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Electron Interaction in Molecules

II. π-Electronic Structure of Some Aromatic Hydrocarbons and their Derivatives*

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An idea of electron interaction in molecule has been applied to the SCF MO calculations of the π-electronic structure of some complex aromatic hydrocarbons and their derivatives. The theoretical results for singlet and triplet transition energies, first ionization potentials and bond lengths agree fairly well with the experimental data. A correlation equation between the valence state ionization potential and the one center electron repulsion integral has been proposed. It has been shown that the electron repulsion in molecule is considerably smaller than in free atom. The present calculation shows that we can treat sulphur as a normal hetero-atom analogous to oxygen and nitrogen.

Une idée sur l'interaction électronique dans une molécule a été appliquée à des calculs SCF MO de la structure électronique π de quelques hydrocarbures aromatiques complexes et de leurs dérivés. Les résultats théoriques concernant les énergies des transitions singulet et triplet, les premiers potentiels d'ionisation et les longueurs de liaisons sont en très bon accord avec les données expérimentales. Une équation est proposée, corrélant le potentiel d'ionisation de l'état de valence et l'intégrale de répulsion électronique monocentrique. On a montré que la répulsion électronique dans une molécule est considérablement plus faible que dans un atome isolé. Notre travail montre que l'on peut traiter le soufre comme un hétéroatome normal analogue à l'oxygène et à l'azote.

Bei SCF-MO-Rechnungen zur π-Elektronen-Struktur einiger komplizierter Kohlenwasserstoffe und ihrer Derivate wurde eine Idee zur Elektronenwechselwirkung im Molekül angewandt. Die theoretischen Ergebnisse für Singulett- und Triplettübergänge, Ionisationspotentiale und Bindungslängen stimmen ziemlich gut mit den experimentellen Daten überein. Es wurde eine Beziehungsgleichung zwischen Ionisationspotential im Valenzzustand und dem Einzentrenelektronenwechselwirkungsintegral vorgeschlagen. Es wurde gezeigt, daß die Elektronenwechselwirkung im Molekül vergleichsweise klein gegenüber der des freien Atoms ist. Die vorliegenden Rechnungen zeigen, daß man Schwefel wie ein normales Heteroatom analog zu Sauerstoff und Stickstoff behandeln kann.

Introduction

In order to solve the molecular Schrödinger equation for a complex molecule, we require an appropriate approximation to the molecular wave function. For the problem of organic molecules, there are two fundamental approaches to this problem, one which comes from chemical intuition, valence bond theory. Another is a straightforward extension of the idea of atomic orbitals to the molecule, molecular orbital (MO) theory. It is well recognized that the latter approximation is more suitable and useful for the present quantum chemistry [*32*]. The most

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* Ref. [*26*] is referred to as Paper I of this series.

advanced technique for this theory is LCAO MO SCF procedure, which has been originally developed by ROOTHAAN [*36*] as the application of HARTREE-FOCK treatment in the theory of atomic structure to the molecule.

However, the LCAO MO method has two intrinsic shortcomings. One is that the LCAO scheme greatly overestimates the ionic structures in the chemical bond. Another is the orbital approximation (= one electron approximation). Namely, the MO does not include any co-ordinates associated with interelectronic distances. Therefore we have a problem of electron correlation energy [*37*]. In order to eliminate these shortcomings of the theory, several techniques have been proposed. We may classify them into the following two groups; (A) Semi-empirical estimation of basic integrals over atomic orbitals. This procedure is very easy. However, the proposed parameters should be applicable from molecule to molecule. The Pariser-Parr method [*31*] is one of most successful techniques of this kind. (B) Improvement of wave function. This will account for electron correlation. Configuration interaction technique, method of orthogonalized atomic orbitals [*7*], split p-orbital method [*9, 10*], and extraordinary function [*38*] are classified in this category. The method of electron interaction in molecule described in the previous paper [*26*] will introduce an electron correlation of the first category. In the present paper, this idea has been applied to the SCF MO CI calculations of the π-electronic structure of some complex aromatic hydrocarbons and their derivatives.

Variable β Approximation

Some attempts to estimate the core integral, β, have been reported by several workers [*12, 18, 24, 32*]. As shown in our papers [*13, 28*], a considerable improvement in SCF MO calculations of various conjugated systems has been made by the variable β modification. The procedure for this modification is as follows; The total energy can be expressed by

$$E = E_\sigma + E_\pi + E_c .$$

Total sigma energy can be, to a first approximation, given by

$$E_\sigma = \sum_{\mu>\nu} (\tfrac{1}{2})\, k_{\mu\nu}(\sigma)\, [R_{\mu\nu} - R_{\mu\nu}(s)]^2$$

where $k_{\mu\nu}$ and $R_{\mu\nu}(s)$ are the force constant and single bond distance of μ-ν bond in sp^2 hybridization, respectively. Total π-energy is given by P-P-P theory as

$$E_\pi + E_C = \sum_{\mu>\nu} [q_\mu q_\nu \gamma_{\mu\nu} - (q_\mu N_\nu + q_\nu N_\mu)\, \eta_{\mu\nu} + N_\mu N_\nu \xi_{\mu\nu} + 2\beta_{\mu\nu} p_{\mu\nu} - (\tfrac{1}{2})\, p_{\mu\nu}^2 \gamma_{\mu\nu}] + \\ + F(I_\mu, A_\mu)$$

where

$$\gamma_{\mu\nu} = \int \phi_\mu^2(1)\, (e^2/r_{12})\, \phi_\nu^2(2)\, dv$$

$$\eta_{\mu\nu} = \int \phi_\mu^2(1) \frac{e^2}{r_{1\nu}}\, dv$$

$$\beta_{\mu\nu} = \int \phi_\mu(1)\, H_{\text{core}}\, \phi_\nu(1)\, dv$$

The last term, $F(I_\mu, A_\mu)$ is independent of interatomic distances. q_μ and N_μ are the π-electron density and core charge on μ-th atom, respectively. $p_{\mu\nu}$ and $\xi_{\mu\nu}$ are the bond order and core repulsion associated with μ-ν. To a first approximation, $\gamma_{\mu\nu}$, $\eta_{\mu\nu}$, $\xi_{\mu\nu}$, and $\beta_{\mu\nu}$ may be given by the first two terms of a Taylor expansion with respect to the interatomic distance $R_{\mu\nu}$, because in the π-electron theory we are concerned with $R_{\mu\nu}$ in the range of only 1.34 to 1.52 Å for hydrocarbons. The equilibrium condition requires

$$\frac{\partial E}{\partial R_{\mu\nu}} = \frac{\partial}{\partial R_{\mu\nu}} [E_\sigma + E_\pi + E_c] = 0 .$$

There are two boundary conditions; firstly, we must have $R_{\mu\nu} = R_{\mu\nu}(s)$ at $p_{\mu\nu} = 0$ and secondly, $R_{\mu\nu} = R_{\mu\nu}(d)$ at $p_{\mu\nu} = 1$, where $R_{\mu\nu}(d)$ means the double bond distance. The first condition requires that

$$\frac{\partial}{\partial R_{\mu\nu}} [q_\mu q_\nu \gamma_{\mu\nu} - (q_\mu N_\nu + q_\nu N_\mu)\, \eta_{\mu\nu} + N_\mu N_\nu \xi_{\mu\nu}] = 0 .$$

Therefore, we obtain

$$2p \frac{\partial \beta}{\partial R} - \tfrac{1}{2} p^2 \frac{\partial \gamma}{\partial R} + k[R - R(s)] = 0 \tag{1}$$

for each bond. The second requires that

$$2 \frac{\partial \beta}{\partial R} - \tfrac{1}{2} \frac{\partial \gamma}{\partial R} + k[R(d) - R(s)] = 0 . \tag{2}$$

Combining Eqs. (1) and (2), we obtain

$$R = R(s) - [R(s) - R(d)]\, p + \frac{p(p-1)}{2k} \frac{\partial \gamma}{\partial R} . \tag{3}$$

Integrating Eq. (2) and substituting Eq. (3) into the result, we obtain

$$\beta = \frac{[R(s) - R(d)]}{4} \frac{\partial \gamma}{\partial R} p^2 - \left\{ \frac{k}{2} [R(s) - R(d)]^2 + \tfrac{1}{4}[R(s) - R(d)] \frac{\partial \gamma}{\partial R} \right\} p + \beta_0 . \tag{4}$$

This type of β may be called variable β modification in quadratic form (variable β in Q-form).

When we assume $\gamma = \eta = \xi$, which is the usual approximation in P-P-P theory, the relations given in Ref. [*28*] are obtained, namely

$$\frac{\partial \gamma}{\partial R} = 0 \tag{5}$$

$$R = R(s) - [R(s) - R(d)]p \tag{6}$$

and

$$\beta = -\frac{k}{2} [R(s) - R(d)]^2\, p + \beta_0 . \tag{7}$$

The name variable β modification in linear form (variable β in L-form) will be preferred for this type. The last term in Eq. (3) might be generally negligibly small. For example, when we use NM approximation [*30*], $\partial\gamma/\partial R$ is given by

$$\frac{\partial \gamma}{\partial R} = -\gamma \frac{1}{a + R} .$$

Therefore, for a carbon-carbon bond, we obtain

$$\frac{1}{2k} \frac{\partial \gamma}{\partial R} = -0.033 \text{ Å} .$$

Consequently, to a good approximation, a linear relation exists between the bond length and the bond order.

In the above treatment, we assumed that q_ν and $p_{\mu\nu}$ are independent of individual bond distances, $R_{\mu\nu}$. This assumption might be reasonable. In benzene, for example, the MO's are determined by only the symmetry, and we obtain $q_\nu = 1$ and $p_{\mu\nu} = \frac{2}{3}$ for the ground state. Therefore, q_ν and $p_{\mu\nu}$ should be considered as molecular quantities and not depend on a specific bond distance. For simplicity, variable β in L-form has been used in this paper. Q-form will be examined in the subsequent papers.

Estimation of Electron Repulsions in Molecule

The details of the treatment of electron interaction in molecules was described in paper I [*26*]. According to this idea, we must set up two types of electron repulsion integrals, upper-upper γ^{uu}, and upper-lower γ^{ul} repulsions. As shown in the previous paper [*26*], the following equations duplicate fairly well the experimental data for conjugated hydrocarbons.

$$\gamma^{uu}_{\mu\nu} = 7.88 \frac{R_{\mu\nu} + 2.06}{R_{\mu\nu} + 1.13} [3/(2R_{\mu\nu} + \sqrt{a^2_{\mu\nu} + R^2_{\mu\nu}})] \text{ eV} \tag{8}$$

$$\gamma^{ul}_{\mu\nu} = 7.88 \frac{R_{\mu\nu} + 2.06}{R_{\mu\nu} + 1.13} [1/\sqrt{a^2_{\mu\nu} + R^2_{\mu\nu}}] \text{ eV} \tag{9}$$

where $R_{\mu\nu}$ is the distance between μ-th and ν-th atoms. A parameter $a_{\mu\nu}$ is determined by

$$a_{\mu\nu} = \tfrac{1}{2}(a_\mu + a_\nu)$$

where

$$a_\mu = e^2/\gamma_{\mu\mu} = e^2/(I_\mu - A_\mu)$$

I_μ and A_μ are the valence state ionization potential and electron affinity of μ-th atom, respectively. Their values have been found in the literature [*14, 33, 35*]. However, the literature values seem to be rather large, because they have been estimated from the spectroscopic terms in free atoms, not as atoms in molecules. In a conjugated hydrocarbon, $a_C = 1.50$ Å or $I_C = \gamma_{11} = 9.60$ eV is suitable for a carbon $2p\pi$-AO [*26*]. This corresponds to a 14 percent reduction of the Hinze-Jaffé value ($I_C = 11.16$ eV). There is no means of estimating the valence state ionization potential associated with a single charged heteroatom core in molecule. However, $I_\mu = 0.86 \times$ (Hinze-Jaffé value) might be appropriate.

If we use a Slater type AO, the ionization potential is given by a quadratic form of the effective nuclear charge (Z) [*17*], whereas the one center electron repulsion integral is shown to be proportional to Z [*32*]. Therefore, the valence state ionization potential should be expressed by a quadratic equation with respect to the one center electron repulsion integral, namely

$$I_\mu = a\,\gamma^2_{\mu\mu} + b\,\gamma_{\mu\mu}\,. \tag{10}$$

Using the Hinze-Jaffé value for the $2p\pi$ AO and the experimental value [*22*] for the lone pair of the oxygen atom, we obtain

$$I_\mu = 0.0606\,\gamma^2_{\mu\mu} + 0.328\,\gamma_{\mu\mu} \tag{11}$$

Table 1. *Parameters*

Core	I_μ(eV)	A_μ(eV)	$\gamma_{\mu\mu}$(eV)	a_μ(Å)
C^+	9.60	0.00	9.60	1.50
O^{++}(–OH)	30.88	10.85[a]	20.03	0.719
O^{++}(–OCH_3)	29.54	10.00[a]	19.54	0.737
N^{++}(–NH_2)	27.88	8.97[a]	18.91	0.761
N^{++}(–$NHCH_3$)	26.70	8.24[a]	18.46	0.780
N^{++}[–$N(CH_3)_2$]	26.00	7.82[a]	18.18	0.792
S^{++}(–SH)	22.16	9.44[a]	12.72	1.132
S^{++}(–SCH_3)	21.15	8.69[a]	12.46	1.155

Benzene derivatives: $\beta_{CC} = -0.51p - 2.04$ eV
$\beta_{CN} = -0.53p - 2.24$ eV
$\beta_{CO} = -0.56p - 2.44$ eV
Naphthalene derivatives: $\beta_{CC} = -0.51p - 1.90$ eV
$\beta_{CO} = -0.56p - 2.27$ eV
Anthracene and phenanthrene: $\beta_{CC} = -0.51p - 1.84$ eV
Pyrene: $\beta_{CC} = -0.51p - 1.82$ eV
Coronene: $\beta_{CC} = -0.51p - 1.70$ eV

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[a] Ref. [*41*].

or

$$A_\mu = 0.0606\,\gamma^2_{\mu\mu} - 0.672\,\gamma_{\mu\mu}\,. \tag{12}$$

It should be noted that Eq. (11) fits the Hinze-Jaffé values for other second row atoms. Consequently, we can use Eq. (11) as a general correlation equation between I and γ for second row elements in the π-type valence state.

As shown in the previous paper [*29*], for a doubly charged core, such as the core for a lone pair or the nitrogen in nitro group, we must assign the first ionization potential to the valence state electron affinity. The method of electron interaction in molecule gives a satisfactory result not only for transition energies, but also for the first ionization potential of molecules [*26*]. Therefore, we can use the experimental ionization potential of CH_3X as the A_μ of the lone pair orbital of hetero atom X in molecule, so that the corresponding $\gamma_{\mu\mu}$ is calculated from Eq. (12).

If we can treat the third row elements as "normal" heteroatoms analogous to oxygen and nitrogen, a similar correlation can be made, using the Pritchard-Skinner value [*35*] and experimental data [*22*] for the sulphur atom, that is

$$I_\mu = 0.160\,\gamma^2_{\mu\mu} - 0.288\,\gamma_{\mu\mu} \tag{13}$$

or

$$A_\mu = 0.160\,\gamma^2_{\mu\mu} - 1.288\,\gamma_{\mu\mu}\,. \tag{14}$$

Using the above equations and the experimental data given by WATANABE et al. [*41*], the parameters associated with the lone pair orbitals of hetero atoms are calculated and summarized in Tab. 1. For one center electron repulsion integrals, the Pariser-Parr approximation [*31*] is used.

Resultats and Discussion

Using the parameters given in Tab. 1, SCF MO calculations (with 10 iterations) of the π-electronic structures of some organic compounds have been carried out.

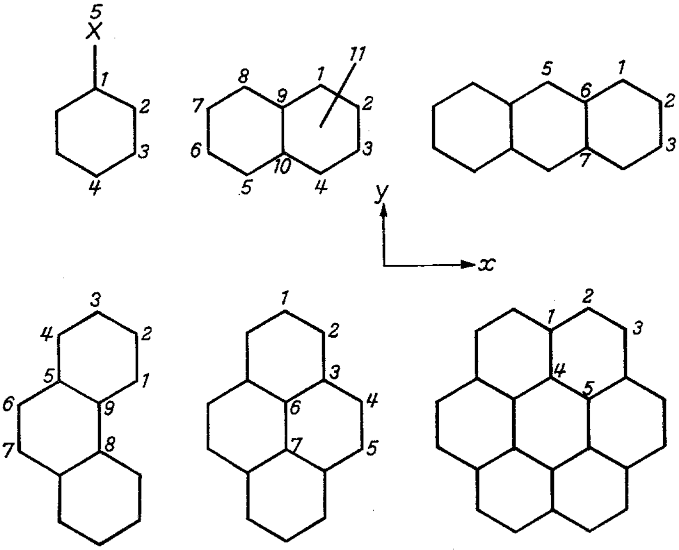

Fig. 1. Numbering of atoms

For mathematical simplicity, the approximation of variable β in L-form, and the same expressions given in Ref. [*28*], has been used. For coronene, $\beta_{\mathrm{CC}} = -0.51\,p - 1.70$ eV is obtained from the ^1B_b transition energy. The numbering of atoms is shown in Fig. 1. Bond lengths and bond angles are taken as 1.40 Å and 120°, respectively.

Ionization potentials and electron affinities. The ionization potential and electron affinity of a molecule are very important theoretically, because they correspond to the negative of Hartree-Fock energies of the highest occupied orbital and the lowest vacant orbital, respectively [*36*]. However, in the usual methods rather large values for ionization potentials are calculated. Experimentally, these quantities are very important for molecular complex formation, such as charge transfer complexes [*5*].

The calculated results are summarized in Tab. 2 and compared with experiment. There is an uncertainty of 0.3—0.4 eV in the experimental ionization potentials, depending on the experimental techniques, such as photoionization or electron impact [*23, 41*]. In the table, the experimental data were obtained from photo-ionization and charge transfer spectra. The agreement between the theory and experiment is quite good in the whole. Unfortunately, experimental electron affinities are not available for most of molecules.

In linear polyacenes, the ionization potential decreases with increasing molecular size. However, there is the rather strange result that the calculated ionization potentials of coronene and pyrene are comparable with that of anthracene, which agrees with experimental data. Furthermore, the ionization potential of phenanthrene is expected to be almost the same as that of naphthalene.

This very interesting result is explained by a perimeter model which tells us that the MO's associated with non zero ring quantum number should be doubly degenerate [*34*]. In a linear polyacene, this degeneracy is removed by the pertur-

Table 2. *Calculated and Experimental Ionization Potentials and Electron Affinities of Some Aromatic Compounds* (eV)

Molecule	Ionization potential Calc.	Ionization potential Expt.	Electron affinity Calc.
Benzene	9.45	9.247[a]	0.15
Naphthalene	8.26	8.10[b]	1.34
Anthracene	7.60	7.37[b]	2.00
Phenanthrene	8.14	8.09[b]	1.46
Pyrene	7.60	7.55[b]	2.00
Coronene	7.66	7.44[b]	1.94
Phenol	8.47	8.50[a]	−0.02
Anisol	8.29	8.22[a]	−0.06
Aniline	8.09	7.70[a]	−0.08
Dimethylaniline	7.71	—	−0.16
Benzenethiol	8.26	8.33[a]	−0.03

[a] Ref. [*41*]. [b] Ref. [*4*].

bation of cross rinks and molecular shape, so that one of the highest occupied orbitals in the perimeter model is raised. Phenanthrene is iso-π-electronic with anthracene, but has rather round molecular shape. Therefore, the separation of the two orbitals associated with the same number of nodes (Platt's ring quantum number [*34*]) is expected to be smaller than that in anthracene, as shown in Fig. 2. It will generally be concluded that in iso-π-electronic hydrocarbons, the first ionization potential of a round shape molecule is larger than that of a linear molecule.

Electronic spectra. The transition energies have been calculated by including configuration interaction between all singly excited configurations within D eV of lowest excited (singlet or triplet) states. The calculated transition energies, intensities, and polarizations are summarized in Tabs. 3—5. The value of D (2.0—3.0 eV) used in each CI calculation is specified in tables. Comparing with the previous papers [*28*] in which we used NM approximation and adjusted theoretical integrals, a considerable improvement is found in the singlet — triplet transition energies. Agreement between calculated results and the experimental data is satisfactory.

Concerning the singlet states, we have obtained practically the same conclusions with other calculations using NM approximation [*27, 28*]. It should be noted that

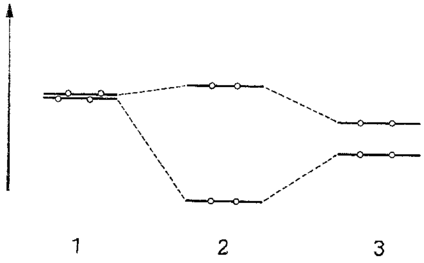

Fig. 2. Highest occupied orbitals of iso π-electronic molecules of 14 carbons: 1. Perimeter model; 2. Anthracene; 3. Phenanthrene

Table 3. *Transition Energies* (eV) *and Intensities of Benzene Derivatives* (D = 3.0 eV)

	Transition energy						
Molecule	Singlet		Triplet		Oscillator strength		Polarization
	Calc.	Obs.[a]	Calc.	Obs.[b]	Calc.	Obs.[a]	
Phenol	4.52	4.59	3.53	3.54	0.033	0.020	x
	5.71	5.82	3.81	—	0.150	0.132	y
	6.56	6.70	4.06	—	0.951	0.636	x
	6.64	6.93	4.89	—	1.159	0.467	y
	7.90	—			0.002	—	y
	7.96	—			0.099	—	x
Anisol	4.46	4.59	3.53	3.50	0.042	0.023	x
	5.63	5.78	3.73	—	0.199	0.175	y
	6.51	6.68	4.05	—	0.874	0.585	x
	6.62	6.90	4.93	—	1.137	0.371	y
	7.81	—			0.003	—	y
	7.86	—			0.158	—	x
Aniline	4.39	4.40	3.54	3.32	0.048	0.028	x
	5.50	5.39	3.69	—	0.264	0.144	y
	6.40	6.40	4.03	—	0.732	0.510	x
	6.60	6.88	4.93	—	1.085	0.570	y
	7.66	7.87			0.295	0.68	x
	7.70				0.008		y
Dimethylaniline	4.23	4.30	3.42	—	0.065	0.044	x
	5.33	5.15	3.48	—	0.348	0.256	y
	6.27	6.25	3.99	—	0.540	0.350	x
	6.59	6.88	4.90	—	1.044	0.575	y
	7.48	7.68			0.453	0.81	x
	7.49				0.016		y
Benzenethiol	4.44	4.58	3.43	—	0.033	0.013	x
	5.41	5.30	3.73	—	0.268	0.347	y
	6.38	6.22	4.03	—	0.708	0.398	x
	6.54	6.79	4.84	—	0.924	0.587	y
	7.49	7.30			0.103	0.438	y
	7.56				0.359		x

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[a] Ref. [*15*] [b] Ref. [*21*]

the same expressions of variable β in L-form can be used for both the present method and NM approximation. Present calculation shows that in anthracene the very weak ${}^1L_b$ absorption is expected to be appear in the same region as the medium ${}^1L_a$ absorption. It is interesting to note that the calculated energy associated with the transition from the ground state to the lowest triplet state of a derivative having an auxochromic substituent is not appreciably different from that of the parent hydrocarbon.

Although LONGUET-HIGGINS [*19*] showed that there are two pd^2 hybrids in sulphur atom appropriate for conjugation with carbon $2p\pi$ AO, the present normal hetero atom treatment gives rather good results for electronic spectra and ionization potential of benzenethiol. In aniline, dimethyl aniline, and benzenethiol,

Table 4. *Transition Energies* (eV) *and Intensities of Naphthalene and Naphthols* ($D = 3.0$ eV)

Molecule	Transition energy Singlet		Triplet		Oscillator strength		Polarization[c]
	Calc.	Obs.[a]	Calc.	Obs.	Calc.	Obs.[a]	
Naphthalene	3.98	3.97[e]	2.73	2.64[b]	0	0.002[e]	x
	4.51	4.51[e]	3.42	—	0.246	0.11[e]	y
	5.34	—	3.61	—	0	—	
	5.50	—	3.98	—	0	—	
	5.54	5.63[e]	4.66	—	1.946	1.70[e]	x
	5.74	—	5.76	—	0	—	
	6.07				0.861		y
	6.95				0		
α-Naphthol	3.89	3.86	2.60	2.55[d]	0.025	0.016	−7°
	4.24	4.29	3.43	—	0.245	0.102	80°
	5.16	5.40	3.46	—	0.460	0.328	0°
	5.32	—	4.01	—	0.013	—	135°
	5.58	—	4.12	—	0.638		0°
	5.60	5.80	5.11	—	0.715	0.892	0°
	6.08				0.684		90°
	6.70	—			0.032	—	0°
β-Naphthol	3.85	3.78	2.66	2.62[d]	0.038	0.021	126°
	4.43	4.54	3.36	—	0.186	0.081	115°
	5.18	—	3.54	—	0.169	—	−8°
	5.38	5.53	3.76	—	1.371	1.06	16°
	5.52	—	4.22	—	0.355	—	−6°
	5.70	—	4.56	—	0.160	—	21°
	5.91	—			0.750	—	105°
	6.74	—			0.059	—	111°

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[a] Ref. [*3*] [b] Ref. [*21*]

[c] Numerical value gives an angle between the transition moment vector and x-axis of the molecule. [d] Ref. [*2*] [e] Ref. [*16*]

their 2—5 transitions have appreciable values of transition moments and should appear near 7.5 eV region. Observed spectra near 7.5 eV region in these compounds [*15*] are probably assigned to this type of transitions.

Bond lengths. The bond orders and π-electron densities associated with the ground state configuration will indicate the utility of the theory for the calculation of molecular properties of ground state molecules. These quantities for benzene derivatives are summarized in Tab. 6. The molecular diagrams of naphthols are shown in Fig. 3. Unfortunately, there are no very accurate structural informations for these compounds. However, the molecular structures of some polycyclic aromatic hydrocarbons were determined very accurately by X-ray crystallography or electron diffraction technique. Carbon-carbon bond lengths of conjugated systems can be calculated from the equation, $R_{CC} = 1.517 - 0.180\,p$ [*28*]. The calculated results are summarized in Tab. 7 and compared with the experimental data. The present method gives almost the same results as the previous calculations based on NM approximation [*27*, *28*]. Agreement between calculated results

Table 5. *Transition Energies* (eV) *and Intensities of Complex Hydrocarbons*

Molecule	Transition energy				Oscillator strength		Polarization
	Singlet		Triplet				
	Calc.	Obs.	Calc.	Obs.[a]	Calc.	Obs.	
Anthracene	3.58	—	1.80	1.82	0	—	x
(D = 3.0 eV)	3.59	3.34[b]	2.99	—	0.313	0.10[b]	y
	4.50	—	3.35	—	0	—	
	4.79	—	3.60	—	0	—	
	4.81	—	4.11	—	0	—	
	4.84	4.83[b]	4.65	—	2.523	2.28[b]	x
	5.19	—	4.81	—	0.044	—	y
	5.36	—			0	—	
	5.87	5.61[b]			0.604	0.28[b]	y
	6.21	—			0	—	
Phenanthrene	3.58	3.75[b]	2.60	2.68	0	0.003[b]	x
(D = 3.0 eV)	4.27	4.23[b]	3.37	—	0.459	0.18[b]	y
	4.54	—	3.39	—	0	—	
	4.91	4.91[b]	3.72	—	1.260	1.09[b]	y
	5.00	—	3.77	—	0.425	—	x
	5.32	—	3.86	—	0.436	—	x
	5.36	—	4.07	—	0	—	
	5.60	5.83[b]	4.50	—	0.449	0.60[b]	y
	5.87	—			0	—	
	5.89	—			0	—	
	6.58	6.62[b]			0.494	0.59[b]	x
Pyrene	3.49	3.33[c]	2.04	2.08	0	0.0016[c]	x
(D = 3.0 eV)	3.64	3.71[c]	3.21	—	0.675	0.33[c]	y
	4.10	—	3.26	—	0	—	
	4.27	—	3.32	—	0	—	
	4.77	4.55[c]	3.49	—	0.954	0.35[c]	x
	4.90	—	3.83	—	0	—	
	5.00	—	3.89	—	0	—	
	5.08	—	4.27	—	0	—	
	5.25	5.14[c]	4.77	—	1.485	0.85[c]	y
	5.33	—			0	—	
	5.98	—			0	—	
	6.47	6.26[c]			1.046	—	y
Coronene	3.04	2.74[c]	2.51	2.37	0	—	x
(D = 2.0 eV)	3.51	3.67[c]	2.89	—	0	0.19[c]	y
	3.94	—	2.89	—	0	—	
	3.96	—	3.07	—	0	—	
	4.19	4.18[c]	3.33	—	3.894	1.34[c]	x, y
	4.35	—	3.54	—	0	—	
	5.06	—			0	—	
	6.11	—			1.135	—	x

[a] Ref. [*21*] [b] Ref. [*16*] [c] Ref. [*39*]

and experimental data is quite good, except for the phenanthrene 4—5 and 5—6 bonds. However, it should be noted that the X-ray data corresponds to the molecular structure in solid state, which might include special intermolecular interactions through the strong crystal field.

Table 6. *π-Electron Densities (q_μ) and Bond Orders ($p_{\mu\nu}$) of Benzene Derivatives*

	Phenol	Anisol	Aniline	Dimethyl Aniline	Benzenethiol
q_1	0.964	0.967	0.977	0.986	0.980
q_2	1.066	1.075	1.077	1.093	1.059
q_3	0.991	0.990	0.989	0.986	0.992
q_4	1.032	1.038	1.040	1.050	1.031
q_5	1.889	1.866	1.851	1.804	1.887
p_{12}	0.627	0.619	0.614	0.598	0.627
p_{23}	0.674	0.675	0.676	0.679	0.674
p_{34}	0.663	0.662	0.661	0.659	0.662
p_{15}	0.338	0.370	0.388	0.443	0.337

In conclusion, the π-electronic spectra, both singlets and triplets, first ionization potentials, and bond lengths can be satisfactorily calculated by the method based on an idea of electron interaction in molecule. From the present calculation, it should be concluded that the electron repulsion in molecule should be considerably reduced by the polarisable molecular field. In the subsequent papers, the present idea will be applied to other conjugated systems, such as non-alternant hydrocarbons, anions, cations, etc.

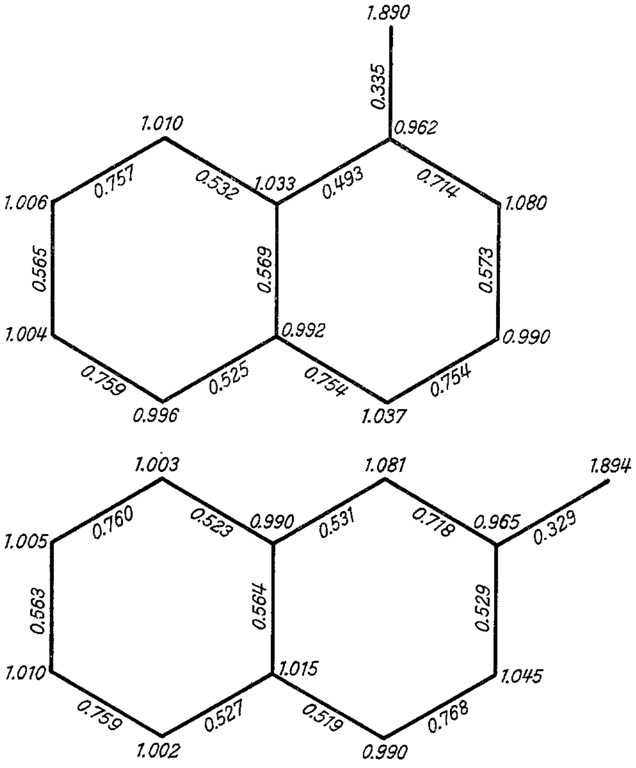

Fig. 3. Molecular diagrams of naphthols

Table 7. *Bond Lengths of Some Polycyclic Hydrocarbons*
($R_{CC} = 1.517 - 0.180p$)

Molecule	Bond	Bond order	Bond length (Å)	
			Calc.	Obs.
Naphthalene	1—2	0.761	1.380	1.364[a]
	1—9	0.524	1.423	1.421
	2—3	0.562	1.416	1.415
	9—10	0.568	1.415	1.418
Anthracene	1—2	0.792	1.374	1.368[a]
	1—6	0.478	1.431	1.436
	2—3	0.521	1.423	1.419
	5—6	0.620	1.405	1.399
	6—7	0.516	1.424	1.428
Phenanthrene	1—2	0.723	1.387	1.383[b]
	1—9	0.578	1.413	1.425
	2—3	0.603	1.408	1.398
	3—4	0.726	1.386	1.381
	4—5	0.570	1.414	1.457
	5—6	0.438	1.438	1.390
	5—9	0.594	1.410	1.404
	6—7	0.832	1.367	1.372
	8—9	0.408	1.444	1.448
Pyrene	1—2	0.670	1.396	1.380[c]
	2—3	0.619	1.406	1.420
	3—4	0.423	1.441	1.442
	3—6	0.552	1.418	1.417
	4—5	0.842	1.365	1.320
	6—7	0.481	1.430	1.417
Coronene	1—2	0.498	1.427	1.444[d]
	1—4	0.600	1.409	1.381
	2—3	0.789	1.375	1.362
	4—5	0.488	1.429	1.438

[a] Ref. [*8*] [b] Ref. [*40*] [c] Ref. [*6*] [d] Ref. [*1*].

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References

[*1*] Almenningen, A., O. Bastiansen, and F. Dyvik: Acta crystallogr. **14**, 1056 (1961).
[*2*] Azumi, T.: Bull. chem. Soc. Japan **35**, 788 (1962).
[*3*] Baba, H., and S. Suzuki: Bull. chem. Soc. Japan **34**, 82 (1961).
[*4*] Birks, J. B., and M. A. Slifken: Nature **191**, 761 (1961).
[*5*] Briegleb, G.: Elektronen Donator-Acceptor Komplexe. Berlin: Springer 1961.
[*6*] Cameron, A., and J. Trotter: Acta crystallogr. **18**, 636 (1965).
[*7*] Coulson, C. A., and I. Fischer: Philos. Mag. **40**, 386 (1949).
[*8*] Cruickshank, D. W. J., and R. A. Sparks: Proc. Roy. Soc. [London] **A258**, 270 (1960).
[*9*] Dewar, M. J. S., and N. L. Hojvak: J. chem. Physics **34**, 1232 (1961).

[*10*] —, and C. F. WULFMAN: J. chem. Physics **29**, 158 (1958).
[*11*] EVANS, D. F.: J. chem. Soc. [London] **1960**, 1735.
[*12*] FISCHER-HJALMARS, I.: Molecular orbitals in chemistry, physics, and biology, (Ed. by LÖWDIN, P. O., and B. PULLMAN), p. 361. New York: Academic Press 1964.
[*13*] FOX, J. L., S. P. LABERGE, K. NISHIMOTO, and L. S. FORSTER: Acta Biochem. Biophysics (To be published).
[*14*] HINZE, J., and H. H. JAFFÉ: J. Amer. chem. Soc. **84**, 540 (1962).
[*15*] KIMURA, K., and S. NAGAKURA: Molecular Physics **9**, 117 (1965).
[*16*] KLEVENS, H. B., and J. R. PLATT: J. chem. Physics **17**, 470 (1949).
[*17*] KLOPMAN, G.: J. Amer. chem. Soc. **86**, 1463 (1964).
[*18*] KON, H.: Bull. chem. Soc. Japan **28**, 320 (1954).
[*19*] LONGUET-HIGGINS, H. C.: Trans. Faraday Soc. **45**, 173 (1949).
[*20*] LÖWDIN, P. O.: Physic. Rev. **97**, 1509 (1955).
[*21*] MCCLURE, D. S.: J. chem. Physics **17**, 905 (1949).
[*22*] MOORE, C.: Atomic energy levels, Vol. 1, Circ. 467. Washington: National Bureau of Standards 1949.
[*23*] MORRISON, J. D., and A. J. C. NICHOLSON: J. chem. Physics **20**, 1021 (1952).
[*24*] MULLIKEN, R. S.: J. Chim. physique **46**, 497 (1949).
[*25*] MURRELL, J. N.: The theory of the electronic spectra of organic molecules. London: Methuen 1963.
[*26*] NISHIMOTO, K.: Theoret. chim. Acta [Berl.] **5**, 74 (1966).
[*27*] —: J. physic. Chem. **67**, 1443 (1963).
[*28*] —, and L. S. FORSTER: Theoret. chim. Acta [Berl.] **3**, 407 (1965); **4**, 155 (1966).
[*29*] —, and R. FUJISHIRO: Bull. chem. Soc. Japan **31**, 1036 (1958).
[*30*] —, and N. MATAGA: Z. physik. Chem. [Frankfurt] **12**, 335; **13**, 140 (1957).
[*31*] PARISER, R., and R. G. PARR: J. chem. Physics **21**, 466, 767 (1953).
[*32*] PARR, R. G.: Quantum theory of molecular electronic structures. New York: W. A. Benjamin, Inc. 1963.
[*33*] PILCHER, G., and H. A. SKINNER: J. inorg. nucl. Chem. **24**, 937 (1962).
[*34*] PLATT, J. R.: J. chem. Physics **17**, 484 (1949); **18**, 1168 (1950).
[*35*] PRITCHARD, H. O., and H. A. SKINNER: Chem. Rev. **55**, 745 (1955).
[*36*] ROOTHAAN, C. C. J.: Rev. mod. Physics **23**, 61 (1951).
[*37*] SINANOGLU, O.: Advances in chemical physics, Vol. 6, p. 315, (Ed. by PRIGOGINE, J.). New York: Interscience Publishers 1964.
[*38*] SNYDER, L. C., and R. G. PARR: J. chem. Physics **28**, 1250 (1958); **34**, 1661 (1961).
[*39*] TANAKA, J.: Bull. chem. Soc. Japan **38**, 86 (1965).
[*40*] TROTTER, J.: Acta crystallogr. **16**, 605 (1963).
[*41*] WATANABE, K., T. NAKAYAMA, and J. MOTTL: J. quant. Spectrosc. Radiat. Transfer **2**, 369 (1959).

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