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Charge-Transfer Complexes of Maleic Anhydride and Dichloromaleic Anhydride with Various Aromatic Compounds

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Absorption, fluorescence and fluorescence excitation spectra were measured at room temperature and at low temperature for charge-transfer complexes containing maleic anhydride and dichloromaleic anhydride as electron acceptors. Benzene, toluene, mesitylene, durene, hexamethylbenzene, aniline, dimethylaniline, naphthalene and anthracene were used as electron donors. The charge-transfer absorption and fluorescence bands were observed for these complexes, their peak positions being linearly dependent upon the ionization potentials of donors for the same electron acceptor. From the comparison of the charge-transfer absorption or fluorescence peaks of maleic anhydride complexes with the corresponding values of dichloromaleic anhydride complexes, the difference in electron affinity between these two electron acceptors was obtained to be 0.4 eV. The electronic structures of the maleic anhydride complexes with benzene, naphthalene and anthracene were studied theoretically by considering the configuration interaction among the ground, locally-excited and charge-transfer configurations. The stable geometrical configurations in the ground and lower excited states of the complexes were discussed by the aid of the energy levels calculated for various relative orientations between electron donor and acceptor.

Maleic anhydride (abbreviated hereafter to MA) is one of the most important dienophilic substances in the Diels-Alder reaction. The charge-transfer (abbreviated hereafter to CT) complexes between MA and some aromatic hydrocarbons are suggested to take part in some Diels-Alder photoreactions.[1] This seems to be supported by the fact that MA and benzene which can form a CT complex is led to the Diels-Alder reaction.[2] The reaction is sensitized by benzophenone, and is inhibited by benzil.[2,3] The triplet-energy transfer from the sensitizer to the CT complex and therefore the sensitization of the Diels-Alder reaction may be possible, if the lowest triplet state of the former is higher than that of the latter. In this connection, it seems to be important to determine the positions of the lower excited states, especially the lowest triplet state, of CT complexes containing MA as an electron acceptor.

In the present work, we have undertaken to measure the absorption and emission spectra of the complexes between MA and various electron donors such as benzene, toluene, mesitylene, durene, hexamethylbenzene, aniline, dimethylaniline, naphthalene and anthracene. Furthermore, to clarify the character of the MA complexes, the study has been extended to complexes containing dichloromaleic anhydride (DCMA) which is stronger as an electron acceptor than MA.

Furthermore, from the theoretical point of view, we have undertaken to study by the semi-empirical MO method the electronic structures of CT complexes between MA and benzene, naphthalene or anthracene, the calculated energy of CT excited states being discussed in connection with the Diels-Alder photoreaction mechanism.

Experimental

Commercially available MA (Wako, reagent grade) and DCMA (Tokyo Kasei, reagent grade) were purified by sublimation *in vacuo* and by zone refining. Benzene, toluene, mesitylene, aniline and dimethylaniline (abbreviated hereafter to DMA) were purified by distillation. Commercially available durene, hexamethylbenzene (abbreviated hereafter to HMB), naphthalene and anthracene were purified by repeated recrystallizations from ethanol. A mixture 1 : 1 of ethyl ether and isopentane (abbreviated hereafter to EP) was used for the spectrophotometric study at low temperature. The single crystals of complexes between MA or DCMA and aromatic hydrocarbons were prepared by mixing the acceptor and one of the donors in methylene chloride or chloroform and by evaporating slowly the solvent at room temperature.

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[1] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc, New York (1965), p. 193.

[2] D. Bryce-Smith, A. Gilbert and B. Vickery, *Chem. Ind.* (London), **1960**, 2060; D. Bryce and J-E. Lodge, *J. Chem. Soc.*, **1962**, 2675; D. Bryce-Smith and A. Gilbert, *ibid.*, **1965**, 918.

[3] G. S. Hammond and W. M. Hardham, *Proc. Chem. Soc.*, **1963**, 63.

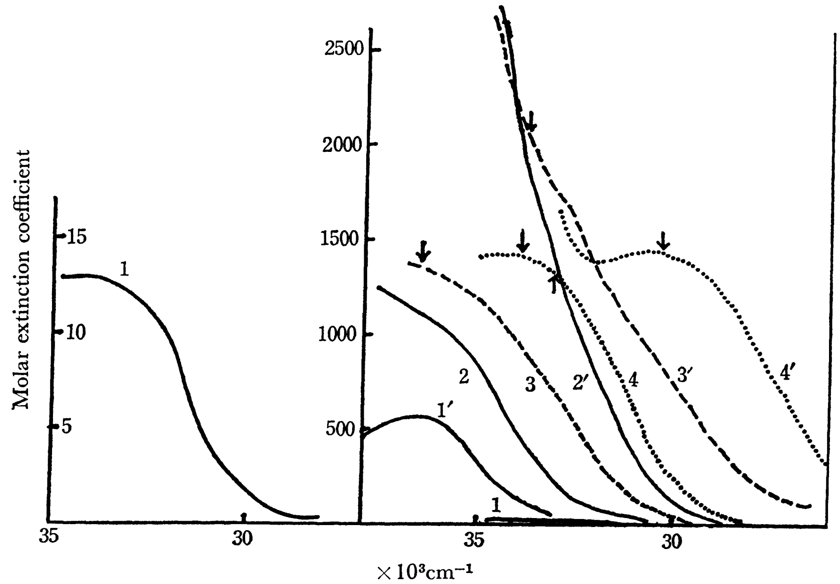

Fig. 1. The absorption spectra of MA and DCMA in various solvents at room temperature.

Curves 1, 2, 3, and 4 are for the MA solutions in chloroform, benzene, toluene and mesitylene, respectively. Curves 1', 2', 3' and 4' are for the DCMA solutions in chloroform, benzene, toluene and mesitylene, respectively.

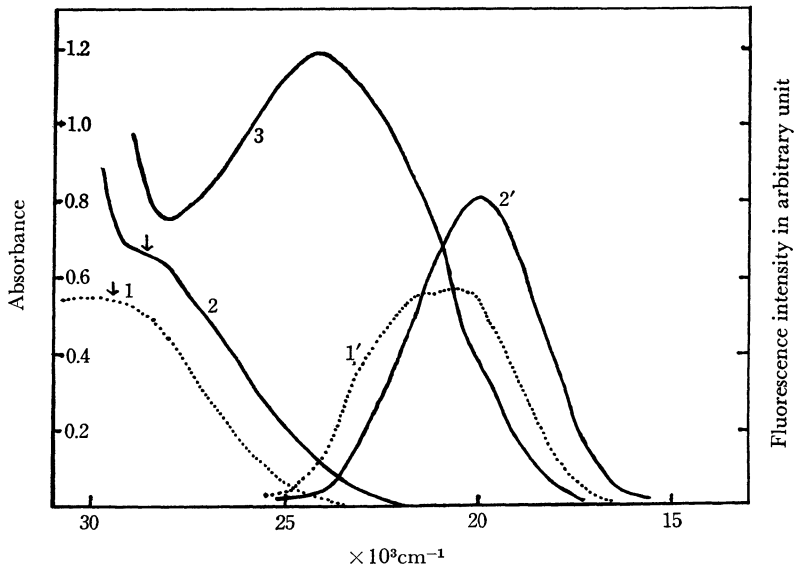

Fig. 2. The absorption and fluoresecnce spectra of some MA complexes at room temperature (in chloroform) and at liquid nitrogen temperature (in rigid EP solution), respectively.

Curve 1, absorption for the MA (0.93×10^{-1} mol/*l*)-durene (0.33×10^{-2} mol/*l*) solution.

Curve 2, absorption for the MA (0.93×10^{-1} mol/*l*)-HMB (0.83×10^{-2} mol/*l*) solution.

Curve 3, absorption for the MA (0.93×10^{-1} mol/*l*)-DMA (5.3×10^{-2} mol/*l*) solution.

Curves 1' and 2' are the fluorescence spectra of the MA complexes with durene and HMB, respectively.

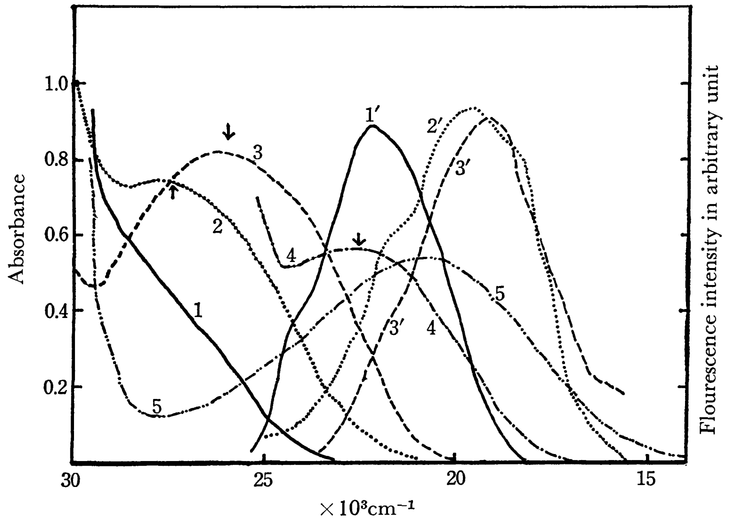

Fig. 3. The absorption and fluorescence spectra of some DCMA complexes at room temperature (in chloroform) and at liquid nitrogen temperature (in rigid EP solution), respectively.

Curve 1, absorption for the DCMA (0.55×10^{-2}mol/*l*)-durene (0.42×10^{-1} mol/*l*) solution.

Curve 2, absorption for the DCMA (0.55×10^{-2} mol/*l*)-HMB (1.1×10^{-1} mol/*l*) solution.

Curve 3, absorption for the DCMA (0.50×10^{-1} mol/*l*)-naphthalene (0.45×10^{-1} mol/*l*) solution.

Curve 4, absorption for the DCMA (0.50×10^{-1} mol/*l*)-anthracene (0.27×10^{-2} mol/*l*) solution.

Curve 5, absorption for the DCMA (0.50×10^{-1}mol/*l*)-DMA (1.5×10^{-1} mol/*l*) solution.

Curves 1′, 2′, and 3′ are the fluorescence spectra of the complexes with durene, HMB and naphthalene, respectively. The DCMA-durene complex exhibits considerably strong phosphorescence and curve 1′ is the difference between the total emission and the phosphorescence.

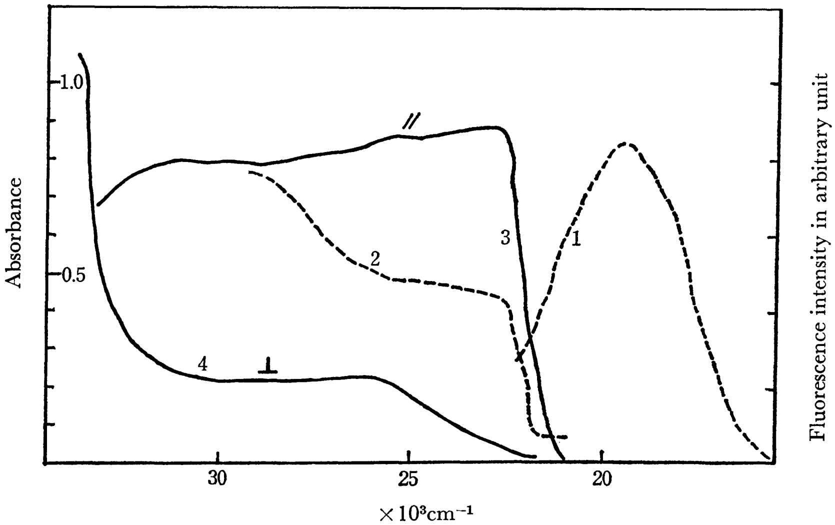

Fig. 4. The fluorescence (curve 1), fluorescence excitation (curve 2) and polarized absorption (curves 3 and 4) spectra of the DCMA-HMB crystal. The polarized absorption was measured in the direction parallel and perpendicular to the crystal growth axis.

TABLE 1. ABSORPTION MAXIMA AND IONIZATION POTENTIALS OF DONORS

Donor	Acceptor	State	Temperature	ν_m	I_D*
MA	Mesitylene	in mesitylene	r.t.	34.0 (10^3 cm^{-1})	8.39 (eV)
MA	Durene	in chloroform	r.t.	31.8	8.03
MA	HMB	in chloroform	r.t.	28.6	7.85
MA	DMA	in chloroform	r.t.	24.0	7.14
DCMA	Mesitylene	in mesitylene	r.t.	30.8	8.39
DCMA	Durene	in chloroform	r.t.	27.8	8.03
DCMA	HMB	in chloroform	r.t.	26.2	7.85
DCMA	Anthracene	in chloroform	r.t.	22.7	7.37
DCMA	DMA	in chloroform	r.t.	20.8	7.14
MA	Aniline	powder	100°K	30.2	7.69
DCMA	HMB	single crystal	77°K	23.2**	7.85

* V. I. Vedeneyev, L.V. Gurvich, V. N. Kondrat'yev, V. A. Madevdev and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold Ltd., London (1966).

** The peak of the polarized absorption parallel to the crystal growth axis.

TABLE 2. FLUORESCENCE MAXIMA AND IONIZATION POTENTIALS OF DONORS

Donor	Acceptor	State*	ν_m	I_D
MA	Mesitylene	in EP	22.4 (10^3 cm^{-1})	8.39 (eV)
MA	Durene	in EP	20.9	8.03
MA	HMB	in EP	20.0	7.85
DCMA	Mesitylene	in EP	22.3	8.39
DCMA	Durene	in EP	19.8	8.03
DCMA	HMB	in EP	19.2	7.85
MA	Aniline	powder	21.3	7.69
DCMA	HMB	single crystal	19.5	7.85

* Fluorescence was measured at 77°K in all cases.

Absorption spectra of solutions and of thin films on quartz plates[4] were measured with a Cary recording spectrophotometer Model 14M. Polarized absorption spectra of small single crystals were measured with a microspectrophotometer constructed in our laboratory.[5]

Emission spectra at liquid nitrogen temperature were measured with a JASCO Model CT-50 grating monochromator with an RCA 1P28 or EMI 9529A photomultiplier tube as a detector, glassy solutions or crystals being irradiated by a high pressure 500 W Hg lamp combined with Toshiba UV D1A and UV D2 filters in order to select 3650 Å light which excites the CT complexes only. The fluorescence spectra and their excitation spectra of powder samples (MA-aniline) were measured with an Aminco-Bowman spectrophotofluorometer (4-8202B) located at Government Chemical Industrial Research Institute.*[1]

The spectra observed with the MA and DCMA complexes are shown in Figs. 1, 2, 3 and 4, and the peak positions of the absorption and emission spectra are tabulated in Tables 1 and 2.

Theoretical

In the present paper, the interaction between electron donor and acceptor is taken into account by the configuration interaction among the ground, CT and locally-excited (abbreviated hereafter to LE) configurations.[6,7] For this calculation we need the MO's of each component. We adopt the SCF MO's of MA calculated by S. Hosoya and H. Hosoya by the aid of the Pariser-Parr-Pople method.*[2] The electron donors taken in the present theoretical study are benzene, naphthalene and anthracene.

For the sake of simplicity, we consider only the highest two occupied MO's (ϕ_1, ϕ_2 and θ_1, θ_2) and the lowest two vacant MO's (ϕ_3, ϕ_4 and θ_3, θ_4) of MA and aromatics. The wave functions

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4) T. Sakata and S. Nagakura, This Bulletin, **42**, 1497 (1969).

5) J. Tanaka, *ibid.*, **36**, 833 (1963).

*[1] We should like to express our sincere thanks to Dr. Akira Kuboyama, Government Chemical Industrial Research Institute, for his kindness in permitting us to use the instrument.

6) S. Iwata, J. Tanaka and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 894 (1966).

7) S. Iwata, J. Tanaka and S. Nagakura, *ibid.*, **89**, 2813 (1967).

*[2] We are greatly indebted to Dr. Haruo Hosoya and Mrs. Sumie Hosoya for their kindness in permitting us to use their unpublished theoretical result.

of the ground and lowest CT configurations[8)] are given by the Slater-type determinant

$$\Phi_{\mathrm{G}} \;\;= |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\theta_1\bar{\theta}_1\theta_2\bar{\theta}_2|$$

$$\Phi_{\mathrm{CT}_1} = 1/\sqrt{2}\{|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\theta_1\bar{\theta}_1\theta_2\bar{\phi}_3| - |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\theta_1\bar{\theta}_1\bar{\theta}_2\phi_3|\}$$

$$\Phi_{\mathrm{CT}_2} = 1/\sqrt{2}\{|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\theta_1\bar{\phi}_3\theta_2\bar{\theta}_2| - |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\bar{\theta}_1\phi_3\theta_2\bar{\theta}_2|\}$$

$$\Phi_{\mathrm{CT}_3} = 1/\sqrt{2}\{|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\theta_1\bar{\theta}_1\theta_2\bar{\phi}_4| - |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\theta_1\bar{\theta}_1\bar{\theta}_2\phi_4|\}$$

$$\Phi_{\mathrm{CT}_4} = 1/\sqrt{2}\{|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\theta_1\bar{\phi}_4\theta_2\bar{\theta}_2| - |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\bar{\theta}_1\phi_4\theta_2\bar{\theta}_2|\}$$

In addition to the above-mentioned configurations, the following LE configurations corresponding to the lower excited states of the component molecules are taken into consideration.

$$\Phi_{\mathrm{L}_1}^{\mathrm{MA}} = \Phi^{\mathrm{MA}}(\phi_2{}^{-1}\phi_3) \quad (5.96\ \mathrm{eV})$$

for local excitation in MA

$$\Phi_{\mathrm{L}_1}^{\mathrm{B}} = 1/\sqrt{2}\{\Phi^{\mathrm{B}}(\theta_1{}^{-1}\theta_4) - \Phi^{\mathrm{B}}(\theta_2{}^{-1}\theta_3)\} \quad (4.71\ \mathrm{eV})$$

for ${}^1B_{2\mathrm{u}}$ local excitation in benzene

$$\Phi_{\mathrm{L}_1}^{\mathrm{N}} = 1/\sqrt{2}\{\Phi^{\mathrm{N}}(\theta_1{}^{-1}\theta_3) - \Phi^{\mathrm{N}}(\theta_2{}^{-1}\theta_4)\} \quad (4.06\ \mathrm{eV})$$

for ${}^1B_{3\mathrm{u}}{}^-$ local excitation in naphthalene

$$\Phi_{\mathrm{L}_2}^{\mathrm{N}} = \Phi^{\mathrm{N}}(\theta_2{}^{-1}\theta_3) \quad (4.45\ \mathrm{eV})$$

for ${}^1B_{2\mathrm{u}}{}^+$ local excitation in naphthalene

$$\Phi_{\mathrm{L}_1}^{\mathrm{A}} = \Phi^{\mathrm{A}}(\theta_2{}^{-1}\theta_3) \quad (3.31\ \mathrm{eV})$$

for ${}^1B_{2\mathrm{u}}{}^+$ local excitation in anthracene

$$\Phi_{\mathrm{L}_2}^{\mathrm{A}} = 1/\sqrt{2}\{\Phi^{\mathrm{A}}(\theta_1{}^{-1}\theta_3) + \Phi^{\mathrm{A}}(\theta_2{}^{-1}\theta_4)\} \quad (4.93\ \mathrm{eV})$$

for ${}^1B_{3\mathrm{u}}{}^+$ local excitation in anthracene

The energies of the LE configurations are taken from the transition energies observed with MA, benzene,[9a)] naphthalene[9b)] and anthracene.[9b)] Their values are given in the parentheses after the wave functions of the corresponding LE configurations.

The energies of the CT configurations, the ground configuration energy being taken as the standard, is obtained as follows, for example, for the CT_1 configuration:

$$\begin{aligned} E_{\mathrm{CT}_1} &= \varepsilon(\phi_3) - \varepsilon(\theta_2) - \iint \phi_3(1)\phi_3(1)\frac{e^2}{r_{12}}\theta_2(2)\theta_2(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \\ &= I(\theta_2) - A(\phi_3) - C_{23} \end{aligned}$$

where $\varepsilon(\phi_3)$ and $\varepsilon(\theta_2)$ are the orbital energies, and $I(\theta_2)$ and $A(\phi_3)$ are the ionization potential of the donor and the electron affinity of the acceptor, respectively. The ionization potentials of benzene, naphthalene and anthracene are 9.245, 8.10 and 7.37 eV, respectively.[10)] The electron affinity of MA can be determined to be 0.6 eV from the peak of the first CT band of MA-DMA complex on the assumption that the Coulomb term in Eq. (1) given later is 3.6 eV.[11)] The electron affinity for the second lowest vacant orbital can be determined from the value for the lowest vacant orbital by assuming that the difference in the electron affinity is equal to that in the corresponding SCF orbital energies. The off-diagonal matrix elements of the total electron Hamiltonian each of which represents the interaction between two different configurations can be evaluated.[12)] For example, those between the CT configuration and the ground or LE configurations can be represented in terms of the core resonance integral β which is approximately represented by the following equation:[13)]

$$\beta = -KS_{ij}$$

where K is an experimental parameter and S_{ij} is the overlap integral between the electron donating orbital θ_i and the electron accepting orbital ϕ_j. It is represented by the sum of the overlap integrals between the Slater type atomic orbitals. We set K equal to 10.[6,7)]

By solving secular equations constructed by the above-mentioned diagonal and off-diagonal matrix elements, we evaluate the energies of the ground and lower excited states for the MA complexes with benzene, naphthalene and anthracene,[14)] taking various geometrical configurations under the following limitations;

1) The molecular planes of electron donor and acceptor are parallel with each other and their distance is 3.4 Å.

2) The C=C bond of MA is parallel to the symmetry axis parallel to a bond of each donor molecule.

Results and Discussion

Complexes in Solution. The absorption spectra of MA and DCMA in chloroform, benzene, toluene and mesitylene are shown in Fig. 1. A very weak absorption of MA (curve 1 in Fig. 1) due to an n-π^* transition[15)] appears at 31000 cm^{-1}—34000

[8)] Since the wave functions include spin functions, strictly speaking, these configurations should be called the "zero-order ground singlet state" and the "zero-order CT singlet state." Here we use "configuration" instead of "zero-order singlet state" because of simplicity.

[9)] a) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949). b) E. Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin (1952).

[10)] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957); J. B. Birks and M. A. Slifkin, *Nature*, **191**, 761 (1961).

[11)] This is the value calculated for the benzene-tetracyanobenzene system on the point-charge approximation.[7)] On this approximation, this value is applicable to various donor-acceptor systems taking structures of parallel molecular planes 3.4 Å distant.

[12)] J. A. Pople, *Proc. Phys. Soc.*, **68A**, 81 (1955); H. C. Longuet-Higgins and J. N. Murrell, *ibid.*, **68A**, 601 (1955).

[13)] For example, R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[14)] Actual calculations were performed by the aid of an electronic computer FACOM 202 of our institute. The authors' thanks are due to the Mr. Yasuho Ishida for his assistance in writing the program.

[15)] From the low value of the molar extinction coefficient and from the analogy with similar carbonyl compounds, the absorption band near the 360 mμ is clearly attributed to the n-π^* transition.

cm^{-1} in chloroform. In the other solvents, MA exhibits a new band conceivably due to the CT interaction with surrounding molecules. The situation is the same for the DCMA solutions.

Concerning the electron donors other than benzene, toluene and mesitylene, absorption and fluorescence spectra were measured with ternary solutions containing electron donor and acceptor in chloroform, with the results shown in Figs. 2 and 3 for the MA and DCMA complexes, respectively. A new absorption band neither due to electron donor nor acceptor is observed for the MA complexes with HMB and DMA and for the DCMA complexes with DMA, anthracene, HMB and durene. Furthermore, a shoulder appears for the MA complex with durene, and for the DCMA complex with naphthalene. In order to certify that these bands and shoulders are due to the CT transition, we examine the relationship between the peak positions and the ionization potentials of donors.

The peak wave numbers of the CT bands for a series of complexes with a fixed electron acceptor are related to the ionization potentials (I_D) of donors by the following equation:

$$h\nu_{CT} = I_D - C_1 + \frac{C_2}{I_D - C_1} \tag{1}$$

where C_1 and C_2 are constants to be determined experimentally. C_1 is mainly composed of two factors, the electron affinity of the electron acceptor (A_A) and the Coulomb attraction between the donor and acceptor orbitals (C): that is to say, $C_1 = A_A - C$. Using the observed ionization potentials of the donors and taking the CT band maximum of the MA-DMA or DCMA-DMA complex as the standard, we can calculate the CT band positions for the MA and DCMA complexes. They are indicated by the arrows in Figs. 1, 2 and 3. The calculated peak positions are in good agreement with the observed ones. This supports the CT assignment of the absorption bands under consideration.

Figures 2 and 3 show that the fluorescence spectrum of each complex in EP solution at liquid nitrogen temperature satisfies the mirror image relation with the CT absorption spectrum observed for the chloroform solution at room temperature. This means that the observed fluorescence spectra are of the CT character.

From Eq. (1), we may expect that a linear relation can be approximately satisfied between ν_{CT} and I_D in the case where the latter is changed in a rather narrow range. Plotting these two quantities for both the fluorescence and the absorption spectra observed for a series of complexes containing the fixed electron acceptor, we obtain a straight line relationship, as is shown in Fig. 5. From this figure, it is found that the lines for the absorption maxima observed for the MA and DCMA complexes are parallel with each other and they cross the ordinate with the energy difference of ~0.4 eV. This is mainly due to the difference in C_1 in Eq. (1) between the DCMA and MA complexes. That is to say, the electron affinity of DCMA may be higher by ~0.4 eV than that of MA.

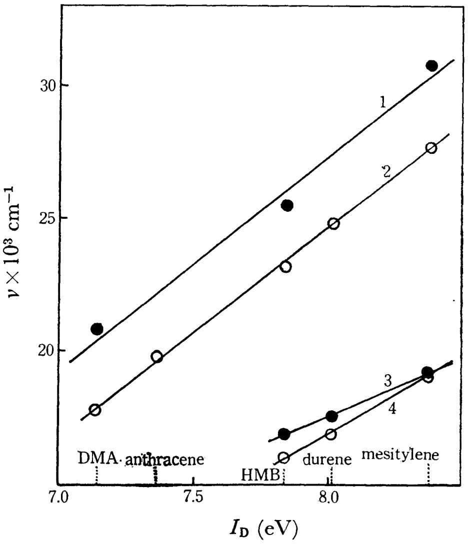

Fig. 5. The plot of the absorption and fluorescence maxima for the MA and DCMA complexes in solution against the ionization potentials (I_D) of donors.

1 and 2; absorption maxima—I_D polts for the MA and DCMA complexes, respectively.

3 and 4; fluorescence maxima—I_D plots for the MA and DCMA complexes, respectively.

Complexes in Solid State. The polarized absorption was measured with a single crystal of the DCMA-HMB complex, for the purpose of obtaining an additional support for the CT assignment of the band at ~22000 cm^{-1}. The needlelike crystal of this complex is unstable and decomposed within a few days at 5°C. Therefore the measurement was carried out as quickly as possible after the crystallization. The result is shown in Fig. 4. Furthermore, the fluorescence and fluorescence excitation spectra of this crystal measured at liquid nitrogen temperature are also shown in this figure. An absorption at 22000 cm^{-1} is polarized parallel to the crystal growth axis with the dichroic ratio more than 4. Since crystals of this kind usually grow up in the direction perpendicular to the planes of the stacked component molecules, the above result seems to mean that the transition moment of the band is directed perpendicular to the molecular plane. This supports the interpretation that the absorption band at ~22000 cm^{-1} is the CT one and therefore the corresponding fluorescence at ~20000 cm^{-1} is of the same character.[16]

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[16] The similar experimental work has been carried out for the single crystal of the DCMA-durene complex. In this case too, the CT absorption polarized parallel to the crystal growth axis is observed.

Theoretical Result. The energies of the ground and lowest CT states were calculated for the MA complexes with benzene, naphthalene and anthracene by the method described in the "Theoretical" part. Concerning the MA complex with benzene, the stable geometrical configuration of the ground state is predicted to be similar to that of the lowest CT state. In both the ground and the lowest CT state, the center of the C=C double bond of MA is located above the point close to the center of benzene. However, the gradient of energy surface is about 10 times steeper in the excited state than in the ground state.

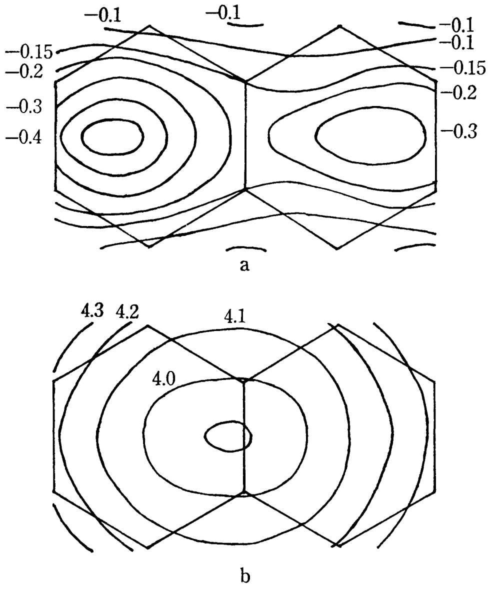

Fig. 6. The dependence of energy (in eV) on the geometrical configuration for the MA-naphthalene complex.
a, ground state
b, lowest CT state

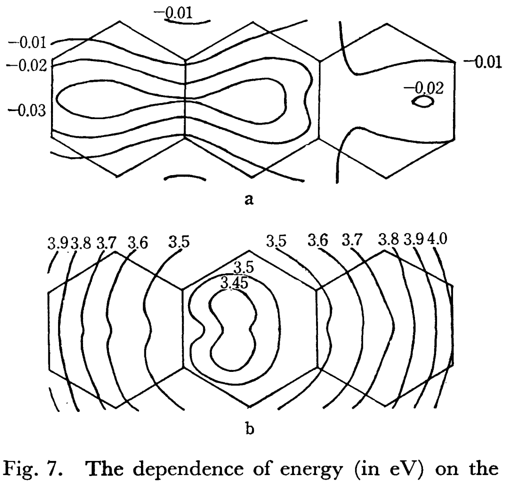

Fig. 7. The dependence of energy (in eV) on the geometrical configuration for the MA-anthracene complex.
a, ground state
b, lowest CT state

Theoretical results on the MA complexes with naphthalene and anthracene are shown in Figs. 6 and 7, respectively. These figures show energy contour maps for the ground and lowest CT state, which are obtained by plotting the state energies against the positions of the center of the C=C bond of MA.

The MA-naphthalene and MA-anthracene complexes in the ground state have, respectively, two and three energy minima which are located near the center of each benzene ring, while in the excited state they have only one minimum near the center of donor molecule. As an example, the stable geometrical structure of the MA-anthracene complex predicted by the present theoretical consideration is shown in Fig. 8. According to this figure, the MA molecule moves to the energy minimum position above the center of the anthracene molecule in the excited state from the position above one of the end benzene rings in the ground state. This seems to be interesting in connection with the fact that in the Diels-Alder reaction the C=C double bond of MA reacts with anthracene on the 9 and 10 positions. The positions of photochemical dienophile addition in this case seems to be reason-

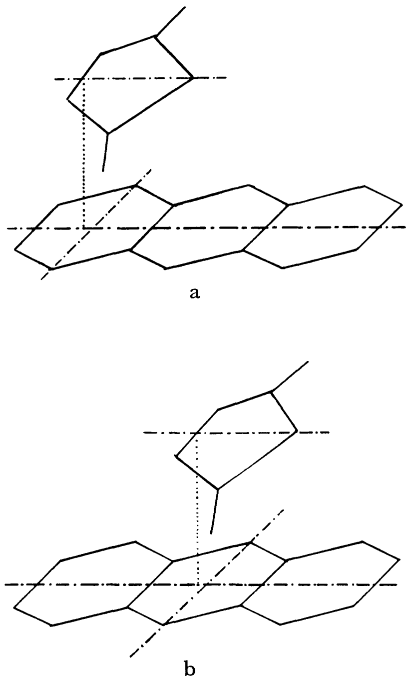

Fig. 8. The stable geometrical configuration of the MA-anthracene complex.
a, ground state
b, lowest CT state

ably explained by assuming that the reaction occurs through the excited CT state of the complex.

Next, we add a brief descrption on the mechanism of thermal Diels-Alder reaction of MA. In view of the electron accepting ability mentioned above, it may be considered that the CT interaction takes part in the reaction. That is to say, in the initial stage of the reaction, we can except the formation of the π (outer)-complex which takes the structure shown in Fig. 8a.[17] In this stage the degree of the electron transfer from anthracene to MA may be small. With the progress of the reaction, the CT degree may increase and the system may approach gradually the structure shown in Fig. 8b. Therefore in the stage of the actual formation of the new C–C bonds between MA and anthracene, the system may probably take the structure similar to that in Fig. 8b.[18] Thus, by the aid of CT state structure shown in Fig. 8b we can explain reasonably the fact that the thermal dienophile addition occurs at the 9 and 10 positions of anthracene.

We are greatly indebted to Dr. Keitaro Yoshihara, the Institute for Solid State Physics, for his helpful advice.

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[17] The present discussion is made on the assumption that the thermal Diels-Alder reaction proceeds through the π (outer)-complex in the initial stage.

[18] The actual process of the bond formation is not clear. There are two possibilities that the two C–C bonds are simultaneously formed, and that each of them is formed separately and the bond formation proceeds in the two steps. In the latter case, we may expect the inner (σ)-complex formation in which electron transfer occurs to a great extent and a new C–C bond is formed between MA and anthracene.