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Charge-Transfer Transitions Associated with Tricyanovinyl Aromatics[1]

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Four tricyanovinyl aromatic compounds were spectroscopically investigated in various phases. The solid-state spectra distinctly display both intra- and inter-molecular charge-transfer bands in the visible region. The formation of the charge-transfer self-complex is, however, markedly hindered in the fluid phases. The dual charge-transfer properties were also examined for these compounds.

When an electron-accepting moiety is directly bonded to an electron-donor molecule within a single electronic conjugate system, the uppermost filled valence orbital will be akin to that of the unsubstituted electron donor, the lowest vacant orbital being localized in the electron-accepting group.[3,4] As can easily be predicted from such an electronic structure, the first absorption band originates from the so-called intramolecular charge-transfer transition, *i.e.*, the transition between the two orbitals denoted above.

In some cases, specific intermolecular interactions are additionally observed for such a compound. The simultaneous presence of the intra- and inter-molecular charge-transfer transitions was first observed for 2,4,6-trinitro-*p*-terphenyl.[5] In a previous paper, we ourselves reported that two anisyl-*p*-benzoquinones form charge-transfer self-complexes in the solid state.[6] In this article, we would like to present other typical examples of intramolecular charge-transfer compounds, tricyanovinyl aromatics.

Experimental

Tetracyanoethylene (TCNE) often reacts with aromatic compounds to give the corresponding tricyanovinyl aromatics. Four tricyanovinyl aromatic compounds were prepared according to the method developed by Sausen *et al.*[7] The reaction products of *N*,*N*-dimethylaniline (DMA), pyrrole, indole, and 2,6-xylenol (xylenol) were *p*-(tricyanovinyl)-*N*,*N*-dimethylaniline (TCV-DMA), 2-(tricyanovinyl)-pyrrole (TCV-pyrrole), 2-(tricyanovinyl)-indole (TCV-indole), and 4-(tricyanovinyl)-2,6-xylenol (TCV-xylenol), respectively. All the absorption spectra were taken by using a Beckman DK-2A spectrophotometer.

Results and Discussion

Figures 1—4 show the absorption spectra of TCV-DMA, TCV-pyrrole, TCV-indole, and TCV-xylenol respectively in two phases. Every solution spectrum is composed of a single absorption band in the visible region. The absorption peaks are located at 19500 cm^{-1} ($\varepsilon_{\mathrm{max}}=5.78\times10^4$), 23800 cm^{-1} ($\varepsilon_{\mathrm{max}}=2.59\times10^4$), 21900 cm^{-1} ($\varepsilon_{\mathrm{max}}=2.13\times10^4$), and 23900 cm^{-1} ($\varepsilon_{\mathrm{max}}=2.88\times10^4$) for TCV-DMA, TCV-pyrrole, TCV-indole, and TCV-xylenol respectively in chloroform.

A similar tendency in transition energies is found among the charge-transfer bands of the TCNE complexes with parent aromatic compounds. The combinations of TCNE with DMA, pyrrole, indole, and xylenol induce the characteristic charge-transfer bands with maxima at 14300, 18800, 18600, and 19100 cm^{-1} respectively in chloroform. These values could not be observed accurately enough, since these donor-acceptor systems are quite reactive in solution. However, these charge-transfer bands are consistent with the first bands of the tricyanovinyl compounds in that a similar orderliness in transition energies is found in both cases. Such parallelism enables one to assign the latter bands to the intramolecular charge-transfer transitions. It is strongly suggested that the ionization potentials of the parent compounds increase in this order: $\mathrm{DMA} \ll \mathrm{indole} \le \mathrm{pyrrole} < \mathrm{xylenol}$. Actually, the vertical ionization potential of DMA (7.51 eV)[8] is much

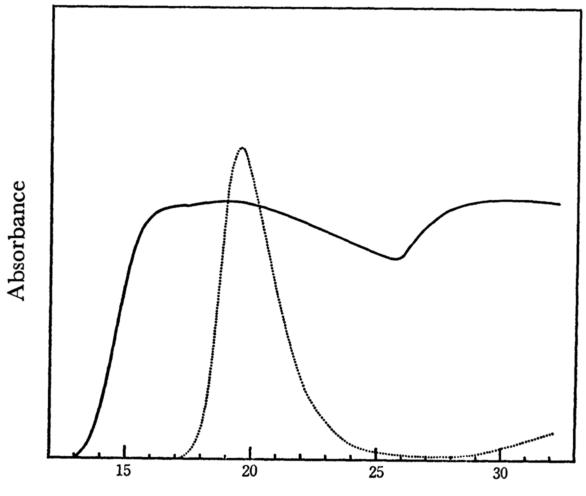


Fig. 1. Absorption spectra of TCV-DMA in chloroform solution (······), and in the solid state (——).

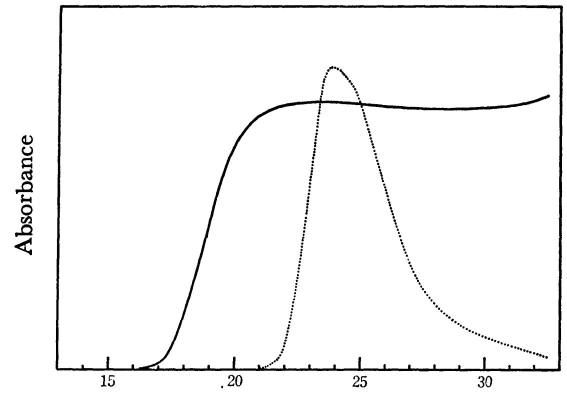


Fig. 2. Absorption spectra of TCV-pyrrole in chloroform solution (······), and in the solid state (——).

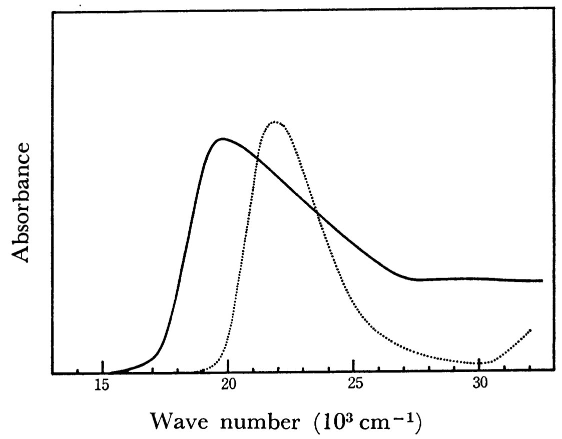
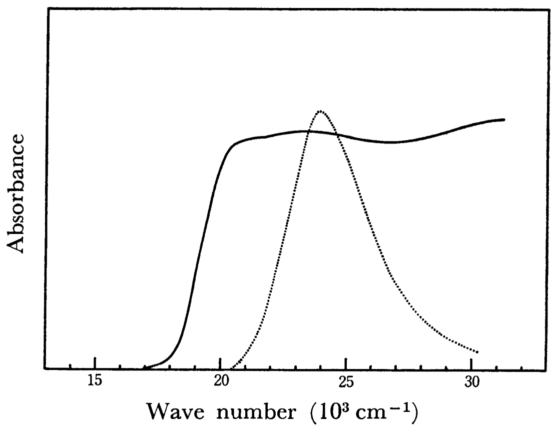


Fig. 3. Absorption spectra of TCV-indole in chloroform solution (······), and in the solid state (——).



Fig· 4. Absorption spectra of TCV-xylenol in chloroform solution (······), and in the solid state (——).

lower than that of pyrrole (8.21 eV),[9] though the other ionization potentials have not yet been determined. The smooth and isolated contour of the absorption band also characterizes the intramolecular charge-transfer transition. These absorption bands are very asymmetric, indicating that the 0–0 transitions are the strongest.

In view of the above discussion, the electron-donating orbital is supposedly located in the aromatic portion, whereas the tricyanovinyl group acts as an electron acceptor. Therefore, we can fully expect, in solution, the formation of the self-complex, where there would be a finite overlap between the donor orbital of one molecule and the acceptor orbital of a second molecule. However, the absorption spectra obtained over a 10^2-fold range of concentrations did not show any failure to obey Beer's law. No new bands were detected in the solution spectra.

If one takes into consideration the fact that 2,4,6-trinitro-*p*-terphenyl (TNTP) forms a self-complex in solution,[5] the behavior of tricyanovinyl compounds appears somewhat unusual. For example, the donor portion of TCV-DMA has more electron-donating ability than that of TNTP (diphenyl). The vertical ionization potential of diphenyl is 8.41 eV,[10] which is higher by 0.9 eV than that of DMA. On the other hand, the electron affinity of the trinitrophenyl moiety is considered to be similar to, or, more probably, less than that of the tricyanovinyl group, as will be discussed later. Since the contrast between the donor and acceptor orbitals is more striking for the tricyanovinyl compound, the dimerization in solution must have been hindered by some other effects, such as the unfavorable shapes of the molecular orbitals concerned.

On the other hand, the TCV-DMA crystal is deep blue and is in marked contrast with the deep red solution of the same compound. As is shown in Fig. 1, the gross absorption spectrum of the solid TCV-DMA is quite different from the solution spectrum in that the lower-energy part near 16000 cm^{-1} is much intensified in the former spectrum. The absorption peak around 19000 cm^{-1} in the solid-state spectrum corresponds well to the 19500 cm^{-1} band in the solution spectrum; it is assigned to the intramolecular charge-transfer transition.

Here, it must be noted that the intensified component near 16000 cm^{-1} is considered to be another absorption band. The presence of the two different bands is supported by the shape consideration of the spectrum. There is a distinct break, *i.e.*, an inflection point, around 17500 cm^{-1} in the solid-state spectrum. As may easily be seen, the intensity of the additional band on the low-energy side is comparable to that of the main band arising from the intramolecular transition. The first band can be attributed with little difficulty to the intermolecular transition. The spectral shape of TCV-xylenol also suggests that the solid-state spectrum consists of two different absorption bands in the visible region. By analogy with the case of TCV-DMA, the low-energy portion of the spectrum is considered to be due to the intermolecular interactions.

However, it is not clear whether or not the solid TCV-indole has the same spectral features. The whole spectrum appears to be composed of a single absorption band. The intramolecular absorption is supposedly covered by the predominant intermolecular charge-transfer band.

In connection with the above spectral behavior, one should remember the crystal structure of (2,2-dicyanovinyl)-ferrocene.[11] In the structure, the short distance between the dicyanovinyl moiety and the cyclopentadienyl ring of the adjacent molecule suggests, though not decisively, a donor-acceptor interaction analogous to that found in the molecular complex of ferrocene with TCNE. For another dicyanomethylene compound, 9-(dicyanomethylene)-2,7-dinitrofluorene, such self-complexing is postulated as giving rise to enhanced photoconductivity.[12] Therefore, the intermolecular interactions associated with tricyanovinyl compounds can similarly be considered to be of the charge-transfer type.

Various properties of tricyanovinyl compounds were first systematically studied by Sausen *et al.*[7] They compared these compounds with the corresponding dicyanovinyl compounds. It was then found that the investigated tricyanovinyl compounds show transition energies in ethanol about 0.4 eV lower than those of the dicyanovinyl counterparts. The extinction coefficients are smaller for the former group of compounds.

These facts imply that the tricyanovinyl group is considerably stronger as an electron acceptor than the dicyanovinyl group, and is probably stronger than the dicyanomethylene moiety. The larger electron affinity would more stabilize the charge-transfer self-complex, at least, in the crystal.

One might safely say that the self-complex formation is attained to 100 per cent in the crystal, if it is formed at all. Accordingly, the intensity of the additional band, *i.e.*, the intermolecular charge-transfer band, is comparable to that of the intramolecular charge-transfer band, as was suggested before.

However, the deep blue TCV-DMA crystal easily turns red upon being ground softly with sodium chloride. The dispersed material clearly shows the monomeric spectrum. The low-energy portion of the absorption spectrum diminishes rapidly on grinding. The evaporated film also shows a substantial decrease in the contribution of the intermolecular charge-transfer interactions to the spectrum. Such effects are also encountered among the other three tricyanovinyl compounds, though the change in color is rather modest. This aspect of the compounds in turn emphasizes the fragility of the charge-transfer interactions in the crystal as in solution.

The colors of the molten tricyanovinyl compounds are all similar to those of the corresponding solutions. The monomeric behavior of these compounds even in the pure melts would explain the behavior in solution, where the molecular association constants are obviously negligible. A free molecular motion seems easily to liberate these compounds from the dimerization in fluid phases. Such a situation is quite the same as for *o*-anisyl-*p*-benzoquinone.[6]

In order to estimate further the dual charge-transfer properties, *i.e.*, the electron-donating and -accepting abilities, of tricyanovinyl compounds, we examined the absorption spectra of the mixtures of these compounds with other typical electron donors and acceptors. Figure 5 shows the absorption spectra of TCV-pyrrole in the liquid DMA. The gross absorption spectra are very similar to the other solution spectra of this compound. However, a long absorption tail is noticeably preceded by the main band. For the four tricyanovinyl compounds, an absorption tail always begins at about 15000 cm^{-1}. Accordingly, the absorption tail of TCV-DMA is almost degenerate with the main band in DMA.

Such an absorption tail can be considered as a part of the charge-transfer band arising from the intermolecular interactions. In other words, it is related to the transition from the highest filled orbital of DMA to the lowest vacant orbital of the tricyanovinyl compound. The absorption tail is dependent on the ionization potential of the electron donor. When aniline is employed as a solvent, the edge of the absorption tail advances to about 16500 cm^{-1}. The absorption spectra taken in α-methylnaphthalene do not show any absorption tails. Instead, the absorbance in the higher-energy region around 25000 cm^{-1} increases to some extent. Considering that the absorption tails are preserved at almost the same photon energies in a given solvent for the four tricyanovinyl compounds, the electron-accepting ability should be similar among them. This fact further supports the previously-mentioned idea that the acceptor orbital is mainly localized in the tricyanovinyl moiety of the compound.

Since the absorption peak of the charge-transfer band could not be detected in these systems, the accurate estimate of the electron affinity was made difficult for the tricyanovinyl compound. However, by comparing the absorption edge of any compound to those of many other electron acceptors in the same donor solvent, it is not impossible to determine roughly the electron affinity of the compound. In the present case, the absorption edge of 1,3,5-trinitrobenzene (TNB) is found to fit well that of TCV-pyrrole in DMA, as is shown in Fig. 5. Therefore, the electron affinity of the tricyanovinyl compound is estimated to be similar to that of TNB, which is approximately 1.9 eV.[13]

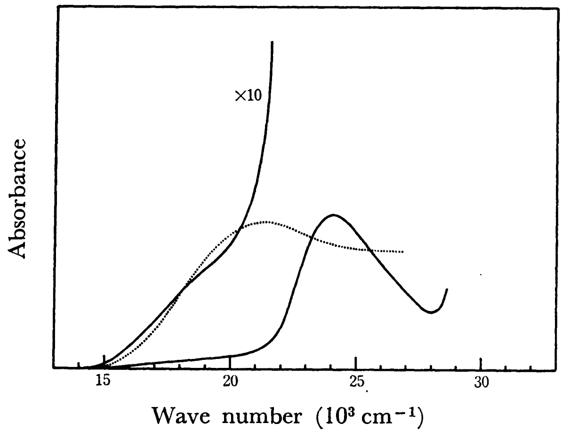


Fig. 5. Absorption spectra of TCV-pyrrole (——), and TNB (······) in DMA solution.

On the other hand, no combinations of such tricyanovinyl compounds with typical electron acceptors, such as TCNE and chloranil, exhibited any intermolecular interactions supported by the absorption bands. The ordinarily-prepared solution is seemingly too deficient in concentration for the intermolecular charge-transfer to be observed. The small association constants between them are easily inferrable from the case mentioned above, where the additional absorption band of the tricyanovinyl compound is still weak in a pure donor solvent, such as DMA. If any strong acceptor were employed as a solvent, the charge-transfer band could be appreciably detected. At present there are no solvents suitable for this purpose. However, the absorption band of the self-complexed TCV-DMA in the solid suggests that the ionization potential of the isolated TCV-DMA is not very different from that of DMA and is possibly somewhat smaller than that.

In summary, tricyanovinyl aromatics are typical intramolecular charge-transfer compounds. Though they are considered to be at once good electron acceptors and good electron donors, every aspect of the absorption spectra is consistent with quite small association constants of these compounds, either with any other partner molecules or with themselves.

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