Charge-Transfer Complex Formation between Stilbenes and 7,7,8,8-Tetracyanoquinodimethane

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Formation of intermolecular charge-transfer complexes between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and two different series of stilbene derivatives has been studied spectroscopically at 25 °C in 1,2-dichloroethane. The compounds of Series I include stilbene and stilbene derivatives which have fused phenyl rings on one end of the central ethylene structure and a phenyl ring on the other end. The other Series, II, is comprised of stilbenes which have various para substituents on one of the two phenyl rings. The equilibrium constant, K_C^{AD}, and the molar extinction coefficient, ϵ_λ^{AD}, were determined using the Scott equation. The values of the charge-transfer transition frequency, ν_{AD}, and K_C^{AD} correlated well respectively with the ionization potentials of the fused rings of Series I or of the compounds of Series II and with the values of σ_p, the Hammett constants of the Series II substituents. *trans*-4-N,N-Dimethylaminostilbene and *trans*-4-nitrostilbene were found to be able to participate in electron transfer reaction with TCNQ forming the corresponding anion radical, TCNQ⁻:

Introduction

Formation of charge-transfer complexes between π-donors and π-acceptors has been a subject of numerous reports, since Mulliken,[1,2] Benesi and Hildebrand[3] and others[4-10] made theoretical and experimental contribution to the understanding of charge-transfer phenomena between donors and acceptors. In general, π-acceptors contain electron-withdrawing groups and π-donors electron-donating substituents.

Iodine, 2,3-dichloro-5,6-dicyano-p-benzoquinone, fluoranil, tetracyanoethylene and TCNQ are some of the important examples of acceptors. Representative examples of π-donors include benzene, stilbene, tetrathiofulvalene and their derivatives. Owing to the many systematic studies reported, the relationship between the structure of a compound and its ability to accept or donate π-electrons in complex formation is relatively well established. The electron affinities of acceptors, the ionization potentials of donors and the Hammett constants of substituents are the most important properties with regard to structure and reactivity in charge-transfer complex formation.[7]

In 1970's it was also found that some of charge-transfer complexes are electro-conducting. Good charge-transfer complex conductors are formed between good donor and acceptor pairs whose molecular shapes are flat.[11-13]

In this investigation we have studied the formation of charge-transfer complexes between TCNQ and two series of *trans*-stilbenes whose structures are shown below:
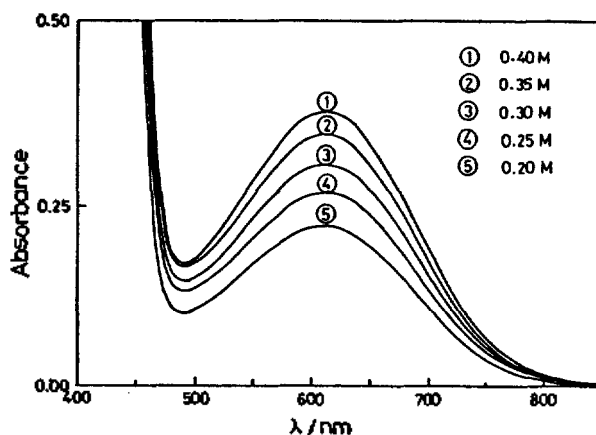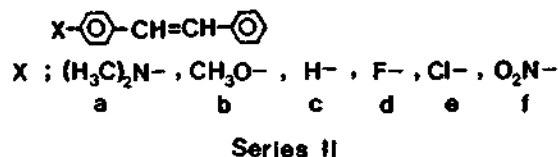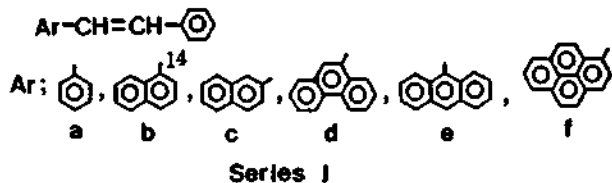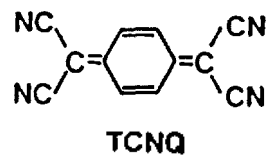
Ar–CH=CH–⬡

Ar : ⬡, ⬡⬡[14], ⬡⬡, ⬡⬡, ⬡⬡⬡, ⬡⬡⬡
     a   b   c   d   e   f

Series I

X–⬡–CH=CH–⬡

X : $(H_3C)_2N-$, CH_3O- , $H-$, $F-$, $Cl-$, O_2N-
     a   b   c   d   e   f

Series II

Figure 1. Absorption spectra of *trans*-stilbene (Ia)/TCNQ solutions in 1,2-dichloroethane at various donor concentrations (Concentration of TCNQ was 1.0×10^{-3}M).

① 0.40 M
② 0.35 M
③ 0.30 M
④ 0.25 M
⑤ 0.20 M

TCNQ

Compounds I have fused rings on the one end of the central ethylene, while compounds II contain various para substituents on one of the phenyl rings.

Complex formation between TCNQ and stilbene derivatives was studied by u.v.-visible spectrometry. The equilibrium constant, K_C^{AD}, and molar extinction coefficient, ϵ_λ^{AD}, of complexes were determined using a modified Benesi-Hildebrand equation,[3] the Scott equation[4]:
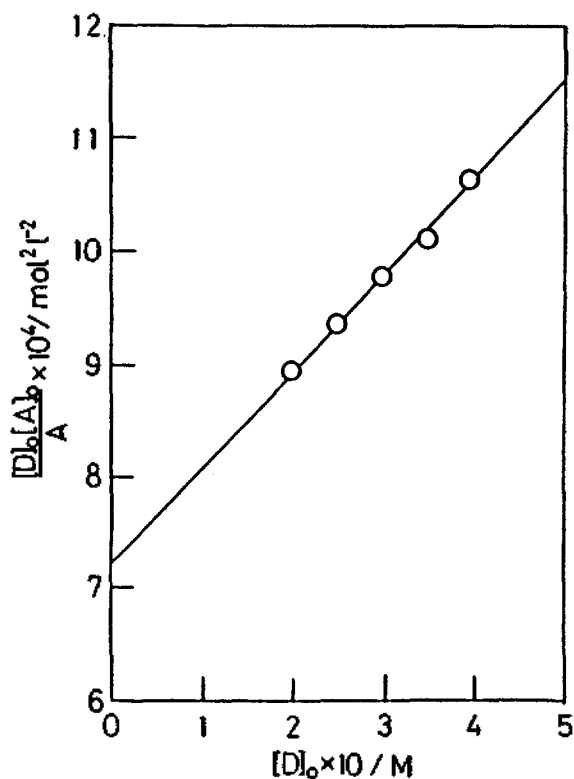
$$\frac{[A]_o [D]_o}{A} = \frac{1}{K_C^{AD} \cdot \epsilon_\lambda^{AD}} + \frac{[D]_o}{\epsilon_\lambda^{AD}}$$

where $[A]_o$ and $[D]_o$ are the initial concentrations of an acceptor and a donor, respectively, and A is the absorbance of the charge-transfer band. This equation is valid for the case of $[D]_o \gg [A]_o$ and where the donor and acceptor pair forms an 1:1 complex.

Table 1. Formation Constants (K_c^{AD}) for the Charge-transfer Complexes Between Series I compounds and TCNQ

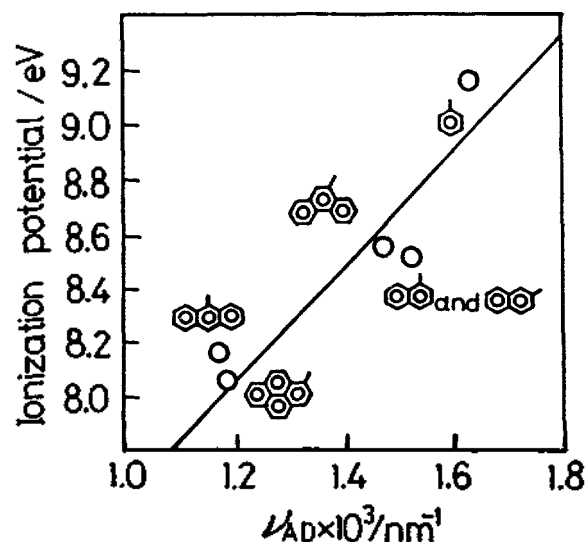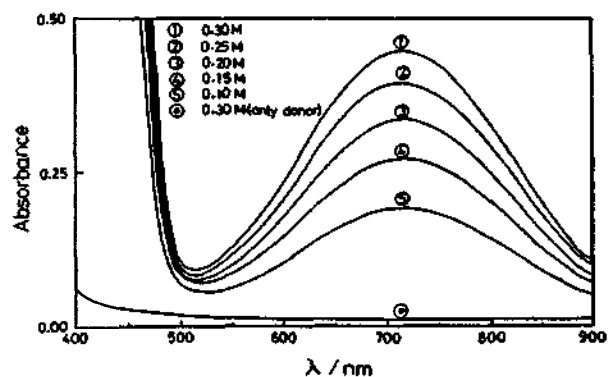| Compounds	λ_{max}^{D}/nm	λ_{max}^{AD}/nm	ϵ_λ^{AD}/lmol^{-1}cm^{-1}	K_c^{AD}/lmol^{-1}
Ia	320	611	1199	1.14
Ib*	325	658	588	2.40
Ic	334	660	1278	2.04
Id	320	680	890	2.76
Ie	350	855	536	5.50
If	372	850	1381	9.81

* Data quoted from reference 14.

Figure 2. Scott's plot for *trans*-stilbene (Ia)/TCNQ solutions in 1,2-dichloroethane.

Figure 3. Relationship between ν_{AD} and ionization potential.

Figure 4. Absorption spectra of *trans*-4-methoxystilbene (IIb)/ TCNQ solutions in 1,2-dichloroethane at various donor concentration (*; spectrum of *trans*-4-methoxystilbene (IIb) at 0.30 M).

Results and Discussion

Complex Formation between Series I Compounds and TCNQ. All of the Series I compounds, when mixed with TCNQ in 1,2-dichloroethane, exhibited distinct charge-transfer absorption bands in the visible region (Figure 1 and Table 1). Figure 2 shows the Scott's plot for the *trans*-stilbene (Ia)/TCNQ pair, from which the values of K_c^{AD} and ϵ_λ^{AD} were obtained to be 1.14 1 mol^{-1} and 1199 1 mol^{-1}cm^{-1}, respectively. Neither donor nor acceptor absorbs any light at wavelength greater than 500 nm. The satisfactory linear plot is an indication of the formation of an 1:1 donor-acceptor complex.

Similar experiments and analyses were performed for the pairs formed by the remaining Series I compounds and TCNQ. The results are summarized in Table 1. The values of K_c^{AD} and λ_{max}^{AD} increased with the number of fused rings in the donor molecules. This implies that the ability of a compound to donate π-electron to the acceptor molecule, TCNQ, increases with the number of fused rings, while the energy of charge-transfer band decreases. When we plot the values of

ν_{AD}, *i.e.* of 1/ λ_{max}^{AD} against the ionization potentials of the fused rings,[6,10] a linear relationship is approximated as shown in Figure 3. This observation is in line with Weiss' hypothesis[15] that a low ionization potential of a donor molecule stabilizes the complex. Similar observations were made earlier for many other donor-acceptor series,[16] especially when steric hindrance was absent. We, however, could not observe any correlation between the values of ϵ_λ^{AD} and the structures of donors.

Complex Formation between Series II Compounds and TCNQ. The compounds of Series II also formed 1:1 complexes with TCNQ. Representative spectra and Scott's plot are shown in Figures 4 and 5 for *trans*-4-methoxystilbene (IIb) and TCNQ pair. The values of K_c^{AD} and ϵ_λ^{AD} obtained for this pair from Figure 5 were 1.65 1 mol$^-$ and 1305 1 mol^{-1}cm^{-1}, respectively. They are included in Table 2 together with values for other Series II pairs. The values of K_c^{AD} and λ_{max}^{AD} increase with the electron donating power of the stilbene substituent. This relationship can be clearly presented when the values of log K_c^{AD} and ν_{AD} are plotted against the Hammett σ_p values[17,18] of the substituents and the ionization potentials of the donors respectively (Figure 6).

As expected, the lower is the σ_p value, the higher is the value of K_c^{AD}. A linear relationship seems to exist between
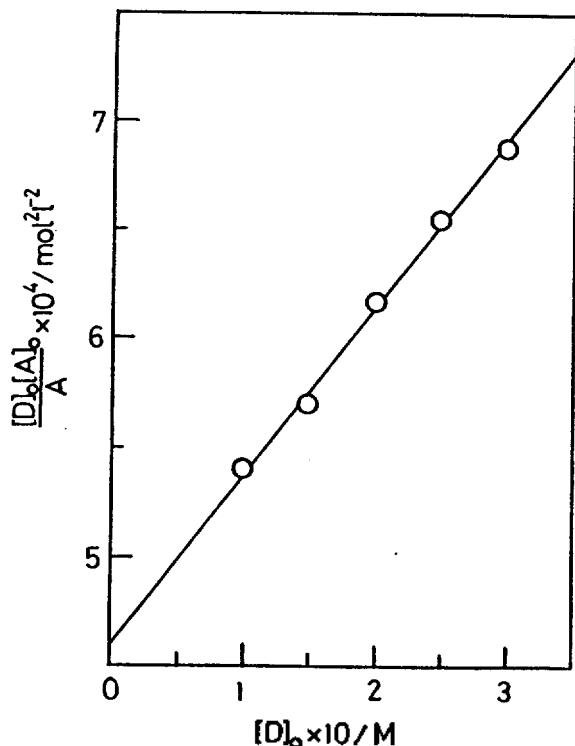
Figure 5. Scott's plot for *trans*-4-methoxystilbene (IIb)/TCNQ solutions in 1,2-dichloroethane.

Figure 7. Time dependence of absorption spectra of *trans*-4-N,N-dimethylaminostilbene(IIa) $(1.0 \times 10^{-3}$ M)/TCNQ $(1.0 \times 10^{-3}$ M) in 1,2-dichloroethane.

Table 2. Formation Constants(K_c^{AD}) for the Charge-transfer Complexes Between Series II compounds and TCNQ

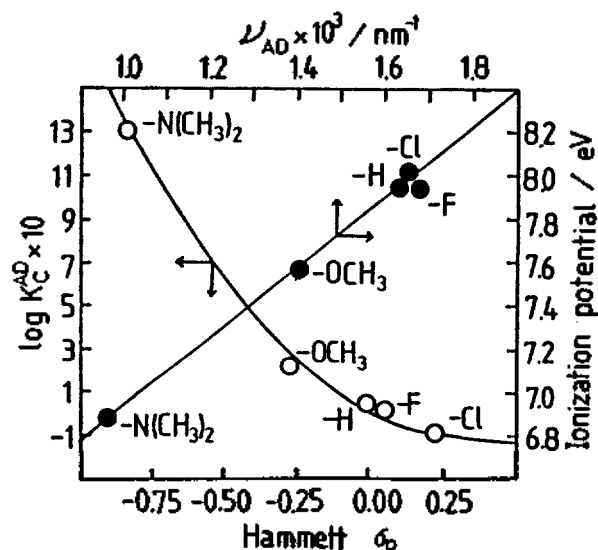| Compounds	λ_{max}^{D}/nm	λ_{max}^{AD}/nm	ϵ_{λ}^{AD}/1mol^{-1}cm^{-1}	K_c^{AD}/1mol^{-1}
IIa	348	1045	1278	20.0
IIb	317	715	1305	1.65
IIc	320	6₁1	1199	1.14
IId	340	599	859	1.06
IIe	348	605	1244	0.82

Figure 6. Plots of log K_c^{AD} vs. σ_p and ν_{AD} vs. ionization potential.

ν_{AD} and ionization potential of the donors, though the number of data is rather limited. The experimental points for *trans*-4-N, N-dimethylaminostilbene(IIa)/TCNQ pair are not shown in the figure for the reason to be discussed below.

Electron Transfer Reaction between trans-4-N,N-Dimethylaminostilbene(IIa) or trans-4-Nitrostilbene(IIf) and TCNQ. The u.v.-visible spectrum of the *trans*-4-N,N-dimethylaminostilbene(IIa) and TCNQ pair was peculiar in that it initially revealed a charge transfer absorption band at λ_{max} = 470nm, but then its intensity slowly decreased with time. Meanwhile, three groups of new bands, with λ_{max} of 685, 749 and 851nm appeared and their intensities grew with time (Figure 7). Comparing the absorption profile of these
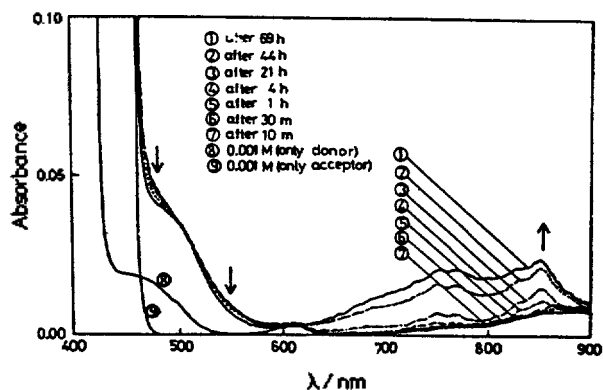
new absorption bands with that of Li$^+$TCNQ$^-$, we arrived at the conclusion that TCNQ anion radicals, TCNQ$^-$, probably are formed by an electron transfer reaction between the donor and the acceptor. It was reported previously by Melby *et al.*[5] that a similar electron transfer reaction occurred between N,N,N',N'-tetramethyl-*p*-phenylenediamine and TCNQ to form TCNQ$^-$ and Wurster's blue cation radical. Tomono *et al.*[19] also studied electron transfer reactions between amines and TCNQ, concluding that electron transfer proceeded through direct reaction between the donor and the acceptor, but not through complex formation. We, however, do not yet have enough experimental evidence to propose a reaction mechanism for our observation.

Figure 7 also indicates that, under the condition used in this investigation, the electron transfer reaction between *trans*-4-N,N-dimethylaminostilbene(IIa) and TCNQ is very slow. Therefore, we tried to determine the values of K_c^{AD} and ϵ_{λ}^{AD} of this pair in spite of the electron transfer reaction observed. We found that spectroscopic analysis of the complex solutions at λ_{max} of 1045 nm, after being kept for 30 minutes at room temperature, gave a satisfactory Scott's plot. From this, the values of 20.0 1 mol^{-1} and 1278 1 mol^{-1}cm^{-1} were obtained for K_c^{AD} and ϵ_{λ}^{AD} respectively (Table 2).

We performed a preliminary study on the electron transfer reaction. An equimolar mixture $(2.18 \times 10^{-3}$M) of *trans*-4-N,N-dimethylaminostilbene (IIa) and TCNQ in 1,2-dichloroethane was refluxed under a nitrogen atmosphere. The concentration increased with time of the TCNQ$^-$ formed was spectroscopically followed at a wavelength of 851 nm. The molar extinction coefficient of TCNQ$^-$, determined using a Li$^+$TCNQ$^-$ solution was 1.52×10^5 1 mol^{-1}cm^{-1}. This value was used for the quantitative analysis of the electron transfer reaction. The experimental results shown in Figure
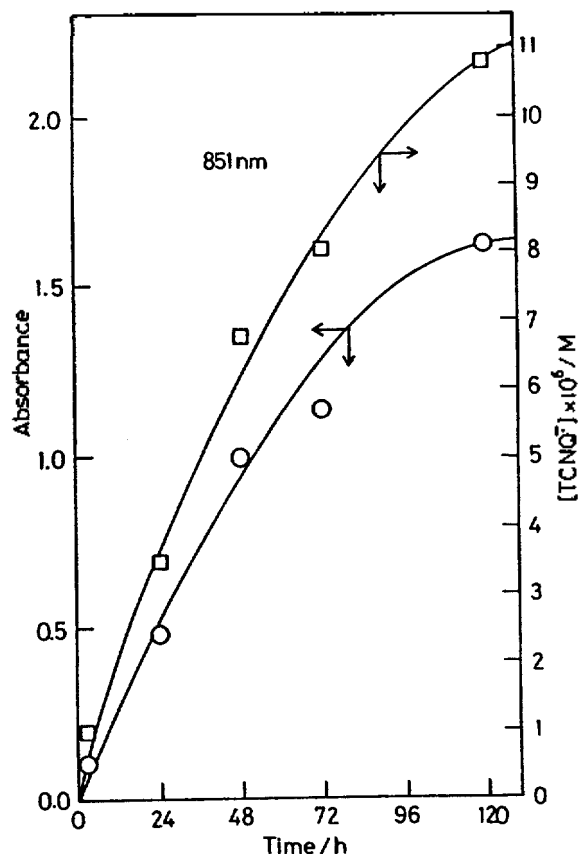
Figure 8. Time dependence of TCNQ⁻ formation in a mixture of *trans*-4-N,N-dimethylaminostilbene (IIa) and TCNQ in 1,2-dichloroethane.

8 reveal a linear relationship, in the early stage of reaction, between the concentration of TCNQ⁻ formed and the reaction time, and then a diminished rate of increase in the concentration of TCNQ⁻ with time.

Finally we also observed the formation of TCNQ· from the mixtures of *trans*-4-nitrostilbene (IIf) and TCNQ. The electron transfer reaction between the two compounds was much faster than that between the previous pair. This caused difficulties in the determination of the values of K_c^{AD} and ϵ_λ^{AD}. On standing, the mixture formed an insoluble material which was believed to be the salt resulted from the electron transfer reaction. We have a strong indication that the nitro group, but not the conjugated aromatic part of the molecule, is playing a major role in this reaction.[20] This conclusion is drawn from the observation that, even when nitromethane, instead of *trans*-4-nitrostilbene, was mixed with TCNQ in 1,2-dichloroethane, the formation of TCNQ⁻ was evident in spectroscopic studies. Further research is needed before any further discussion on this reaction can be presented.

Conclusion. The following conclusions can be drawn from the present investigation: (1) All of the stilbene derivatives examined in this study formed charge-transfer complexes with TCNQ. (2) Well defined values of K_c^{AD} and ϵ_λ^{AD} could be obtained by u.v.-visible spectroscopic analysis of the donor-acceptor solutions using the Scott equation. (3) The values of K_c^{AD} and ν_{AD} could be correlated with the Hammett σ_p values (Series II) of the substituents and the ionization potentials of the donors (Series I and II). (4) *trans*-4-N,N-Dimethylaminostilbene (IIa) and *trans*-4-nitrostilbene (IIf) undergo electron transfer reaction with TCNQ.

Experimental

Synthesis of Stilbene Derivatives. All of the stilbenes used in the present study are known compounds and were prepared by literature procedures.[21-26] The trans compounds of 2-(2-phenylethenyl)naphthalene(Ic), 9-(2-phenylethenyl)phenanthrene (Id), 9-(2-phenylethenyl)anthracene(Ie), 1-(2-phenylethenyl)pyrene (If), 4-N,N-dimethylaminostilbene (IIa), 4-fluorostilbene (IId), 4-Chlorostilbene (IIe), and 4-nitrostilbene (IIf) were prepared by reacting benzyltriphenylphosphonium chloride and the corresponding aldehydes (Aldrich) in ethanol or *t*-butanol using sodium ethoxide or *t*-butyllithium as a base. All of the initial Wittig reaction products were digested in a dilute iodine solution in benzene. The final products were recrystallized from ethanol. Their melting points were identical to literature values and their i.r. and n.m.r. spectra were consistent with the expected structures.

trans-4-Methoxystilbene[27], however, was prepared via a modified Wittig reaction. Benzyl chloride was first reacted with triethylphosphite to form diethylbenzylphosphonate, which was then reacted with *p*-methoxybenzaldehyde (Aldrich) in DMF using sodium methoxide as a base. The crude product was recrystallized from ethanol. Its melting point (135 °C) was in agreement with the literature value and its i.r. and n.m.r. spectra were consistent with the expected structure.

Spectroscopic Study of Complex Formation. All of the spectroscopic study of complexation between TCNQ and the various stilbenes were made at 25 °C on a Cary 17D u.v.-visible spectrometer. 1,2-Dichloroethane was the solvent used throughout the present investigation.

The acceptors' concentration was kept constant either at 1.0×10^{-3}M or 1.0×10^{-4}M and the donors' concentrations were varied from 0.1M to 0.4M. Five to eight solutions of different concentrations were employed for spectroscopic analyses. The solutions were allowed to stand at room temperature for 12 hours before use. The solution of IIa and TCNQ, however, was allowed to stand only for 30 minutes before use in order to minimize the effect of the possible electron transfer reaction between the pair as known for N,N, N',N'-tetramethyl-*p*-phenylenediamine and TCNQ.[5,19] The values of K_c^{AD} and ϵ_λ^{AD} were obtained from the Scott's plot. The slope and the intercept of the plots were estimated using a least mean square method.

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Spectra of Piroxicam

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Solvent Dependence of Absorption and Fluorescence Spectra of Piroxicam. A Possible Intramolecular Proton Transfer in the Excited State

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The spectral properties of piroxicam in different solvents are similar to those of its skeletal precursor, HMBDC. The maximum absorption and emission wavelengths strongly depend on the hydrogen bonding ability of the solvent, and it is shown that intramolecular hydrogen bonding between the –OH and the ortho carbonyl group of the parent benzothiazine ring plays an important role in the solvent-dependence of their spectroscopic properties. The fluorescence spectra in aprotic nonpolar solvent exhibit abnormally large Stokes-shifted ($\sim 9{,}000 \text{cm}^{-1}$) emission bands in contrast to the spectra in water. In ethanol, dual emission bands with two different fractional components of lifetimes have been observed. These results suggest that the abnormally red-shifted emission is attributed to the proton transferred form of an intramolecularly hydrogen-bonded closed conformer.

Introduction

Piroxicam (4-hydroxy-2-methyl-N-2-pyridine-1 ,2H-benzothiazine-3-carboxamide-1,1-dioxide), a non-steroidal and anti-inflammatory drug has been shown to cause cutaneous photosensitivity in some patients[1-4]. Even though its photosensitizing properties have not been understood, the photosensitization can be expected to occur with respect to red blood cells like many other photosensitizing drugs[5,6]. Thus the photosensitization may involve piroxicam in various microenvironmental conditions which depend on its incorporation into the red blood cells. In order to understand the photochemistry and the photophysics of piroxicam with respect to the photosensitization mechanism in biological molecules, it is of primary importance to investigate its electronic properties in various solvents such as nonpolar or polar solvents and/or hydrogen bonding solvents. Thus we have investigated the spectroscopic properties of piroxicam in various solvents.

It is the purpose of this paper to show that piroxicam displays absorption spectra and quite unusual fluorescence spectra both of which strongly depend upon the hydrogen bonding ability of the solvent at room temperature. The comparison with the solvent dependence of fluorescence properties obtained for a skeletal precursor of piroxicam, HMBDC (4-hydroxy-2-methyl-1,2- λ -benzothiazine-1,1-dioxide-3-methyl-carboxylate) infers to a possibility of the occurrence of an excited state intramolecular proton transfer from the hydroxyl group of the benzothiazine ring to the carbonyl portion of the amide group of the side chain. The latter plays an important role in the observation of an abnormally red-shifted fluorescence emission of piroxicam in nonpolar solvent.

Piroxicam   HMBDC