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The influence of hydrogen bonding on the photoinduced interaction of 9-anthracenecarboxylic acid and xanthene dye esters

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Abstract

The interaction of 9-anthracenecarboxylic acid with xanthene esters in chloroform solution was studied using emission spectra, fluorescence lifetime, IR spectra and ^{1}H NMR spectra. The results show that there exists both dynamic and static fluorescence quenchings. Dynamic quenching is a diffusion controlled process while static quenching is affected by hindrance of substituents adjacent to the hydroxyl groups in the xanthene moiety. Thus an intermolecular hydrogen bond interaction model between the hydroxyl groups of xanthene dye esters and 9-anthracenecarboxylic acid is proposed, and this is supported by IR and ^{1}H NMR spectra data. The binding constant for fluorescein and 9-anthracene carboxylic acid is 982 M^{-1}, while it is only 81 M^{-1} for the eosin ester and 9-anthracenecarboxylic acid. No apparent static interaction was observed in methanol solution. This may be explained in terms of hydrogen bonding between the hydroxyl group of methanol to anthracenecarboxylic acid, being in competition with that from the hydroxy group of the xanthene dye esters to 9-anthracene carboxylic acid. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrogen bond; Xanthene dyes; Aryl carboxylic acid

1. Introduction

Supermolecular systems consisting of non-covalently interacted donors and acceptors for the mimic of photosynthesis have attracted much attention [1–13]. Whilst these systems have attained extensive developments, there is much work in this area to be done. Here, we offer a simple intermolecular hydrogen-bonding interaction model between the hydroxyl groups of esterified xanthene dyes (Fig. 1) and the aryl carboxylic acid. This report focuses on the structure of the interaction model and the steric hindrance effect on the stability of the intermolecular hydrogen bond.

2. Experimental

^{1}H NMR spectra at 400 MHz were taken for $CDCl_3$ solutions of the esters of the xanthene dyes and 9-anthracenecarboxylic acid ($\sim 1\times10^{-3}$ M) on a Varian XL-400 spectrometer. IR spectra were

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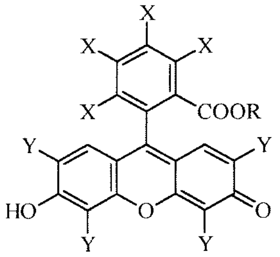

I . 4FlOH : R=n-Bu ; X=H ;

II . 2EoOH : R=Et ; X=H ;

III . 2RbOH : R=Et ; X=Cl ;

Fig. 1. Structures of the xanthene dye esters.

obtained at room temperature on a Perkin–Elmer 983 spectrophotometer. Electronic spectra were recorded on a Hitachi-160 spectrophotometer. Fluorescence spectra were taken on a Perkin–Elmer LS-5 fluorimeter interfaced to a 3600 Data Station. Samples for fluorescence measurements were at 10^{-6} M concentration in 1-cm cuvettes. Fluorescence lifetimes were determined using a HORIBA NAES-1100 single-photon counting apparatus. Redox potentials for the model compounds were measured by means of a cyclic voltammeter with a pyrolytic graphite as working electrode, platinum bridged by saturated KCl solution as counter electrode, and Ag/AgCl (saturated KCl) reference electrode. 0.1 M LiCl was employed as the electrolyte for solutions of 10^{-4} M in MeOH.

The singlet energy was determined from the overlap of the normalized absorption and emission spectra. 9-Anthracene carboxylic acid was an Aldrich product and was recrystallized from benzene prior to use. The xanthene dye esters and 9-anthracenecarboxylic acid were prepared as previously described [14–16]. Solvents for all spectroscopic experiments were dried and redistilled.

3. Results and discussion

3.1. Energetic

The singlet state energy and redox potentials of the model compound were determined. Table 1 shows that the singlet state energy of 9-anthracenecarboxylic acid (74 kcal/mol) is higher than that of the esters of the xanthene dyes (< 56 kal/mol).

Table 1
The singlet state energy and redox potentials of model compounds

	Es (ev)	*Eox(D)* (ev)	*Ere(A)* (ev)
ANCOOH[a]	3.18	0.95	−1.74
4FLOH (I)	2.40	0.91	−1.20
2EoOH (III)	2.28	0.80	−1.4

[a] ANCOOH: 9-Anthracenecarboxylic acid

When the xanthene dyes are excited, there will be no energy transfer between the xanthene dyes and 9-anthracenecarboxylic acid. We can calculate the free energy changes (ΔG) of ET reactions using the Rehm–Weller equation [17];

$$\Delta G = Eox(D) - Ere(A) - E_{0,0} - C$$

where $Eox(D)$ is the oxidation potential of the donor, $Ere(A)$ is the reduction potential of the acceptor; $E_{0,0}$ is the singlet state energy of the sensitizer; C is the solubilizing energy of $D+-$A$-$, and can be regarded as 0.06 ev or 1.4 kcal/mol in a polar solvent. [18]. According to this equation, if the esterified xanthene dyes act as sensitizer and electron donor, and 9-anthracenecarboxylic acid is the acceptor, the free energy change is −0.34 ev for fluorescein, and is −0.38 ev for eosin. This indicates that electron transfer from the lowest excited states of esterified xanthene dyes to the ground state of 9-anthracenecarboxylic acid is feasible. In contrast, if the xanthene dyes act only as electron donors, the free energy changes will be larger than 0, and the ET process is inhibited thermodynamically.

For dynamic fluorescence quenching, a Stern–Volumer linear relationship can be applied:

$$F_0/F = \tau^0/\tau = 1 + Kd[Q] = 1 + \tau^0 Kq[Q]$$

where F_0 and F are the fluorescence intensities in the absence and the presence of a quencher (Q), respectively; Kd is the Stern–Volumer constant, kq is the rate constant for fluorescence quenching, and τ^0 and τ are the fluorescence lifetimes in the absence and the presence of Q, respectively (Fig. 2). If static quenching due to the formation of non-fluorescent ground-state complex competes with a dynamic process, the Stern–Volumer equation is modified as [19]:

$$F^0/F = \left(1 + Kq\tau^0[Q]\right)(1 + Ks[Q])$$

where Ks is the binding constant of the ground state complex, and Kq is the rate constant for dynamic fluorescence quenching. The dynamic portion of the observed quenching can be determined by lifetime measurements, viz. $\tau^0/\tau = 1 + \tau^0 Kq[Q]$. The results are shown in Table 2.

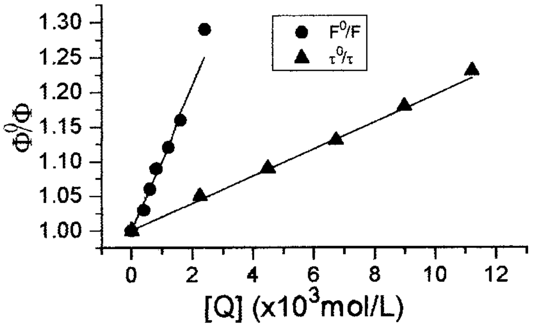

Fig. 2. Fluorescence quenching of the ethyl ester of eosin by anthracenecarboxylic acid in chloroform.

Table 2
Fluorescence quenching rate constants of the xanthene dye esters by anthracenecarboxylic acid and its ester in $CHCl_3$

	Kq (9-ANCOOH) M^{-1} S^{-1} (EXP)	Kq (9-ANCOOR) M^{-1} S^{-1} (EXP)	Ket^{cal}[a]	Ks
4FLOH	1.33×10^{10}	2.7×10^{9}	1.36×10^{10}	982
2EoOH	1.67×10^{10}	9.8×10^{9}	1.42×10^{10}	81

[a] Calculated according to Refs. [20,21].

Table 2 shows that the dynamic quenching is a diffusion controlled process, $Kq \sim 10^{10}$, which is near to the theoretical value. Moreover, there obviously exists a ground state interaction between the esterified xanthene dyes and 9-anthracenecarboxylic acid; for fluorescein and 9-anthracenecarboxylic acid, the binding constant is 982 M^{-1}, while for eosin and 9-anthracenecarboxylic acid the value is 81 M^{-1}.

Fluorescence quenching experiments in methanol were also carried out and the results are shown in Fig. 3.

The rate constant of the fluorescence quenching of the esterified fluorescein by 9-anthracenecarboxylic acid is 2.5×10^{10}, while it is 4.7×10^{10} for the esterified eosin. These values are for the diffusion controlled process that does not contain static interaction. This result is quite different from that observed in chloroform. In order to ascertain the driving force in forming the ground-state complexes in chloroform, we carried out on ^1H NMR experiments on mixed solutions of the xanthene dye esters and 9-anthracenecarboxylic acid in $CDCl_3$. The chemical shifts of the active protons are shown in Table 3.

Table 3 shows that the chemical shifts of the active protons change to a large degree after mixing. For esterified fluorescein and 9-anthracenecarboxylic acid, the active protons shift from 9.5 ppm (proton of the hydroxyl group of esterified fluorescein (I) and 3.7 ppm (proton of the carboxylic

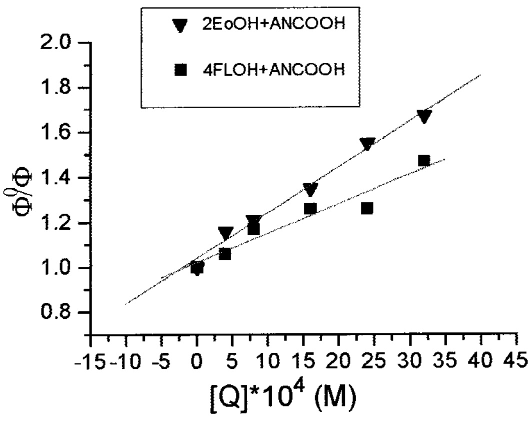

Fig. 3. Fluorescence quenching of the esters of xanthene dyes by anthracenecarboxylic acid in methanol.

acid of 9-anthracenecarboxylic acid/(ANCOOH) to 7.5 ppm. For the ester of eosin (II) and ANCOOH, the active protons shift from 6.6 ppm (II)and 3.7 ppm (ANCOOH) to 2.6 ppm. For the ester of Rose Bengal (III) and ANCOOH, they shift from 6.6 ppm (III) and 3.7 ppm (ANCOOH) to 2.2 ppm. We propose an intermolecular hydrogen bonding interaction model to explain these experimental results, and this can be expressed in Fig. 4.

The difference of the chemical shifts of the active protons in each mixing solution can be attributed to the different steric hindrance effects of the different substituents (H, Br, I). For fluorescein, adjacent to the hydroxyl group are small hydrogen atoms (Fig. 1), while for eosin and Rose Bengal they are bromo and iodo substituents. The hydrogen-bonding ring between the esterified fluorescein and 9-anthracenecarboxylic acid can rotate to some degree, and is not located in the heavy shielding field of the xanthene and anthracene rings. This causes the protons of the hydrogen-bonded ring to up shift, from 9.5 to 7.5 ppm. For the eosin and 9-anthracenecarboxylic acid pair, due to the steric hindrance of the large bromine atoms, the hydrogen-bonded ring cannot rotate greatly, and is almost perpendicular to the xanthene ring and the anthracene ring. Thus, the protons of the hydrogen-bonded ring are in the more heavily shielded field of the xanthene and anthracene ring moieties. They shift from 6.6 ppm (proton of the hydroxyl group of eosin) to 2.6 ppm (protons of the mixing solution). For the same reason, the active protons of the Rose Bengal shift from 6.5 ppm (unmixing solution) to 2.15 ppm (mixing solution). Moreover, protons '1 and 8' of the anthracene ring and the head methyl protons of the ester of the xanthene dyes, shift to upfield or downfield. The results are listed in Table 4.

Table 3
Chemical shifts of the protons in the mixed solutions of the xanthene dye esters and 9-anthracenecarboxylic acid ($CDCl_3$; 10^{-3} M)

Compound	Chemical shift (ppm)	Compound	Chemical shift (ppm)
(I) 4FLOH	9.5	ANCOOH	3.7
(II) 4FLOH/ ANCOOR (1:1)	9.5	4FlOH/ ANCOOH (1:1)	7.5
(III) 2EoOH/ ANCOOR (1:1)	6.5	2EoOH/ ANCOOH (1:1)	2.6
(IV) 2RbOH/ ANCOOR (1:1)	6.6	2RbOH/ ANCOOH (1:1)	2.2

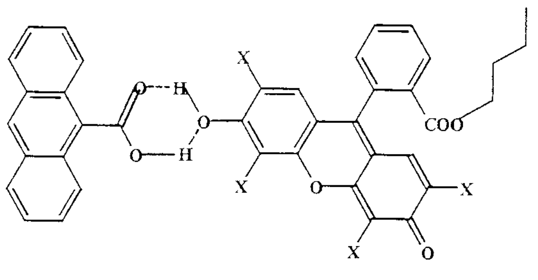

Fig. 4. Hydrogen-bonding interaction of the esterified xanthene dyes and 9-anthracenecarboxylic acid in chloroform.

Table 4 shows that the chemical shifts of protons '1 and 8' of the ester of anthracene carboxylic acid are at 8.57 ppm. For a dilute solution of 9-anthracenecarboxylic acid (2×10^{-3} M), proton '1 and 8' are also at 8.56 ppm, while for a more concentrated solution (4×10^{-3} M), they shift to 8.3 ppm. This may be explained that in the more concentrated solution, dimerization of 9-anthracene carboxylic acid [22] causes protons '1 and 8' to be in the shielding field of the opposite anthracene ring cycle, and they will then upshift to some degree. Table 4 also shows that the protons '1 and 8' of anthracene ring still shift upfield in the mixed solutions, even though the concentration of 9-anthracenecarboxylic acid is more dilute (2×10^{-3} M). If this results from the dimerization of 9-anthracenecarboxylic acid, it should not influence the protons of the head methyl group of the esterified xanthene dyes. However, the head methyl protons of these dyes shift to downfield: for the butyl esterified fluorescein from 0.78 to 0.95 ppm; for the ethyl ester of eosin from 1.18 to 1.58 ppm; for the ethyl esterified Rose Bengal from 1.10 to 1.60 ppm. These values declude the influence of the dimerization of anthracenecarboxylic acid, but, nevertheless, our proposed intermolecular hydrogen-bonding interaction model can explain these results very well. The interaction of esterified xanthene dyes and 9-anthracenecarboxylic acid may strengthen the unshielding field, and thus the head methyl protons of the xanthene dye esters shift to downfield. The IR spectra further confirm our assumption; data are shown in Table 5.

Table 5 shows that for concentrated 9-anthracenecarboxylic acid solution (4×10^{-3} M), there are two absorption peaks, one at 1730 cm^{-1} and another at 1690 cm^{-1}. It has been reported [23] that two peaks are observed (one at 1740–1743 cm^{-1} and another at 1700 cm^{-1}) in a concentrated hexane solution of benzoic acid; the peak at 1740–1743 cm^{-1} is ascribed to the monomer of benzoic acid while the peak of 1700 cm^{-1} is ascribed to the dimer. Here, we can also ascribe the peak at 1730 cm^{-1} to the monomer of 9-anthracenecarboxylic acid and the peak of 1690 cm^{-1} to the dimer. For dilute solution (2×10^{-4} M), the carbonyl absorption peak is at 1730 cm^{-1}, because the dimer portion at this concentration is very small. However for mixed solutions, we cannot observe these two peaks, and find one broadened peak at 1710 and 1711 cm^{-1} for fluorescein/9-anthracenecarboxylic acid, and eosin/anthracenecarboxylic acid respectively. Comparing the spectra of the xanthene dye ester solutions with those of the mixed solutions, we find that the spectra of the mixed solutions at short wavenumber (near 1700 cm^{-12}) increases to some degree, while the spectra at longer wavenumber (near 1730 cm^{-1}) are almost the same. It have reported [23] that the peak at 1700 cm^{-1} can be the attributed to the double hydrogen bonds effect on the carbonyl group, so it is also apparent that in our system, there also exist double hydrogen bonds interactions.

Our interaction model can satisfactorily explain the fluorescence quenching results in chloroform. The atoms adjacent to the hydroxyl group of fluorescein are all relatively small hydrogen atoms, and hindrance is very weak. Thus the hydrogen-bonded ring can form easily, and the binding constant is larger, 982 M^{-1}. However for eosin, the groups adjacent to the hydroxyl group are large bromine atoms and thus steric hindrance will be great. This hinders the formation of the hydro-

Table 4
Chemical shifts of protons '1 and 8' of anthracene and the head methyl protons of the xanthene dye esters ($CDCl_3$; 2×10^{-3} M)

	ANCOOR	ANCOOH 4.0×10^{-3} M	ANCOOH	4FLOH	4FLOH ANCOOH (1:1)	EoET	EoET + ANCOOH (1:1)	RbET	RbEt + ANCOOH (1:1)
Chemical shifts of proton1 and 8 of anthracene ring (ppm)	8.57	8.32	8.56		8.3		8.29		8.35
Chemical shifts of head methyl protons of the esterified xanthene dyes (ppm)				0.78	0.95/0.78	1.18	1.18/1.58	1.0	1.0/1.26

Table 5
The IR C=O peak of the mixing solutions of esterified xanthene dyes and 9-anthracenecarboxylic acid: ($CHCl_3$;4×10^{-4} M)

	2EoOH (II)	2EoOH + ANCOOH (II)	4FLOH (I)	4FLOH + ANCOOH (II)	ANCOOH 2×10^{-3} M	ANCOOH 4×10^{-3} M
ν (C=0) cm^{-1}	1710	1710	1711	1711	1730	1730/1690

gen-bonded ring, and the binding constant is therefore smaller, 81 M^{-1}. Our interaction model can only be applied to static interaction. For dynamic fluorescence quenching in chloroform, they are also controlled by the diffusion rate constant.

The reason why we did not observe ground-state interaction of the esterified xanthene dyes and 9-anthracene carboxylic acid in methanol can be related to the different solvent hydrogen bonding ability. Chloroform has no hydrogen bonding ability, and cannot compete with the hydrogen bond ability of the hydroxyl group on the xanthene dyes, and so in chloroform hydrogen bonding interaction between the xanthene dye esters and 9-anthracenecarboxylic acid can occur. However, methanol has a very strong hydrogen bonding ability and can compete with that of the hydroxyl group of xanthene dyes; the static interaction of the esterified xanthene dyes and 9-anthracenecarboxylic acid is then negligible in methanol.

4. Conclusions

The fluorescence quenching of xanthene dye esters by 9-anthracenecarboxylic acid consists of both a diffusion controlled dynamic process and static interaction in $CHCl_3$. An intermolecular hydrogen-bonding interaction model between the hydroxyl groups of the xanthene dye esters and 9-anthracenecarboxylic acid is proposed. Due to the weak hindrance of hydrogen atoms adjacent to the hydroxyl group in the fluorescein molecule, the binding constant for esterified fluorescein and 9-anthracene carboxylic acid is 982 M^{-1}, which is larger than that for the ester of eosin and 9-anthracene carboxylic acid, 81 M^{-1}, because of the large steric hindrance factors of the bromine atoms adjacent to the hydroxyl group. However, in methanol, due to the great hydrogen bonding ability of the solvent, the static interaction of the esters of the xanthene dyes and 9-anthracene carboxylic acid is negligible. The results of this study will be helpful for the designing of supermolecular systems in which exist hydrogen bonding interaction of carboxylic acid and hydroxyl groups.

Acknowledgements

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