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Electron transfer singlet quenching and exciplexes in the photoreaction of substituted anthracenes with indole derivatives

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Abstract

The effect of substituents on the singlet quenching and photoreaction of anthracene with indole derivatives was investigated in acetonitrile and *n*-heptane solutions at 298 K. The photoreaction proceeds by the quenching of the excited singlet of anthracene by the indoles. Bimolecular quenching rate constants in acetonitrile follow a Rehm–Weller type correlation. In the nonpolar solvent *n*-heptane, the rate constants are of the same order of magnitude than those in acetonitrile. However, methyl substitution at the N heteroatom of the indole greatly reduces the quenching in this solvent. In these cases, exciplex emission was observed. These differences in quenching capacity may be explained by a charge transfer interaction followed by proton transfer in the excited state, when it is available at the N–H bond. A nonreactive decay route and exciplex emission is operating in the case of the N–CH_3 derivatives. Photobleaching quantum yields were also determined in heptane. The substitution by methyl or cyano groups at 9 and 10 positions on the anthracene ring decreases the reaction quantum efficiency.

Keywords: Electron transfer; Exciplexes; Anthracenes; Indole

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1. Introduction

The reactions of excited states of aromatic hydrocarbons with aliphatic and aromatic amines are well documented [1]. In the case of polycyclic aromatic hydrocarbons (PAHs), these reactions lead to non-cyclic addition of the amine to the aromatic rings, with the subsequent loss of conjugation and photobleaching of the PAH. Particularly, the photoreactions of anthracenes with amines has been the subject of several papers [2–5]. In polar solvents, the initial step in these reactions is an electron transfer from the amine to the excited state of the PAH [6]. The photobleaching of PAHs caused by nitrogen heterocycles has been less investigated. We have been interested in the detailed mechanism of the reaction of excited singlet pyrene with indole both in homogeneous [7,8] and heterogeneous media [8,9]. More recently, an investigation of the structural factors and solvent effect on the photoreaction of anthracene with indole was published [5]. The photoreaction proceeds by the quenching of the excited singlet of anthracene by the indole. A correlation of the rate constants with the redox potential of the indole derivative was found in acetonitrile. However, in nonpolar media, the rate constants markedly decreased upon methyl substitution on the N atom of the indole ring. It was also observed that the photobleaching efficiency was higher in nonpolar solvents, and that it was nearly totally suppressed by the *N*-methyl substitution [5].

In this paper, we present results on the effect of substitution on the anthracene ring. Methyl and cyano groups at the positions 9 and 10 greatly influence the quenching rate constants and the photoreaction yield. Several indole derivatives were also employed in order to clarify the effect of *N*-methyl substitution on the quenching. Bimolecular quenching rate constants were determined in acetonitrile and *n*-heptane. In the polar medium, they were found to follow a Rehm–Weller type correlation with the free energy change for an electron transfer process. In heptane, exciplex emission was observed in cases when the reactive decay of the charge transfer intermediate is blocked by methyl substitution.

2. Experimental

Anthracene, 9-methylanthracene, 9,10-dimethylanthracene, 9-cyanoanthracene and 9,10-dicyanoanthracene were

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from Aldrich and were used without further purification. It was checked that their photophysical properties coincide with those reported in the literature. Indole, 1,2-dimethylindole and 3-methylindole, from Sigma, were purified by recrystallization. 1-Methylindole from Aldrich was purified by fractional distillation under nitrogen. The solvents acetonitrile and *n*-heptane were from Sintorgan, HPLC grade, and they were used as received.

Stationary fluorescence quenching experiments were carried out with an Spex Fluoromax spectrofluorometer. Fluorescence lifetime were measured with the time-correlated single-photon counting technique on an Edinburgh Instruments OB900 equipment.

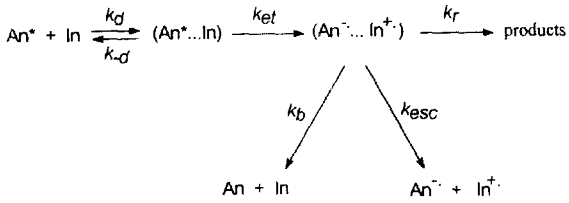
The continuous photolysis experiments were carried out with a 150-W Xe lamp coupled to a grating monochromator (Photon Technology International). Irradiation wavelength was chosen to coincide with the maximum of the lower energy UV band of the anthracenes. Photobleaching quantum yields were determined with Aberchrome 540 actinometer as described earlier [8].

All measurements were performed in deaerated solutions at 298 K.

3. Results and discussion

3.1. Singlet quenching in acetonitrile

The quenching by indole derivatives of anthracene and 9,10 substituted anthracenes was measured in acetonitrile and in *n*-heptane. Bimolecular quenching rate constant k_q, were determined experimentally from Stern–Volmer plots of fluorescence intensity or by measuring the anthracene fluorescence lifetime τ, as a function of indole concentration. Replicate runs produced values that were within 5%. The values of k_q in acetonitrile are collected in Table 1.



Scheme 1.

In our previous work, we have established by laser flash photolysis experiments that the quenching of anthracene by indole in acetonitrile is an electron transfer reaction [5]. This is confirmed here by the substituents effect on the rate constants. The rate constants increase with the electron acceptor capability of the anthracene and with the electron donating ability of the indole, as measured by their redox potentials in acetonitrile. They reach the diffusion limit for the cyanoanthracenes, while they fall down with methyl substitution. The detailed mechanism may be written as Scheme 1.

According to the reaction scheme, the rate constant becomes

$$k_q = \frac{k_d k_{et}}{k_{-d} + k_{et}} \quad (1)$$

Eq. (1) may be reordered to

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{K_D k_{et}} \quad (2)$$

where k_d is the diffusional rate constant and $K_D = k_d/k_{-d}$ is the equilibrium constant for the formation of the precursor complex. For uncharged reactants, K_D depends only on r_{12}, the donor–acceptor distance in the precursor complex. Usually, K_D is in the range 0.5–0.8 M^{-1} [10].

The electron transfer rate constant k_{et} may be written as [11]

$$k_{et} = \kappa \nu_n \exp(-\Delta G^*/RT) \quad (3)$$

where κ is the transmission coefficient (unity for an adiabatic reaction) and ν_n is a nuclear frequency factor (usually between 10^{12} and 10^{13} s^{-1}). The activation Gibbs energy derived from the Marcus classical theory for electron transfer [11], is given by

$$\Delta G^* = \frac{\lambda}{4}\left[1 + \frac{\Delta G^0}{\lambda}\right]^2 \quad (4)$$

where ΔG^0 is the overall Gibbs energy change for the electron transfer process.

The reorganization energy λ, has two contributions:

$$\lambda = \lambda_{in} + \lambda_{out} \quad (5)$$

Table 1
Bimolecular quenching rate constants of anthracenes excited singlet by indoles in acetonitrile at 298 K

	k_q (10^9 M^{-1} s^{-1})				
	Indole (1.21 V)	1-Methylindole (1.20 V)	1,2-Dimethylindole (1.09 V)	2-Methylindole (1.07 V)	3-Methylindole (1.04 V)
Anthracene	5.6	5.6	14.0	14.7 [a]	26.0
9-Methylanthracene	0.80	0.65	8.9	9.3	16.0
9,10-Dimethylanthracene	0.04	0.16	1.96		5.6
9-Cyanoanthracene	26.0	21.0			30.9
9,10-Dicyanoanthracene	25.0	22.0			24.0

[a] From Ref. [5].

The inner term, λ_{in} arises in structural changes on going from the equilibrium configuration of the reactants to that of the products. The second term, λ_{out} is called the solvent reorganization energy, and it is the major contribution to the total reorganization energy for electron transfer reactions involving rigid organic molecules. When a dielectric continuum model is applied, the solvent contribution, assuming spherical shape for the reactants, λ_{out} can be written as [11]

$$\lambda_{out}=e^2\left(\frac{1}{2r_i}+\frac{1}{2r_2}-\frac{1}{r_{12}}\right)\left[\frac{1}{\varepsilon_{op}}-\frac{1}{\varepsilon_s}\right] \qquad (6)$$

where ε_{op} and ε_s are the optical and static dielectric constants respectively, and $r_{12}=r_1+r_2$ is the sum of the molecular radii of the reactants.

According to Rehm and Weller [12], the Gibbs energy change in the electron transfer process can be calculated from the redox potentials of the donor $E_{(D/D^+)}$ and acceptor $E_{(A/A^-)}$, and the energy of the excited state involved

$$\Delta G^0=E_{(D/D^+)}-E_{(A/A^-)}-E^*+\frac{Z_1Z_2}{\varepsilon_s r_{12}} \qquad (7)$$

where E^* is the energy of the singlet excited state of the anthracenes, and the last term represents the coulombic energy necessary to form an ion pair with charges Z_1 and Z_2 in a medium of dielectric constant ε at a distance r_{12}. In the present case, ΔG^0 was calculated with the reduction potentials and excited state energies of the anthracenes as reported in the literature [13]. There are some discrepancies in the literature about the oxidation potential of the indoles [14]. We have used in Eq. (7) the values given in Table 1. They are based on a value of 0.97 V in water vs. NHE for indole, measured by cyclic voltammetry [15]. For the methyl-substituted indoles we employed the relative values derived from pulse radiolysis kinetic measurement [14,16]. The values were normalized to 0.97 V for indole and referred to the SCE by adding 0.241 V. The coulombic term was taken as −0.05 eV, assuming a separation distance of 0.8 nm.

A log plot of the quenching rate constants in MeCN as a function of ΔG^0 can be seen in Fig. 1. The solid line was calculated with Eqs. (2)–(7) and the parameters k_d, $K_D\nu_n$ and λ set to 2.5×10^{10} M^{-1} s^{-1}, 1×10^{13} s^{-1} and 0.90 eV, respectively. The value of k_d agrees well with the diffusion limit in acetonitrile [13]. The values of the other two parameters are typical for an electron transfer process in this solvent [17].

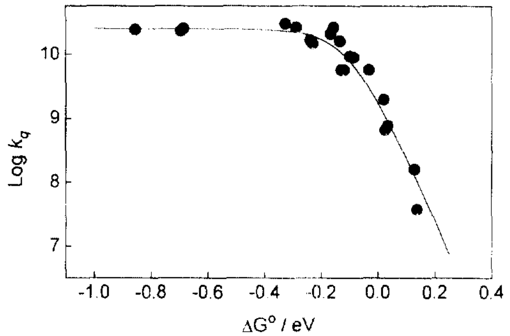


Fig. 1. Bimolecular quenching rate constants as a function of the overall Gibbs energy change for the electron transfer reaction in acetonitrile.

3.2. Singlet quenching in n-heptane

In the nonpolar solvent, *n*-heptane, the rate constants are of the same order of magnitude than those in acetonitrile. The values are presented in Table 2. For a given indole derivative, they increase with the electron acceptor capacity of the anthracene approaching the diffusional limit in this solvent for the cyanoanthracenes. However, while in acetonitrile the rate constants for indole and the 1-methyl derivative are very close; in *n*-heptane, the rate constants for 1-methylindole are very much lower than those for indole itself. Since the oxidation potentials of both compounds are practically the same, this variance must arise from some mechanistic differences in the nonpolar medium.

It is well known that polycyclic aromatic hydrocarbons and their derivatives form emissive exciplexes with electron donors in nonpolar solvents. Exciplex emission was previously observed for cyano-substituted anthracenes quenched by 1,3-cyclohexadiene and 1,2-dimethoxybenzene in methylcyclohexane [18]. However, for indole and its derivatives, the only reported exciplex is for the quenching of pyrene and 9-cyanopyrene by 1,2-dimethylindole [19]. In our previous studies of pyrene quenching by indole in solvents of varying polarity [7,8], exciplex emission was not observed. In the present case, however, when anthracene derivatives are quenched by *N*-methyl substituted indoles, a new red shifted fluorescence band appears at high quencher concentration,

Table 2
Bimolecular quenching rate constants of anthracenes excited singlet by indoles in *n*-heptane at 298 K

	k_q (10^9 M^{-1} s^{-1})				
	Indole	1-Methylindole	1,2-Dimethylindole	2-Methylindole	3-Methylindole
Anthracene	10.6	0.63	4.3 [a]	13.9 [a]	16.0
9-Methylanthracene	0.57	0.09			10.0
9,10-Dimethylanthracene	–	0.07			3.5
9-Cyanoanthracene	28.8	16.6	21.3	21.4	26.9
9,10-Dicyanoanthracene	28.3	24.5	23.1	25.0	28.2

[a] From Ref. [5].

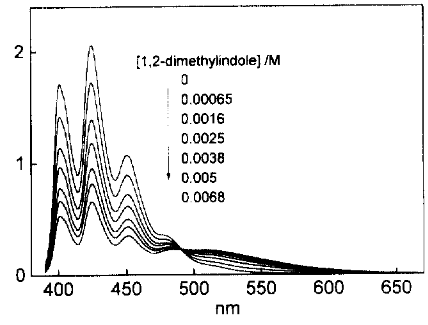


Fig. 2. Quenching of 9-cyanoanthracene fluorescence by 1,2-dimethylindole in heptane.

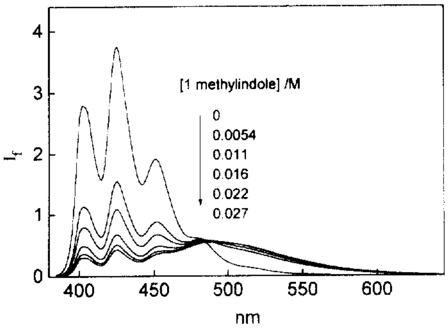


Fig. 3. Quenching of 9-cyanoanthracene fluorescence by 1-methylindole in heptane.

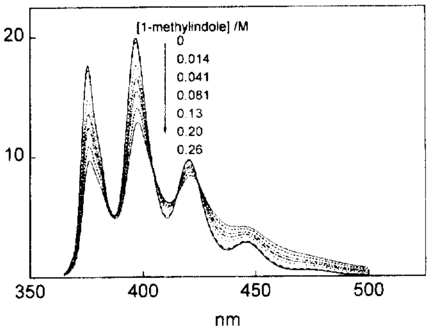
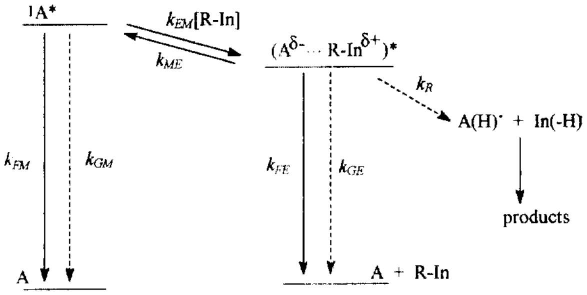


Fig. 4. Quenching of anthracene fluorescence by 1-methylindole in heptane.

that can be ascribed to an exciplex emission. Figs. 2 and 3 show typical examples where an iso-emissive point is clearly observed. The exciplex emission in the case of anthracene and methylanthracenes is submerged under the monomer emission, and the effect manifests as an increase in the bands of longer wavelengths (Fig. 4). The position of the exciplex emission, for the four systems where it can be clearly established, is presented in Table 3. It can be seen that it moves to the red as the charge transfer state is more stabilized according to the redox potentials. This behavior is typical of a polar exciplex.

Table 3
Emission maxima of the exciplex band (nm)

	1-Methylindole	1,2-Dimethylindole
9-Cyanoanthracene	497	513
9,10-Dicyanoanthracene	570	595



Scheme 2.

On the other hand, in the case of quenching by N–H indoles, only a decrease of the anthracene bands is observed. This is similar to the behavior of the pyrene–indole system. These observations may be explained by the following mechanism for the quenching process in heptane (Scheme 2), where $(A^{\delta-}\ldots R-In^{\delta+})$ stands for the polar exciplex and A(H)· and In(−H)· are the anthryl and indolyl radicals formed from the exciplex.

As suggested before [5], the lower rate constants and the lack of reactivity for *N*-methyl derivatives in heptane is what may be expected from an extrapolation of the behavior in polar solvents. The electron transfer operating in acetonitrile is now replaced by the formation of a polar emissive exciplex. What is anomalous is the high quenching efficiency of the N–H derivatives. In Scheme 2, following Birks' [20] nomenclature, k_{FE} and k_{GE} are the radiative and nonradiative rate constants for the exciplex decay. When $R=CH_3$, these are the only deactivation routes. However, when R = H, a new proton transfer process offers a new and very fast decay route for the exciplex. In this case, $k_R \gg k_F + k_{EM}$ and the exciplex emission is not observed.

Time-resolved measurements of the fluorescence decay at the emission wavelengths of 9-cyanoanthacene local excited state (403 nm) and those corresponding to the exciplex were performed for the case of the quenchers 1-methylindole and 1,2-dimethylindole. For the latter, the decay at 403 nm follows a single exponential kinetics from which a rate constant results in agreement with the result of stationary fluorescence intensity measurements. For the exciplex emission, the typical bi-exponential growth and decay is observed. This is indicative of a non-reversible exciplex mechanism, i.e., $k_{FE} + k_{GE} \gg k_{ME}$. The diffusion limit value of the quenching rate constant in Table 2 for this system is also in agreement with the very fast decay of the exciplex. On the other hand, when the same experiments were carried out with 1-methylindole, the emission at 403 nm decays by a bi-exponential law. For this quencher, the rate constant from static measurements is lower than the diffusion limit, and the return to the local excited state competes with the exciplex decay to ground state.

3.3. Photochemical reaction

A detailed study of the influence of the solvent polarity and indole structure on the quantum yield of anthracene

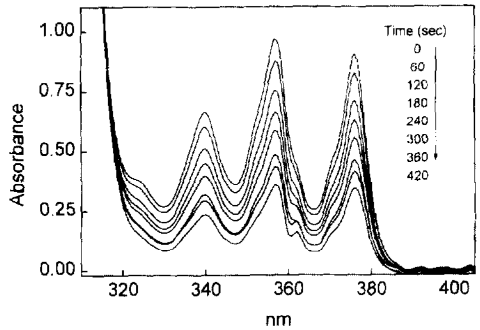


Fig. 5. Photobleaching of anthracene in the presence of 3-methylindole.

Table 4
Quantum yields of anthracenes photobleaching by 3-methylindole in n-heptane at 298 K

	Φ_r
Anthracene	0.37
9-Methylanthracene	0.28
9,10-Dimethylanthracene	0.14
9-Cyanoanthracene	0.19
9,10-Dicyanoanthracene	0.02

photobleaching in the presence of indoles was previously published [5]. However, the effect of the substitution on the anthracene ring was not investigated.

When the anthracene derivatives are irradiated in the UV band of maximum intensity in the region 330–440 nm in the presence of 3-methylindole in n-heptane, the absorption spectrum of the anthracene decreases in intensity without any apparent change in the spectral shape. A typical example is shown in Fig. 5. Under similar conditions of irradiation in the absence of indole, the photobleaching was negligible.

The photobleaching quantum yield Φ_r was determined with the actinometer Aberchrome 540 as described in Section 2. In Table 4, the quantum yields for the same fraction of singlet quenching of several anthracene derivatives by 3-methylindole in n-heptane are collected.

The quantum yields decrease when the positions 9, or 9 and 10 on the anthracene are substituted. This decrease is due to two factors. First, the photobleaching may be understood as a radical, or radical ion addition in a polar solvent, to positions 9 and 10 of the hydrocarbon. This breaks the structure of the anthracene chromophore, and accordingly, the typical absorption bands of the conjugated aromatic rings diminish in intensity. When these positions are blocked by substituents, the attack by reactive species is less efficient, and the photobleaching is diminished. Second, it may be observed in Table 4 that the quantum efficiency of the cyanoanthracenes is much less than that of the methyl anthracenes. These may be explained by the higher electron acceptor capacity of the cyano derivative as compared with the methyl-substituted anthracene. Accordingly, the energy level of the exciplex is lower in the case of the cyanoanthracenes. Therefore, considering the energy gap law, the decay from this polar intermediate to ground state, k_{GD} should favorably compete with the reaction pathway, k_R and the quantum yield decreases.

In summary, we have shown that the excited state quenching of anthracenes by methyl-substituted indoles follows an electron transfer kinetics in acetonitrile. In n-heptane, the results may be explained by the formation of a polar exciplex. The decay of the exciplex depends strongly on the substitution on the N atom of the indole ring. When it is methyl-substituted, exciplex emission is observed. This emission is absent for the N–H indoles. For the latter, the quenching rate constants and photoreaction yield are very much higher than those of the methyl-substituted derivatives. This behavior may be explained by a fast H atom transfer reaction as an alternative route for the exciplex decay. The effect of substitution on the anthracene ring on the photochemistry in heptane may be explained by the same exciplex mechanism.

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