

# ULTRAVIOLET ABSORPTION SPECTRA OF MONOSUBSTITUTED BENZENES<sup>1</sup>: A CORRELATION BY REACTIVITIES AND RESONANCE PARAMETERS

C. N. RAMACHANDRA RAO

*R. B. Wetherill Laboratory of Chemistry, Purdue University, Lafayette, Indiana, U.S.A.*

THE ultraviolet absorption spectra of benzene and its mono- and disubstituted derivatives may be represented as an approximately regular progression of at least three bands, namely, the secondary, first primary and second primary bands, in the order of decreasing wavelength. In early work, the ultraviolet spectra of substituted benzenes were always discussed in terms of the displacement of the secondary band. Doub and Vandenberg<sup>2</sup> showed that the first primary band (also known as the B-band) is capable of displacement to the edge of the visible region and that it provides a basis for a more logical interpretation of benzenoid absorption.

The displacing effect of a substituent on the primary band of benzene ( $\Delta\lambda = \lambda - 203.5$ , where  $\lambda$  is the wavelength corresponding to the first primary absorption maximum of the substituted benzene in  $m\mu$ ) has been considered to an extent, a measure of its electron donating or withdrawing power. In this communication, a correlation of the ultraviolet absorption spectra of monosubstituted benzenes with the electrical properties of the substituents has been presented. Hammett's  $\sigma$  values<sup>3</sup> and Brown's  $\sigma^+$  values<sup>4,5</sup> have been made use of as substituent constants for purposes of correlation. In general, the substituent constant,  $\sigma$ , is considered to be the measure of the ability of the substituent to change the electron density at the reaction centre. While a negative value of the substituent indicates an increase in the electron density, a positive value indicates a decrease. Greater the effect of the substituent on the electron density, larger is the numerical value of  $\sigma$ . The  $\sigma^+$  values are the substituent constants developed by Brown and Okamoto<sup>4,5</sup> suitable for electrophilic reactions. Since electrophilic reactions provide far greater opportunity for resonance contributions by the substituent, the difference between  $\sigma$  and  $\sigma^+$  values is attributed to such resonance.

When the  $\Delta\lambda$  values of monosubstituted benzenes were plotted against either *para*- $\sigma$  or *para*- $\sigma^+$  values, an approximately linear relationship was found. This relationship can be expressed as:

$$\Delta\lambda = \rho\sigma \quad (1)$$

where  $\rho$  is the slope of the line.  $\rho$  is a measure of the sensitivity of the equilibrium or

the transition to change in the electron density. Since  $\Delta\lambda$  for benzene itself is zero, one gets two straight line plots with different slopes, one for the electron withdrawing groups (positive  $\sigma$  values) and another for the electron donating groups (negative  $\sigma$  values). Accordingly,  $\rho$  is positive or negative depending on the sign of the  $\sigma$  values.

The wavelength changes in the primary band of benzene appear to be caused by resonance and steric interactions rather than coulombic interactions. In monosubstituted or *para*-disubstituted benzenes, the steric effects can be assumed to be negligible and consequently the resonance interactions will be mainly responsible for the observed changes. Recently, Taft<sup>6,7</sup> has proposed a quantitative separation of the Hammett  $\sigma$  value to independent inductive and resonance contributions according to the equation:

$$\sigma = \sigma_I + \sigma_R \quad (2)$$

$\sigma_I$  is the inductive component and  $\sigma_R$ , the resonance component, can be considered to be a measure of the free energy effect resulting from the ability of the substituent to repel or attract electrons through resonance interaction with the  $\pi$ -orbital of the benzene system. A plot of the  $\Delta\lambda$  of monosubstituted benzenes against the *para*-resonance parameters of the substituents (*para*- $\sigma_R = \sigma_{para} - \sigma_I$ ) is found to be reasonably linear (cf. Fig. 1). A similar rela-

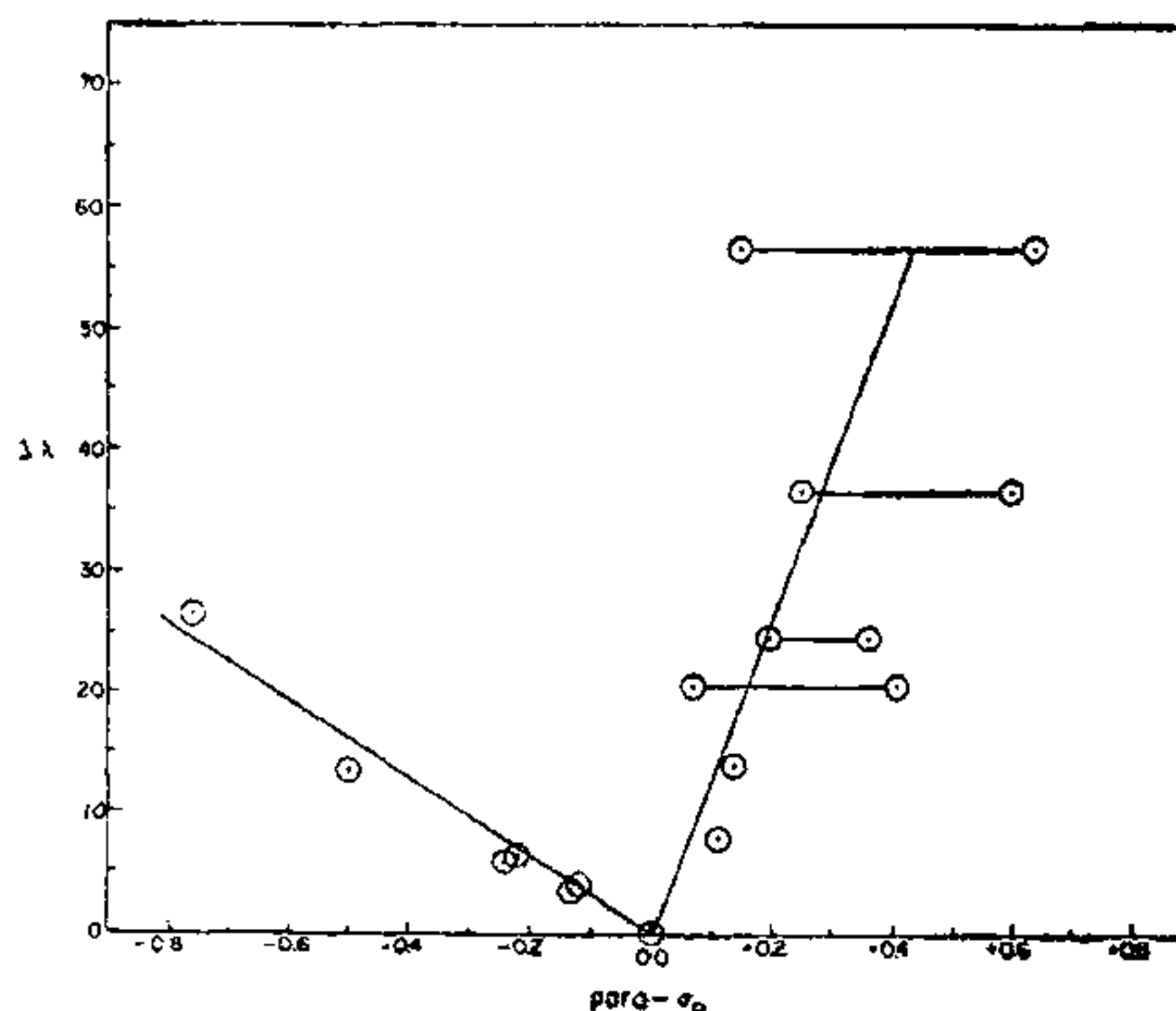


FIG. 1. Correlation of the displacement of the primary band of benzene with resonance parameters of substituents.



tionship is also observed when one employs  $\text{para-}\sigma_R^+$  ( $\text{para-}\sigma_R^+ = \sigma^+_{\text{para}} - \sigma_I$ ). No straightforward relationship of  $\Delta\lambda$  with inductive parameters was apparent. In general, the linear plots follow the equation:

$$\Delta\lambda = \sigma_R \rho_R \quad (3)$$

The values of  $\rho_R$  are about 130 and -32 for the electron withdrawing ( $+\sigma_R$ ) and electron contributing ( $-\sigma_R$ ) substituents, respectively. When  $\sigma_R^+$  values are used for the correlation, the slope is about -17 for the electron donating groups. In all these correlations it has been tacitly assumed that hydrogen acts like a substituent possessing the same value of the substituent constant (0.00) or the resonance parameter (0.00) and the  $\Delta\lambda$  value (zero) when opposed to either *ortho-para* or *meta-orienting* groups. However this assumption follows from the definition of  $\sigma$  or  $\sigma_R$  and  $\Delta\lambda$ , since all these quantities are relative to hydrogen as standard. Doub and Vandenberg<sup>2</sup> have made a similar observation and have in fact assigned a displacing effect to this hypothetical chromophore. In Fig. 1 for the groups CN, NO<sub>2</sub>, COCH<sub>3</sub> and COOC<sub>2</sub>H<sub>5</sub>, Hammett  $\sigma_R$  values are shown for a lower limit and the "dual"  $\sigma_R$  values for an upper limit. It is clear that a value in between these two limits would reasonably correlate the  $\Delta\lambda$  values for the CN, NO<sub>2</sub> and COCH<sub>3</sub> groups. The extrapolated values of  $\sigma_R$  for these three groups are about 0.16, 0.29 and 0.44 respectively. A similar observation has been made by Taft<sup>7</sup> in correlating the nuclear magnetic shielding parameters,  $\delta^p$ , for *meta*- and *para*-substituted fluorobenzenes by inductive and resonance parameters. It may be apt to mention at this juncture that while the inductive effect should essentially be independent of the reaction, the resonance contribution would be expected to vary with the electronic demands of the reaction. It is interesting to note that for monosubstituted benzenes, larger the numerical value of the resonance parameter of the substituent, greater is the magnitude of the displacement of the primary band.

Doub and Vandenberg<sup>2</sup> reported a linear relationship between their derived displacement values ( $\delta\lambda_0$ ) and the differential polarizabilities of Price<sup>8</sup> ( $\Delta\sigma = \sigma_{\text{para}} - \sigma_{\text{meta}}$ ).  $\Delta\sigma$  is actually a measure of the resonance contribution of a substituent in view of the fact that the *meta- $\sigma$*  values in many cases are nearly equal to the inductive parameters. This is in variance with

Price's view, that  $\Delta\sigma$  depends primarily on electrostatic effects. It is found that a plot of  $\delta\lambda_0$  versus *para- $\sigma_R$*  exhibits a relationship very similar to that of  $\Delta\lambda$  discussed above.

The correlations presented above clearly point out that the wavelength shifts caused by the substituents on benzene are a measure of resonance effects, that is, of effects associated with the directional displacement of electrons to or from the ring depending on the electron withdrawing or contributing nature of the group. Recent work,<sup>9</sup> after the publication of Rao's correlation<sup>10</sup> of the ultraviolet absorption spectra of disubstituted benzenes with reactivities, has shown that it is essential to consider the resonance parameters in the case of disubstituted benzenes also. A detailed report on the correlations of the ultraviolet absorption spectra of disubstituted benzenes with reactivities and resonance parameters and their applicability to studies of mechanisms of reactions and to estimations of electrical properties of groups will be published in the near future. Preliminary investigations<sup>11</sup> have shown that the dipole moments of substituted benzenes show similar relationships with substituent constants. As can be expected, in the correlation of the dipole moments, the overall electronegativities of the substituents (combination of resonance and inductive parameters) seem to be more applicable.

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