THE NEAR-ULTRAVIOLET ABSORPTION SPECTRA OF MONOALKYL-SUBSTITUTED BENZENES[1]

HYPERCONJUGATION AND THE BAKER–NATHAN EFFECT

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The near-ultraviolet absorption spectra in the vapor of toluene, ethylbenzene, the *n*- and iso-propylbenzenes, and the *n*-, *sec*-, and *tert*-butylbenzenes have been obtained. It is found that the 0–0 shifts, the intensity, and the internal distribution of intensity are of such a nature as to indicate that the methyl group hyperconjugates to the greatest extent and the *tert*-butyl group to the least extent with the ring. This is the spectroscopic analogue of the Baker–Nathan effect, that the methyl group is a stronger directing group for ortho–para substitution in the ring than is the *tert*-butyl group.

INTRODUCTION

Substituted benzenes have spectra in the near-ultraviolet region which are closer to the visible and are more intense than is the spectrum of benzene. In general, greater wave-length shift and greater intensification are observed for those substituents which have large directing power toward a subsequent electrophilic substituent. The directing substituents have mobile electrons which can resonate with or migrate into the ring, such as substituents having unshared pairs of electrons on the alpha atom, —F, —Cl, —OH, $—NH_2$[2] and unsaturated groups which are conjugate to the ring, such as $—CH{=}CH_2$. An inductive effect related to the electron affinity of the substituent also operates, either in the same direction or opposite to the resonance effect.

A. L. Sklar (16) has discussed in detail the effect of migration of electrons from substituent to the ring on the intensity of the spectra. He shows that the intensity is a function of the extent of migration, which in turn depends on the presence of non-bonded electrons in suitably oriented *p* orbitals as well as on the electron affinity of the substituent.

K. F. Herzfeld (8) has obtained similar expressions for the term values of the ground and excited states as a function of the extent of migration. His formulae indicate that for these compounds the wave-length shift parallels the intensification.

Alkyl substituents, while not possessing formal unshared pairs of electrons or a structure which is conjugate to the ring, can nevertheless resonate with the

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[1] Presented at the Symposium on Color and the Electronic Structure of Complex Molecules which was held under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society at Northwestern University, Evanston and Chicago, Illinois, December 30 and 31, 1946.

[2] For the spectra of C_6H_5F, C_6H_5Cl, C_6H_5OH, and $C_6H_5NH_2$ see references 6, 10, 16, and 21.

ring in what has been called "hyperconjugation" by Mulliken, Rieke, and Brown (13). Here the single bonds on the α-carbon atom may act as electron donors to the ring. The methyl group has approximately the same effect on intensity, wave-length shift (15), and directing power as has the chlorine atom. Sklar (16) has calculated the intensity of absorption in the near-ultraviolet region for toluene and has obtained excellent agreement with experiment.

Little has been published on the effect of the structure of alkyl groups on the spectrum. The treatment of hyperconjugation mentioned above deals with the ground state and the over-all effect of alkyl groups on acceptor bonds. It does not emphasize differences between alkyl groups except to state "... the computed contribution to the total x conjugation energy per bond is practically the same for $—CH_3$ linked to $C{=}C$ as for $—CH_2—$. . . ."

TABLE 1

Dipole moments

R	RCl (20)	RC_6H_5 (2)
	D	*D*
Methyl	1.87	0.37
Ethyl	2.05	0.58
n-Propyl	2.10	
Isopropyl	2.15	0.65
n-Butyl	2.09	
sec-Butyl	2.12	
tert-Butyl	2.13	0.70

The difference in structure of the alkyl groups should be more apparent for the excited state (8). The electronic excitation in mononuclear aromatic spectra is of the form

$$x_1^2x_2^2x_3^2 \rightarrow \begin{cases} x_1^2x_2^2x_3x_4 \\ x_1^2x_2^2x_3x_5 \\ x_1^2x_2x_3^2x_4 \\ x_1^2x_2x_3^2x_5 \end{cases}$$

where the x's represent molecular orbitals for the π electrons of the ring. The energy of these orbitals is in the following order:

$$E(x_1) < E(x_2) = E(x_3) < E(x_4) = E(x_5) \qquad (7, 12)$$

Thus the excited state, having a vacant low-lying orbital, is a more enthusiastic electron acceptor than the ground state. (Qualitatively this accounts for the fact that the excited state is lower lying when electrons migrate into the ring.) Phenomena involving the excited state should be much more affected by differences in the electron-donating power of the substituent.

ELECTRON AFFINITIES AND POLARIZABILITIES OF ALKYL GROUPS

The dipole moments given in table 1 seem to indicate differences in the polarizabilities and perhaps the electron affinities of the various alkyl groups.[3] Sklar (16) has estimated the electron affinity of the methyl group to be 1.8 e.v. Applying the same method of calculation to other alkyl groups, the values given in table 2 were found.[4] The significance of these calculations is obscure, since it assumes that the excess positive and negative charges are localized on either end of the halogen-carbon bond. Furthermore, zero dipole moments have been reported for all paraffins. However, these data do seem to indicate that the ease of electron withdrawal is in the order $CH_3 < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$. One might expect then that, other factors being constant, the intensity and the wave-length shift of the spectra will follow the same order. That this is not the case will be seen from the data presented below.

TABLE 2

Estimated electron affinities

ALKYL GROUP	ELECTRON AFFINITIES
	e.v.
Methyl	1.8
Ethyl	1.4
n-Propyl	1.0
Isopropyl	~1.0

EXPERIMENTAL DATA

In figure 1 are plotted the wave lengths of the 0–0 bands from the spectra of various alkyl-substituted benzenes, both in the vapor state and in solution. The vapor data are from Robertson, Chuoke, and Matsen (14) and the solution data from the reports of the American Petroleum Institute, Project 44 (1). The 0–0 band in benzene is forbidden, but its position in the vapor state has been calculated by Sponer, Nordheim, Sklar, and Teller (17) to be 2625 A. We have estimated the 0–0 band in solution to be 2640 A. from a comparison of the solution and vapor data for the substituted benzenes. It will be seen that the largest shift is for toluene and that *tert*-butylbenzene is shifted least from the position occupied by benzene.

The word "intensity" is generally taken to mean the integrated intensity for the entire electronic transition. However, equally interesting information

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[3] The authors wish to acknowledge a conversation with Professor G. W. Wheland on this point.

[4] It was not possible to carry out the calculations for higher members of the series because the pertinent dipolo-moment data were lacking. In the course of these calculations the electron affinities of $—NO_2$ and —CN were estimated in an attempt to acquire more data to aid in the determination of the slopes of the charge *versus* electron affinity lines for the higher alkyl groups. These were found to be 6.5 for $—NO_2$ and 7.0 for —CN.

can be obtained from the intensities of the individual bands. In figure 2 are plotted the molar extinction coefficients for the 0–0 bands. As was mentioned above, the 0–0 band in benzene is missing; consequently its extinction coefficient is zero. These extinction coefficients are calculated from the reports of the American Petroleum Institute Project 44 (1). Work on absolute intensities in the vapor phase has begun in this Laboratory; up to this time there has been established only the trend in the curve after toluene. It will be seen that the extinction coefficients of the 0–0 bands show the same sort of dependence on the substituent as was observed for the wave lengths of these bands.

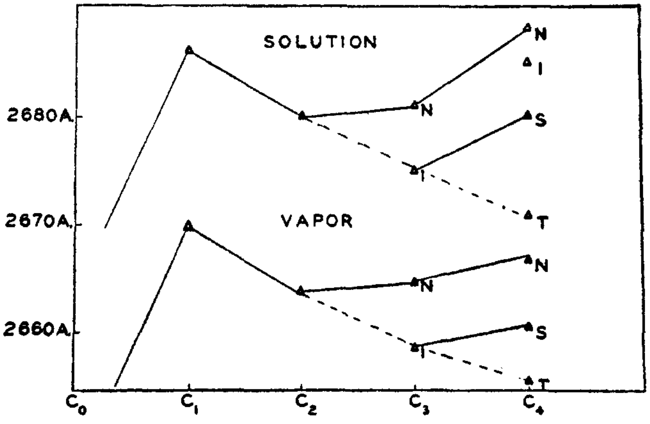

FIG. 1. Wave lengths of the 0–0 bonds in monoalkyl-substituted benzenes

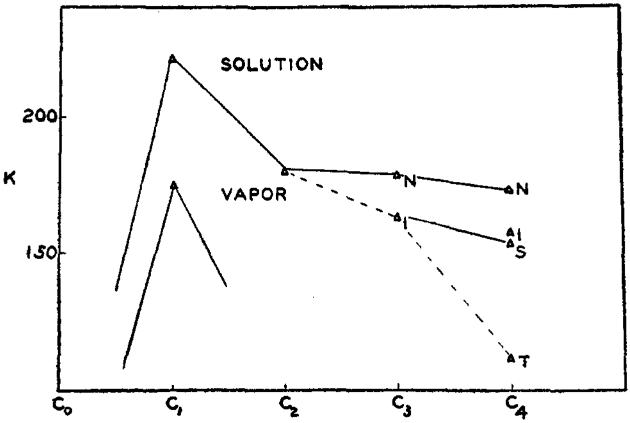

FIG. 2. Extinction coefficient (moles per liter) of the 0–0 bonds of monoalkyl-substituted benzenes.

Further evidence of this trend in the spectra may be obtained by comparing the relative intensities of several of the bands in each spectra with the relative intensities in other spectra. It has been stated that the spectrum of a monosubstituted benzene is composed of two sub-spectra (18): One, which is allowed in benzene, is composed of bands involving one of the e_g^+ vibrations (6*b* in Wilson's

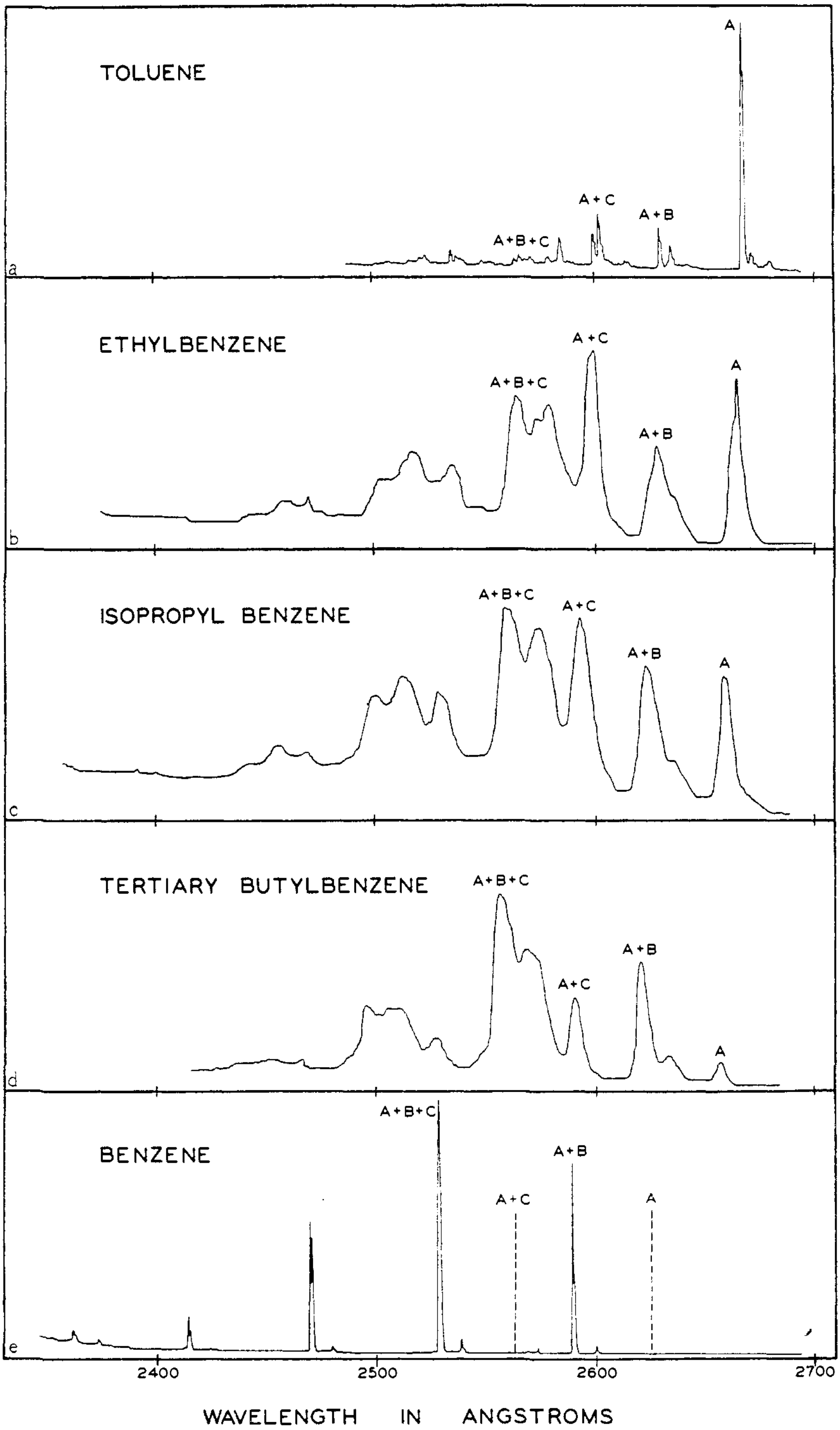

FIG. 3. Microphotometer tracings of the spectra of monoalkylbenzenes. The density scale varies from compound to compound.

notation; frequency, 500 cm.$^{-1}$), hereafter referred to as *B*. The 0–0 band, hereafter referred to as *A*, is missing. Thus the benzene spectrum is made up of the following strong bands: $A + B$, $A + B + C$, $A + B + 2C$, etc. (see figure 3e). The second sub-spectrum, which does not appear in benzene, is the one which is made allowed by the migration of electrons into the ring. The 0–0 band, *A*, appears under these conditions. In addition the vibration *C* may appear as $A + C$, $A + 2C$, etc. Certain other vibrations which are totally symmetric for the monosubstituted benzenes appear in the same manner as *C* (see figures 3a, 3b, 3c, 3d). These figures are microphotometer tracings of the vapor-phase spectrographs. The ordinate in this figure is proportional to the intensity of absorption, but the scale from one tracing to another is not comparable, since the exposure of the plate and the sensitivity of the microphotometer were set so as to bring out the optimum contrast.

From the discussion above it is to be expected that compounds with substituents which permit extensive electron migration into the ring will have spectra in which the second or substitution sub-spectrum, *A*, $A + C$, $A + 2C$, etc., is relatively more intense. It is seen from a comparison of the spectra in figure 3 that this spectrum becomes relatively less intense in going down the series from toluene to *tert*-butylbenzene.[5]

DISCUSSION

The wave-length shift, the variation of intensity of the 0–0 bands, and the internal distribution of intensity all indicate that the migration of electrons from substituent to the ring becomes smaller as the hydrogen atoms in toluene are progressively replaced by alkyl groups. Since the availability of electrons as indicated by the dipole-moment data increases at the same time, this does not seem to be an electrostatic or inductance effect. It seems necessary to postulate that hyperconjugation with the ring decreases as the hydrogens in the methyl group of toluene are successively replaced by alkyl groups. This implies that the electrons in a C—H bond are less localized than in a C—C bond. The formal difference between the two types of bonds is that in a C—H bond a hybridized *s*–*p* orbital on carbon overlaps an *s* orbital on hydrogen, while in the C—C bond a hybridized *s*–*p* orbital overlaps another orbital of the same kind. It is hoped to discuss this problem in more detail in a later paper.

DIRECTING POWER OF ALKYL SUBSTITUENTS

Studies on the relative directing power of alkyl substituents provide confirmation for the interpretation of the spectra presented above. The earliest experiments were concerned with the orientation of electrophilic substituents in the *p*-alkyltoluenes. It was found that the substituent entered predominantly into the position ortho to the methyl group, indicating that the methyl group possessed directing power greater than that of the other alkyl groups. On the basis of these and other experiments Baker and Nathan stated that the electron-releasing power of a methyl group substituted on benzene is superior

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[5] These data may be taken as evidence for the existence of two sub-spectra in monosubstituted benzenes.

to that of other alkyl groups, even though the reverse is true when the substitution is on an aliphatic group (19). Recently Deasy (4) has summarized much of the data relative to hyperconjugation in general and the Baker-Nathan effect in particular. More recently de la Mare and Robertson (5) have measured the relative rate constants for the chlorination and the bromination of alkylbenzenes and found them to be in the order methyl > ethyl > isopropyl > *tert*-butyl. Berliner and Bondhus (3) carried out a competitive bromination of toluene and *tert*-butylbenzene and found that the ratio of the monobrominated toluene to the monobrominated *tert*-butylbenzene in the product was four to one. In neither case was the ortho–para ratio determined, so that some question of steric hindrance might be raised. It is believed by both sets of authors, however, that the factor does not affect the qualitative conclusions which can be drawn: namely, that the electron-donating power of an alkyl substituent decreases as the number of hydrogen atoms on the α-carbon atom is decreased, giving further evidence for the Baker–Nathan effect.

Thus the spectroscopic and chemical data are in accord. Since the spectroscopic data parallel the chemical data so closely, even with regard to small effects of the type discussed here, one is led to the conclusion that the excited state produced in aromatic compounds by the absorption of light must resemble in a number of ways the transition state for the substitution reactions.

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