperature. This salt was converted to other salts by metathetical precipitation from aqueous solution or by neutralization of an aqueous solution of $(H_3^+O)_2$-$B_{10}H_{10}^{-2}$ with the appropriate metal hydroxide. The $(H_3^+O)_2B_{10}H_{10}^{-2}$ was prepared by cation exchange in water. $K_2B_{10}D_{10}$ was prepared from $K_2B_{10}H_{10}$ by repeated exchange with acidic deuterium oxide.[19] The preparation of *p,p'*-dimethoxyazobenzene, for use in ^1H n.m.r. studies, was carried out as previously[20] described. Acetonitrile was purified by passage through an acid ion-exchange column followed by treatment with silica gel and distillation from benzenediazonium tetrafluoroborate followed by distillation from P_2O_5.

Stoichiometry. The triethylammonium salt of $B_{10}H_{10}^{-2}$ was recrystallized from water and dried at $100°$

(12) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964).

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(19) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(20) J. H. Collins and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 4708 (1962).

over P_2O_5 in vacuo for 12 hr. A standard solution of this salt was prepared by diluting 0.0322 g. (0.100 mmole) to the mark in a 100-ml. volumetric flask with acetonitrile. The p-methoxybenzenediazonium hexafluorophosphate was recrystallized from aqueous acetonitrile and gave needles of m.p. 149–150° dec. (lit.[17] m.p. 149° dec.). A standard solution was prepared by diluting 0.0180 g. (0.0643 mmole) to the mark in a 100-ml. volumetric flask with acetonitrile. To 1 ml. of the above $B_{10}H_{10}^{-2}$ solution in 10-ml. volumetric flasks was added amounts of diazonium solution which varied from 0.20 to 5.0 ml. After dilution to the mark with acetonitrile, the optical density was measured at 515 mμ. The optical densities became constant beyond 0.94 equiv. of added aryldiazonium ion.

General Procedure for the Coupling Reaction. $K_2B_{10}H_{10}$ (10 g., 51 mmoles) was dissolved in 1 l. of acetonitrile[21] and cooled to $-35°$, whereupon 13.8 g. (0.051 mole) of p-bromobenzenediazonium tetrafluoroborate in 50 ml. of acetonitrile was added slowly with stirring. The solution rapidly turned yellow and then became deep purple. After 0.5 hr. the solution was allowed to warm to room temperature and concentrated to about 25 ml., whereupon 6.7 g. (0.053 mole) of a purple solid, whose infrared spectrum was identical with that of KBF_4, was isolated by filtration. The filtrate was passed through a 300-g. column of acid-washed alumina and concentrated to near dryness. The solid obtained was dissolved in 300 ml. of distilled water containing several milliliters of 0.10 N HCl and filtered. About 15 ml. of of a 50% aqueous tetramethylammonium chloride solution was slowly added with stirring. The insoluble tetramethylammonium salt of the monoprotonated azo dye (I) precipitated and was collected by filtration, washed with water, ethanol, and ether, and dried in vacuo over P_2O_5; yield, 17.7 g., 92%. *Anal.* Calcd. for $C_{10}H_{26}N_3B_{10}Br$: C, 31.90; H, 6.96; N, 11.16; B, 28.74; Br, 21.23; equiv. wt., 376. Found: C, 32.14; H, 7.05; N, 11.05; B, 28.60; Br, 21.20; equiv. wt., 370.

After passing through the alumina column, a second preparation was dissolved in 50 ml. of distilled water containing several grams of potassium hydroxide, and after filtration about 10 ml. of 5 M tetramethylammonium chloride solution was added. The somewhat soluble tetramethylammonium salt of the azo dye (II) precipitated and was recrystallized from water to give an analytical sample. *Anal.* Calcd. for $C_{14}H_{37}N_4$-$B_{10}Br$: C, 37.40; H, 8.30; N, 12.46; B, 24.07; Br, 17.78; equiv. wt., 450. Found: C, 37.14; H, 8.25; N, 12.16; B, 23.92; Br, 17.54; equiv. wt., 446.

Other members of the I and II series were prepared by the same procedure and their properties are given in Table I.

The Reaction in Aqueous Solution. To 0.100 g. (0.45 mmole) of p-methoxybenzenediazonium tetrafluoroborate dissolved in 5 ml. of water was added 0.100 g. (0.51 mmole) of $K_2B_{10}H_{10}$ in 5 ml. of slightly acidic water. The yellowish solid which precipitated was separated by filtration and washed with water. The material redissolved upon addition of base and was reprecipitated upon acidification. Addition of the yellowish solid, while still moist, to either acetonitrile or

acetone, gave deep purple solutions from which p-CH_3O-I could be isolated as its tetramethylammonium salt in the usual manner. An infrared spectrum showed strong absorption near 2220 cm.$^{-1}$. A sample of the solid was dried for further studies but detonated. A comparable sample prepared from benzenediazonium tetrafluoroborate and $K_2B_{10}H_{10}$ was washed repeatedly with water and then dried in vacuo over P_2O_5 at room temperature for several hours. The sample was weighed and dissolved in 25 ml. of water containing a slight molar excess of NaOH (to promote solubility), passed through an acidic cation-exchange column, and titrated with standard base.[22] The equivalent weight so obtained was 153 (calcd. for $C_6H_5N_2)_2B_{10}H_{10}$, 164). Benzenediazonium tetrafluoroborate, when treated in this manner, gave an equivalent weight of 181 (calcd., 192). A similar sample derived from p-bromobenzenediazonium ion decomposed violently (although not explosively) while still moist. The handling of these materials is therefore discouraged.

Competitive Coupling Experiments Using $B_{10}H_{10}^{-2}$ and $B_{10}D_{10}^{-2}$. A solution of 0.100 g. (0.45 mmole) of p-methoxybenzenediazonium tetrafluoroborate dissolved in 5 ml. of acetonitrile was added dropwise at $-25°$ to 50 ml. of an acetonitrile solution of 0.750 g. (3.75 mmoles) of a $K_2B_{10}H_{10}$–$K_2B_{10}D_{10}$ mixture whose infrared absorption at 2450 (B–H) and 1830 cm.$^{-1}$ (B–D) was 1.02 : 1.00. The reactants were stirred and maintained between -25 and $-30°$ for 30 min., whereupon the acetonitrile was removed in vacuo and the product taken up in water of pH 5. The monoprotonated azo dye was isolated as its triethylammonium salt and washed repeatedly with water to remove the excess unreacted materials. An infrared spectrum of the protonated azo dye formed then showed the intensities of the 2450- and 1830-cm.$^{-1}$ bands to be 1.04 : 1.00, which represent a statistical distribution of deuterium assuming that the ratios of the extinction coefficients of B–H and B–D are the same in $B_{10}H_{10}^{-2}$ and p-CH_3O-I.

Exchange of $B_{10}H_{10}^{-2}$ and $B_{10}D_{10}^{-2}$ in the Yellow Intermediate. A solution of 0.100 g. (0.45 mmole) of p-methoxybenzenediazonium tetrafluoroborate dissolved in 5 ml. of water was added to a slightly acidic solution of 0.100 g. (0.51 mmole) of $K_2B_{10}H_{10}$ in 10 ml. of water. A yellow solid rapidly precipitated and was collected by filtration followed by repeated washing with distilled water. It was then pressed fairly dry and added to a stirred solution of 0.500 g. (2.43 mmoles) of $K_2B_{10}D_{10}$ in 500 ml. of acetonitrile at $-35°$. This solution was stirred at $-35°$ for 0.5 hr. and allowed to warm gradually to room temperature. The solvent was then removed in vacuo and the product taken up in water. An aqueous solution of triethylammonium chloride was added and the precipitated solid collected and washed with water to remove the more soluble triethylammonium salt of $B_{10}H_{10}^{-2}$. An infrared spectrum of the p-CH_3O-I indicated the ratio of intensities of the 2450-cm.$^{-1}$/1830-cm.$^{-1}$ bands to be about 1:5. The yield of azo dye was 82%.

General Procedure of pK_a Determinations. A standard solution of azo dye in 100 ml. of distilled water was prepared and equal aliquots diluted to the mark in volumetric flasks with 0.05 N KOH, 0.05 N HCl, and

(21) For preparative work acetonitrile was distilled over CaH_2 and not further purified.

(22) The added NaOH is converted to H_2O in this procedure and therefore does not influence the neutralization equivalent.

buffer solutions of varying, but known, pH in the vicinity of the pK_a of the dye. Optical density *vs.* wave-length curves were recorded for all solutions over a range of wave lengths which included the maximum for the acid and base forms of each compound. The pK_a values were then evaluated in the several buffer solutions using the method of simultaneous equations required when the base and its conjugate acid have overlapping absorptions.[23] Averaged values for the eight compounds are reported in Table II and are shown plotted against σ-values[24,25] in Figure 4.

Spectroscopic Studies. Samples of the various compounds were dissolved in acetonitrile or in acetone–water mixtures of the appropriate compositions, and the position of their visible absorption bands was determined using a Cary Model 14 recording spectrophotometer. Transition energies were calculated from the expression[11] $E_t = 285,900/\text{Å}$. Data for E_t *vs.* substituent are listed in Table II. Data for E_t *vs.* Z values for p-CH$_3$O-I and -II in acetone–water mixtures are recorded in Table III.

N.m.r. Spectra. ^{1}H spectra were recorded at 60 Mc./sec. on a Varian Model A-60 spectrometer with acetonitrile as solvent. Chemical shifts were measured relative to solvent and are listed as p.p.m. relative to tetramethylsilane. The ^{11}B spectra were obtained at 19.3 Mc./sec. on a Varian Model HR-60 spectrometer with acetonitrile or water as solvent. Chemical shifts were calculated relative to an external boron trifluoride etherate standard.

General Procedure for the Hydrosulfite Reduction of the Dyes. Four grams (15 mmoles) of unsubstituted I as its K$^+$ salt was dissolved in 100 ml. of water and the pH adjusted to about 12 by the addition of KOH pellets. Sufficient base was added to maintain the pH at about 12, along with 5.0 g. of Na$_2$S$_2$O$_4$. After

(23) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962.
(24) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 184.
(25) P. W. Wells, *Chem. Rev.*, **63**, 171 (1963).

stirring 30 min. the solution was acidified to pH 0.5, and after an additional 15 min. it was filtered. Aqueous tetramethylammonium chloride was added, whereupon 2.4 g. of (CH$_3$)$_4$NB$_{10}$H$_9$NH$_3$ (77%) precipitated and was collected by filtration. Recrystallization from dimethyl sulfoxide–water afforded an analytical sample. *Anal.* Calcd. for B$_{10}$C$_4$H$_{24}$N$_2$: C, 23.1; H, 11.5; N, 13.5; B, 51.9; equiv. wt., 208. Found: C, 25.4; H, 11.8; N, 13.4; B, 49.9; equiv. wt., 201. The filtrate was made basic and extracted with two 25-ml. portions of ether. The ether was concentrated to about 15 ml. and HCl added. Aniline hydrochloride, 1.1 g. (54%), precipitated and was collected by filtration. Its infrared spectrum was identical with an authentic sample.

10-NH$_3^+$-I. Acetonitrile (50 ml.) containing 3.7 g. (1.9 mmoles) of benzenediazonium tetrafluoroborate was added to a solution of 4.0 g. (1.9 mmoles) of (CH$_3$)$_4$NB$_{10}$H$_9$NH$_3$ in 1 l. of acetonitrile and stirred at room temperature overnight. The acetonitrile was removed *in vacuo* and the product taken up in methanol. The product was precipitated by addition of water and recrystallized from aqueous methanol to give 1.5 g. (32%) of 10-NH$_3$-I. *Anal.* Calcd. for C$_6$H$_{17}$N$_3$B$_{10}$: B, 45.2. Found: B, 44.1. An aqueous solution of the base form was prepared by extraction of an ethereal solution of the acid with aqueous KOH.

1,10-(H$_3$N)$_2$B$_{10}$H$_8$. Reduction of 10-NH$_3^+$-I with excess tin in a 30:70 hydrochloric acid–methanol solvent afforded 1,10-(H$_3$N)$_2$B$_{10}$H$_8$ in 48% yield. The excess tin was removed by filtration and the solvent removed *in vacuo*. The product was recrystallized from aqueous ethanol and gave, after drying at 100° *in vacuo*, an infrared spectrum which was superimposable with that of an authentic sample.

Trends in Transition Metal Ion–Ligand Covalency from Nuclear Magnetic Resonance Contact Shifts

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N.m.r. contact shifts are reported for a series of transition metal ion complexes of hexamethylphosphoramide. Evidence is reported to indicate that several of these complexes exist as tetrahedral complexes in the solvent nitrobenzene. The effect of excess ligand on the species in solution is investigated. The contact shifts also indicate that pronounced changes occur when several of the complexes are dissolved in some acidic and basic solvents. The n.m.r. contact shifts of the tetrahedral complexes are interpreted as indicating an increase in covalent bonding ability for the series Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II). The electron spin–nuclear spin coupling constants are found to correlate with the respective metal ion ionization potentials and with the first formation constant for some oxygen donors with the respective metal ions.