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

Molecular Orbital Theory and Spectra of Monosubstituted Benzenes. I. The Resonance Effect[1]

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Introduction

Molecular orbital calculations have been made on monosubstituted benzenes by Hückel,[2] Wheland and Pauling[3,4] for the purpose of interpreting the orienting effects of substituents in the benzene ring. Sklar[5] and Herzfeld[6] have calculated the intensity and the wave length of ultraviolet absorption, respectively. In this paper a combination of molecular orbital and perturbation theory is used to derive general expressions for the resonance energy, resonance moment, and the intensity and wave length of ultraviolet absorption. These quantities are subsequently evaluated in terms of the parameters of Wheland and Pauling.

The effect of substituents on the properties of the benzene molecule have been discussed in terms of a resonance and an inductive effect. For most molecules the spectrosopic properties are adequately described in terms of the resonance effect alone. However, there is evidence that in certain molecules the inductive effect is of the same magnitude as the resonance effect. These will be treated in Paper IV of this series.

General Theory

The molecular π-orbitals χ_j in a monosubstituted benzene, C_6H_5X may be taken as linear combinations of the $2p\pi$ atomic orbitals of the ring carbon atoms and the attached atom X. These atomic orbitals will be denoted by ϕ_k ($k = 1, 2, \ldots, 7$) where the numbering follows that of the atoms (see Fig. 1). This approximation (LCAO) is embodied in equation (1)

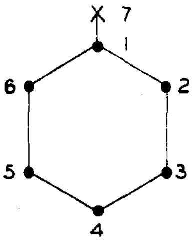

Fig. 1.

$$\chi_j = \sum_{k=1}^{7} A_{jk}\phi_k \qquad (1)$$

However, it is more convenient to express the MO's χ_j as linear combinations of seven orbitals ψ_i of which the first six are orthogonal LCAO benzene orbitals while $\psi_7 = \phi_7$, as in equation (2).

$$\chi_j = \sum_{i=1}^{7} \lambda_{ji}\psi_i \qquad (2)$$ [7]

The seven ψ_i's are as shown in Table I.

TABLE I

Wave function[a,b]	Symmetry[c]	
	D_{6h}	C_{2v}
$\psi_1 = (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)/\sqrt{6}$	A_{1u}	A_1
$\psi_2 = (\phi_2 + \phi_3 - \phi_5 - \phi_6)/\sqrt{4}$	E_{2g}	B_1
$\psi_3 = (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)/\sqrt{12}$	E_{2g}	A_1
$\psi_4 = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/\sqrt{4}$	E_{1u}	B_1
$\psi_5 = (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)/\sqrt{12}$	E_{1u}	A_1
$\psi_6 = (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)/\sqrt{6}$	B_{2g}	A_1
$\psi_7 = \phi_7$	—	A_1

[a] Mayer and Sklar, *J. Chem. Phys.*, **6**, 645 (1938), and ref. 2. [b] The numbering of the benzene orbitals is in the order of increasing energy on perturbation by an electronegative substituent, as determined below. [c] The benzene π-electron system belongs to point group D_{6h} while the monosubstituted system is in C_{2v}.

The energies and forms of the correct orbitals χ_j (equation 2) may be obtained approximately by perturbation theory using the orbitals ψ_i as bases. If the interaction between ring and atom X is regarded as a perturbation, then each orbital χ_j of the perturbed system will be associated with a particular orbital ψ_j of the unperturbed system.

According to standard second order perturbation theory,[8] the energy E_j of an electron in χ_j is given by the equation

$$E_i = H_{ii} - \sum_{i \neq j} \frac{H_{ji}^{\ 2}}{H_{ii} - H_{ii}} \qquad (3)$$

Here $H_{ii} = \int \psi_i H \psi_i d\tau$, etc., where H is the effective one-electron Hamiltonian.[9]

From the C_{2v} symmetry classification given in Table I, together with the orthogonality of the benzene orbitals, it follows that all integrals of the type $H_{ij} (i \neq j)$ vanish or may be assumed negligible except H_{17}, H_{37}, H_{57} and H_{67}. Hence

$$E_j = H_{jj} + \frac{H_{j7}^{\ 2}}{H_{jj} - H_{77}};\ j = 1, 2, \ldots, 6 \qquad (4)$$

and

$$E_7 = H_{77} + \sum_{i=1}^{6} \frac{H_{7i}^{\ 2}}{H_{77} - H_{ii}} \qquad (5)$$

A discussion of the range of validity of perturbation theory is given in Appendix I.

The wave functions χ_j are given by the standard formula

$$\chi_j = \psi_j - \sum_{i \neq j} \frac{H_{ji}\psi_i}{H_{ii} - H_{jj}} \qquad (6)$$

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(1) Presented in part before the San Francisco Meeting of the American Chemical Society, April, 1949.

(2) Hückel, *Z. Physik*, **72**, 310 (1931).

(3) Wheland and Pauling, THIS JOURNAL, **57**, 2086 (1935).

(4) Wheland, *ibid.*, **64**, 900 (1942). See also Ploquin, *Bull. soc. chim.*, France, **15**, 640 (1948); Lyons, *Research*, **2**, 589 (1949).

(5) Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

(6) Herzfeld, *Chem. Revs.*, **41**, 233 (1947).

(7) Dewar, *Proc. Cambridge Phil. Soc.*, **45**, 638 (1949), has discussed these group functions. The monosubstituted benzene corresponds to his case *i*.

(8) See, for example, Pauling and Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 191 ff.

(9) Perturbation theory fails when H_{77} is close in value to any of the H_{ii} and in certain cases it may be necessary to solve a secular equation; see Appendix I.

Comparing this with equation (2) above we see that

$$\lambda_{jj} = 1 \tag{7}$$

and

$$\lambda_{ji} = \frac{H_{ji}}{H_{jj} - H_{ii}} \tag{8}$$[10]

From these equations, one can, in principle, determine the π-electron distribution in the orbital ψ_j; and hence, the resonance moment, directing power, and intensity and wave length of ultraviolet absorption.

Applications

The Herzfeld Formulas.—The theory will now be used to derive formulas for the resonance energy and excitation energy first obtained by Herzfeld. These derivations do not require migration of the substituent electrons into unoccupied benzene orbitals as does the Herzfeld approach. The energy of the ground state $\chi_1^2\chi_2^2\chi_3^2\chi_7^2$ is given by

$$E_g = 2\sum_{j=1}^{3} E_j + 2E_7 \tag{9}$$

Substitution of equations (4) and (5) yields

$$E_g = 2\sum_{j=1}^{3} H_{jj} + 2H_{77} + 2\sum_{j=1}^{3}\frac{H_{j7}^{\ 2}}{H_{jj} - H_{77}} + 2\sum_{i=1}^{6}\frac{H_{7i}^{\ 2}}{H_{77} - H_{ii}} \tag{10}$$

The third and fourth terms on the right side of the equation represent the perturbation of the ring by the substituent and *vice versa*. The sum of these terms gives the "excess resonance energy," ΔRE, of the system

$$\Delta RE = 2\sum_{i=4}^{6}\frac{H_{7i}^{\ 2}}{H_{77} - H_{ii}} \tag{11}$$

where the summation extends over those orbitals of the benzene ring which are unoccupied in the ground state. Equation (11) is identical to that given by Herzfeld.

The energies H_{44}, H_{55}, H_{66} of the unperturbed benzene orbitals, χ_4, χ_5 and χ_6, lie high (they are unoccupied in the ground state) relative to the energy of the unperturbed substituent. Thus, the excess resonance energy of C_6H_5X should be small and relatively insensitive to H_{77}, *i. e.*, to the electronegativity of the substituent. On the other hand, the electronic spectrum, the dipole moment and the chemical reactivity involve the lower orbitals ψ_1 to ψ_3, which are more strongly perturbed; so these properties are quite sensitive to the electronegativity of X.

Herzfeld describes the electronic excitation responsible for the ultraviolet absorption as

$$\chi_1^2\chi_2^2\chi_3^2\chi_7^2 \longrightarrow \chi_1^2\chi_2^2\chi_3\chi_7^2\chi_5$$[11]

If electron interaction is neglected, the change in energy in this transition is, according to equation (4)

$$\Delta E = H_{55} - H_{33} + \frac{H_{57}^{\ 2}}{H_{55} - H_{77}} - \frac{H_{37}^{\ 2}}{H_{33} - H_{77}} \tag{12}$$

To the same approximation the energy of the corresponding excitation in benzene is

$$H_{55} - H_{33}$$

so the difference in excitation energy $\Delta(\Delta E)$ between C_6H_5X and C_6H_6 should be

$$\Delta(\Delta E) = \frac{H_{57}^{\ 2}}{H_{55} - H_{77}} - \frac{H_{37}^{\ 2}}{H_{33} - H_{77}} = h\Delta\nu \tag{13}$$

which is identical to the equation given by Herzfeld.

Evaluation of Integrals.—In order to apply the theory, it is necessary to assign values to the quantities H_{ii} and H_{ij}. Instead of a direct calculation of these quantities, the scheme of Wheland and Pauling will be used. In their notation $H_{11} = \alpha + 2\beta$, $H_{22} = H_{33} = \alpha + \beta$, $H_{44} = H_{55} = \alpha - \beta$, $H_{66} = \alpha - 2\beta$, and $H_{77} = \alpha + \delta\beta$ where $\alpha = \int\phi_k H\phi_k d\gamma$, and $\beta = \int\phi_k H\phi_{k+1} d\gamma$ for $k < 7$. It will also be assumed that $\int\phi_1 H\phi_7 d\gamma = \beta$, although as indicated below, this is not a good assumption in all cases. From the definition of β it will be seen that $H_{17} = H_{67} = \beta/\sqrt{6}$ and $H_{37} = H_{57} = \beta/\sqrt{3}$. The parameter δ is a measure of the electronegativity of the substituent. Its value may be estimated by assuming that H_{77} is approximately the ionization energy of a simple compound containing atom (or group) X. Ionization energies have been recently tabulated by Price.[12] Mulliken[13] has assigned a value of −7.2 e. v. for the benzene α and −3.0 e. v. for the benzene β. In Table II are listed three sets of values for δ, one calculated from the ionization energies, I, of the series of compounds HX, taking $\delta = (7.2 - I)/\beta$, one from the compounds CH_3X calculated in the same manner and the third a "best value" chosen to give the best fit to the spectroscopic data and the resonance energies (see Tables III and IV).

TABLE II

	HX		CH_3X		Best
	Ionizn. energy	δ	Ionizn. energy	δ	value δ^a
F	..	...	15.0	2.6	5
CH_3[b]	13.1	2.0	11.6	1.4	2.9
Cl	12.8	1.9	11.3	1.4	2.5
OH	12.6	1.8	10.8	1.2	1.8
NH_2	10.8	1.2	9.8	0.9	1.6
SH[c]	10.5	1.1	9.7	0.8	1.7

[a] Best value obtained from perturbation theory. Use of the exact solution of the secular equation yields slightly different values. See Paper III. [b] The methyl group does not possess an unshared pair of electrons and so does not formally belong to the groups treated here. It may be considered to have a virtual unshared pair of electrons which interact with the ring through hyperconjugation. [c] The properties of this group are discussed in Paper II.

Substitution for the H_{ij} in equations (4) and (5) yields

$$\begin{aligned}
E_1 &= \alpha + 2\beta - \frac{\beta}{6(\delta - 2)} \\
E_2 &= \alpha + \beta \\
E_3 &= \alpha + \beta - \frac{\beta}{3(\delta - 1)} \\
E_4 &= \alpha - \beta \\
E_5 &= \alpha - \beta - \frac{\beta}{3(\delta + 1)} \\
E_6 &= \alpha - 2\beta - \frac{\beta}{6(\delta + 2)} \\
E_7 &= \alpha + \delta\beta + \frac{\delta(\delta^2 - 3)\beta}{(\delta^2 - 1)(\delta^2 - 4)}
\end{aligned} \tag{14}$$

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(10) On the inclusion of overlap in the perturbation theory, this equation becomes for $i \neq 7$

$$\lambda_{7i} = \frac{H_{7i} - S_{7i}H_{77}}{H_{77} - H_{ii}}$$

the equivalent of equation (19) in Sklar's paper, obtained by another approach

$$\lambda_i = \frac{\rho_i - S_i\omega}{\omega - \omega_i}$$

(11) The excited state may actually be a mixture of several states; see section on oscillator strength.

(12) Price, *Chem. Revs.*, **41**, 257 (1947).

(13) Mulliken, *Phys. Rev.*, **74**, 736 (1948).

Excess Resonance Energy

The excess resonance energy may be obtained directly from equation (11). In order to eliminate the resonance integral, the ratio of the excess resonance energy to the resonance energy of benzene, (2β) will be calculated.

$$\frac{\Delta RE}{RE_B} = \frac{1}{6}\,\frac{3\delta + 5}{(\delta + 1)(\delta + 2)} \qquad (15)$$

In Table III are given the observed quantities and those calculated from the "best values" of δ in Table II.

TABLE III

Compound	$\Delta RE/RE_B$ Calcd. from best value δ	Observed[a]
C_6H_5F	0.08	..
$C_6H_5CH_3$	.11	0.00
C_6H_5Cl	.13	..
C_6H_5OH	.15	.22
$C_6H_5NH_2$	.17	.24

[a] From values tabulated in Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.

Absorption Frequency.—In order to calculate the wave length and intensity of the near ultraviolet absorption of a monosubstituted benzene, the nature of the transition must be established. In benzene the excitation of an electron from the highest filled orbital in the ground state to the lowest unoccupied orbital would produce an excited singlet and triplet state each with fourfold orbital degeneracy. When electron repulsion is included in the Hamiltonian, the degenerate wave functions mix, some of the degeneracy is removed and there result three singlet and three triplet states. The energies of excitation calculated without the electron repulsion is thought to give the average height of the actual states.[14] In the monosubstituted benzene the original orbital degeneracy does not exist, since it is removed by the perturbation of the substituent. In this case it will be assumed that the energy of excitation averaged over the four theoretical orbital states will give the average height of the actual levels. Thus

$$\chi_2 \longrightarrow \chi_4 \quad \Delta E = -2\beta \qquad (16a)$$

$$\chi_2 \longrightarrow \chi_5 \quad \Delta E = -2\beta - \frac{\beta}{3(\delta + 1)} \qquad (16b)$$

$$\chi_3 \longrightarrow \chi_4 \quad \Delta E = -2\beta + \frac{\beta}{3(\delta - 1)} \qquad (16c)$$

$$\chi_3 \longrightarrow \chi_5 \quad \Delta E = -2\beta - \frac{\beta}{3(\delta + 1)} + \frac{\beta}{3(\delta - 1)} \qquad (16d)$$

$$\Delta E_{av} = h\nu = -2\beta + \frac{\beta}{3(\delta^2 - 1)} \qquad (17)$$

The ν is the frequency of a transition from the ground state to a hypothetical state located at the average height of the actual excited states.

By analogy to the corresponding state ($^1B_{2u}$) in benzene,[15] the wave function of the lowest-lying singlet is given approximately by

$$\psi_e = (\psi_a + \psi_b)/\sqrt{2} \qquad (18)$$

where ψ_a corresponds to $\chi_1{}^2\chi_2{}^2\chi_3\chi_4\chi_7{}^2$ and ψ_b to $\chi_1{}^2\chi_2\chi_3{}^2\chi_5\chi_7{}^2$.[16] In the approximation given by equation (18), provided one neglects electronic interaction, the excitation energies to the center of gravity and to the lowest-lying of the mixed singlet excited states are identical and should be given by equation (17). The excitation energy above that of benzene is one-half of that which would have been obtained on the basis of Herzfeld's assumption that only the excited state $\chi_1{}^2\chi_2{}^2\chi_3\chi_5\chi_7{}^2$ is involved. (Compare equation (16d) with equation (17).)

The relative shift in frequency between ν of equation (17) and the corresponding mean frequency in benzene, $\nu_B = -2\beta/h$, is given by

$$\frac{\nu_B - \nu}{\nu_B} = \frac{1}{6(\delta^2 - 1)} \qquad (19)$$

It will now be assumed that the relative shift so computed is applicable without serious error to a comparison between the actual lowest singlet levels of benzene and any substituted benzene, even though strong electron interactions are present in both. The quantity $(\nu_B - \nu)/\nu_B$ as calculated from equation 19, is listed in Table IV using the best value δ from Table II together with the values calculated from the observed O–O bands of the near ultraviolet absorption.

TABLE IV

	$\frac{\nu - \nu_B}{\nu_B}$ Calcd. from best value δ[a]	Obsd.
C_6H_5F	0.007	0.007
$C_6H_5CH_3$	.02	.02
C_6H_5Cl	.03	.03
C_6H_5OH	.07	.05
$C_6H_5NH_2$	.11	.11

[a] From values tabulated in ref. 6.

Oscillator Strength.—Characterization of the lowest-lying excited state by $\psi_e = (\psi_a + \psi_b)/\sqrt{2}$ leads to the following expressions for the oscillator strength of the transition to that state.[17]

$$f = 1.085 \times 10^{11}\nu\left(\int \chi_3 x \chi_4 d\gamma + \int \chi_2 x \chi_5 d\gamma\right)^2 \qquad (20)$$

Here the x axis lies in the plane of the molecule perpendicular to the figure axis.[15] The transition moments for the other axes are zero. The quantity ν is in wave numbers. An approximate expression is

$$f \cong 1.085 \times 10^{11}\nu\,(r/2\,(\lambda_{33} - \lambda_{55}))^2 \qquad (21)$$

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[14] Roothaan and Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).

[15] Mulliken, *ibid.*, **7**, 353 (1939). Professor Mulliken has informed the writer of certain minor errors in this paper. The corrections are embodied above.

[16] For a more accurate discussion of the relative magnitude of the coefficients of ψ_a and ψ_b for a monosubstituted benzene, see Appendix II.

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

The carbon–carbon distance in benzene is given by r. By perturbation theory $\lambda_{33} = \lambda_{55} = 1$; so the transition is forbidden for all values of δ. However, the perturbation wave functions are not yet normalized. An approximate normalization is given by

$$\lambda_{jj}^2 + \lambda_{j7}^2 = 1$$

the λ_{j7} being given by equation (7). Then, to the first approximation

$$f = 0.092\ (\delta^2/(\delta^2 - 1)^4) \qquad (22)$$

The oscillator strengths as obtained experimentally and from equation (22) using the best value δ from Table II are given in Table V.

TABLE V

	Calcd.	Oscillator strength Obsd.
C_6H_5F	0.00002	0.009[b]
$C_6H_5CH_3$	.0003	.001,[a] .003[b]
C_6H_5Cl	.0008	.001,[a] .003[b]
C_6H_5OH	.01	.02[a]
$C_6H_5NH_2$	.04	.03[a]

[a] Reference 17. [b] Sponer and Lowe, *J. Opt. Soc. Am.*, **39**, 840 (1949). The vibrational contribution to the intensity has been neglected.

Directing Power and Resonance Moment.—Molecular orbital theory had led to an interpretation of the directing power of monosubstituted benzenes.[3,4] As a result of the interaction between substituent and ring, there is built up on the latter an excess of negative charge. Wheland and Pauling have calculated the distribution of charge, finding that the electron density is greater at the two, six and four (ortho and para) positions in the ring and, further, that the effect is greater for smaller values of δ. This is in agreement with the observation that these compounds are ortho-para directors and that phenol and aniline, which have small δ values, exercise a strong directing influence.

The separation of charge produces a multipole which to a first approximation may be considered a dipole with the excess charge in the ring localized at the center.[18] The "resonance moment" is defined as the difference between the dipole moment of a monosubstituted benzene and the corresponding alkyl compound. It measures roughly the dipole moment due to the migration of electrons from substituent to ring and may be approximated by the expression

$$\text{resonance moment} = 2e(r + R)(1 - \lambda_{77}^2 - \lambda_{17}^2 - \lambda_{37}^2) \qquad (23)$$

where e is the charge on the electron and $r + R$ is the distance from substituent to the center of the ring. In the lower range the coefficients, λ_{ij}, particularly λ_{17} and λ_{77}, must be evaluated from secular equation solutions for energy. See Appendix I. Wheland and Pauling have calculated the π-electron charge on the substituent to be 1.91, 1.96 and 1.98 for $\delta = 2$, 4 and 6. Taking an average value of $r + R = 2.4$ Å., the resonance moments become 1.03, 0.46 and 0.23 D. An exact comparison with experiment cannot be made since there is no agreement among the several workers. For example, values of 0.31 to 0.91 D have been reported for chlorobenzene. These values are sufficient to indicate that the δ's used for the correlation of intensity and frequency of absorption and resonance energies produce resonance moments of the correct order of magnitude.

To the accuracy of the treatment given here, it is reasonably satisfactory to set $\int \phi_1 H \phi_7 d\gamma$ equal to β. There are at least two instances in which it is suggested from the experimental data that $|\int \phi_1 H \phi_7 d\gamma|$ must be less than $|\beta|$. The first of these is the compound C_6H_5SH, whose wave length shift, intensity and directing power are less than for aniline even though H_2S and CH_3SH have a lower ionization energy than NH_3 and CH_3NH_2, respectively. Secondly, the overlap of the functions ϕ_1 and ϕ_7 can be reduced (thereby reducing the magnitude of $\int \phi_1 H \phi_7 d\gamma$) by the steric effects of ortho substitution in dimethylaniline and similar compounds. In these cases there has been observed a decrease in the resonance moment,[19] and in the wave length and intensity of absorption.[20a,b]

Discussion

A perturbation treatment of MO theory of monosubstituted benzenes making use of the experimentally evaluated parameter, δ, provides a semi-quantitative description of the resonance energies, absorption frequencies, absorption intensities and resonance moments.

The perturbation theory enables one to obtain certain properties of monosubstituted benzenes as simple functions of the parameter δ. An exact solution of the secular equation does not provide these simple functions. However, a plot of the energy levels as a function of δ obtained from the secular equations does give an easily interpretable representation (see Fig. 2 and Appendix I). One can see from an inspection of this figure that the larger the value of δ the smaller the perturbation of the ring; that the lower levels are perturbed more than the upper levels so the frequency of absorption should become smaller as δ becomes smaller; and that since the benzene spectrum is forbidden the greater the perturbation the more allowed the spectrum, so that the spectrum becomes more intense for lower values of δ.

The parameter δ absorbs the effect of many of

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(18) The excess electrical density is concentrated on the two ortho and the para positions. Consequently, there is no net dipole perpendicular to the axis of the molecule. The moments along the axis are additive and assuming a total charge of ρ distributed equally among the three positions, the sum is $\rho/3\ (2r + R + 2(r/2 + R)) = \rho(r + R)$. Here r is the carbon–carbon distance in benzene and R, the distance from substituent to the ring carbon atom number one.

(19) Ingham and Hampson, *J. Chem. Soc.*, 981 (1939).

(20) (a) Remington, THIS JOURNAL, **67**, 1838 (1945); (b) Brown and Reagan, *ibid.*, **69**, 1032 (1947).

the approximations made. For example, the resonance integral between ring and substituent is actually smaller than between two adjacent ring carbon atoms. If the correct value of the resonance integral were used, smaller δ values would be needed; these would, in fact, match more closely the δ's obtained from the ionization energy. Further the use of the empirical parameter δ enables one to extend the range of the perturbation theory.

Comparison of the experimental values of the monosubstituted benzenes with those of benzene itself cancels out certain large-scale approximations in the theory. The β determined spectroscopically is usually different from the one determined from resonance energies. However, β does not enter into the present theory except to determine the amount of mixing in the excited state functions.

Comparison with benzene also renders the neglect of overlap less serious since overlap is neglected in the benzene treatment also. The same can be said for the neglect of electron repulsion.

The greatest effect of substitution on the benzene ring seems to be on the one-electron levels. Consequently, experimental comparisons are set up which emphasize this effect. In this way the perturbation can be studied without working up the complete benzene and monosubstituted benzene problems.

It will be noted that the theory predicts $f = 1 \times 10^{-5}$ for C_6H_5F while the observed value is 9×10^{-3}. This high intensity is believed to be due to the inductive effect (also operative in C_6H_5Cl) and will be discussed in detail in Paper IV of this series.

I wish to acknowledge the kind help of Professors Mulliken and Longuet-Higgins.

Appendix I

Secular Equation.—Since perturbation theory fails when H_{77} is approximately equal to H_{11}, it will be necessary to solve the secular equation to obtain energies for the range of δ values where this is true. The secular equation is of seventh order since there are seven ψ_i's. It, however, factors into two first and one fifth order equation since the benzene functions are orthogonal and only ψ_1, ψ_3, ψ_5 and ψ_6 have the correct symmetry to interact with ψ_7.

$$\begin{vmatrix} \alpha+\beta-E & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \alpha-\beta-E & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha+2\beta-E & 0 & 0 & 0 & \beta/\sqrt{6} \\ 0 & 0 & 0 & \alpha+\beta-E & 0 & 0 & \beta/\sqrt{3} \\ 0 & 0 & 0 & 0 & \alpha-\beta-E & 0 & /\beta\sqrt{3} \\ 0 & 0 & 0 & 0 & 0 & \alpha-2\beta-E & \beta/\sqrt{6} \\ 0 & 0 & \beta/\sqrt{6} & \beta/\sqrt{3} & \beta/\sqrt{3} & \beta/\sqrt{6} & \alpha+\delta\beta-E \end{vmatrix} = 0$$

The fifth order block gives, on expansion

$$\delta = \frac{A(A^2-3)}{(A^2-4)(A^2-1)} - A, \text{ where } A = \frac{\alpha - E}{\beta}$$

The five roots are plotted against δ in Fig. 2. On the right side of the figure the levels are, beginning with the lowest, E_7, E_1, E_3, E_5 and E_6. The unperturbed or zero-order energy levels are given by dotted lines. The real levels do not cross as is to be expected from the no-crossing rule. E_2 and E_4 are not drawn in but would be represented by straight lines parallel to the base at energies $\alpha + \beta$ and $\alpha - \beta$, respectively. For states seven and one the perturbation theory breaks down at $\delta < 3$; for state three at $\delta < 2$; while for the remainder of the states the perturbation theory gives essentially the same results as does the secular equation. States one and seven are not involved in the calculation of resonance energy, intensity or frequency of absorption.

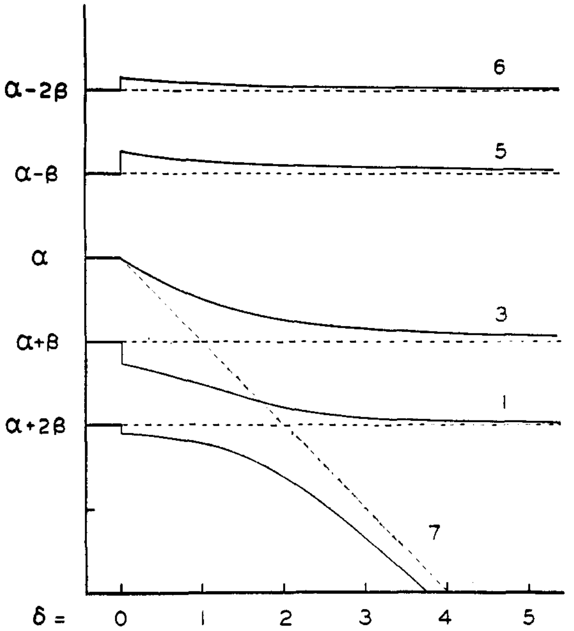

Fig. 2.—The energy levels of the C_6H_5X system as a function of δ. The light dotted lines are the zero order levels. The numbers on the right hand side index the levels.

Appendix II

A question may be raised with regard to the mixing of the zero order excited states, ψ_a and ψ_b. For benzene ψ_a and ψ_b are degenerate so that mixing with equal coefficients follows automatically, but for the monosubstituted benzene ψ_a and ψ_b are not degenerate and equal mixing need not be expected. A change in the amount of mixing will not affect appreciably the center of gravity of the excited states nor, consequently, the position of the spectrum, but, it will have an effect on the intensity of the transition.

Let the trial function be

$$\psi = C_a\psi_a + C_b\psi_b$$

where ψ_a and ψ_b are the antisymmetrized functions for the excited states $\psi_1{}^2\psi_2{}^2\psi_3\psi_4\psi_7{}^2$ and $\psi_1{}^2\psi_3{}^2\psi_2\psi_5\psi_7{}^2$. Let H^t be the total Hamiltonian including electron repulsion.

The resulting energies and coefficients are

$$\frac{E^{+}_{e}}{E^{-}_{e}} = (H_{aa}{}^{t} + H_{bb}{}^{t})/2 \pm {}^{1}/_{2} \sqrt{(H_{aa}{}^{t} - H_{bb}{}^{t})^2 + 4H^{t}{}_{ab}{}^{2}}$$

and

$$C_a/C_b = H^{t}{}_{ab}/(E - H^{t}{}_{aa})$$

To evaluate $H^{t}{}_{aa}$, $H^{t}{}_{bb}$ and $H^{t}{}_{ab}$ one writes the antisymmetrized functions

$$\psi_a = \frac{1}{\sqrt{8!}} \sum_{P} (-1)^{P}\, P\chi_1(1)\chi_1(2)\chi_2(3)\chi_2(4)\chi_3(5)\chi_4(6)\chi_7(7)\chi_7(8)$$
$$\times\, 2^{-1/2}\alpha(1)\beta(2)\alpha(3)\beta(4)[\alpha(5)\beta(6) - \alpha(6)\beta(5)]\alpha(7)\beta(8)$$

$$\psi_b = \frac{1}{\sqrt{8!}}$$
$$\sum_{P} (-1)^{P}\, P\chi_1(1)\, P\chi_1(1)\chi_1(2)\chi_3(3)\chi_3(4)\chi_2(5)\chi_5(6)\chi_7(7)\chi_7(8)$$
$$\times\, 2^{-1/2}\alpha(1)\beta(2)\alpha(3)\beta(4)[\alpha(5)\beta(6) - \alpha(6)\beta(5)]\alpha(7)\beta(8)$$

The total Hamiltonian H^t may be broken up into two parts, $H^t = H + H^1$ where $H^1 = \sum_{\substack{\gamma=1\\ \mu<\gamma}}^{8} \frac{e^2}{r_{\gamma\mu}}$ and $H = \sum_{\gamma=1}^{8} H\gamma$. $H\gamma$ is the Hamiltonian for the γth electron excluding electron repulsion.

The operator H averaged over each of the antisymmetrized orbitals ψ_a and ψ_b yields the sum of the one electron energies since all exchange integrals vanish by virtue of the orthogonality of the χ's. Then

$$H_{aa} - H_{bb} = \frac{2\beta}{3(\delta^2 - 1)}$$

Further

$$H_{ab} = 0$$

The electron repulsion terms are: $H^{1}{}_{aa} - H^{1}{}_{bb} = (\Gamma_{2222} - \Gamma_{3333}) + 2\,(\Gamma_{1122} - \Gamma_{1133}) + 2(\Gamma_{1144} - \Gamma_{1155}) + 2(\Gamma_{2244} - \Gamma_{3355}) + (\Gamma_{1313} - \Gamma_{1212}) + (\Gamma_{1515} - \Gamma_{1414}) + (\Gamma_{3535} - \Gamma_{2727}) + (\Gamma_{5757} - \Gamma_{4747})$

and

$$H^{1}{}_{ab} = -\Gamma_{2435}$$

where

$$\Gamma_{i^1j^1k^1l^1} = \int\!\!\int \chi_{i^1}(\gamma)\,\chi_{j^1}(\gamma)\,\frac{e^2}{r_{\gamma\mu}}\,\chi_{k^1}(\mu)\,\chi_{l^1}(\mu)\,d\tau_\gamma d\tau_\mu = \sum_{i,j,k,l} \lambda_{i^1 i}\lambda_{j^1 j}\lambda_{k^1 k}\lambda_{l^1 l}\gamma_{ijkl}$$

and

$$\gamma_{ijkl} = \int\!\!\int \phi_i(\gamma)\phi_j(\gamma)\,\frac{e^2}{r_{\gamma\mu}}\,\phi_k(\mu)\phi_l(\mu)\,d\tau_\gamma d\tau_\mu$$

Evaluation of these expressions is a formidable task and will not be attempted here. Since all the terms in $H^{1}{}_{aa} - H^{1}{}_{bb}$ appear as differences between closely related integrals, it will be assumed that $H^{1}{}_{aa} - H^{1}{}_{bb}$ is only a small part of the total difference $H^{t}{}_{aa} - H^{t}{}_{bb}$. Then

$$C_a/C_b = 1/(1 - K)$$

where

$$K = \delta\beta/3H^{1}{}_{ab}\,(\delta^2 - 1)$$

With the normalization condition $C^{2}{}_{a} + C^{2}{}_{b} = 1$

$$C_a = \frac{1}{\sqrt{2}\sqrt{1 - K + \frac{K^2}{2}}}$$

The expression for the dipole strength becomes

$$Q = \sqrt{2}\,(C_a\textstyle\int\chi_3 \times \chi_4 d\tau + C_b\int\chi_2\,(x\chi_5\,d\tau)$$
$$\cong \sqrt{2}\,(C_a\lambda_{33} - C_b\lambda_{55})r/2$$
$$= \frac{1}{\sqrt{1 - K + \frac{K^2}{2}}}\left(\frac{-2\delta}{3(\delta^2 - 1)^2} + K\lambda_{55}\right)r/2$$

When K can be neglected the expression reduces to that used in equation (21). Since K is a positive quantity it decreases the magnitude of the term in the bracket but increases its coefficient. The former effect will probably predominate which indicates that the assumption of equal mixing gives intensities which are too high. This will be most noticeable at low δ values.

Summary

A molecular orbital calculation of the resonance energy, intensity and frequency of absorption and resonance moment of monosubstituted benzenes has been made and the results compared with experiment.

Expressions for extent of migration and frequency of absorption first obtained by Sklar and Herzfeld, respectively, are obtained by a perturbation treatment.

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Molecular Orbital Theory and Spectra of Monosubstituted Benzenes. II. Thiophenol

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

It has been shown[1,2,3] that the intensity and wave length of the near ultraviolet absorption of a monosubstituted benzene are strongly dependent upon the ionization energy of the substituent. For substituents with an ionization energy greater than that of benzene, the lower the ionization energy of the substituent, the higher is the intensity and the longer is the wave length of the substituted benzene. In Table II of Paper I[1] is given a list of ionization energies from which it can be concluded that the ionization energy of the –SH group is lower than that of the $-NH_2$ and –OH groups. It is, therefore, to be expected that the intensity and wave length of absorption would be in the order $C_6H_5SH > C_6H_5NH_2 > C_6H_5OH$. Sklar[2] predicted a "large intensification" of the spectrum of thiophenol.

The vapor spectrum of thiophenol has not been reported previously. The solution spectrum of thiophenol has been published by Böhme and Wagner.[3a]

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[1] Matsen, THIS JOURNAL, 72, 5243 (1950).

[2] Sklar, *J. Chem. Phys.*, 7, 984 (1939).

[3] Herzfeld, *Chem. Revs.*, 41, 233 (1947).

[3a] Böhme and Wagner, *Ber.*, 75, 606 (1942).