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Interaction of the Excited Singlet State of 1,4- and 1,8-Dimethoxynaphthalene with Some Organic Compounds: A Fluorescence-Quenching Study

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Summary. The fluoroescence quenching of 1,4-dimethoxynaphthalene (**1**) and 1,8-dimethoxynaphthalene (**2**) by tetraphenylporpyrin (**3**), 9,10-diphenylanthracene (**4**), and 3-cyano-4-phenyl-6-(*p*-tolyl)-pyridin-2-one (**5**) has been studied in chloroform solution. The quenching occurs *via* a resonance energy transfer mechanism. The rate constant for the energy transfer (k_{ET}) of donor **2** is slower than that of **1** by the same acceptors, indicating that the steric effect dominates the ionization potential effect in all systems. The calculated critical transfer distances (R_0) are 17–72 Å. In contrast, charge transfer is the predominant pathway of electronic deexcitation in the fluorescence quenching of donors **1** and **2** by 7,7,8,8-tetracyanoquinone-dimethane (**6**) in chloroform. The roles of temperature and geometrical structure of the donors on the efficiency of fluorescence quenching of **1** and **2** by acceptor **6** have also been studied.

Keywords. Energy transfer; Charge transfer; Fluorescence quenching; Dimethoxynaphthalenes.

Wechselwirkung des angeregten Singlett-Zustands von 1,4- und 1,8-Dimethoxynaphthalin mit einigen organischen Verbindungen: eine Untersuchung zur Fluoreszenzlöschung

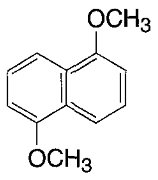
Zusammenfassung. Die Löschung der Fluoreszenz von 1,4-Dimethoxynaphthalin (**1**) und 1,8-Dimethoxynaphthalin (**2**) durch Tetraphenylporphyrin (**3**), 9,10-Diphenylanthracen (**4**) und 3-Cyano-4-phenyl-6-(*p*-tolyl)-pyridin-2-on (**5**) in Chloroform wurde untersucht. Die Löschung verläuft über einen Resonanzenergietransfermechanismus. Die Geschwindigkeitskonstante für den Energietransfer (k_{ET}) ist bei gleichem Akzeptor für den Donor **2** niedriger als für **1**. Daraus läßt sich schließen, daß in allen untersuchten Systemen der sterische Effekt über den Effekt des Ionisierungspotentials dominiert. Die berechneten kritischen Transferdistanzen betragen 17–72 Å. Im Gegensatz zu diesen Beobachtungen verläuft der vorherrschende Relaxationsmechanismus bei der Fluoreszenzlöschung von **1** und **2** durch 7,7,8,8-Tetracyanochinon-dimethan (**6**) über einen *charge-transfer*-Prozeß. Die Einflüsse von Temperatur und Geometrie der Verbindungen auf die Effizienz der Fluoreszenzlöschung von **1** und **2** durch den Akzeptor **6** wurden ebenfalls untersucht.

Introduction

Interest in the spectroscopic, photophysical, and electron transfer reactions of dimethoxynaphthalenes has resulted in several articles in the literature during the past years [1–7]. Examples are the involvement of the charge transfer mechanism in the fluorescence quenching of 1,5-, 2,3- and 2,6-dimethoxynaphthalenes by a series of π-acceptors [1, 2]. In the same studies, ground state properties of these complexes were mainly correlated with evaluation of molecular quantities such as molar absorption coefficients, equilibrium constants, transition dipole moments, oscillator strength values, thermodynamic standard reaction quantities, and dissociation energies of the charge transfer complexes. It has also been found that charge transfer is the predominant pathway in the quenching of 2,6-dimethoxynaphthalene by methylchloroacetate and 2-chloroacetamide [3]. *Quina et al.* [4] have reported the quenching of 1,4- and 2,6-dimethoxynaphthalene by chloroacetonitrile in acetonitrile solution, where radical cations were observed by flash spectroscopy. However, near-diffusion-controlled rate constants were found for the fluorescence quenching of 1,4-dimethoxynaphthalene by N-tosylmethylamine in benzene and acetonitrile, though no exciplex emission was observed [5].

In an important recent study, we have found that both 1,4- and 1,8-dimethoxynaphthalene form 1:1 charge transfer complexes with some π-acceptors [6]. The stability of these complexes depends on the electron affinities of the acceptors in addition to the geometrical structure of the donor. Moreover, *Wong* and *Arnold* [7] have reported the spectroscopic and photo-CIDNP studies of charge transfer complexes of 1,4-, 1,5-, and 2,3-dimethoxynaphthalenes with 1,2-dicyanoethylene. However, a survey of the literature suggested that very little studies have dealt with the energy transfer process.

In this paper, we present results of quenching studies designed to investigate the role of the quenchers on the quenching mechanism as well as the steric influence on the reactivity of 1,4- and 1,8-dimethoxynaphthalenes.



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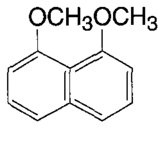

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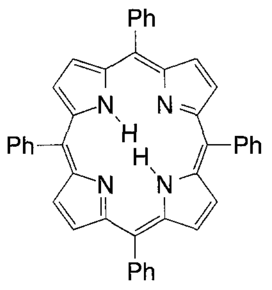

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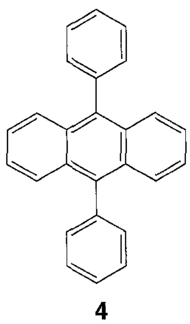

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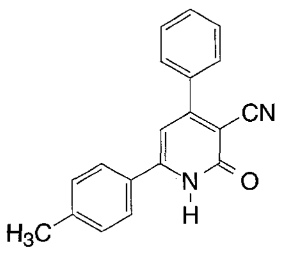

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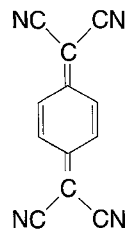

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Results and Discussion

The fluorescence of electronically excited **1** and **2** in chloroform is strongly quenched by a number of organic compounds like **3**–**5**, having excited singlet states lying energetically low enough to be populated by transfer of electronic energy available in the donors. Figure 1 represents the decrease in fluorescence intensity of $1.8806 \times 10^{-4} M$ donor **2** as the concentration of **3** increases. In all cases, the unquenched part of the fluorescence had the same spectral distribution as that observed in absence of the quencher. No new emission was detected in $CHCl_3$, indicating the absence of exciplex fluorescence. It is important to note that within the wavelength of measurements up to 700 nm no additional absorption bands could be observed in the mixed solutions of the donors and the acceptors **3**–**5** in chloroform. This behavior indicates the absence of ground state complexes between the fluorophores and the quenchers.

The quenching process obeys the *Stern-Volmer* (SV) relationship [8]

$$I_0/I = 1 + K_{SV} = 1 + k_{ET}\tau_0[Q]$$

where I_0 and I are the relative fluorescence intensities in absence and presence of the quencher Q, K_{SV} is the SV quenching rate constant, τ_0 is the fluorescence lifetime of the fluorophore in absence of the quencher, and k_{ET} is the bimolecular rate constant of the energy transfer. Linear regression according to the above relation leads to a good linear representation with correlation coefficients of 0.979–0.999; the *Stern-Volmer* plots are shown in Figs. 3 and 4. For donors **1** and **2** with acceptors **3**–**5** in chloroform, k_{ET} was calculated from K_{SV} values and the measured fluorophor lifetimes ($\tau_0 = 5.31 \pm 0.018$ ns for **1** and 3.07 ± 0.011 ns for **2**). As an example, the time-decay curve of **2** is shown in Fig. 2. The experimental results are summarized in Table 1, where the SV rate constants K_{SV}, the quenching rate constants for the energy transfer (k_{ET}), and correlation coefficients (r) are given.

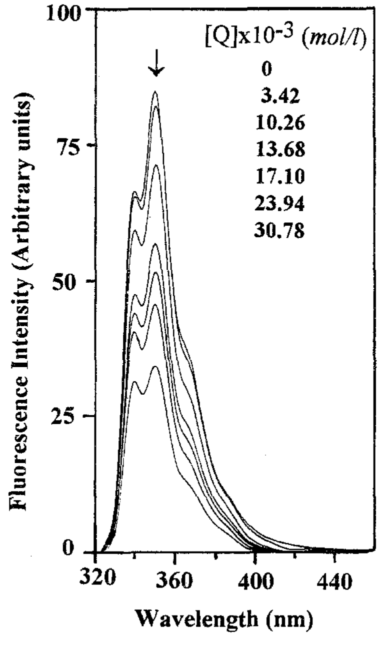

Fig. 1. Emission spectra of $1.8806 \times 10^{-4} M$ donor **2** in chloroform ($\lambda_{ex} = 330$ nm) in absence and presence of quencher **3** at 298 K

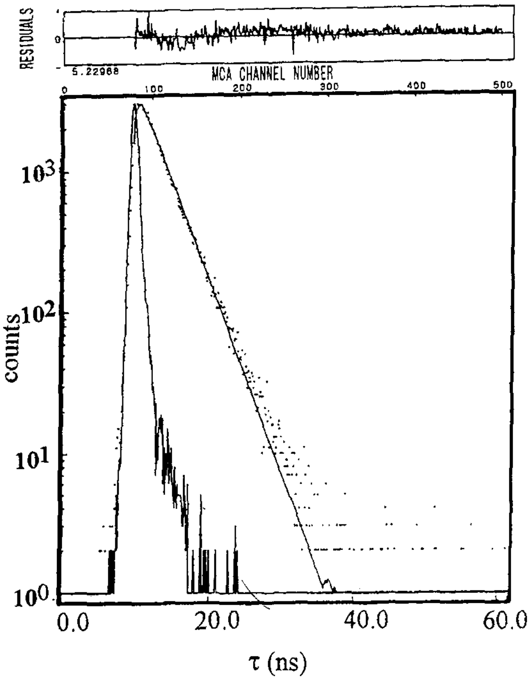

Fig. 2. Fluorescence decay curve of **2**, excited at 330 nm; the best fit provided a decay time of 3.07 ± 0.011 ns

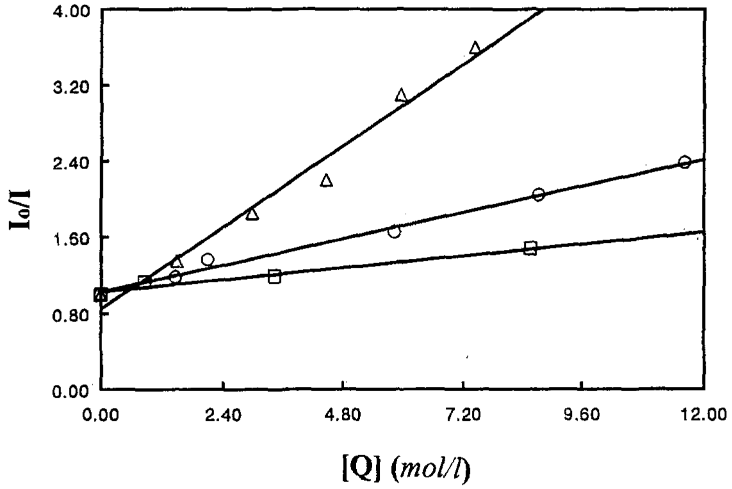

Fig. 3. *Stern-Volmer* plots of the fluorescence quenching of 1.9657×10^{-4} *M* donor **1** by acceptors **3** (□, $[Q] \times 10^{-4}$), **4** (○, $[Q] \times 10^{-5}$), and **5** (△, $[Q] \times 10^{-5}$); $\lambda_{ex} = 318$ nm in chloroform

As shown in Table 1, the k_{ET} values are higher than the limiting diffusion rate constant k_{diff} in chloroform ($k_{diff} = 1.2 \times 10^{10}\ M^{-1}\,s^{-1}$). This indicates a diffusionless mechanism for energy transfer [9].

On the other hand, the K_{SV} values and therefore the rate of energy transfer k_{ET} from **1** and **2** to different acceptors increase as the area of overlap between donor emission and absorption spectra of the acceptor increases. Figures 5a,b show the overlap between the emission spectra of **1** and **2** and the absorption spectra of **1**–**3**.

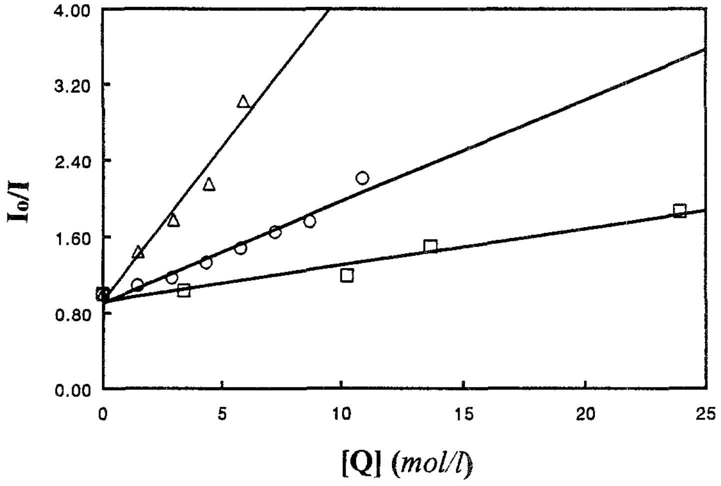

Fig. 4. *Stern-Volmer* plots of the fluorescence quenching of $1.8806\times10^{-4}\,M$ donor **2** by acceptors **3** (□, $[Q]\times10^{-3}$), **4** (○, $[Q]\times10^{-4}$), and **5** (△, $[Q]\times10^{-5}$); $\lambda_{ex}=330$ nm in chloroform

Table 1. Energy transfer data for donors **1** and **2** to organic acceptors **3**–**5** in chloroform at 25 °C

donor	acceptor	$K_{SV}/10^4$	$k_{ET}(M^{-1}s^{-1})$	r	R_0(Å)
1	**5**	3.207 ± 0.381	1.045×10^{13}	0.980	46
1	**4**	1.189 ± 0.022	2.224×10^{12}	0.999	72
1	**3**	0.059 ± 0.002	1.113×10^{11}	0.997	19
2	**5**	2.556 ± 0.377	4.814×10^{12}	0.979	31
2	**4**	0.681 ± 0.080	2.219×10^{12}	0.981	26
2	**3**	0.025 ± 0.003	8.324×10^{10}	0.977	17

Furthermore, k_{ET} values for the quenching of **1** with various acceptors are significantly larger than those obtained for **2**. These observations may be attributed to steric hindrance, due to the adjacent methoxy groups in positions 1 and 8 in **2** which hamper the energy transfer process.

The critical transfer distance R_0 have been calculated by applying the following relation [9]

$$R_0^6=\frac{1.25\times10^{-25}x\phi_f}{n^4}\int_0^\infty\frac{F_D(\tilde{\nu})\varepsilon_A(\tilde{\nu})}{(\tilde{\nu})^4}d\tilde{\nu}$$

where ϕ_f is the emission quantum yield of the donor in absence of the acceptor, n is the solvent refractive index, $F_D(\tilde{\nu})$ is the normalized distribution of the donor emission at wavenumber $\tilde{\nu}$ (cm^{-1}), $\varepsilon(\tilde{\nu})$ is the decadic molar absorption coefficient of the acceptor, and R_0 is the distance at which energy transfer and emission processes are equally probable.

From Table 1, it can be seen that the R_0 values are higher than that for collisional energy transfer in which R_0 is in the range of 4–6 Å [10]. The high value of the critical

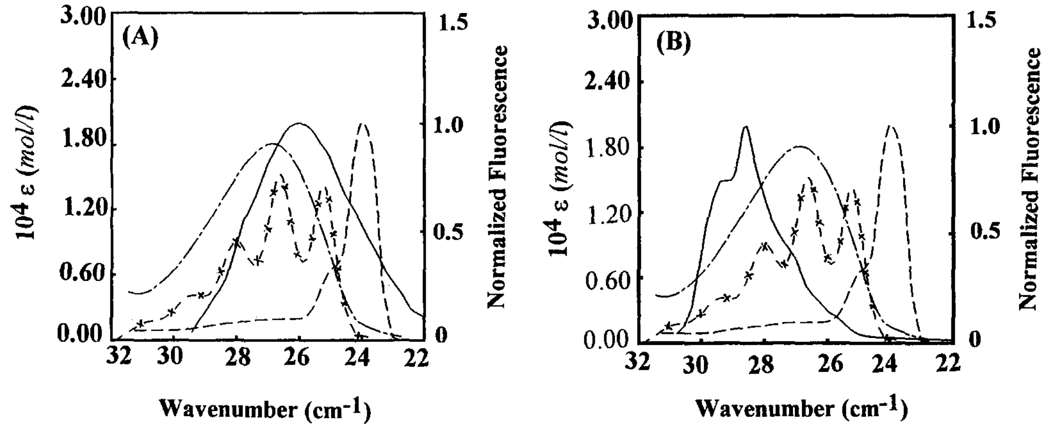

Fig. 5. Spectral overlap of the fluorescence emission of donor **1** (**a**, —) and donor **2** (**b**, —) with the acceptor absorption curves of **3** (–––), **4** (– × –), and **5** (–––)

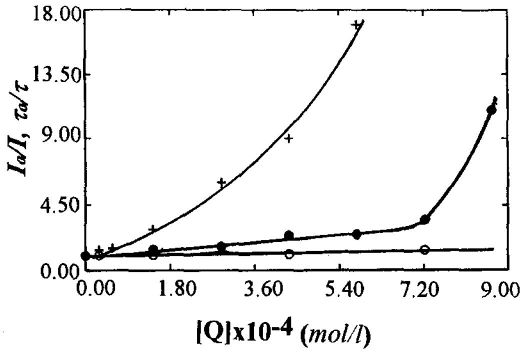

Fig. 6. *Stern-Volmer* plots for the quenching of the excited singlet donors **1** and **2** by **6** (+); ● relative fluorescence intensity (I_0/I); ○ relative fluoresence lifetime (τ_0/τ)

transfer distance as well as the quenching rate constant indicate that the underlying quenching mechanism for these systems is that of resonance energy transfer, due to long-range dipole–dipole interaction between excited donor and ground state acceptor molecules.

The quenching of the fluorescence of **1** and **2** was also observed after the addition of **6**. *Stern-Volmer* plots for the excited singlet state quenching based on steady state emission measurements are shown in Fig. 6. It can readily be seen that the linear dependence takes place only at rather low quencher concentrations. With increasing quencher concentration, the plots show upward deviation from linearity indicating that the quenching involves a static mechanism. Thus, the slopes of the curves depicted in Fig. 6 are determined at low quencher concentrations.

The fluorescence lifetime of **2** is almost independent of the quencher concentration. As an approximation, the main lifetime components were used for the SV plots (τ_0/τ) as shown in Fig. 6. The slopes of the SV plot based on the lifetime are very small in comparison with those of the plots based on the emission intensities. This result shows that the quenching cannot occur by a dynamic process, but involves a static process under the present concentration conditions (1.4446 10^{-4} *M* to 8.6679 10^{-4} *M*). Generally, static and dynamic quenching can be distinguished by their

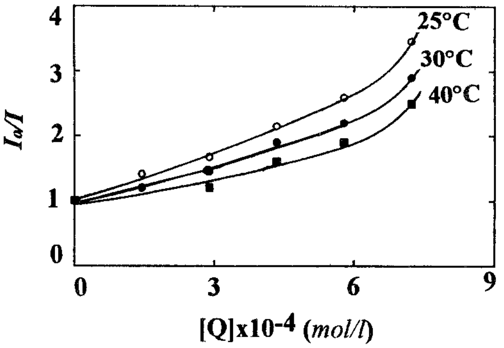

Fig. 7. *Stern-Volmer* plots of donor **2** with acceptor **6** in chloroform at various temperatures

Table 2. Fluorescence quenching data of donors **1** and **2** with acceptor **6** in chloroform at 25 °C

donor	$k_{SV}/10^4$	$k_q/10^{12}(M^{-1}s^{-1})$	r
1	1.987 ± 0.202	3.742	0.983
2	0.321 ± 0.037	1.046	0.974

different dependence on the temperature. The effect of temperature on quenching has been investigated over the temperature range of 25–40 °C. The increase of temperature leads to a decrease of the quenching efficiency (Fig. 7). This behavior gives distinct evidence that the excited singlet state of **2** is quenched by a static process [9]. Similar behavior has been observed for **1**.

An important feature which arises from the data in Table 2 is a considerable higher value of the bimolecular quenching rate constant k_q for **1** (about three order of magnitude) than for **2**. This provides further evidence of steric hindrance due to adjacent methoxy groups in positions 1 and 8 in **2** which prevents a good overlap of the appropriate molecular orbitals [11] and therefore hinders the quenching process. A similar steric behavior has been observed previously [6] for ground state complexes of donors **1** and **2** with acceptor **6**. The close similarity of ionization potential values I_p for **1** (7.51 eV) and **2** (7.50 eV) [6] indicates that the ionization potential shows a negligible small effect on k_q, and that the steric effect plays a major role. Also, the k_q values (Table 2) are much larger than the limiting diffusion rate constant k_{diff} in chloroform ($k_{diff} = 1.2 \times 10^{10}\,mol^{-1}\,s^{-1}$). As has been previously mentioned, this behavior suggests that diffusion is not involved in the quenching mechanism. It is difficult to explain such high values of k_q solely in terms of singlet–singlet energy transfer. As evidenced by absorption and emission spectra, quencher **6** has a lower energy than that of **1** and **2**, so resonance energy transfer is excluded.

In the view of the above observations, it is possible to state that there is no clear evidence of any effects other than charge transfer operating on the quenching of the excited states of **1** and **2** by acceptor **6** [9]. This conclusion is supported by ground state absorption spectra between the donors and acceptor **6**, where a new absorption band appears at longer wavelength [6] as a result of the formation of ground state complexes. This indicates that the quenching of donors **1** and **2** by acceptor **6** occurs as a result of the formation of non-fluorescing ground state charge transfer complexes between the reactants [9].

Experimental

Dimethoxynapthalenes **1** and **2** were synthesized and purified as described earlier [6]. Compound **3** (Aldrich) was used as received. Compound **4** (Aldrich) was purified by recrystallization and subsequent TLC using glass-backed silica gel as the stationary phase just prior to use. **3** was kindly supplied by Dr. *A. Attia* of this university and used without additional purification. **6** (Aldrich) was purified by sublimation. Chloroform (spectroscopic grade from Merck) was used without further purification and was found to be transparent within the wavelength studied.

Steady state fluorescence measurements were acquired with a Shimadzu RF 540 spectrometer equipped with a thermostated cell housing. The excitation wavelength was 318 nm and 330 nm for **1** and **2**, respectively. To avoid the reabsorption of the emitted radiation by the acceptor (inner filter effect) as a result of overlapping of acceptor absorption and donor emission, the measured data was corrected using a procedure described elsewhere [12]. Excited-state lifetimes were measured at the Chemistry Laboratory, Kyoto-Institute of Technology, Japan, using the technique of time-correlated single-photon counting (channel width: 107 ps). The excitation source was a deuterium-filled flash lamp, and the wavelength of excitation used in this work was 318 nm for **1** and 330 nm for **2**. The fluorescence decay curves were analyzed as described earlier [13].

Fluorescence quantum yields were measured at 25 °C in chloroform relative to anthracene, $\lambda_{ex} = 313$ nm ($\phi_f = 0.35$ in cyclohexane [14]), introducing the usual corrections for the instrumental spectral response and the solvent refractive index. The evaluated values were 0.027 and 0.028 for **1** and **2**, respectively.

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