PHOTOINDUCED INTRAMOLECULAR ELECTRON-TRANSFER OF SUBSTITUTED BENZOATE ESTERS OF 9-ANTHRACENEMETHANOL IN METHANOL*

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Abstract: The photoinduced intramolecular electron transfer is a complex phenomena. The role of the solvent and the substituents on the chromophore are important in electron transfer. The higher dipole moment difference between the excited and ground states is direct evidence for such an intramolecular electron transfer. In this study six esters of 9-anthracene methanol were synthesised and characterised. The Stoke shifts in different solvents for three esters were measured and the dipole moment difference between the excited and ground states were estimated. The fluorescence quantum yields in methanol for all the esters were measured. The results are explained by the intramolcular electron transfer in the excited state. The esters where the two chromophores linked by -CH$_2$OCO- group makes the possible interaction of two chromophores in the excited state were studied. The driving force for the electron transfer is therefore relatively strong. The estimated electron transfer rates were correlated with Hammett σ-values with the reaction constant, ρ = + 1.5. This is a strong evidence for the presence of intramolecular electron transfer in the excited state.

Key Words: 9-Anthracene methyl esters, Bichromophoretic compound, fluorescence, Hammett correlation, photoinduced electron-transfer, solvent effects.

INTRODUCTION

The photoinduced electron transfer (PIET) has received much attention during the past two decades. There are several reviews[1] and books[2] published. The intramolecular PIET, however becomes attractive to the scientist, since it is the basic mechanism of biological and chemical - energy conversion processes. Recently there have been many articles[3] published in this field. On electronic excitation of a molecule, the redistribution of charge and possible conformational changes which occur, can result in a net increase or decrease in the dipole moment of the system compared with that of the ground state. The knowledge of excited state charge distribution and dipole moments are important in understanding the photochemical processes. All the methods of determination of dipole moment of an excited state (μ_e) are based on the position change of the spectral band caused by an electric field either external (electrochromism) or internal (solvalochromism). The determination of μ_e by the method of solvalochromism is based on the shift of adsorption and/or fluorescence maxima in different solvents. The optimum results have been obtained by using the

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model proposed by Bakshiev.[4] Based on this model, several reports[5] on fluorescent compounds have appeared in the literature. The dipole moment difference between the excited and ground state, $(\mu_e\text{-}\mu_g)$, is excellent evidence for the intramolecular photoinduced electron transfer processes.

Studies[6] on the bichromophoretic compounds connected by σ-bonds have shown the formation of exciplexes. Most of these studies were done on the systems where the two chromophores are connected by a hydrocarbon chain; $-(CH_2)_n-$. Recently work carried out on the anthracene bichromophoretic compounds in various solvents show the formation of exciplexes.[7] The lower fluorescence quantum yields have been observed in the bichromophoretic compounds where the two chromophores are connected by the ester -C(=O)OC- linkage.[8] These esters are photostable and have shorter lifetimes. Moreover, these compounds give exciplexes emission at longer wavelengths. It was suggested that the exciplex is formed by intramolecular PIET from one chromophore to the other.

Our previous studies[9] on the fluorescence quantum yields of 1-naphthalenemethyl benzoate, 3, have established intramolecular PIET from naphthalene chromophore to the benzoate chromophore. According to the Wellar equation[10] the free energy for the electron transfer (ΔG_{ET}) can be expressed in terms of oxidation potential of the naphthalene chromophore $(E_{1/2}{}^{ox})$ and reduction potential $(E_{1/2}{}^{red})$ of the benzoate chromophore along with the solvent contribution factor, $e^2/4\pi\varepsilon r$.

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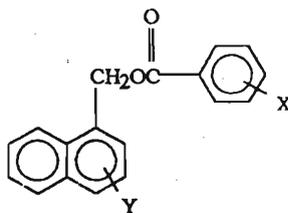
$$\Delta G_{ET} = (E_{1/2}{}^{ox} - E_{1/2}{}^{red} - e^2/4\pi\varepsilon r) - E_{0.0} \qquad ...(1)$$

Here $E_{0.0}$ is the excited state energy of the compound. Therefore, the substituents attached to the two chromophores leads to the change of the above potentials and effects the electron - transfer rates. Studies carried out in our laboratories[9] have established that electron donating groups attached to the naphthalene chromophore and electron withdrawing groups attached to the benzoate chromophore enhances the electron transfer rates. However, the weak fluorescence of these esters makes the estimation of electron transfer rates inaccurate. Therefore, in order to achieve greater accuracy we decided to carry out further studies with anthracene esters. In this paper we report the synthesis

of the 9-anthracenemethyl acetate (AnCH$_2$OCOCH$_3$), **1**, and 9-anthracenemethyl benzoate esters (AnCH$_2$OCOPh), **2a-e**, and their fluorescence measurements. We have also determined the (μ_e - μ_g) for the compounds **1**, **2a** and **2c**.

METHODS AND MATERIALS

Absorption spectra were obtained using a Jasco V - 560 UV/Visible spectrophotometer. GC/MS studies were done on a Hewlett Packard 5890 Series II Gas Chromatograph with column temperature programmed from 50°C to 250°C using a Hewlett Packard 5989A Mass spectrometer. Infrared spectra were recorded on a Jasco FT/IR - 5300 and are given in wave numbers (cm^{-1}). ^{1}H nmr spectra were obtained on Bruker ACF 200 instrument at 200 MHz with chemical shifts relative to TMS. Fluorescence studies were done using a RF - 5000 Shimadzu Spectrofluorimeter at 25°C, and spectra were corrected. All the chemicals except 9-anthracene methanol (Aldrich) were purchased from Fluka. All the solvents used in spectroscopic measurements are either of Analar grade or GP grade (purified by distillation).

General method for preparation of esters **1, 2a-e** : The esters were prepared by a common method as outlined in Scheme 1.
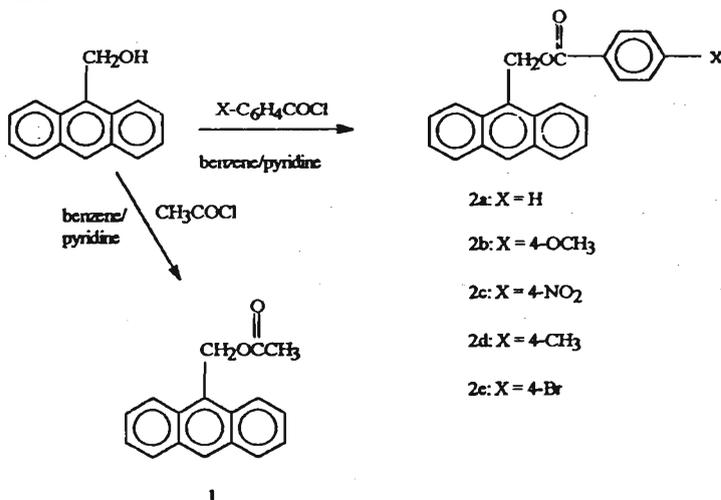
Scheme 1: Preparation of Esters 1 and 2a-e.

To a solution of alcohol (10 mmol) in 50 ml of benzene and 1 ml of pyridine, a solution of acid chloride (12 mmol) in 20 ml of benzene was added. After leaving overnight, the mixture was poured into 50 ml of water and the organic layer separated. This layer was dried and evaporated to give an oil or solid. This crude product was chromatographed on silica gel with 30% dichloromethane:hexane as eluent.

9-anthracenemethyl acetate,1: mp = 90-92 ^{0}C, ^{1}H nmr (CDCl$_3$) δ : 2.08(s,3H) 6.15(s,2H), 7.35-7.58(m,4H), 8.03(d,2H,J=4.5Hz), 8.32(d,2H,J=4.5Hz), 8.51(s,1H), IR (CCl$_4$) cm^{-1}: 1732, 1232, 1209, 790, GC/MS (m/e): 251(9), 280(52), 191(100), 190(20.25), 189(30), 179(19), 178(12), 176(8), 95(7).

9-anthracenemethyl benzoate,2a: mp=56-58^{0}C, ^{1}H nmr(CDCl$_3$)δ: 6.36(s,2H), 7.29-7.58(m,7H), 8.00-8.20(m,4H), 8.44(d,2H,J=4Hz), 8.54(s,1H), IR (CCl$_4$) cm^{-1} : 1713, 1258, 1101, 795, GC/MS (m/e): 312(74), 193(28), 192(22), 191(100), 190(24), 189(30), 179(9), 155(9), 105(42), 77(33).

9-anthracenemethyl-4´ -methoxybenzoate, 2b: mp = 128-130^{0}C, ^{1}H nmr(CDCl$_3$) δ : 3.8(s,3H), 6.36(s,2H), 6.83(d,2H,J=4.5Hz), 7.49-7.58(m,4H), 7.95(d,2H, J=4Hz), 8.05(d,2 H,J=4Hz), 8.44(d,2H,J=4Hz), 8.54(s,1H), IR (CCl$_4$) cm^{-1} : 1705, 1258, 1101, 795, GC/MS (m/e): 342(54), 192(20), 191(100), 190(26), 189(37), 179(11), 178(10), 105(38), 77(26), 51(13).

9-anthracenemethyl-4´ -nitrobenzoate 2c: mp = 120-122^{0}C, ^{1}H nmr (CDCl$_3$) δ: 6.47(s,2H), 7.45-7.66(m,6H), 8.04(t,2H,J=8Hz), 8.16(d,2H,J=4Hz), 8.42(d,2H,J=9Hz), 8.58(s,1H), IR(CCl$_4$) cm^{-1}: 1718, 1531,1272,1102,776. GC/MS (m/e): 357(34), 192(20), 191(100), 167(51), 137(12), 121(25), 109(15), 76(22), 75(25), 74(20), 65(100), 53(15), 51(30).

9-anthracenemethyl-4´ -methylbenzoate 2d: mp = 131-132^{0}C, ^{1}H nmr (CDCl$_3$) δ: 2.2(s,3H) 6.36(s,2H), 7.50-7.20(m,6H), 8.00-7.80(m,4H), 8.20(d,2H,J=4Hz), 8.45(s,1H), IR(CCl$_4$) cm^{-1} : 1720, 1284, 1101, 776. GC/MS (m/e): 326(10), 192(20), 191(100), 190(21), 179(12), 178(10), 105(32), 77(29), 51(18).

9-anthracenemethyl-4´ -bromobenzoate 2e: mp = 74-75^{0}C, ^{1}H nmr (CDCl$_3$) δ: 6.34(s,2H), 7.50-7.82(m,8H), 8.05(d,2H,J=4Hz), 8.30(d,2H,J=4Hz), 8.44(s,1H), IR(CCl$_4$) cm^{-1} : 1716, 1265, 1108, 786. GC/MS (m/e): 390(5), 388(4), 192(22), 191(100), 190(28), 179(10), 105(38), 77(28), 51(15).

RESULTS

Absorption studies: The absorption spectra of 1x10^{-5} mol dm^{-3} solutions of the esters **1** and **2a - e** in cyclohexane, dioxane, chloroform, dichloromethane, tetrahydrofuran, acetonitrile and methanol respectively were recorded at 25^{0}C. Nitrogen gas was bubbled through the solutions for 20 min, prior to recording the spectra. The data are presented in Tables 1 and 2.

Fluorescence studies: The emission spectra of esters in the above solutions were recorded and the data are presented in Tables 1 and 2. The samples were purged

with N_2 for 20 min before measurements were taken. The fluorescence quantum yields of esters **1** and **2a-e** dissolved in methanol were determined using anthracene $(\phi_f = 0.4)$ in methanol as the standard. The singlet state energies were determined by the position of the 0,0 band using the overlap between the emission and excitation spectra.

Table 1: **The absorption** $^a(\lambda_a)$ **and emission** $^b(\lambda_e)$ **maxima of the compounds 1, 2a and 2c in different solvents.**

Solvent	1		2a		2c		
	λ_a(nm)	λ_e(nm)	λ_a(nm)	λ_e(nm)	λ_a(nm)	λ_e(nm)	^{c}F
cyclohexane	384.0	391.6	383.8	390.8	384.4	390.0	-0.0026
dioxane	385.5	394.0	385.2	393.6	385.3	394.8	-0.0024
chloroform	386.8	396.0	387.0	396.0	387.2	396.0	0.3706
dichloromethane	386.2	396.0	385.8	396.0	385.9	396.4	0.5903
tetrahydrofuran	385.2	393.2	385.0	392.8	385.1	396.8	0.5491
acetonitrile	383.6	396.8	388.0	392.8	387.6	393.2	0.8593
methanol	383.7	391.0	385.1	392.7	383.0	394.6	0.8237

^{a}The longest wavelength band maxima were taken.
^{b}The shortest wavelength band maxima were taken.
^{c}Values taken from reference number 13.

Determination of the dipole moment difference $(\mu_e - \mu_g)$ *between the excited and ground state*: The $(\mu_e - \mu_g)$ for the esters **1,2b** and **2c** were determined by the method of solvatochromism. Bakshievs formula has been used in our studies:

$$\nu_a - \nu_f = 2F (\mu_e - \mu_g)/h\tau a_0^3 \qquad \qquad ...(2)$$

where ν_a and ν_f are respectively the absorption and emission maximum wave numbers in cm^{-1}, μ_e and μ_g are the dipole moments of the ground and excited state respectively.

$$F = [(D -1) / (D - 2) - (n^2 + 2)/(n^2 +2)] (2n^2 + 1)/ (n^2 +2) \qquad ...(3)$$

where D is the dielectric constant of the solvents and n is the refractive index of the solvent.

Table 2: The emission properties of compounds 1 and 2a-e in methanol.

Compound	Singlet state energies $E_{0,0}$ (kJ mol^{-1})	Quantum yield of fluorescence	[a] % of fluorescence quenching by electron transfer	[b] k_{et}^X/k_{et}^H	$\log(k_{et}^X/k_{et}^H)$	[c] σ
1	306.5	0.300				
2a, X = H	309.7	0.280	6.0	1.00	0.00	0.00
2b, X = 4-OCH$_3$	309.7	0.292	2.7	0.39	-0.41	-0.29
2c, X = 4-NO$_2$	310.7	0.028	90.7	1.36×10^2	+2.14	+1.21
2d, X = 4-CH$_3$	310.2	0.287	4.3	0.64	-0.19	-0.17
2e, X = 4-Br	310.1	0.270	10.0	1.56	+0.19	+0.21

[a] estimated values using the equation (8) in the text.

[b] estimated values using the equation (9) in the text.

[c] values taken from reference number 13.

DISCUSSION

The solute-solvent properties and solvent polarity functions are shown in Table 1. The dielectric constant and the refractive indices of solvents at 25⁰C are taken from the literature.[11] Figure 1 shows correlation between the solvent shifts and the solvent polarity function F for the esters **1**, **2b** and **2c**. Statistical treatment of the correlation of solvent spectral shifts for the esters have been performed for all the solvents. Solvents such as dioxane, acetonitrile and methanol show deviation from the Bakshievís correlation. By eliminating these solvents, the slope of the Stokes shift versus F were calculated as 1.27, 1.55 and 1.93 for the compounds **1**, **2a** and **2c**. From these values it is clear that there is s charge separation in these esters when they are in the excited states. Also the charge separation is higher for **2c** than for **2a**. This suggests that the charge transfer is more in compound **2c** than in **2a**.
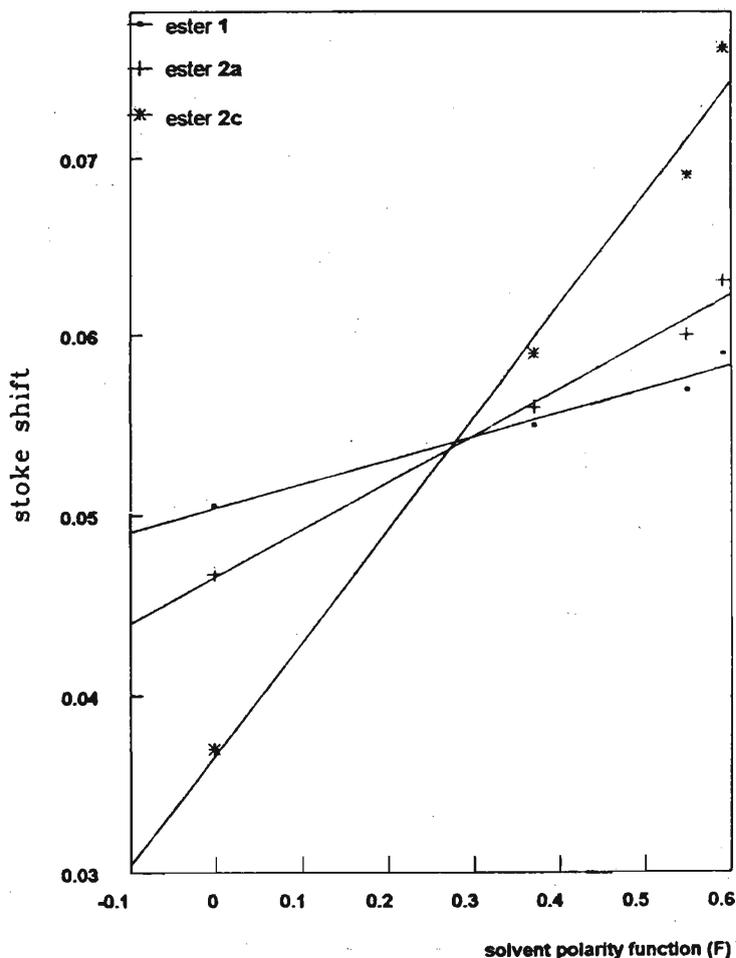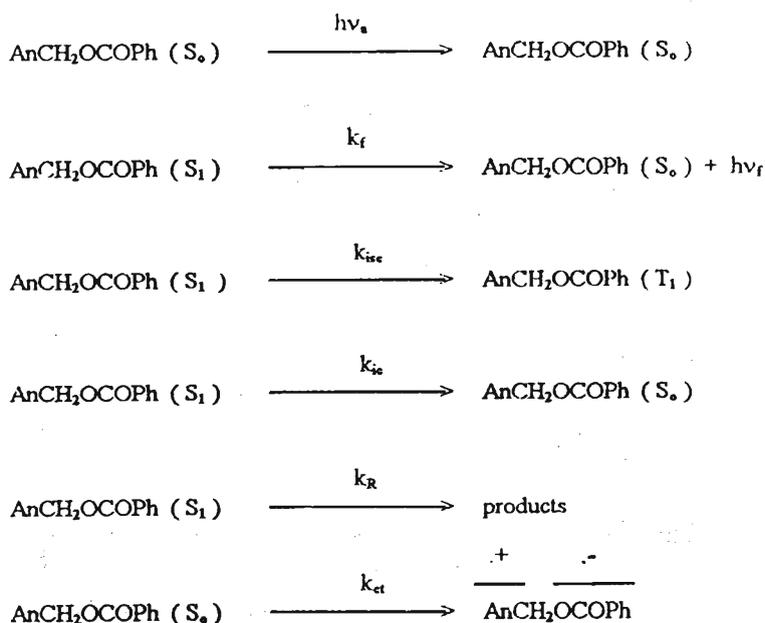

Figure 1: Bakshiev's correlation between the Stoke shifts and the solvent polarity function (F) for esters 1, 2a and 2c.

As mentioned in the introduction the lower fluorescence quantum yield of 1-naphthyl methyl benzoate esters were due to the intramolecular electron-transfer from the naphthalene chromophore to the benzoate chromophore. Table 1 shows the change of fluorescence quantum yield of **2** in methanol with different substituents on the benzoate chromophore. According to the Wellar equation (equation 1), the energy of the electron transfer is dependent on the oxidation potential of the electron donor and reduction potential of the electron acceptor. The electron withdrawing groups on the benzoate chromophore, **2c** and **2e**, show lower fluorescence quantum yields, supporting the intramolecular electron-transfer from anthracene chromophore to the benzoate chromophore. For instance, the free energy of the electron transfer process for compound **2a** has been calculated as -320 kJ mol^{-1} by using Weller equation along with the oxidation potential of anthracene (-1.82V wrt SCE),[7] reduction potential of methyl benzoate (2.12 V wrt SCE)[12] and singlet state energy of 309.7 kJ mol^{-1}. The negative value for the free energy of the electron transfer indicates that the process is feasible. The lowering of fluorescence quantum yields in benzoate compared to that of acetate can be explained by the electron transfer process. The electron withdrawing group on the benzoate chromophore, in esters **2c** and **2e**, gives a lower reduction potential. This enhances the intramolecular electron transfer rates lowering the fluorescence quantum yields compared to that of unsubstituted **2a**. On the other hand the electron donating substituents on the benzoate ring, in esters **2b** and **2d**, increase the reduction potential making the electron transfer less favourable. This results in an increase in the fluorescence quantum yields when compared to that of unsubstituted ester **2a**.

$$AnCH_2OCOPh \ (S_o) \xrightarrow{\ h\nu_a\ } AnCH_2OCOPh \ (S_o)$$

$$AnCH_2OCOPh \ (S_1) \xrightarrow{\ k_f\ } AnCH_2OCOPh \ (S_o) + h\nu_f$$

$$AnCH_2OCOPh \ (S_1) \xrightarrow{\ k_{isc}\ } AnCH_2OCOPh \ (T_1)$$

$$AnCH_2OCOPh \ (S_1) \xrightarrow{\ k_{ic}\ } AnCH_2OCOPh \ (S_o)$$

$$AnCH_2OCOPh \ (S_1) \xrightarrow{\ k_R\ } products$$

$$AnCH_2OCOPh \ (S_o) \xrightarrow{\ k_{et}\ } \overset{.+}{AnCH_2} \overset{.-}{OCOPh}$$

Scheme 2: Mechanism for the irradiation of 9-anthracenemethyl benzoate in methanol.

The mechanism outlined in the Scheme 2, can be used for the quantitative explanation of the results. According to the mechanism there are five different pathways for the disappearance of the excited state. S_1 of the benzoate esters with rate constants k_f, k_{isc}, k_{ic}, k_R and k_{et}. The following equation can be easily derived for the quantum yield of fluorescence of benzoate ester using the steady state conditions:

$$\phi_f^B = \frac{k_f}{k_f + k_{ISC} + k_{IC} + k_R + k_{et}} \qquad (3)$$

The fluorescence quantum yield for ester **1**, can be given as follows:

$$\phi_f^A = \frac{k_f^o}{k_f^o + k_{ISC}^o + k_{IC}^o + k_R^o + k_{et}^o} \qquad (4)$$

making the reasonable assumption that the rates of disappearance of the excited state of the acetate and benzoate esters are similar except for the difference in the rate of electron transfer.

Since there is no intramolecular electron transfer for the acetate, one can derive the equations (5) and (6).

$$\frac{\phi_f^A}{\phi_f^B} = 1 + \tau k_{et} \qquad ...(5)$$

$$\phi_{et} = 1 - \frac{\phi_f^B}{\phi_f^A} \qquad ...(6)$$

Here $\tau = k_f^o / k_f^o + k_{ISC}^o + k_{IC}^o + k_R^o + k_{et}^o = k_f / k_f + k_{ISC} + k_{IC} + k_R$, is the lifetime of the acetate ester and is a constant.

From equation (5),

$$\left(\frac{\phi_f^A}{\phi_{fB}} - 1 \right) \alpha \ k_{et} \qquad ...(7)$$

From equation (6), the percentage of fluorescence quenching in the substituted benzoate esters can be expressed as,

$$\text{The percentage of Fluorescence quenching} = \left(1 - \frac{\phi_f^B}{\phi_f^A} \right) \times 100 \qquad \ldots(8)$$

The values for the percentage of quenching of fluorescence by intramolecular electron-transfer can be estimated by equation (8) and are given in Table 2. The variation of percentage of quenching of the fluorescence with the Hammett σ[13] values is given in Figure 2.
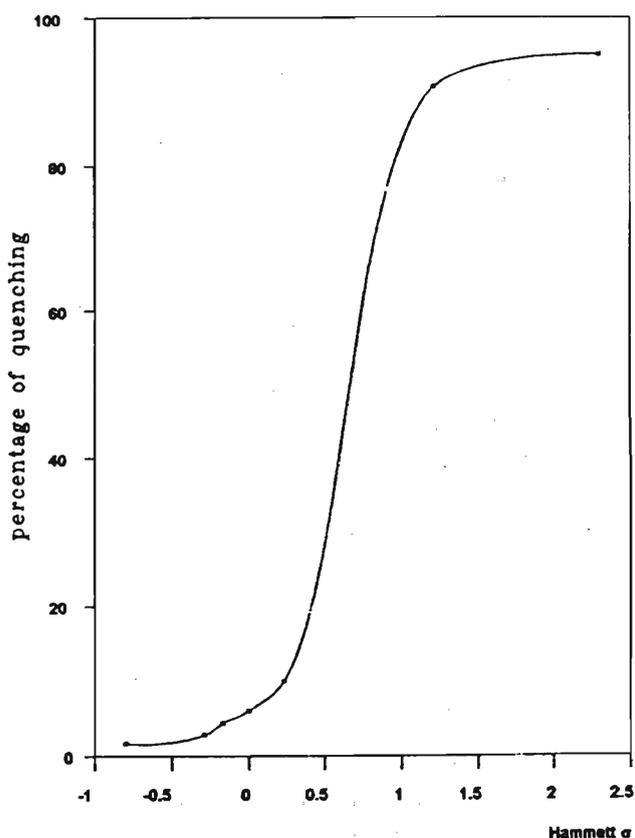

Figure 2: **Plot between percentage of quenching and Hammett σ.**

Taking the electron transfer rates for unsubstituted and substituted esters as k_{et}^H and k_{et}^X respectively and using the equation (7), one can derive:

$$\left(\frac{\phi_f^A}{\phi_f^B} - 1 \right)_X \Bigg/ \left(\frac{\phi_f^A}{\phi_f^B} - 1 \right)_H = k_{et}^X / k_{et}^H \qquad \ldots(9)$$

According to the Hammett linear free energy relation (LFER),[14]

$$\log (k_{et}^X / k_{et}^H) = \rho\sigma \qquad\qquad ...(10)$$

where the ρ and σ are the reaction constant and the substituents constants respectively.

The values for the above equation are given in Table 3. The log (k_{et}^X / k_{et}^H) were plotted against the reaction constant, σ and a linear plot was obtained as given in Figure 3.
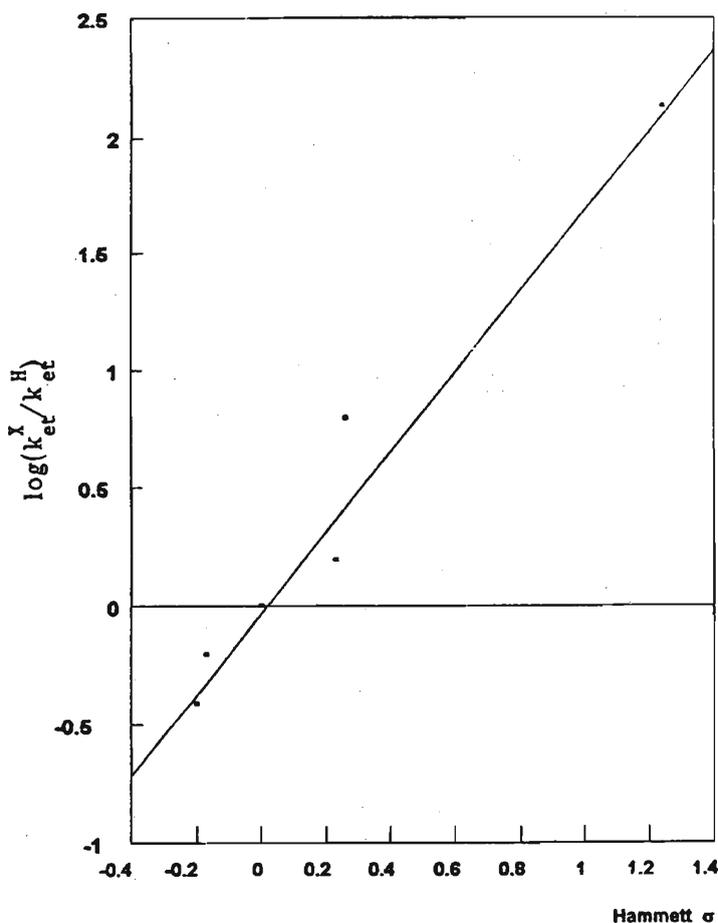

Figure 3: log (k_{et}^x / k_{et}^H) versus Hammett σ.

A straight line suggests the validity of the proposed mechanism although alternatives are not completely ruled out. The -CH$_2$OCO- linkage between the anthracene chromophore and benzene chromophore gives an efficient overlapping of the orbitals. The s-cis configuration is necessary for the efficient

overlapping of the orbitals. The linear plot between the k_{et}^X/k_{ct}^H and σ is very good evidence for the overlapping of the orbitals of the anthracene and benzoate chromophores and hence intramolecular electron transfer from the one to the other. The reaction constant ρ is calculated as 1.53. The electron-transfer takes place from the excited state surface. Therefore the substituents have very little effect on the absorption spectra However, the emission spectra will be greatly affected by a variation of the substituent. Indeed, the electron-transfer is the controlling factor for the fluorescence quantum efficiencies. High ρ-values ($\rho > 1$) are frequently reported for the ionisation reactions in which the developing charge is in direct conjugation with the substituent on the aromatic ring. Indeed, direct conjugation would be better modelled by Okomota[15] σ^- relationships. The ρ-values higher than 4.0 are reported[17] and these higher values were explained by the direct conjugations.

In this study we attempted LFER correlations with σ^- and σ. Our best fit is with Hammett σ, which gave ρ-value of +1.5 (r = 98.9%) for k_{et} . This suggests that the electron-transfer from the anthracene chromophore to the benzoate chromophore takes place with some charge delocalization into the benzene ring.

Acknowledgement

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