

calculations were directed at an exploration of the possibility that  $\nu_{10}$  or  $\nu_{11}$  of the *cis* isomer was to be found at a significantly different frequency from that predicted by the zero-order calculations. It seems, however, that a splitting of less than  $60 \text{ cm.}^{-1}$  is to be expected between this pair of frequencies even though the fundamentals are members of the same symmetry class. This result provided further support for the assignments discussed above for  $\nu_{10}$  and  $\nu_{11}$ .

Diagrams of the atom displacements in the normal coordinates for the planar modes, as derived from the zero-order calculations, are given in ref. 7.

*cis-trans Stability.* Although *cis*-CFHCFH<sup>15</sup> and *cis*-CCIHCCI<sup>16</sup> have been found to be relatively more stable than the corresponding *trans* isomers, equilibrium data are not as yet available for the CF-CICFCl isomerization. The one qualitative attempt,

(15) N. C. Craig and E. A. Entemann, *J. Am. Chem. Soc.*, **83**, 3047 (1961).

(16) R. E. Wood and D. P. Stevenson, *ibid.*, **63**, 1650 (1941).

mentioned above, to obtain a significant change in a mixture of nearly equal amount of *cis-trans* isomers produced little change. Our calculation of statistical thermodynamic functions for both isomers gave results little different from those previously reported by Mann and Plyler.<sup>4</sup> For the *cis* to *trans* reaction  $\Delta S^\circ$  is  $0.20 \text{ cal./mole } ^\circ\text{K.}$  throughout the temperature range 200 to  $1500^\circ\text{K.}$  We must therefore tentatively conclude that *cis*- and *trans*-CFCICFCl are about equally stable and the enthalpy change for this isomerization is practically zero.

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## Perturbation of Singlet-Triplet Transition Energies<sup>1</sup>

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Contribution from the Department of Chemistry of the University of Washington, Seattle, Washington. Received April 5, 1965

*The first singlet-triplet transition energies for various substituted butadienes have been measured. A red shift found consistently going with 1- or 1,4-substitution but not consistently with 2- or 2,3-substitution is taken as evidence of hyperconjugation. A major conflicting possibility for explaining spectral shifts is internal dispersion forces. The dispersion force effect here is minimized because the transition studied has almost zero transition moment. A valence bond theory of perturbation of  $\pi$ -electron systems is developed and used to explain the results. A formula for free valence or residual affinity can be adapted from another, complementary, expression which automatically appears in the theory. It is judged more approximate to emphasize the complementary expression, which is called fixed valence. The fixed valence for a site is the sum of the Dirac-Penney bond orders of all bonds in the unperturbed molecule involving that site. The perturbation energy for radical attack is found to be inversely proportional to the fixed valence.*

### Introduction

Hyperconjugation in the original sense<sup>3,4</sup> is almost certainly to be reckoned with, as can be inferred from the magnitudes of relevant overlap integrals or from

(1) This research was supported in part by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research.

(2) Department of Chemistry, University of Oregon, Eugene, Ore.

(3) R. S. Mulliken, C. A. Rieke, and W. A. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(4) See also G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 149.

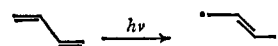
wave functions deduced from certain e.s.r. results. Thus to look for a direct energetic effect attributable to hyperconjugation may be somewhat redundant, but certainly not entirely so. Much of the supposed experimental evidence for hyperconjugation has been questioned: small effects can so easily have several plausible causes.

Evidence from spectral shifts would seem to be pertinent. The characteristic dye-like ions



have absorptions which shift markedly as the nitrogen atoms are alkylated. This could be caused by hyperconjugation, but also by changes in the effective ionization potential of nitrogen on alkylation (which changes are partly explicable through hyperconjugation),<sup>5</sup> or by internal dispersion forces; so an examination of spectral shifts for dyes may not be especially fruitful.

Here we shall be looking for hyperconjugation by examining spectral shifts<sup>6</sup> for a singlet-triplet transition: the first singlet-triplet transition in substituted butadienes. The transition may be represented

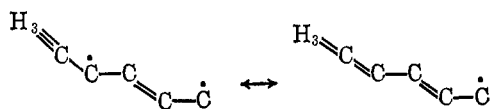


In the excited state there are electrons anti-paired but essentially non-interacting at the 1- and 4-positions. Thus changing hydrogen for methyl in the 1-position,

(5) M. Goeppert-Mayer and K. J. McCallum, *Rev. Mod. Phys.*, **14**, 248 (1942), explain spectral shifts in the Wurster's salts on this basis.

(6) Measurements were made by the Evans technique: D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

say, could cause a preferential stabilization of the excited state (with red shift) mainly attributable to hyperconjugation in the original sense.



No comparable effect would be expected with substitution of a methyl in the 2-position.

Referring to the competing effects expected in the case of spectral shifts for dyes, there seems to be no reason for expecting appreciable changes in effective ionization potential of the carbons on alkylation beyond what could be attributed to hyperconjugation. Moreover, internal dispersion forces are expected to have a minimal effect here. The reason is that for these forces to cause a red shift, typically an excited state is considered to have mixed with it an excited state not much higher in energy in which a perturbing group is excited and the parent substance has returned to the ground state. The mixing is governed by a product of transition moments, for the parent substance and for the perturber, divided by the *difference* in excitation energies; but the transition moment is essentially zero for a singlet-triplet transition. True, for this case, there is mixing with states in which the perturber is excited and the triplet is also excited, but these are expected not to contribute greatly owing to the *additive* appearance of two excitations in the energy denominator.

For interpretation of the measured spectral shifts, a valence bond perturbation method (developed below) will be used. Through the use of pairing theory one is able to deal with singlets and triplets on an equal basis. The perturbation energy turns out to be related to a parameter of the unsubstituted molecule called the *fixed valence*.<sup>7</sup>

### Experimental Section

The spectra were taken using a commercial<sup>8</sup> high-pressure absorption cell with a 5-cm. light path. The cell was fashioned so as to fit directly into the compartment of a Cary 14 recording spectrophotometer.

A solution sample was placed in the cell and the spectrum taken. Oxygen was then admitted and the spectrum again recorded. The spectrum was retaken after removal of the oxygen to check for irreversibly induced absorption bands. The pressure of oxygen used was in the range of 2000 to 2300 p.s.i. The butadiene spectrum was taken in the gas phase also using the Cary 14 and in chloroform; all others were taken in chloroform solution.

Most of the compounds were obtained commercially and were routinely distilled prior to use.

### Results

In general, the 0-0 band width was about 15-20  $m\mu$ . The 0-0 band generally appeared on the tail of a more intense band (judged to be a charge-transfer band connected with the oxygen perturbation) and could not be located as precisely as for butadiene. As the number of

(7) Fixed valence is closely related to free valence or *residual affinity* (W. Moffitt, *Trans. Faraday Soc.*, **45**, 316, 373 (1949)) though in a complementary fashion. Earlier work with residual affinity had not established the connection with the perturbation energy.

(8) Supplied by the American Instrument Co., Silver Spring, Md.

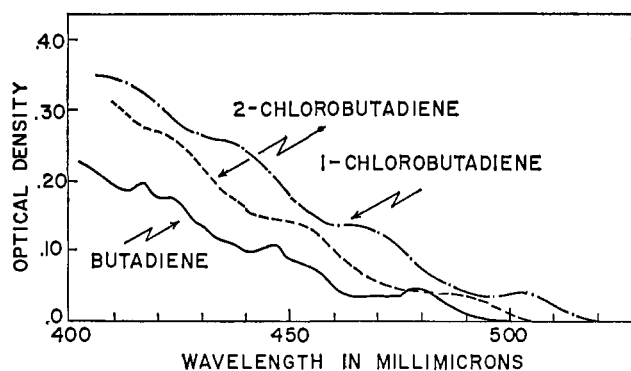


Figure 1. Typical singlet-triplet absorptions of dienes. Spectra were recorded in chloroform (0.6 *M*) with a path length of 5 cm. and in the presence of oxygen at around 2300 p.s.i. The molar extinctions are *ca.*  $10^{-2}$ .

substituents was increased, the intense band shifted to longer wave lengths and could completely screen the singlet-triplet vibrational structure (e.g., in 2,5-dimethyl-2,4-hexadiene).

Typical spectra are shown in Figure 1. The locations of the 0-0 bands for the various compounds studied are given in Table I. Note that there is a red

Table I. Locations of 0-0 Bands of the N-T<sub>1</sub> Transition in Substituted Butadienes<sup>a</sup>

Butadiene	478
Isoprene	476
2,3-Dimethylbutadiene	473
1,3-Pentadiene <sup>b</sup>	483
2,4-Hexadiene	487
Chloroprene	488
1-Chlorobutadiene	503
2,3-Dichlorobutadiene	486
1-Methoxybutadiene	505
2,4-Hexadien-1-ol	481
Bis(2,2'-dibutadiene)	493
Cyclopentadiene	492
1,3-Cyclohexadiene <sup>c</sup>	545

<sup>a</sup> All spectra (in  $m\mu$ ) were taken in chloroform. The 0-0 band of butadiene comes at 478  $m\mu$  also in the vapor. <sup>b</sup> *trans*. There are bands for *cis* at 490 and 499  $m\mu$ . <sup>c</sup> Evans<sup>6</sup> reports a value of 535  $m\mu$ . We have checked our value but have not come to any conclusion about the discrepancy.

shift accompanying 1- or 1,4-substitution (butadiene to *trans*-1,3-pentadiene, +5  $m\mu$ ; to 2,4-hexadiene, +9  $m\mu$ ) and a blue shift for 2- or 2,3-substitution (butadiene to isoprene, -2  $m\mu$ ; to 2,3-dimethylbutadiene, -5  $m\mu$ ). Similar comparisons may be made. Thus chloroprene shows a red shift, but 1-chlorobutadiene shows a considerably greater red shift. Again, the 2,3-dichlorobutadiene band lies a bit to the blue of chloroprene. The five-membered ring compound, cyclopentadiene, absorbs (492  $m\mu$ ) close to where *cis*-1,3-pentadiene absorbs (490-499  $m\mu$ ).

For the six-membered ring, 1,3-cyclohexadiene, absorption comes considerably to the red (545  $m\mu$ ). Such an effect has been noticed by Price and Walsh<sup>9</sup> looking at the N-V<sub>1</sub> transition (232  $m\mu$  for the five- and 248  $m\mu$  for the six-membered ring compound)

(9) W. C. Price and A. D. Walsh, *Proc. Roy. Soc. (London)*, **A179**, 201 (1941). Also, tangible departure from planarity in the ground state has been observed: S. S. Butcher, *J. Chem. Phys.*, **42**, 1830 (1965).

and correlated by them with the abnormally low value of the ionization potential found for the six-membered ring compound. Presumably strain in the ground state is relieved on ionization and excitation to the  $V_1$  state, and from the result here also on excitation to the  $T_1$  state.

The value featured in Table I for 1,3-pentadiene is for *trans*. The spectrum of pure *cis* has been examined and has an odd appearance which suggests two 0-0 bands, at 490 and 499  $m\mu$ . These could be for *s-trans* and *s-cis* conformational isomers.

It is apparent that steric effects can be even more pronounced than effects attributable to hyperconjugation. Nevertheless, it seems reasonable to conclude that the entries in Table I as a whole show a red shift accompanying substitution in the 1-position which shift is unmatched by a comparable one going with substitution in the 2-position. Further argument to the effect that this could well be caused by hyperconjugation will be delayed until after the valence-bond perturbation theory is presented.

### Theory

The  $\pi$ -electron Hamiltonian for the unperturbed system is taken as a sum of terms over all pairs of adjacent orbitals.

$$H_0 = -B \sum_{m < n} \mathcal{R}_{mn}$$

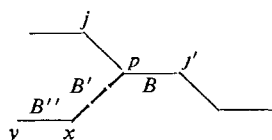
Here  $B$  is the "bond integral" or exchange integral and  $\mathcal{R}_{mn}$  is an operator which exchanges spins going with orbitals  $m$  and  $n$ .<sup>10</sup> All bonding interactions are assumed equivalent. The site which is being perturbed, e.g., substitution of an adjacent hydrogen by a methyl, will be called the  $p$ th, and we can rewrite  $H_0$  to feature this site.

$$H_0 = -B \left( \sum_j \mathcal{R}_{pj} + \text{other terms} \right)$$

The explicit sum is over all orbitals adjacent to and capable of bonding with the  $p$ th in the unperturbed molecule. The perturbation is taken as

$$H_1 = -B' \mathcal{R}_{px} - B'' \mathcal{R}_{xy}$$

where  $B'$  is the exchange integral connecting the  $p$ th orbital with the perturbing orbital (and may be considered to be small) and  $B''$  is the exchange integral connecting the  $x$ th orbital with a  $y$ th. ( $B''$  would be expected to be about the same as  $B$ .) An electron in the  $x$ th orbital would be perfectly paired with one in the  $y$ th when  $B' = 0$ . The various quantities are summarized in the diagram



The unperturbed wave function,  $|\psi_0\rangle$ , will be taken as one of the exact valence bond functions for  $H_0$ , denoted  $\varphi$ , multiplied by the function for perfectly paired spin orbitals  $X_x$  and  $X_y$

$$|\psi_0\rangle = N(1 - \mathcal{R}_{xy})X_x X_y \varphi$$

(10) W. T. Simpson, "Theories of Electrons in Molecules," Prentice-Hall, Inc., New York, N. Y., 1961, p. 97.

( $N$  is a normalizing factor.) The perturbation method is based on a variation calculation in which  $X_x$  is mixed with a spin orbital at  $p$ . The many-electron function to be mixed with  $|\psi_0\rangle$  may then be taken<sup>11</sup> as

$$|\psi_1\rangle = \mathcal{R}_{xp} |\psi_0\rangle$$

The apparatus of the linear variation method will take care of phase and nonorthogonality. Also, it can be shown that  $|\psi_1\rangle$  has the same multiplicity as  $|\psi_0\rangle$ .

To set up the secular equation we first consider  $\langle \psi_0 | H | \psi_0 \rangle$  or

$$\begin{aligned} \langle \psi_0 | H_0 + H_1 | \psi_0 \rangle &= E + \langle \psi_0 | H_1 | \psi_0 \rangle = \\ &E + B'' - B' \langle \psi_0 | \mathcal{R}_{px} | \psi_0 \rangle = \\ &E + B'' - \frac{B'}{2} \end{aligned}$$

Here  $E$  is, so to speak, the exact energy of the unperturbed system and  $B'' - \frac{1}{2}B$  is the  $xy$  bond energy minus the exchange repulsion between an electron in  $X_x$  and one in  $X_p$ , each being always paired or anti-paired elsewhere. The  $xy$  bond is included in  $H_1$  so that  $B''$  will appear explicitly, rather than in  $E$ .

The off-diagonal element  $\langle \psi_1 | H | \psi_0 \rangle$  may be written

$$\begin{aligned} \langle \psi_0 | \mathcal{R}_{px} H_0 + \mathcal{R}_{px} H_1 | \psi_0 \rangle &= \\ E \langle \psi_0 | \mathcal{R}_{px} | \psi_0 \rangle + \langle \psi_0 | \mathcal{R}_{px} H_1 | \psi_0 \rangle &= \\ \frac{E}{2} - B' - B'' \langle \psi_0 | \mathcal{R}_{px} \mathcal{R}_{xy} | \psi_0 \rangle &= \frac{E}{2} - B' + \frac{B''}{2} \end{aligned}$$

Here we have used  $H_0 |\psi_0\rangle = E |\psi_0\rangle$ ,  $\langle \psi_0 | \mathcal{R}_{px} | \psi_0 \rangle = \frac{1}{2}$ ,  $\mathcal{R}_{px}^2 = 1$ , and  $\langle \psi_0 | \mathcal{R}_{xy} | \psi_0 \rangle = -\langle \psi_0 | \psi_0 \rangle$ . The nonorthogonality integral  $\langle \psi_1 | \psi_0 \rangle$  is  $\frac{1}{2}$  and the integral  $\langle \psi_1 | \psi_1 \rangle$  is 1.

This leaves the integral  $\langle \psi_1 | H | \psi_1 \rangle$ , which is the interesting one. First there is the part

$$\begin{aligned} \langle \psi_0 | \mathcal{R}_{px} H_0 \mathcal{R}_{px} | \psi_0 \rangle &= \\ -B \langle \psi_0 | \mathcal{R}_{px} \left( \sum_j \mathcal{R}_{pj} \right) \mathcal{R}_{px} + \mathcal{R}_{px} (\text{other terms}) \mathcal{R}_{px} | \psi_0 \rangle &= \\ -B \langle \psi_0 | \sum_j \mathcal{R}_{xj} + (\text{other terms}) | \psi_0 \rangle \end{aligned}$$

Here we have used the theorem

$$\mathcal{R}_{ab} \mathcal{R}_{bc} \mathcal{R}_{ab} = \mathcal{R}_{ac}$$

and have commuted  $\mathcal{R}_{px}$  past the other terms (terms connecting the sites not involving  $p$ ). Now we use the fact that spin orbitals  $X_x$  and  $X_j$  are each paired or anti-paired elsewhere, so that  $\langle \psi_0 | \sum_j \mathcal{R}_{xj} | \psi_0 \rangle = \langle \psi_0 | \sum_j \frac{1}{2} | \psi_0 \rangle$  where the sum is over the orbitals in the unperturbed system adjacent to  $p$ . We also add and subtract  $B \sum_j \mathcal{R}_{pj}$ . Then

$$\langle \psi_1 | H_0 | \psi_1 \rangle = E + B \langle \psi_0 | \sum_j (\mathcal{R}_{pj} - \frac{1}{2}) | \psi_0 \rangle$$

The second part of the matrix element is

$$\begin{aligned} \langle \psi_1 | H_1 | \psi_1 \rangle &= \\ -B' \langle \psi_0 | \mathcal{R}_{px} \mathcal{R}_{px} \mathcal{R}_{px} | \psi_0 \rangle - B'' \langle \psi_0 | \mathcal{R}_{px} \mathcal{R}_{xy} \mathcal{R}_{px} | \psi_0 \rangle &= \\ -\frac{B'}{2} - \frac{B''}{2} \end{aligned}$$

(11) A function resembling this one has been used by Murrell in an investigation of the enhancement of S-T absorption by  $O_2$ : J. N. Murrell, *Mol. Phys.*, 3, 319 (1960).

and the secular equation becomes

$$\begin{vmatrix} E - \frac{B'}{2} + B'' - \lambda & \frac{E}{2} + \frac{B''}{2} - B' - \frac{\lambda}{2} \\ E + B \langle \psi_0 | \sum_j (R_{pj} - 1/2) | \psi_0 \rangle - \frac{B'}{2} - \frac{B''}{2} - \lambda & \end{vmatrix} = 0$$

Now

$$-^{2/3} \langle \psi_0 | (R_{pj} - 1/2) | \psi_0 \rangle$$

is the Dirac-Penney bond order between sites  $p$  and  $j^{12}$  so that we are dealing with the sum of bond orders from the  $p$ th site to all adjacent sites in the unperturbed molecule. Let us write the sum of Dirac-Penney bond orders as  $V_p$ . Then

$$\langle \psi_0 | \sum_j (R_{pj} - 1/2) | \psi_0 \rangle = -^{3/2} V_p$$

and the secular equation now is seen to involve  $V_p$ . We make the further abbreviation

$$-\mu = E - \frac{B'}{2} + B'' - \lambda$$

which makes  $\mu$  the perturbation energy, and the secular equation takes the final form

$$\begin{vmatrix} -\mu & -^{3/4} B' - \mu/2 \\ -^{3/2} (B'' + V_p B) - \mu & \end{vmatrix} = 0$$

If we wish to consider the perturbation accompanying radical attack, we can at this point set  $B'' = 0$  (and  $-\mu = E - (B'/2) - \lambda$ ).<sup>13</sup>

The lowest root of the secular equation, to the second order in  $B'$ , is

$$\mu_p \approx \frac{3}{8} \frac{(B')^2}{B'' + V_p B}$$

The residual affinity, previously defined,<sup>7</sup> is

$$f_p = 1 - V_p$$

The perturbation energy (units of  $B'$ ) for radical attack ( $B'' = 0$ ) may now be written as involving  $f_p$

$$\frac{\mu_p}{B'} \approx \frac{3}{8} \left( \frac{B'}{B} \right) \frac{1}{V_p} = \frac{3}{8} \left( \frac{B'}{B} \right) \frac{1}{1 - f_p} \sim \frac{3}{8} \left( \frac{B'}{B} \right) (1 + f_p)$$

Considering the exceptional nature of the radical-attack case, and the fact that  $V_p$  occurs in the denominator in the energy expression generally, but not always standing by itself, one gets the idea that it would be better to think of  $V_p$  as fundamental. Instead of thinking of a perturbation proportional to free valence, one would think of a perturbation decreased by and sometimes inversely proportional to  $V_p$ . A name for  $V_p$ , the sum of Dirac-Penney bond orders over all bonds in the unperturbed molecule to the  $p$ th site, is *fixed valence*.<sup>14</sup>

(12) W. G. Penney, *Proc. Roy. Soc. (London)*, **A158**, 306 (1937).

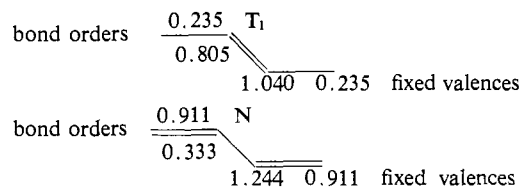
(13) Radical attack on a triplet can give a doublet or a quartet. Further consideration shows that in this way we automatically deal with the doublet.

(14) Conceivably one might sometimes want to use the sum of Hückel theory bond orders in the present context as an approximation to  $V_p$ . However, this would not be helpful for singlet-triplet transitions because Hückel excited states are averages between singlet and triplet.

## Application

The final secular equation for  $\mu$  gives the exact perturbation energy in the cases of radical attack and attack by a vinyl group if the unperturbed system is ethylene in its ground state—this because singlets for allyl radical and butadiene are described fully in the valence bond method ( $\pi$  electrons only) by two linearly independent functions. The secular equation is only approximate for other cases, and the formula above for the lowest root of course involves an additional approximation. The perturbation formula has been checked in the perturbed butadiene case by comparing with some full valence bond calculations and has been found to be very close.

To compare theory with experiment it is mainly necessary to have at hand the Penney-Dirac bond orders for the unperturbed system—here for butadiene. These bond orders and the fixed valences as obtained by standard methods for the lowest singlet and the lowest triplet states are given in the diagram



The bond orders and fixed valences are seen to be consistent with the approximate picture suggested by the valence bond structures. The perturbation energies mostly are governed by a fixed valence around unity, except for the 1- and 4-positions in the triplet. Here the fixed valence is only 0.235 so the perturbation energy would be comparatively large.

$$T_1 \quad \mu \approx \frac{3}{8} \frac{(B')^2}{B'' + 0.235B}$$

$$N \quad \mu \approx \frac{3}{8} \frac{(B')^2}{B'' + 0.911B}$$

Having the triplet stabilization the larger thus produces a red shift, and this is essentially what is observed.

The theory does not predict a blue shift for substitution at the 2- (or 3-) position, whereas such a shift can be detected for alkyl substitution. This may mean that the blue shifts are steric. An additional possibility arises because we have been assuming no bond alteration in butadiene. A qualitative assessment of the probable effect of including bond alternation has been attempted, the conclusion being that the minor red shift predicted for substitution at the 2-position would become less and might even turn into a blue shift.

We can make some actual numerical estimates, calculating back from observed spectral shifts and using the difference between the  $\mu$  values above. A spectral shift of 10  $m\mu$  is taken as representative. With the main band around 500  $m\mu$  this is 0.05 e.v. A fair value for  $B$  is 2 e.v. The  $\pi$  component of the three bonds to hydrogen in methyl could well have a  $B''$  value between  $B$  and  $2B$ . If the former we find that a 10- $m\mu$  shift implies  $B'/B \approx 1/2$  and, if the latter, it implies  $B'/B \approx 1/8$ . These ratios should be similar to ratios of the corresponding nonorthogonality integrals, which in turn are squares of overlap integrals. The overlap between the  $\pi$  component of methyl and a true  $\pi$

orbital is thus found to be in the range 0.7–0.3, which is all right as to magnitude even if somewhat high.

All this, we believe, tends to confirm the idea that the red shifts, especially going with 1- and 1,4-disubstitution, are caused principally by hyperconjugation.

*Acknowledgment.* We wish to thank Dr. Angelo Lamola for supplying us with pure *cis*- and pure *trans*-1,3-pentadiene; Dr. Carl Aufdermarsh for 1-chlorobutadiene, 2,3-dichlorobutadiene, and bis-2,2'-dibutadiene; and Dr. T. W. Koenig for helpful discussion.

## Application of Linear Free Energy Relations to Electronically Excited States of Monosubstituted Phenols

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*Protolytic dissociation of phenol and sixteen monosubstituted phenols in the lowest triplet and first excited singlet states has been investigated by means of fluorescence, phosphorescence, and ultraviolet absorption spectra. A treatment of the experimental data by means of the Hammett and Taft equations is presented. It is shown that excited-state acidities can be correlated well with ground-state substituent constants. Further evidence is provided for the concept that conjugative effects are much more important, relative to inductive effects, in electronically excited states than in the ground state. Direct resonance interactions between meta substituents are shown to be considerably more significant in excited singlet states than in the ground state; an approximate calculation of the magnitude of the effect is presented.*

### Introduction

The influence of substituent groups upon the rates and equilibria of reactions of aromatic compounds in their ground electronic states has received much study. Considerably less attention has been directed toward substituent effects on reactions of electronically excited molecules. Photochemical studies of Havinga<sup>2</sup> and Zimmerman<sup>3</sup> indicated that substituent effects in electronically excited states may not always be predictable from ground-state chemical behavior.

Acidities of electronically excited molecules can be studied by fluorescence spectroscopy. In many cases, very striking changes in acidity are brought about by electronic excitation.<sup>4</sup> Although acidities of many aromatic compounds have been determined in excited states, substituent effects upon excited-state acidities have received comparatively little attention. Bartok, Lucchesi, and Snider<sup>5</sup> reported that the excited-state dissociation constants of phenol, *p*-chlorophenol, and *p*-cresol could not be correlated with Hammett sub-

stituent constants; more recently however, this conclusion has been rescinded.<sup>6</sup> Jaffé and Jones<sup>7</sup> have recently reported a treatment of excited-state acidities by means of the Hammett equation. Using data obtained solely from absorption spectra, these authors noted that, for a number of different types of compounds, excited-state acidities could be "correlated by the Hammett equation with moderate precision."<sup>7</sup>

The goal of the present study was to examine in detail the influence of substituents upon the excited-state dissociation of one class of compounds, monosubstituted phenols. We were particularly interested in ascertaining which factors improved (or decreased) a correlation of excited-state acidities with ground-state substituent parameters.

### Experimental Section

The compound *p*-hydroxyphenyltrimethylammonium iodide was synthesized by the procedure of Hünig<sup>8</sup> and then converted to the chloride, as described by Hepler.<sup>9</sup> The synthesized compound was analyzed volumetrically for chloride; the experimental percentage chloride was 19.07%, compared with the theoretical value of 18.89%. All other phenols were commercial samples, purified by one or more of the following procedures: recrystallization, vacuum sublimation, vacuum distillation, column chromatography, or fractional freezing.

Water was purified by distillation from alkaline permanganate; absolute ethanol was distilled over reagent grade KOH which had been previously washed with ethanol to remove surface impurities.

Whenever feasible, ground-state dissociation constants for the phenols were taken from the literature. When this was not possible,  $pK_a$  values were determined spectrophotometrically,<sup>10</sup> using carbonate and borate buffers described by Biggs.<sup>11</sup>

Ultraviolet absorption spectra were measured using either a Bausch and Lomb Spectronic 505 or Cary

(1) (a) National Science Foundation Predoctoral Fellow, 1962–1965. Financial support from the Purdue Research Foundation is gratefully acknowledged. (b) Author to whom inquiries should be addressed at Indiana University, Bloomington, Ind.

(2) E. Havinga, R. O. de Jongh, and W. Dorst, *Rec. trav. chim.*, **75**, 378 (1956).

(3) H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963); H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963).

(4) For a review, see A. Weller, *Progr. Reaction Kinetics*, **1**, 189 (1961).

(5) W. Bartok, P. J. Lucchesi, and N. S. Snider, *J. Am. Chem. Soc.*, **84**, 1842 (1962).

(6) W. Bartok, quoted by H. H. Jaffé, H. L. Jones, and M. Isaks, *ibid.*, **86**, 2934 (1964).

(7) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965).

(8) S. Hünig, *Chem. Ber.*, **84**, 1056 (1952).

(9) H. C. Ko, W. F. O'Hara, T. Hu, and L. G. Hepler, *J. Am. Chem. Soc.*, **86**, 1003 (1964).

(10) R. A. Robinson in "Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 16.

(11) A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1956).