Organic Quantum Chemistry. XXXIII. Electronic Spectra and Rotational Barriers of Vinylborane, Allyl Cation, and Related Compounds[1-3]

Norman L. Allinger* and John H. Siefert

Contribution from the Departments of Chemistry, University of Georgia, Athens, Georgia 30601, and Wayne State University, Detroit, Michigan 48202. *Received March 21, 1974*

Abstract: The geometries of the ground states and the rotational barriers have been studied for vinylborane and the di- and trivinylboranes by the INDO method. For vinylborane itself, *ab initio* calculations have also been carried out. Using these geometries, the VESCF method for the π system has been developed so that after configuration interaction, including all singly and doubly excited configurations, calculations of the electronic spectra are possible. These calculations have been applied to a number of more complicated unsaturated boron derivatives. Similar studies on the related allyl ions are briefly mentioned. The calculated spectra show large systematic errors which are believed to be due mainly to hyperconjugation, which is not taken into account.

Although the total literature concerning boron compounds is substantial, at the time this work was undertaken published quantum mechanical calculations on unsaturated boron compounds, in which boron was the only heteroatom, were very scarce. Vinylborane[4-7] and phenylborane[8-10] were the only compounds for which studies had been reported.

Some calculations concerning electronic spectra of conjugated carbonium ions, which are isoelectronic with boron compounds, have also been reported. These have met with limited success.[11,12] In this paper, we will discuss the application of the VESCF method to the calculation of the electronic spectra of both conjugated organoboron compounds and the corresponding carbonium ions.

Since the compounds we will be concerned with are planar, or nearly so, the π-electron approximation will be satisfactory for calculations involving electronic spectra. The calculation method used herein is the variable electronegativity self-consistent field (VESCF) method.[13] In order to obtain good spectra, a configuration interaction is then carried out using the ground configuration and all singly and doubly excited configurations. The details of this method have been previously reported and used for hydrocarbons.[14,15]

For purposes of determining some structural quantities which are poorly known experimentally if at all, we have made use of the standard INDO method,[16] while the *ab initio* calculations were done with the aid of the program[17] IBMOL-4.

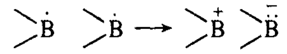
Determination of the VESCF Parameters

The VESCF method has previously been described for hydrocarbons. The parameters and methods are carried over here unchanged, except for carbons attached to boron which are affected by σ induction. The effective nuclear charges and ionization potentials used for carbon to which are attached these combinations of hydrogen, sp^2, or sp^3 hybrid orbitals are collected in Table I.

The ionization potential (I) and one center repulsion integral (Γ) of a carbon are related to its effective nuclear charge by the same equations we have previously used.[13]

$$I = 0.8409Z^2 + 5.4861Z - 15.1718$$
$$\Gamma = 11.08(Z/3.25)$$

The parameters for boron were evaluated in an analogous way. First, the one-center repulsion integral was evaluated following Pariser and Parr.[18] The pairing of two electrons in the p orbital of a boron atom is taken to be the energy of the following reaction.



This corresponds to the ionization potential minus the electron affinity of boron in the trtrπ valence state. The reason that this valence state was chosen is that it is the atomic valence state which most closely represents the state of the atom in the molecule and has an electron in its p orbital. The ionization potential of the boron p orbital in this valence state is 8.33 eV, and the electron affinity is 1.42 eV.[19] The one center repulsion integral is therefore 6.91 eV. The effective nuclear charge corresponding to this value is the Slater charge 2.6, so the effective nuclear charge and the one center repulsion integral are related by

$$\Gamma = 6.91(Z/2.6)$$

In the present work, we are interested in the energy needed to strip the electrons from the p orbital of an atom in the π-electron system. In previous works,[20] this energy has corresponded to the ionization potential of an atom, but since boron has an empty p orbital, this energy corresponds to its electron affinity.

The relationship between the electron affinity and the effective nuclear charge was found using the same ionization processes (Table II) as were used in determining the ionization potential curve for carbon,[13] except that in this case the ionization potentials (I_X) are corrected to boron (I_B) rather than carbon by a factor of B/X. The factor B/X is a ratio of the nuclear charge of boron to that of the species being corrected to boron.

$$I_B(Z) = I_X(Z)(B/X)$$

This results in a set of equations of the form

$$I = AZ^2 + BZ + C$$

where Z is the effective nuclear charge corresponding to the ionization process in question. The equations are solved for A, B, and C giving the equation relating the effective nuclear charge and electron affinity of boron.

$$I = 0.6310Z^2 + 4.1145Z - 11.3821$$

The final problem encountered in the parameterization of the method for the boron atom is the determination of the effective nuclear charges of the boron atom and the carbon atoms adjacent to it.

The first step in this parameterization was to determine the effective nuclear charge of a boron atom bound to three

Table I. Parameters of Carbon Orbitals

	Z	I
$H_2\dot{C}C$	3.132	10.25941
$MeH\dot{C}C$	3.022	9.08670
$Me_2\dot{C}C$	2.938	8.20488
$H\dot{C}C_2$	3.183	10.81003
$Me\dot{C}C_2$	3.073	9.62788
$\dot{C}C_3$	3.250	11.54000

Table II. Points Used to Determine Ionization Potential Curve

Process	Z	X	I_X	I_B
$B^- \rightarrow B$	2.25	3	1.07	1.07
$C \rightarrow C^+$	3.25	4	11.54	8.655
$N^- \rightarrow N^{2+}$	4.25	5	29.17	17.502

Table III. The Calculated Uv Spectrum of Trivinylborane with the Vinyl Groups Twisted to Different Degrees in the Same Direction[a]

Twist, deg	λ_1, nm	f_1	λ_2, nm	f_2
0	217	0.71	182[b]	0.00
10	218	0.69	183	0.00
20	219	0.66	186	0.01
30	219	0.63	193	0.02
40	217	0.54	204	0.94

[a] $R_{C-B} = 1.519$ Å, $R_{C-C} = 1.34$ Å; $Z_B = 2.35$, $Z_C = 3.189$. [b] In our preliminary studies (Table III), this band was calculated to be at 182 nm. In our final calculations (Table VI), this band was calculated to be at 191 nm.

Table IV. Calculated Electronic Spectra of Planar Vinylboranes at Different Effective Nuclear Charges of Boron and the α Carbon

	Z_B	Z_{C_α}	λ, nm
Trivinyl	2.3	3.288	195
	2.4	3.255	205
	2.5	3.222	240
	2.6	3.189	271
Methyldivinyl	2.2	3.239	193
	2.3	3.239	208
	2.4	3.239	225
	2.5	3.239	245
	2.6	3.239	266
Dimethylvinyl	2.2	3.249	186
	2.3	3.249	199
	2.4	3.249	205
	2.5	3.249	237

sp^2 carbon atoms. The compound used for these calculations was a planar model of trivinylborane. While trivinylborane is believed to be nonplanar, our preliminary studies show that twisting the vinyl groups has essentially no effect on the long wavelength band of the spectrum (see Table III). The effective nuclear charges for the boron atom and the α carbon were arbitrary and were chosen in the range of values with which we will be dealing. The carbon-boron bond length was assumed to be equal to the sum of the single bond covalent radii of boron and carbon (1.519 Å), and the carbon-carbon bond length was assumed to be 1.34 Å.

The only planar conformations considered were the "swastika" or "propeller" type. In trivinylborane this is clearly the most stable planar conformation, as any other configuration would have severe interactions between the terminal vinyl protons of two vinyl groups. Armstrong and Perkins have indicated that the "swastika" configuration is also preferred in methyldivinylborane.[7]

The fact that twisting the vinyl substituents does not change the position of the long wavelength band is interesting, particularly because this band is due to the vinyl boron transition, and one might expect it should be affected greatly by twisting the vinyl groups. The reason that the band is essentially stationary is that twisting the substituents changes the energy of the molecular orbitals involved very slightly and identically. For example, on going from the planar to the 30° twist conformer of trivinylborane, the vinyl molecular orbital changes from −11.63 to −11.76 eV in energy, while the orbital involving the boron atom makes a comparable change from −1.68 to −1.80 eV.

The reason for the invariance of the energy differences between these orbitals lies in the fact that orbitals 2, 3, 5, and 6 are almost entirely double bonds, while 4 is mostly boron. On the other hand, orbitals 1 and 7 are mixtures of the different atomic orbitals.

Therefore, the energies of orbitals 1 and 7 are quite sensitive to twisting, because the coefficients of these orbitals change with twist. On the other hand, because the nature of orbitals 2, 3, 4, 5, and 6 does not change (2, 3, 5, and 6 remain double bonds, and 4 remains boron upon twisting), transitions between these orbitals should show very little shift on twisting, which is as observed. The lowest energy transitions involve degenerate transitions to orbital 4 from orbitals 2 and 3 and are insensitive to twist. The next one, at 182 nm (see footnote *b*, Table III) in the planar conformation, involves a transition from orbital 1 to orbital 4 and therefore is quite sensitive to twist, shifting to 204 nm in the 40° twist conformer.

Calculations of the spectrum of planar trivinylborane were done using several different effective nuclear charges for the boron atom. In all cases, the effective nuclear charge of each α-carbon atom was assumed to have been changed by a magnitude of 0.33 times that of the boron atom and in the opposite direction, so

$$Z_C = Z_{C_0} - 0.33 Z_B$$

where Z_{C_0} = effective nuclear charge of the carbon atom if the boron has no inductive effect = 3.189, and Z_B = change in Z_B from the atomic Z_{B_0} of 2.6 = $Z_{B_0} - 2.6$.

The results of these calculations (see Table IV) were then plotted. The calculated spectrum was found to agree with the 234-nm band which has been observed in the gas phase[6] at $Z_B = 2.48$ and $Z_{C_\alpha} = 3.229$.

The total effect of the three vinyl groups in trivinylborane on the effective nuclear charge of the boron atom is −0.12. This was broken down into contributions of the individual vinyl groups as follows. The first vinyl group is assumed to have an effect of −0.06 or half of the total. The second vinyl group is assumed to have an effect of −0.04. The third vinyl group is assumed to have an effect of −0.02. The fact that each additional group added to an atom has a smaller effect on its effective nuclear charge than the previous group has been observed in the case of methylated sp^2 carbon atoms.[13]

The two vinyl groups of methyldivinylborane should, therefore, have a total effect of −0.10 on the effective nuclear charge of the boron atom. The effective nuclear charge of each α carbon is then increased by 0.05 to make $Z_{C_\alpha} = 3.189 + 0.05 = 3.239$. The effect of the methyl group on Z_B was then determined by calculations on methyldivinylborane altering Z_B and holding $Z_{C_\alpha} = 3.239$. The results of these calculations (see Table IV) were plotted. The calculated spectrum correlates with the band at 221 nm which has been observed in the gas phase[4,5] when $Z_B = 2.38$, so the methyl group shifts Z_B by −0.12.

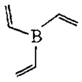
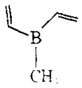
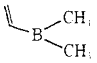
Similar fitting to experiment[4,5] for dimethylvinylborane indicated that the two methyl groups shift the effective nuclear charge of the boron atom by −0.27.

These results indicate that in the vinylboranes the substitution of a methyl group on boron decreases its effective nuclear charge by 0.12, and the addition of a second methyl

Table V. Effective Nuclear Charges of Substituted Boron Atoms and Changes in the Effective Nuclear Charges of Their α Carbons

Substitution	Z_B	$\Delta Z_{C\alpha}$
$(\text{C sp}^2)_3\text{B}$	2.48	0.04
$(\text{C sp}^2)_2\text{B}(\text{C sp}^3)$	2.38	0.05
$(\text{C sp}^2)\text{B}(\text{C sp}^3)_2$	2.35	0.06

Table VI. Calculated and Observed Gas-Phase Spectra of the Vinylboranes

	Calculated (planar)			Observed[4,5]		
Compd	λ, nm	E, eV	f	λ, nm	E, eV	f
	234 234 191[a]	5.30 5.30 6.49	0.36 0.36 0.00	234 2.15	5.31 5.77	0.33 0.04
	221 197	5.61 6.30	0.47 0.09	221 201	5.61 6.17	0.31 0.11
	207	5.99	0.34	196	6.30	0.28

[a] This band is calculated for planar trivinylborane, while the observed band corresponds to a twist of 40–50°.

group will decrease the effective nuclear charge of the boron atom by an additional 0.15. This is contrary to what is known[13] in the case of methyl-substituted sp^2 carbons and contrary to intuition. The second methyl group should decrease the effective nuclear charge of the boron atom by about two-thirds as much as the first methyl group. In order to be in agreement with this fact and still correlate with the observed spectra, we gave the first methyl substituent an effect of −0.12, and the second an effect of −0.07. The values for the effective nuclear charges finally settled on are given in Table V.

One discrepancy with intuition results from such a treatment of the effective nuclear charges. An sp^2 hybridized carbon atom seemingly donates electrons to an sp^2 hybridized boron in the σ framework of the molecule. The ionization potentials of sp^2 orbitals on boron and carbon are 11.29 and 15.62 eV, respectively, indicating that boron should donate electrons to carbon in the σ framework of the molecule. The reason for this discrepancy may be that because of the twisting of the vinyl groups of the vinylboranes there may not be complete σ–π separation. That is, some hyperconjugative σ–π electron donation from carbon to boron may occur, and because our calculations are incapable of handling such interactions, they are reflected in our initial effective nuclear charges.

The spectra of planar trivinylborane, methyldivinylborane, and dimethylvinylborane were calculated using the parameters in Table V. The results are compared with the observed spectra in Table VI. The agreement is satisfactory except for the short wavelength band of trivinylborane. This band was found by a Gaussian analysis of the gas phase spectrum of trivinylborane and has been assigned to an electronic transition rather than vibrational fine structure. This band is quite sensitive to the twisting of the vinyl substituents, and our calculations indicate that a twist of 20–40° may be present in trivinylborane. Such a twist would not only make the calculated wavelength of this transition correlate better with experiment but would also tend to make the calculated oscillator strength be more in line with experiment by making the transition very slightly allowed.

Electronic Spectra of Organoboron Compounds

The spectra of the simple vinylboranes used in the parameterization are summarized in Table IX. Very few additional experimental spectra are available for organoboron compounds. We will first discuss the compounds for which such data are available in order to demonstrate the validity of our calculations; then we will discuss the spectra of several compounds for which no experimental data exist.

Table VII. Electronic Spectrum of Diisopropyldiboracyclopentanobenzene (I)

Calculated			Observed[21,a]		
λ, nm	E, eV	f	λ, nm	E, eV	Log ϵ
300	4.14	0.14	304	4.08	2.99
231	5.38	0.18	249	4.98	3.70
222	5.58	0.00			
199	6.24	0.08	207	5.99	4.24
192	6.47	0.80			

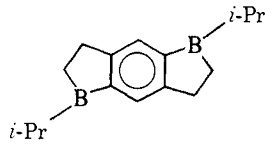
[a] Corrected to the gas phase using experimental oscillator strengths.[22]

Table VIII. Electronic Spectrum of 9-Ethylborafluorene

Calculated			Observed[24-26,a]		
λ, nm	E, eV	f	λ, nm	E, eV	log ϵ
341	3.64	0.03	387	3.20	2.25
269	4.61	0.07	293	4.23	3.65
247	5.03	0.00	256	4.84	4.15
217	5.73	0.85			
215	5.78	0.07	(Strong end absorption at 225 nm)		
205	6.05	0.01			
202	6.15	0.27			
193	6.42	0.15			

[a] Corrected to the gas phase using experimental oscillator strength and molar refractivity in place of polarizability.

The electronic spectrum of *B,B'*-diisopropyldiboracyclopentanobenzene (I) has been observed by Koster.[21] Our calculation assumed carbon–carbon bond lengths of 1.397 Å and carbon–boron bond lengths of 1.519 Å, the sum of the single bond covalent radii of carbon and boron. The C–C–C bond angles of the six-membered ring were all assumed to be 120°, and the C–C–B bond angle of the five-membered ring was assumed to be 108°. The results of our calculations may be found in Table VII. The agreement between the experimental and calculated values is reasonable. An additional calculation of the spectrum of *B,B'*-diisopropyldiboracyclopentanobenzene used a C–B bond length of 1.500 Å. We found that the calculated spectrum of this compound was quite insensitive (±0.03 eV) to the carbon–boron bond length over this range.



I

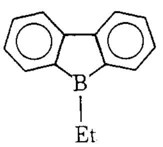
We then turned our attention to more complex systems, starting with 9-ethylborafluorene (II). Again we assumed the C–C–C bond angles in the six-membered rings to be 120° and the angles of the five-membered ring to be as close as possible to 108°. The carbon–carbon bonds of the six-membered rings were taken to be 1.397 Å, and the carbon–carbon bond between the two rings was taken to be 1.47 Å. The latter bond length was chosen, because our preliminary studies indicated a bond order of 0.27 between these two carbon atoms, which corresponds to a bond length of 1.47 Å, according to the method of Allinger and Graham.[23] Table VIII summarizes the results of our calculations. The results are in fair agreement with experiment.

We also calculated the spectrum of 3-phenyl-3-benzoborapin (III). In this case, two conformers were considered.

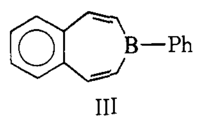
Table IX. Electronic Spectrum of Benzoborapin

	Calculated			Observed[27,a]		
	λ, nm	E, eV	f	λ, nm	E, eV	Log ε
				342	3.63	4.21
	309	4.02	0.06	327	3.79	4.22
				317	3.91	3.98
	287	4.33	0.02	290	4.28	4.45
				270	4.59	4.68
Planar	243	5.11	0.59	226	5.49	4.50
	229	5.41	0.25			
	210	5.91	0.05			
	199	6.22	1.21			
	394	3.15	0.02			
	342	3.63	0.01			
Tub	260	4.77	0.01			
	247	5.02	0.01			
	239	5.19	0.06			
	217	5.72	0.01			
	201	5.19	0.25			

[a] Corrected for cyclohexane solvent.[22]



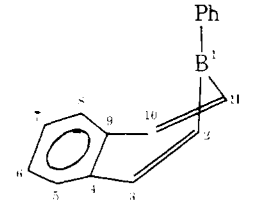
II



III

The first was planar with carbon–carbon bond lengths of 1.397 Å in the six-membered ring, while the bond lengths of the seven-membered ring were determined by the method of Allinger and Graham.[23] The C_2–C_3 and C_{10}–C_{11} bonds were, therefore, taken to be 1.365 Å, and the C_3–C_4 and C_9–C_{10} bonds were taken to be 1.443 Å. The carbon–boron bond lengths were considered to be 1.519 Å. The rings were considered to be as close as possible to regular polygons. This resulted in the bond angles of the seven-membered ring being slightly distorted because of the alternating bonds. The phenyl substituent was omitted from our calculations, because our program will only handle 14 atoms, and the boron was treated as a tri-sp^2 substituted boron atom (Z_{eff} = 2.48). The phenyl substituent should give a very slightly perturbed benzene spectrum which should be added to our calculated results. In addition, it may cause some slight shift in the spectrum, because it will lengthen the conjugated system.

The other conformation considered was a tub-type conformation (IV). The bond lengths of the seven-membered ring were obtained by the method of Allinger and Graham.[23] The bond angles were adjusted so that they were as close as possible to 120°. The results of our calculations are given in Table IX.



IV

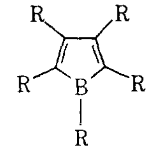
Our spectral calculations are more consistent with the planar conformer. The 342, 327, and 317 nm bands appear to be a vibronic progression centered about 327 nm. This corresponds to our calculated 309 nm band. It is difficult to tell whether the 290 and 270 nm bands are due to two separate transitions (one being from the phenyl substituent which was not included in our calculation) or are due to vibrational fine structure. Either way, these bands correspond to the calculated transition at 287 nm. The band observed at 226 nm corresponds to the two calculated transitions at 243 and 229 nm.

Table X. Calculated Electronic Spectra

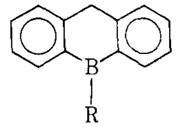
	λ, nm	E, eV	f
B-Alkylborole	306	4.05	0.03
	206	6.04	0.01
	167	7.44	0.12
	161	7.69	0.32
9-Methyl-10-hydro-9-boraanthracene	252	4.92	0.06
	239	5.20	0.09
	234	5.31	0.33
	215	5.77	0.01
	196	6.32	0.01
	195	6.35	0.69
B-Alkylborirene	160	7.73	0.04
	147	8.41	0.45
B-Alkylboraperinaphthene	339	3.65	0.26
	294	4.22	0.06
	277	4.47	0.06
	231	5.36	0.00
	218	5.69	0.07
	212	5.85	0.47
	204	6.09	0.04

The calculated oscillator strengths of the two long wavelength bands are in complete disagreement with experiment. The calculated values indicate that these are very slightly allowed transitions, while the observed log ε values are quite large. This may be due to a slow tailing off of the large short wavelength bands, with the long wavelength bands being shoulders on this tail. We do not have a complete spectrum in our possession, so all we can do is speculate that this may be the cause of the problem. A more likely possibility is that the phenyl substituent perturbs the system so as to give the large oscillator strengths which are observed, which is the case when benzene is compared with biphenyl, for example. The calculations in Table XII are, of course, for the parent system.

We have also carried out spectral calculations on two other known types of organoboron compounds for which no spectral data have yet been reported. These are borole (V) and 10-hydro-9-boraanthracene[28] (VI). The known members of these groups of compounds are Vb, VIb, and VIc.



Va, R = H
b, R = C_6H_5



VIa, R = H
b, R = C_6H_5
c, R = CH_3

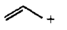
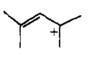
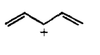
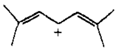
The calculation was carried out for B-alkylborole rather than the known pentaphenylborole (Vb). The carbon–boron bond length was taken to be 1.519 Å, the two side carbon–carbon bonds were taken to be 1.34 Å, and the bond opposite the boron atom was taken to be 1.50 Å.

The calculation performed on 9-methyl-10-hydro-9-boraanthracene (VIc) assumed a planar geometry with carbon–carbon bond lengths of 1.519 Å and carbon–carbon bond lengths of 1.397 Å. All bond angles were considered to be as close to 120° as possible.

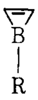
The results of these calculations may be found in Table X.

Calculations were also carried out for two systems, of which classes no members are yet known, B-alkylborirene (VII) and B-alkylboraperinaphthene (VIII). These two compounds are of great interest to the organic chemist. Borirene represents the simplest potentially aromatic organo-

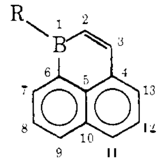
Table XI. Allyl and Pentadienylium

	Calculated			Observed[30,a]		
Ion	λ, nm	E, eV	f	λ, nm	E, eV	Log ϵ
	234	5.30	0.53			
	235	5.29	0.51	288	4.31	4.03
	322	3.85	0.92			
	281	4.41	0.03			
	341	3.64	0.89	363	3.42	4.00[28]
	263	4.71	0.05			

[a] Corrected for H_2SO_4 solvent.[22]



VII



VIII

boron compound, while boraperinaphthene is a potentially aromatic species which is isoelectronic with the peri-naphthenyl cation, which is known to be a relatively stable ion.[29]

The carbon-carbon bonds of the naphthalene system were assumed to be 1.397 Å. The C_2-C_3 and C_3-C_4 bond distances were determined by the method of Allinger and Graham[23] to be 1.357 and 1.454 Å, respectively. The carbon-boron bonds were taken to be 1.519 Å. The bond angles were taken to be as close as possible to those of a regular polygon.

The results of these calculations are also given in Table X.

It is interesting to note that borirene shows only very short wavelength absorption and will be transparent in ordinary solution spectra. Weak long wavelength bands due to σ-π^* transitions may be observed similar to that observed in dimethylvinylborane.[5]

Electronic Spectra of Carbonium Ions. A Comparison with Organoboron Compounds

The electronic spectra of several carbonium ions were calculated for comparison purposes. In all cases, we assumed geometries in which all carbon-carbon bond lengths were 1.397 Å, and all bond angles were either 120° or were considered to be the angles of regular polyhedra. The results of these calculations are shown along with the observed data[30,31] in Tables XI-XII. In some cases, the observed data are for alkylated derivatives of the ions. In these instances, calculations have been carried out on both the substituted and unsubstituted ions.

The charges of the carbonium ions were initially spread over the entire ion so that the starting effective nuclear charge of a carbon atom is given by

$$Z = Z_0 + (0.35)(1/n)$$

where Z_0 is the effective nuclear charge which the carbon would have in a neutral molecule, and n is the number of atoms in the π-electron system. The second portion of the equation is the Slater shielding of one electron divided by the number of atoms in the π system.

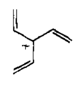
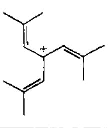
Several different twist conformers of the trivinylmethyl ion were used in our calculations (see Table XII). Because the only observed data available are for the tri(2,2-dimethylvinyl)methyl ion, we also included it in our calculations.

In general, the VESCF method gave rather poor spectral results for carbonium ions (see tables). The discrepancies between the calculated and observed spectra may be in part due to our having assumed the carbon-carbon bond lengths of the ions to be 1.397 Å. However, a recent *ab initio* calculation[32] of the geometry of allyl ion indicates that the carbon-carbon bond lengths are 1.385, a value similar to the one we chose.

An important reason for the discrepancies between the calculated and observed spectra of the alkylated derivatives of simple carbonium ions (see Table XI) is that hyperconjugative effects certainly are more important in carbonium ions. Our calculations assume that the effect of an alkyl substituent is the same in the ion as it was in the neutral molecule. Because the hyperconjugation effectively extends the length of the conjugated system, it should lead to red shifts as observed. Hyperconjugative effects should be most important in small, highly allkylated ions, where the positive charge is concentrated on relatively few atoms. In larger ions the charge is spread over more atoms, and hyperconjugation becomes less important.

A comparison of the spectra of organoboron compounds

Table XII. Trivinylmethyl Ions

		Calculated			Observed[31,a,b]		
Ion	Twist, deg	λ, nm	E, eV	f	λ, nm	E, eV	Log ϵ
	0	369	3.36	0.32			
		368	3.37	0.32			
		228	5.44	0.30			
		227	5.46	0.31			
		224[c]	5.54	0.00			
	20	369	3.36	0.32			
		369	3.36	0.32			
		228	5.44	0.27			
		228	5.44	0.27			
		224[c]	5.54	0.01			
	50	352	3.52	0.35			
		351	3.53	0.35			
		242[c]	5.12	0.00			
		222	5.58	0.10			
		221	5.61	0.11			
	50	362	3.43	0.37	330	3.76	4.65
		362	3.43	0.37			
		233[c]	5.32	0.00			
		220	5.64	0.09			
		220	5.65	0.09			

[a] Corrected for H_2SO_4 solvent.[22] [b] Models suggest a twisting of 20-40° probably is present in this ion. [c] This band is due to the V_{14} transition and is shifted to the red as the vinyl groups are twisted, while the other transitions are shifted to the blue.

with those of the corresponding carbonium ions shows that, in general, the carbonium ions absorb at a significantly longer wavelength than do the boron compounds. The greatest part of this difference is doubtlessly due to the lower electronegativity of boron as compared with carbon, which causes a carbonium ion to accept a pair of electrons from a neighboring π-electron system more readily than boron. This results in the π-electron systems of carbonium ions being more extensively delocalized than those of organoboron compounds.

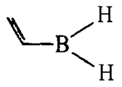
It is concluded that organoboron compounds have electronic properties which differ quite significantly from those of the corresponding carbonium ions. Any comparison between organoboron compounds and their corresponding carbonium ions must be made with caution.

Geometries of the Vinylboranes and Allyl Ions

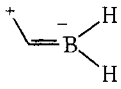
It has been assumed for some time that the vinylboranes are planar.[4-7] This assumption is based on the facts that the allyl cation is planar,[32-38] and the boron atom is isoelectronic with the carbonium ion. Our first attempts at calculating the electronic spectra of organoboranes were thus directed at a planar model of dimethylvinylborane.

Since we planned to deal with several rather large molecules, our early attempts at calculating the spectra of organoboranes were made using a self-consistent-field method and only singly excited configuration interaction.[39] Using this method, we encountered a great deal of difficulty when we attempted to parameterize the program so that the observed spectrum of vinylborane[4,5] would match our calculated spectrum. We therefore decided to give more serious consideration to the geometries of these compounds.

Upon examining the resonance structures which contribute to vinylborane, one finds a single Kekulé form (IXa), together with a charge-separated species (IXb). The latter is expected to be only a minor contributor. Because IXb is the resonance contributor which would hinder rotation about the boron-carbon bond one might not be surprised to find that this rotation requires relatively little energy. One would expect that the rotational barriers here should be reflected in the π-bond orders. If one compares the π-bond orders for ethylene, allyl ion, and for the B-C and C-C bonds of dimethylvinylborane, they have the following values: 1.00, 0.71, 0.35, and 0.94.



IXa



IXb

It was therefore decided to subject dimethylvinylborane and vinylborane as well as the dimethylallyl ion and allyl ion to CNDO[40] and INDO[16] conformational studies. The CNDO and INDO methods are both self-consistent-field, all-valence-electron calculations. In the CNDO scheme, differential overlap between any two atomic orbitals is neglected, while in the INDO method the differential overlap between two orbitals on one center is retained in all electronic integrals. The programs used are available from the Quantum Chemical Program Exchange[41] and were run on a CDC 6400 computer.

The first step in our study was to calculate the energies of vinylborane, dimethylvinylborane, and allyl ion, and the dimethylallyl ion with the vinyl group twisted with respect to the boron or positively charged carbon. This was done at 10° increments from 0 to 90°. The bond lengths chosen for this first phase of the study were 1.34 Å for the carbon-carbon double bond and 1.519 Å for the carbon-boron or the carbon-positively charged carbon bond. The C-H and B-H bond lengths were taken to be 1.08 Å, and the C-Me and B-Me bond lengths were assumed to be 1.56 Å.[42] In the final calculations, the C-Me bond length was reduced to 1.51 Å, which is a more realistic value. The bond angles were all taken to be normal sp^2 (120°) angles about boron and unsaturated carbon and sp^3 (109.5°) angles about saturated carbon.

According to these calculations, the allyl ion is planar, the dimethylallyl ion is twisted between 20 and 30°, and both vinylborane and dimethylvinylborane are twisted 90°. While the CNDO and INDO methods both gave the same qualitative results, the CNDO method predicts that the planar conformations are less stable relative to the 90° conformations than does the INDO method.

The next step was the minimization of the energies with respect to bond lengths. This was done with respect to both bonds of the unsaturated portions of the molecules, using the INDO method. The minimization was carried out on the planar and 90° forms of the allyl ion, vinylborane, and dimethylvinylborane. Since the dimethylallyl ion appears to be twisted slightly, and the angle of twist may vary with the bond lengths, this ion was minimized in its planar, 10, 20, 30, and 90° forms.

The minimizations were carried out by calculating the energy of a compound using three different bond lengths. It was assumed that bond length *vs.* energy is a parabolic function of the form

$$E = Ar^2 + Br + C$$

The resulting set of equations was solved for A, B, and C. The derivative dE/dr was taken and set equal to zero

$$dE/dr = 2Ar + B = 0$$

The bond length when the derivative is zero is the minimum energy bond length.

The same calculation was then carried out on the other bond of the unsaturated system, maintaining the first bond at its minimum energy length. The procedure was repeated until the bond lengths were consistent to within 0.007 Å (Table XIII).

In all cases except for the dimethylallyl ion, the minimum energy conformer is either planar or twisted 90°. The angle of twist in the minimum energy conformer of the dimethylallyl ion was calculated using the energies of the 10, 20, and 30° twisted forms. The energy *vs.* angle of twist was assumed to be approximately a parabolic function in this region. By solving a set of equations similar to those used for the bond lengths, the angle of twist corresponding to a minimum energy was found to be 30°. The rotational barriers obtained from these calculations may be found in Table XIV.

The rotational barriers of several substituted allyl ions have been determined through the use of low-temperature

Table XIII. Energies and Geometries (INDO) at Minimum Energy Bond Lengths

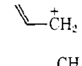
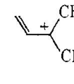
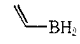
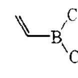
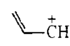
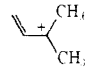
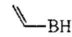
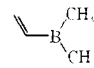
Compound	Twist, deg	R_{12}, Å	R_{23}, Å	E, hartrees
	0	1.369	1.369	−23.7294
	90	1.329	1.380	−23.6980
	0	1.355	1.418	−40.6822
	10	1.350	1.415	−40.6827
	20	1.351	1.413	−40.6838
	30	1.348	1.411	−40.6842
	90	1.331	1.415	−40.6777
	0	1.336	1.488	−21.0469
	90	1.327	1.480	−21.0498
	0	1.334	1.527	−37.9868
	90	1.328	1.512	−37.9959

Table XIV. Rotational Barriers of Allyl Ions and VinylboranesCalculated by INDO

Compd	Twist, deg	E, hartrees	ΔH^*, kcal/mol
	0 90	−23.7294 −23.6980	19.7
	30 90	−40.6842 −40.6777	4.1
	0 90	−21.0469 −21.0498	−1.8[a]
	0 90	−37.9868 −37.9959	−5.7[a]

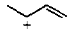
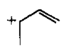
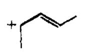
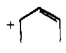
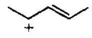
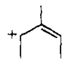
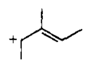
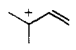
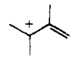
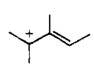
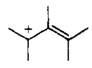
[a] A negative barrier indicates the perpendicular form is more stable than the planar form.

Table XV. Theoretical Evaluations of the Rotational Barrier of the Allyl Ion

ΔH^*, kcal/mol	Method	Ref
38	Dewar	36
29	NDDO	36
42	*Ab initio*	35
11	CNDO	43[a]
34.8	*Ab initio*	32[a]

[a] Energy minimized with respect to bond length.

Table XVI. Rotational Barriers of Allyl Cation and Methylated Derivatives

	a	b	c	Steric	$\Delta G^*_{\text{elect}}$	ΔG^*_{obs}	ΔG^*_{calc}
	1	0	0	0			27.9
	1	1	0	0			21.3
	1	1	0	1.6			19.7
	1	1	1	1.6	23.9	22.3	22.9
	1	1	1	6.0	24.7	18.7	18.5
	1	1	1	0			24.5
	1	1	1	6.0	24.1	18.1	18.5
	1	1	1	1.6	25.2	23.6	22.9
	1	2	0	1.6			13.1
	1	2	0	2.6	14.3	11.7	12.1
	1	2	1	2.6	18.4	15.8	15.3
	1	2	2	7.0	20.8	13.8	14.1

nmr spectroscopy.[34,38,43] Only the ΔG^* values are usually available.

The free energies of activation have also been determined by nmr.[43] In a few cases the ΔG^* and E_a values were obtained and are very similar, which means that the entropies of activation are quite low for this type of rotation.

It has been shown that adding a methyl group to the 2-position of the 1,3-dimethylallyl ion does little to change its free energy of isomerization.[43] Because of this and the fact that the rotational barrier of the 1,1,2-trimethylallyl ion has been found to be 11.7 kcal, it has been estimated that the rotational barrier of the 1,1-dimethylallyl ion should be 12.5–13.5 kcal/mol. If this is true, then our calculated rotational barrier is somewhat low.

No experimental value has been found for the rotational barrier of the allyl ion. There are, however, theoretical values which have been determined by several methods (Table XV).[32,33,36,44]

Although *ab initio* studies should give the best theoretical evaluation of the rotational barrier of the allyl ion, the study by Peyerimhoff and Buenker[33] did not minimize the energy with respect to bond length. An *ab initio* study done by Pople[32] using the 6-31G (see footnote *a*, Table XV) basis set in which the energy was minimized with respect to geometry indicates a rotational barrier of 34.8 kcal/mol for the allyl ion. This value seems somewhat high in light of the available experimental evidence regarding substituted allyl ions (see below).[34,38,42] Solvation and ion pairing would be expected to stabilize the transition state (where the charge is more localized) more than the ground state, which may account for some of the discrepancy.

The available rotational barriers for substituted allyl ions are summarized in Table XVI. We can use these numbers to try to estimate by extrapolation what the barrier would be for the parent allyl ion. Schleyer has previously given attention to this problem, and has noted that the presence of a methyl group or a 1,1-dimethyl grouping leads to a lowering of the rotational barrier. This is because the positive charge is largely localized on one center when the group has twisted 90°, and one or more methyl groups on that center will stabilize the charge more here than in the delocalized planar form. Thermodynamic arguments were used to deduce the stabilization obtained by attaching a methyl group to a carbonium center, and it was concluded that the addition of each methyl stabilizes the twisted ion by 12–14 kcal/mol more than the planar allyl ion. Using this approximation Schleyer deduced that the rotational barrier for the parent allyl ion will be 38–43 kcal/mol.[37] A good *ab initio* result, with geometry optimization, gives this result as 34.8 kcal/mol.[32] Since inclusion of configuration interaction in the calculation would be expected to lower the *ab initio* energy of the twisted form of the allyl ion more than it lowers the energy of the planar form, this value should perhaps best be looked upon as an approximate upper limit for the rotational barrier.

It is possible to deduce the rotational barrier of allyl ion by another approximate method. The approach is as follows. We will call the rotational barrier in the parent allyl ion *a*. Each methyl added to the 1 position is assumed to lower the energy by an increment *b*. (This would be the quantity for which Schleyer finds the value −12 to −14 kcal/mol). In addition, each methyl attached at the 3 position is assumed to change the rotational barrier by an increment *c*. One might guess that the value for *c* would most likely be small and positive. The reasoning is that adding the methyls to the other end tends to push the electron density back toward the C_1–C_2 bond, raising the bond order and hence the rotational barrier.

The observed rotational barriers are a combination of the electronic effects (*a*, *b*, and *c*, above), together with the steric effects present. Schleyer suggests[38] that the methyl-methyl interaction like in the last ion in Table XVI amounts to about 6.0 kcal/mol. Similarly, the methyl-hydrogen interaction in the third ion amounts to about 1.6 kcal/mol.[38,45] Additionally, the 1,2-dimethyl interaction as in the last ion amounts to about 1.0 kcal/mol. All of these interactions are relieved in going to the rotational energy maximum, and hence they serve to lower the observed barrier. From the observed values for ΔG^*, after subtracting out the steric effects, we arrive at the numbers listed in Table XVI as $\Delta G^*_{\mathrm{elect}}$; these are the components of the barrier attributed to electronic effects. One now has seven simultaneous equations, containing three unknowns, and these were solved by the method of least squares. The values obtained were $a = 27.9$, $b = -6.6$, and $c = +3.2$.

Having the values for a, b, and c, and knowing the steric effects, one can calculate the rotational barrier for each of the ions in Table XVI. Where experimental values are available, the agreement is good (the experimental values are only claimed to be ±1 kcal/mol). For the cases where no experimental values exist, the calculated values constitute predictions. The values found for a and b give the value for the rotational barrier of the parent allyl ion as 27.9 kcal/mol. From the scatter in the experimental values, it is estimated that this number is accurate to within 3 or 4 kcal/mol. This is consistent with the *ab initio* value, and in reasonable agreement with the value arrived at by Schleyer. The INDO value of 19.7 kcal/mol seems definitely too low, although not alarmingly so. The value calculated by molecular mechanics (1971 force field) is 26.3 kcal/mol.

Thus it would seem that the rotational barriers calculated by the INDO method for both the allyl and dimethylallyl ions are about 6–10 kcal too low. This error suggests that a systematic error in the INDO calculations is present, which is likely to be carried over from the allyl ions to the vinyl boranes.

It has been pointed out that CNDO type calculations tend to give low values for the resonance stabilization of the allyl ion.[43] In addition the method has been shown to give unsatisfactory results for several unsaturated molecules which have low rotational barriers.[46,47] Because of the similarities between the CNDO and INDO methods, it would not be surprising to encounter this difficulty in INDO calculations. However, because of the larger number of integrals retained, the INDO method might be expected to give better results.

There are no experimental data available on the rotational barriers of vinylborane and dimethylvinylborane. The results of our INDO calculations show both of these to be more stable in the 90° twist form, vinylborane by 1.8 kcal/mol and dimethylvinylborane by 5.7 kcal/mol.

It was obvious that if the systematic error in the allyl ions is carried over to the vinylboranes, it is possible that both vinylborane and dimethylvinylborane are more stable in the planar form. The results of our VESCF-CI calculations indicate that this is so.

An *ab initio* study of vinylborane was carried out in our laboratory using the minimum energy (by INDO) bond lengths. The details of the calculation followed previously published procedures.[48] Such calculations avoid many of the simplifications and approximations of the INDO method, and the results should be more reliable. These calculations gave a rotational barrier of 16.2 kcal/mol favoring the planar conformer.

After completion of this work, a paper by Williams and Streitwieser[49] appeared which gave the results of an *ab initio* calculation using the STO-3G basis set of Pople, for both the planar and 90° rotated forms of vinylborane. The bond lengths used by these workers differ slightly from ours. They found a rotational barrier of 8.8 kcal/mol, favoring the planar structure. We showed earlier that our basis set not only required less computer time but also gave a lower total energy than the STO-3G basis.[49] Accordingly, our total energy for the planar form (−102.61065 hartrees) is considerably better than that of Streitwieser (−102.0361 hartrees). This is, of course, no guarantee that our rotational barrier is better.

Since some of the results which have been discussed are contradictory and may confuse the issue, it would be best to conclude our discussion by reiterating what we believe to be its important points. First, we conclude that while allyl ion is planar, with a substantial rotational barrier (calculated 19.7 kcal/mol by INDO, most probable value about 28 kcal/mol), 1,1-dimethylallyl ion definitely has a much smaller rotational barrier (calculated 4.1 kcal/mol by INDO, most probable value about 13 kcal/mol) and may be twisted some (probably less than 30°) in the ground state.

Vinylborane is also planar, with a much smaller rotational barrier than that found for allyl ion (8.8 and 16.2 kcal/mol by *ab initio*). Dimethylvinylborane, methyldivinylborane, and trivinylborane are probably not planar, with the vinyl groups in each case being twisted from the plane by perhaps 30° or so (rotational barriers may be 4 kcal/mol or so).

The VESCF method reproduced reasonably well the electronic spectra of the planar vinyl boron compounds. The same method does not reproduce well the spectra of the carbonium ions, where it is indicative of trends, but suffers from a large systematic error. The main reason for this error is believed to be hyperconjugation, which is not included or allowed for in the calculations. While this interaction is minor in the boron compounds, it is serious in the carbonium ions.

References and Notes

(1) For paper XXXII, see N. L. Allinger, J. T. Sprague, and T. Liljefors, *J. Amer. Chem. Soc.*, **96**, 5100 (1974).
(2) Supported by Grant GP-15263 from the National Science Foundation.
(3) (a) Abstracted from the Ph.D. dissertation submitted by J.S. to Wayne State Univertisy, Nov 27, 1973.
(4) C. D. Good and D. M. Ritter, *J. Amer. Chem. Soc.*, **84**, 1162 (1962).
(5) D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, **4**, 69 (1966).
(6) D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, **4**, 352 (1966).
(7) D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, **5**, 11 (1966).
(8) D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, **5**, 215 (1966).
(9) D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, **5**, 222 (1966).
(10) D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, **8**, 138 (1967).
(11) R. Zahradnik, J. Pancir, and A. Krohn, *Collect. Czech. Chem. Commun.*, **34**, 2831 (1969).
(12) J. Michl, R. Zahradnik, and P. Hochmann, *J. Phys. Chem.*, **70**, 1732 (1966).
(13) N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, **87**, 2081 (1965).
(14) N. L. Allinger, J. C. Tai, and T. W. Stuart, *Theor. Chim. Acta*, **8**, 101 (1967).
(15) J. C. Tai and N. L. Allinger, *Theor. Chim. Acta*, **12**, 261 (1969).
(16) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967).
(17) The program was a version made available to us by Professors I. G. Csizmadia and S. Wolfe.
(18) R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).
(19) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).
(20) J. C. Tai and N. L. Allinger, *Theor. Chim. Acta*, **15**, 133 (1969).
(21) R. Koster, private communication, June 9, 1971.
(22) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).
(23) N. L. Allinger and J. C. Graham, *J. Amer. Chem. Soc.*, **95**, 2523 (1973).
(24) R. Koster, G. Benedikt, W. Fenzl, and K. Reinert, *Justus Liebigs Ann. Chem.*, **702**, 197 (1967).
(25) R. Koster and G. Benedikt, *Angew. Chem.*, **75**, 419 (1963).
(26) R. Koster, G. Benedikt, W. Larbig, K. Reinert, and G. Rotermund, *Angew. Chem.*, **75**, 1079 (1963).
(27) E. E. van Tamelen, G. Brieger, and K. G. Untch, *Tetrahedron Lett.*, 14 (1960).
(28) P. Jutzi, *J. Organometal. Chem.*, **19**, P1 (1969).
(29) R. Pettit, *J. Amer. Chem. Soc.*, **82**, 1972 (1960).
(30) N. C. Deno and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **86**, 1871 (1964).
(31) T. S. Sorenson, *Can. J. Chem.*, **43**, 2744 (1965).
(32) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 6531 (1973).
(33) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **51**, 2528 (1969).
(34) N. C. Deno, R. C. Haddon, and E. N. Nowak, J. *Amer. Chem. Soc.*, **92**, 6691 (1970).
(35) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **90**, 6082 (1968).
(36) N. C. Baird, *Tetrahedron*, **28**, 2355 (1972).
(37) V. Buss, R. Gleiter, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3927 (1971).
(38) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).
(39) F. A. Van-Catledge and N. L. Allinger, *J. Amer. Chem. Soc.*, **91**, 2582 (1969).
(40) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

(41) QCPE 91, CNDO/2, by G. A. Segal, and QCPE 141, CNINDO, by P. A. Dobosh.

(42) "Tables of Interatomic Distances and Configurations in Molecular and Ions," *Chem. Soc., Spec. Publ., Suppl.*, **No. 18** (1965).

(43) J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, **92**, 4025 (1970).

(44) H. Kollmar and H. O. Smith, *Theor. Chim. Acta*, **20**, 65 (1971).

(45) J. Packer, J. Vaughan, and E. Wong, *J. Amer. Chem. Soc.*, **80**, 905 (1958).

(46) O. Gropen and H. M. Seip, *Chem. Phys. Lett.*, **11**, 445 (1971).

(47) D. Perahia and A. Pullman, *Chem. Phys. Lett.*, **19**, 73 (1973).

(48) N. L. Allinger and M. J. Hickey, *Tetrahedron*, **28**, 2157 (1972).

(49) J. E. Williams, Jr., and A. Streitwieser, Jr., *Tetrahedron Lett.*, 5041 (1973).

Temperature Variation of the H_R Acidity Function in Aqueous Sulfuric Acid[1]

M. J. Cook, N. L. Dassanayake, C. D. Johnson,* A. R. Katritzky,* and T. W. Toone

Contribution from the School of Chemical Sciences, University of East Anglia, Norwich, England.

Received October 25, 1973

Abstract: The variation of the H_R acidity function with temperature has been defined by the extent of ionization of triarylcarbinol indicators at temperatures of 25, 40, 60, 80, and 90°. The correlation of H_R and temperature is expressed by an empirical equation which should have important applications in mechanistic investigation. A linear relationship is found between the pK_{R^+} values at 25° and ΔH_{25}.

Previously, we have reported investigations on the variation of H_0 in aqueous sulfuric acid with temperature[2] and the correlation of the pK_a values of the nitroaniline indicators with ΔH_{25} in a linear free energy-enthalpy correlation.[3] In continuation of these studies, we have now obtained data on the temperature dependency of the H_R scale in aqueous sulfuric acid. This variation had previously been investigated by Arnett and Bushick;[4] however, their results extended only to 45°. They concluded that the H_R scale becomes steadily more negative with increasing temperature for solutions above 65% but that it behaved erratically and discontinuously in lower concentrations. For example H_R for 20% H_2SO_4 was reported as -1.69 (0°), -1.70 (15°), -1.33 (30°), and -1.49 (45°). These conclusions appeared suspect for at least two reasons: (i) there is no analogy with the temperature variation of the H_0 scale,[2] the work of Gel'bshtein[5] being incorrect, and (ii), although the erratic behavior made it difficult to interpolate for 25°, if this is done approximately then significant discrepancies are found with the results reported by Deno[6] for the single temperature of 25°. Values of H_R at elevated temperatures would be most useful for the elucidation of carbonium ion type reactions carried out in aqueous sulfuric acid above room temperature. We ourselves are particularly interested in the variation of nitronium ion concentration with temperature, for more explicit elucidation of nitration studies in heteroaromatic compounds,[7] following Moodie and Schofield's demonstration[8] that the acidity variation of the rate constants for such nitrations are given by eq 1. Unfortunately,

$$\log k_2 = -(H_R + \log a_{H_2O}) + \text{constant} \tag{1}$$

extrapolation of Arnett's H_R scale to higher temperatures is impossible because of the discontinuous variation reported (see figure quoted above for 20% H_2SO_4). It was therefore essential to reinvestigate the temperature variation of H_R. Our studies have now shown that the earlier conclusions[4] are incorrect; the H_R scale is proved to be a well-behaved continuous function of temperature and does indeed show considerable analogy to the temperature dependence of the H_0 scale.

Throughout these investigations, the experimental techniques and methods of calculation outlined in the previous paper[2] were employed. No modification or extension was required. Random checks on instrument reproducibility using the results of the initial paper entirely confirmed their accuracy.

Errors. Correlation coefficients and standard deviations shown in the tables were calculated by standard formulas.[9,10]

Experimental Section

Materials. Sulfuric and hydrochloric acids were Analar grade reagents. Water was purified as previously.[2]

The triphenylmethanol indicators used for the determination were 4,4′,4″-trimethoxy, 4,4′-dimethoxy (as chloride) (solutions made up with the chloride), 4-methoxy-4′-methyl, 4-methoxy (as chloride), 4,4′,4″-trimethyl, 4-methyl, unsubstituted, 4,4′,4″-trichloro, 4-nitro, 3,3′,3″-trichloro (as chloride), 4,4′-dinitro (as chloride), 4,4′,4″-tris(trimethylammonium) (as perchlorate), and 4,4′,4″-trinitro. These were prepared and purified by standard procedures. Their analyses corresponded with their molecular formulas and their melting points agreed with previous workers.[9] Synthetic difficulties often encountered in this field were found here—intractable gum and tar formation from which products crystallized reluctantly in low yield. It has been suggested[9a] that the trinitrocarbinol is unstable; our observations confirmed this and showed that it is also light sensitive. Stock solutions of this compound were therefore kept in the dark at −80°. The measurements on the indicator showed that the results were accurate up to and at 60°, but above this, at 80°, they were less reliable and impossible to obtain at 90°, because decomposition had become so rapid. Extensive checks on all the other indicators showed them to be stable in all strengths of sulfuric acid at 90°.

Methods. The preparation of solutions and their spectrophotometric determination were carried out precisely as described previously.[2,9] Medium effects on uv spectral characteristics were in all cases negligible.

Results. The pK_{R^+} values for the anchoring indicator, 4,4′,4″-trimethoxytriphenylcarbinol were measured in aqueous HCl. They are recorded in Table I. Table II gives indicator data. Measurements of I ($[R^+]/[ROH]$) were made for the whole indicator series, in aqueous sulfuric acid, at temperatures of 25, 40, 60, 80, and 90°. Readings for each indicator were made at two or three different wavelengths, and each set of determinations was duplicated. The averaged values of log I were then plotted on large scale graph paper and values read off at close intervals of acidity as given in Table III, which also contains the complete set of data for the first two indicators of the series, from which the accuracy and repro-