Electronic Spectra of Substituted Aromatic Hydrocarbons. I. Phenol and Aniline

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(Received July 22, 1960)

Recent advances in both theoretical[1-4] and experimental[5,6] studies have made it possible to understand fully the origin of the electronic spectra of aromatic hydrocarbons. On the other hand, it appears that no satisfactory interpretations have been given to the spectra of substitution products of the aromatics other than benzene. The present series of papers are concerned with systematic analyses of the electronic spectra of substituted aromatic hydrocarbons, especially hydroxyl and amino derivatives.

As to the spectra of monosubstituted benzenes, a number of theoretical investigations have been carried out[7-13]. There remain, however, unsettled problems even concerning

1) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).
2) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).
3) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).
4) N. Mataga, K. Nishimoto and S. Mataga, This Bulletin, **32**, 395 (1959).
5) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).
6) D. S. McClure, ibid., **22**, 1668 (1954); J. W. Sidman, ibid., **25**, 115 (1956).
7) A. L. Sklar, ibid., **7**, 984 (1939).
8) K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).
9) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).
10) S. Nagakura and H. Baba, ibid., **74**, 5693 (1952).
11) L. Goodman and H. Shull, *J. Chem. Phys.*, **27**, 1388 (1957).
12) K. Nishimoto and R. Fujishiro, This Bulletin, **31**, 1036 (1958).
13) Y. I'Haya, *J. Am. Chem. Soc.*, **81**, 6120, 6127 (1959).

the qualitative assignment of the observed absorption bands. In this paper, a molecular orbital (MO) calculation has been made of the π-electronic spectra of phenol and aniline. Herein a semiempirical method of calculation is developed, which will be applied also to naphthalene derivatives in the next paper.

Method of Calculation

The so-called simple LCAO MO theory originally proposed by Hückel is inadequate for dealing with molecules in their excited states. The more rigorous theoretical method, which is based on the correct many-electron Hamiltonian, has been developed to account for the electronic spectra of unsaturated compounds. Although the latter method has been simplified by Pariser and Parr[14] and Pople[2], it seems troublesome to apply it directly to such complex molecules as monosubstituted naphthalenes.

In this calculation an eclectic method is adopted; namely, the simplicity of the Hückel theory is retained, and at the same time it is somewhat modified by reference to the rigorous theoretical method so as to allow for electronic interaction. Thus, MO's are determined by the simple LCAO procedure; configurational wave functions are built up as antisymmetrized products of these MO's, configuration interaction being taken into account.

In the simple LCAO procedure, the energy of an MO is expressed in termes of the resonance integral $\beta\,[\equiv\beta_{\mathrm{CC}}]$. In the present calculation, the evaluation of this integral is made, after the scheme of Goodman and Shull[11], in the following way.

According to the simple LCAO MO theory, the energy required for exciting an electron from an occupied MO ϕ_i to an unoccupied MO ϕ_k is given by

$$\Delta E = e_k - e_i = (m_k - m_i)\,\beta \qquad (1)$$

Here, e_i and e_k are the energies of the MO's ϕ_i and ϕ_k, respectively; $e_i = \alpha + m_i\beta$ and $e_k = \alpha + m_k\beta$, where $\alpha\,[\equiv\alpha_{\mathrm{C}}]$ is the Coulomb integral of a carbon atom.

In the rigorous theory, configurational wave functions are obtained as antisymmetrized products of molecular spin-orbitals. Such wave functions for the lowest energy configuration and for the singlet configuration resulting from the excitation $\phi_i \rightarrow \phi_k$ are denoted by V_0 and V_{ik}, respectively. The energies associated with these wave functions are

$$E(V_0) = \int V_0^* \mathbf{H} V_0 \, \mathrm{d}v, \quad \text{etc.}$$

where $\mathbf{H}$ is the complete many-electron Hamiltonian. Deriving an expression for the excitation energy $\Delta E = E(V_{ik}) - E(V_0)$ by the self-consistent field method, Mulliken pointed out that the energy quantity which is acceptable as the energy of the excited MO ϕ_k is dependent not only upon the MO ϕ_k, but also upon the MO ϕ_i from which the excitation occurs[15]. On the contrary, the orbital energy e_k in Eq. 1 does not depend on ϕ_i.

In view of this situation, let the resonance integral be regarded as a quantity depending upon both i and k, and be designated as $\beta_{i\rightarrow k}$ instead of β. Then, the following relation may be assumed to hold[16]

$$(m_k - m_i)\,\beta_{i\rightarrow k} = E(V_{ik}) - E(V_0) \qquad (2)$$

If the purely theoretical quantity, $E(V_{ik}) - E(V_0)$, is replaced by an appropriate experimental one, $\beta_{i\rightarrow k}$ will immediately be determined, for the values of m_i and m_k can be obtained from the simple MO procedure.

In this study only the singlet transitions will be treated.

Results of Calculation

Molecular Orbitals. — The MO's have been determined by the simple LCAO MO theory with neglect of overlap integrals.

In the parent hydrocarbon, benzene, the following four MO's are responsible for the lower electronic transitions:

$$\phi_2^0 = (1/2)\,(\chi_2 + {}_3\chi - \chi_5 - \chi_6) \qquad (3a)$$

$$\phi_3^0 = (1/\sqrt{12})\,(2\chi_1 + \chi_2 - \chi_3 - 2\chi_4 - \chi_5 + \chi_6) \qquad (3b)$$

$$\phi_4^0 = (1/\sqrt{12})\,(2\chi_1 - \chi_2 - \chi_3 + 2\chi_4 - \chi_5 - \chi_6) \qquad (3c)$$

$$\phi_5^0 = (1/2)\,(-\chi_2 + \chi_3 - \chi_5 + \chi_6) \qquad (3d)$$

where χ_p is the pth carbon $2p\pi$ atomic orbital; the superscript zeros refer to the parent hydrocarbon; ϕ_2^0, ϕ_3^0 and ϕ_4^0, ϕ_5^0 are degenerate pairs of MO's, viz., $e_2^0 = e_3^0 = \alpha + \beta$, $e_4^0 = e_5^0 = \alpha - \beta$.

In the calculation of the MO's of a monosubstituted benzene, the Coulomb integral α_{X} of the substituent X is taken as

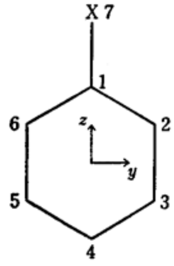

Fig. 1.

14) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

15) R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949); R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

16) A more detailed discussion on this point is given in H. Baba and S. Suzuki, ibid., **32**, 1706 (1960).

$$\alpha_X = \alpha + \delta_X \beta$$

The MO's and their energies are calculated for various values of the parameter δ_X. Let the MO of the monosubstituted benzene corresponding to ϕ_i^0 of the parent hydrocarbon be designated as ϕ_i, and suppose that the substituent X is attached to the carbon atom 1, as shown in Fig. 1. Then, the MO's ϕ_2 and ϕ_5 of symmetry type a_2 are identical with ϕ_2^0 and ϕ_5^0, respectively[17]; the MO's ϕ_3 and ϕ_4 are of symmetry type b_1. The variation of the MO energies with the magnitude of δ_X was reported by Matsen[9].

Configuration Energies.—Owing to the high symmetry (D_{6h}) of benzene, V_{24}^0, V_{35}^0 and V_{25}^0, V_{34}^0 are degenerate pairs of configurations, and the interaction of the configurations of each pair is automatically introduced to give excited states, the characteristics of which are shown in Table I. Referring to this table, one obtains

TABLE I. EXCITED STATES OF BENZENE

Symmetry D_{6h}	Symmetry C_{2v}*	Wave function	Observed excitation energy**, eV.
B_{2u}	B_2^-	$\frac{1}{\sqrt{2}}(V_{24}^0 - V_{35}^0)$	4.88
B_{1u}	A_1^+	$\frac{1}{\sqrt{2}}(V_{25}^0 + V_{34}^0)$	6.14
E_{1u}	B_2^+	$\frac{1}{\sqrt{2}}(V_{24}^0 + V_{35}^0)$	6.74
	A_1^-	$\frac{1}{\sqrt{2}}(V_{25}^0 - V_{34}^0)$	

* In this column are given symmetry types for the subgroup C_{2v} of D_{6h}. The plus or minus sign refers to the manner in which two configurations combine with each other.

** Taken from Ref. 18.

$$E(V_{24}^0) = E(V_{35}^0) = \frac{1}{2}\{W^0(B_{2u}) + W^0(E_{1u})\}$$
$$= E(V_0^0) + 5.81 \text{ eV}.$$
$$E(V_{25}^0) = E(V_{34}^0) = \frac{1}{2}\{W^0(B_{1u}) + W^0(E_{1u})\}$$
$$= E(V_0^0) + 6.44 \text{ eV}.$$

in which $W^0(B_{2u})$, for instance, represents the energy of the B_{2u} state of the parent hydrocarbon, benzene. Since $m_2^0 = m_3^0 = 1$, $m_4^0 = m_5^0 = -1$, it follows from Eq. 2 that

$$\beta_{2\to4}^0 = \beta_{3\to5}^0 = -2.905 \text{ eV.} = \beta^0(B_2) \quad (4a)$$
$$\beta_{2\to5}^0 = \beta_{3\to4}^0 = -3.22 \text{ eV.} = \beta^0(A_1) \quad (4b)$$

In the monosubstituted benzene, the energies of the B_2 configurations, V_{24} and V_{35}, are no longer equal to each other; the same is the case with the energies of the A_1 configurations, V_{25} and V_{34}. In evaluating the energies of these configurations, the assumption is made that

$$\beta_{2\to4} = \beta_{3\to5} = \beta^0(B_2) \quad (5a)$$
$$\beta_{2\to5} = \beta_{3\to4} = \beta^0(A_1) \quad (5b)$$

Then the energies $E(V_{ik})$'s for the configurations V_{ik}'s are readily derived on the basis of Eq. 2, since m_i and m_k can be obtained from the simple MO calculation.

Configuration Interaction.—The matrix element of the total Hamiltonian **H** between V_{ik} and V_{jl} is, in general, given by

$$\{V_{ik} \mid V_{jl}\} = \int V_{ik}^* \mathbf{H} V_{jl} \, dv$$
$$= 2[ki \mid jl] - [kl \mid ji] \quad (i \neq j,\ k \neq l) \quad (6)$$

with

$$[ij \mid kl] = \int \phi_i^*(1)\phi_k^*(2)(e^2/r_{12})\phi_j(1)\phi_l(2)\,dv \quad (7)$$

The orthonormal MO's determined by the simple MO theory are used for the calculation of the above matrix element. On the assumption of zero differential overlap, the integral $[ij \mid kl]$ may be expressed in terms of integrals over atomic orbitals of the form

$$(pp \mid qq)$$
$$= \int \chi_p^*(1)\chi_q^*(2)(e^2/r_{12})\chi_p(1)\chi_q(2)\,dv \quad (8)$$

The integrals of this type were evaluated by Pariser and Parr's method[14]. Necessary values of the valence-state ionization potentials and electron affinities for carbon, oxygen and nitrogen atoms were taken from the table of Pritchard and Skinner[19]. The values of the integrals $(11 \mid 11)_{CC}$ and $(11 \mid 22)_{CC}$ were slightly modified in the following manner.

To the approximation adopted in the present calculation, one obtains

$$\{V_{24}^0 \mid V_{35}^0\} = (1/12)\{(11 \mid 11)_{CC} + 3(11 \mid 22)_{CC}$$
$$- (11 \mid 33)_{CC} - 3(11 \mid 44)_{CC}\}$$
$$= (1/2)\{W^0(E_{1u}) - W^0(B_{2u})\} \quad (9a)$$
$$\{V_{25}^0 \mid V_{34}^0\} = (1/12)\{(11 \mid 11)_{CC} - 9(11 \mid 22)_{CC}$$
$$+ 11(11 \mid 33)_{CC} - 3(11 \mid 44)_{CC}\}$$
$$= (1/2)\{W^0(B_{1u}) - W^0(E_{1u})\} \quad (9b)$$

17) Monosubstituted benzenes belong to symmetry group C_{2v}. The group-theoretical notation used in this paper is the same as that of G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Company, Inc., New York (1945), p. 106. The y and z axes are chosen as in Fig. 1 and the x axis is perpendicular to the molecular plane.

18) H. B. Klevens and J. R. Platt, "Technical Report, Laboratory of Molecular Structure and Spectra, Univ. of Chicago", Part One (1953-1954), p. 145.

19) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, 55, 745 (1955).

in which the superscript zeros refer, as before, to benzene. Pariser and Parr's method gives $(11|33)_{CC}=5.470$ eV. and $(11|44)_{CC}=4.894$ eV. Inserting these values into Eqs. 9a and 9b and using the experimental values, quoted in Table I, for $W^0(B_{2u})$, etc., one may determine those values of $(11|11)_{CC}$ and $(11|22)_{CC}$ which simultaneously satisfy Eqs. 9a and 9b. The result is

$$\left.\begin{aligned}(11|11)_{CC}&=11.212\text{ eV.}\quad(10.84\text{ eV.})\\(11|22)_{CC}&=6.700\text{ eV.}\quad(7.392\text{ eV.})\end{aligned}\right\}\qquad(10)$$

the values obtained by the method of Pariser and Parr being given in parentheses.

The matrix elements $\{V_{24}|V_{35}\}$ and $\{V_{25}|V_{34}\}$ for the monosubstituted benzene are calculated to be

$$\begin{aligned}\{V_{24}|V_{35}\}&\\=(1/2)(-g_{22}+g_{33})&\{(11|11)_{CC}-(11|33)_{CC}\}\\+(3/2)(g_{32}-g_{23})&\{(11|22)_{CC}-(11|44)_{CC}\}\end{aligned}\qquad(11a)$$

$$\begin{aligned}\{V_{25}|V_{34}\}&\\=(-g_{22}+g_{33})&\{(1/2)(11|11)_{CC}-(11|22)_{CC}\\&+(3/2)(11|33)_{CC}-(11|44)_{CC}\}\\+(1/2)(g_{32}-g_{23})&\{(11|22)_{CC}-(11|44)_{CC}\}\\-(g_{11}-g_{44})&\{(11|22)_{CC}-(11|33)_{CC}\}\\-g_{77}&\{(22|77)_{CX}-(33|77)_{CX}\}\end{aligned}\qquad(11b)$$

Here $g_{pq}=c_{3p}c_{4q}$, in which c_{ip} is the coefficient of the atomic orbital χ_p in MO ϕ_i. The matrix elements have been computed for various values of δ_X, the results being shown in Fig. 2. Actually, the curve for $\{V_{25}|V_{34}\}$ was obtained by assuming X to be NH_2. It should be noted in this connection that, while $\{V_{24}|V_{35}\}$ does not contain any terms associated with the substituent X, $\{V_{25}|V_{34}\}$ does contain such terms (see Eq. 11b). Accordingly, a deviation from the above-mentioned curve may occur when X is taken to be OH instead of NH_2. An examination on this point, however, revealed that the deviation is so small as to be virtually negligible. Consequently the curve in question can be applied to the case of the hydroxyl substituent as well as to the amino substituent.

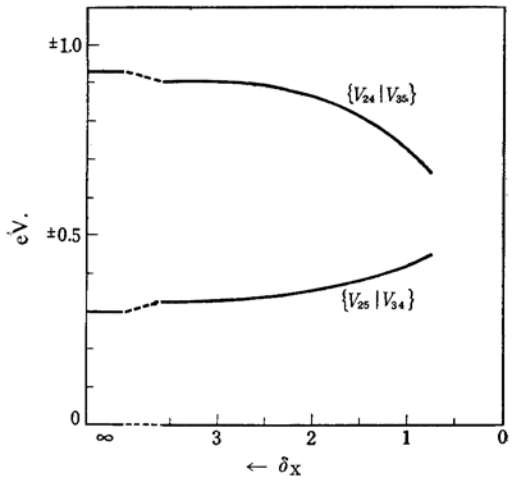

Fig. 2. Relation of the configuration interaction integrals to δ_X. The plus and minus signs on the scale numbers of the ordinate correspond to $\{V_{24}|V_{35}\}$ and $\{V_{25}|V_{34}\}$, respectively.

State Energies.—The interaction between the two B_2 configurations, V_{24} and V_{35}, gives two B_2 states, B_2^+ and B_2^-. Similarly A_1^+ and A_1^- states arise from the interaction of V_{25} and V_{34}. The dependencies of the energies of these states upon δ_X are shown in Fig. 3, together with the observed excitation energies[18,20] for phenol and aniline.

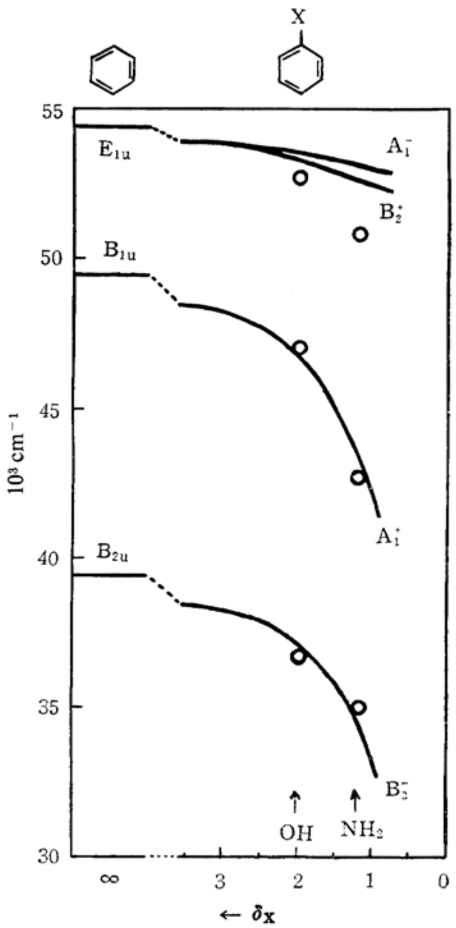

Fig. 3. Relation of the energies of the excited states to δ_X. The observed energies are represented by circles.

20) American Petroleum Institute Research Project 44, Ultraviolet Spectral Data, Serial No. 171.

Oscillator Strengths.—The oscillator strengths, f, have been calculated by the use of the well-known relation[21]

$$f = 1.085 \times 10^{11}\, \nu \mathbf{Q}^2 \qquad (12)$$

where ν is wave number in cm^{-1} and $\mathbf{Q}$ is transition moment in cm. The results are graphed in Fig. 4. The directions of the

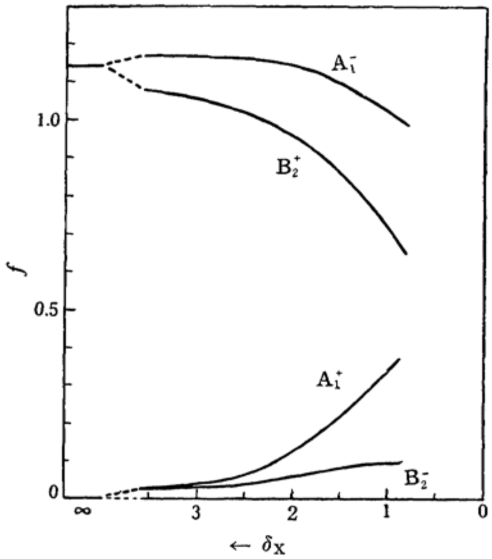

Fig. 4. Relation of f values to δ_X.

transition moments are known from the symmetry types of the excited states concerned. Thus the moments of the transitions to the $B_2^{\pm}$ states are perpendicular to the C_1-X axis, while those of the transitions to the $A_1^{\pm}$ states lie along the direction of the C_1-X axis.

Changes of Electron Density Accompanying Electronic Transitions.—The changes of the π-electron density at the substituent X, Δq_X, accompanying the electronic transitions have been calculated as functions of δ_X. The results

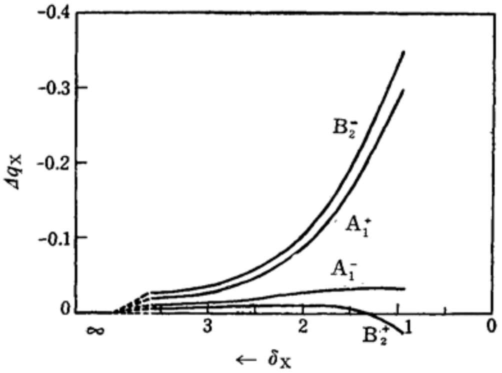

Fig. 5. Relation of Δq_X values to δ_X.

are shown in Fig. 5. The calculation of the electron density is based on the definition of Pariser[3].

Summary of Calculation.—In the preceding sections several theoretical quantities, e. g., configuration interaction integrals and energies of excited states, have been given as functions of the parameter δ_X to see the general trend of the substitution effects. However, in order to find the values of these quantities for a particular molecule, one must assign a suitable value to δ_X. In this calculation the values of δ_X for phenol and aniline have been determined in such a way that the calculated excitation energies might be in best agreement with the observed. This led to the following parameter values (cf. Fig. 3):

$$\text{phenol,} \quad \delta_O = 2.0 \qquad (13a)$$

$$\text{aniline,} \quad \delta_N = 1.2 \qquad (13b)$$

Other theoretical quantities than the excitation energies are also derived by using these parameter values. The calculated results thus obtained for phenol and aniline are summarized in Tables II and III, together with available experimental data.

Discussion

It is seen from Table III that the degrees of configuration mixing in the wave functions of the excited states are considerably changed upon substitution. As was pointed out by Goodman and Shull[11], this fact is of basic importance in discussing the effect of substitution on the excitation energies and intensities.

In making the assignment of the electronic transitions of the substituted benzenes, particularly of aniline, a problem is raised concerning the nature of the excited state for the transition corresponding to the $A_{1g} \rightarrow B_{1u}$ transition of benzene. Murrell[22] regarded the absorption band at 42700 cm^{-1} in aniline as due to a transition to an electron transfer state characteristic of this molecule. According to the present calculation, the above band is attributed to the transition to the A_1^+ state of aniline which corresponds to the B_{1u} state of benzene. As is seen from the data on Δq_N of Table III, this transition is accompanied by an electron transfer, but its amount is much smaller than that in the electron transfer transition of Murrell. Moreover, there occurs an electron transfer also in the transition to the B_2^- state, the amount of which is comparable to that in the case of the transition to the A_1^+ state. Inspection of the calculated values of Δq_X will show that there is no substantial difference between the natures of

21) R. S. Mulliken and C. A. Rieke, *Repts. Progr. Phys.*, **8**, 231 (1941).

22) J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 969 (1955).

TABLE II. ORBITAL ENERGIES AND ORBITALS FOR PHENOL AND ANILINE

	i	Orbital energy $(e_i-\alpha)/\beta$	Orbital ϕ_i
Phenol	3	0.755	$0.477\chi_1+0.372(\chi_2+\chi_6)-0.197(\chi_3+\chi_5)-0.520\chi_4-0.384\chi_7$
	4	-1.108	$0.569\chi_1-0.224(\chi_2+\chi_6)-0.321(\chi_3+\chi_5)+0.580\chi_4-0.183\chi_7$
Aniline	3	0.575	$0.356\chi_1+0.387(\chi_2+\chi_6)-0.133(\chi_3+\chi_5)-0.463\chi_4-0.569\chi_7$
	4	-1.143	$0.559\chi_1-0.200(\chi_2+\chi_6)-0.330(\chi_3+\chi_5)+0.577\chi_4-0.238\chi_7$

TABLE III. EXCITED STATES OF PHENOL AND ANILINE

	Symmetry	Wave function	Excitation energy, cm^{-1}		f		Δq_X
			calcd.	obs.*	calcd.	obs.**	calcd.
Phenol	B_2^-	$0.495V_{24}-0.869V_{35}$	37200	36700	0.059(0.018)	0.0213	-0.103
	A_1^+	$0.487V_{25}+0.873V_{34}$	46800	47000	0.125(0.037)	0.103	-0.087
	B_2^+	$0.869V_{24}+0.495V_{35}$	53400	52700	0.956(0.29)		-0.011
	A_1^-	$0.873V_{25}-0.487V_{34}$	53600		1.142(0.34)		-0.027
Aniline	B_2^-	$0.366V_{24}-0.931V_{35}$	34500	35000	0.091(0.027)	0.026	-0.273
	A_1^+	$0.356V_{25}+0.935V_{34}$	43400	42700	0.289(0.087)	0.17	-0.233
	B_2^+	$0.931V_{24}+0.366V_{35}$	52700	50800	0.773(0.23)		$+0.006$
	A_1^-	$0.935V_{25}-0.356V_{34}$	53200		1.051(0.32)		-0.034

* Taken from Refs. 18 and 20.
** Values for phenol are obtained from the unpublished data of the present author, and those for aniline from the data of Ref. 20.

the 42700 cm^{-1} band of aniline and of the 47000 cm^{-1} band of phenol. Thus, as to the origin of the aniline band, the present interpretation is somewhat different from Murrell's. A further experimental examination is desirable for reaching a final conclusion.

In both phenol and aniline, the calculated energy levels of the B_2^+ and A_1^- states are situated close to each other. This suggests that the 52700 cm^{-1} band of phenol, or the 50800 cm^{-1} band of aniline, consists of two absorptions corresponding to the excitations to the B_2^+ and A_1^- states.

The calculated values of the oscillator strengths may account for the general feature of the effect of the substitution on the band intensities, but their absolute values are too high. A correction factor of 0.30 was introduced, which is the ratio of f_{obs} to f_{calcd} for the $A_{1g}\rightarrow E_{1u}$ transition in benzene; the corrected values are given in parentheses in Table III.

In making a comparison of the calculated and observed f values, one should keep the following point in mind. Both the $A_{1g}\rightarrow B_{2u}(B_2^-)$ and $A_{1g}\rightarrow B_{1u}(A_1^+)$ transitions in benzene are theoretically forbidden, i. e., $f_{calcd}=0$; whereas f_{obs} values for these transitions were found to be 0.0014 and 0.10, respectively[18]. This discrepancy was shown to be due to the distortion of the ring by unsymmetrical vibrations[23]. A part of the f_{obs} values for the corresponding transitions of the substituted benzenes may come from such a ring distortion effect[24]. This is not taken into consideration in deriving the f_{calcd} values. If allowance is made for the contribution from the ring distortion effect, the f_{obs} values for phenol and aniline are known to be in fairly good agreement with the corrected values of f_{calcd}.

The calculation of Δq_X provides useful information about the charge distributions in the excited states. It is seen in Table III that all the Δq_X values are negative except for that associated with the B_2^+ state of aniline, and that the magnitudes of Δq_X for the B_2^- and A_1^+ states are noticeably greater than those for the B_2^+ and A_1^- states. In the ground state of the substituted benzenes under consideration, the substituent has a formal positive charge on account of the migration of the non-bonding pair of electrons into the benzene ring[25]. It will be expected from the calculation that the transitions to the B_2^- and A_1^+ states are accompanied by an appreciable increase of the said positive charge. This expectation is consistent with the observation that the absorption bands corresponding to the transitions to the B_2^- and A_1^+ states are distinctly shifted to the longer wavelengths by the formation of a hydrogen bond between phenol or aniline and

23) A. L. Sklar, *J. Chem. Phys.*, **5**, 669 (1937); M. Goeppert-Mayer and A. L. Sklar, ibid., **6**, 645 (1938); H. Sponer, G. Nordheim, A. L. Sklar and E. Teller, ibid., **7**. 207 (1939).
24) A. L. Sklar, ibid., **10**, 135 (1942).
25) The charge distribution in the ground state of aniline will be shown in the next paper.

a proton-accepting substance, e. g., dioxane[26].

In consideration of the electronegativities of oxygen and nitrogen, the magnitudes of the Coulomb integral parameters δ_O and δ_N, given in Eqs. 13a and 13b, appear to be reasonable. However in the present treatment no allowance has been made for the inductive effect of the substituent group on the ring carbon atoms, which is to be taken into account in a more precise calculation; further, the resonance integral β_{CX} has been assumed to be equal to β_{CC}. Accordingly, the values of δ_O and δ_N should be regarded as effective ones. At any rate, in view of its practical nature, the present method of calculation is expected to be useful for dealing with the spectra of substitution products of complex organic compounds.

26) H. Baba and S. Suzuki, to be published in *J. Chem. Phys.*

Summary

The electronic spectra of monosubstituted benzenes are examined from the viewpoint of semi-empirical MO theory. To allow for electronic interaction, the simple LCAO method is refined in the light of purely theoretical procedure, configuration interaction being included. The refined method is particularly convenient for dealing with the spectra of substituted organic compounds.

The origins of the absorption bands for phenol and aniline are clarified on the basis of the calculated excitation energies, oscillator strengths and changes of charge distribution accompanying electronic transitions. The nature of the second excited state of aniline is discussed in detail, in connection with the problem of electron transfer.

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