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PRESSURE EFFECT ON THE EDA COMPLEXES IN SOLUTION

BY TOSHIHIRO NAKAYAMA

The intermolecular charge-transfer spectra of the complexes between tetracyanoethylene (TCNE) and methyl substituted benzenes in various solvents have been studied under high pressure at 25°C. Both the equilibrium constant K and the molar absorption coefficient ε increased with increasing pressure. The volume change of the complex formation in carbon tetrachloride was in the range of $-3.4\sim-14.1$ cm³/mol for the various donors, benzene, toluene, mesitylene and hexamethylbenzene (HMB), and these negative values could be mainly interpreted by the contraction of the distance between the donor and the acceptor (TCNE) on the complex formation. The enhancement of ε by pressure $\varepsilon_{max(p)}/\varepsilon_{max(1)}$ was *ca* 1.2 at 1500 kg/cm² for most EDA complexes, and it was discussed by taking into account both the solute-solvent interaction and the decrease of the donor-acceptor distance by pressure. Nearly linear red shift of absorption maximum λ_{max} with pressure was observed for benzene, toluene and mesitylene up to 1500 kg/cm². However, λ_{max} of HMB complex shifted to lower frequency with pressure at first and then turned to higher frequency. The turning pressure was solvent dependent: around 800 kg/cm² in carbon tetrachloride and 4500 kg/cm² in *n*-pentane. The spectral shift was considered from the viewpoint of not only the effect of solvent property but also the change of resonance interaction between the donor and acceptor caused by compression.

Introduction

The charge-transfer (CT) or electron-donor-acceptor complexes (EDA complexes) are characterized by an intense absorption spectrum in the visible or ultraviolet region. Since Mulliken[1)] described the CT forces in terms of the resonance between a no-bond and a dative structures, his theory has been widely applied to many interesting works on molecular complexes[2~4)]. According to this theory, the stability of the complex and the energy of the intermolecular CT absorption sensitively depend on the extent of the overlap between the orbitals of donor and acceptor molecules.

It is well known from the experimental results that, on going from vapor to liquid, the equilibrium constant K and the spectral properties (absorption maximum λ_{max} and absorption coefficient ε_{max}) of a weak complex show quite remarkable changes[5,6)]. That is, the CT bands of such complexes as

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3) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, London (1969)
4) R. S. Mulliken and W. B. Person, "Molecular Complexes", John Wiley & Sons, New York (1969)
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6) M. Kroll, *J. Amer. Chem. Soc.*, **90**, 1097 (1968)

tetracyanoethylene (TCNE)-aromatic and iodine-aromatic hydrocarbons show red shift of 1000 to 4000 cm^{-1} and the enhancement of ε_{max} of 2 to 8 folds upon the phase change from vapor to liquid.

Similarly, the application of high pressure should induce change in some properties of an EDA complex. The effect of high pressure on the electronic absorption spectra of EDA complexes has been noted both in solid[7~11] and in liquid[12~15]. Gott and Maisch[12] investigated the spectral properties of aromatic hydrocarbons-TCNE complexes in dichloromethane at high pressures, but contrary to Mulliken's prediction[1] they observed the decrease in K with increasing pressure for the benzene-TCNE complex. For many π-π complexes, both K and ε were found to increase with pressure[13~15].

In the previous papers[14,15], it was found that, in carbon tetrachloride, the absorption spectrum of the EDA complex between hexamethylbenzene (HMB) and TCNE first showed the slight red shift with increasing pressure and turned to the blue shift at higher pressure, while the complexes formed between benzene, toluene or mesitylene and TCNE showed only the red shift up to 1600 kg/cm^2*. Moreover, the turning pressure of red-to-blue shift found in carbon tetrachloride is lower than those in dichloromethane[12,13] and polymer matrix[9]. The red shift with increasing pressure might be partly explained by the change of solvent property, such as refractive index, caused by pressure. Bayliss[16] gave a theoretical base of the red shift with the increase of refractive index at atmospheric pressure. Robertson *et al.*[17] derived the theoretical relation between the frequency shift and the density of solvent, and applied it successfully to $\pi\pi^*$ absorption in some aromatic hydrocarbons under high pressure. Shuler[18] derived the relation from the simple free electron model that the shortening of the intermolecular distance resulted in the red shift, and predicted that the pressure would shift the CT absorption maximum to lower frequency. But for the blue shift, only the ambiguous explanations were given. Ewald[13] suggested the following hypothesis: the ground state has a shallow and broad potential curve, while the excited state has a much deeper potential curve. The blue shift could be explained if the difference between the equilibrium separations of the ground and excited states is so small that under compression excitation raises the complex to the repulsive region of the excited state potential curve. However, the present author has previously suggested the importance of the change of resonance energy with pressure between the no-bond and the dative structures.

The present paper deals with the study of the HMB-TCNE complex in several solvents (n-pentane, n-hexane, n-heptane, chloroform and 1,2-dichloroethane) to elucidate the pressure-induced

* 1 kg/cm^2 = 0.9807 × 10^5 Pa

7) W. H. Bently and H. G. Drickamer, *J. Chem. Phys.*, **42**, 1573 (1965)
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14) T. Nakayama and J. Osugi, *This Journal*, **45**, 79 (1975)
15) T. Nakayama, M. Sasaki and J. Osugi, *ibid.*, **46**, 57 (1976)
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17) N. W. Robertson, O. E. Weigang and F. A. Matson, *J. Molecular Spectro.*, **1**, 1 (1957)
18) K. E. Shuler, *J. Chem. Phys.*, **20**, 1865 (1952)

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changes of K, ε_{max} and λ_{max} for this complex by pressure.

Experimentals

All the experimental procedures and apparatus used up to 1600 kg/cm^2 were the same as those in the previous paper[14]. At higher pressure than 1600 kg/cm^2, a Drickamer type high pressure optical cell[19] was used, which was adapted to a Union Giken RA 405 spectrophotometer. Pressure was measured with a calibrated manganin coil, which was inserted in the high pressuae vessel.

TCNE and HMB were purified by the same method described previously[15]. n-Hexane was washed successively with concentrated sulfuric acid, dilute sodium hydroxide and water. Adding potassium hydroxide, it was distilled before use. 1, 2-Dichloroethane was washed with dilute sodium hydroxide and water, dried over calcium chloride and distilled before use. n-Pentane, n-heptane and chloroform (Spectrograde reagent, Nakarai Chemicals Ltd.) were used without further purification.

The solutions containing large excess of HMB (10-60 mM) over TCNE (0.1 mM) were prepared so as to give the suitable absorbances at various pressures. The concentrations of the solutes in n-hexane, n-heptane, chloroform and 1, 2-dichloroethane were corrected for compression at high pressure by the Tait equation[20]. In n-pentane, the relative volume at high pressure with reference to 1 atm was estimated by the graphical method, using the values at 30°C[21].

Results

Spectra: Fig. 1 shows the typical absorption spectra of the HMB-TCNE complex in chloroform. In any solvents used here, the absorbance was largely enhanced with increasing pressure. And also, the pressure scarcely caused either the broadening or the sharpening of the absorption bands, but it only caused slight shifts of the spectra. The former result coincided with the fact that the half-width of the absorption band was nearly constant at various pressures. Such tendency of spectra is common to other TCNE-methylsubstituted benzene systems in carbon tetrachloride[14,15]. As shown in Fig. 2, the relative increases of the absorbance at the maximum exceeded those due to the compression. The absorption maxima of HMB-TCNE at 1 atm are 528 in n-pentane, 529 in n-hexane, 530 in n-heptane, 535 in 1, 2-dichloroethane and 540 nm in chloroform. The frequency shift of the absorption maximum at high pressure is shown in Figs. 3 and 4, together with the previous results. Except for the HMB-TCNE complex, other complexes only show the red shift in carbon tetrachloride. The HMB-TCNE complex first shows the red shift with increasing pressure and turns to the blue shift at higher pressure in several solvents.

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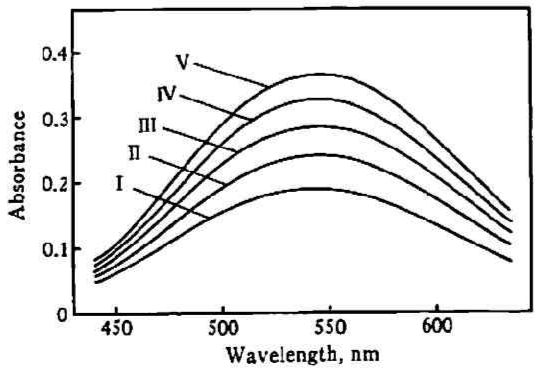

Fig. 1 Absorption spectra of the HMB-TCNE complex in chloroform at various pressures at 25°C
I: 1 atm, II: 800 kg/cm^2, III: 1600 kg/cm^2, IV: 2400 kg/cm^2, V: 3200 kg/cm^2

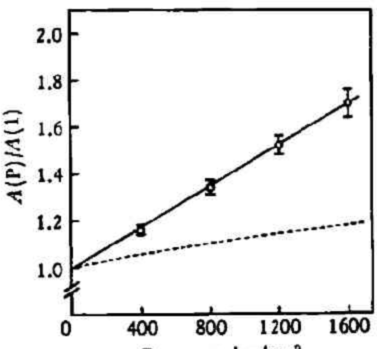

Fig. 2 Increase of the absorbance at absorption maximum as a function of pressure in 1,2-dichloroethane. The broken line is the square of the relative density of solvent.

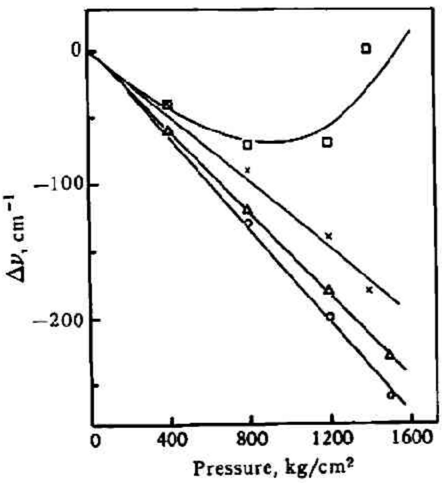

Fig. 3 Frequency shift of some TCNE complexes in carbon tetrachloride as a function of pressure
○: benzene, △: toluene, ×: mesitylene, □: HMB

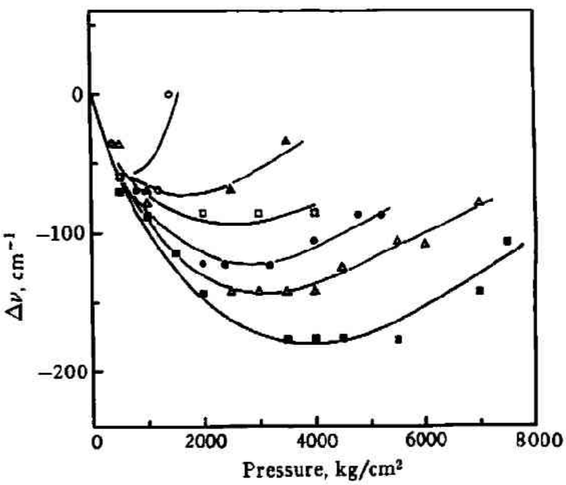

Fig. 4 Frequency shift of the HMB-TCNE complex in various solvents as a function of pressure
○: carbon tetrachloride, ▲: 1,2-dichloroethane, □: chloroform, ●: *n*-heptane, △: *n*-hexane, ■: *n*-pentane

Equilibrium measurement: Foster and Kulevsky[22] suggested that from the result of the optical measurement, a 2:1 complex as well as a 1:1 complex between HMB and TCNE existed in carbon tetrachloride. However, it was concluded that the existence of the 2:1 complex was negligible compared with the 1:1 complex in this experimental concentration range. Since the component molecules have no absorption in the visible region and Beer's law is held for this complex, Scott's equation (1)[23]

22) R. Foster and K. Kulevsky, *J. Chem. Soc., Faraday I*, 1427 (1973)
23) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956)

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can be applied for a series of solutions in which HMB exists in large excess.

$$\frac{[A]_0[D]_0 l}{A}=\frac{1}{\varepsilon}[D]_0+\frac{1}{K\varepsilon}. \quad (1)$$

In Eq. (1), $[A]_0$ and $[D]_0$ are the initial concentrations of TCNE and HMB, respectively, and A the absorbance with the optical pathlength of l at the absorption maximum at each pressure. Scott's plots in 1, 2-dichloroethane at various pressures are shown in Fig. 5, and the values of K and ε_{max} are estimated from the slopes and the intercepts. The same procedure was carried out for n-hexane and chloroform solutions. The values of K and ε_{max} at high pressure are given in Table 1. The equilibrium

Table 1 Equilibrium constants, spectroscopic parameters and volume changes for HMB-TCNE complex in various solvents at 25°C

Solvent	1, 2-dichloroethane			chloroform			n-hexane		
P/kg cm^{-2}	K / l mol^{-1}	$\varepsilon_{max}\times10^{-3}$ / cm^{-1} l mol^{-1}	f	K / l mol^{-1}	$\varepsilon_{max}\times10^{-3}$ / cm^{-1} l mol^{-1}	f	K / l mol^{-1}	$\varepsilon_{max}\times10^{-3}$ / cm^{-1} l mol^{-1}	f
1	21.7	3.49	0.08	24.7	4.32	0.10	77.1	5.87	0.11
400	24.7	3.65	0.08	27.3	4.77	0.11	78.6	6.03	0.12
800	28.8	3.76	0.09	29.4	4.92	0.11	77.8	6.34	0.12
1200	31.0	4.03	0.09	30.8	5.09	0.12	78.2	6.63	0.13
1600	34.2	4.21	0.10	33.6	5.13	0.12	78.8	6.82	0.14
2000	—	—	—	35.6	5.26	0.12	—	—	—
ΔV/cm^3 mol^{-1}		−11.4			−9.0			−4.3	

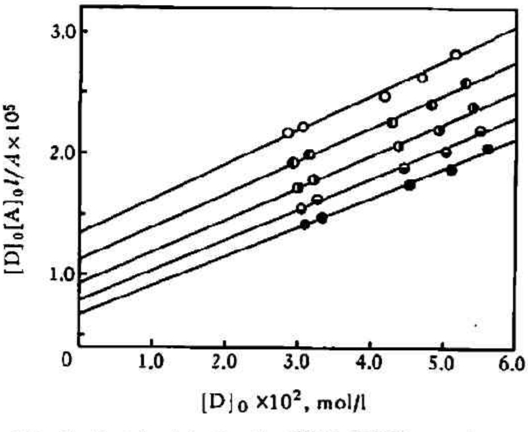

Fig. 5 Scott's plots for the HMB-TCNE complex in 1, 2-dichloroethane at various pressures at 25°C
○: 1 atm, ◐: 400 kg/cm², ◖: 800 kg/cm², ◒: 1200 kg/cm², ●: 1600 kg/cm²

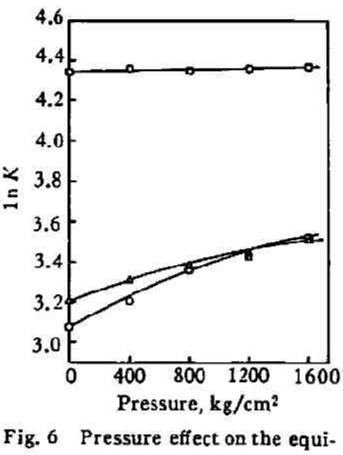

Fig. 6 Pressure effect on the equilibrium constants of the HMB-TCNE complex in various solvents
○: 1, 2-dichloroethane,
△: chloroform,
□: n-hexane

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constants in these solvents at 1 atm are smaller than that in carbon tetrachloride ($140 M^{-1}$)[15].

The oscillator strength f is also calculated from the relation.

$$f=4.319\times10^{-9}\times\Delta\nu_{1/2}\times\varepsilon_{max}, \tag{2}$$

where $\Delta\nu_{1/2}$ is the halfwidth of the absorption band. Pressur edependence of ln K is shown in Fig. 6. The volume change ΔV for the complex formation was calculated by using the following equation,

$$\left(\frac{\partial \ln K}{\partial P}\right)_T=-\frac{\Delta V}{RT}+\Delta\alpha\cdot\beta, \tag{3}$$

where $\Delta\alpha$ is the difference of the number of molecules accompanying the complex formation, and the compressibility of the solution β is approximated to that of solvent.

Discussion

Equilibrium constants and spectral properties of TCNE-methyl substituted benzene complexes at atmospheric pressure: The values of K, ε_{max} and λ_{max} of a series of complexes of TCNE as an acceptor are presented in Table 2. A linear relation is held between $h\nu_{CT}$ and the donor ionization potential I_p as seen in Fig. 7. The values of K, ε_{max} and λ_{max} are all increased from top to bottom as shown in Table 2.

Table 2 Equilibrium constants, spectroscopic parameters, and volume changes for the EDA complexes in carbon tetrachloride at 25°C : acceptor is TCNE

Donor	$K/l\,mol^{-1}$	$\varepsilon^{max}/10^3 cm^{-1} l\,mol^{-1}$	λ_{max}/nm	I_p^c/eV	$\Delta V/cm^3/mol$
Benzene[a]	0.964	2.21	385	9.24	− 3.4
Toluene[a]	1.92	2.22	411	8.82	− 4.9
Mesitylene[b]	12.8	2.40	464	8.40	− 7.1
HMB[b]	140	5.16	534	8.0	−14.1

a, ref. (11) ; b, ref. (12) ; c, ref. (26).

According to Mulliken's valence bond description of an EDA complex, the wave functions of the ground state (ψ_N) and excited state (ψ_E) are given by Eqs. (4) and (5), respectively,

$$\psi_N=a\psi_0(D, A)+b\psi_1(D^+A^-), \tag{4}$$

$$\psi_E=a^*\psi_1(D^+A^-)-b^*\psi_0(D, A), \tag{5}$$

where $\psi_0(D, A)$ is the wave function of the no-bond structure and $\psi_1(D^+A^-)$ is that of the dative structure. For a weak complex, the energies of the ground state W_N and the excited state W_E are derived from Eqs. (4) and (5),

$$W_N\simeq W_0-\frac{|W_{01}-W_0S_{01}|^2}{W_1-W_0}, \tag{6}$$

$$W_E\simeq W_1+\frac{|W_{01}-W_1S_{01}|^2}{W_1-W_0}, \tag{7}$$

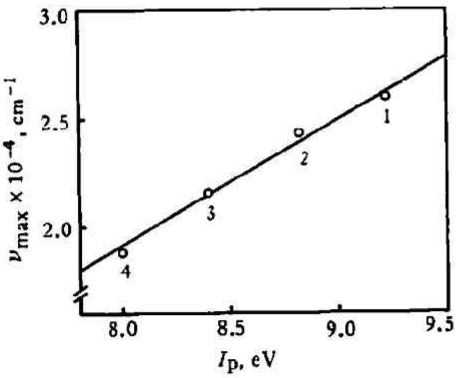

Fig. 7 A plot of the frequency of the CT band for some TCNE complexes in carbon tetrachloride *vs.* the ionization potentials of the donors
1: benzene, 2: toluene,
3: mesitylene, 4: HMB

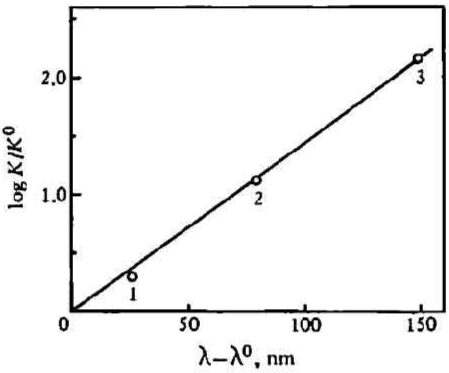

Fig. 8 A plot of $\log K/K^\circ$ *vs.* the wavelength for some TCNE complexes in carbon tetrachloride. K° is a value for benzene-TCNE complex
1: toluene, 2: mesitylene, 3: HMB

where W_0 and W_1 are the energies of the no-bond and the dative structures, respectively, W_{01} the resonance integral between $\psi_0(D, A)$ and $\psi_1(D^+A^-)$, and S_{01} the overlap integral. The charge-transfer band corresponds to the transition $\psi_E \leftarrow \psi_N$.

The difference between W_1 and W_0 is given by the following equation,

$$W_1 - W_0 \simeq I_p - E_A - \frac{e^2}{R_{DA}}, \qquad (8)$$

where E_A is the electron affinity of an acceptor, and the Coulombic term e^2/R_{DA} can be usually taken to be constant for a series of similar donors. Therefore, the following approximation can be obtained if the acceptor is fixed:

$$h\nu_{CT} \simeq I_p - C_1 + \frac{C_2}{I_p - C_1}, \qquad (9)$$

The constants C_1 and C_2 are characteristic of the acceptor. Conversely, for the complexes of one kind of donor the similar relation may be held between $h\nu_{CT}$ and the electron affinity of the acceptor[24].

In case of fixed acceptor, the linear relation of the form,

$$h\nu_{CT} = mI_p + n, \qquad (10)$$

provides a better empirical fit to each set of data than the curved relation given by Eq. (9). It was found for various sets of complexes[25] that the value of m was less than unity. For methyl substituted benzene-TCNE complexes in carbon tetrachloride, the empirical relation between $h\nu_{CT}$ and I_p was obtained from Fig. 7,

24) J. B. Nagy, O. B. Nagy and A. Bruylants, *J. Phys. Chem.*, **78**, 980 (1974)
25) See for instance. (a) H. M. McConnel, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953), (b) G. Reichenbach, S. Satini and G. G. Aloisi, *J. Chem. Soc., Faraday I*, 95, (1977)

$$h\nu_{CT}(eV)=0.711I_p-3.32. \quad (11)$$

Merrifield and Philips[26] reported that $h\nu_{CT}=0.487I_p-1.30$ for the same system in dichloromethane.

A linear relationship was experimentally found between I_p and the free energy change of complex formation ΔG[26]. And Arimoto and Osugi[27] pointed out that the plot of $\log K$ *vs.* ν_{CT} for the vinyl ether-TCNE complexes gave a straight line. In the present case, however, the plot of $\log K/K^0$ (benzene as a standard donor) *vs.* ν_{CT} seems to have a slight curvature.

Since it was found in many cases that the entropy change ΔS was a nearly linear function of the enthalpy change ΔH[25], we can not, strictly speaking, base the discussion on the well allowed assumption that ΔS remains unvariable for a series of complexes. However, the change of ΔH predominates so that the change of the free energy change ΔG may be nearly proportional to the change of ΔH. The stabilization energy of complex is approximately expressed as

$$\begin{aligned}\Delta W&=W_N-W_0\\ &\simeq-\frac{|W_{01}-W_0S_{01}|^2}{W_1-W_0}.\end{aligned} \quad (12)$$

The enthalpy change ΔH of a complex formation is not, of course, equal to ΔW. But when we consider only the difference of ΔH between two weak complexes in one solvent, the solvation energy may be cancelled each other, since the electronic ground state of the weak complex is of low polarity. Ultimately, the following relation is given between two complex formation equilibria in a solvent:

$$\log K/K^0\propto-(\Delta W-\Delta W^0). \quad (13)$$

Moreover, $\Delta W\simeq|W_{01}-W_0S_{01}|^2/h\nu_{CT}$ since (W_1-W_0) would be nearly equal to $h\nu_{CT}$ for a weak complex. Thus, Eq. (13) becomes

$$\log K/K^0\propto1/\nu_{CT}-1/\nu^0_{CT}=\lambda-\lambda^0. \quad (14)$$

The validness of Eq. (14), which is shown in Fig. 8, suggested that the variation of K is mainly due to the variation in the CT force.

McConnel *et al.*[25] found a linear relation between ε_{max} and λ_{max} for a series of the complexes between benzene and halogens. Nagy *et al.*[24] also obtained the similar correlation that the oscillator strength f decreased with ν_{max} for the complexes between acenaphthene-cyclic anhydrides. In both cases, it was found that f or ε_{max} increased with λ_{max}. In the present case, it seems that ε_{max} increases, though not linearly, with λ_{max}. In general, the transition moment on an EDA complex consists of two factors. The first is proportional to the dipole moment of the transferred electron and is also related to the stabilization of the ground state through the coefficient a*b: that is, the resonance stabilization energy ΔW raises the transition moment. The second is a factor dominant in a contact charge-transfer complex which does not require any overlap of van der Waals volumes of a donor and an acceptor, but the overlap between the bonding orbital of a donor and the antibonding orbital of an acceptor[28,29].

26) R. E. Merrifield and W. D. Philips, *J. Amer. Chem. Soc.*, **80**, 2778 (1958)
27) T. Arimoto and J. Osugi, *This Journal*, **44**, 25 (1974)
28) L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, **78**, 4839 (1957)
29) J. N. Murrell, *Quart. Rev.* (*London*), **15**, 191 (1961)

Contact charge-transfer theories predict that ε_{max} should increase with temperature. The latter effect was found to be strong in the complexes of σ-acceptors such as halogens. In the π-π complex as in present case, since ε_{max}'s were only slightly changed with temperature and these complexes had a face-to-face structure affording maximum overlap of the π orbitals, only the consideration of the former factor is sufficient, and thus the change of ε_{max} with a number of methyl-substituents are mainly explained by the increased stabilization energy.

From above discussion, it is concluded that the decrease in the ionization potential of donor results in the increases in all values of K, ε_{max} and λ_{max}.

As to HMB-TCNE complex, the values of K and ε_{max} remarkably indicated the solvent effect as seen in Tables 1, 2 and 167.0 M^{-1}, 5540 $cm^{-1}M$ in n-pentane, while varying the solvent had no effect on the halfwidth of the absorption band. The values of K and ε_{max} in polar solvents, such as 1, 2-dichloroethane and chloroform, were smaller than in non-polar solvents such as carbon tetrachloride, n-pentane and n-hexane. This trend in K is incompatible with the suggestion that the partially charged solute should be stabilized in polar solvent. Moreover, varying the solvent induces the changes in K which are not so largely reflected in the values for the heat of formation, which are -23.8 in chloroform and -27.3 kJ/mole in n-pentane. It is likely that solvent molecules are specifically oriented in the vicinity of the partially charged complex, or that the competitive donor-solvent or acceptor-solvent complex in 1, 2-dichloroethane and chloroform reduces the apparent equilibrium constant. Furthermore, the variation in K with solvent can be also attributed to the assumption of ideal solution, or to the neglect of higher complexes. It can be said that when the role of solvent is not considered, a reasonable explanation of the changes in various properties for the EDA complex is not found.

Pressure effect on the equilibrium constant: It is seen that the absorbances of HMB-TCNE complex in various solvents increase with increasing pressure. As a matter of fact, the increase in the concentration of solute caused by compression can produce the enhancement of absorption. Only if the above compression effect was considered, the ratio of absorbance at P kg/cm^2 to that at 1 atm should be roughly equal to the square of the relative density of solvent since the complex is in equilibrium with the two component molecules in solution. However, the observed increase of the absorbance can be attributed not only to the compression effect as shown in broken line in Fig. 2, but to the increases in K and ε_{max} with pressure as seen in Table 1. These trends in K and ε_{max} are obviously similar to the previous results of TCNE-methyl substituted benzene complexes in carbon tetrachloride.

The increase in K with increasing pressure can be reasonably explained by Mulliken's original description that a π-π complex has slightly shorter intermolecular distance than the van der Waals separation. From the X-ray diffraction studies of Wallwork[30] the weak π-π complexes generally have the parallel plane configuration where the donor and the acceptor molecules alternate, and it was found that their interplaner separation within a stack was indeed shorter than the van der Waals

30) S. C. Wallwork, *J. Chem. Soc.*, 494 (1961)

separation. Although the above fact was observed only in crystal, the expectation that the intermolecular distance of a π-π complex in solution also becomes shorter than the sum of the van der Waals radii of the componenet molecules is reasonable. So, the contraction of distance between components on the complex formation, namely, the negative value of the volume change ΔV shown in Table 2 for the complex formation explains the fact that K increases with increasing pressure. The volume change ΔV can be roughly estimated by the following equation,

$$\Delta V = -N\pi r^2 \Delta d, \tag{15}$$

where N is the Avogadro number, and the contraction Δd of the interplaner distance on the complex formation is assumed to occur along the axis of a symmetrical cylinder of the radius r equal to the van der Waals radius of a HMB molecule. Taking the value of 0.01 or 0.02 nm[31] for Δd and 0.59 nm[32] for r, ΔV for HMB-TCNE complex is calculated to be -7 or $-13\,cm^3/mol$. This is comparable with the experimentally obtained values, that is, -11.4 in 1, 2-dichloroethane and -9.0 in chloroform, and $-14.1\,cm^3/mol$ in carbon tetrachloride[15]. But the anomalous value of $-4.3\,cm^3/mol$ in n-hexane can not be reasonably explained yet.

There is a progressive decrease of ΔV in carbon tetrachloride with the number of methyl substituents as seen in Table 2, and the extent of decrease for each methyl substituent was about -1.8 cm^3/mol. This tendency is reasonably explained as follows: Δd probably becomes larger with the strength of the CT force which is roughly reflected on the stability of the complex. Namely, the methyl substitution will make ΔV more negative. Moreover, even assuming that Δd remains constant, the overlapped volume between the donor and the acceptor will reliably become larger with the number of methyl substituents.

Pressure effect on the absorption coefficient: Some increases in the integrated absorbance $\int \varepsilon_\nu d\nu$ on going from gaseous state to solution may be expected because of the change of the effective electric field affected on the molecule. This effect is roughly predicted according to Chako's simplified equation[33],

$$\frac{f_s}{f_g} = \left(\frac{n^2+2}{3}\right)^2 \frac{1}{n}, \tag{15}$$

where f_s and f_g are the integrated absorbance in solution and gas, respectively, and n the refractive index of solvent. Using the value of $n=1.4$ which is common to most solvents, f_s/f_g can be estimated to be around 1.24. However, using the literature values of $\varepsilon_{max(g)}$ in gas phase[6], the experimentally determined $\varepsilon_{max(s)}$ in solution gave the ratio of $f_s/f_g = \varepsilon_{max(s)}/\varepsilon_{max(g)}$ of 2.7~5.0 for methyl substitueted benzene-TCNE complexes[14,15,26]. So, the increase in f_s or ε_{max} in solution may be partly explained by Eq. (15), but mostly has to be attributed to other reasons. Unfortunately, convincing explanation can not be given yet, though many authors[34] have recognized and discussed the difference

31) These values were estimated from X-ray diffraction studies for several π-π complexes.
32) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press (1960)
33) N. Q. Chako, *J. Chem. Phys.*, **2**, 644 (1934)
34) See ref. (4) Chapter 7

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of absorption coefficients of an EDA complex between gas phase and solution, probably because the solvent may have the significant and specific effect on the EDA complex. In fact, any meaningful correlation has not been found between ε and the macroscopic solvent property.

But applying pressure in solution might have an advantage that these specific effects were possibly removed or minimized. Accordingly, a rough estimation of increase in the integrated absorbance under pressure is made by using Eq. (15). The refractive index n of carbon tetrachloride at desired pressure was obtained by the interpolation of literature values[35]. For 1, 2-dichloroethane, n was estimated from Lorentz-Lorenz relation $(n^2-1)/(n^2+2)=4N\pi\rho\alpha/3M$, assuming to be applicable even at high pressure. The density ρ was calculated from the Tait equation[20]. And for n-hexane, n was determined by two method: one is to use the Lorentz-Lorenz relation, and the other is to estimate from the dielectric constant D at 20°C under high pressure[36], using the relation $n^2=D$. Both methods gave much the same values of $\{(n^2+2)/3\}^2/n$ for n-hexane. The ratio of f at P kg/cm^2 to that at 1

Taole 3 Comparison of the molar absorption coefficient with Chako's function for TCNE-methyl substituted benzene complexes

(1)

Solvent	carbon tetrachloride					n-hexane	
P/kg cm^{-2}	$\varepsilon_{max}(P)/\varepsilon_{max}(1)$ [a] Benzene	Toluene	Mesitylene	HMB	$f(P)/f(1)$ [b]	$\varepsilon_{max}(P)/\varepsilon_{max}(1)$ [a] HMB	$f(P)/f(1)$ [b]
400	1.04	1.05	1.09	1.01	1.02	1.03	1.01
800	1.10	1.15	1.18	1.05	1.04	1.08	1.02
1200	1.16	1.18	1.27	1.09	1.06	1.13	1.03
1400	—	—	1.29	1.11	1.06	—	—
1500	1.22	1.20	—	—	1.07	—	—
1600	—	—	—	—	—	1.16	1.04

(2)

Solvent	1, 2-dichloroethane		chloroform	
P/kg cm^{-2}	$\varepsilon_{max}(P)/\varepsilon_{max}(1)$ [a] HMB	$f(P)/f(1)$ [b]	$\varepsilon_{max}(P)/\varepsilon_{max}(1)$ [a] HMB	$f(P)/f(1)$ [b]
400	1.05	1.01	1.10	1.01
800	1.08	1.02	1.14	1.02
1200	1.15	1.03	1.18	1.03
1600	1.21	1.03	1.19	1.04
2000	—	—	1.22	1.05

a, determined by experimental absorption coefficient.
b, calculated from Chako's equation (15), by considering the change of n at each pressure.

35) K. Vedam, *Proc. 4th Int. Conf. High Press.*, 596 (1974)
36) H. Hartmann, A. Neumann and G. Rink, *Z, Phys. Chem., N. F.*, **44**, 204 (1965)

atm should be equal to $\varepsilon_{max(P)}/\varepsilon_{max(1)}$ as found from Eq. (2), for pressure has little effect on the half-width of the absorption band. As seen in Table 3, the observed ratio of $\varepsilon_{max(P)}/\varepsilon_{max(1)}$ appears a little larger than $f(P)/f(1)$ calculated according to Eq. (15), and the increase in ε_{max} is partly explained by the change of the refractive index of solvent with increasing pressure. Since the potential energy curve of the ground state of a π-π complex is broad, the CT bond is probably more compressible than the orbinary chemical bond. That is, it is expected that there occurs a decrease in the donor-acceptor distance of the complex with increasing pressure, which increases the overlap between the π orbitals of the donor and the acceptor molecules. The increasing overlap will qualitatively lead to the enhancement of the transition moment[1]. Also in the solid media in which both the environmental change and the further complexation by pressure were assumed to be absent, the increase in ε by compression was considered to be brought about by the decrease in the donor-acceptor distance[7,9].

Spectral shift: The extent of pressure induced-spectral shift is almost comparable to that of solvent shift. The nature of the interaction in solution which affects the states involved in the electronic transition is complicated and not well understood as yet. Various theories have been put forward in order to correlate the frequency shift with solvent properties. One of them was proposed by McRae[37], who derived an approximate expression concerning the frequency shift in transfer from gas to solution. By taking into account the dipole interaction as the perturbation, Eq. (16) was given.

$$\Delta\nu_s=(AL_0+B)\frac{n^2-1}{2n^2+1}-C\left(\frac{D-1}{D+2}-\frac{n^2-1}{n^2+2}\right). \tag{16}$$

In this equation $|\Delta\nu_s|$ is the magnitude of red shift when a solute is transferred from gas to solution, n the refractive index, D the dielectric constant of the solvent, and (AL_0+B) and C are constants characteristic of the solute. In non-polar solvents in which the second term in Eq. (16) can be neglected because n^2 is assumed to be equal to D, McRae's equation could be reduced to a form similar to Bayliss' one[16]. Fig. 9 shows a fairly good linearity between ν_{CT} and $(n^2-1)(2n^2+1)$ for HMB-TCNE. And ν_{CT} extrapolated to zero is in agreement with that in gas phase[6]. Aihara *et al.*[38] also found that there were linear relations between ν_{CT} and $(n^2-1)(2n^2+1)$ for TCNE-aromatic hydrocarbons. Applying this relation to the pressure-induced shift of a non-polar solute can account for the pressure dependence of the difference of solvation energies between two electronic states. According to Eq. (16), increasing pressure should always result in a red shift, since n increases with pressure.

The intermolecular CT transition of such a weak π-π complex as was studied in the present work is expected to depend on pressure itself because the CT force between a donor and an acceptor as well as solvation energy is influenced by pressure as described below.

From Eqs. (6) and (7), the expression for the CT transition energy is

$$h\nu_{CT}=W_1-W_0+\frac{|W_{01}-W_0S_{01}|^2+|W_{01}-W_1S_{01}|^2}{W_1-W_0}. \tag{17}$$

37) E. C. McRae, *J. Phys. Chem.*, **61**, 562 (1957)
38) J. Aihara, M. Tsuda and H. Inokuchi, *Bull. Chem. Soc. Japan*, **42**, 1824 (1969)

Assuming that the overlap integral S_{01} is negligible, the second term in Eq. (17) can be approximated by

$$\frac{|W_{01}-W_0S_{01}|^2+|W_{01}-W_1S_{01}|^2}{W_1-W_0}=\frac{2W_{01}^2}{W_1-W_0}. \tag{18}$$

Therefore, the pressure-induced shift of the CT absorption frequency of an EDA complex in solution is given by

$$\Delta\nu_{CT}=\Delta(W_1-W_0)+2\Delta\left(\frac{W_{01}^2}{W_1-W_0}\right)+\Delta\nu_s. \tag{19}$$

The last term represents the shift due to the change of solvation energy by pressure and is expected to make a red shift contribution as understood from the above discussion of solvent shift. The first term of Eq. (19) represents the changes of the energy difference between the no-bond and the dative structures. Taking into account that the intermolecular separation is less than the ordinary van der Waals separation, W_0 increases at higher pressure, since the donor-acceptor distance is contracted into the repulsive region of potential curve. On the other hand, W_1 decreases with the decrease of the intermolecular distance because the Coulombic attraction is still dominant in the dative structure. Hence, the term $\Delta(W_1-W_0)$ contributes to a red shift. The second term in Eq. (19) which arises from the CT interaction, contributes to a blue shift, since the denominator (W_1-W_0) decreases in a weak complex and the resonance integral W_{01} is expected to increase by compression. Namely, for similar

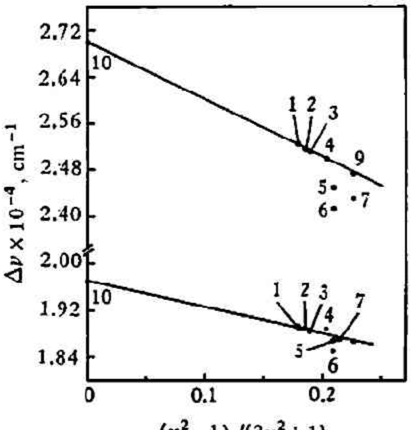

Fig. 9 A plot of the frequency of the CT band *vs.* $(n^2-1)/(2n^2+1)$
●: HMB-TCNE,
○: toluene-TCNE
solvent:
1: *n*-pentane, 2: *n*-hexane,
3: *n*-heptane, 4: cyclohexane,
5: 1,2-dichloroethane,
6: chloroform,
7: carbon tetrachloride,
8: toluene, 9: benzene,
10: gas phase[1]

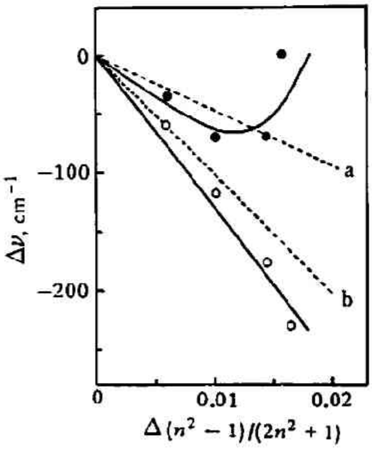

Fig. 10 Frequency shift of the CT band under pressure *vs.* refractive index of carbon tetrachloride. The broken lines a for HMB-TCNE and b for toluene-TCNE are obtained from Fig. 9
●: HMB-TCNE,
○: toluene-TCNE

complexes, the stronger the complex, the smaller is $W_1 - W_0$, the greater is W_{01}, and hence the larger the contribution of a blue shift.

$\Delta\nu_s$ by compression makes a contribution of a smaller red shift for HMB-TCNE than for toluene-TCNE as shown in Fig. 9. As seen in Fig. 10, the extent of the pressure-induced spectral shift for the toluene-TCNE complex is comparable with that of the solvent shift, while the HMB-TCNE complex shows a blue shift at higher pressure. And also as seen in Fig. 3, a stronger complex shows a smaller red shift. These results are consistent with the above considerations which suggest larger contribution from the CT interaction for a stronger complex. Therefore, the spectrum becomes a smaller red shift or a blue shift for more stable complex, for example, the HMB-TCNE complex.

For the HMB-TCNE complex, the pressure induced spectral shifts in n-pentane, n-hexane and n-heptane show larger red shifts in comparison with those in chloroform and 1, 2-dichloroethane, while K's in n-pentane, n-hexane and n-heptane are larger than in chloroform and 1, 2-dichloroethane as shown in Table 1 and Fig. 4. Although this fact can not be explained from the CT interaction, it is likely that there exists some specific solute-solvent interaction. As discussed in the solvent effect for HMB-TCNE complex, it is likely that there existes some specific solute-solvent interaction. Therefore, the pressure-induced spectral shift in the various solvents can not be satisfactorily explained.

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Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto 606, Japan