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The Absorption and Fluorescence Spectra of the Ion-Pairs of 1,2,4,5-Tetracyanobenzene with Several Methyl Substituted Benzenes

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The absorption and fluorescence spectra and the fluorescence decay times were measured at 77 K for the photoirradiation products of the 1,2,4,5-tetracyanobenzene (TCNB) complexes with hexamethylbenzene (HMB), durene, mesitylene, and toluene. The absorption spectra of the photoproducts are similar in shape to that of the TCNB anion and have maxima at 469, 467, 466, and 465 nm for the TCNB complexes with HMB, durene, mesitylene, and toluene, respectively. The fluorescence maximum wavelengths and decay times of the photoproducts are also similar to those of the TCNB anion (505 nm, 19.6 ns for the TCNB–mesitylene system; 505 nm, 20.7 ns for the TCNB-toluene system). The red shift of the absorption maximum and the decrease in the fluorescence decay time by changing the electron donors from toluene to HMB are discussed in terms of ion-pair formation.

Only a few electron donor–acceptor (EDA) complexes have been found to emit fluorescence in fluid solutions and even those which are fluorescent in nonpolar fluid solutions become nonfluorescent in polar fluid solutions.1,2) In connection with the fluorescence quenching, the ionic dissociation of EDA complex in their excited states has been studied.3) Sofue and Nagakura4) reported that flash irradiation of 1,2,4,5-tetracyanobenzene (abbreviated hereafter to TCNB) in such polar solvents as diethyl ethyl ether and acetonitrile at room temperature produces the TCNB anion. Achiba *et al.*5) studied in more detail the TCNB complexes with tetrahydrofuran and other complexes (in dichloromethane) and observed charge-transfer (CT) bands. Furthermore, they found that the ionization takes place by the excitation in the CT band. Masuhara *et al.*6) reported that such weak CT complexes as the TCNB–toluene system dissociate spontaneously into ions in their excited CT singlet states in polar solvents.

In the present paper, we report that TCNB complexes with methyl substituted benzenes in diethyl ether-isopentane (1: 1) mixed solvent produce stable ion-pairs at 77 K by excitation in their CT bands.7) Subsequent to our study, Achiba and Kimura also obtained similar results for TCNB-2-methyltetrahydrofuran.8)

Experimental

Commercially available TCNB (Frinton, GR grade) used as an electron acceptor was purified by sublimation *in vacuo.* Hexamethylbenzene (abbreviated hereafter to HMB) (Tokyo Kasei, GR grade) was purified by repeated recrystallizations and thereafter by sublimation *in vacuo.* Durene (Tokyo Kasei, GR grade) was purified by repeated recrystallizations from ethanol, and thereafter by repeated zone refinings (about 50 times). Spectrograde toluene (Dotite) was used without further purification. Commercially available mesitylene (Tokyo Kasei, GR grade) was purified by distillation. Diethyl ether and isopentane were purified by the usual methods. The samples in a mixed solvent of diethyl ether–isopentane (1: 1) (hereafter abbreviated to EP) were excited by a 100 W high-pressure mercury lamp at 77K. By using appropriate filters, the samples were exposed to and excited by light with a frequency corresponding to the CT band. The absorption spectra of the photoproducts were measured by the use of a Cary recording spectrophotometer, model 14R. The fluorescence spectra were measured with a grating monochromator (Spex model 1704) with an EMI 9558B photomultiplier as a detector and a 100 W high-pressure mercury lamp as the excitation source. Fluorescence lifetimes were measured by using a dye laser (4-methylumbelliferone; 460 nm) pumped by an Avco Everett model 950 nitrogen laser (peak power, 100 kW; pulse width, 10 ns) as a pulsed excitation light source and by using an HTV 1P28 photomultiplier combined with an oscilloscope (Hitachi, model V1000) as a detector.

Results and Discussion

TCNB in EP at 77 K was directly irradiated by a 100 W high-pressure mercury lamp. Several minutes after the excitation, the irradiated portion of the sample was colored. The absorption and emission spectra of the photoproduct are shown in Figs. 1 and 2, respectively. The absorption spectrum with a maximum at 460 nm9) and with a vibrational structure is quite similar to that of the TCNB anion in acetonitrile.4) Therefore the photoproduct can safely be assigned to the TCNB anion. The fluorescence spectrum is broad and structureless, with a maximum at 500 nm. The fluorescence lifetime was found to be 21.3 ns.

The TCNB–HMB system in EP was irradiated at 77 K by a 100 W high-pressure mercury lamp through a Toshiba UV-39 filter and a TCNB (in methylene chloride) solution filter. With these filters, the complex was

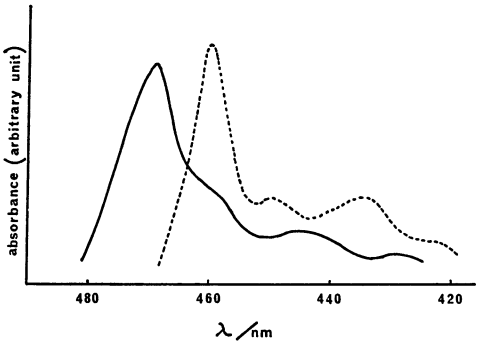

Fig. 1. The absorption spectra of the irradiated EP solution of TCNB (---) and the TCNB–HMB complex (—) at 77 K.

excited only in its CT band. After the irradiation of the sample for several minutes, we obtained a photoproduct with an absorption maximum at 469 nm (Fig. 1). The absorption spectrum of the photoproduct resembles that of the TCNB anion, although the former slightly shifts to longer wavelengths and is a little broader than the latter. The concentrations of the photoproducts were found to be proportional to the exciting light intensity. Therefore, the photo-process is a one photon process.

Table 1. The maximum wavelengths of the absorption and fluorescence spectra (λ_a and λ_f, respectively), Stokes shifts ($\Delta\nu$), and the fluorescence lifetimes (τ_f) observed with the TCNB anion and the ion-pairs of the TCNB anion and the methyl substituted benzene cations

Donor	λ_a(nm)	λ_f(nm)	$\Delta\nu$(10^3 cm^{-1})	τ_f(ns)
HMB	469			
Durene	467			
Mesitylene	466	505	1.66	19.6
Toluene	465	505	1.70	20.7
TCNB anion only	460	500	1.74	21.3

Similar measurements have been made with the systems containing TCNB as an electron acceptor and durene, mesitylene, and toluene as electron donors; their absorption maxima were observed at 467, 466, and 465 nm, respectively (see Table 1). Thus, the absorption maxima of the photoproducts shift to longer wavelengths with the increasing number of the methyl groups in the donor.

The photoproducts have another common feature: they emit intense fluorescence. The fluorescence spectra and decay times of the photoproducts were measured for the TCNB–mesitylene and TCNB–toluene systems.$^{10)}$ The observed fluorescence spectra are shown in Fig. 2, and the maximum wavelengths, Stokes shifts, and decay times are given in Table 1. The fluorescence spectra of the photoproducts$^{11)}$ shift only slightly to longer wavelengths and their fluorescence decay times are only a little shorter compared with the corresponding quantities of the TCNB anion in EP. The Stokes shifts obtained from the absorption and emission spectra of the photoproducts are 1660 and 1700 cm^{-1} for the TCNB–mesitylene and TCNB–toluene systems, respectively. These values are similar to the value for the TCNB anion, 1740 cm^{-1}. The fluorescence excitation spectra were measured with the TCNB–mesitylene and TCNB–toluene systems. Their maximum positions agree well with those of absorption spectra of the respective systems within the limitations of experimental error and their vibrational structures are similar to that of the corresponding absorption spectra.

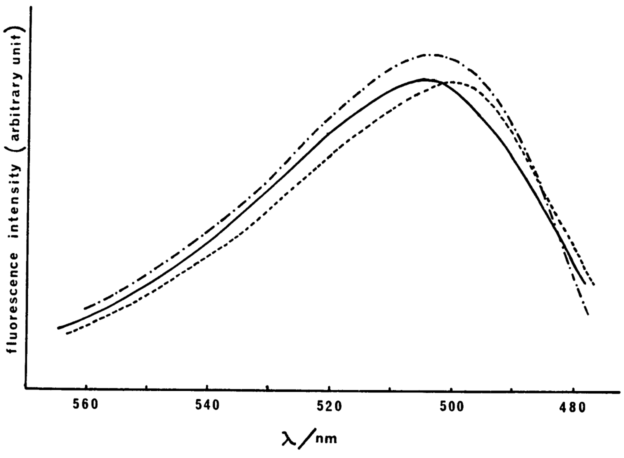

Fig. 2. The fluorescence spectra of the TCNB anion (------) and of the ion-pairs: TCNB$^-$–toluene$^+$(——) and TCNB$^-$-mesitylene$^+$(-·-·-) at 77 K.

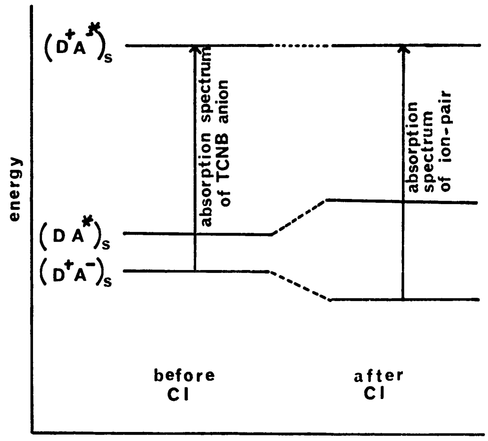

Fig. 3. The schematic energy diagrams of the ion-pair before and after configuration interaction. ( )$_s$ indicates the state after solvation.

The above-mentioned results for the absorption and fluorescence spectra, the fluorescence decay times, and the fluorescence excitation spectra show that the photoproducts are the TCNB anion perturbed by some chemical species. From the fact that a counter cation is formed in a pair with the TCNB anion for the electron-donor-acceptor system at 77 K in the rigid medium, it is reasonable to consider that the perturbing chemical species is the donor cation which forms an ion-pair with the TCNB anion. The identification of the photoproducts is supported by the following considerations about the peak wavelengths of the absorption spectra and the fluorescence decay times.

(i) In the ion-pair, the zero-order locally (within TCNB) excited state (DA*) is probably located above the zero-order ion-pair state (D^+A^-), and the two can interact. This interaction stabilizes the ion-pair state and increases the transition energy of the absorption band of the TCNB anion (see Fig. 3). The interaction depends on the energy separation, ΔE, and overlap, S, between the appropriate orbitals belonging to D and A. With the decreasing ionization potential, I_p, of the donor, namely, with the increase in the number of the methyl groups on the donor, $n(CH_3)$, the D^+A^- state becomes lower and ΔE increases. Furthermore, with the increase in $n(CH_3)$, the distance between the TCNB anion and the donor cation may increase because of the increasing steric hindrance, and S is expected to decrease.$^{12)}$ Thus, we can expect that the stabilization of the D^+A^- state due to the interaction with the DA* state decreases with the increase in $n(CH_3)$. From this we can explain the observed shift of the absorption maximum with $n(CH_3)$ of the donor.[13)]

(ii) The decrease in the fluorescence decay time with the decreasing I_p of the donor may be tentatively explained in the following way: The radiative transition moment may decrease with the increasing DA* character of the ion-pair in the ground state, which is represented by D^+A^-, since the observed fluorescence corresponds to an allowed transition of the TCNB anion. As described above, the contribution of the DA* state to the ground state of the ion-pair increases with the decrease in $n(CH_3)$. Thus, the decrease in the radiative lifetime of S_1 with the decreasing I_p of donor can be explained. A similar tendency was also observed for the TCNB complexes with methyl substituted benzenes in both fluid and rigid nonpolar solvents, and was explained in the same way.[2)]

Thus the TCNB complexes with methyl substituted benzenes produce stable ion-pairs at 77 K by excitation in their CT bands.

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9) The absorption band at 460 nm shifts to 462 nm at room temperature (295 K) for a degassed solution.

10) The fluorescence spectra of the photoproducts could not be measured for the TCNB–HMB and TCNB–durene systems. It is difficult to separate them from the fluorescence spectra of the corresponding molecular complexes because of the large overlap.

11) The fluorescence spectra are broad (bandwidth 1700—1800 cm^{-1}) and structureless while the corresponding absorption spectra show a vibrational structure. This implies that a rather large change in the geometrical configuration of the photoproduct and in the orientation of the surrounding solvent molecules takes place in the excited state.

12) Since the ion-pair is formed by the excitation in the charge-transfer absorption band of the complexes in the rigid solvents, it is reasonable to consider that no solvent molecule intervenes between the TCNB anion and the donor cation. The molecular planes of the components in the ion-pair may be parallel with each other as are those in the parent complex. The exchange interaction between the components may exist in both the ion-pair and the parent CT complex, although it may decrease in the former.

13) The fact that the photoproduct of the TCNB–EP system shows its absorption maximum at a shorter wavelength (460 nm) than the TCNB–toluene complex can be explained by the interaction between D^+A^- and DA*. The ΔE value may conceivably be larger for the TCNB–diethyl ether than for the TCNB–toluene. The finding that the fluorescence decay time is longer for the TCNB–EP system than for the TCNB–toluene system can be explained along the same lines.