The Electronic Structure of the Electron-donor-acceptor System in the Excited State. The Exciplex and the Fluorescent State of EDA Complex

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(Received April 17, 1975)

The semiempirical SCF-MO-CI calculation was applied to the electron donor-acceptor (EDA) interaction in 9,10-dicyanoanthracene and naphthalene system which exhibits the exciplex fluorescence and also the fluorescence due to the EDA complex stable in the ground state. On the basis of energy contour maps of the ground and excited states and of electronic transitions in the EDA system, the relaxation process from the F.C. excited state of the EDA complex to an identical fluorescent state with the exciplex was discussed on the intermolecular interaction, and also on the intramolecular interaction in (9,10-dicyanoanthracene)-$(CH_2)_3$-(naphthalene) systems.

There are numerous investigations relating to the electronic and geometrical structures of excimers. Excimers are believed to have a sandwich structures and to be stabilized by the exciton as well as charge resonance interaction. For exciplex it has been thought that the CT interaction is more important than the exciton interaction from many points of view.[1] Most molecular orbital calculation of the EDA complex as well as the exciplex were based on the configuration interaction between the ground and locally excited states of each component molecule including the charge transfer interaction, which is so called the method of "composite molecules".[2] On the other hand, some of investigators attempted to calculate the electronic structure of the EDA complex as a single conjugate system of π-electrons.[3,4]

Ohta, Kuroda and Kunii reported a method to calculate the electronic structure of the EDA complex, where the complex was treated as a single conjugated system of π-electrons.[6] The electronic state was calculated by the semiempirical SCF-MO-CI method within π-electron approximation by including all β terms. They accounted well for electronic transitions of the EDA complex of tetracyanoethylene with polycyclic aromatic hydrocarbons by this method.[5,6]

We have reported both exciplex and EDA complex fluorescence in the same EDA systems of 9,10-dicyanoanthracene (DCA) and naphthalenes.[7-9] The previous paper suggested that the geometrical arrangement between the excited electron acceptor and the ground state donor in the primary process of the exciplex formation was different from that of the Frank-Condon (F.C.) excited state of the corresponding EDA complex formed in the ground state.[7] In the intermolecular system, however, the fluorescence behavior of EDA complex and exciplex led to the conclusion that the fluorescent state of the exciplex may be identical with that of the corresponding EDA complex.[8] On the other hand, the geometrical conversion from their F.C. excited state of the EDA complex to the fluorescent state is sterically forbidden in the intramolecular system of 1-(9,10-dicyano-β-anthryl)-3-(α or β-naphthyl)propane.[9]

In this paper, the electronic interactions between 9,10-dicyanoanthracene and naphthalene both in the ground and excited states were calculated by assuming the complex as a single π-conjugate system. On the basis of energy contour maps of the ground and excited states and of electronic transitions in this EDA system, the electronic and geometrical structures of the fluorescent state of the exciplex and the EDA complex were discussed.

Method of calculation

The Pariser-Parr-Pople type semiempirical LCAO-SCF-MO's including configuration interaction of the EDA complex are calculated by assuming the complex as a single π-conjugate system. The molecular orbitals of the complex are calculated within the zero-differential-overlap approximation but with the including all two center resonance integrals.[5,6] In this method two center resonance integrals were evaluated by Katagiri-Sandorfy's formula,[10]

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

where C_μ is one center penetration integral and $S_{\mu\nu}$ is the overlap integral of atomic orbitals. If two atomic orbitals are associated to same molecule in these systems, $S_{\mu\nu}$ is evaluated from single Slater atomic orbitals, and if two atomic orbitals are associated to different molecule, we used SCF-atomic orbitals.[11] Two center repulsion integrals, $\gamma_{\mu\nu}$, were evaluated by Nishimoto-Mataga's formula,[12] and one center repulsion integrals, $\gamma_{\mu\mu}$, were estimated according to the Pariser-Parr's method.[13] Core energy, $H_{\mu\mu}$, is assumed to be minus of the ionization potential, which is given by Hinze and Jaffe.[14] Intermolecular core-core repulsion integrals, $\gamma_{\mu\nu}{}^c$, were estimated by following Dewar-Klopman's formula modified by Ohta *et al.*[5,15,16]

$$\gamma_{\mu\nu}{}^c = \gamma_{\mu\nu} + \left(\frac{1}{R_{\mu\nu}} - \gamma_{\mu\mu}\right)\exp\left[\alpha(R_{\mu\nu} - D_\mu - D_\nu)\right] \tag{2}$$

Table 1 shows parameters used here which were also adopted in the calculations of the EDA complexes between tetracyanoethylene (TCNE) and various polycyclic aromatic hydrocarbons and also various excimers of aromatic hydrocarbons.[5,6]

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Table 1. Used parameters in this calculation

	$H_{\mu\mu}$ (eV)	$\gamma_{\mu\mu}$ (eV)	C (eV)	D (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

$\alpha=-1.75$

The iteration of SCF-MO calculation was repeated, until the deviation in the total electronic energy by iteration becomes less than $10^{-4}\%$. For the prediction of electronic transitions, the CI calculation was carried out taking into consideration of the forty lowest singly excited configurations. The character of MO and the nature of the electronic transition in the bimolecular system are derived with same procedures as those references.[5,6]

The ground state total energy of each geometrical conformation was calculated by subtracting the total energy of component molecules (DCA and naphthalene) from summation of the electronic and core-core repulsion energies. The total energy in the first excited singlet state was evaluated from the total energy in the ground state and the first electronic transition energy.[5,6]

The energy contour maps of the ground and the first singlet excited state were depicted by moving a center of naphthalene on DCA molecule, where the intermolecular distance was assumed to be 3.4Å and molecular planes were parallel each other.[17] The calculation to depict one contour map was performed with 20 conformations taking into account of symmetry. The angle between the long axes of DCA and naphthalene, θ, were adopted to be 30°, 60°, and 90°, as shown in Fig. 1. Actual computation was carried out by the use of HITAC 8700/8800 operating system of the University of Tokyo.

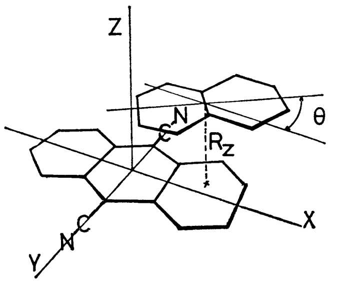
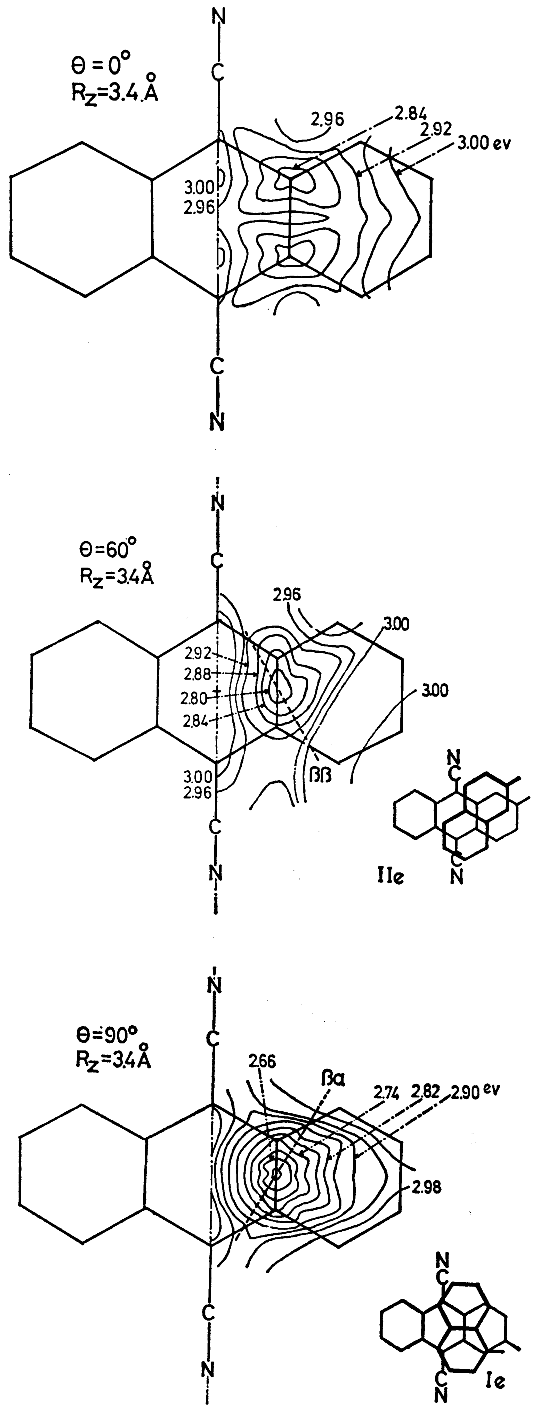


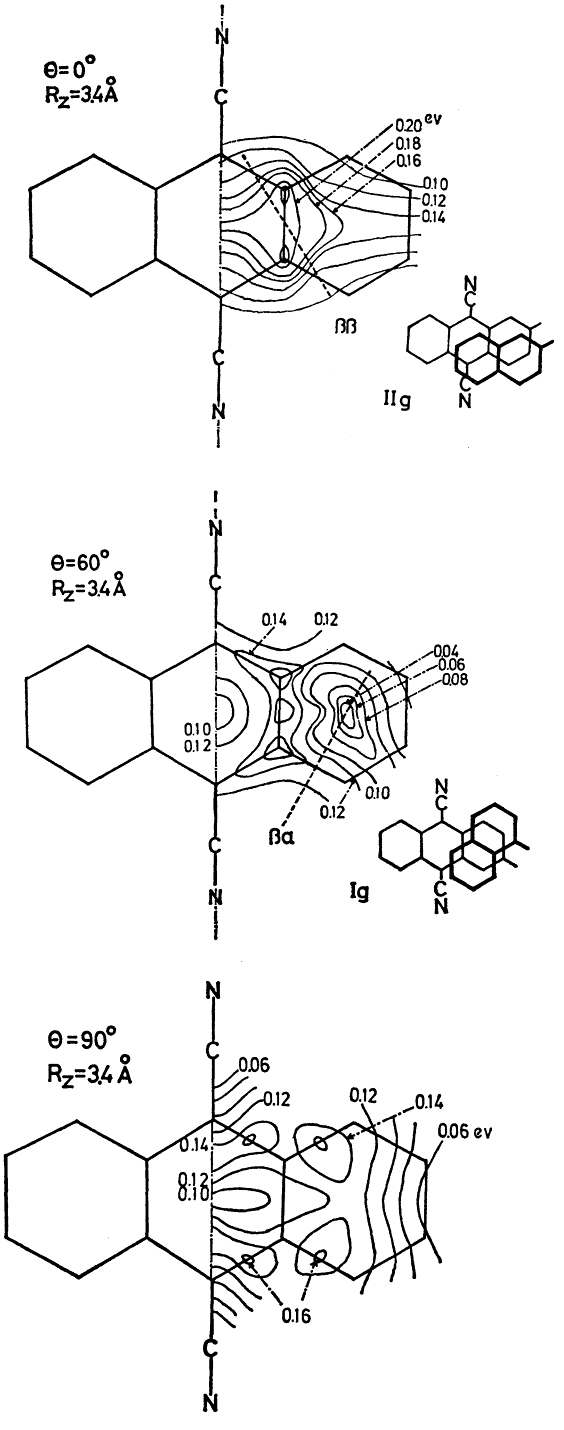
Fig. 1. The conformation and the geometrical parameters used for these calculations, where θ is the angle between the long axes and R_z is distance between the molecular planes (parallel) of these component molecules.



Figs. 2—4. The energy contour maps in the excited states for each angle of θ.

Results

The energy contour maps of the first excited singlet state obtained in the DCA and naphthalene system are shown in Figs. 2—4 for $\theta=0°$, 60°, and 90°, respectively. Although there are minimum points in the excited state for $\theta=0°$ and 60°, the most stable structure in the excited state is in the conformation of $\theta=90°$ as shown in Figs. 4. The ground state energy contour maps also shown in Fig. 5—7 for each angle of θ. Here, the most stable geometries in the excited state are represented by Ie and IIe and those geometries in the ground state are Ig and IIg as shown in Figs. 3—6. Unfortunately, there is no minus point of the total energy in the ground state which might mean a stabilization in the complex formation in the ground state. However, this is not important in this stage because we don't take into account explicitly a solute–solvent interaction and fix an intermolecular distance at 3.4 Å. It seems that the relative total energy is more important in the EDA complex formation. Inspection of these energy contour maps reveals that the most stable



Figs. 5—7. The energy contour maps in the ground states for each angle of θ.

structure in the ground state is in the conformation of $\theta=60°$, as shown in Fig. 6.

The nature of excitation was estimated by following equation which are identical with those described in the previous paper by Ohta, Kuroda and Kunii,[6]

$$\left.\begin{aligned}\mathrm{LE(D^*A)} &= \sum_{ij} b_{ij}{}^2{}_{,m} D_i D_j,\\ \mathrm{LE(DA^*)} &= \sum_{ij} b_{ij}{}^2{}_{,m} A_i A_j,\\ \mathrm{CT(D^+A^-)} &= \sum_{ij} b_{ij}{}^2{}_{,m} D_i A_j,\\ \mathrm{CT(D^-A^+)} &= \sum_{ij} b_{ij}{}^2{}_{,m} A_i D_j,\end{aligned}\right\} \tag{3}$$

Table 2. The electronic excitation energies, oscillater strengths and characters of transition of the lowest three excitations

Structure	Excitation energy (eV)	Oscillater strength	Character of Transition[a)] CT(D^+A^-)	LE(DA*)
Ig	2.96 (418 nm)	0.42	24%	74%
	3.16 (392)	0.15	66	28
	3.46 (358)	0.02	49	42
Ie	2.50 (495)	0.17	48	52
	3.41 (363)	0.02	43	45
	3.43 (361)	0.23	42	55
IIg	2.78 (446)	0.27	43	56
	3.22 (384)	0.17	46	53
	3.38 (366)	0.10	52	46
IIe	2.62 (472)	0.15	45	53
	3.10 (400)	0.22	46	52
	3.57 (347)	0.02	31	34

a) Residual characters are LE(D*A) and CT(D^-A^+) in mere trace amount.

where D_i, D_j, A_i, and A_j are expressed in Eq. (4), and $C_{i\mu}$ is coefficient of the atomic orbital, and $b_{ij,m}$ are coefficient of each excitation (i-th MO→j-th MO, Φ_{ij}) in CI calculation of the m-th excited state (Eq. (5)).

$$D_i = \sum_{\mu=1}^{n_d} C_{i\mu}{}^2,\quad A_i = \sum_{\mu=n_d+1}^{n_d+n_a} C_{i\mu}{}^2 \tag{4}$$

$$\Psi_m = \sum_{ij} b_{ij,m}\Phi_{ij} \tag{5}$$

In Eq. (4), n_a and n_d are given numbers to atoms in acceptor and donor molecules, respectively. The electronic transition and the character of transition are listed in Table 2 for several structures including Ig and Ie as mentioned above. The character of transition and oscillater strength are remarkably varied with the conformation of the EDA complex. These electronic transition characters summarized in Table 2 represent that the first electronic transition (absorption) from the ground state conformation (Ig or IIg) and also transition (fluorescence) from the excited singlet state (Ie or IIe) are the CT transition (D→A) equally mixed with the local excitation (^1L_a) of DCA.

Discussion

The great difference between the inter- and intramolecular systems is their degrees of freedom. In the intermolecular system each component molecule can take any conformation with no restriction. Therefore, the molecular conformation in the intermolecular EDA system may be dependent only on the electronic interaction in the ground state and also in the excited state of this system. Since the exciplex is the electronic interaction between the ground and the excited state molecules, the fluorescent conformation of the exciplex may be the energy minimum conformation in the energy contour map of the excited state. The energy minimum conformation for $\theta=90°$ seems to be most stable in the excited state than those for $\theta=0°$ and 60°, as shown in Figs. 2—4. Then, the exciplex and the

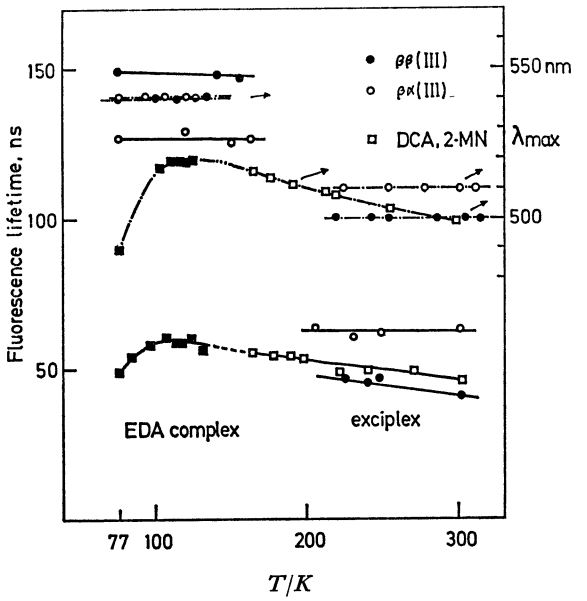


Fig. 8. The temperature dependence of the EDA complex and exciplex fluorescence maxima and fluorescence lifetimes of $\beta\alpha$-, $\beta\beta$(III) and DCA, 2-methylnaphthalene (2-MN) systems in 3-methylpentane. The broken lines and solid lines refer to the right and left ordinates, respectively. (extracted from the previous papers, Refs., 7) and 8)).

fluorescent state of the EDA complex, as will be mentioned later, seem to be in the geometrical conformation of Ie.

DCA and various naphthalenes form the corresponding EDA complex in the ground state as reported in the previous papers.[7-9] The fluorescence maxima and lifetimes of the exciplex (above∼150 K) and EDA complex (below∼120 K) were reported to continuously vary in the intermolecular system of DCA-naphthalenes, while these maxima and lifetimes were also reported to change discontinuously in the intramolecular system of 1-(9,10-dicyano-β-anthryl)-3-(α or β-naphthyl)propane (abreviated to $\beta\alpha$- and $\beta\beta$(III)) in the temperature region of 180—200 K.[7,8] The fluorescence behavior is illustrated in Fig. 8 extracted from previous papers for subsequent discussion. In the energy point of view, the conformation of these EDA complexes might be Ig for $\theta=60\ ^\circ$ as mentioned in the last section. Mataga and Murata,[18] and also Kobayashi *et al.*[19] reported that in fluid media the geometrical conformation of the F.C. excited state of the EDA complex of tetracyanobenzene (TCNB) and aromatic hydrocarbons reorient to a great extent to a fluorescent conformation. On the other hand, Itoh and Mimura demonstrated an experimental evidence of an identical fluorescent state of the exciplex and the EDA complex in the DCA and alkylnaphthalene system.[8] The geometrical conversion from the F.C. excited state of the complex (Ig) to the fluorescent equilibrium state (Ie) may be smoothly achieved in fluid media at low temperature. In the rigid matrix at 77 K, however, the fluorescence of the EDA complex seems to be from an non-relaxed or incompletely relaxed state near F.C. excited state of the EDA complex as mentioned in the previous paper.

As mentioned last section, the electronic transitions of the local excitation (^1L_a) and the CT transition are comparably mixed each other, and the electronic transition character of the first transition is dependent very much on the geometry. These results calculated here are consistent with the experimental results of the photoelection study that the fluorescence of the EDA complex of these systems has considerable CT character reported in the previous papers.[20-22] Furthermore, the electronic transition in Ig are in agreement with the absorption spectra of the EDA complexes of the DCA-naphthalene systems at 77 K.

In the intramolecular systems of $\beta\alpha$- and $\beta\beta$(III), the geometrical conformation between DCA and naphthalene moieties are restricted by trimethylene chain. The allowed traces of a center of naphthalene over the DCA molecule with an approximate spacing of 3.4 Å are shown by dotted lines in energy contour maps for $\beta\alpha$- and $\beta\beta$(III), respectively. A molecular model suggests that $\beta\alpha$(III) does not take the conformation of $\theta=0\ ^\circ$, while $\beta\beta$(III) does not take $\theta=90\ ^\circ$. Therefore, the geometry of the exciplex of the former may be Ie and that of the latter is IIe. On the other hand, the ground state geometry of $\beta\alpha$(III) seems to be Ig and that of $\beta\beta$(III) seems to be IIg by considering a steric hindrance of the trimethylene conformation.

In the intermolecular interaction, the geometrical conversion from the F.C. excited state of the EDA complex (Ig) to the fluorescent state (Ie) is not restricted in the fluid media, as mentioned above. In the intramolecular interaction, however, this kind of the geometrical conversion retaining the space of the electron donor and acceptor, *e.g.* Ig→Ie in $\beta\alpha$(III) and IIg→IIe in $\beta\beta$(III) seem to be forbidden by the trimethylene chain. As the result, the fluorescent state of the EDA complex in $\beta\alpha$- and $\beta\beta$(III) may be approximately the F.C. excited state of the complex formed in the ground state which are completely different from that of the corresponding exciplex. The electronic transitions calculated based on the geometrical conformations of Ig and IIg are consistent with the electronic absorption spectra and fluorescence polarizations of the corresponding EDA complexes reported previously.[22]

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