Electronic Interactions in Triple Exciplex of the 1,4-Dicyanobenzene and Naphthalene System

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Semiempirical SCF-MO-CI caluculation was carried out for the 1,4-dicyanobenzene (DCB) and naphthalene system which is known to form exciplex (DA)* and triple exciplex (D_2A)*. Potential energy curves of the electronic interactions between excimer and electron acceptor molecule, and between exciplex and electron donor molecule were constructed. The results show that the array of component molecules in the triple exciplex is DDA, and the stabilization energy of triple exciplex is $\approx$0.4 eV from the excimer and $\approx$0.2 eV from the exciplex. They are in line with results reported on the experiment of exciplex and triple exciplex formation.

The system of 1,4-dicyanobenzene (DCB) and naphthalene exhibits exciplex fluorescence and also triple exciplex fluorescence as reported by Beens and Weller. They suggested from the solvent effect of the fluorescence spectra that the array of component molecules in the triple exciplex is not DAD but DDA.[1] Mimura and Itoh also reported the triple exciplex formation in 1,4-dicyanobenzene and dinaphthylpropane(DNP) where an array of the triple exciplex was proposed to be DDA from a steric factor of the trimethylene chain in DNP.[2] They reported on the mechanism of triple exciplex formation in the DCB and several alkylnaphthalene systems. In high concentration of electron donor ($>10^{-2}$ M), the triple exciplex was formed from excimer of alkylnaphthalene and DCB as well as from exciplex and alkylnaphthalene, while the triple exciplex formation from exciplex and electron donor in the concentration below $\approx 10^{-2}$ M is predominant in another process.[3] The dissociation process from the triple exciplex to the exciplex is so fast that the fluorescence rise of the triple exciplex and double exponential decay of the exciplex fluorescence are observed. The fluorescence rise as well as two-component decay of the exciplex was observed in the system of DCB and alkylnaphthalene which exhibits no triple exciplex fluorescence. This was explained by the exciplex formation through triple exciplex *via* the excimer in high concentration of electron donor.[3] A similar investigation was reported by Grellman and and Suckow in connection with the formation of triplet state of anthracene in the diethylaniline and anthracene system.[4]

Most molecular orbital calculations of the electron-donor-acceptor (EDA) complex as well as the exciplex are based on the configuration interaction between the ground and locally excited states of each component molecule, including the charge transfer interaction (CT) which is called the method of "composite molecules." On the other hand, some attempts have been made to calculate the electronic structure of the EDA complex as a single conjugate system of π-electrons.[5-7] The method of calculation of molecular orbital is almost the same as reported, namely the Pariser-Parr-Pople type semiempirical LCAO-SCF-MO method including CI.[7] We have calculated the trimolecular system as well as bimolecular system as a single molecule.

In this paper we discuss the electronic structure of triple complex in both the ground state and the excited state. The potential energy curves obtained revealed the correlation between four excited species, excited monomer, exciplex, excimer and triple exciplex.

Method of Calculation

The method of calculation and the parameters used are the same as in the previous paper.[7] It was also assumed that π-electron approximation is applicable to the triple complex. Two center resonance integrals were evaluated for the two molecules neighboring each other in the triple complex, but neglected for the two molecules far from each other. Two center resonance integrals were evaluated by following the Katagiri-Sandorfy formula:[8]

$$H_{\mu\nu} = \frac{1}{4}(C_\mu + C_\nu + \gamma_{\mu\mu} + \gamma_{\nu\nu} - 2_{\mu\nu})S_{\mu\nu}, \quad (1)$$

where C_μ is one center penetration integral and $S_{\mu\nu}$ is the overlap integral between atomic orbitals and evaluated from single Slater atomic orbitals. When two atomic orbitals are associated with different molecules, we use SCF-atomic orbitals.[9] Two center repulsion integrals $\gamma_{\mu\mu}$ were evaluated by the Nishimoto-Mataga formula,[10] and $\gamma_{\mu\mu}$ were estimated according to the Pariser-Parr method.[11] Core energy, $H_{\mu\mu}$ is assumed to be the negative of the ionization potential, given by Hinze and Jaffé.[12] Intermolecular core-core repulsion integrals $\gamma^{\circ}_{\mu\nu}$ were estimated by following the Dewar-Klopman formula[13] modified by Ohta *et al.*[6]

$$\gamma^{\circ}_{\mu\nu} = \gamma_{\mu\nu} + \left(\frac{1}{R_{\mu\nu}} - \gamma_{\mu\mu}\right)\exp\left[\alpha(R_{\mu\nu} - D_\mu - D_\nu)\right]. \quad (2)$$

Parameters used in this calculation (Table 1) are the same as those previously reported. The nature of electronic transition was estimated by the following equations which are almost the same as reported.[7]

$$\mathrm{LE}(M_1{}^*M_2M_3) = \sum_{ij} b^{a_2}_{ij} m^1_i m^1_j, \quad (3)$$

$$\mathrm{CT}(M_1^+M_2^-M_3) = \sum_{ij} b^{a_2}_{ij} m^1_i m^2_j, \quad (4)$$

where M_i is i-th molecule in the complex and b^a_{ij}, m^1_i are given by Eqs. 5 and 6, respectively.

$$m^1_i = \sum_{\mu=1}^{n_1} c^2_{i\mu} \quad (5)$$

$$\Phi_a = \sum_{ij} b^a_{ij} \Psi_{ij} \quad (6)$$

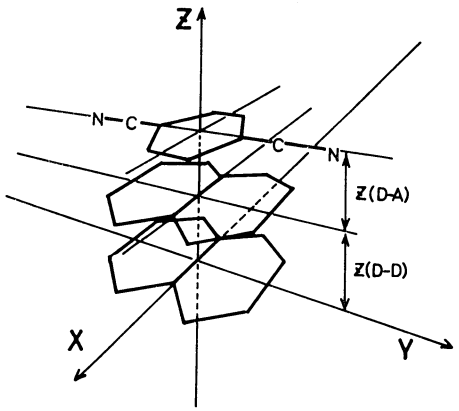


Fig. 1. The conformation and the geometrical parameters used for these calculations where Z(D–D) and Z(D–A) are distances between the molecular planes (parallel) of these component molecules.

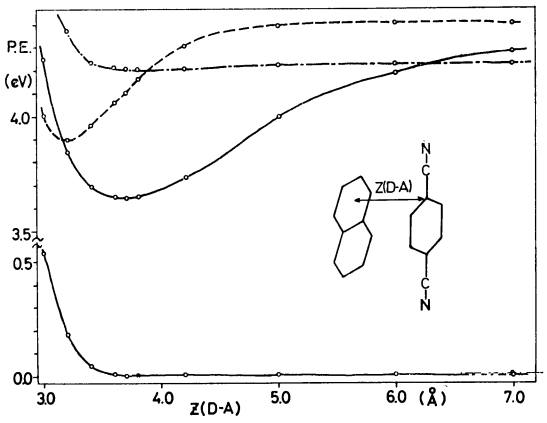


Fig. 2. Potential curves of complex (DA). In the excited state, ——, – – –, and ---- indicate mainly (D^+A^-), (D*A) ^1L_b, and (DA*), respectively.

TABLE 1. PARAMETERS USED IN THE CALCULATION

	$H_{\mu\mu}$(eV)	$\gamma_{\mu\mu}$(eV)	C_μ(eV)	D_μ(a.u.)	ζ
C^+	−11.16	11.13	14.5	2.0	1.625
N^+	−16.18	11.52	20.0	1.0	1.950
		$\alpha = -1.75$			

where n_1 indicates the number of atoms in molecule 1, Φ_a the wave function of a-th electronic excited state, and Ψ_{ij} a configuration promoting an electron from i-th MO to j-th MO.

In the actual calculation of the electronic structures, molecular planes of each component molecule in the complex were assumed to be both parallel to each other and also to the long axes of each component molecule as shown in Fig. 1. The geometrical change from the standard conformation, such as component molecules being twisted together around an axis perpendicular to the molecular planes, did not affect so much the energy of the excited state of molecular complex. The iteration of SCF-MO calculation was repeated until the deviation in the total electronic energy became less than 10^{-4}%. For evaluation of the electronic transition energy and the oscillator strength of each transition, forty lowest singly excited configurations were taken into account. The calculation was carried out by the HITAC 8700/8800 operating system of the University of Tokyo.

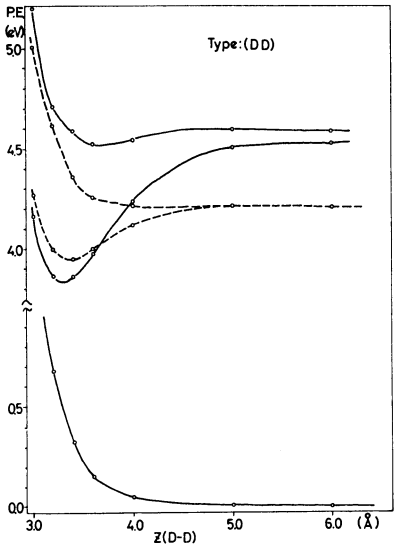


Fig. 3. Potential curves of dimer (DD). In the excited state, —— indicates levels including ^1L_a exciton interaction and charge resonance interaction, and ---- indicates levels including ^1L_b exciton interaction and charge resonance interaction.

Results and Discussion

Potential energy curves of the ground state and the excited state of complex (DA) are shown in Fig. 2. The abscissa indicates the distance between electron donor D and electron acceptor A. The complex in the ground state is unstable between D and A. With decreasing distance of each component molecule (D and A), a charge transfer state (CT-state) is stabilized in the potential energy surface, crossing a potential energy curve of locally excited state (LE-state) of the electron donor at 6.2 Å. This indicates that an electron transfer state mixes with the LE state at 6.2 Å in association with the excited electron donor D and the electron acceptor A to form the exciplex (DA)*. A prominent feature of (DA)* is that the CT character of the first excited state amounts to 98—100% at any distance below ≈6 Å of Z(D–A).

The potential energy curves of the naphthalene dimer, (DD), both in the ground and excited states are shown in Fig. 3. The abscissa indicate the distance between two naphthalene molecules. The dimer (DD) is unstable in the ground state, while it is stabilized by the exciton interaction mixed with the charge resonance interaction. The mixing ratio of the molecular exciton interaction with the charge resonance interaction is 1 : 1 for all the excited states. The first excited state of the dimer stabilized from the monomer is the state including ^1L_a exciton interaction (not ^1L_b exciton interaction) in a D_{2h} symmetry.[14]

The potential energy curves of the ground state and the excited state are shown in Fig. 4 for the case of an interaction of the exciplex and the donor molecule to form the array of DDA of the triple exciplex. The intermolecular distance between a centered electron

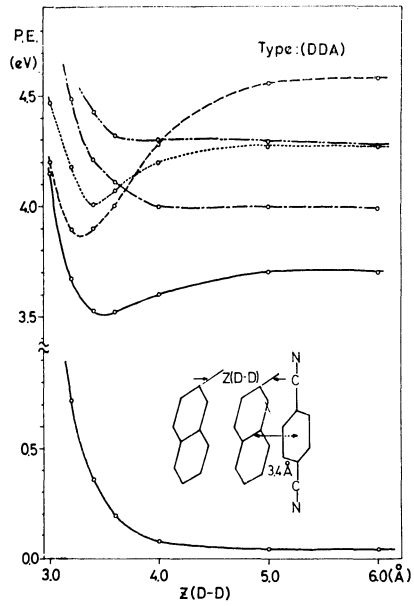


Fig. 4. Potential curves of complex (DDA). Variable parameter is Z(D–D) and Z(D–A) is constant (3.4 Å). In the excited state, ——, – – –, – – –, and ····· indicate mainly (D···D$^+$A$^-$), (D···DA*), excimer (^1L_a) and excimer (^1L_b) levels, respectively.

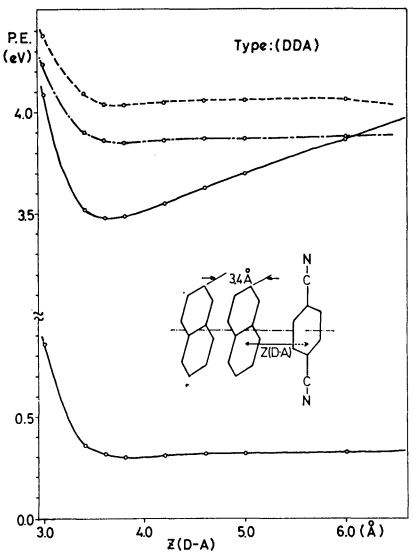
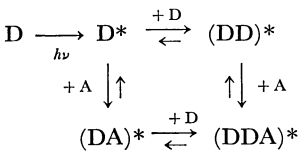


Fig. 5. Potential curves of complex (DDA). Variable parameter is Z(D–A) and Z(D–D) is constant (3.4 Å). In the excited state, ——, – – –, and – – – indicate mainly (D$^+$D···A$^-$)↔(DD$^+$···A$^-$), excimer (^1L_a), and excimer (^1L_b) levels, respectively.

donor and a terminal electron acceptor is set to be constant (3.4 Å), and the intermolecular distance between two electron donors as is variable (Z(D–D) as abscissa). The triple complex is repulsive in the ground state. However, there is a shallow minimum in the first excited state of DDA which implies the triple exciplex formation in the excited state.

Figure 5 shows the potential energy curves of the ground state and the excited state of electronic interaction between the excimer and the electron acceptor to also form the array of DDA, where the intermolecular distance between electron donors in the dimer is constant (3.4 Å) and the intermolecular distance between centered electron donor and terminal electron acceptor changes (Z(D–A) as abscissa). The first excited singlet state (S_1 state) of this triple complex at the distance between D and A of 7.0 Å is almost first LE state of naphthalene dimer, namely excimer state. The charge transfer from the excimer to the electron acceptor occurs at the D–A distance ≈6 Å, then the CT state is stabilized by coulomb interaction between (DD)$^+$ and A$^-$. The energy gap of the triple exciplex from the excimer state of naphthalene was found to be *ca.* 0.4 eV.

It was suggested in the nano-second time resolved fluorescence investigation on the triple exciplex formation in the intermolecular system of DCB-alkylnaphthalene that the triple exciplex is formed *via* exciplex in a dilute solution of the electron donor ($<10^{-2}$ M), and the triple exciplex is also formed *via* excimer in a high concentration of the electron donor ($>10^{-1}$ M) (see Scheme 1).



Scheme 1.

It was also verified that the dissociation process from the triple exciplex, (DDA)*, to the exciplex, (DA)*, is significant at room temperature. These results are clarified by the MO calculations described above. Since the energy gap of the stable triple exciplex, (DDA)*, from the exciplex, (DA)*, is 0.2 eV (≈4.6 kcal/mol), the triple exciplex (DDA)* and the exciplex (DA)* might coexist at room temperature, and the stable triple exciplex (Type: DDA) would be formed from the exciplex even in the considerably dilute solution of electron donor. On the other hand, the energy gap between the excimer state of naphthalene and the more stable triple exciplex (Type: DDA) in the excited state is 0.4 eV (≈9.2 kcal/mol) as shown in Fig. 5. The energy gap calculated is so great that the naphthalene excimer can not coexist thermodynamically with the triple exciplex of the array of DDA at room temperature. The triple exciplex formation *via* the excimer as well as *via* the exciplex with increasing concentration of electron donor greater than 10^{-1} M was mentioned. Subsequently, the triple exciplex *via* the excimer may dissociate easily to the exciplex at room temperature due to the small stabilization energy (≈0.2 eV) of the triple exciplex.

The potential energy curves of the ground state and the excited states for the array of component molecules, DAD, are given in Fig. 6. The intermolecular distance between a centered electron acceptor and one of two electron donors is constant (3.4 Å), while that between A and D varies (Z(A–D) as abscissa). The triple complex in the array of DAD is stable neither in the ground state nor in the first excited state. The exciplex (DA)* seems to be unperturbed by the approach of another

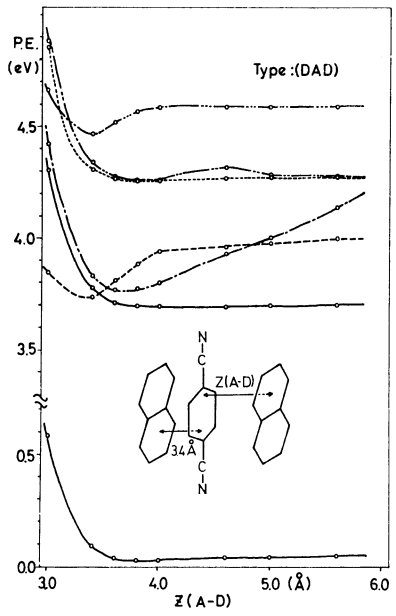


Fig. 6. Potential curves of complex (DAD). Variable parameter is Z(A–D), and Z(D–A) is constant (3.4 Å). In the excited state, ——, ———, ----, _____, and —·—·— indicate mainly ($D^+A^-\cdots D$), ($DA^-\cdots D^+$), ($DA^*\cdots D$), ($D^*A\cdots D$)↔($DA\cdots D^*$) (^1L_b) and ($D^*A\cdots D$) (^1L_a), respectively.

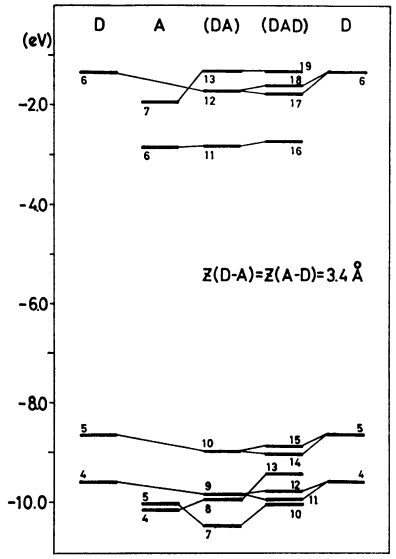


Fig. 7. Origins of SCF-MOs of complexes (DA) and (DAD) from SCF-MOs of component molecules.

D molecule leading to the formation of DAD. The calculated results concerning with the array of the triple exciplex are in line with the experimental results of the intramolecular triple exciplex formation in 1,3-dinaphthylpropane (DNP) and DCB system and also with the suggestion by Beens and Weller.[1] In the intramolecular system, it is impossible that triple exciplex takes an array of DAD because of trimethylene chain of DNP.[2]

The first electronic transition energies calculated in D, (DD), (DA) and (DDA) are summarized in Table 2 in comparison with the results from their fluorescence

Table 2. The first electronic transition energies (eV)

	D[a]	(DA)[a]	(DD)	(DDA)
Calcd	4.11	3.65	3.53	3.16
Obsd[b]	3.68	2.95	3.09	2.58

a) D and A are naphthalene and 1,4-dicyanobenzene, respectively. b) Obtained from the fluorescence maxima of respective excited species in 2-MN and DCB system.

Table 3. Characters of first electronic transition in several D–D distances of the triple complex (Type; D···DA)

Character of transition	Z(D-D)/Å			
	3.4	4.0	5.0	6.0
(D*···DA)	0.03%	0.01%	0.00%	0.00%
($D^+\cdots D^-A$)	0.75	0.72	0.26	0.02
($D^+\cdots DA^-$)	55.00	55.69	20.82	1.35
($D^-\cdots D^+A$)	0.03	0.01	0.00	0.00
(D···D*A)	0.60	0.56	1.00	1.24
($D\cdots D^+A^-$)	43.15	42.57	77.20	96.53
($D^-\cdots DA^+$)	0.01	0.00	0.00	0.00
($D\cdots D^-A^+$)	0.02	0.02	0.03	0.04
(D···DA*)	0.42	0.42	0.69	0.82

Table 4. Characters of first electronic transition in several A–D distances of the triple complex (Type; DA···D)

Character of transition	Z(A-D)/Å			
	3.4	4.0	5.0	6.0
(D*A···D)	0.39%	1.14%	1.26%	1.26
($D^+A^-\cdots D$)	19.54	88.53	97.71	97.88
($D^+A\cdots D^-$)	0.39	0.23	0.01	0.00
($D^-A^+\cdots D$)	0.69	0.03	0.04	0.04
(DA*···D)	57.99	0.80	0.83	0.82
($DA^+\cdots D^-$)	0.69	0.01	0.00	0.00
($D^-A\cdots D^+$)	0.39	0.12	0.00	0.00
($DA^-\cdots D^+$)	19.54	9.12	0.14	0.01
($DA\cdots D^*$)	0.39	0.02	0.00	0.00

spectra, where the molecular distance of component molecules are all 3.4 Å. The calculated transition energies are compared with those of fluorescence maxima, transition energy obtained in this kind of MO calculation being usually compared with that of electronic absorption spectra. Decrease in the transition energy in the order D>(DA)>(DD)>(DDA) is in line with that of transition energy from their fluorescence spectra, though all the energies were calculated to be *ca.* 0.5—0.6 eV greater than those of the corresponding fluorescence maxima, and the observed energy of (DD) is a little greater than that of (DA). Characters of the electronic transition of the lowest excitation in several D–D distance of the triple complex of DDA are given in Table 3. When donor molecule approaches the exciplex which has great CT-character (D^+A^-), the electronic configuration ($D^+\cdots DA^-$) gradually mixes with (D···

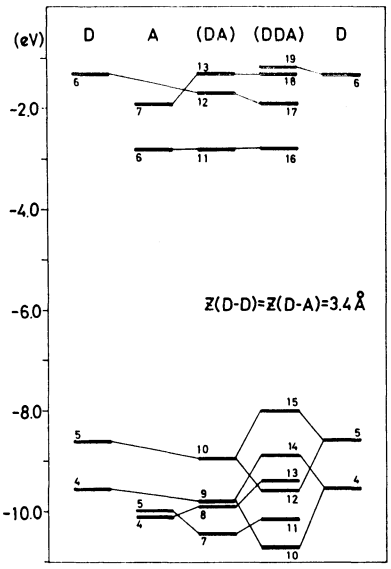


Fig. 8. Origins of SCF-MOs of complexes (DA) and (DDA) from SCF-MOs of component molecules.

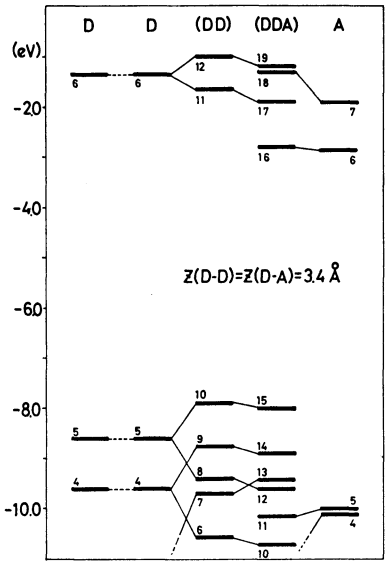


Fig. 9. Origins of SCF-MOs of dimer (DD) and complex (DDA) from SCF-MOs of component molecules.

D^+A^-). The dipole moment of the exciplex was calculated to be 16.16 D, while that of the triple exciplex was 18.13 D at the most stable molecular distance shown in Figs. 2 and 4. If the donor molecule approaches the exciplex to form (DDA)*, the donor molecule shares a positive charge with the another D molecule in the (D^+A^-) of the exciplex leading to form (($DD)^+A^-$). It is necessary to stabilize the triple exciplex that two electron donors interact with each other effectively when the exciplex associates with another electron donor. In the symmetric triple exciplex (DAD)* formation (Fig. 6), however, the CT state of ($DA^-\cdots D^+$) does not mix with ($D^+A^-\cdots D$), the electronic structure of which is almost the same as that of the initial exciplex (D^+A^-) (Table 4). The first excited state of triple complex ($DA\cdots D$) maintains the CT character of the exciplex (DA)* in approaching another D molecule. Figures 7—9 show the molecular orbitals and their correlations obtained in each conformation. Higher occupied orbitals of triple complexes (DDA) and (DAD) and the complex (DA) are supplied from electron donor molecule. In (DAD) alignment, the interaction between the highest occupied molecular orbital (HOMO, 5th MO) of electron donor and HOMO (10th MO) of the complex (DA) which consists of mostly HOMO (5th MO) of electron donor is not so great. They form 14 and 15th MO's (Fig. 7). However, the great interaction occurs between 5th MO of D molecule and 10th MO of the complex (DA) which is supplied from the electron donor (Fig. 8) in DDA alignment. In the electronic interaction between (DD) and A, the electronic attribution of MO's of component molecules to MO's of the triple complex in DDA alignment is obvious (Fig. 9). The 14 and 15th MO's of the triple complex are supplied from the dimer. Since there is no chance for the two electron donors interacting with each other in DAD alignment, the symmetric exciplex of (DAD) would be unstable.

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