Here

$$A = (\alpha - E)/\beta$$

The energies as functions of δ are plotted as full lines in Fig. 4. For comparison, the energies of the system C_6H_5X have been plotted as heavy dotted lines in the same figure. The light dotted lines represent the zero order levels. The perturbed levels are indexed on the right by the zero order levels from which they originate.

In the compounds $(C_6H_5)_2X$ the corresponding excited states are

$$\chi_3\psi_4, \chi_3\psi_4', \ \psi_2\chi_5 \text{ and } \psi_2'\chi_5$$[4]

These states are assumed to mix in the same way as do the states in the corresponding B_{2u} state in benzene. Thus, there are two excited states, one for each ring characterized by $\chi_3\psi_4 + \psi_2\chi_5$ and $\chi_3\psi_4' + \psi_2'\chi_5$. The assumptions that the excitation energy calculated from the molecular orbitals is the excitation energy of the center of gravity of the excited states, and that the lowest of these varies as does the center of gravity, lead to the expression

$$\frac{\nu_B - \nu}{\nu_B} = \frac{2 - [A_5 - A_3]}{4} = \frac{2\beta - [E_3 - E_5]}{4\beta}$$

where ν_B and ν are the frequencies of the 0–0 bands in benzene and the $(C_6H_5)_2X$ compound, respectively.

From an inspection of Fig. 4, it can be seen that the frequency shift is approximately the same for C_6H_5X and $(C_6H_5)_2X$. The results of the actual calculations are given in Table I. These appear to be in reasonably good agreement with experiment as well as can be judged by the diffuse spectra.

TABLE I

Compound	δ	$(\nu_B - \nu)/\nu_B$
C_6H_5OH	1.8	0.05
$C_6H_5OC_6H_5$	1.8	.05
C_6H_5SH	1.1	.08
$C_6H_5SC_6H_5$	1.1	.08
$C_6H_5NH_2$	0.8	.10
$C_6H_5NHC_6H_5$	0.8	.10

The intensity cannot be calculated by the methods used for C_6H_5X because the perturbation of the benzene levels is too great. However, if one accepts the general observation that the greater the perturbation of the benzene levels the higher is the intensity of absorption, there is qualitative agreement with experiment: namely, that the absorption of the $(C_6H_5)_2X$ is more intense than for the C_6H_5X and that the order of intensity is the same in both series.

Summary

The spectra of compounds of the type $(C_6H_5)_2X$ are presented and compared with the corresponding C_6H_5 spectra. The former are more intense, but lie at approximately the same wave length as do the latter. Conclusions drawn from crude molecular orbital theory are shown to be in qualitative agreement with experiment.

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(4) There are also one-electron states belonging to representation B_{1u}, $1/\sqrt{2}\,(\psi_3 - \psi_3')$ and $1/\sqrt{2}\,(\psi_5 - \psi_5')$, from and to which excitation can occur, producing the excited molecular states $1/\sqrt{2}\,(\psi_3 - \psi_3')\psi_4$, $1/\sqrt{2}\,(\psi_3 - \psi_3')\psi_4'$, $\psi_2\, 1/\sqrt{2}\,(\psi_5 - \psi_5')$ and $\psi_2'\, 1/\sqrt{2}\,(\psi_5 - \psi_5')$. Since none of these one-electron states interact with the substituent, they are not perturbed and the benzene type transition discussed above is forbidden. It has yet to be established that these states do not interact in any way with the states to which the benzene type transition is allowed.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, THE UNIVERSITY OF TEXAS]

Molecular Orbital Theory and the Near Ultraviolet Absorption Spectrum of Monosubstituted Benzenes. IV. The Phenyl Halides and the Inductive Effect

BY W. W. ROBERTSON AND F. A. MATSEN

Introduction

The intensities and wave lengths of the near ultraviolet absorption of monosubstituted benzenes with an unshared pair of electrons on the substituent are quite well described by molecular orbital theory.[1] For most of the compounds considered, the resonance interaction between the substituent and the ring is the important effect and others, such as the inductive effect, can be neglected. On this basis the spectral properties can in general be correlated with the difference in the ionization energies of the substituent and benzene. The smaller the difference in the ionization energies, the greater is the perturbation of the benzene levels, the longer the wave length and the higher the intensity of the near ultraviolet absorption. For the phenyl halide series the wave lengths lie in the order predicted by this generalization. However, it appears that the intensities lie in the reverse order. Consequently, a further study of the problem is indicated.

Wheland and Pauling[2] have discussed the directing properties of the substituent from the standpoint of molecular orbital theory.

Experimental

The vapor spectra were obtained on a three-meter grating with Eastman Kodak Co. 103-0 plates and were scanned with a Leeds and North-

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(1) Matsen, THIS JOURNAL, **72**, 5243 (1950).

(2) Wheland and Pauling, *ibid.*, **57**, 2086 (1935).

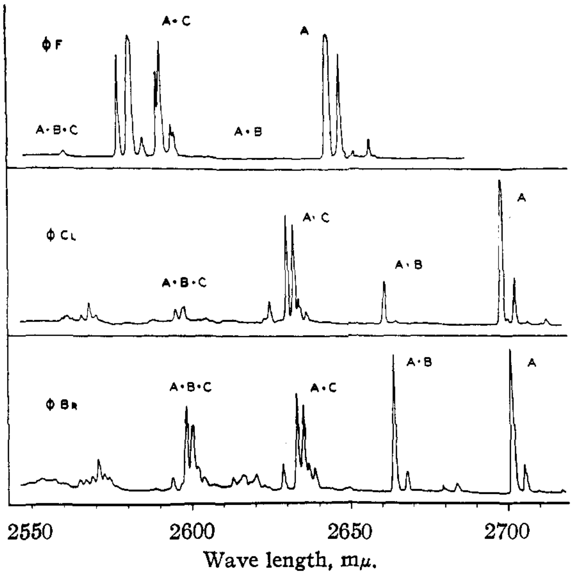

Fig. 1.—Microphotometer tracings of the near ultraviolet absorption spectra of the vapors of fluorobenzene, chlorobenzene and bromobenzene.

rup microphotometer (see Fig. 1). Eastman "white label" compounds redistilled just before use were employed in the investigation. The solution spectra were obtained in ethyl alcohol on a Beckman quartz spectrophotometer (see Fig. 2).

Discussion

An inspection of Table I in reference 1 shows that the ionization energies of the halide atoms are in the order F > Cl > Br. On the basis of the resonance effect alone, it is concluded that the intensities and the wave lengths should lie in the order $C_6H_5Br > C_6H_5Cl > C_6H_5F$. This is actually the order of the wave lengths of the 0–0 bands: C_6H_5Br 2702.2 Å. > C_6H_5Cl, 2689.1 Å. > C_6H_5F, 2643.5 Å.[3]

Solution spectra of the phenyl halides have been obtained by various workers and tabulated by Braude.[4] These show the maximum extinction coefficients to be C_6H_5F, 1650 > C_6H_5Cl, 310 > C_6H_5Br, 245, in contradiction to the predictions made on the basis of resonance effect. The A.P.I. spectra,[5] using isoöctane as solvent, yield: C_6H_5F, 1061 > C_6H_5Cl 236 > C_6H_5Br, 200. Sponer[6] and co-workers report an oscillator strength for fluorobenzene of 8.9×10^{-3} and for chlorobenzene of 3.0×10^{-3}. These authors, as well as Sklar,[7] have also called attention to the anomaly presented by the resonance interpretation of the spectra. The data obtained in ethyl alcohol and presented in Fig. 2 give the same order of intensity.[8]

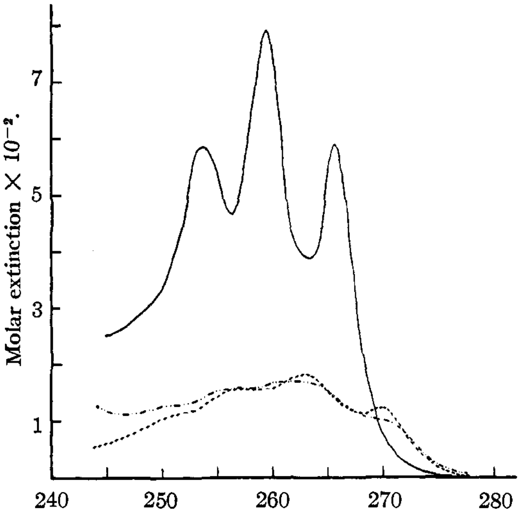

Fig. 2.—Solution spectra of fluorobenzene (——) chlorobenzene (----) and bromobenzene (-.-.-.) in ethanol.

It has been shown[9] that the oscillator strength of the monosubstituted benzenes correlates with the intensity distribution among the vibrational bands. The benzene spectrum is electronically forbidden, but absorption occurs because of the perturbing action of an unsymmetrical vibration of symmetry E_g^+ of approximately 520 cm.$^{-1}$, which appears strongly in the benzene spectrum. This band will be labeled A + B in Fig. 1. The 0–0 band (labeled A) is missing in benzene, as are all transitions involving totally symmetric vibrations only (labeled A + C). When substitution is made on the benzene ring the electronic transition becomes allowed. The entire spectrum becomes more intense; A and A + C become relatively more intense, while A + B and A + B + C become relatively less intense. If the substituent perturbs the ring very strongly, as in styrene, A, A + C, etc., become very strong while A + B and A + B + C become of negligible intensity. Thus the ratio of the intensity of A + B to the intensity of A + C, I(A + B)/I(A + C), for a given monosubstituted benzene gives a measure of the forbiddenness of the electronic transition.

The vapor spectra of C_6H_5F,[10] C_6H_5Cl[11] and C_6H_5Br[12] have been analyzed and published. Comparative microphotometer tracings have not been heretofore presented. These are given so that a comparison of the intensities of the various bands in the spectrum of a given compound can be made.

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(3) See tabulation in Herzfeld, *Chem. Revs.*, **41**, 233 (1947).

(4) Braude, *Ann. Reports*, **42**, 125 (1945).

(5) American Petroleum Institute Research Project 54 at the National Bureau of Standards; Catalogue of Ultraviolet Spectrograms, Serial Nos. 296, 300 and 304, Duke University.

(6) Sponer and Lowe, *J. Opt. Soc. Am.*, **39**, 840 (1949).

(7) Sklar, *Rev. Mod Phys.*, **14**, 232 (1942).

(8) The maxima of the solution spectra presented in Fig. 2 are lower than those reported by previous workers, which is a consequence of the use of ethyl alcohol as a solvent. Polar solvents tend to level off the structure of solution spectra.

(9) Matsen, Robertson and Chuoke, *Chem. Revs.*, **41**, 273 (1947).

(10) Wollman, *J. Chem. Phys.*, **14**, 123 (1946).

(11) Sponer and Wollman, *ibid.*, **9**, 816 (1941).

(12) Masaki, *Bull. Chem. Soc. Japan*, **11**, 246 (1936).

The vapor spectra of Fig. 1 show clearly that the ratio I(A + B)/I(A + C) is in the order $C_6H_5Br > C_6H_5Cl > C_6H_5F$, from which it is concluded that the forbiddenness of the transition is in the same order. (No conclusion can be drawn with respect to C_6H_5I because of its diffuseness.)

The vapor spectra and additional solution spectra confirm the conclusion that the order of allowedness and intensity of the spectra is $C_6H_5F > C_6H_5Cl > C_6H_5Br$. Since this is not the order predicted by the resonance effect alone, it therefore seems necessary to consider the inductive effect and its relation to spectra.

Theory

The frequency and intensity of absorption will be calculated by the use of LCAO MO's. The MO's are taken to be

$$\chi_j = \sum_{i=1} A_{ji}\,\psi_i \quad j = 1, 2, \ldots, 7 \qquad (1)$$

where

$$\begin{aligned} \psi_1 &= \phi_1 \\ \psi_2 &= (\phi_2 + \phi_6)/\sqrt{2} \\ \psi_3 &= (\phi_3 + \phi_5)/\sqrt{2} \\ \psi_4 &= \phi_4 \\ \psi_5 &= \phi_7 \\ \psi_6 &= (\phi_2 - \phi_6)/\sqrt{2} \\ \psi_7 &= (\phi_3 - \phi_5)/\sqrt{2} \end{aligned} \qquad (2)$$

Here ϕ_k is the 2pπ function on the kth atom.[13,14] The seventh order representation (1) factors into a fifth and a second order representation since ψ_6 and ψ_7 are antisymmetric under reflection through a plane perpendicular to the plane of the benzene ring and containing the figure axis, while orbitals ψ_1, ψ_2, ψ_3, ψ_4 and ψ_5 are symmetric with respect to this operation.

The usual approximations are made: namely, that all resonance integrals are equal and that the overlap integrals may be neglected. The second order energy equation is

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} \qquad (3)$$

where α is the coulomb integral over a normal carbon atom and β the resonance integral between two adjacent atoms. The roots are

$$\begin{aligned} E_2 &= \alpha + \beta \\ E_4 &= \alpha - \beta \end{aligned} \qquad (4)$$

The numbering of the levels is that used for benzene. The energies and the associated wave functions are independent of the substituent and are the same as for benzene itself. As in references one and two the coulomb integral over the substituent is taken to be

$$H_{77} = \alpha + \delta\beta \qquad (5)$$

where δ is a positive quantity which for the halogens lies between two and five. The quantity δ varies roughly as do the substituent ionization energies; it will be evaluated from spectroscopic data.

To take account of the inductive effect it is assumed that the high electron affinity of the substituent polarizes the C–X bond in such a way as to raise the electron affinity on carbon atom one. Thus

$$H_{11} = \alpha + \delta_1\beta \qquad (6)$$

where δ_1 is a positive quantity roughly proportional to but smaller than δ. The fifth order equation is then

$$\begin{vmatrix} \alpha + \delta\beta\text{-E} & \beta & 0 & 0 & 0 \\ \beta & \alpha + \delta_1\beta\text{-}E & \sqrt{2}\beta & \beta & 0 \\ 0 & \sqrt{2}\beta & \alpha\text{-}E & \beta & 0 \\ 0 & \beta & \beta & \alpha\text{-}E & \sqrt{2}\beta \\ 0 & 0 & 0 & \sqrt{2}\beta & \alpha\text{-}E \end{vmatrix} = 0 \qquad (7)$$

The roots of this equation and the coefficients A_{ji} of equation (1) were obtained to a first approximation on a secular equation solver of the Frost and Tamres type.[15] The secular equation was then expanded and solutions to four significant figures were obtained by trial. Using these energy values the A_{ji} were obtained to three significant figures, again by trial, from the simultaneous equations represented by the secular equation (7).

The frequency of the O–O band, ν, is conveniently referred to the corresponding benzene frequency ν_B

$$(\nu_B - \nu)/\nu_B = (2\beta - (E_3 - E_5))/4\beta \qquad (8)$$

where E_3 and E_5 were obtained from the secular equation. Equation (8) is discussed in some detail in reference (1).

The oscillator strength[16] is given by

$$f = 1.085 \times 10^{11}\nu Q^2$$

where ν is the frequency of absorption. For excitation of the benzene ring[1]

$$Q = \int \chi_3 r\, \chi d\tau + \int \chi_2 r \chi_5 d\tau$$

where

$$\chi_2 = \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$$

$$\chi_4 = \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6)$$

and for χ_3 and χ_5

$$\chi_j = A_{j1}\phi_1 + A_{j2}(\phi_2 + \phi_6)/\sqrt{2} + A_{j3}(\phi_3 + \phi_5)/\sqrt{2} + A_{j4}\phi_4 + A_{j5}\phi_7$$

then

$$f = 1.085 \times 10^{11}\,\nu\,\frac{3}{8}\,r^2(A_{32} - A_{33} + A_{52} + A_{53})^2 \qquad (9)$$

Fortunately, the frequency is relatively insensitive to the inductive effect (*i.e.*, to δ_1). Consequently, δ could be evaluated by setting

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[13] For the numbering system see Fig. 1, ref. 1.

[14] In the earlier papers of this series the MO's were constructed from the substituent orbital ϕ_7 and the six benzene orbitals. This combination was chosen since it was the most suitable for the perturbation development. The combination used above is more convenient for the direct (non-perturbation) calculation of intensities.

[15] Frost and Tamres, *J. Chem. Phys.*, **15**, 383 (1947). The instrument was built at the University of Chicago from an improved design developed there.

[16] Mulliken and Rieke, "Reports on Progress in Physics," Vol. VIII, p. 231, 1941.

$\delta_1 = 0.1\delta$ and calculating $(\nu_B - \nu)/\nu_B$ for a range of δ (see Fig. 3). Comparison with the experimental values yield for C_6H_5Br, $\delta = 2.4$ for C_6H_5Cl $\delta = 2.5$ and for C_6H_5F $\delta = 5.0$. With these, f was calculated for various values of δ_1. These are plotted for C_6H_5Cl and C_6H_5F in Figs. 4 and 5 together with $(\nu_B - \nu)/\nu_B$.

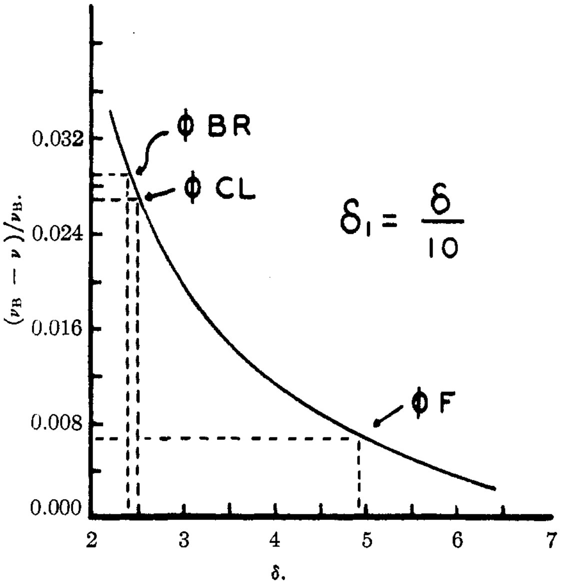

Fig. 3.—Relative wave length as a function of δ, with $\delta_1 = 1/10\delta$.

It will be seen, as was stated above, that $(\nu_B - \nu)/\nu_B$ is quite insensitive to δ_1, the inductive effect. Consequently, the resonance treatment alone gives the experimentally observed order for the $(\nu_B - \nu)/\nu_B$ among the phenyl halides. The f values are, however, extremely sensitive to δ_1. The inductive and resonance effects act in opposition, and for certain combinations of δ_1 and δ the f value may even become zero. For large values of δ_1, the inductive effect predominates and the f values can become very large. In fluorobenzene, because of the large value of δ, the resonance effect is small and is easily overcome by the large inductive effect. The experimental value[5] of $f = 8.9 \times 10^{-3}$ is fitted by a $\delta_1 = 1.1$.

The f value taken for chlorobenzene[17] is 2×10^{-3}. With the value of $\delta = 2.5$ obtained from the frequency, this can be fitted by $\delta_1 = 0.8$ and not lower. While it is true that the f value does increase at very low values of δ_1, its maximum value in this region ($\delta_1 = 0$) is only one-fifth of the experimental value, which seems to indicate that the intensity is not primarily a resonance effect phenomenon.

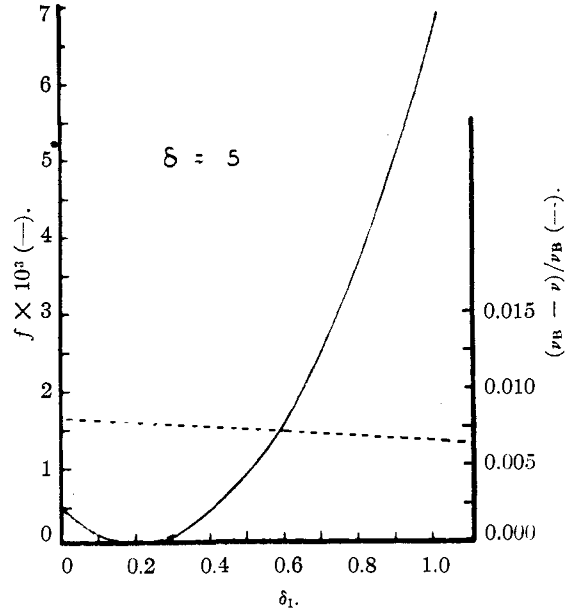

Fig. 4.—Wave length and frequency as a function of δ_1 for $\delta = \delta$.

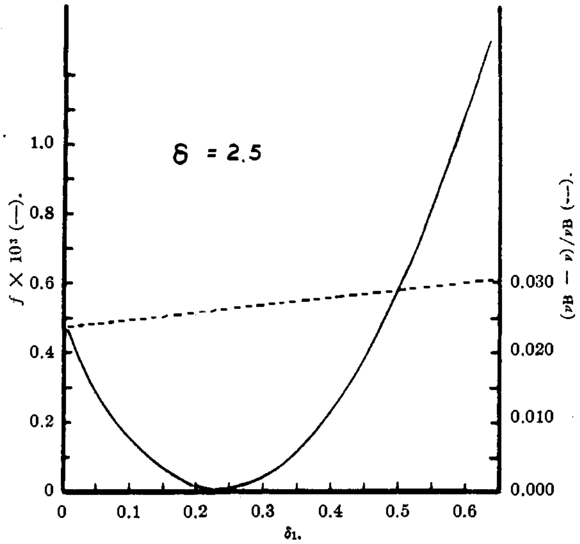

Fig. 5.—Wave length and intensity as a function of δ_1 for $\delta = 2.5$.

The experimental f value of bromobenzene is not known but the spectrum is weaker than that of chlorobenzene and from an inspection of Fig. 2 it is estimated to be 1.5×10^{-3}. This f value is satisfied by $\delta_1 = 0.6$. The results are summarized

	$(\nu_B - \nu)/\nu_B$	$f \times 10^3$	δ	δ_1
C_6H_5F	0.007	8.9	5	1.1
C_6H_5Cl	.025	2	2.5	0.8
C_6H_5Br	.027	1.5	2.4	0.6

Conclusions

The inductive effect, when combined with the resonance effect in the crude molecular orbital theory, provides a very satisfactory description

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[17] This is an average of the value given by Sponer and Lowe[6] and that listed by Mulliken and Rieke, ref. 16. The vibrational contribution to the intensity has been neglected.

of the spectral properties of the phenyl halides. The necessary δ's are in the order which would be expected from consideration of ionization potentials, and the δ_1's in turn bear a reasonable relation to these δ's. One also concludes from these studies that while the frequency is primarily a resonance effect, the intensity of these compounds is due primarily to an inductive effect.

Summary

Vapor and solution near ultraviolet absorption spectra of the phenyl halides are presented.

The position and intensity are calculated by crude molecular orbital theory in which allowance has been made for the inductive effect.

Austin, Texas Received February 20, 1950

[Contribution from the Departments of Chemistry and Physics, The University of Texas]

Molecular Orbital Theory and Spectra of Monosubstituted Benzenes. V. Styrene, Phenylacetylene and Phenylcyclopropane

By J. F. Music[1] and F. A. Matsen

Molecular orbital theory[2] has been shown to provide a reasonably satisfactory description of the near-ultraviolet absorption of monosubstituted benzenes having a substituent with two unshared $p\pi$ electrons on the α-atom. It is the purpose of this paper to extend the treatment to monosubstituted benzenes with hydrocarbon substituents possessing unsaturation, in particular, styrene, phenylacetylene and phenylcyclopropane.

Outline of the Calculations

The Secular Equation.—The MO's may be constructed from linear combinations of the atomic $2p\pi$ functions, ϕ, on each atom

$$\chi_j = \sum_{i=1}^{n} C_{ji}\phi_i \qquad (1)$$

However, for convenience in the solution of the secular equation, the MO's will be taken as linear combinations of functions which are themselves made up of the ϕ's

$$\chi_j = \sum_{i=1}^{8} \lambda_{ji}\,\psi_i \qquad (2)$$

Here ψ_1 through ψ_6 are orthogonal benzene functions[2] and ψ_7 and ψ_8 are substituent functions which are orthogonal to each other and will be particularized for a given molecule.

Variation treatment and the usual assumptions[2] lead to a secular equation in terms of α and β, which are defined as

$$\alpha = \int \phi_i H \phi_i \, d\tau$$
$$\beta = \int \phi_i H \phi_j \, d\tau$$

for atom i adjacent to j—otherwise taken as zero. The elements of the secular equation are of the form

$$H_{pp} = \alpha + n_i\beta_p$$
$$H_{ss} = \alpha + n_i\beta_s$$
$$H_{ps} = N_i\,\beta_{ps}$$

Here p indexes a phenyl ring function and s, a substituent function. The symbol n_i is a positive or negative integer. After the substitution which follows, the n_i's are seen to be the eigenvalues of the zero order problem for benzene and the substituent. For the benzene levels $n_1 = +2$, $n_2 = n_3 = +1$, $n_4 = n_5 = -1$ and $n_6 = -2$. The quantity N_i is the product of the normalization factors and the coefficients of ϕ_1 and ϕ_7 in ψ_s and ψ_p and will be evaluated for the particular molecule.

These elements of the secular equation can be brought into a simpler form on division by β_p and by making the following substitutions

$$A = \frac{\alpha - E}{\beta_p},\ \gamma_1 = \frac{\beta_{ps}}{\beta_p} \text{ and } \gamma_2 = \frac{\beta_s}{\beta_p}$$

The secular equation factors into a second and a sixth order equation. The second order block has roots $A = \pm 1$ and is independent of the substituent. The sixth order block follows

$$\begin{array}{c|cccccc|}
 & (1) & (3) & (5) & (6) & (7) & (8) \\
(1) & A+2 & 0 & 0 & 0 & B & C \\
(3) & 0 & A+1 & 0 & 0 & D & E \\
(5) & 0 & 0 & A-1 & 0 & D & E \\
(6) & 0 & 0 & 0 & A-2 & B & C \\
(7) & B & D & D & B & A+n_7\gamma_2 & 0 \\
(8) & C & E & E & C & 0 & A+n_8\gamma_2
\end{array} = 0 \qquad (3)$$

The numbers in parentheses indicate the functions from which the term at the intersection arises. Thus

$$B = \frac{H_{17}}{\beta_p} = \frac{H_{71}}{\beta_p} = \frac{H_{67}}{\beta_p} = \frac{H_{76}}{\beta_p} = N_i\gamma_1$$

Corresponding definitions obtain for C, D and E. This block yields the equation

$$\begin{aligned}(A^2 - 1)(A^2 - 4)(A + n_7\gamma_2)(A + n_8\gamma_2) - \\ 2A(A^2 - 1)[C^2(A + n_7\gamma_2) + B^2(A + n_8\gamma_2)] - \\ 2A(A^2 - 4)[D^2(A + n_8\gamma_2) + E^2(A + n_7\gamma_2)] + \\ 4A^2[D^2C^2 - B^2E^2] - 8BCDEA^2 = 0 \qquad (4)\end{aligned}$$

In equation (4) all constants except the γ_i may be evaluated from specified ψ's.

Evaluation of γ_i.—It may be assumed that the resonance integral, β, is proportional to the over-

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[1] du Pont Fellow, The University of Texas, 1949–1950.

[2] Matsen, This Journal, **72**, 5243 (1950).