A MO Theoretical Study of Organic Dyes I. Effect of Chemical Softness on the Electronic Spectra

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In order to obtain reasonable results for the π-electronic spectra of organic dyes with simple semi-empirical MO methods, a new approximation for the two-center electron repulsion integral (new gamma) is proposed which takes the chemical softness of the π-conjugated system into account. New gamma was successfully applied to PPP calculations of the electronic spectra of linear polyenes, simple cyanines, and simple merocyanines. The calculated results agree satisfactorily with the experimental data. On the contrary, a calculation based on the conventional PPP parameters gives shorter wavelengths for the absorption maxima of the electronic spectra of charge-resonance systems, such as cyanines and merocyanines. Furthermore, they give very strange electronic spectral shifts for merocyanines (see text), due to an inbalance between the one- and two-electron parts of the electronic transition energy.

Along with the surprising progress of computer, high quality *ab initio* MO calculations can be carried, allowing an elucidation of the optimized geometry, chemical bondings, and various molecular properties of a given molecule. Thus, the computer-assisted theoretical design of molecules has become possible today. Modern chemistry will thus be successfully developed through the cooperation of theory, computer, and experiment. However, at the present this dreamful aspect of modern chemistry based on *ab initio* MO calculations is restricted to the molecule in the ground state and the small size molecule in the excited state. The *ab initio* MO calculation of the electronic spectra of a larger molecule is very expensive and impractical. For this reason, various semiempirical MO methods are still being widely used to calculate the electronic spectra of organic dyes.[1)] PPP calculations provide reasonable results for the electronic spectra of benzene and naphthalene derivatives. However, they give rather poor results for larger π-conjugated systems and molecule having a strong intramolecular chargetransfer interaction, such as indigo. Thus, the calculations using the conventional PPP parameters give rather shorter wavelengths of the absorption bands.[1)] Furthermore, the calculated separation between the first and second absorption bands of a given dye molecule is larger than that from the experimental data. The reason for this might be attributable to either an electron correlation problem or many electron problems in mobile π-electron systems. The results for the electronic spectra calculated by usual semiempirical MO methods suggest that there is a larger screening effect for π-electron interactions in larger conjugated systems with many mobile π-electrons.

In order to calculate reasonable results for the π-electronic spectra of organic dyes with simple semiempirical MO methods, we propose a new approximation for the two-center electron repulsion integral (new gamma) which takes the chemical softness of a π-conjugated system into account. We shall apply it to PPP calculation of the electronic spectra of organic dyes.

There are many examples showing how a simple semiempirical method which is essentially based on intuitive considerations may prove to be much more successful than a rigorous theoretical approach. A pertinent example is the frontier electron theory which treats only HOMO and LUMO as the active MO's for a chemical reaction.[2)] In general, a simpler model is useful for a qualitative understanding of the nature of the molecular world and would provide useful concepts or principles. On the other hand, very accurate numerical calculations usually provides detailed information concerning individual molecule or molecular interaction. In our works we have used simpler semiempirical MO methods. We sometimes need detailed information concerning the molecular geometries and molecular interaction energies. In such cases, we refer to *ab initio* MO calculations.

Effective Interaction between Two π-Electrons in Organic Dyes

Let us designate a bare interaction V_0 when two electrons repel each other at the circumstance with no other electrons and the effective interaction V_{eff} when they interact with each other at a polarizable molecular potential field formed by many other electrons. Here, we consider only π-electrons explicity. It is thus assumed that σ-electrons form a σ-core potential field with the inner-shell electrons and nuclei. There are, of course, Σ–Π interactions, and V_0 is screened or weakened by this interaction.[3)]

In an investigation of the effective electron repulsion, it is convenient to consider two kinds of regions in the molecular potential field. One is the intraatomic region which is associated with one-center electron repulsion integral $(\gamma_{\mu\mu})$,

$$\gamma_{\mu\mu}=\int\int\phi_\mu^2(1)(1/r_{12})\phi_\mu^2(2)\mathrm{d}\tau_{12} \tag{1}$$

where ϕ_μ is 2pπ-AO of μ-th atom and r_{12} is the distance between electrons 1 and 2. Another one is the interatomic region which is associated with the two-center electron repulsion integral ($\gamma_{\mu\nu}$),

$$\gamma_{\mu\nu} = \int\int \phi_\mu^2(1)(1/r_{12})\phi_\nu^2(2)\mathrm{d}\tau_{12}. \tag{2}$$

In the interatomic region, two electrons repel each other at the polarizable many-electron molecular potential field. When each atom provides only one π-electron to the molecular potential field, one-center electron repulsion integral represents the repulsion between two π-electrons in an anionic atmosphere, while the two-center electron repulsion integral calculates the electron repulsion in an almost neutral atmosphere.

In the intraatomic region, the repulsion between two π-electrons at the μ-th atom can be expressed by the one-center electron repulsion integral ($\gamma_{\mu\mu}$). It is given by the following Pariser-Parr approximation;[4)]

$$\gamma_{\mu\mu} = I_\mu - A_\mu, \tag{3}$$

where I_μ and A_μ are the valence state ionization potential (VSIP) and the electron affinity, respectively. Using this approximation, one can take into account of an important electron correlation effect in the intraatomic region.

In the interatomic region, two electrons repel each other at the polarizable many-electron molecular potential field. An effective electron-electron interaction in the many-electron system can be investigated by RPA (see below) which is one of the field theoretical techniques.[5)]

Let us suppose a "hydrogen metal" composed of an equal number of electrons and protons. The protons oscillate at the lattice positions. The electrons move about and repel each other. As an electron moves, on account of the strong Coulomb interaction, it will be attracted by protons for a while and moves off, then be replaced by another electron. This dynamical interaction causes a virtual polarization which can be investigated by quantum electrodynamics, many-body techniques or field theoretical methods.[5)]

In quantum electrodynamics, a "bare" electron interacting with photons acquires a cloud of virtual photons around it, converting it into a "dressed" electron. In a metal, an electron is dressed by a cloth composed of various types of interactions, such as Coulomb interaction and polarizations. These interactions can be described by the Feynman diagrams.[5)] The interaction between real particles in (k,ω) space is called a "bare" interaction (V_q), while that between "dressed" particles is referred to as an "effective" interaction, ($V_{\mathrm{eff,q}}$). An electron gas was introduced in the early works of metals as theoreticians' "dream metal" consisting of N electrons moving against a smeared-out positive-charge background. In the electron gas model, the most important Feynman diagrams involve the "polarization diagrams", in which the interaction causes the medium to become "virtually polarized" in all possible ways. When the sum of all possible polarization diagrams can be carried out, a so-called "random phase approximation" (RPA) is obtained. The functional form of RPA may be written as[5)]

$$V_{\mathrm{eff(RPA)}}(k,\omega) = V_\mathrm{q}/(1+V_\mathrm{q}\pi_0(q,\omega)), \tag{4}$$

where $\pi_0(q,\omega)$ comes from the polarization interaction. This has the form of an interaction taking place between two charges in a dielectric, with

$$\varepsilon_{\mathrm{RPA}}(k,\omega) = 1 + V_\mathrm{q}\pi_0(q,\omega) \tag{5}$$

being the frequency-dependent, or so-called "generalized", dielectric constant. In the extreme case (small q and $\omega=0$) one can obtain by the Fourier transform a well-known Abraham potential[6)] or Yukawa potential,

$$V_{\mathrm{eff}}(r) = (e^2/r)e^{-\lambda r}, \tag{6}$$

which is a shielded Coulomb interaction. Unfortunately, we can not obtain from Eq. 4 the analytical form of the effective electron-electron interaction in a finite π-conjugated system. Therefore, based on a formal comparison of Eq. 4 with NM-gamma (two-center electron repulsion integral with our approximation[7)]), we propose a new gamma using the chemical softness of a π-conjugated system. Eq. 4 can be rewritten as

$$V_{\mathrm{eff(RPA)}}(k,\omega) = 1/(V_q^{-1} + \pi_0(q,\omega)). \tag{7}$$

NM-gamma is given by

$$\gamma_{\mu\nu} = e^2/(R_{\mu\nu} + a_{\mu\nu}), \tag{8}$$

where $R_{\mu\nu}$ is the interatomic distance between the μ-th and ν-th atoms; $a_{\mu\nu}$ is given by

$$a_{\mu\nu} = 2e^2/(I_\mu - A_\mu + I_\nu - A_\nu). \tag{9}$$

Using the Pople approximation[8)] for the two-center electron repulsion integral,

$$V = \gamma_{\mu\nu,\mathrm{Pople}} = e^2/R_{\mu\nu}, \tag{10}$$

Eq. 8 can be rewritten as

$$\gamma_{\mu\nu} = 1/(V^{-1} + (a_{\mu\nu}/e^2)). \tag{11}$$

A comparison of Eq. 7 with Eq. 11 suggests that $a_{\mu\nu}/\mathrm{e}^2$ corresponds to a kind of polarizability which measures the chemical softness at the interatomic region between the μ-th and ν-th atoms in a molecule (see Appendix). Parr and Pearson pointed out that $(I-A)/2$ measures the absolute chemical hardness of an atom or molecule.[9)] Yang and Parr[10)] discussed the softness of atom by the inverse of $(I-A)$. One can thus say that $a_{\mu\nu}/e^2$ is a measure of the chemical softness at the interatomic region between the μ-th and ν-th atoms in a π-conjugated system. The chemical softness of a π-conjugated system becomes larger when the number of mobile π-electrons increases, since the polarizability of the π-electron cloud increases. Furthermore, the intramolecular charge transfer interaction (IMCT) would result in a considerable increase in the chemical softness. In order to take into account the effect of the chemical softness of a π-conjugated system on the two-center electron repulsion integral, the chemical softness parameter k is introduced in Eq. 8 as

$$\gamma_{\mu\nu} = e^2/(R_{\mu\nu} + ka_{\mu\nu}). \qquad (12)$$

PPP calculations of the electronic spectra of benzene, naphthalene and their derivatives using NM-gamma ($k=1$ in Eq. 12) well reproduce their experimental data.[1] We can thus estimate the chemical softness of a π-conjugated system from the point of view of a benzene standard ($k=1$).

We applied Eq. 12 to PPP calculations of the electronic spectra of some prototype dyes, such as linear polynes, simple cyanines, and simple merocyanines. A PPP calculation with variable β approximation[11] was carried out. The PPP parameters used in this paper were as follows[12];

	I(eV)	A(eV)
C	11.16	0.03
N(N(Me$_2$)$_2$)	14.12	1.78
O	17.70	2.47

$$\beta_{CC} = -0.51P_{\mu\nu} - 2.00 \text{ eV}$$
$$\beta_{CN} = -0.53P_{\mu\nu} - 2.20 \text{ eV}$$
$$\beta_{CO} = -0.56P_{\mu\nu} - 2.40 \text{ eV}$$

The value of the calculated transition energy greatly depends on the number of excited configurations taken in the CI (configuration interaction) calculation. In this paper, we calculated only the electronic transition from HOMO to LUMO, because all of the molecules that we investigated were linear conjugated systems or one-dimensional systems. This approximation may be called the two-orbital model. In a one-dimensional system, the π-MO's are non-degenerated and the longest wavelength absorption band can be, to a good approximation, assigned to a HOMO-LUMO transition. In an aromatic compound or a two-dimensional system, such as benzene, the HOMO's and LUMO's are degenerated or nearly degenerated in two fold, respectively. Therefore, a four-orbital model might be recommended in this case. In this model, four singly excited configurations constructed by the two highest occupied and the two lowest unoccupied orbitals are used in the CI calculation. As a result, we expect four absorption bands in the longest wavelength region for an aromatic compound, which agrees with the experimental data.[13]

Results and Discussion

A. Linear Polyenes. The electronic spectra of linear polyenes (H–(CH=CH)$_n$–H(n=1—10)) are calculated by PPP method using three types of two-center electron repulsion integrals: NM-gamma (Nishimoto–Mataga approximation[7]), OK-gamma (Ohno–Klopman approximation[14]), and new-gamma (Eq. 12). The calculated absorption wavelengths are shown in Fig. 1 and are compared with the experimental data.[15] It can be seen from this figure that the calculation using NM-gamma gives longer wavelengths than the experimental ones. The reason for this may be as follows: In polyenes, π-electrons are not very mobile at the ground state, since a given linear polyene can be qualitatively described by a bond alternative structure. Thus the π-electrons are localized in the region of double bonds, so that the π-conjugated system might be chemically harder than benzene. Therefore, in a calculation using new-gamma we tentatively set k=0.9. As can be seen from Fig. 1, the calculated results are improved.

B. Simple Cyanines. The electronic spectra of simple cyanines (N(Me)$_2$–(CH=CH)$_n$–CH=N$^+$(Me)$_2$ (n=1—8)) were calculated by the PPP method with three types of two-center electron repulsion integrals. The calculated absorption wavelengths are shown in Fig. 2 and are compared with the experimental data.[16] This figure shows that a calculation using the usual PPP parameters gives shorter wavelength than that of experimental ones. Cyanine is described as the following charge resonance system;

$$\mathrm{N(Me)_2{-}(CH{=}CH)_{\mathit{n}}{-}CH{=}N^+(Me)_2} \leftrightarrow$$
$$\mathrm{N^+(Me)_2{=}CH{-}(CH{=}CH)_{\mathit{n}}{-}N(Me)_2}.$$

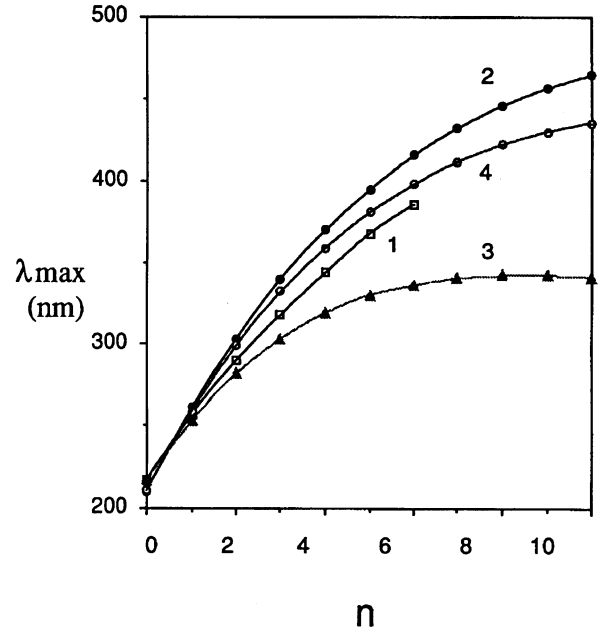

Fig. 1. A plot of absorption wavelengths calculated by PPP method with various types of two-center electron repulsion integrals vs. n of linear polyenes, CH$_2$=CH–(–CH=CH–)$_n$–CH=CH$_2$. 1; Experimental value, 2; NM-gamma, 3; OK-gamma, 4; New-gamma.

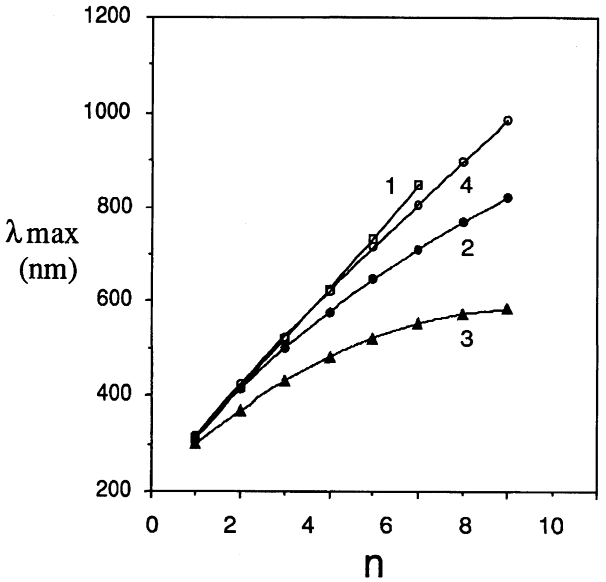

Fig. 2. A plot of absorption wavelengths calculated by PPP method with various types of two-center electron repulsion integrals vs n of simple cyanines, N-$(Me)_2$-(-CH=CH-$)_n$-CH=$N^+(Me)_2$. 1; Experimental value, 2; NM-gamma, 3; OK-gamma, 4; New-gamma.

Therefore, π-electrons move almost freely in the whole molecular framework and form a polarizable π-electron sea. The chemical softness of a π-electron sea might increase with an increase in the number of π-electrons. Therefore in a calculation using new-gamma we tentatively set $k=0.1n+1.0$. As can be seen from Fig. 2, this model seems to be successful.

C. Simple Merocyanines. Merocyanines are known as the important dyes in the field of photography. The electronic spectra of simple merocyanines (N-$(Me)_2$-$(CH=CH)_n$-CH=O (n=1—10)) were calculated by the PPP method using three types of two-center electron repulsion integrals. The calculated absorption wavelengths are shown in Fig. 3 and are compared with the experimental data.[16] It should be noted that a calculation using OK-gamma gives a very strange spectral shift (Fig. 3). Thus, when the value of n is over 4, the calculated λ decreases with an increase in n. This is due to an inbalance between the one- and two-electron parts of the electronic transition energy. Details concerning this strange result should be referred in a subsequent paper. Merocyanines have the following strong intramolecular charge transfer interaction:

$$N(Me)_2\text{-}(CH{=}CH)_n\text{-}CH{=}O \leftrightarrow N^+(Me)_2{=}CH\text{-}(CH{=}CH)_n\text{-}O^-.$$

Therefore, the chemical softness of a π-electron sea might increase with an increase in the number of π-electrons. In a calculation using new-gamma we set $k=0.1n+1.0$ just as in the case of cyanines. As can be seen from Fig. 3, this model seems to be successful.

Quantitative criterion for the determination of the

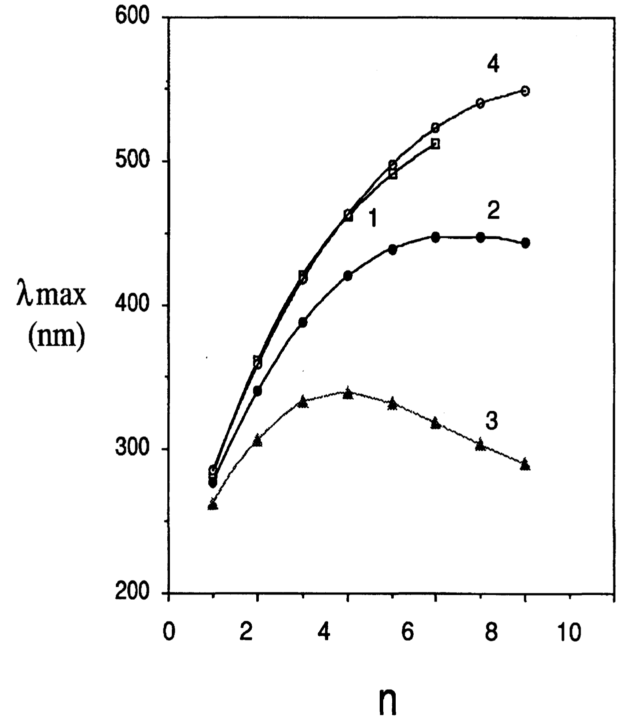

Fig. 3. A plot of absorption wavelengths calculated by PPP method with various types of two-center electron repulsion integrals vs n of simple merocyanines, $N(Me)_2$-(-CH=CH-$)_n$-CH=O. 1; Experimental value, 2; NM-gamma, 3; OK-gamma, 4; New-gamma.

value of the chemical softness parameter k (Eq. 12) has not yet been established. After some trials, however, we will be able to propose one. However, the qualitative criteria are as follows: (1) The value of k increases with an increase in the number of mobile π-electrons. (2) In the case of an organic dye molecule having a strong intramolecular charge transfer interaction between electron-donor and -accepter groups, such as in indigo, the value of k becomes quite large (the value of k is about 2 for indigo[17]).

Conclusion

In order to investigate the π-electronic spectra of organic dyes with simple semi-empirical MO methods, a new approximation for a two-center electron repulsion integral (new gamma) is proposed which takes the chemical softness in the interatomic region of a π-conjugated system into account. Although new gamma (Eq. 12) has the simplest form, it provides reasonable results for the PPP calculations of the π-electronic spectra of organic dyes. Thus, as we will report in the subsequent papers, PPP calculations of organic dyes, such as indigo and quinones, using new gamma will provide reasonable results for their π-electronic spectra, compared to those using conventional PPP parameters which usually give shorter wavelengths for their absorption maxima. In particular, the usual PPP parameters give some strange results concerning the electronic spectra of simple merocyanines, due to an inbalance between the one- and two-electron energy parts of the electronic transition energy.

Appendix

Chemical Softness at the Interatomic Region. Chemical softness may be a measure of the polarizability of given systems, such as atoms, molecules and local areas in molecules. Let us consider the following polarization at the interatomic region between the μ-th and ν-th atoms in the π-conjugated system:

$$-\mu\text{--}\nu- \;\longrightarrow\; -\overset{+}{\mu}-\overset{-}{\nu}- \tag{A1}$$

This polarization requires an amount of energy ($\Delta E_{\mu\nu}$) given by

$$\Delta E_{\mu\nu} = I_{\mu} - A_{\nu}. \tag{A2}$$

A smaller $\Delta E_{\mu\nu}$ corresponds to larger chemical softness at the interatomic region, since polarization may easily occur. There is another type of polarization at the interatomic region represented by

$$-\mu\text{--}\nu- \;\longrightarrow\; -\overset{-}{\mu}-\overset{+}{\nu}- \tag{A3}$$

accompanying the following energy change:

$$\Delta E_{\nu\mu} = I_{\nu} - A_{\mu}. \tag{A4}$$

Therefore, the energy change associated with the polarization at the interatomic region may be given by

$$\begin{aligned} \Delta E_{\mu\nu} &= (\Delta E_{\mu\nu} + \Delta E_{\nu\mu})/2 \\ &= (I_{\mu} - A_{\nu} + I_{\nu} - A_{\mu})/2. \end{aligned} \tag{A5}$$

Using Eq. 9, Eq. A5 can be rewritten as

$$\Delta E_{\mu\nu} = e^2/a_{\mu\nu} \tag{A6}$$

With an increase of the number of mobile π-electrons, the value of I_{μ} decreases and that of A_{μ} increases, since the ionized state is stabilized at the polarizable media. Therefore, in this case, the chemical softness is amplified.

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