BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 645—650 (1966)

Calculation of the Three π–π^* Absorptions of Conjugated Systems by Hückel MO Method

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(Received April 22, 1965)

Correlation relations between the Hückel molecular orbital energies and the absorption wavelengths of the ${}^1L_a$, ${}^1L_b$, and ${}^1B_b$ species of an alternant hydrocarbon are presented. After a small modification, the present relations are applied fairly well to the calculations of the electronic spectra of α-substituted hydrocarbon and *N*-heterobenzenes. This shows us that the nature of the electronic spectra of these compounds are very similar with those of parent hydrocarbon. On the other band, the calculation for β-substituted derivatives does not give good results, although the agreement between the calculated and observed values is semi-quantitatively satisfactory. This should be attributed to the complicated configuration interaction scheme between the lower excited configurations of the molecule.

It is widely recognized that the Hückel molecular orbital theory¹⁾ (HMO theory) provides very useful theoretical information for the prediction of the various ground state properties of the conjugated molecules, such as bond distances, reactivity, resonance energy, and dipole moment, in spite of its appalling simplicity. However, only a few attempts²⁾ made to positively treat the electronic spectra of the aromatic compounds by HMO theory, because this theory does not explicitly, but only implicitly, take the electron repulsions into account. It would be, however, very convenient when we can calculate the electronic spectra of these compounds in the framework of HMO theory.

The present paper shows that there is a possibility for the prediction of the main three absorptions of a given aromatic compound in the near ultraviolet or visible region by HMO theory, when we set up an appropriate HMO transition energy - absorption wavelength relationship, just as in the case of the bond length calculation for which we usually use Coulson's bond order - bond length relation.³⁾ In this paper, first of all, we will provide some relationships between HMO transition energies and the absorption wavelengths of ${}^1L_a$, ${}^1L_b$, and ${}^1B_b$ species for the alternant hydrocarbon. Secondly, we will apply these relations to some *N*-heterocycles and aromatic derivatives. All of the HMO calculations are carried out by the IBM 7090 computer of the University of Pittsburgh.

HMO Energy - Absorption Wavelength Relations

Alternant Hydrocarbons.—The spectra of an aromatic hydrocarbon in the longer wavelength region has usually three absorption maxima: weak, medium, and intense bands, which on an empirical basis Clar⁴⁾ classified as α-, *p*-, and β-bands, respectively. However, on a theoretical point of view, a spectroscopic symbolism developed by Platt⁵⁾ on the basis of free electron model is more convenient for the classification of the absorption bands. According to this nomenclature, the ${}^1L_a$ band (Clar's *p*-band) is associated with a transition from the highest occupied MO, ψ_1, to the lowest vacant MO, $\psi_{1'}$. A convention given in the previous paper⁶⁾ is used for numbering of MO. In HMO theory, the MO energy associated with *i*th MO, ψ_i, is expressed by

$$\psi_i; \quad \varepsilon_i = \alpha + m_i\beta \tag{1}$$

where α and β are conventional Coulomb and resonance integrals, respectively. The eigenvalue m_i is a root of the secular determinant. The HMO transition energy associated with ${}^1L_a$ absorption is, therefore, given by

$$E({}^1L_a) = (m_1 - m_{1'})\beta$$

or

$$\Delta m = E({}^1L_a)/\beta = m_1 - m_{1'} \tag{2}$$

For the convenience, an excited configuration associated with one electron transition from an

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1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York (1961).

2) For example, Ref. 1, p. 202.

3) C. A. Coulson, *Proc. Roy. Soc.*, **A169**, 413 (1939).

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

5) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949); *J. Opt. Soc. Am.*, **43**, 252 (1953).

6) K. Nishimoto and R. Fujishiro, This Bulletin, **37**, 1660 (1964).

TABLE I. CALCULATED AND OBSERVED ABSORPTION WAVELENGTHS FOR HYDROCARBONS (in mμ)

	$\lambda(^1L_a)$		$\lambda(^1L_b)$		$\lambda(^1B_b)$	
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
Acetylene	161	166*	—	—	—	—
Ethylene	174	174[1]	—	—	—	—
Benzene	190	190[2],*	264	264[2]	179	179[2]
Naphthalene	283	285[2]	316	315[2]	221	221[2]
Anthracene	380	375[2]	352	—	253	252[2]
Tetracene	478	471[2]	378	—	276	274[2]
Pentacene	579	582[2]	396	428[2]	294	303[2]
Phenanthrene	286	293[2]	361	345[2]	261	251[2]
Chrysen	320	319[2]	374	360[2]	273	267[2]
Picene	328	329[2]	406	376[2]	303	287[2]
3, 4-Benzphenanthrene	320	315[2]	394	372[2]	273	281[2]
Benzanthracene	354	359[2]	411	385[2]	307	390[2]
Pyrene	358	334[2]	372	372[2]	270	272[2]

1) P. G. Wilkinson and H. L. Johnston, *J. Chem. Phys.*, **18**, 190 (1950).

2) E. Clar, "Polycyclic Hydrocarbons," Vols. 1 and 2, Academic Press, New York (1964).

* See text.

occupied orbital, ψ_i, to a vacant orbital, ψ_j, is represented by χ_{i-j} in this paper. In an alternant hydrocarbon, the two excited configurations, $\chi_{1-2'}$ and $\chi_{2-1'}$ are degenerate, namely

$$\Delta m = m_1 - m_{2'} = m_2 - m_{1'} \qquad (3)$$

and interact each other by the first order configuration interaction, as shown in Fig. 1. This configuration interaction gives rise to a highly allowed intense ^1B_b band (Clar's β band) and a very weak ^1L_b band (Clar's α-band). According to the Pariser-Parr-Pople theory,[7] in which the electron repulsions are explicitly taken into account, the energy associated with a singlet electronic transition $^1\chi_{i-j}$ is given by:

$$\Delta E_{i-j} = \varepsilon_j{}^F - \varepsilon_j{}^F - [ii|jj] + 2[ij|ij] \qquad (4)$$

where $\varepsilon_i{}^F$ and $[ij|kl]$ are the Hartree-Fock orbital energy associated with ψ_i and the electron repulsion integral over MO's, respectively. The peculiar degeneracy in an alternant hydrocarbon,

$$\Delta E_{1-2'} = \Delta E_{2-1'}$$

is still valid in Pariser-Parr-Pople treatment. However, the comparison of Eq. 2 with Eq. 4 makes clear that in the discussion of electronic spectra, the conventional resonance integral β does not have its original meaning, which is a characteristic integral for a given carbon-carbon bond, but it is a complicated function of electron repulsion integrals and core integrals over atomic orbitals. The value should, therefore, depend on the molecular shape and varies from molecule to molecule. However, as shown in the previous paper,[6] in linear polyacene series the value of ε_i and $[ij|kl]$ monotonously decreases with increase in the molecular size.

This suggests that in a linear polyacene series there are some relationships between the wavelengths of three main absorptions, $\lambda(^1L_a)$, $\lambda(^1L_b)$, and $\lambda(^1B_b)$, and the corresponding Δm values of Eqs. 2 and 3. The plot of the absorption wavelength against the $1/\Delta m$ in Fig. 2 shows excellent correlations. The correlations are satisfactorily represented by:

$$\lambda(^1L_a) = 474(\Delta m)^{-1/2} - 145 \text{ m}\mu \qquad (5)$$

$$\lambda(^1L_b) = 428(\Delta m)^{-1} + 50 \text{ m}\mu \qquad (6)$$

$$\lambda(^1B_b) = 358(\Delta m) \text{m}\mu \qquad (7)$$

respectively. Rather similar relations have been found by Streitwieser,[1] except for ^1L_a species. The calculated wavelengths for various hydrocarbons are compared with the experimental data in Table I. The agreement between the calculated and observed values is satisfactory in the whole. From Eq. 5, the conventional resonance integrals for ethylene and acetylene are estimated as $\beta_{C=C} = 1.1\beta$ and $\beta_{C\equiv C} = 1.2\beta$, respectively. In benzene and acetylene, the configurations $\chi_{1-1'}$ and $\chi_{2-2'}$ are degenerate and interact each other. This gives rise to a weak ^1L_a and strong ^1B_a absorptions. Therefore, the calculated $\lambda(^1L_a)$ should be compared with the harmonic mean of the observed $\lambda(^1L_a)$ and $\lambda(^1B_a)$.

The correlation equations, 5 and 7, have the following noteworthy features; that is, the transition energy associated with the ^1B_b species is proportional to the corresponding HMO energy ($\beta = -3.46$ eV.), whereas $\lambda(^1L_a)$ varies linearly with the inverse square root of Δm. This seems to suggest us that when we use the valence bond language the excitation from the ground state to the ^1L_a state may be described by the change in the covalent structure and that to ^1B_b state may be represented by the change from covalent to

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[7] K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York (1963), p. 116.

charge resonance structure. Indeed, every ^1L_a absorption of a hydrocarbon is accompanied with the vibrational fine structure which is resulted from a vibronic coupling. Whereas, the ^1B_b absorption is usually consisted of only one sharp and high peak, as the absorption band in a charge resonance system, e. g. cyanine analogs⁽⁸⁾ and some organic ions.⁽⁹⁾ In polyacene series, the ^1L_a absorption is polarized to the direction of the molecular short axis.⁽¹⁰⁾ On the other hand, the ^1L_b and ^1B_b absorptions are polarized in the direction of the molecular long axis. Consequently, the electron displacement in the ^1L_a species is limited at the largest in 2.78 A, however in the latter species the largest electron displacement will be proportional to the number of benzene rings. This situation may partly be responsible to such characteristic shifts as represented by the correlation equations.

α-Substituted Hydrocarbons.—In an aromatic derivative, the peculiar degeneracy of the two excited configurations, $\chi_{1-2'}$, and $\chi_{2-1'}$, of the parent hydrocarbon is removed by the perturbation of the substituent. Furthermore, this perturbation leads to an interaction between all configurations. However, as pointed out in the previous paper,⁽⁶⁾ in α-substituted hydrocarbon which has an auxochromic substituent in the α-position, such as α-naphthol, $\chi_{1-2'}$ strongly interacts with $\chi_{2-1'}$, but only slightly with $\chi_{1-1'}$, so that the nature of the π—π* absorption is practically the same as that of the parent hydrocarbon. We will, therefore, be able to calculate the $\lambda(^1L_a)$ of an α-derivative from Eq. 5. On the other hand, the calculations of the $\lambda(^1L_b)$ and $\lambda(^1B_b)$ are very difficult, because there is no means of estimating the interaction energy between the configurations $\chi_{1-2'}$ and χ_{2-1}. The configurational energy associated with $\chi_{1-2'}$ is approximately given by a harmonic mean of the hypothetical $\lambda(^1B_b)$ and $\lambda(^1L_b)$, which are calculated from Eqs. 6 and 7, using $\Delta m = m_1 - m_{2'}$. Similarly, the energy of $\chi_{2-1'}$ is estimated. One approximation is that a geometric mean of $\Delta m_{1-2'}$ and Δm_{2-1} is assigned to Δm. However, this approximation has not any theoretical background, but only an intuitive analogy with a well-known approximation for the interaction energy between two different molecules.⁽¹¹⁾ In summarizing, the three absorption wavelengths of an α-substituted hydrocarbon are calculated from the following equations;

$$\lambda(^1L_a) = 474(\Delta m_1)^{-1/2} - 145\ \mathrm{m}\mu \tag{8}$$

$$\lambda(^1L_b) = 428(\Delta m_2)^{-1} + 50\ \mathrm{m}\mu \tag{9}$$

$$\lambda(^1B_b) = 358(\Delta m_2)^{-1}\mathrm{m}\mu \tag{10}$$

where

$$\Delta m_1 = m_1 - m_{1'}$$

$$\Delta m_2 = \sqrt{(m_1 - m_{2'})(m_2 - m_{1'})}$$

TABLE II. PARAMETERR FOR HMO CALCULATION

Atom core (X)	δ_X	Bond (XY)ᵃ⁾	k_{XY}
C^+	0	C$\underset{\cdots}{-}$C	1
N^+	0.5	C$\underset{\cdots}{-}$N	1.05
N^{2+}	1.0	N$\underset{\cdots}{-}$N	1.10
O^{2+}	1.5	C-NH_2	0.8
F^{2+}	2.0	C-OH	0.7
		C-F	0.6

a) $\underset{\cdots}{-}$ means an aromatic bond.

The HMO calculations are carried out using the parameters given in Table II. In Table II, the conventional Coulomb and resonance integrals are expressed as follows;

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

$$\beta_{XY} = k_{XY} \beta$$

where δ_X and k_{XY} are the characteristic constants for atom core X and bond X-Y, respectively. It would be reasonable to compare α_X with the diagonal element of the Hartree-Fock operator, F_{XX}, over the π-AO of atom X. F_{XX} should be considered as the effective electronegativity of atom X in the molecule.⁽¹²⁾ To a first approximation, α_X is, therefore, given by the valence state electronegativity, which was circumstantially investigated by Prichard and Skinner⁽¹³⁾ and Hinze and Jaffé⁽¹⁴⁾. According to their study, the electronegativity in a given valence state increases almost linearly with the atomic number in the same period. The δ_X values given in Table II are in accord with their results. The calculated absorption wavelengths for some α-derivatives are compared with the experimental values in Table III. Table III shows that the simple correlations are still applicable to the prediction of the three main absorptions of these compounds.

Benzene Derivatives and *N*-Heterobenzenes.—In the calculation of benzene's $\lambda(^1L_a)$, we have used the harmonic mean of observed $\lambda(^1L_a)$ and $\lambda(^1B_b)$ as the reference, because they come from two degenerated configurations $\chi_{1-1'}$ and $\chi_{2-2'}$. In benzene derivatives and *N*-heterobenzenes, we can not neglect the configuration interaction between $\chi_{1-1'}$ and $\chi_{2-2'}$. Fortunately, this configuration interaction energy has, however, practically the same value with that of benzene.⁽⁶,¹²,¹⁵⁾ So that, in good approximation, the $\lambda(^1L_a)$ of a benzene derivative or a *N*-heterobenzene is given by

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10) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).
11) M. Kurata, "Polymer Physics," Ed. by Phys. Soc. Japan, Asakura Shoten, Tokyo (1963), p. 71.
12) N. Mataga and K. Nishimoto, *Z. Physik. Chem. (Frankfult)*, **13**, 140 (1957).
13) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).
14) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
15) K. Nishimoto and R. Fujishiro, This Bulletin, **31**, 1036 (1958).

TABLE III. CALCULATED AND OBSERVED ABSORPTION WAVELENGTHS FOR α-SUBSTITUTED HYDROCARBONS (in mμ)

Hydrocarbon	Substituent	$\lambda(^1L_a)$ Calcd.	$\lambda(^1L_a)$ Obs.	$\lambda(^1L_b)$ Calcd.	$\lambda(^1L_b)$ Obs.	$\lambda(^1B_b)$ Calcd.	$\lambda(^1B_b)$ Obs.
Naphthalene	NH_2	305	317[3]	327	332[3]	231	242[3]
	OH	291	289[3]	320	322[3]	225	230[3]
	F	285	291[4]	318	316[4]	223	—
Anthracene	NH_2	394	397[5]	358	368[5]	258	260[5]
	OH	382	389[3]	354	—	255	253[3]
	F	378	—	353	—	254	—

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

4) T. Iredale and J. W. White, *Trans. Faraday Soc.*, **56**, 1719 (1960).

5) S. Suzuki and H. Baba, This Bulletin, **37**, 519 (1964).

TABLE IV. CALCULATED AND OBSERVED ABSORPTION WAVELENGTHS OF BENZENE DERIVATIVES AND *N*-HETEROBENZENES (in mμ)

Parent compound	Substituent	$\lambda(^1L_a)$ Calcd.	$\lambda(^1L_a)$ Obs.	$\lambda(^1L_b)$ Calcd.	$\lambda(^1L_b)$ Obs.	$\lambda(^1B_b)$ Calcd.	$\lambda(^1B_b)$ Obs.
Benzene	NH_2	227	234[6]	285	286[6]	196	197[6]
	OH	213	213[6]	273	272[6]	186	190[6]
	F	207	204[7]	268	266[7]	182	—
	H	204	204[2]	264	264[2]	179	179[2]
Pyridine	2-OH	209	205[8]	269	269[8]	183	—
	3-OH	212	216[8]	273	276[8]	186	—
	4-OH	212	222[8]	272	235[8]	185	—
	H	201	—	261	251[8]	177	—
Pyridazine	—	200	—	259	246[8]	177	—
Pyrimidine	—	198	—	255	243[8]	175	—
Pyrazine	—	198	—	257	260[8]	172	—
s-Triazine	—	189	—	247	222[8]	174	—
s-Tetrazine	—	191	—	251	252[8]	166	—

6) H. Baba, This Bulletin, **34**, 76 (1961).

7) K. Bowden and F. A. Braude, *J. Chem. Soc.*, **1952**, 1068.

8) S. F. Mason, ibid., **1959**, 1247, 1253; **1957**, 5010.

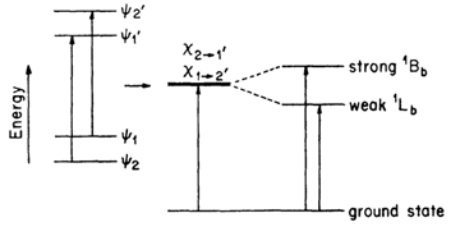

Fig. 1. First order configuration interaction in an alternant hydrocarbon.

$$\lambda(^1L_a) = 2\Big/\left[\frac{1}{\lambda_1}+\frac{1}{\lambda_2} - \sqrt{\left(\frac{1}{\lambda_1}-\frac{1}{\lambda_2}\right)^2+(0.701)^2\times 10^{-6}}\,\right]\ \mathrm{m}\mu$$

where

$$\lambda_1 = 474(\varDelta m_3)^{-1/2} - 145$$

$$\lambda_2 = 474(\varDelta m_4)^{-1/2} - 145$$

$$\varDelta m_3 = m_1 - m_{1'}$$

$$\varDelta m_4 = m_2 - m_{2'}$$

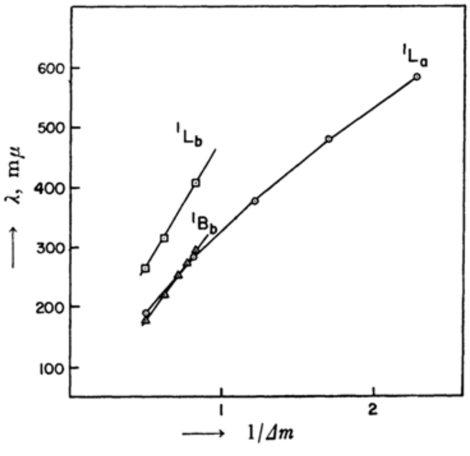

Fig. 2. Absorption spectra of linear polyacenes and the inverse of HMO energy differences:
— : Calculaled line.
○, □, △: Experimental data

TABLE V. CALCULATED AND OBSERVED ABSORPTION WAVELENGTHS OF MISCELLANEOUS COMPOUNDS (in mμ)

Parent compound	Substituent	$\lambda(^1L_a)$ Calcd.	$\lambda(^1L_a)$ Obs.	$\lambda(^1L_b)$ Calcd.	$\lambda(^1L_b)$ Obs.	$\lambda(^1B_b)$ Calcd.	$\lambda(^1B_b)$ Obs.
Quinoline	H	279	275[9]	314	315[9]	220	232[9]
	2-OH	278	270[10]	321	324[10]	227	224[10]
	3-OH	287	270[10]	325	330[10]	230	—
	4-OH	283		316		222	—
	5-OH	292	—	321	323[10]	226	242[10]
	6-OH	291	—	316	—	230	227[10]
	7-OH	285	263[10]	325	333[10]	229	227[10]
	8-OH	295	—	321	305[10]	226	242[10]
Isoquinoline	H	282	280[9]	314	320[9]	220	217[9]
	1-OH	286	—	317	—	222	—
	3-OH	293	—	321	—	226	—
	4-OH	293	295[10]	320	330[10]	225	230[10]
	5-OH	294	303[11]	321	328[11]	226	234[11]
	6-OH	285	286[11]	328	300[11]	232	229[11]
	7-OH	290	301[11]	326	333[11]	230	224[11]
	8-OH	291	304[11]	318	334[11]	224	233[11]
Phenanthrene	H	286	293[2]	361	345[2]	261	251[2]
	1-OH	295	308[12]	367	335[12]	267	245[12]
	2-OH	286	292[12]	368	355[12]	268	255[12]
	3-OH	292	305[12]	364	355[12]	264	248[12]
	4-OH	292	302[12]	368	340[12]	268	245[12]
	9-OH	295	305[12]	366	355[12]	266	248[12]
Azulene	—	361	352[13]	389	659[13]	286	279[13]

9) R. Muller and F. Dorr, *Z. Elektrochem.*, **63**, 1150 (1959).
10) S. F. Mason, *J. Chem. Soc.*, **1957**, 5010.
11) K. Nakanishi, M. Ohashi and H. Koike, This Bulletin, **34**, 533 (1961).
12) C. Djerassi, H. Bendes and P. Sengupta, *J. Org. Chem.*, **20**, 1046 (1955).
13) J. F. Tilney-Bassett and W. A. Waters, *J. Chem. Soc.*, **1959**, 3123.

In Table IV, the calculated absorption wavelengths of a number of benzene compounds are shown and compared with the experimental data. Generally speaking, the agreement between them is satisfactory, except for the $\lambda(^1L_b)$'s of *s*-triazine and 4-OH pyridine.

Micellaneous Compounds.—As pointed out in the previous paper,[6] in β-substituted derivatives, such as β-naphthol, all of the lower excited configurations interact strongly each other, so that the transition characteristics of the parent hydrocarbon are completely lost. Namely, we can not represent the ^1L_a species by $\chi_{1-1'}$ and so on. In attempts to explain the electronic spectra of a β-derivative, we have therefore to consider the interaction among all configurations. It would be, however, desirable to examine to what extent we can expect the electronic spectra of a β-derivative, making the same assumption with an α-derivative. In Table V, the calculated absorption wavelengths for quinoline, isoquinoline, phenanthrene, and their hydroxy derivatives, using Eqs. 8—10 are given and compared with the experimental values. Generally speaking, although the agreement between calculated and observed values is semiquantitatively satisfactory, it is not quite so good as that of α-derivative.

In order to explain the electronic spectra of a β-derivative by HMO theory, we have to set up other correlation equations considering the complicated configuration interactions. The present correlation equations predict fairly well the $\lambda(^1L_a)$ and $\lambda(^1B_b)$ of azulene as shown in Table V. The scheme of configuration interaction in a derivative having a chromophor, such as $-NO_2$, $-NO$, $-COR$, etc., is an intricate problem. However, the preliminary calculation shows that the ^1L_a absorptions of such derivatives are satisfactorily calculated by Eq. 8.

Conclusion

The results of this study indicate that the HMO method is applicable to the prediction of the three π-π^* absorptions of conjugated systems, when we set up the appropriate relationships. Simple correlation equations provided in the present study are particularly useful for the alternant hydrocarbons and their α-derivatives having an auxochromic group and also for some *N*-heterocycles. In order to predict the electronic spectra of β-derivatives and the derivatives having a chromophor, we have to set up other relationships considering the complicated configuration interaction scheme.

The author gratefully wishes to acknowledge the many kindneses and the most generous financial support of the Mellon Institute which has made his extremely enjoyable stay at the Institute possible.