Nature of the π-Electronic Spectra of Aromatic Compounds.[1] *I. Aromatic Hydrocarbons and Their Hydroxyl Derivatives*

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It is very interesting, for several reasons, to carry out the systematic theoretical analysis of the π-electronic spectra of aromatic compounds in the visible and near-ultraviolet regions. First, the spectra of aromatic hydrocarbons show some remarkable regularities.[2,3] There is, for instance, a noticeable empirical relation, pointed out by Clar,[2] between the wavelengths of the weakest band and the strongest band in the spectrum of an aromatic hydrocarbon. Second, the effect of the substitution on the spectrum of the parent hydrocarbon depends largely upon the position at which the substituent is attached to the molecule.[4] Thirdly, the π-electronic spectrum of a *N*-heterocycle bears a noteworthy resemblance to that of the corresponding hydrocarbon,[4,5] although the replacement of –CH=

1) Presented in part at the International Symposium on Molecular Structure and Spectroscopy, Tokyo, Japan, September, 1962.

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2) E. Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin (1952).

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4) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, New York (1951).

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with –N= brings little change in the intensity and frequency of the spectrum of the parent hydrocarbon.

Recently, many excellent theoretical works on the π-electronic spectra of aromatic hydrocarbons have been published.[6-13] However, very few systematic theoretical studies of the nature of the π-electronic spectra of aromatic derivatives have been made, except for benzene derivatives.[14-20] In previous papers[21,22] we have studied the electronic spectra of phenol, α- and β-naphthols by the ASMO-CI method. Our theory expected that all the ^1L_b absorptions would be polarized in the direction perpendicular to their C–O bond axes. Our next interest has been to study the electronic spectra of more complicated derivatives, such as anthrols and nitroanthracenes. However, it is hard to study them by the ordinary ASMO-CI method.

The primary purpose of the present study is, therefore, to propose a theoretical procedure for the systematic study of the nature of π-electronic spectra of aromatic derivatives with a minimum of theoretical effort. The method is based on a limited LCMO approximation. It has been generally recognized that the Pariser-Parr's theory[11] is the best semi-empirical ASMO theory at present. However, the theory gives a rather unsatisfactory result for the transition energy of the benzene B_{2U} spectrum. This result is attributable to the estimation of two center-electron repulsion integrals, $\gamma_{\mu\nu}$. Recently, we have proposed an approximation[23] for the estimation of $\gamma_{\mu\nu}$ within the framework of zero differential overlap approximation, and we have successfully applied it to the SCF calculation of benzene *N*-heterocycles[23,24] and to the ASMO calculation of the electronic structure of some aromatic hydroxyl derivatives.[21,22,25]

In this paper, we will, first, study and elucidate the π-electronic spectra of several catacondensed hydrocarbons, whose general formula is $C_{4n+2}H_{2n+4}$, and will examine the existence of the Clar relation, by means of the ASMO-CI method. Next, we will study the effect of the substitution of a hydroxyl group on the nature of the π-electronic spectrum of the parent hydrocarbon. In subsequent papers, we will apply the present method to the aromatic nitro derivatives and the aromatic *N*-heterocycles.

Theoretical Procedure

The procedure of calculation may be summarized as follows: First, we calculate the eight lowest excited states, four of which are singlets and the others, triplets, of the parent hydrocarbon by means of the ASMO-CI method. The configurational wave function associated with a given electron configuration is represented by an antisymmetrized product of the Hückel molecular orbitals (HMO), which are obtainable in Ref. 26. The ground state wave function and the energy are described by the symbols Ψ_0 and H_0 respectively. The excited configurational function associated with the transition of one electron from an occupied orbital, ϕ_i, to a vacant orbital, $\phi_{k'}$, and the corresponding configurational energy are represented by $^1\chi_{ik'}$ and $^1H_{ik',ik'}$ or by $^3\chi_{ik'}$ and $^3H_{ik',ik'}$ respectively. (Here, the superscripts 1 and 3 indicate singlet and triplet respectively.)

It is interesting to note that the number of nodal planes, perpendicular to the molecular plane, of a given HMO is closely related to the orbital ring quantum number in the free electron theory.[6] It may, therefore, be closely connected with the selection rule for the transition. To a first approximation, it is, therefore, reasonable to assume that the "optical electrons" are those in the higher occupied orbitals, which have n nodal planes perpendicular to the molecular plane, and that the transitions from these orbitals to the lower vacant orbitals, which have $(n+1)$ nodal planes, are primarily responsible for the absorption spectrum in the longest wavelength regions.

For an aromatic hydrocarbon, there are two such higher occupied orbitals and two lower vacant orbitals, so that we can have four kinds of transitions from their combinations. In

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8) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc.*, (*London*), **A67**, 795 (1954).
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19) L. Goodman and H. Shull, ibid., **27**, 1388 (1957).
20) I. Fischer-Hjalmer, *Ark. für Fys.*, **21**, 123 (1962).
21) K. Nishimoto and R. Fujishiro, This Bulletin, **31**, 1036 (1958).
22) K. Nishimoto, *J. Phys. Chem.*, **67**, 1443 (1963).
23) K. Nishimoto and N. Mataga, *Z. physik. Chem.* (*Frankfurt*), **12**, 335 (1957).
24) N. Mataga and K. Nishimoto, ibid., **13**, 140 (1957).
25) K. Nishimoto and R. Fujishiro, This Bulletin **35**, 905 (1962).
26) C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," C. N. R. S. and I. C. I., Ltd., Paris (1955).

order to discuss the spectra of aromatic compounds systematically, it will be convenient to use the following notation: 1) The higher one of the two higher occupied orbitals in a hydrocarbon is designated as ϕ°_1, and the other as ϕ°_2. 2) The lower one of the two lower vacant orbitals is designated as $\phi^\circ_{1'}$ and the other as $\phi^\circ_{2'}$. As Coulson-Rushbrook[27] and Longuet-Higgins[28] have pointed out, in an alternant hydrocarbon the molecular orbitals appear in pairs. Because of this peculiar property, the configurations $\chi_{12'}$ and $\chi_{21'}$ are degenerate. Therefore, we have the following relation:

$$H_{12',12'}=H_{21',21'} \tag{1}$$

In addition, because of the molecular symmetry, the configurations $\chi_{11'}$ and $\chi_{22'}$ combine together, as do as $\chi_{12'}$ and $\chi_{21'}$. As a result, the excited state should be divided into two classes, which may be expressed as follows:

$$\left.\begin{aligned}
\Psi(\mathrm{L_a}) &= A\chi_{11'}+B\chi_{22'}\\
\Psi(\mathrm{B_a}) &= B\chi_{11'}-A\chi_{22'}\\
\Psi(\mathrm{L_b}) &= \frac{1}{\sqrt{2}}(\chi_{12'}-\chi_{21'})\\
\Psi(\mathrm{B_b}) &= \frac{1}{\sqrt{2}}(\chi_{12'}+\chi_{21'})
\end{aligned}\right\} \tag{2}$$

where the letter in parenthesis is Platt's notation characterizing the nature of the excited state.

The interconfigurational energy, $H_{ik',jl'}$ which is given by

$$H_{ik',jl'}=\int \chi_{ik'}H\chi_{jl'}\mathrm{d}\tau \tag{3}$$

where H is the total Hamiltonian, is calculated by the method described in our previous paper.[25] The present calculations concern the interaction between only a few configurations, so it is not necessary to use a constant value of the semi-empirical parameter β_{CC}, which is a core integral over the neighboring carbon $2p\pi$AO's from molecule to molecule, since the β_{CC} value should depend more or less upon how many configurations are taken into account. As a matter of convenience, the value of β_{CC} is chosen here for each hydrocarbon to fit the observed absorption maxima of either the ^1B_b or ^1L_b species.

When the HMO's of the parent hydrocarbon are written as $\phi^\circ_{2n+1}, \cdots, \phi^\circ_1, \phi^\circ_{1'}, \cdots, \phi^\circ_{(2n+1)'}$ and those of the substituent, as $\theta_1, \cdots, \theta_m$, the HMO of an aromatic derivative, ψ_i, is exactly represented by the linear combinations of these unperturbed MO's:

$$\psi_i=\sum_k b_{ik}\phi^\circ_k+\sum_j b_{ij}\theta_j \tag{4}$$

However, since we are concerned with the electronic spectra of aromatic derivatives in the longest wavelength regions, we will be able satisfactorily to explain them by considering only the higher occupied and the lower vacant unperturbed MO's, which make the most important contribution to the lowest excited states of the molecule. From this point of view, we introduce a limited LCMO approximation and express ψ_i as:

$$\begin{aligned}\psi_i=C_{i2}\phi^\circ_2+C_{i1}\phi^\circ_1+C_{i1'}\phi^\circ_{1'}+C_{i2'}\phi^\circ_{2'}\\ +C_{is}\theta_s+C_{is'}\theta_{s'}\end{aligned} \tag{5}$$

where θ_s and $\theta_{s'}$ are the highest occupied and the lowest vacant HMO of a substituent respectively. C_{ij} is a coefficient to be determined by the variation principle, using appropriate parameters.

When the substituent is an auxochromic group, such as OH, NH_2, or $N(CH_3)_2$, there is no $\theta_{s'}$ (if we neglect the hyperconjugation effect). Therefore, in this case, ψ_i should be necessarily expressed by the linear combination of five unperturbed MO's:

$$\begin{aligned}\psi_i=C_{i2}\phi^\circ_2+C_{i1}\phi^\circ_1+C_{i1'}\phi^\circ_{1'}\\ +C_{i2'}\phi^\circ_{2'}+C_{is}\theta_s\end{aligned} \tag{6}$$

where θ_s is the lone pair orbital centered at the substituent. In the case of hydroxyl derivatives, we assume the conventional Coulomb integral, α_O, for the hydroxyl group to be:

$$\alpha_O=\alpha+1.5\beta$$

and the conventional resonance integral to be:

$$\beta_{CO}=0.7\beta$$

These are the values reported in our previous paper.[21]

The Hartree-Fock-like orbital energy associated with ψ_i is given by:

$$\bar{\varepsilon}_i=\int \psi_i F\psi_i\mathrm{d}\tau \tag{7}$$

where F is the Hartree-Fock operator, whose general expression has been given in Roothaan's article,[29] for the system. For the sake of simplicity, $\bar{\varepsilon}_i$ is estimated by the following approximation:

$$\begin{aligned}\bar{\varepsilon}=&(C^2_{i2}-C^2_{i2'})\bar{\varepsilon}^\circ_2+(C^2_{i1}-C^2_{i1'})\bar{\varepsilon}^\circ_1\\ &+C^2_{is}\bar{\varepsilon}^\circ_s+C^2_{is'}\bar{\varepsilon}^\circ_{s'}\\ &+2C_{is}[(C_{i2}\pm c_{i2'})H_{2s}+(C_{i1}\pm C_{i1'})H_{1s}]\\ &+2C_{is'}[(C_{i2}\pm C_{is'})H_{2s'}+(C_{i1}\pm C_{i1'})H_{1s'}]\end{aligned}$$

where the upper and lower signs are associated with the α- and β-substitution respectively.

27) C. A. Coulson and G. S. Rushbrook, *Proc. Camb. Phil. Soc.*, **36**, 193 (1940).
28) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).
29) C. C. J. Roothaan, *Revs. Modern Phys.*, **23**, 69 (1951).

Interaction energies, H_{2s}, H_{1s}, $H_{2s'}$ and $H_{1s'}$, are approximated by:

$$H_{2s}=\int \psi^{\circ}{}_2(1)\,H_{\mathrm{core}}(1)\,\theta_s(1)\,\mathrm{d}\tau$$

$$H_{1s}=\int \psi^{\circ}{}_1(1)\,H_{\mathrm{core}}(1)\,\theta_s(1)\,\mathrm{d}\tau$$

$$H_{2s'}=\int \psi^{\circ}{}_2(1)\,H_{\mathrm{cere}}(1)\,\theta_{s'}(1)\,\mathrm{d}\tau$$

$$H_{1s'}=\int \psi^{\circ}{}_1(1)\,H_{\mathrm{core}}(1)\,\theta_{s'}(1)\,\mathrm{d}\tau$$

$\bar{\varepsilon}^{\circ}{}_2$, $\bar{\varepsilon}^{\circ}{}_1$, $\bar{\varepsilon}^{\circ}{}_s$ and $\bar{\varepsilon}^{\circ}{}_{s'}$ are the Hartree-Fock-like orbital energies associated with $\psi^{\circ}{}_2$, $\psi^{\circ}{}_1$, θ_s and $\theta_{s'}$ respectively. Therefore, the configurational energy is given by;

$$^{1,3}H_{ik',ik'}=\bar{\varepsilon}_{k'}-\bar{\varepsilon}_i-[ii\mid k'k']+[ik'\mid ik'] \pm [ik'\mid ik'] \qquad (9)$$

where

$$[ik\mid jl]=\int \psi_i(1)\psi_k(1)\frac{e^2}{r_{12}}\psi_j(2)\psi_l(2)\,\mathrm{d}\tau$$

The plus and minus signs are combined with the singlet and triplet configurations respectively. The interconfigurational energy is simply approximated by:

$$^{1,3}H_{ik',jl'}=-[ij\mid k'l']+[ik'\mid jl'] \pm [ik'\mid jl'] \qquad (10)$$

This approximation means that a given configuration interacts with other configurations through only the electron repulsion term in the total Hamiltonian.

In the calculation of the molecular integrals of a hydroxyl derivative, we use the following approximation:

1) $\bar{\varepsilon}^{\circ}{}_s$ has a constant value of -11.649 eV., the value of the integral over the oxygen $2p\pi$ atomic orbital (AO) with respect to the Hartree-Fock Hamiltonian of phenol.[21]

2) The core integral over the neighboring carbon and oxygen $2p\pi$AO's is assigned a constant value of -1.664 eV., which is estimated as $0.7\times(\beta_{\mathrm{CC}}$ of benzene).

3) The electron repulsion integrals over AO's are calculated by the method described in our previous papers.[21,25]

For convenience, we lay down the following rule for the numbering of the MO's of a derivative. We name the orbital which contains θ_s to the extent of more than 50%, ϕ_s, and the orbital which contains $\psi^{\circ}{}_2$ to the extent of more than 50%, ϕ_2, and so on. Using this rule, the excited state wave function for an aromatic derivative can be adequately given by the linear combination of six configurations:

$$\Psi_a=d_{a1}\chi_{11'}+d_{a2}\chi_{22'}+d_{a3}\chi_{12'}+d_{a4}\chi_{21'}+d_{a5}\chi_{s1'}+d_{a6}\chi_{1s'} \qquad (11)$$

The coefficient d_{at} is to be determined by the variation principle.

In order to study the π-electronic spectra of aromatic compounds systematically, we use Platt's nomenclature[6] and set up the following somewhat artificial criterion for the assignment of the electronic transitions: we describe the excited state which is characterized by $d_{a1}>0$, $d_{a2}>0$ and $d^2{}_{a1}+d^2{}_{a2}>0.5$ as the L_a species. Here, d_{a1} is a coefficient which appeared in Eq. 11. The state which is characterized by $d_{a3}>0$, $d_{a4}>0$ and $d^2{}_{a3}+d^2{}_{a4}>0.5$, we designate as the B_b species. The criteria are arranged in Table I. In the table, C-T

Table I. Assignment of the electronic transition in aromatic compounds

State	Characterization		
L_a	$d_{a1}>0$	$d_{a2}>0$	$d^2{}_{a1}+d^2{}_{a2}>0.5$
L_b	$d_{a3}>0$ or $d_{a3}<0$	$d_{a4}<0$ or $d_{a4}>0$	$d^2{}_{a3}+d^2{}_{a4}>0.5$
B_b	$d_{a3}>0$	$d_{a4}>0$	$d^2{}_{a3}+d^2{}_{a4}>0.5$
B_a	$d_{a1}>0$	$d_{a2}<0$	$d^2{}_{a1}+d^2{}_{a2}>0.5$
$(C\text{-}T)_1$	$d^2{}_{a5}>0.5$		
$(C\text{-}T)_2$	$d^2{}_{a6}>0.5$		

indicates an intramolecular charge transfer state. When we use these criteria, we will be able to assign theoretically the π-electronic excited states of a conjugated system without any trouble.

In the present calculations, the excited state wave function of a hydroxyl derivative is approximated by the linear combination of only four configurations, $\chi_{11'}$, $\chi_{22'}$, $\chi_{12'}$ and $\chi_{21'}$, for two reasons. First, ϕ_s is located deep

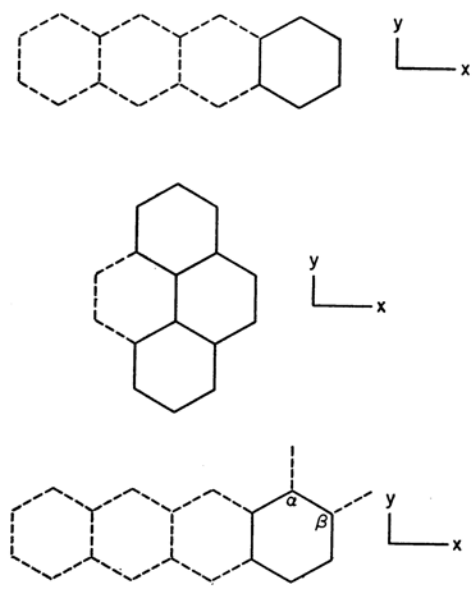

Fig. 1. Structures of aromatic hydrocarbons and their hydroxyl derivatives.

TABLE II. CALCULATED EXCITATION ENERGIES, OSCILLATOR STRENGTHS AND POLARIZATIONS

Excited state	Excitation energy, eV.		Oscillator strength		Polarization
	Calcd.	Exptl.	Calcd.	Exptl.	
			Benzene		
$\Psi(^1L_b)$	4.880	4.88[a]	0	0.0014[a]	x
$\Psi(^1L_a)$	6.119	6.14[a]	0	0.10 [a]	y
$\Psi(^1B_b)$	6.941	6.74[a]	1.186	—	x
$\Psi(^1B_a)$	6.941	6.74[a]	1.186	—	y
$\Psi(^3L_a)$	3.143	3.65[b]	0	—	
$\Psi(^3B_b)$	4.880	—	0	—	
$\Psi(^3L_b)$	4.012	—	0	—	
$\Psi(^3B_a)$	4.012	—	0	—	
			Naphthalene		
$\Psi(^1L_b)$	3.990	3.99[c]	0	0.002[c]	x
$\Psi(^1L_a)$	4.236	4.51[c]	0.273	0.10 [c]	y
$\Psi(^1B_b)$	5.608	5.62[c]	2.119	1.70 [c]	x
$\Psi(^1B_a)$	6.185	—	0.854	—	y
$\Psi(^3L_a)$	2.279	2.64[d]	0	—	
$\Psi(^3B_b)$	3.990	—	0	—	
$\Psi(^3L_b)$	3.485	—	0	—	
$\Psi(^3B_a)$	4.065	—	0	—	
			Anthracene		
$\Psi(^1L_a)$	3.300	3.31 [e]	0.363	0.10 [f]	y
$\Psi(^1L_b)$	3.649	—	0	—	x
$\Psi(^1B_b)$	4.930	4.930[e]	2.848	2.28 [f]	x
$\Psi(^1B_a)$	6.098	6.66 [f]	0.756	0.65 [f]	y
$\Psi(^3L_a)$	1.510	1.85 [g]	0	—	
$\Psi(^3B_b)$	3.649	—	0	—	
$\Psi(^3L_b)$	3.328	—	0	—	
$\Psi(^3B_a)$	4.482	—	0	—	
			Tetracene		
$\Psi(^1L_a)$	2.786	2.63[e]	0.400	0.98[f]	y
$\Psi(^1L_b)$	3.507	—	0	—	x
$\Psi(^1B_b)$	4.520	4.52[e]	3.411	1.85[f]	x
$\Psi(^1B_a)$	6.070	5.88[f]	0.728	0.45[f]	y
$\Psi(^3L_a)$	1.125	1.27[h]	0	—	
$\Psi(^3B_b)$	3.507	—	0	—	
$\Psi(^3L_b)$	3.292	—	0	—	
$\Psi(^3B_a)$	4.768	—	0	—	
			Phenanthrene		
$\Psi(^1L_b)$	3.797	3.59[e]	0	0.003[f]	x
$\Psi(^1L_a)$	4.119	4.24[e]	0.566	0.18 [f]	y
$\Psi(^1B_b)$	4.874	4.94[e]	1.072	1.09 [f]	x
$\Psi(^1B_a)$	4.934	6.62[f]	1.174	0.59 [f]	y
$\Psi(^3L_a)$	2.451	2.68[i]	0	—	
$\Psi(^3L_b)$	3.174	—	0	—	
$\Psi(^3B_b)$	3.797	—	0	—	
$\Psi(^3B_a)$	3.457	—	0	—	
			Pyrene		
$\Psi(^1L_b)$	3.276	3.34[e]	0	—	x
$\Psi(^1L_a)$	3.490	3.72[e]	0.673	—	y
$\Psi(^1B_b)$	4.560	4.56[e]	1.263	—	x
$\Psi(^1B_a)$	5.171	5.14[e]	1.449	—	y
$\Psi(^3L_a)$	1.722	—	0	—	
$\Psi(^3L_b)$	2.926	—	0	—	
$\Psi(^3B_b)$	3.276	—	0	—	
$\Psi(^3B_a)$	3.674	—	0	—	

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b) H. Shull, *J. Chem. Phys.*, **17**, 295 (1949).
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d) J. Ferguson, T. Iredale and J. A. Taylor, *J. Chem. Soc.*, **1954**, 3160.
e) Reference 2.
f) Reference 3.
g) M. R. Padhye, S. P. McGlynn and M. Kasha, *J. Chem. Phys.*, **24**, 588 (1956).
h) S. P. McGlynn M. R. Padhye and M. Kasha, ibid., **23**, 593 (1955).
i) K. Kanda and B. Shimada, *Spectrochim. Acta*, **13**, 211 (1959).

TABLE III. CALCULATED INTERCONFIGURATIONAL ENERGIES FOR HYDROCARBONS (in eV.)

	Benzene	Naphthalene	Anthracene	Tetracene	Phenanthrene	Pyrene
$^1H_{11',11'}-H_0$	6.5301	4.3695	3.3768	2.8454	4.2380	3.6639
$^1H_{22',22'}-H_0$	6.5301	6.0517	6.0213	6.0104	4.8150	4.9968
$^1H_{11',22'}$	−0.4113	−0.4916	−0.4578	−0.4372	−0.2882	−0.5120
$^1H_{12',12'}-H_0$	5.9107	4.7991	4.2895	4.0136	4.3354	3.9180
$^1H_{12',21'}$	1.0307	0.8092	0.6404	0.5064	0.5386	0.6420
$^3H_{11',11'}-H_0$	3.5775	2.3155	1.5188	1.1286	2.5590	1.7373
$^3H_{22',22'}-H_0$	3.5775	4.0285	4.4733	4.7652	3.3494	3.6584
$^3H_{11',22'}$	−0.4341	−0.2526	−0.1608	−0.1078	−0.3114	−0.1748
$^3H_{12',12'}-H_0$	4.4459	3.7373	3.4883	3.3994	3.4854	3.1012
$^3H_{12',21'}$	−0.4341	−0.2526	−0.1608	−0.1078	−0.3114	−0.1748

and apart from the others. Secondly, the interconfigurational energies between $\chi_{s1'}$ and the other configurations are relatively small.

The core structures and the molecular axes of hydrocarbons and their hydroxyl derivatives are shown in Fig. 1. Here, we assume that each molecular framework is made of the appropriate regular hexagon systems, with the constant bond length of 1.397 Å, the experimental carbon-carbon bond distance for benzene.[30]

The intensity of the absorption associated with the one-electron transition from Ψ_o to Ψ_a is calculated by:[31]

$$f = 1.085 \times 10^{11} \tilde{\nu}_{oa} (D_{oa})^2 \qquad (12)$$

where $\tilde{\nu}_{oa}$ is the frequency of the transition in cm^{-1}. $\vec{D}_{oa}$ is the transition moment defined by:

$$\vec{D}_{oa} = \int \Psi_o \sum e_i r_i \Psi_a \mathrm{d}\tau \qquad (13)$$

where e_i and r_i are the charge and the position vector of the i-th charged particle respectively. $\vec{D}_{oa}$ gives the direction of the polarization of the absorption band. Therefore, we usually use $\vec{D}_{oa}$ in assigning and classifying the electronic spectrum of a molecule.

Results and Discussion

The spectrum of a hydrocarbon in the visible and near ultraviolet regions usually contains four main absorptions. On the basis of a free electron model (perimeter model), Platt[6] classified these bands as ^1L_b, ^1L_a, ^1B_b and ^1B_a respectively. There is the following remarkable empirical relation, pointed out by Clar,[2] between the wavelength maxima of the weak ^1L_b band and the very strong ^1B_b band:

$$\lambda(^1L_b)/\lambda(^1B_b) = 1.35 \qquad (14)$$

The calculated results of hydrocarbons are summarized in Table II, where they are also compared with the experimental data. The calculated interconfigurational energies are collected in Table III. The results are in satisfactory agreement with the experimental findings. The calculated $\lambda(^1L_b)/\lambda(^1B_b)$ values are given in Table IV. The results lead to this correlation equation:

$$\lambda(^1L_b)/\lambda(^1B_b) = 1.36 \pm 0.06 \qquad (15)$$

That is, the present theory suggests approximately the existence of the Clar relation.

TABLE IV. CALCULATED RATIO OF THE WAVELENGTH OF ^1L_b SPECIES, $\lambda(^1L_b)$, TO THE WAVELENGTH OF ^1B_b, $\lambda(^1B_b)$

Molecule	$\lambda(^1L_b)/\lambda(^1B_b)$
Benzene	1.42
Naphthalene	1.41
Anthracene	1.35
Tetracene	1.29
Phenanthrene	1.28
Pyrene	1.39

Semi-empirically estimated β_{CC} values are collected in Table V. A plot of β_{CC} against n, the number of carbon atoms included in a given hydrocarbon, gives a good correlation, as is shown in Fig. 2. The correlation line is given by:

$$\beta_{CC}(n) = 0.571 \times 10^{-0.0522n} + 2.100 \text{ eV}. \qquad (16)$$

Alternant aromatic hydrocarbons can be broadly divided into two isomeric series: One is the linear series in which the rings are arranged linearly, as in anthracene. The other

TABLE V. SEMI-EMPIRICALLY ESTIMATED β_{CC} VALUES FOR HYDROCARBONS

Molecule	β_{CC} (in eV.)
Benzene	−2.3777
Naphthalene	−2.2310
Anthracene	−2.2062
Tetracene	−2.1673
Phenanthrene	(−2.2062)
Pyrene	−2.1863

30) B. P. Stoicheff, *Can. J. Phys.*, **32**, 339 (1954).
31) R. S. Mulliken and C. A. Rieke, *Rep. Progr. Phys.*, **8**, 231 (1941).

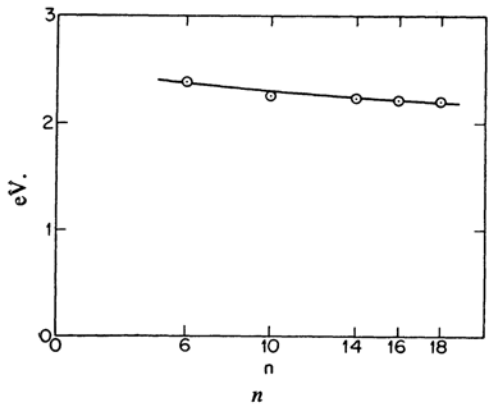

Fig. 2. A plot of β_{CC} against the number of carbon atom, n, contained in the hydrocarbon.

is the angular series, of which phenanthrene is the first member. As is shown in Fig. 4, in the linear series there is a steady displacement of the group of the maxima towards longer wavelengths with the increasing length of the conjugated system.

The molecules of the linear series have symmetry planes along both their short and long axes. The transition moments for allowed transitions can, then, be either perpendicular or parallel to the long axis of the molecule (x-axis in Fig. 1) or, alternatively, allowed transitions have either transverse or longitudinal polarization. The present calculation expects that the transitions from the ground state to $\Psi(^1L_a)$ or to $\Psi(^1B_a)$ will be polarized in the direction of the molecular y-axis, whereas the transitions from the ground state to $\Psi(^1L_b)$ or to $\Psi(^1B_b)$ will have the polarizations in the direction of the molecular x-axis. In assigning the spectrum of phenanthrene, there

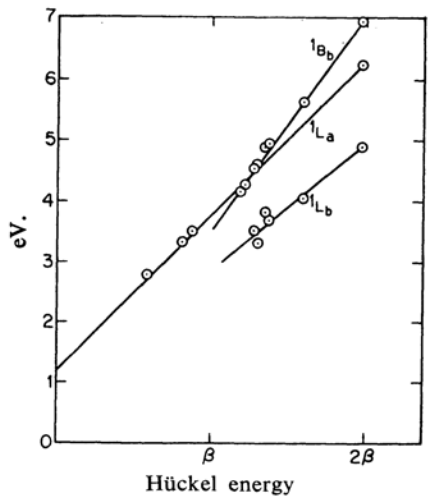

Fig. 3. A plot of the calculated singlet frequency against the corresponding Hückel energy.

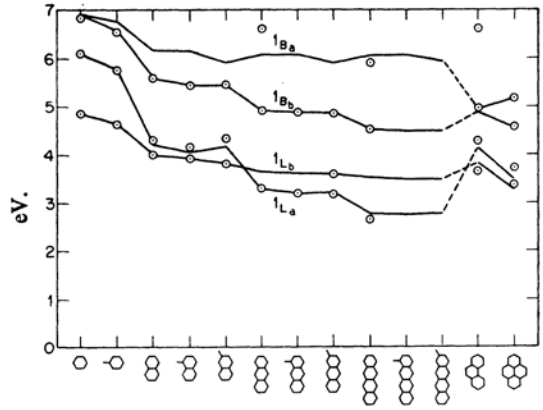

Fig. 4. Comparison of calculated and experimental singlet states. The experimental values are represented by circles.

is a puzzling question. We can treat it as a modified naphthalene spectrum. However, in the light of our theoretical results, it seems better to regard the spectra of phenanthrene and pyrene as modified biphenyl spectra. Their molecular axis should, therefore, be fixed as in Fig. 1 for the study of the electronic spectra. Unfortunately, with a few exceptions, the experimental polarizations are unknown.

The present calculation anticipates that the transition from the ground state to the $\Psi(^1L_b)$ will be forbidden if the molecule rests at the equilibrium configuration. However, the molecule continuously vibrates around the equilibrium positions with rather small amplitudes, and some of the vibrations may instantaneously break down the molecular symmetry. As a result, the forbidden ^1L_b absorption would barely appear through the coupling with such vibrations, accompanied by the vibrational fine structure as in the benzene 260 mμ absorption.

Our results show that the intensity of the ^1L_a absorption should increase with the length of the conjugated system. However, the observed oscillator strengths have practically the same value from molecule to molecule. Moreover, the calculated oscillator strength associated with the ^1B_b absorption seems somewhat larger than the observed values. The reason for this is probably to be found partly in the limited configuration interaction treatment and partly in the point charge approximation.

It is interesting to examine whether or not any interrelationships exist between the calculated frequency and the corresponding orbital energy difference in the Hückel theory. A plot of the calculated frequency against the corresponding Hückel energy gives a rather good correlation, as Fig. 3 shows.

Our approximation for two center electron

TABLE VI. CALCULATED EXCITATION ENERGIES, OSCILLATOR STRENGTHS OF AROMATIC HYDROXYL DERIVATIVES

The theoretical results are compared with experimental data.

Excited state	Excitation energy eV.		Oscillator strength	
	Calcd.	Exptl.	Calcd.	Exptl.
		Phenol		
$\Psi(^1L_b)$	4.672	4.55[a]	0.0146	0.0213[a]
$\Psi(^1L_a)$	5.792	5.83[a]	0.113	0.103[a]
$\Psi(^1B_b)$	6.626	6.53[a]	0.976	—
$\Psi(^1B_a)$	6.799	—	1.231	—
$\Psi(^3L_a)$	3.088	—	0	—
$\Psi(^3L_b)$	3.905	—	0	—
$\Psi(^3B_b)$	4.804	—	0	—
$\Psi(^3B_a)$	3.869	—	0	—
		α-Naphthol		
$\Psi(^1L_b)$	3.906	3.86[c]	0.0059	0.016[c]
$\Psi(^1L_a)$	4.065	4.29[c]	0.335	0.102[c]
$\Psi(^1B_b)$	5.462	{5.40[c] 5.80	1.952	{0.328[c] 0.892
$\Psi(^1B_a)$	6.178	—	0.863	—
$\Psi(^3L_a)$	2.152	—	0	—
$\Psi(^3L_b)$	3.418	—	0	—
$\Psi(^3B_b)$	3.931	—	0	—
$\Psi(^3B_a)$	4.059	—	0	—
		β-Naphthol		
$\Psi(^1L_b)$	3.834	3.78[c]	0.0412	0.0211[c]
$\Psi(^1L_a)$	4.187	4.54[c]	0.199	0.0811[c]
$\Psi(^1B_b)$	5.490	5.53[c]	2.191	1.06 [c]
$\Psi(^1B_a)$	5.912	—	0.863	—
$\Psi(^3L_a)$	2.248	—	0	—
$\Psi(^3L_b)$	3.371	—	0	—
$\Psi(^3B_b)$	3.809	—	0	—
$\Psi(^3B_a)$	4.062	—	0	—
		α-Anthrol		
$\Psi(^1L_a)$	3.216	3.19[j]	0.391	—
$\Psi(^1L_b)$	3.613	—	0.0027	—
$\Psi(^1B_b)$	4.867	4.90[j]	2.740	—
$\Psi(^1B_a)$	6.097	—	0.761	—
$\Psi(^3L_a)$	1.458	—	0	—
$\Psi(^3L_b)$	3.295	—	0	—
$\Psi(^3B_b)$	3.620	—	0	—
$\Psi(^3B_a)$	4.481	—	0	—
		β-Anthrol		
$\Psi(^1L_a)$	3.230	3.56[j]	0.321	—
$\Psi(^1L_b)$	3.612	3.16[j]	0.0255	—
$\Psi(^1B_b)$	4.873	4.88[j]	2.988	—
$\Psi(^1B_a)$	5.906	—	0.756	—
$\Psi(^3L_a)$	1.496	—	0	—
$\Psi(^3L_b)$	3.258	—	0	—
$\Psi(^3B_b)$	3.589	—	0	—
$\Psi(^3B_a)$	4.424	—	0	—
		1-OH Tetracene		
$\Psi(^1L_a)$	2.738	—	0.413	—
$\Psi(^1L_b)$	3.487	—	0.0014	—
$\Psi(^1B_b)$	4.488	—	3.339	—
$\Psi(^1B_a)$	6.069	—	0.730	—
$\Psi(^3L_a)$	1.101	—	0	—
$\Psi(^3L_b)$	3.273	—	0	—
$\Psi(^3B_b)$	3.490	—	0	—
$\Psi(^3B_a)$	4.768	—	0	—
		2-OH Tetracene		
$\Psi(^1L_a)$	2.754	—	0.282	—
$\Psi(^1L_b)$	3.478	—	0.0082	—
$\Psi(^1B_b)$	4.492	—	3.592	—
$\Psi(^1B_a)$	5.936	—	0.724	—
$\Psi(^3L_a)$	1.118	—	0	—
$\Psi(^3L_b)$	3.246	—	0	—
$\Psi(^3B_b)$	3.474	—	0	—
$\Psi(^3B_a)$	4.726	—	0	—

a) Reference a in Table II.
c) Reference c in Table II.
j) Reference 34.

repulsion integrals seems to be adequate for the calculation of singlet states, but not for triplet states. There is a reason for this. Our approximation has been found from the benzene singlet spectrum by a trial and error procedure. As Linnett indicated in his book,[32] the electron correlation in the singlet state differs entirely from that in the triplet state. It is probable that our approximation implicitly includes the electron correlation in the singlet state, therefore, it perhaps does not explain the electron correlation in the triplet state.

In the present calculations, we have introduced the following two somewhat drastic approximations: for a molecule, the core integral, β_{CC}, has been fixed at a constant value, and only the four lowest excited configurations have been taken into account. The observed distances in a polyacene are usually not the same.[33] It is natural that the value of β_{CC} should vary with the variation in the bond distances. However, in this paper, we have used HMO's in which the bond dependence of the resonance integral has been neglected. Therefore, so far as we use HMO's in the theory, a constant β approximation may be reasonable. In order to improve the theory, we have to apply the SCF-MO theory with reference to the bond distance dependence of core integrals.

Next, we will consider the excited states of

32) J. W. Linnett, "Wave Mechanics and Valency," Methuen and Co., London (1960).
33) F. Ahmad and D. J. W. Cruickshank, *Acta Cryst.*, 5, 852 (1952).

TABLE VII. CALCULATED INTERCONFIGURATIONAL ENERGIES FOR AROMATIC HYDROXYL DERIVATIVES (in eV.)

	Phenol	α-Naphthol	β-Naphthol	α-Anthrol	β-Anthrol	1-OH Tetracene	2-OH Tetracene
$^1H_{11',11'}-H_0$	6.0608	4.1911	4.2159	3.2916	3.3109	2.7967	2.8081
$^1H_{22',22'}-H_0$	6.5301	6.0517	5.7708	6.0213	5.8312	6.0104	5.8812
$^1H_{12',12'}-H_0$	5.2722	4.5599	4.7915	4.1873	4.2952	3.9619	4.0241
$^1H_{21',21'}-H_0$	6.0255	4.8086	4.6442	4.2922	4.1838	4.0136	3.9454
$^1H_{11',22'}$	−0.4452	−0.5011	−0.4641	−0.4609	−0.4258	−0.4378	−0.4091
$^1H_{11',12'}$	0	0	0.0884	0	0.0377	0	0.0211
$^1H_{11',21'}$	0	0	−0.1123	0	−0.0470	0	−0.0157
$^1H_{22',12'}$	0	0	0.1063	0	0.0666	0	0.0250
$^1H_{22',21'}$	0	0	−0.0099	0	0.0272	0	0.0324
$^1H_{12',21'}$	0.9016	0.7681	0.7809	0.6249	0.6358	0.4996	0.5063
$^3H_{11',11'}-H_0$	3.3794	2.1819	2.3121	1.4664	1.5099	1.1045	1.1231
$^3H_{22',22'}-H_0$	3.5775	4.0285	3.9746	4.4733	4.4148	4.7652	4.7226
$^3H_{12',12'}-H_0$	4.1106	3.5803	3.6629	3.4133	3.4700	3.3585	3.3953
$^3H_{21',21'}-H_0$	4.5989	3.7684	3.5410	3.5020	3.3734	3.4050	3.3228
$^3H_{11',22'}$	−0.3776	−0.2385	−0.2285	−0.1563	−0.1590	−0.1060	−0.1079
$^3H_{11',12'}$	0	0	−0.1000	0	−0.0275	0	−0.0107
$^3H_{11',21'}$	0	0	0.1803	0	0.0954	0	0.0651
$^3H_{22',12'}$	0	0	−0.0841	0	−0.0142	0	0.0002
$^3H_{22',21'}$	0	0	0.1073	0	0.0168	0	−0.0002
$^3H_{12',21'}$	−0.3776	−0.2385	−0.2285	−0.1563	−0.1590	−0.1060	−0.1079

the hydroxyl derivatives. Generally speaking, the absorption spectra of aromatic hydroxyl derivatives in the near ultraviolet regions closely resemble those of the parent hydrocarbons,[4,34] except that the absorption bands are usually shifted to somewhat longer wavelengths. However, in the polycyclic hydroxyl derivatives, not all the possible positions of substitution are identical, so the various groups of absorption bands (^1L_b, ^1L_a, ^1B_b and ^1B_a) are not always shifted to the same extent. For example, there is a noticeable difference between the spectral changes caused by the substitutions at the α- and β-positions. In this paper, the effect on the electronic spectrum of the substitution of a hydroxyl group at the α- or β-position of the parent hydrocarbon has been studied.

The calculated results of the hydroxyl derivatives are summarized in Table VI, where they are also compared with the experimental data. The calculated interconfigurational energies are collected in Table VII. The theoretical singlet frequencies are in satisfactory agreement with the experimental findings. It is suprising that the interconfigurational energies for α-hydroxyl derivatives are practically the same as those for the parent hydrocarbons. Their calculation is, however, an elaborate task, so it is convenient, for a first approximation, to use the latter in place of the former.

The substitution of a hydroxyl group on the parent hydrocarbon has the following effects: first, it breaks out the molecular symmetry of D_{2h} or D_{6h} and removes the peculiar degeneracy of the two configurations, $\chi_{12'}$ and $\chi_{21'}$. As a result, the theoretical oscillator strength of the ^1L_b absorption is not zero, but has a definite value. Furthermore, all the excited configurations will interact with each other. Secondly, a lone-pair orbital of the substituent conjugates with the π-electron system of the parent hydrocarbon. This usually results in something of a spectral red shift. Figure 4 shows the interrelation between the lower singlet states. The present theory suggests that the ^1L_a bands of the parent hydrocarbons are most sensitive for the α-substitution, whereas the β-substitution has no significant effect on them. On the other hand, the ^1L_b bands are

TABLE VIII. POLARIZATIONS OF THE ELECTRONIC TRANSITIONS IN AROMATIC DERIVATIVES

Molecule	Polarization $\Psi_0 \rightarrow \Psi(^1L_a)$	$\Psi_0 \rightarrow \Psi(^1L_b)$	$\Psi_0 \rightarrow \Psi(^1B_b)$	$\Psi_0 \rightarrow \Psi(^1B_a)$
Phenol	90°	180°	180°	90°
α-Naphthol	86°	180°	180°	89°
α-Anthrol	85°	180°	180°	89°
1-OH Tetracene	86°	180°	180°	89°
β-Naphthol	99°	115°	181°	78°
β-Anthrol	97°	72°	181°	79°
2-OH Tetracene	94°	41°	181°	80°

Note: Numerical value gives an angle between the transition moment vector and x-axis of the molecule.

34) H. Baba and S. Suzuki, This Bulletin, 34, 82 (1961); 35, 683 (1962).

remarkably affected by the β-substitution, while they are only slightly influenced by the α-substitution. It is interesting to note that the effect of substitution gradually decreases with the length of the parent conjugated systems.

We have a special interest in the effect of substitution on the direction of the polarization of the electronic transition of the parent hydrocarbon, because the nature of the electronic excited states of the molecule is frequently discussed on the basis of the polarization of the electronic transition.

The calculated results are summarized in Table VIII. Our calculations show that, in α-derivatives, in spite of the absence of D_{2h} or D_{6h} symmetry each absorption band should be polarized in the direction of the short or long molecular axis of the parent hydrocarbon systems. That is, the characteristics of the spectrum of the parent hydrocarbon are not changed in this case. On the other hand, in β-derivatives, the nature of the spectrum of parent hydrocarbons is considerably lost, because all the excited configurations interact strongly with each other. In β-naphthol, for example, the ^1L_b species contains a configuration $\chi_{11'}$ to the extent of about 26% and is polarized approximately in the direction perpendicular to the carbonoxygen bond. Moreover, the present theory expects that, if we try to assign the excited states of β-anthrol on the basis of the experimental polarization, it will be impossible to distinguish the ^1L_a and ^1L_b bands. Unfortunately, no experiments connected with the polarization of the electronic transition in the aromatic hydroxyl derivative have yet given us any results. In β-derivatives the direction of polarization moves gradually towards that of the parent hydrocarbon with an increase in the length of the conjugated system.

The calculated oscillator strength of the α-derivative exhibits a striking contrast to that of the β-derivative. Namely, by α-substitution, the ^1L_a absorption is intensified, whereas the ^1B_b absorption is slightly weakened. On the contrary, the β-substitution has the effects of intensifying the latter absorption and weakening the former absorption. Moreover, the ^1L_b absorption is considerably intensified by the β-substitution, while it is only slightly increased in intensity by the α-substitution. These results are in accord with the experimental data.[4]

The theoretical results for phenol, α- and β-naphthols in the present theory are in satisfactory agreement with those based on the ASMO-CI method.[21,22] This fact suggests that the present theory is reasonable and adequate for the purpose of making a systematic study of the electronic spectra of aromatic derivatives with a minimum of theoretical effort.

Summary

The π-electronic spectra of a number of aromatic hydrocarbons and their hydroxyl derivatives have been theoretically studied by the ASMO-CI method within the framework of a limited LCMO approximation. The calculated singlet frequencies are in satisfactory agreement with the experimental findings. The experimental Clar relation is obtained theoretically. The present theory suggests that the substitution of a hydroxyl group at the α-position of the parent hydrocarbon has effects of a substantial red shift in the ^1L_a band and a rather small shift in the ^1L_b band, but the band characteristics are practically the same as those of the parent hydrocarbon. On the other hand, the substitution at the β-position has the effect of mixing the ^1L_a species with the ^1L_b species to a considerable extent, so that the band characteristics of the parent hydrocarbon should be considerably modified by this type of substitution. In the light of the present theory, it is better to regard the spectra of phenanthrene and pyrene as modified biphenyl spectra. A plot of the calculated frequency against the corresponding Hückel energy gives a rather good correlation.

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