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Solvent Effects of Charge-transfer Complexes

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The solvent effects of charge-transfer complexes were examined in various solvents. During the course of investigations pertaining to aromatic-TCNE complexes, Brownstein's and McRae's formulae were found to be valid. The gas-phase spectra of these charge-transfer complexes may be regarded as the origin of the solvent effects. The anomalous behaviour of carbonyl solvent molecules was also discussed.

It has been easily assumed that increasing the solvating power of a medium for a charge-transfer (CT) complex should shift the CT-band of the absorption spectra to a lower energy region.[1] Contrary to this prediction, however, it is often found that an increase in solvent polarity results in the shift of the CT-band to higher energy region.[2] Specific interaction between the charge-transfer complex and the surrounding solvent causing these blue shifts should thus also be considered as significant in these systems.[3]

Several explanations have been proposed for these solvent effects: some of them emphasized the small heat of formation, ΔH, of the complex, which implies that the complex-binding can be looser with little change in the surroundings.[4]

Davis and Symons believed a charge redistribution in the ground state of the complex to be responsible for the blue shift in polar solvents.[3] Therefore, they concluded that the commonly-accepted concept regarding solvent shifts on the absorption spectra of charge-transfer complexes has to be abandoned. Weiss proposed that a donor-acceptor complex can be considered as an electron-hole pair in correlation with the theory of Wannier exciton, but his theory also seems to be unsuccessful.[5] One of the purposes of the present work is to reexamine the solvent effects of the charge-transfer complexes; another is to locate the absorption spectra of the gaseous complexes in the solvent diagrams for various relationships.

Experimental

Naphthalene, durene, diphenyl and pyrene used in this work were recrystallized and zone-refined materials. Stilbene was twice recrystallized from ethanol. Tetracyanoethylene (TCNE) was synthesized according to the method of Ref. 6 and purified by recrystallization

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[1] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

[2] H. W. Offen and M. S. F. A. Abidi, *J. Chem. Phys.*, **44**, 4642 (1966).

[3] K. M. C. Davis and M. C. R. Symons, *J. Chem. Soc.*, **1965**, 2079.

[4] J. Czekalla and K. O. Meyer, *Z. Physik. Chem. (Frankfurt)*, **27**, 185 (1961).

[5] J. J. Weiss, *Phil. Mag.*, **8**, 1169 (1963).

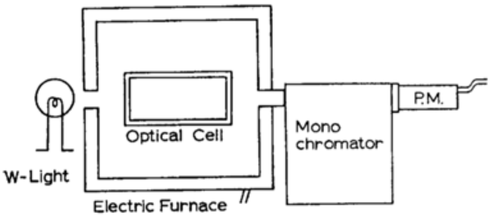
[6] "Organic Syntheses," Coll. Vol. IV, p. 877 (1963).

from chlorobenzene and by sublimation.

The solutions of charge-transfer complexes were prepared by mixing the respective components to appropriate concentrations. The absorption spectra were measured using a Cary Model 14 spectrophotometer.

The optical data for the charge-transfer complexes in the gas phase were obtained with an Aminco 4-8401 monochromator. TCNE and equimolecular aromatic hydrocarbon were placed in a quartz cell 7 cm or 40 cm long, which was then sealed after evacuation. The cell was heated to an appropriate temperature in a large, 50-kW electric furnace, and the absorption spectra were measured rapidly, as Fig. 1 shows schematically. The light source was a 200-W Wolfram lamp.

Survey of Gas-phase Spectra. In a previous paper, we have already reported some of the general features of the absorption spectra in the gas phase.7) In this article, we will describe the individual characteristics in detail, as Figs. 2—7 show, in comparison with those of the carbon tetrachloride solution. The CCl_4 solvent is the most popular non-polar solvent. In general, gas-phase spectra are very similar to those in the solution in respect to shape and width. Moreover, the gaseous spectra of the complexes have no vibrational structures, such as are often found in the gaseous spectra of simple molecules. Exceptionally, the durene-TCNE complex (Fig. 3) has an asymmetric spectrum in solution.



Apparatus for Spectrophotometry

Fig. 1. The apparatus for spectrophotometry of gaseous charge transfer complexes.

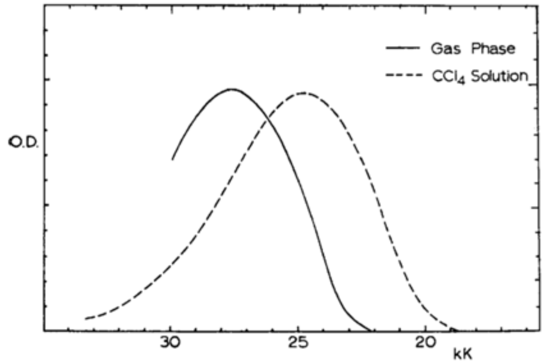


Fig. 2. The gaseous spectrum of toluene-TCNE.

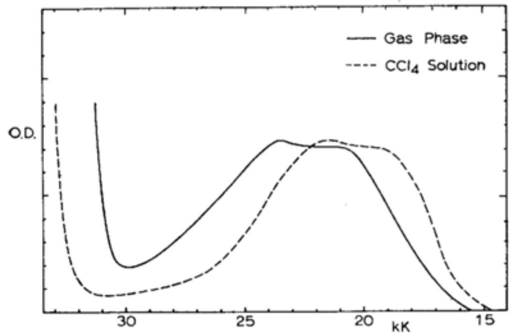


Fig. 3. The gaseous spectrum of durene-TCNE.

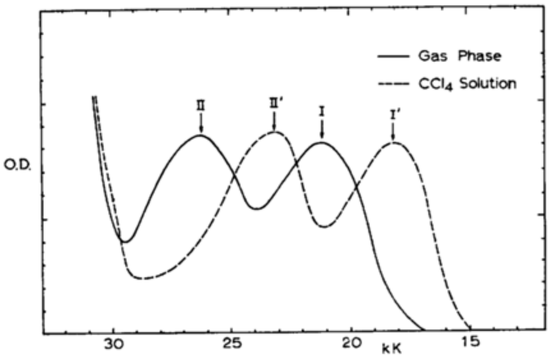


Fig. 4. The gaseous spectrum of naphthalene-TCNE.

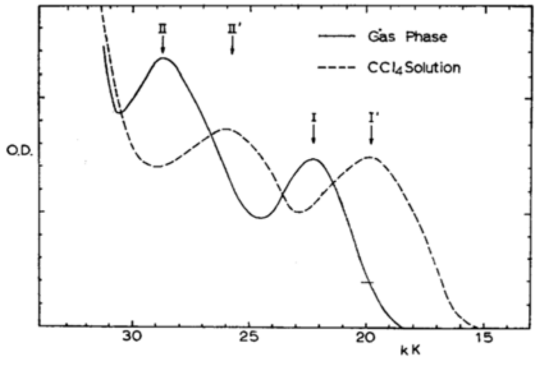


Fig. 5. The gaseous spectrum of diphenyl-TCNE.

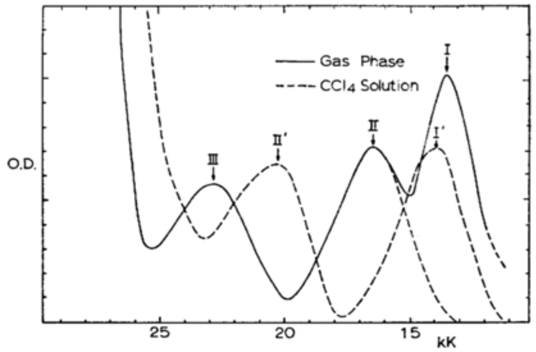


Fig. 6. The gaseous spectrum of pyrene-TCNE.

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7) J. Aihara, M. Tsuda and H. Inokuchi, This Bulletin, **40**, 2460 (1967).

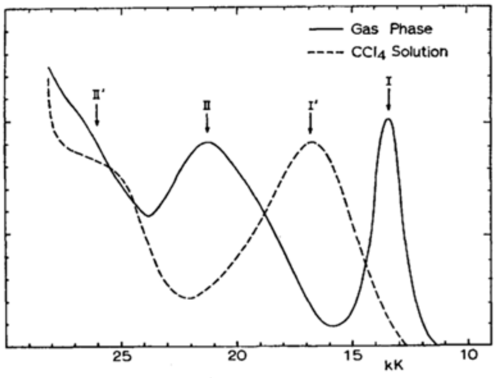

Fig. 7. The gaseous spectrum of stilbene-TCNE.

However, in the gas phase it is reproduced within the range of the structures in the solution. This suggests that the location of the 0–0 band in the gaseous spectrum is at the same position as in the solution specturm.

Therefore, the following conventional method was adopted to treat the data: the absorption maxima were taken as the position for the 0–0 band, and the peaks were assigned by comparing the spectra in carbon tetrachloride with those in the gas phase.

The absorption spectra of the naphthalene-TCNE complex are shown in Fig. 4. This complex has two charge-transfer bands, which may be interpreted as transitions from the highest occupied orbital of naphthalene to the lowest and the second lowest vacant orbitals of TCNE. The complexes of diphenyl (Fig. 5), pyrene (Fig. 6), and stilbene (Fig. 7) with TCNE are the same. The intensity ratio of the two bands is kept nearly constant between gas and solution.

Pyrene-TCNE complex has obviously different features. In the gas phase, the absorption spectra has three bands in the visible region, while in the solution only two bands are observed. In the pyrene-TCNE complex, we may except the lowest energy band for the following reasons. In the first place, the location of this band has a fairly good reproducibility, but it is poor in its intensity ratio in relation to other bands. The shapes of the first and the second bands in the solution are apparently comparable respectively to those of the second and the third bands in the gas phase. Moreover, the solvent effect to be described in the next section supports this interpretation. It is probable that the first gaseous band may be ascribed to that produced by the reaction or decomposition of the complex. An anomaly is also found in the stilbene-TCNE complex, so the first band is ommitted for the same reasons. In these two cases these phenomena appeared in nearly the same wavelength region. All the gaseous data are summarized in Table 1. Each shows a red gas-to-solution shift.

TABLE 1. THE LIST OF CT-BANDS OF TCNE CHARGE-TRANSFER COMPLEXES

Donor	CT-band (kK) in gas phase	CT-band (kK) in CCl_4 solution	Gas-to-solution shift (kK)
Toluene	27.6	24.7	−2.9
Durene	20.8	19.2	−1.6
Naphthalene	21.1	18.0	−3.1
	26.3	23.0	−3.3
Diphenyl	22.2	20.0	−2.2
	28.6	25.7	−2.9
	13.5	—	—
Pyrene	16.5	14.0	−2.5
	23.0	20.5	−2.5
	13.4	—	—
Stilbene	21.1	16.8	−4.3
	—	26.0	—

Discussion

It is very interesting to ascertain where the gaseous data are located in the solvent diagrams. As has been mentioned before, if the solvent effect is substantially abnormal, solvation itself is a theme of importance.

Several authors have attempted to relate the solvent shift of absorption spectra to the rate of the solvolysis reaction.[8] Following Kosower's idea, Brownstein developed an empirical relationship which obviously resembles the so-called Hammett rule.[9] He estimated an S-value for each solvent comparable to Hammett's σ value.

Brownstein's rule is expressed as follows.

$$SR = \frac{\nu_0 - \nu_E}{\nu_0} \tag{1}$$

where R is a constant characteristic of the system, where ν_E is the value in a given solution, and where ν_0 is the value obtained for ethanol as a standard.

To survey the general behaviour of the solvent effect of the charge-transfer bands, we adopted this rule for the naphthalene-TCNE complex. Figure 8 shows Brownstein's relation; a general correlation is found between the spectral shift and the S-value. From this validity to the complex, R is determined to be -0.433, a value which is fairly large in comparison with ordinary π–π^* or n–π^* transitions. The spectra from a gaseous specimen deviates much to the higher energy region, and so do those in ethyl-acetate and acetone. Some of these data were first cited in Refs. 2 and 10.

Next, we applied these data to the McRae relation, one of the most popular formulae of the solvent effect, expression of which is:[11]

$$\Delta h\nu \cong (AL_0 + B)\frac{n^2-1}{2n^2+1} + C\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) \tag{2}$$

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[8] E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

[9] S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).

[10] G. Briegleb, J. Czekalla and G. Reuss, *Z. Physik. Chem. (Frankfurt)*, **30**, 316 (1961).

[11] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

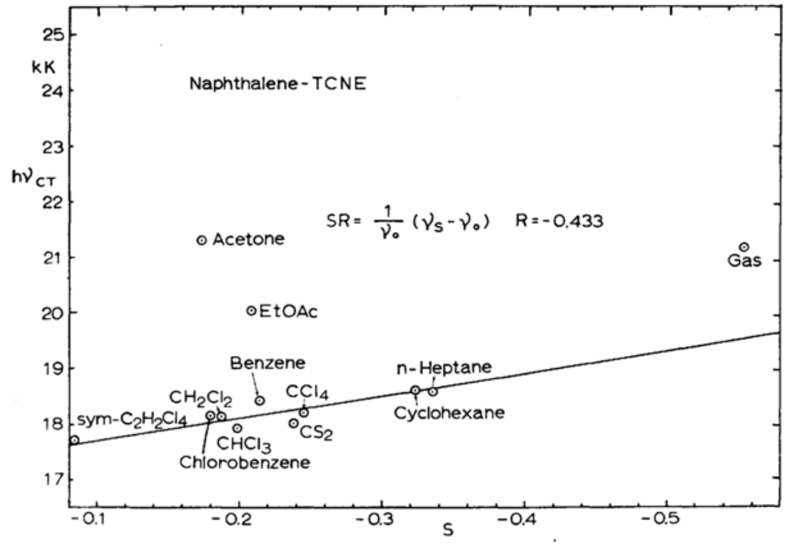

Fig. 8. The Brownstein's plots for naphthalene-TCNE.

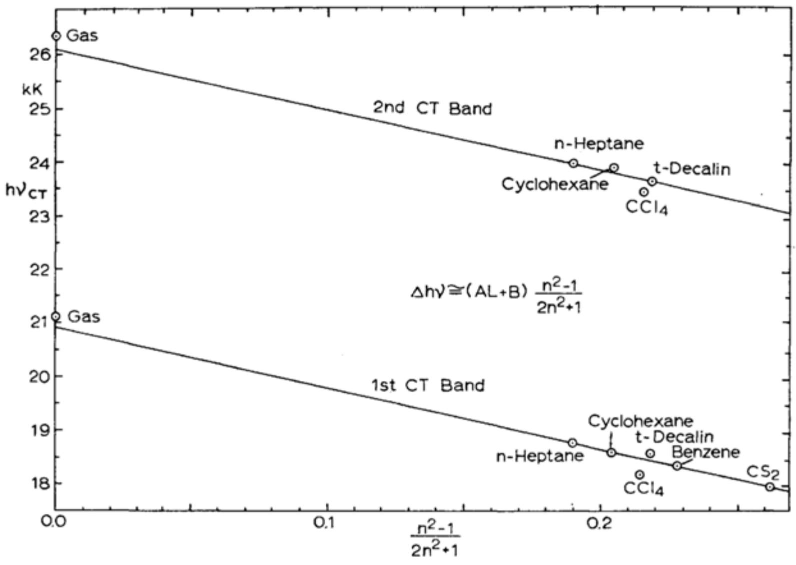

Fig. 9. The non-polar solvent effect of naphthalene-TCNE.

where n is the refractive index and where ε is the dielectric constant of the solvent. (AL_0+B) and C are constants characteristic of the solute. We plotted the absorption maxima in non-polar solvents, in which case the second term can be disregarded because $n^2 \cong \varepsilon$. The n and ε values were taken from Refs. 12 and 13. In Fig. 9 we found a fairly complete linearity between spectral shifts and $n^2-1/2n^2+1$ and obtained 11.00 kK as the (AL_0+B) value.

This means that, in these complexes, interaction between the solute-induced dipole and the solvent-induced dipole and/or between the solute dipole and the solvent-induced dipole is very large, compared to the general trend of solvent shifts. The wave numbers extrapolated to zero agree with the gaseous data.

Offen and Abidi suggested that there is no correlation between the magnitude of the shift and the refractive index or dielectric constant,[2] but this complex seems to behave normally, at least in non-polar solvents. Accordingly the nature of the complex is substantially the same in the gaseous state and in solution. Probably the large (AL_0+B)

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12) A. D. E. Pullin, *Spectrochim. Acta*, **16**, 12 (1960).

13) "Organic Solvents," 2nd Ed., Interscience Publishers, New York (1955).

value reflects the abnormal blue shift of the gas phase in Brownstein's relation.

Using this value, we tried to obtain the *C*-value of McRae's formula; therefore $h\nu_{\mathrm{CT}}-(AL_0+B)\frac{n^2-1}{2n^2+1}$ is plotted against $\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}$ in Fig. 10. Several disordered solvents appeared among the polar solvents. This term indicates part of the solute dipole-solvent dipole interaction; explicitly, *C* is expressed as $2\mu_g(\mu_g-\mu_a)/a^3$, where μ_g and μ_a are the dipole moments of the ground state and the excited state respectively, and where *a* is the cavity radius of the solvent. As to the naphthalene-TCNE complex, the dipole moment of the ground state is reported to be 1.28 D, while that of the excited state can be assumed to be 10—15 D on the basis of the data of the excited hexamethylbenzene-TCNE complex.[4,14] Accordingly, the value of *C* must be negative in a normal case. Figure 10 shows a group of solvents which exhibit a good linear correlation between those whose gradient is −490 cm^{-1}. This group consists mainly of halo-alkanes and alkenes.

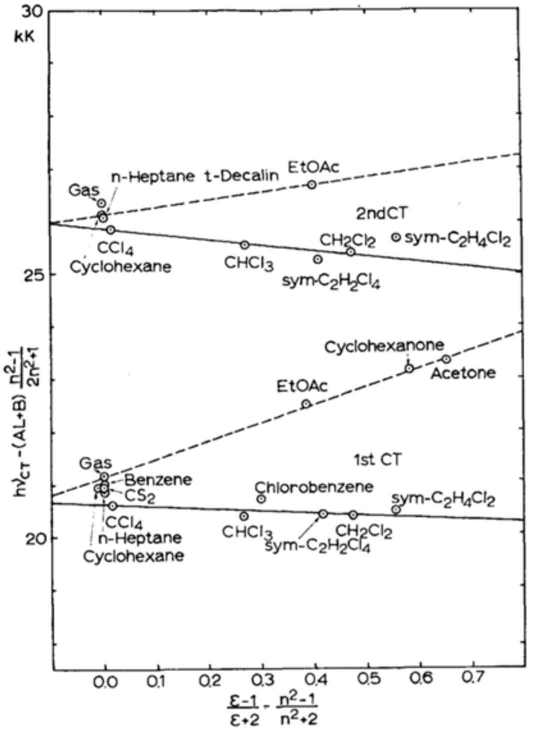

Fig. 10. The polar solvent effect of naphthalene-TCNE.

For these solvents, we can estimate the charge distribution of the complex to be nearly constant. Now let us estimate the Coulomb term contributing to the charge-transfer transition. $h\nu_{\mathrm{CT}}$ is frequently approximated by the expression;[15]

$$h\nu_{\mathrm{CT}}=I_{\mathrm{D}}-E_{\mathrm{A}}-\frac{e^2}{R_{\mathrm{DA}}}-P \tag{3}$$

where I_{D} is an ionization potential of the donor, where E_{A} is the electron affinity of the acceptor, and where *P* is the polarization energy due to solvent molecules. R_{DA} indicates the distance between donor and acceptor molecules. When we apply this formula to the heptane solution, we can deduce *P* directly from Fig. 9 as the value of the spectral shift, 0.50 eV. The electron affinity of TCNE is 2.60 eV if we take as the standard *p*-benzoquinone, whose value, 1.40 eV, was recently determined by a magnetron method.[16] Therefore, the Coulombic ion-pair attraction term results in 2.38 eV.

Ikemoto calculated the molecular orbitals of this complex in the crystalline phase.[17] According to him, the Coulomb energy of the first band may be estimated to be 3.32 eV. The decrease in the Coulombic interaction suggests that there exists a looser complex in both the gas and the solution with a larger intermolecular distance. However, the charge distribution in the complex may be considerably different from that in the solid state, so the displacement between the two components can not be estimated straightforwardly.

From the above results, the spectral shifts may all be ascribed to a simplification of McRae's formula. The possibility of some orientational isomers in the gas phase or in the various solvents is not very important.[18] If a different form of charge-transfer isomers exists, those isomers may be expected to produce a secondary shift compared to the usual dipole-polarization shifts. The only questionable point is that the plots for the non-polar solvents in Fig. 9 are slightly displaced upward from the linearity of the regular solvents.

On the other hand, the plots for the oxygen-containing solvents are mainly dispersed to the blue side. This irregularity is in good accord with the trend in Brownstein's relationship. Generally the values found in ethyl acetate, acetone, and cyclohexanone are far remove from those in methylene chloride.[2,19] Therefore, we can conclude that these groups behave abnormally, so special theoretical attention should be given to them.

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14) G. Briegleb, J. Czekalla and G. Reuss, *Z. Physik. Chem. (Frankfurt)*, **30**, 333 (1961).

15) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

16) L. Farragher and F. M. Page, *Trans. Faraday Soc.*, **62**, 3072 (1966).

17) I. Ikemoto, private communication.

18) J. R. Gott and W. G. Maisch, *J. Chem. Phys.*, **39**, 2229 (1963).

19) H. W. Offen and A. H. Kadhim, *ibid.*, **45**, 269 (1966).

How can we examine this phenomenon? As Bayliss pointed out, this point-dipole model, in a uniform medium, is not the best approximation.[1] In the case of the charge-transfer complex especially, these solvents may change the nature of the complex.

Using the above data of the normal solvation, the cavity radius of the solvent is calculated to be 6.60±0.30 Å. This radius is quite large. In this connection the typical solvents have molecular radii in the range of from 2.0 to 4.0 Å. Therefore, a solvent which does not have a very marked partial moment may be regarded as a continuous medium.

TABLE 2. THE RESULTS OF SOLVENT EFFECT FOR THE CHARGE-TRANSFER COMPLEXES

Species	Band	AL_0+B (kK)	C (kK)	C'** (kK)	a (Å)
Naphthalene-TCNE					
	1st CT	−11.07	−0.49	~3.44	6.60
	2nd CT	−10.72	−1.08	~1.50	
Azulene*	1_{L_b}	− 0.131	0.286	—	3—4
	1_{L_a}	− 2.734	0.209	—	
	1_{B_b}	− 7.154	0.000	—	

* Cited from W. W. Robertson, A. D. King, Jr., and O. E. Weiganger, Jr., *J. Chem. Phys.*, **35**, 464(1961).

** Determined from the dotted line in Fig. 10.

However, some polar solvent molecules will tend to become oriented so as to stabilize these partially-charged complexes through stereospecific solvation; that is, the solvent molecules around the complex may take such orientations that maximum attractions between the solvent and the solute molecules are obtained. In forming such a local field, the proper geometrical conditions of solvent molecules as well as proper polarities are necessary.[20]

Moreover, a new interaction of carbonyl compounds was reported a few years ago.[21] An oxygen atom in the carbonyl group is closely attached to the carbon atom of the same group in the neighbouring molecule. The usual van der Waals distance between them is expected to be at least 3.1 Å, according to Pauling's list of van der Waals radii.[22] However, those of chloranil, parabanic acid, and aloxan are 2.85, 2.77, and 2.79 Å respectively. Such an effect may be expected also in acetone, ethyl acetate, cyclohexanone, and so on. Carbonyl group has an ionic character of several tens per cent, too.

If we proceed to develop such an idea, the concept of a local field formed by the surroundings acting on the complex in the direction from the acceptor molecules to the donor molecules, the ground state of the complex is further polarized.[23] This explanation is somewhat related to those by Davis and Symons, and Offen and Abidi, who also suggested the enhancement of the mixing of the dative bond.[2,3] In the present case, the carbonyl solvent molecules around the complex may take such orientations as described above. It is probable that these interactions are large enough to invert the direction of the solvent shifts.[22] The dotted

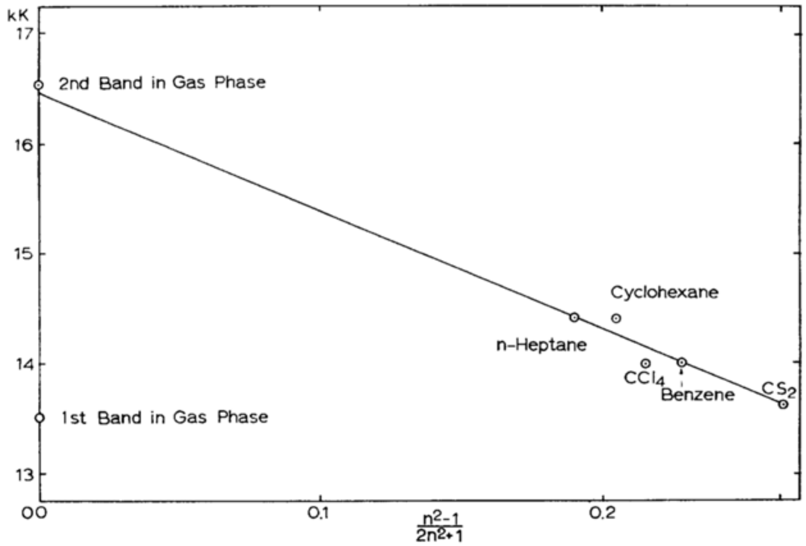

Fig. 11. The non-polar solvent effect of pyrene-TCNE.

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20) G. Briegleb and T. Schachowskoy, *Z. Physik. Chem.*, **B19**, 255 (1932).

21) W. Bolton, *Acta Cryst.*, **16**, 166 (1963).

22) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed. Cornell Univ. Press, New York (1960).

23) S. Yomosa, *Progr. Theor. Phys. Supplement.*, No. 40, 249 (1967).

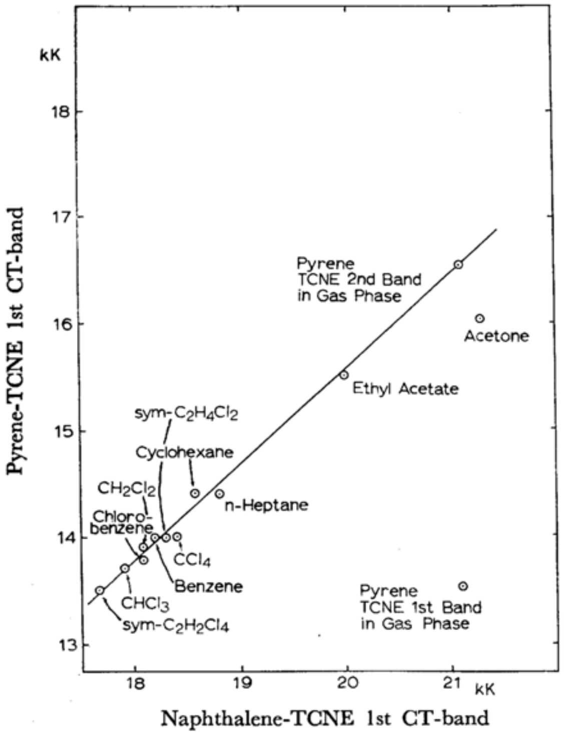

Fig. 12. The correlation between naphthalene-TCNE and pyrene-TCNE.

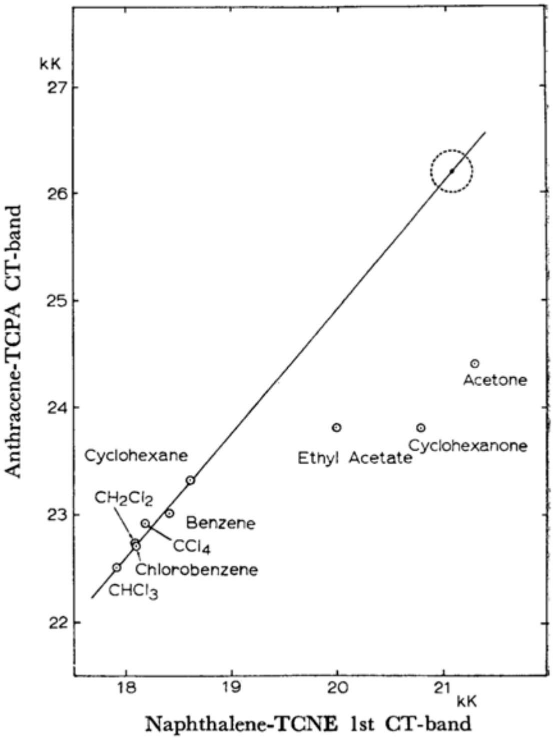

Fig. 13. The correlation between naphthalene-TCNE and anthracene-TCPA.

line in Fig. 10 suggests the possibility of such a case.

So far we have discussed mainly the naphthalene-TCNE complex, but the parallelism of solvation is widely valid among a variety of complexes.[2] In Fig. 11 another example is shown, here the first band of the gaseous pyrene-TCNE complex can be omitted as a band originating for a different reason.

We can ascertain another correlation between the spectral shifts of naphthalene-TCNE and pyrene-TCNE complexes. The results shown in Fig. 12 also give support to the above reasoning as to the first band of the gaseous pyrene-TCNE complex. The first band of the gaseous stilbene-TCNE complex is omitted for the same reason.

In Fig. 13 the correlation with a different type of complex, that is, the anthracene-TCPA (tetrachlorophthalic anhydride) complex, is examined. The gaseous spectrum of this complex could not be observed because of overlapping with that of component molecules as a result of the blue shift. However, the location of the peak is assumed to be around the dotted circle.

In both these diagrams, the carbonyl solvent behaves independently as before. We must leave further investigation of this problem to later. In this step, however, we should stress the regularity of the solvent effect and the location of gaseous spectra as a standard of that effect.