Table 1 Equilibrium constants and spectroscopic parameters for the EDA-complexes of mesitylene-TCNE and HMB-TCNE in carbon tetrachloride at 25°C

Press.	mesitylene-TCNE				HMB-TCNE		
kg/cm²	K l. mole⁻¹	$\varepsilon_{max}\times 10^{-3}$ cm⁻¹ l. mole⁻¹	f	λ_{max} nm	K l. mole⁻¹	$\varepsilon_{max}\times 10^{-3}$ cm⁻¹ l. mole⁻¹	λ_{max} nm
1	12.8	2.40	0.070	464	140	5.16	534
	8.54±0.340[a]	3.057±0.093[a]			123±8.8[a]	5.14±0.140[a]	
400	13.3	2.61	0.077		177	5.20	
800	14.0	2.84	0.084		205	5.42	536
1200	14.9	3.04	0.089		229	5.63	
1400	15.7	3.09	0.093	468	242	5.73	534

a ; ref. 8

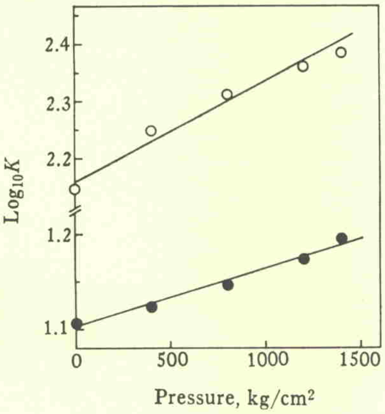

Fig. 6 Pressure effect on the equilibrium constants
●: mesitylene-TCNE,
○: HMB-TCNE

Consideration

As seen in Fig. 3 and Table 1, the enhancement of absorption with pressure can be ascribed not only to the increase of concentrations of solutes caused by compression but also to the increase of K and ε_{max}. Taking into account that K and λ_{max} are 0.964 l/mole and 385 nm for benzene-TCNE, and 1.92 l/mole and 411 nm for toluene-TCNE complexes1), it seems to be concluded that the higher the transition energy $h\nu_{ct}$ of the EDA-complex, the smaller its equilibrium constant K. The similar trend was reported in a series of aromatic hydrocarbon-TCNE complexes in dichloromethane14). However, the inverse trend was observed in vinyl ether-TCNE comlexes15). The increase of K with pressure can be interpreted by Mulliken's original description16) that both the no-bond and dative structures have smaller intermolecular distance than the sum of the van der Waals radii of the component molecules. Actually, it was confirmed in solid state by X-ray diffraction studies2). Since the same fact is

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14) R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, **80**, 2778 (1958)
15) T. Arimoto and J. Osugi, *This Journal*, **44**, 25 (1974)
16) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952)

expected in solution, the volume change for the complex formation will be negative, which results in the increase of K with pressure.

As seen in Table 2, the values of ΔV became more negative with the increasing number of substituents of the donor. This tendency seems to be reasonable, since the molecular size of the donor might become larger with the number of substituents.

Table 2 Volume changes for the EDA-complex formations of TCNE and spectral shift induced by pressure in carbon tetrachloride at 25°C

Donor	$-\Delta V$, cm^3/mole	Spectral shift
Benzene	3.4	red
Toluene	4.9	red
Mesitylene	7.1	red
HMB	14.1	red-blue

Several authors have attempted to account for the influence of solvent on the spectra of neutral-neutral EDA-complexes. Since the excited state of the complex is considerably more polar than the ground state, it has been predicted that increasing solvent polarity should cause a red shift as a consequence of increased stabilization of the polar excited state. This prediction, however, was not in accord with the experimental facts that the spectral shift did not correlate with the dielectic constant as a measure of solvent polarity. McRae17) derived theoretically the following expression for the frequency shift caused by the dipole interaction, using the solvent perturbation theory;

$$\Delta h\nu \cong (AL+B)\frac{n^2-1}{2n^2+1}-C\left(\frac{D-1}{2D+1}-\frac{n^2-1}{2n^2+1}\right), \qquad (3)$$

where $(AL+B)$ and C are constants characteristic of a solute, and n is the refractive index and D the dielectric constant of solvent, and $\Delta\nu$ is the amount of the red shift from vapor phase to solution. Since the second term can be disregarded because $n^2=D$ in nonpolar solvent, McRae's expression should be simplified to a form similar to Bayliss' equation3) derived by using the model of an oscillating point dipole in a continuum medium. Accordingly, the following relation was obtained:

$$\Delta h\nu \propto \frac{n^2-1}{2n^2+1} \qquad (4)$$

Actually, Voigt18) and Aihara *et al.*19) found a good linear correlation between the spectral shift of EDA-complex and $(n^2-1)/(2n^2+1)$ in various solvents. Furthermore, Ham9) has applied this relation to his pressure studies of aromatic hydrocarbon-iodine comlexes in n-heptane, but his results failed to be extrapolated to the vapor phase. On the other hand, Robertson *et al.*20) derived theoretically the relaiton, $\Delta\nu \propto \rho$ where ρ is the density of solvent, for non-polar solute in non-polar medium and recognized that this relation held good for some aromatic hydrocarbons in n-heptane under high pres-

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17) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957)

18) M. Voigt, *ibid.*, **70**, 598 (1966)

19) J. Aihara, M. Tsuda and H. Inokuchi, *Bull. Chem. Soc. Japan*, **42**, 1824 (1969)

20) W. W. Robertson, O. E. Weigang and F. A. Matson, *J. Molecular Spectro.*, **1**, 1 (1957)