and has been applied by us to the case of an ion with finite size and water molecules with real dipoles.

As in most existing theories, polarizabilities of the ions have not been considered. From a classical viewpoint, the orientated water dipoles can induce a dipole in the ion proportional to the polarizability of the ion. The total ionic field would then contain contributions from both the ion and the induced dipole fields. This contribution to the total ionic field would nevertheless be very small for most ions considered here.

It is hoped that the model adopted here for ions in the liquid phase will prove as successful in its application to other solvent systems as more experimental solvation energies become available, particularly as the solvent structure is likely to be less complex than that of water.

Charge-Transfer Interaction in Tetracyanoethylene Complexes of Pyrene and Naphthalene

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Abstract: Theoretical treatments were made on the charge-transfer interaction between donor and acceptor in the tetracyanoethylene (TCNE) complex of naphthalene and that of pyrene with the consideration of the effect of interaction of higher energy charge-transfer configurations, and structural models were proposed for these complexes. The spectrophotometric investigation was carried out on the formation of the pyrene–TCNE complex in carbon tetrachloride. The dipole moment of the pyrene–TCNE complex was experimentally determined as 2.0 D. These experimental results and the corresponding data on the naphthalene–TCNE complex are compared with the results of theoretical treatment. It is shown that theoretical predictions consistent with the observations are obtainable when the higher energy charge-transfer configurations are taken into account.

The interaction between electron donor and acceptor in a molecular complex can be well understood by the charge-transfer theory developed by Mulliken.[1] According to the theory, the electronic structure of a 1:1 complex can be described as the resonance hybrid between the "no-bond structure" and the "dative structure." The ground-state wave function of a complex is generally expressed as

$$\Psi_N(\mathrm{D \cdot A}) = a\Phi_0(\mathrm{D \cdot A}) + b\Phi_1(\mathrm{D^+ \cdot A^-})$$

where $\Phi_0(\mathrm{D \cdot A})$ and $\Phi_1(\mathrm{D^+ \cdot A^-})$ are respectively the wave function of the no-bond structure and that of the dative structure. A simplifying assumption has been usually adopted on the wave function of the dative structure; namely, it can be approximately described with the wave function of the lowest energy charge-transfer configuration, *i.e.*, the state where an electron has been transferred from the highest occupied molecular orbital of the donor to the lowest vacant molecular orbital of the acceptor. A number of investigations on the molecular complexes have been carried out on the basis of this assumption. This simplifying assumption is quite useful; however, its general validity is obviously questionable. The significance of higher energy charge-transfer configurations, including back charge-transfer configurations, has been pointed out by Mulliken[2] and several other investigators.[3–5]

In a previous paper[4] we have shown that the mixing of higher energy charge-transfer configurations is of great importance in the case of the pyrene–tetracyanoethylene complex, particularly in the appearance of its multiple charge-transfer bands. Seemingly this is the case not only in this particular complex, but also in many other π complexes which involve polycyclic aromatics as the electron donor. Thus it is of particular interest to elucidate various aspects associated with the effect of the mixing of higher energy charge-transfer configurations by making a detailed study on some typical examples of these complexes. The complexes which involve naphthalene or pyrene as the donor and tetracyanoethylene (TCNE) as the acceptor seem to be most suited for this purpose, since, firstly, the component molecules possess a rather simple molecular structure with high symmetry, and, secondly, we can expect that the charge-transfer interaction between the donor and acceptor plays an important role in the intermolecular binding in these complexes because TCNE is a nonpolar molecule with a very high electron affinity.

Spectrophotometric investigations on the complex formation in carbon tetrachloride have been already carried out in detail on the naphthalene–TCNE complex.[6,7] The dipole moment of this complex also has been determined. Compared with this, available experimental data are limited on the pyrene–TCNE complex. Therefore, in the present study, we have carried out the spectrophotometric investigation on the

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(1) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

(2) R. S. Mulliken, *J. Chim. Phys.*, **61**, 20 (1963).

(3) J. N. Murrell, *J. Am. Chem. Soc.*, **81**, 4839 (1959).

(4) H. Kuroda, I. Ikemoto, and H. Akamatu, *Bull. Chem. Soc. Japan*, **39**, 1842 (1966).

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

(6) G. Briegleb, J. Czekalla, and G. Reuss, *Z. Physik. Chem.* (Frankfurt), **30**, 334 (1961).

(7) G. D. Johnson and R. E. Bowen, *J. Am. Chem. Soc.*, **87**, 1655 (1965).

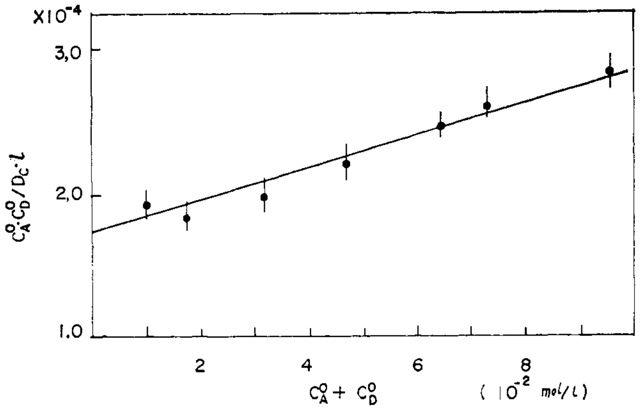

Figure 1. Benesi-Hildebrand-Scott plots for the pyrene-TCNE system (in carbon tetrachloride solution, at 45°).

complex formation between pyrene and TCNE in carbon tetrachloride solution, and determined the heat of formation and the dipole moment of the 1:1 complex of pyrene and TCNE, so that the comparison between the naphthalene-TCNE and pyrene-TCNE complexes is possible. We have made theoretical considerations on the charge-transfer interactions in these complexes, with special attention on the effect of the mixing of higher energy charge-transfer configurations, and examined the possibility of obtaining theoretical predictions on the electronic structures of these complexes consistent with the observations.

Experimental Section

Pyrene was purified by the successive application of recrystallizations from a xylene solution and from an acetic anhydride solution, alumina column chromatography, and finally sublimation *in vacuo*. Naphthalene and TCNE were purified by sublimation *in vacuo* after recrystallization. Carbon tetrachloride was dried over calcium chloride, distilled carefully, and bubbled with dry nitrogen immediately before it was used.

The visible and ultraviolet absorption spectra of solutions were observed by a Hitachi EPS-2U recording spectrophotometer. For the purpose of determination of the equilibrium constant, however, the absorbance was directly read at each wavelength with a Hitachi-Perkin-Elmer 135 UV-VIS spectrophotometer by using 10-cm cylindrical silica cells and a thermostated cell holder. The temperature of the cell was controlled with an accuracy of ±0.2°. The absorption spectra of the crystals were observed with a microspectrophotometer which has been described in a previous paper.[8]

The measurement of dielectric constant was made with an apparatus of the heterodyne-beat method, which had been designed so as to show a high sensitivity for the detection of small change in dielectric constant.[9] The cell used in the present study had two silver-plated cylindrical electrodes. The capacitance of this cell was about 89 pf. The accuracy of measurement of dielectric constant change was ±0.00005. The temperature of solution was kept at 30.2 ± 0.02° during the measurement of dielectric constant. The density of solution was measured by using an Ostwald pycnometer. The error expected in the observed molar polarizability was about 0.002 cm^3.

The numerical calculations in the theoretical part of the present paper were made by using an electronic computer, HITAC 5020E, at the computer center, University of Tokyo.

Experimental Results

Complex Formation Equilibrium. The equilibrium constant, K^c, for the formation of the 1:1 complex was determined from the analysis of the spectrophotometric data by using Scott's equation, a modification of the Benesi-Hildebrand equation

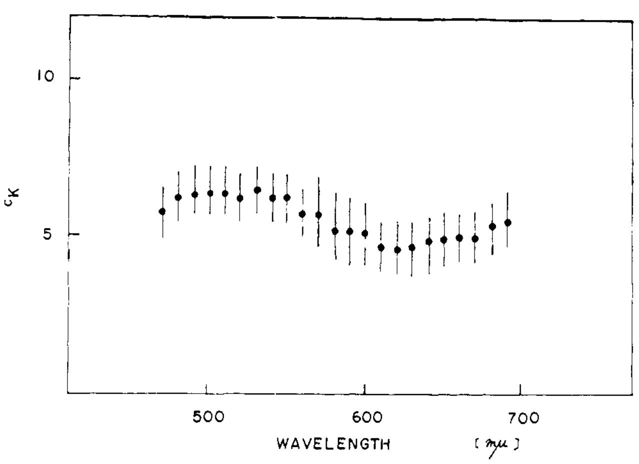

Figure 2. Variation of K^c with wavelength for the pyrene-TCNE system (45°).

$$\frac{C_A^0 C_D^0}{D_c l} = \frac{1}{K^c \epsilon} + \frac{1}{\epsilon}(C_D^0 + C_A^0) \qquad (1)$$

where $D_c = D - \epsilon_A C_A^0 - \epsilon_D C_D^0$, $\epsilon = \epsilon_c - \epsilon_A - \epsilon_D$, D is the measured optical density, l is the length of optical path, C_D^0 and C_A^0 are the initial concentrations of donor and acceptor, and ϵ_D, ϵ_A, and ϵ_c are the molar extinction coefficients. This equation is applicable when the 1:1 complex only is formed; otherwise the plots of $(C_D^0 C_A^0 / D_c l)$ *vs.* $(C_D^0 + C_A^0)$ will deviate from linearity. The linearity of this kind of plots has been always regarded as evidence of the presence of only 1:1 complex. Recently, however, it has been shown by Johnson and Bowen that the linearity of Benesi-Hildebrand plots is not a sufficient criterion for the presence of only 1:1 complex.[7] The plots could appear linear within the experimental error even if complexes of other stoichiometries are formed in addition to the 1:1 complex provided that the latter is the principal species, but, in this case, the observed equilibrium constant shows a systematic variation with wavelength. For the pyrene-TCNE complex, the Scott plots were found to be linear as shown in Figure 1, but K^c was dependent on the wavelength.[10]

The variation of K^c at 45° is shown in Figure 2. Similar results were obtained both at 7 and 31°. We can conclude, therefore, that the principal species formed in carbon tetrachloride solution between pyrene and TCNE is the 1:1 complex as expected, but a small fraction of complexes is in the form of different stoichiometries. A similar conclusion has been given for the naphthalene-TCNE complex by Johnson and Bowen.[7] Consequently the observed equilibrium constant may not give the true equilibrium constant in these cases. The deviation from the true equilibrium constant might be quite significant at wavelengths in the tail of charge-transfer band, but it may not be large at wavelengths around the absorption maximum of a charge-transfer band. In effect, the observed value of K^c is nearly constant in the regions around the ab-

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(8) H. Kuroda, T. Kunii, S. Hiroma, and H. Akamatu, *J. Mol. Spectry.*, **26**, 60 (1967).

(9) I. Nakagawa, *Nippon Kagaku Zasshi*, **79**, 1353 (1955).

(10) The observed data were processed with an electronic computer, OKITAC 5090A, at the Data Processing Center of University of Tokyo. The least-squares method was used to determine the value of K^c and ϵ_c.

Table I. Equilibrium Constant (K^c) and Molar Extinction Coefficient (ϵ_{max}) Determined at the Absorption Maximum of the Charge-Transfer Band[a]

Temp, °C	K^c (at 19.9 kK), l./mole	ϵ_{max} 1st CT band	ϵ_{max} 2nd CT band
7	15.6	1270	1050
31	9.0	1160	965
45	6.4	1100	910

[a] $\Delta H = -4.1$ kcal/mole; $\Delta S = -8.8$ cal/deg mole.

Table II. Charge-Transfer Bands of TCNE Complexes of Naphthalene and Pyrene

	Naphthalene–TCNE Solution	Naphthalene–TCNE Crystal[a]	Pyrene–TCNE Solution	Pyrene–TCNE Crystal[a]
Wavenumbers of CT bands				
1st CT band, $\bar{\nu}_1$, kK	18.2	17.5	13.7	12.7
2nd CT band, $\bar{\nu}_2$, kK	23.4	24.5 (sh)	19.9	20.0
Energy difference between two CT bands				
$h\nu_2 - h\nu_1$, ev	0.65	0.87	0.77	0.91
ΔE^d (calcd), ev	0.78		1.0	
Intensity ratio of two CT band $(f_1/f_2)^b$				
Observed	0.86	>5	1.3	0.94
Calculated[c]	...	(2nd CT is forbidden)	...	0.9

[a] In the spectrum polarized in the direction of the crystal axis, along which donor and acceptor are alternately stacked on each other. [b] f_1 and f_2 are respectively the oscillator strength of the first CT band and that of the second CT band. [c] Calculated for the relative orientation found in the crystal structure by using the procedure described in the theoretical part of the present paper. [d] Energy difference between the highest occupied orbital and the next occupied orbital calculated by the SCF MO method.

sorption maximum. In this paper, we shall tentatively assume that the mean value of K^c determined at wavelengths around the absorption maximum of the charge-transfer band is approximately equal to the true equilibrium constant for the formation of the 1:1 complex. These values are given in Table I. By using the values of K^c mentioned above, the heat of formation of the pyrene–TCNE complex was estimated as 4.1 kcal/mole. This is almost equal to the heat of formation of the naphthalene–TCNE complex, which is 4.06 kcal/mole according to Briegleb, *et al.*[6]

Dipole Moment of the Complex. We have determined the dipole moment of the pyrene–TCNE complex from the observations of the dielectric constant on the carbon tetrachloride solutions containing pyrene and TCNE, according to the procedure of analysis developed by Briegleb, *et al.*[6] We obtained 2.0 ± 0.3 D. for the dipole moment of the pyrene–TCNE complex. This is considerably large for a π complex. The dipole moment of the naphthalene–TCNE complex has been reported as 1.28 D.[6] Thus the dipole moment of the pyrene–TCNE complex is appreciably larger than that of the naphthalene–TCNE complex.

Intensity Ratio of Multiple Charge-Transfer Bands. The relative orientation of donor and acceptor in a 1:1 complex formed in solution has been usually assumed as identical with that found in the crystal structure. However, the validity of this assumption is often questionable. The relative orientation could be quite different between the two states since the charge-transfer interaction between the donor and acceptor molecules adjacent to each other is not the only factor that determines the orientation of molecules in the crystal. As we have pointed out in a previous paper,[4] the intensity ratio of multiple charge transfer bands must be sensitively dependent on the relative orientation of donor and acceptor. Accordingly, the ratio observed in the absorption spectrum of a complex will give information on the relative orientation of donor and acceptor. The wavenumbers of charge-transfer bands and the intensity ratio are summarized in Table II.

In the case of the pyrene–TCNE complex, the intensities of the first and second charge-transfer bands are comparable to each other both in the solution spectrum and in the crystal spectrum. However, the intensity ratio is markedly different between the solution and crystal spectra in the case of the naphthalene–TCNE complex; the intensity of the second charge-transfer band is almost equal to that of the first charge-transfer band in the absorption spectrum of the solution, but the second charge-transfer band appears very weakly only as a shoulder in the absorption spectrum of the crystal. This fact clearly indicates that the relative orientation is considerably different in the two states in the case of the naphthalene–TCNE complex. Seemingly we should not presume also for the pyrene–TCNE complex that the relative orientation of donor and acceptor in the isolated 1:1 complex is identical with that in the crystal although the intensity ratio of charge-transfer bands is similar between these two states. We shall consider the geometrical configuration expected for the isolated 1:1 complex from the charge-transfer theory in the later part of the present paper.

Theoretical Consideration of Charge-Transfer Interaction

We shall assume here that the ground-state wave function of a 1:1 complex can be described with a linear combination of the wave function of the no-bond configuration and those associated with charge-transfer configurations, namely as follows

$$\Psi_N(\mathrm{D \cdot A}) = a_0{}^0\Phi_0(\mathrm{D \cdot A}) + \sum_{i,j} b_{ij}{}^0\Phi_{ij}(\mathrm{D^+ \cdot A^-}) + \sum_{k,l} c_{kl}{}^0\Phi_{kl}'(\mathrm{D^- \cdot A^+}) \quad (2)$$

where $\Phi_{ij}(\mathrm{D^+ \cdot A^-})$ is a wave function of a charge-transfer configuration associated with the electron transfer from the ith orbital of donor to the jth orbital of acceptor, and $\Phi_{kl}'(\mathrm{D^- \cdot A^+})$ is a wave function of a back charge-transfer configuration associated with the electron transfer from the lth orbital of acceptor to the kth orbital of donor.

The wave function of the no-bond or ground configuration can be given in the form of a Slater determinant

$$\Phi_0(\mathrm{D}\cdot\mathrm{A}) = |\phi_1\bar{\phi}_1\ldots\phi_i\bar{\phi}_i\ldots\phi_M\bar{\phi}_M\theta_1\bar{\theta}_1\ldots\theta_N\bar{\theta}_N| \quad (3)$$

where ϕ_i is the *i*th molecular orbital of donor and θ_j is the *j*th molecular orbital of acceptor, and *M* and *N* denote the highest occupied orbital of donor and that of acceptor, respectively.[11] Similarly $\Phi_{ij}(\mathrm{D}^+\cdot\mathrm{A}^-)$ and $\Phi_{kl}'(\mathrm{D}^-\cdot\mathrm{A}^+)$ can be expressed as shown in eq 4 and 5. The off-diagonal matrix element for the interaction

$$\Phi_{ij}(\mathrm{D}^+\cdot\mathrm{A}^-) = \frac{1}{\sqrt{2}}\{|\phi_1\bar{\phi}_1\ldots\phi_i\bar{\theta}_j\ldots\phi_M\bar{\phi}_M\theta_1\bar{\theta}_1\ldots \theta_N\bar{\theta}_N| + |\phi_1\phi_1\ldots\theta_j\bar{\phi}_i\ldots\phi_M\bar{\phi}_M\theta_1\bar{\theta}_1\ldots\theta_N\bar{\theta}_N|\} \quad (4)$$

$$\Phi_{kl}'(\mathrm{D}^-\cdot\mathrm{A}^+) = \frac{1}{\sqrt{2}}\{|\phi_1\bar{\phi}_1\ldots\phi_M\bar{\phi}_M\theta_1\bar{\theta}_1\ldots \phi_k\bar{\theta}_l\ldots\theta_N\bar{\theta}_N| + |\phi_1\bar{\phi}_1\ldots\phi_M\bar{\phi}_M\theta_1\bar{\theta}_1\ldots \theta_l\bar{\phi}_k\ldots\theta_N\bar{\theta}_N|\} \quad (5)$$

between the ground and charge-transfer configurations can be approximately given by

$$\langle\Phi_0|H|\Phi_{ij}\rangle = \sqrt{2}\langle\phi_i|H^{\mathrm{core}}|\theta_j\rangle \quad (6)$$

We shall now use the following approximation and introduce a constant, *K*, as an empirical parameter

$$\langle\phi_i|H^{\mathrm{core}}|\theta_j\rangle = -KS_{ij} \quad (7)$$

where $S_{ij} = \int\phi_i(1)\theta_j(1)\,\mathrm{d}\tau_1$. According to the second-order perturbation theory, the ground-state energy can be given by

$$W_N = -\left\{\sum_{i,j}(\langle\Phi_0|H|\Phi_{ij}\rangle)^2/W_{ij} + \sum_{k,l}(\langle\Phi_0|H|\Phi_{kl}'\rangle)^2/W_{kl}'\right\}$$

This can be written as follows by using the approximation described in eq 7.

$$W_N = -2K^2\left\{\sum_{i\leq M}\sum_{j>N}(S_{ij}^2/W_{ij}) + \sum_{k>M}\sum_{l\leq N}(S_{kl}^2/W_{kl}')\right\} \quad (8)$$

In eq 8, W_{ij} is the energy of the charge-transfer configuration $\Phi_{ij}(\mathrm{D}^+\cdot\mathrm{A}^-)$ and W_{kl}' is that of $\Phi_{kl}'(\mathrm{D}^-\cdot\mathrm{A}^+)$; the energy of the ground configuration is taken as the standard. Similarly the following relation can be derived for the dipole moment of the complex in the ground state

$$\mu_N \simeq |e|R\left\{2K^2\left[\sum_{i\leq M}\sum_{j>N}(S_{ij}/W_{ij})^2 - \sum_{k>M}\sum_{l\leq N}(S_{kl}/W_{kl}')^2\right] + K\left[\sum_{i\leq M}\sum_{j>N}(S_{ij}^2/W_{ij}) - \sum_{k>M}\sum_{l\leq N}(S_{kl}^2/W_{kl}')\right]\right\} \quad (9)$$

where *R* is the distance between the molecular centers of donor and acceptor. We have assumed here that both donor and acceptor molecules possess the center of symmetry as they are in the naphthalene–TCNE and pyrene–TCNE complexes. Accordingly the dipole moment of the ground configuration is zero; otherwise the expression will be much complicated. The transition dipole of a charge-transfer band associated with the electron transfer from the *i*th orbital of donor to the *j*th orbital of acceptor will be

$$\mu_{(0,ij)} \simeq \sqrt{2}|e|RK(S_{ij}/W_{ij}) \quad (10)$$

provided that $2K/W_{ij} \gg 1$, and that the mixing of the locally excited configurations can be neglected, which might have a considerable effect on the transition dipole of a charge-transfer band in some cases.

On the bases of the theoretical considerations described above, we have carried out numerical analysis of the charge-transfer interaction in the naphthalene–TCNE and pyrene–TCNE complexes.

Energy of Charge-Transfer Configuration. The energy of each charge-transfer configuration can be estimated by the following relations

$$W_{ij} = I(i) - A'(j) + C(i,j) + P \quad (11)$$

$$W_{kl}' = I'(l) - A(k) + C(k,l) + P \quad (11')$$

where *I*(*i*) is the energy required to take out an electron from the *i*th molecular orbital of donor, *A*(*k*) is the energy gained as an electron is brought to the *k*th molecular orbital of donor, and *I'*(*l*) and *A'*(*j*) are the corresponding values of acceptor. *C*(*i,j*) is the Coulomb energy term, and *P* is the polarization energy term.

We have calculated the self-consistent field molecular orbitals of naphthalene, pyrene, and TCNE.[12] The calculated orbital energies are shown in Figure 3. The values of *I*(*i*) and *A*(*i*) were estimated by assuming the relations

$$I(i) - I^0 = E(M) - E(i) \quad (12)$$

$$A(i) - A^0 = E(M+1) - E(i) \quad (13)$$

where I^0 and A^0 are respectively the observed ionization energy and the electron affinity of the donor, *E*(*i*) is the orbital energy, and *M* and *M* + 1 denote the highest

Table III. The Ionization Energy (*I*) and Electron Affinity (*A*) Assumed in the Calculation.

	Ionization energy, ev	Electron affinity, ev
Naphthalene	8.12[a]	(0.02)[c]
Pyrene	7.55[b]	0.39[d]
TCNE	(10.13)[e]	1.80[b]

[a] K. Watanabe, *J. Chem. Phys.*, **22**, 1565 (1954). [b] Estimated from CT band: G. Briegleb, *Angew. Chem.*, **76**, 326 (1964). [c] Estimated from the ionization energy by assuming the molecular electronegativity as 4.07 ev: R. S. Becker and W. E. Wentworth, *J. Am. Chem. Soc.*, **85**, 2210 (1963). [d] W. E. Wentworth and R. S. Becker, *ibid.*, **84**, 4263 (1962). After we carried out the present calculation, Becker and Chen (*J. Chem. Phys.*, **45**, 2403 (1966)) gave new values of electron affinity: naphthalene, 0.15 ev; pyrene, 0.59 ev. The results of the present calculation, however, will be little affected by the use of these new values. [e] Estimated from the difference in the energies of SCF MO's between TCNE and ethylene. The ionization energy of the latter was taken as 10.52 ev.

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(11) Strictly speaking, the wave function $\Phi_0(\mathrm{D}\cdot\mathrm{A})$ must be the wave function of the perturbed state, but without electron transfer between molecules, because we are not explicitly considering the mixing of the locally excited configuration.

(12) The SCF MO's were calculated by using the program written by Kunii in our laboratory, with the variable-β modification of the Pariser–Parr–Pople method proposed by Nishimoto and Forster.[13]

(13) K. Nishimoto and L. S. Forster, *Theoret. Chim. Acta*, **4**, 155 (1966).

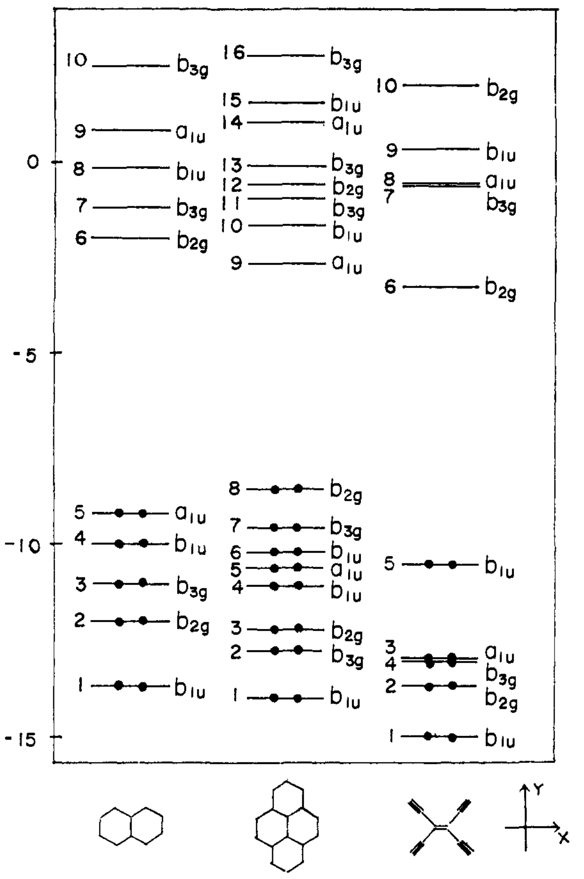

Figure 3. Orbital energies of SCF MO's.

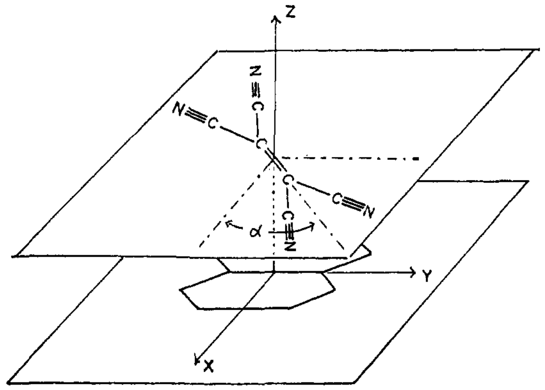

Figure 4.

occupied molecular orbital and the lowest vacant molecular orbital, respectively. The same procedures were used for the acceptor. The values of the ionization energy and the electron affinity assumed in the present study are summarized in Table III.

The Coulomb energy term, $C(i,j)$, was calculated on each geometrical configuration by the following equation with the point-charge approximation.

$$C(i,j) = -\int \phi_i^2(1)\,(e^2/r_{12})\theta_j^2(2)\,d\tau_1 d\tau_2 \qquad (14)$$

The polarization energy term, P, is rather difficult to estimate theoretically, as it depends on the properties of the solvent, as well as on the geometrical configuration of the complex. In the present paper, however, we assumed that it is a constant for each complex: 0.90 ev for the naphthalene–TCNE complex and 1.10 ev for the pyrene–TCNE complex.[14]

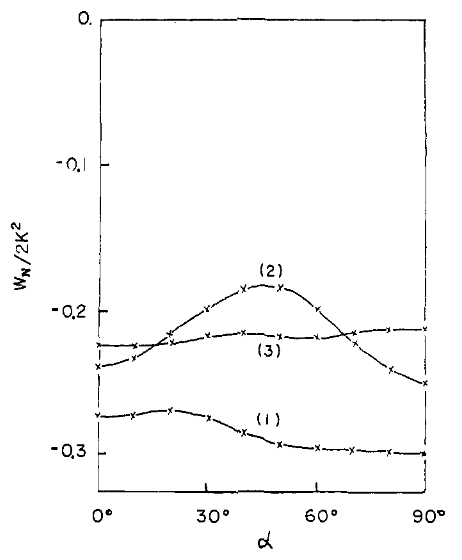

Figure 5. Variation of $W_N/2K^2$ with α, calculated for the naphthalene–TCNE complex: (1) $X = 1.235$ A, $Y = 0$; (2) $X = 0$, $Y = 0$; (3) $X = 1.235$ A, $Y = 0$.

Model of the Geometrical Configuration of the Complex. To calculate the ground-state energy for various assumed geometrical configurations, we looked for the structural model of the isolated 1:1 complex. In this procedure, we assumed that the donor and acceptor molecules are in the closest contact, making their molecular planes parallel to each other; the separation between the molecular planes is taken as 3.32 A as is in the crystal structure of the pyrene–TCNE complex. We took an orthogonal coordinate system, (X, Y, Z), so that the coordinate axes coincide with the symmetry axes of the donor molecule, and defined the angle, α, as shown in Figure 4. Then the geometrical configuration of the complex can be specified by giving the coordinates of the center of TCNE molecule (X, Y, Z) and the angle α. We calculated the relative value of the ground-state energy, defined as ($W_N/2K^2$) according to eq 8, as a function of X, Y, and α. All possible charge-transfer configurations were taken into account in these calculations, 50 configurations for the naphthalene–TCNE complex and 80 configurations for the pyrene–TCNE complex. In the present calculations, we used the self-consistent field molecular orbitals of the donor and acceptor, and the Slater orbitals with the orbital exponents 1.64 and 2.13 au for the 2p atomic orbitals of carbon and nitrogen, respectively.

It has been always assumed that the binding energy associated with the charge-transfer interaction is most sensitively dependent on the relative orientation of donor to acceptor. The geometrical configuration of a complex has been discussed often from the symmetry property of the highest occupied orbital of the donor and that of the lowest vacant orbital of the acceptor. This kind of discussion has its basis in the simplifying assumption that the interaction of the lowest energy

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(14) These values are taken so that the theoretical excitation energy of the first charge-transfer band agrees with the observed value; consequently, they are dependent on the assumed value of the electron affinity of TCNE.

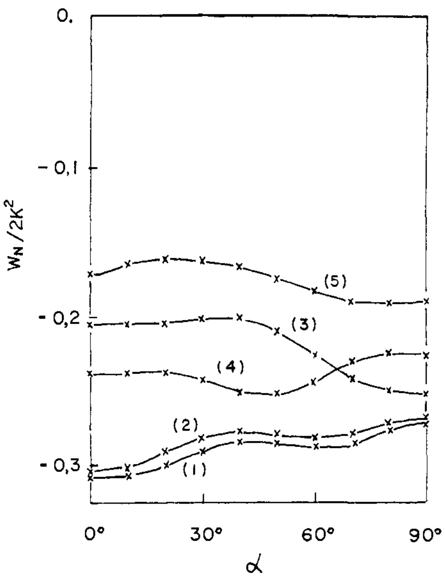

Figure 6. Variation of $W_N/2K^2$ with α, calculated for the pyrene–TCNE complex: (1) $X = 0$, $Y = 2.13$ A; (2) $X = 1.204$ A, $Y = 0$; (3) $X = 0$, $Y = 0$; (4) $X = 0$, $Y = 1.42$ A; (5) $X = 1.204$ A, $Y = 1.42$ A.

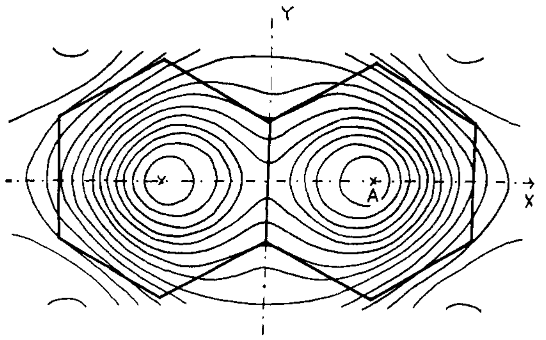

Figure 7. Variation of $\overline{W}_N/2K^2$ with (X, Y), calculated for the naphthalene–TCNE complex: contours at intervals of -0.142; point A, $X = 1.235$ A, $Y = 0$.

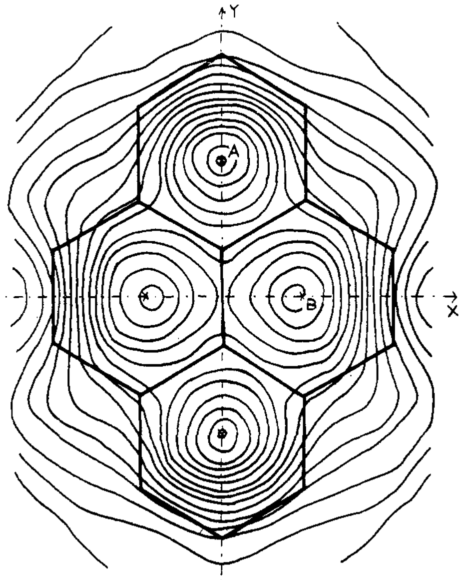

Figure 8. Variation of $\overline{W}_N/2K^2$ with (X, Y), calculated for the pyrene–TCNE complex: contours at intervals of -0.142; point A, $X = 0$, $Y = 2.13$ A; point B, $X = 1.20$ A, $Y = 0$.

charge-transfer configuration only plays an important role in the stabilization of the complex. This assumption is by no means acceptable in the present case. As we have pointed out in a previous paper,[4] the contribution of the lowest energy charge-transfer configuration is only less than 20% of the total binding energy associated with the charge-transfer interaction in the case of the pyrene–TCNE complex. According to the results of the present calculation where all possible charge-transfer configurations are considered, the ground-state energy shows a relatively small variation with α for a given (X, Y, Z) as shown in Figures 5 and 6, the difference between the maximum and minimum being only about 10–20% of the average value of the ground-state energy. This means that the energy barrier hindering the rotation of the TCNE molecule relative to naphthalene or pyrene molecule is less than 1 kcal/mole. If this is the case, there is no reason to suppose a preferred value of α for the orientation of TCNE molecule as far as the charge-transfer interaction only is concerned. As compared with the variation with α, the ground-state energy shows a larger variation with the position of the center of TCNE molecule. Therefore we shall assume here for simplicity that the molecules can be rotated freely relative to each other within their molecular planes and examine the variation of the mean ground-state energy, $\overline{W}_N(X,Y)$, the average of W_N over α for a given coordinate of the molecular center. On the naphthalene–TCNE complex, the calculation was made for 66 points in the coordinate range, $0 \leq X \leq 3.0$ A, $0 \leq Y \leq 1.5$ A. At each point, $\overline{W}_N$ was obtained as the average value of W_N calculated for 18 different values of α, with 10° intervals from 0 to 180°. The result is shown in Figure 7 in the form of an energy contour. There are two potential minima each at the position directly over the center of benzene rings of naphthalene. Although the potential minimum is not deep enough to fix firmly the position of the center of TCNE molecule, we can consider that the 1:1 complex formed in solution will predominantly take the geometrical configuration corresponding to the potential minimum. Therefore we shall presume this structure as the structural model for the naphthalene–TCNE complex. A similar calculation was carried out on the pyrene–TCNE complex. The result is shown in Figure 8. Four potential minima appear at the positions directly over the center of each benzene ring of pyrene. Accordingly we can propose two models in this case: "model A" where $X = 0$ and $Y = \pm 2.13$ A, and "model B" where $X = \pm 1.20$ A and $Y = 0$. These two models are almost equivalent with regard to stability. The relative position of molecular centers found in the crystal structure[15] of the pyrene–TCNE complex corresponds to the model A.

Similarly, in the crystal of the naphthalene–TCNE complex, the position of the center of TCNE molecule relative to the adjacent naphthalene molecule nearly agrees with the potential minimum predicted by the present calculation. In this connection, it is also interesting to see that, in the crystal structure of the perylene–TCNE complex,[16] the center of TCNE mole-

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(15) H. Kuroda, I. Ikemoto, and H. Akamatu, *Bull. Chem. Soc. Japan*, **39**, 547 (1966).

(16) I. Ikemoto and H. Kuroda, *ibid.*, **40**, 2009 (1967).

Table IV. Value of K Estimated from the Observed Dipole Moment

	K, ev
Naphthalene–TCNE	21.8
Pyrene–TCNE	
Model A	24.5
Model B	26.0

Table V. Comparison of the Theoretical Predictions with the Observation

	Naphthalene–TCNE		Pyrene–TCNE		
	Calcd	Obsd	Model A	Model B	Obsd
Transition dipole, A					
1st CT band	0.46	0.36	0.54	0.24	0.34
2nd CT band	0.52	0.33	0.46	0.39	0.25
Oscillator strength ratio[b] (f_1/f_2)	0.62	0.86	0.95	0.21	1.3
Dipole moment, D.	1.29	1.28[a]	1.61	1.32	2.0
CT binding energy, kcal/mole	6.32	...	6.42	6.28	...
Heat of formation (in CCl_4), kcal/mole	...	−4.06[a]	...	...	−4.1

[a] See ref 6. [b] f_1 and f_2 are respectively the oscillator strengths of the first and second CT bands.

cule is located at the position approximately over the center of one of the peripheral benzene rings of perylene, which is also theoretically expected to correspond to the potential minimum associated with the charge-transfer interaction. These facts suggest that the charge-transfer interaction between donor and acceptor molecules plays an important role in the determination of the positions of molecular centers relative to each other, not only in the isolated 1:1 complex but also in the crystal state.

Comparison of Theoretical Predictions with Observation. In order to make theoretical predictions on the numerical values of the binding energy, dipole moment, and transition dipole, we need to introduce an assumption on the numerical value of K. The proportionality between the resonance and overlap integrals is often assumed in the molecular orbital calculation of π-electron systems, where β_{C-C}/S_{C-C} is usually taken as about 10 ev. If this approximation is used also for the intermolecular integrals, the value of K will be 10 ev. It has been pointed out, however, that the intermolecular overlap integrals are markedly underestimated when they are calculated by using the Slater atomic orbitals.[5,17] In effect the overlap integrals calculated in the present study will be about three times larger if the Hartree–Fock atomic orbitals are used. In view of this fact, it seems necessary to employ a value of K considerably larger than 10 ev in order to obtain a reasonable value for the intermolecular resonance integral. We estimated the value of K that makes the theoretical values of dipole moment, calculated on the structural models described in the preceding paragraph, agree with the observed values. The results are given in Table IV. Interestingly the values thus obtained are nearly the same for the pyrene–TCNE complex and for the naphthalene–TCNE complex, and their magnitude, 20–26 ev, also looks quite reasonable from the theoretical point of view. In the present study we shall tentatively take 22 ev as the empirical value of K and calculate the ground-state energy, transition dipole, and others. The results of these calculations are summarized in Table V together with the observed values.

The theoretical values of transition dipole are a little larger than the observed values, but the deviation will be smaller if we take into account the situation that the complexes are not always taking the most stable geometrical configuration. Thus the agreement with the observation can be regarded as being satisfactory. It is also interesting to see that the observed ratio of the intensity of the first charge-transfer band to that of the second one can be explained by the results of the present theoretical calculations. In this respect, model A of the pyrene–TCNE is more plausible than model B. The calculated ground-state energy cannot be directly compared with the observed heat of formation of the complex since the latter involves the energy terms associated with the van der Waals force and the repulsive force as well as the terms associated with the interaction with the solvent. But the calculated value of about 6 kcal/mole seems to be most reasonable. In conclusion, the theoretical predictions obtained in the present study are well consistent with the observation.

Recently Dewar and Thompson[18] have made a systematical comparison of the equilibrium constant on a series of TCNE complexes of polycyclic aromatic hydrocarbons and concluded that the charge-transfer interaction is not a major origin of the intermolecular binding in these complexes. Their conclusion is based on the fact that the plots of log (K^c/K_0^c) *vs.* $(\lambda - \lambda_0)$ are not linear, where K^c and λ are respectively the equilibrium constant and the wavelength of the first change-transfer band of a complex, and K_0^c and λ_0 are those of the reference complex. It should be noticed, however, that the validity of this criterion can be justified only in the case where the contribution of the lowest energy charge-transfer configuration only is predominant and the mixing of higher energy charge-transfer configurations is negligible. As we have shown in the present study, the contributions of higher energy charge-transfer configurations to the stabilization of the ground state are by no means negligible compared with that of the lowest energy charge-transfer configuration in the TCNE complexes of polycyclic aromatics. Therefore the nonlinearity of the plots of log (K^c/K_0^c) *vs.* $(\lambda - \lambda_0)$ could not be regarded as the evidence proving that the charge-transfer interaction is not playing an important role in the binding between donor and acceptor.[19] In the present study, we have not treated the interaction of

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(17) J. L. Katz, S. A. Rice, S. Choi, and J. Jortner, *J. Chem. Phys.*, **39**, 1683 (1963).

(18) M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron, Suppl.*, 97 (1966).

(19) Interestingly, the plots have been found to be linear in the case of TCNE complexes of methylbenzenes where the lowest energy charge-transfer configuration is expected to play a predominant role; see R. E. Merrifield and D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

the ground configuration with locally excited configurations, which have bearing on the origin of the dispersion force. Naturally it is probable that the binding energy due to the dispersion force can be larger than the binding energy associated with the charge-transfer interaction. But we must consider that the contribution of the charge-transfer interaction is of significant importance in the intermolecular binding, at least in the case of TCNE complexes of naphthalene and pyrene, if the binding energy due to the charge-transfer interaction is about 6 kcal/mole as theoretically estimated in the present study.

Studies on Complexes. XII. Charge-Transfer Interactions of Aromatic Hydrocarbon and Azahydrocarbon Acceptors[1]

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Abstract: The strong donor properties of tetrakis(dimethylamino)ethylene (TMAE) are determined by its interactions with π acceptors. Colors of *n*-hexane solutions of this donor with pyrene, anthracene, and perylene are ascribed to intermolecular charge-transfer transitions, where the hydrocarbons function as electron acceptors. Azahydrocarbons similarly produce colors and are stronger acceptors. All association constants for complex formation with the tetraaminoethylene are close to zero, and this is ascribed to the bulk of the TMAE molecule. From these studies and from the published literature, a "perpendicular with a wobble" structure is proposed for TMAE, in which thermally accessible vibrations of the $(CH_3)_2N$ groups occur about a position perpendicular to the $N_2C{=}CN_2$ plane. An earlier proposal that a charge-transfer interaction occurs between the methylbenzenes and anthracene is reinterpreted.

A well-established property of the aromatic hydrocarbons is their Lewis base or electron donor character. As a criterion of this donor strength, their ionization potentials,[2,3] particularly for the highly condensed members, appear low within the series of the numerous measurements[3] for neutral organic molecules. Properties associated with low ionization potentials (I_d), they also exhibit; thus they may be oxidized electrochemically with moderate ease,[4] and they function as strong donors in forming molecular complexes. On oxidation they yield radical cations[5] and they are chemically reactive toward acceptor molecules.

A theoretical rationalization of this donor character comes from the energies of the highest filled π-molecular orbitals, which correspond at least approximately to ionization potentials. On the other hand, from the energies of their lowest unfilled orbitals, which correspond to electron affinities (E_a), weak electron-accepting properties have been predicted. Thus increases in electron affinities with decreasing ionization potential have been proposed[6] so that the sum $I_d + E_a$ is a constant. Moreover, it has been suggested[7] that I_d and E_a expressed as dependencies of the energy of the lowest transitions should be symmetrical about the work function for graphite.

Evidence for accepting properties comes from polarographic reduction potentials[8] and the detection of radical anions.[5,9] Gas-phase, electron-scavenging experiments have been reported in direct, pioneering measurements of electron affinities.[10]

Neutral acceptor–donor interaction as spectral evidence of hydrocarbon acceptor properties has not been presented,[11] and the conclusions of the one study[12] in this area on complexes of condensed aromatics such as anthracene with the methylbenzenes is criticized below.

The energy $h\nu_{CT}$ of the maximum of the charge-transfer transition has been related[13] to a donor ionization

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(1) This work formed part of a presentation to the American Chemical Society, Second Western Regional Meeting, San Francisco, Calif., Oct 1966.

(2) M. E. Wacks, *J. Chem. Phys.*, **41**, 1661 (1964); M. E. Akopyan and F. I. Vilesov, *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **161**, 1110 (1965); (English Transl.) 161, 307 (1965); G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959); H. Kuroda, *Nature*, **201**, 1214 (1964).

(3) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962).

(4) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963); J. Phelps, K. S. V. Santhanam, and A. J. Bard, *ibid.*, **89**, 1752 (1967).

(5) A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959); W. I. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *ibid.*, 3049 (1959); B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

(6) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

(7) F. A. Matsen in "Proceedings of Conference on Carbon," Pergamon Press, New York, N. Y., 1957, pp 21–26, and references therein; R. M. Hedges and F. A. Matsen, *J. Chem. Phys.*, **28**, 950 (1958).

(8) F. A. Matsen, *ibid.*, **24**, 602 (1956); A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962).

(9) G. J. Hoijtink, J. Townsend, and S. I. Weissman, *J. Chem. Phys.*, **34**, 507 (1961); K. Möbius, *Z. Naturforsch.*, **20A**, 1102 (1965); J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

(10) W. E. Wentworth and R. S. Becker, *J. Am. Chem. Soc.*, **84**, 4263 (1962); R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).

(11) Absorptions of a hydrocarbon radical anion with anthracene, pyrene, and chrysene have been tentatively identified as charge-transfer transitions: S. N. Khanna, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 747 (1962). Excess heats of mixing measurements on aromatic hydrocarbon–aliphatic tertiary amine systems have been interpreted as showing specific interaction: H. Kehiaian, Paper C12 presented at the Symposium on the Physical Chemistry of Weak Complexes, Chemical Society Meeting, London, 1967.

(12) W. E. Wentworth and E. Chen, *J. Phys. Chem.*, **67**, 2201 (1963).

(13) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).