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The Electronic Structures of Charge-Transfer Complexes: Application of the Semiempirical SCF-MO-CI Method

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A method is developed to calculate the electronic structure of a molecular complex composed of a π-electron donor and a π-electron acceptor. The complex is treated as a single conjugated system of π-electrons, and its π-electron states are calculated by the semi-empirical SCF-MO-CI method within the π-electron approximation, by including all β terms. The method is applied to the TCNE complexes of polycyclic aromatic hydrocarbons. It is shown that the absorption spectra of these complexes are well predicted by this method. Discussions are given on the mixing of the charge-transfer configurations and the locally-excited configurations.

Es wird eine Methode entwickelt, um die Elektronenstruktur eines Molekülkomplexes aus einem π-Donor und einem π-Akzeptor zu berechnen, und zwar wird er als einheitliches π-Elektronensystem nach einem SCF-Verfahren unter Einschluß aller β-Terme behandelt. Das Verfahren wird auf TCNE-Komplexe von polycyclischen aromatischen Kohlenwasserstoffen angewendet, wobei sich die Absorptionsspektren recht gut ergeben. Diskutiert wird schließlich noch die Kombination von CI- mit lokal-angeregten Konfigurationen.

Développement d'une méthode pour calculer la structure électronique d'un complexe moléculaire entre un donneur et un accepteur d'électrons π. Le complexe est traité comme un système conjugué unique dont les états électroniques sont calculés dans l'approximation π par la méthode semi-empirique SCF MO CI, en tenant compte de tous les termes β. La méthode est appliquée aux complexes des hydrocarbures aromatiques polycycliques avec TCNE. Cette méthode prévoit bien les spectres d'absorption de ces complexes. Discussion du mélange des configurations à transfert de charge avec les configurations localement excitées.

Introduction

The quantum mechanical description of the electronic structure of a molecular complex formed from the interaction between an electron donor and an electron acceptor, was first given by Mulliken in 1952 [1]. In this theory, Mulliken described the electronic structure as a resonance hybrid between the "no-bond structure" and the "dative structure". Since then, this theory has been successfully applied to the explanations of various phenomena associated with the intermolecular charge-transfer interaction.

The electronic spectra of charge-transfer complexes, in particular, the appearance of the charge-transfer band, have often been explained by use of the simplest version of Mulliken's theory. However, it has been also realized that such a treatment is often too simple to give a quantitative prediction, and we need to take into account the interactions with locally-excited configurations as well as those with higher-energy charge-transfer configurations [2].

There can be a quite different approach based on the molecular orbital method, namely to treat a molecular complex as though it forms a single molecule. A simplified treatment of this type has been used by Dewar [3] and by Flurry [4]. But their methods are again too simple to give a quantitative prediction of the electronic spectrum.

Therefore, it seems necessary to develop a more sophisticated treatment based on the self-consistent-field molecular orbital (SCF-MO) method, incorporated with the configuration interaction (CI) calculation. In the present study, we have applied the semiempirical SCF-MO-CI calculation to tetracyanoethylene (TCNE) complexes of aromatic hydrocarbons, and have examined the applicability of the method.

Method of Calculation

The SCF-MO's of a complex are calculated by assuming a complex as a single π-conjugated system. The molecular orbitals are expressed by the linear combination of $2p\pi$ atomic orbitals of atoms in the donor and acceptor, and calculated the semiempirical SCF-MO method of π-electron approximation with the zero-differential-overlap approximation, but with the inclusion of all two-center resonance integrals. This is essentially an extension of the method originally developed for the calculation of π-electron states of a molecule by Flurry and Bell [5].

The semiempirical parameters are evaluated as follows. The two-center resonance integral, $\beta_{\mu\nu}$, is estimated by using Eq. 1, which has been theoretically derived by Katagiri and Sandorfy [6][1].

$$\beta_{\mu\nu} = -(S_{\mu\nu}/4)\,(C_\mu + C_\nu + \gamma_{\mu\mu} + \gamma_{\nu\nu} - 2\gamma_{\mu\nu}) \qquad (1)$$

where C_μ and C_ν are the terms mainly associated with the one-center penetration integrals. Since the value of C_μ is difficult to estimate theoretically, it is treated as an empirical parameter characteristic of the kind of the atom. We have determined its empirical value for carbon atom so that we can obtain a good agreement between the calculated and observed spectra of naphthalene. The value of N^+, N^{++}, O^+ and O^{++} are determined by using *s*-triazine, pyrrole, *p*-benzoquinone and furan, respectively, as the reference compounds. The one-center two electron repulsion integral, $\gamma_{\mu\mu}$, is estimated according to the Pariser-Parr approximation. The assumed values of the above mentioned parameters are listed in Table 1.

The two-center repulsion integral, $\gamma_{\mu\nu}$, is evaluated according to the Nishimoto-Mataga's method [7], namely by Eq. (2)

$$\gamma_{\mu\nu} = 14.3897/(a_{\mu\nu} + R_{\mu\nu}) \quad (\mathrm{eV}) \qquad (2)$$

where $a_{\mu\nu} = 2.0 \times 14.3897/(1/\gamma_{\mu\mu} + 1/\gamma_{\nu\nu})$, $R_{\mu\nu}$ being the distance between the μ-th and ν-th atoms, given in Å unit. This method is used both for the intra- and inter-molecular integrals.

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[1] Although they have used this formula for the nearest neighbor β terms, it can be seen from their derivation that the same formula can be used for the non-nearest neighbor β terms.

Table 1. *Semiempirical constants*

	H_{ii}[a] (eV)	γ_{ii}[a] (eV)	C (eV)	ζ
C^+	−11.16	11.13	14.5	1.625
N^+	−14.12	12.34	23.5	1.95
N^{++}	−26.70	17.44	44.0	2.125
O^+	−17.70	15.23	29.0	2.275
O^{++}	−32.90	21.53	45.0	2.45
C^+ (C≡N)[b]	−12.69	10.09	14.5	1.625
N^+(C≡N)[b]	−16.18	11.52	20.0	1.95

[a] H_{ii} and γ_{ii} are determined according to Pariser and Parr, using the values of ionization potentials and electron affinities by Hinze and Jaffé [14].

[b] H_{ii} and γ_{ii} of C^+ (C≡N) and N^+ (C≡N) are slightly modified in order to fit the calculated excitation energies of TCNE to observed spectrum.

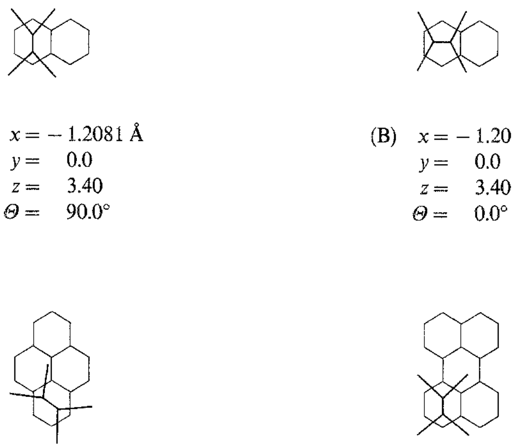
In calculating the overlap integral, $S_{\mu\nu}$, which is required to estimate $\beta_{\mu\nu}$ by Eq. (1), we used the Slater atomic orbitals (STO) with orbital exponents given by Slater [8] when the μ-th and ν-th atoms belong to the same molecule, and SCF-AO's [9] when they belong respectively to different molecules. Of course, it is theoretically desirable to use the SCF-AO's, consistently. Unfortunately, however, we encountered a difficulty ro predict the spectra of the component molecules if we use SCF-AO's for intra-molecular integrals. This is probably due to overestimation of non-nearest neighbor resonance integrals. On the other hand, if we consistently use STO's, the dipole moment of a complex is predicted to be too small and the predicted energy of the first CT band shows a poor agreement with the observation. This is likely to be due to an underestimation of the intermolecular integrals. Therefore, at the present moment, we have adopted a compromise as mentioned above.

In the present treatment, we neglect the interaction between an AO of one molecule and the core of the other molecule. The approximation could be questionable when the interplanar distance between molecules becomes very short, but seems to be acceptable when the distance is not smaller than 3 Å as is usually the case in most charge transfer complexes [10].

The iteration of SCF-MO calculation is repeated until the change in the total π-electron energy by iteration becomes under 0.0001%. For the prediction of transitions, we carry out the CI calculation taking into account the lowest forty singly-excited configurations.

The relative arrangement of the constituent molecules is taken as shown in Fig. 1, according to the crystal structure analysis. In the case of the naphthalene-TCNE, Model *A* corresponds to the relative arrangement found in the crystal structures of the complexes, while Model *B* is constructed so that the central double C=C bond of TCNE is parallel to the long axis of naphthalene.

The results of calculation by the present method on each component molecules are summarized in Table 2. The ionization potential shown here is taken as the negative of the energy of the highest occupied orbital according to Koopman's theorem.



(A) $x = -1.2081$ Å
$y = 0.0$
$z = 3.40$
$\Theta = 90.0°$

(B) $x = -1.2081$ Å
$y = 0.0$
$z = 3.40$
$\Theta = 0.0°$

(C) $x = 0.0$ Å
$y = -2.0925$
$z = 3.323$
$\Theta = -46°$

(D) $x = -1.40$ Å
$y = -2.09$
$z = 3.23$
$\Theta = 90°$

Fig. 1. Relative arrangement of TCNE complexes. (A) and (B) naphthalene-TCNE, (C) pyrene-TCNE, (D) perylene-TCNE. (x, y, z) and Θ mean the relative position of the molecular center and the rotation of TCNE molecule. These are arrangement in the crystals except (B) type of naphthalene-TCNE

Table 2. *Excitation energies* (ΔE) *and ionization potentials (IP) of component molecules (in eV)*

	$\Delta E(f^a)$		IP	
	Calc.	Obs.	Calc.	Obs.
Naphthalene	3.945 (0.006)	3.97 (0.02)	8.556	8.2
	4.337 (0.225)	4.33 (0.18)		
	5.664 (2.041)	5.62 (1.70)		
	6.197 (0.601)	6.51 (0.21)		
	7.232 (0.073)			
	7.963 (0.953)	7.44 (0.8)		
Pyrene	3.449 (0.009)	3.34 (0.0016)	7.815	7.72
	3.553 (0.773)	3.70 (0.33)		
	4.748 (0.934)	4.55 (0.35)		
	5.425 (1.484)	5.15 (0.85)		
	6.092 (0.084)	5.99		
	6.572 (1.311)	6.32		
Perylene	2.839 (0.890)	2.858 (0.33)	7.424	7.15
	3.639 (0.040)	3.65 (–)		
	5.119 (1.634)	4.910 (0.44)		
	5.843 (0.140)	5.481 (0.15)		
	6.016 (0.180)			
	6.166 (1.474)	6.014 (2.17)		
TCNE	4.707 (0.937)	4.55	11.926	–
	5.817 (0.633)			
	7.982 (0.783)			

[a] Oscillator strength.

Results and Discussions

Characters of Molecular Orbitals of a Complex

If the intermolecular interaction between the donor and acceptor is not too strong, we may expect that each molecular orbital of the complex is mainly associated with either one of the constituent molecules. In order to see such a situation, we define the following quantities;

$$D_i=\sum_{\mu=1}^{n_d} c_{i\mu}^2, \qquad A_i=\sum_{\mu=n_d+1}^{n_d+n_a} c_{i\mu}^2 \tag{3}$$

when the i-th MO is described as

$$\psi_i=\sum_{\mu=1}^{n_d+n_a} c_{i\mu}\phi_\mu \tag{4}$$

by numbering the atoms in the donor from 1 to n_d and those in the acceptor from n_d+1 to n_d+n_a. In our approximation, we see that $A_i+D_i=1$.

The molecular orbital is primarily associated with the donor if $D_i>A_i$, and with the acceptor if $A_i>D_i$. The values calculated of the SCF-MO's of the naphthalene-TCNE complex are given in Table 3. We have taken here the arrangement of the two molecules as found in the crystal of the complex, Model A, with the interplanar distance 3.40 Å. It can be seen that the highest occupied molecular orbital of the complex is highly localized on the naphthalene molecule, but

Table 3. *Characters of* SCF-MO's *of the naphthalene*-TCNE *complex*

	Weight of the orbital of the complex		Orbital energy of the complex (eV)		Energy of the corresponding orbital of the component molecules (eV)	
	Donor	*Acceptor*			*Donor*	*Acceptor*
1	0.362	0.638	−19.581	occupied		−17.768
2	0.060	0.940	−16.330			−16.168
3	0.159	0.841	−16.002			−15.658
4	0.012	0.988	−15.446			−15.505
5	0.554	0.446	−14.274		−15.730	
6	0.711	0.289	−12.968		−12.666	
7	0.226	0.774	−11.320			−11.926
8	0.922	0.078	−11.150		−11.048	
9	0.982	0.018	− 9.944		− 9.599	
10	0.957	0.043	− 8.911		− 8.586	
11	0.050	0.950	− 4.195	vacant		− 4.427
12	0.014	0.986	− 2.652			− 2.792
13	0.016	0.984	− 2.519			− 2.596
14	0.987	0.013	− 1.827		− 1.457	
15	0.006	0.994	− 1.676			− 1.803
16	0.984	0.016	− 0.965		− 0.625	
17	0.999	0.001	− 0.187		0.206	
18	0.006	0.994	0.223			0.088
19	0.994	0.006	0.673		1.030	
20	1.000	0.000	1.865		2.263	

the energy is appreciably lowered by the complex formation. On the other hand, the lowest vacant molecular orbital is localized on TCNE molecule, and its energy level is elevated as a result of the complex formation.

Amount of Charge-Transfer and Dipole Moment

As is expected, a small amount of charge transfer occurs in the ground state of the complex. We can estimate this amount by Eq. 5.

$$\Delta Q = \sum_{\mu=1}^{n_d} q_\mu - Q_a = Q_d - \sum_{\mu=n_d+1}^{n_d+n_a} q_\mu \tag{5}$$

where Q_d and Q_a are respectively the total number of π-electrons in the donor and in the acceptor, and q_μ is the π-electron density at the μ-th atom, which is given by

$$q_\mu = \sum_i^{\text{occ}} 2c_{i\mu}^2 . \tag{6}$$

We can calculate the dipole moment of the complex by using the calculated π-electron density.

The results of calculation are given in Table 4. Unfortunately, there is no direct experimental method to determine the amount of charge-transfer. But the experimental value of the dipole moment is known for the naphthalene-TCNE and pyrene-TCNE complexes. In the latter case, the prediction shows good agreement with experiment. An appreciable discrepancy is found in the former case if we take the molecular arrangement found in the crystal. It should be realized that there is a possibility that the actual geometries of the complexes formed in solution are somewhat different from the ones assumed here [2]. As we shall discuss later, the amount of charge-transfer and dipole moment are highly dependent of the interplanar distance in the complex as well as the relative orientation of the molecules. In effect, there is an experimental evidence indicating that the structure of the naphthalene-TCNE complex formed in solution is not fixed as the one shown as the Model *A* in Fig. 1. In the case of Model *B*, the calculated dipole moment becomes smaller than in Model *A*. Thus the discrepancy between the predicted and observed values can be reduced if we take into account the rotation of the TCNE molecule relative to the naphthalene molecule.

Table 4. *Amounts of charge transfer and dipole moments of* TCNE *complexes*

Complex	Interplanar separation (Å)	Amount of CT	Dipole moment (Debye)	
			Calc.	Obs.
naphthalene-TCNE	3.30	0.1109	1.830[a], 1.290[b]	1.28
pyrene-TCNE	3.323	0.1015	1.896	2.0
perylene-TCNE	3.23	0.1605	2.817	

[a] Calculated for the arrangement (A) in Fig. 1.
[b] Calculated for the arrangement (B) in Fig. 1.