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A Study of the Charge-Transfer Complexes. V. The Complexes of Tetracyanoethylene with *trans*-Stilbene and Related Compounds[*1,*2]

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The charge-transfer (CT) absorptions of complexes of tetracyanoethylene with *trans*-stilbene and related compounds were measured both in solution and in solid media. The first and the second CT bands were found to be affected differently by the substituents on the donor molecule; thereupon they were assigned to the transitions of an electron from, respectively, the highest occupied and the second highest occupied orbitals of the donor to the lowest unoccupied orbital of the acceptor. Both the location and the intensity of the first CT band were found to be extremely sensitive to variation in media and temperature. The explanation was arrived at by the use of a model where an acceptor molecule was assumed to associate independently with several different sites of a donor molecule.

In contrast to the presence of abundant information on the charge-transfer (abbreviated to CT hereafter) complexes of condensed aromatic hydrocarbons, no paper has been devoted to the study of the donor properties of linear polyenes and their analogues. In this connection, it is very interesting to investigate the CT complexes of stilbene, the smallest α, ω-diphenylpolyene. In one of the preceding papers of this series, the CT complexes between methyl-substituted *trans*-stilbenes and chloranil or pyromellitic dianhydride have been reported on.[1] The donor strength of stilbene has been found, there, to be strongly dependent on the distortion of the molecular plane. In this paper, a study will be made of the interactions between stilbene derivatives and tetracyanoethylene (TCNE). In order to elucidate the nature of the second CT band, the donor properties of biphenyl, diphenyl ether, and other related compounds will also be investigated.

Experimental

Materials. The diphenyl ether, biphenyl, *p*-terphenyl, and naphthalene were reagent-grade chemicals supplied by the Tokyo Kasei Organic Chemicals Co., and were used after repeated purifications. The cyclohexane and methylene chloride were purchased from the Wako Pure Chemical Co., and were purified by the standard procedure for each solvent. All the other compounds were synthesized in the authors' laboratory by authentic processes, and were repeatedly and carefully purified. The melting points, results of CH analysis, IR and NMR spectra were used to identify the prepared compounds. The purity was checked by gas chromatography, if that was possible.

Spectroscopic Measurements. The solutions of CT complexes were prepared by mixing the respective components to suitable concentrations (donor, 0.01—0.1 mol/*l*; acceptor, 0.005—0.015 mol/*l*). The spectra were measured by a conventional method, using either a Hitachi model EPS-2U or a Shimazu-Bausch & Lomb model SP 505 recording spectrometer. The solid complexes were obtained from the cyclohexane solutions as sharp needles. The crystals were dispersed in starch, and their relative diffuse reflectance measured by a method described before.[2]

Results and Discussion

The wave numbers for the CT absorption bands of the complexes between TCNE and stilbene derivatives in methylene chloride are summarized in Table 1. As may be seen in the table, the two CT absorption bands behave differently upon the introduction of substituents. In the cases of the compounds II, III, and VII, the molecular planes are considered to be distorted due to the presence of steric hindrance. As to the complexes of the compounds in this group, the first CT bands are found at larger wave numbers than that for *trans*-stilbene, while the second bands are found at almost the same positions. The effect of methyl substitution on the benzene ring also gives very important information (compounds IV, V, VI,

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1) H. Shosenji and T. Matsuo, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 802 (1966).

2) Y. Nakayama, Y. Ichikawa and T. Matsuo, This Bulletin, **38**, 1674 (1965).

TABLE 1. THE CHARGE-TRANSFER ABSORPTION BANDS OF TCNE COMPLEXES WITH *trans*-STILBENE AND THE RELATED COMPOUNDS IN METHYLENE CHLORIDE

Donor	The first band (kK)	The second band (kK)
trans-Stilbene (I)	16.6±0.1	25.3±0.2
cis-Stilbene (II)	18.7±0.1	24.8±0.2
trans-α-Methylstilbene (III)	17.3±0.1	25.2±0.2
trans-2-Methylstilbene (IV)	16.7±0.1	23.9±0.2
trans-3-Methylstilbene (V)	16.5±0.1	24.5±0.2
trans-4-Methylstilbene (VI)	15.7±0.1	25.0±0.2
trans-α, α'-Dimethylstilbene (VII)	18.5±0.2	24.8±0.2
trans-4, 4'-Dimethylstilbene (VIII)	14.8±0.1	25.0±0.2
trans-4-Methoxystilbene (IX)	14.3±0.1	23.8±0.3
trans-4, 4'-Dimethoxystilbene (X)	12.8±0.1	21.9±0.2
trans-4, 4'-Dibromostilbene (XI)	16.9±0.1	25.4±0.2
trans-4, 4'-Diacetoxystilbene (XII)	16.8±0.1	25.9±0.3
Styrene (XIII)	20.6±0.1	25.1±0.2
trans-α, ω-Diphenylbutadiene (XIV)	14.9±0.1	24.2±0.3

and VIII). The second CT band shows an appreciable red shift if a methyl group is at 2- or 3-position. The first CT band, on the other hand, is affected by the methyl group at the 4-position. The effects of methyl substitutions, as has been described above, are well correlated to the first-order perturbation effects on the highest occupied and the second highest occupied π-orbitals, as calculated by simple LCAO MO theory. The highest occupied orbital mainly consists of the p-orbitals of the carbon atoms at the 1-, 4-, and α-positions. The second highest occupied orbital, on the other hand, does not involve the carbon atoms of the central double bond. In other words, the second highest occupied orbital is localized at the benzene rings. The methyl substitution at the 4-position and the decrease in conjugation in the C_1-C_α bond are, therefore, expected to have a much larger effect on the energy level of the highest occupied orbital than on that of the second highest occupied orbital. An exactly opposite situation is expected if the substituent is at either the 2- or 3-position. On the basis of the above facts, the first and the second CT bands may be assigned to the electronic transition originating from the highest occupied orbital and that from the second highest occupied orbital of stilbene respectively. By the use of the results of Beveridge and Jaffes' LCAO-SCF-CI computation,3) the second highest occupied orbital of *trans*-stilbene is estimated to be 1.4 eV below the highest occupied orbital.*5 In good agreement with this value, the separation between the first and the second CT bands in Table 1 is found to be 1.1 eV.

In the cases of methoxystilbenes, the second CT band, like the first band, is appreciably affected by the substituent at the 4-position. It may be suggested, then, that the effect of the methoxyl group is somewhat larger than a simple perturbation of the donor orbital. The minor effects of the bromine and acetoxyl groups may be due to the slightly electron-withdrawing natures of these substituents.

The effect of extended conjugation may be seen by examining the absorption bands of the complexes of TCNE with styrene, *trans*-stilbene, and *trans*-α, ω-diphenylbutadiene. The wave number for the first CT band rapidly decreases in the above order of donors. The second CT band, on the other hand, is affected to a much smaller extent.

In order to investigate the nature of these second

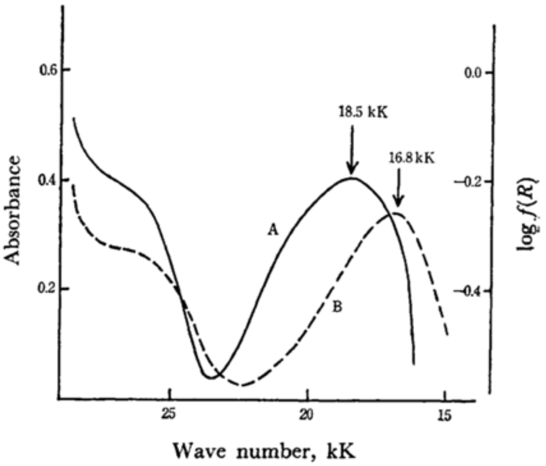

Fig. 1. The CT absorption spectra of TCNE complex with *trans*-stilbene.

A: The diffuse reflectance spectra (the complex, 6 mg; starch, 300 mg). The function $f(R)$ is the Kubelka-Munk function as defined as

$$f(R)=(R-1)^2/2R$$

where R is the relative diffuse reflectance (see Ref. 2 for further detail).

B: The absorption spectra in cyclohexane (the acceptor, 0.03 mol/*l*; the donor, 0.05 mol/*l*).

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3) D. L. Beveridge and H. H. Jaffe, *J. Am. Chem. Soc.*, **87**, 5340 (1965).

*5 The energy for the ^1G state, which corresponds to the excitation of an electron from the second highest occupied orbital to the lowest unoccupied orbital of *trans*-stilbene, was estimated by taking an arithmetic mean of those for the $^1G^-$ and $^1G^+$ states given in Ref. 3.

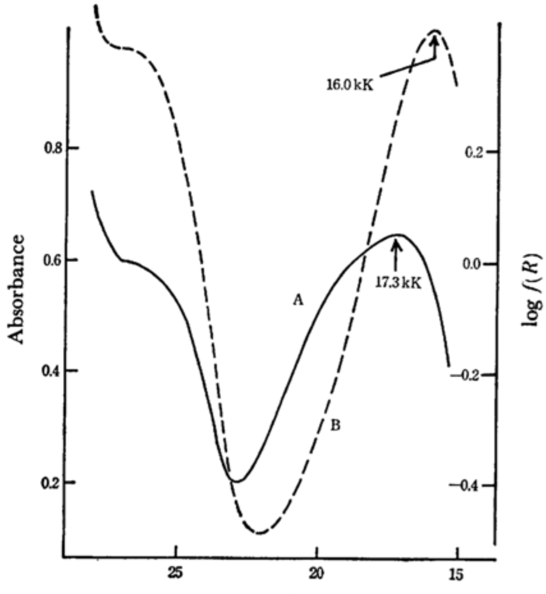

Fig. 2. The CT absorption spectra of TCNE complex with *trans*-4-methylstilbene.

A: The diffuse reflectance spectra (the complex, 9 mg; starch, 300 mg).

B: The absorption spectra in cyclohexane (the acceptor, 0.002 mol/*l*; the donor, 0.05 mol/*l*).

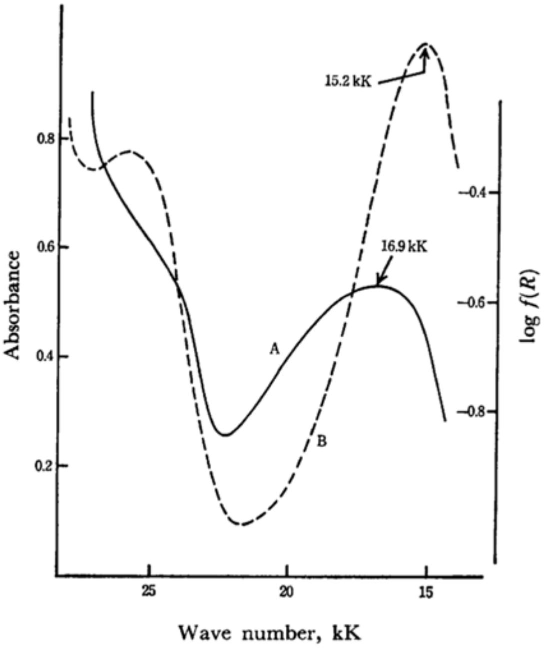

Fig. 3. The CT absorption spectra of TCNE complex with *trans*-4,4′-dimethylstilbene.

A: The diffuse reflectance spectra (the complex, 20 mg; starch, 400 mg).

B: The absorption spectra in cyclohexane (the acceptor, 0.002 mol/*l*; the donor, 0.05 mol/*l*).

CT bands further, the diffuse reflectance spectra of solid complexes have been measured (Figs. 1—3). In comparison with the absorptions in the solutions, the second CT bands of the solid complex appear in slightly lower wave-number regions. The first bands, on the other hand, shifts to considerably higher wave numbers. This blue shift of the CT band is extraordinary, since the frequencies of the absorption bands of crystals of TCNE complexes with polycyclic aromatic hydrocarbons are always lower than those observed with the solutions.4) Even in the case of solid complexes, the CT absorption bands are almost entirely determined by the interactions between donor and acceptor molecules in contact each other. This suggests that the configuration of TCNE complexes of *trans*-stilbene in solid media may be quite different from that in solution.

Analogously to the case of stilbene, many donor molecules with two benzene rings connected by essential single bonds are expected to have second highest occupied orbitals which are localized on

TABLE 2. THE CHARGE-TRANSFER ABSORPTION BANDS OF TCNE COMPLEXES WITH BIPHENYL AND THE RELATED COMPOUNDS IN METHYLENE CHLORIDE

Donor	The first band (kK)	The second band (kK)
Biphenyl	19.9±0.1	25.2±0.2
p-Terphenyl	18.0±0.1	25.5±0.2
Diphenyl ether	20.1±0.1	26.4±0.2
Diphenyl sulfide	17.0±0.1	26.0±0.2
Diphenylamine	13.0±0.1	26.3±0.2

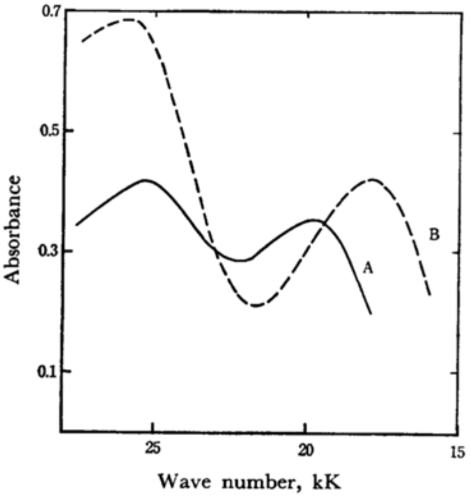

Fig. 4. The CT absorption spectra of TCNE complexes with biphenyl (A) and *p*-terphenyl (B) in methylene chloride.

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4) H. Kuroda, M. Kobayashi, M. Kinoshita and S. Takemoto, *J. Chem. Phys.*, **36**, 457 (1962).

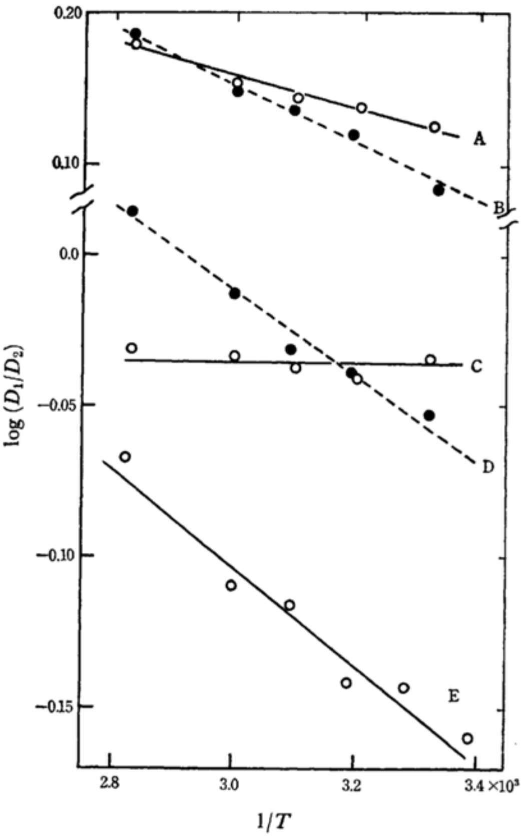

Fig. 5. The temperature dependences of the intensity ratios between the first and the second CT bands.

A: *p*-Terphenyl-TCNE complex
B: *trans*-α-Methylstilbene-TCNE complex
C: Naph-thalene-TCNE complex
D: *trans*-Stilbene-TCNE complex
E: Diphenylamine-TCNE complex

The absorbances at the absorption maxima of the first and the second CT bands are given by D_1 and D_2 respectively.

each benzene ring. The CT bands of TCNE complexes with such donors are summarized in Table 2. In contrast to the large variation in the first CT bands, the second CT bands remain relatively consistent throughout the complexes. In the case of the TCNE-*p*-terphenyl complex, it is also noticed that the intensity ratio between the first and the second CT bands is more than twice that in the TCNE-biphenyl complex (Fig. 4). Furthermore, the intensities of the two CT bands are found to show different temperature dependences, as Fig. 5 shows. The intensity ratio for the naphthalene complex, on the other hand, is independent of the temperature. Therefore, it is obvious that the CT complexes studied here can not be represented by the same single complex for each system and at various states. Briegleb, Czekalla, and Reuss have reported similar observations on the CT complexes of some condensed polycyclic aromatic hydrocarbons, and have suggested that the variation is due to the statistical fluctuation of the conformations.5)

Here the authors would like to suggest a model for the CT complexes. In the case of a donor molecule with a long, conjugated π-electron system, as has been studied here, there are several sites which may be used for association with an acceptor molecule. The donor-acceptor pairs associated at the different sites will give different CT spectra. As the first CT band of the TCNE-stilbene complex shows a large blue shift in solid media, the conformation of the complex in crystal form seems to be less suited to the CT interaction than that in solution. In other words, intermolecular interaction other than CT force are very important in determining the conformations of the complex in solid media. This type of intermolecular interaction is naturally expected to be present even in the case of complex in solution. As a consequence, the relative importance of the sites for the complex formation is expected to be strongly dependent on the nature of the media and on the temperature. The CT spectra of the system may, then, be affected by the same factors.

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5) G. Briegleb, J. Czekalla and G. Reuss, *Z. Phys. Chem. N. F.,* **30**, 316 (1961).