

DEACTIVATION BEHAVIOUR OF ARENES AND HETEROARENES XVI. FLUORESCENCE SELF-QUENCHING OF ANTHRACENE-LIKE COMPOUNDS BY EXCIMER FORMATION

by

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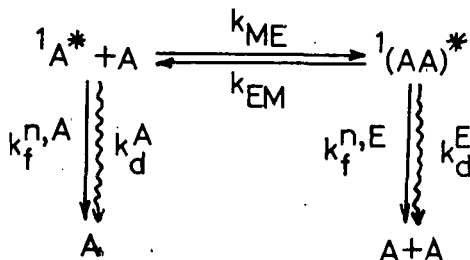
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Using frontal fluorescence excitation, fluorescence quantum yields are accessible even at large fluorophor concentrations provided there is total absorption. This allows to determine the quenching rate constants of fluorescence self-quenching. A suitable method is presented and tested on anthracene and some of its derivatives (2-Me-, 9-Me-, 9-Ph-), the acridizinium ion and 6,7-benzoquinoline. The Stern—Volmer plots agree within the experimental accuracy to those obtained for concentration-dependent fluorescence lifetimes (determined from decay curves and external fluorescence quenching). Consequently a dynamic mechanism has to be formulated for the self-quenching processes examined.

As opposed to other fluorophors studied, the rate constant of self-quenching for 9-phenylanthracene is appreciably smaller than the rate constant of diffusion. This effect is ascribed to steric hindrance of excimer formation.

Introduction

Decreasing fluorescence quantum yields with rising concentration, along with shorter fluorescence lifetimes, are typical for the fluorescence behaviour of many aromatic compounds [1–5]. Detailed studies showed that self-quenching according to (1) is caused by the formation of excimers and their deactivation (radiative k_f^E ; non-radiative k_d^E).



The degree of self-quenching (2) depends on the relationship between the rate constants of all deactivation steps or excimer formation and their back-reactions.

$$\frac{\varphi_{f,0}^A}{\varphi_f^A} = \frac{\tau_{f,0}^{w,A}}{\tau_f^{w,A}} = 1 + k_q^{AA} \tau_f^{w,A} [A] \quad (2)$$

$\varphi_{f,0}^A$; φ^A — limit-value of the fluorescence quantum yield at low concentrations ($[A] < 1 \cdot 10^{-5} \text{ mol l}^{-1}$) or in the case of self-quenching.

$\tau_{f,0}^{w,A}$; $\tau_f^{w,A}$ — unaffected and affected fluorescence decay time, *resp.*, due to self-quenching.

For the rate constant of self-quenching k_q^{AA} holds expression (3).

$$k_q^{AA} = \frac{k_{ME} k_f^{w,E}}{k_{EM} + k_f^{w,E}} \quad (3)$$

$k_f^{w,E}$ — fluorescence decay time of the excimer with

$$k_f^{w,E} = k_f^{n,E} + k_d^E \quad (4)$$

The studies known from the literature of self-quenching of fluorescence are based on concentration-dependent fluorescence lifetimes [6–8]. To prove that fluorescence quenching (1) is purely dynamic, requires to check the validity of (2) to the effect that plotting of the lifetimes and the fluorescence quantum yields will give both values the same Stern-Volmer plots [2, 3, 9, 10]. However, conventional fluorescence observation by right angle excitation does not allow to determine the fluorescence quantum yield at high concentrations owing to the strong filter effect [11, 12] under these conditions of excitation and important reabsorption and reemission influences [12, 13]. Recent investigations into the fluorescence behaviour with frontal fluorescence excitation [12] show that the reabsorption and reemission effects are stable and correctable for this geometrical arrangement (Fig. 1). Based on these results a procedure will be presented which enables the self-quenching at rising concentration to be evaluated on the basis of the fluorescence quantum yields.

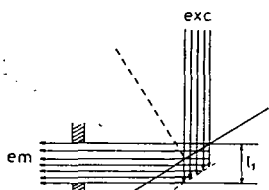


Fig. 1. Optical arrangement in the case of frontal fluorescence excitation

As can be seen from eq. (3) basically two border-line cases exist for the degree of self-quenching:

(i) Deactivation of the excimer is much faster than the back-reactions to $^1A^*$ and

A ($k_f^{w,E} \gg k_{EM}$). Under these conditions self-quenching of fluorescence should be diffusion-controlled [14].

$$k_q^{AA} \approx k_{ME} \approx k_{\text{diff}} = \frac{8RT}{2000\eta} \quad (5)$$

(ii) The back-reaction k_{EM} is faster than the deactivation of the excimer ($k_{EM} \gg k_f^{w,E}$). In this case (6) the extent of fluorescence quenching depends in addition on the location of the equilibrium ($K_c^{ME} = k_{ME}/k_{EM}$), and it holds (7).

$$k_q^{AA} = \frac{k_{ME}}{k_{EM}} k_f^{w,E} = K_c^{ME} k_f^{w,E} \quad (6)$$

$$0 \cong k_q^{AA} < k_{\text{diff}} \quad (7)$$

With reference to the self-quenching of the fluorescence of anthracene (*An*) [2, 4] it is further examined to what extent this self-quenching is affected by exocyclic substitution (2-methylantracene (*2-Me-An*), 9-methylantracene (*9-Me-An*), 9-phenylantracene (*9-Ph-An*)) and endocyclic substitution (acridizinium ion (*Az*), 6,7-benzoquinoline (*BQ*)).

Experimental

The anthracenes used in this study, were commercial products (for purification see [15]). Acridizinium perchlorate was synthesized according to [16] and 6,7-benzoquinoline according to [17]. The solvents were purified by standard procedures [18].

The fluorescence measurements were made on a MPF-2A spektro-fluorimeter (Hitachi-Perkin-Elmer) at 298 K under aerobic conditions. The excitation angle was 30° (cf. Fig. 1). The fluorescence decay curves were recorded by excitation with a nitrogen laser ($\lambda=337.1$ nm) using a Boxcar integrator (for details see [19]).

For the quenching tests $[Q]=1 \cdot 10^{-1} \dots 1 \cdot 10^{-4}$ mol l^{-1} of quencher were added. The self-absorption of the quenchers was in all cases <1% of the fluorophor absorption intensity at excitation wavelength.

For all linear plots, calculations were carried out to adjust for errors in the straight lines.

Results

For studying self-quenching of fluorescence by frontal excitation there must be total absorption inside the path length l_1 . This total absorption depends on a minimum concentration ($[A]$) [12] which does not permit to determine $\varphi_{f,0}$ or an adequate relative fluorescence intensity $I_{f,0}$ because of the presence of self-quenching. Consequently eq. (2) has to be applied in the form of (8).

$$\frac{1}{I_f^A} = \frac{1}{I_{f,0}^A} + \frac{k_q^{AA} \tau_{f,0}^{w,A}}{I_{f,0}^A} [A]. \quad (8)$$

By plotting the reciprocal relative fluorescence intensities *versus* fluorophor concentration, a straight line is obtained, and the quenching rate constant k_q^{AA} is determined from the quotient obtained from the slope and ordinate section, divided by the fluorescence decay time, $\tau_{f,0}^{w,A}$ (Table I).

Table I

Fluorescence quantum yields and fluorescence lifetimes of investigated compounds

	Solvent	$\varphi_{f,0}^A$	$\tau_{f,0}^{w,A}$ [ns]
<i>An</i>	benzene	0.26 ^{a)}	4.3 ^{a)}
<i>2-Me-An</i>	benzene	0.30	4.8
<i>9-Me-An</i>	benzene	0.33	5.2 ^{a)}
<i>9-Ph-An</i>	benzene	0.53	5.1 ^{a)}
<i>Az</i>	methanol	0.52 ^{b)}	4.4 ^{b)}
<i>BQ</i>	ethanol	0.62	11.6

^{a)} [2]; ^{b)} [20].

Figures 2-7 show the functions (8) for the studied fluorophors. Linearity is observed above a given concentration $[A]_t$, as expected, whereas below $[A]_t$ the recorded fluorescence intensities are smaller than suggested by the plotted straight line. This is attributable to the fact that the condition of total absorption inside l_1 (Fig. 1) is no longer satisfied for $[A] < [A]_t$. This also explains the change of shape of the fluorescence band in this concentration range, since the otherwise stable reabsorption effect is becoming weaker, as indicated by the growing intensity in the short-wave part of the spectrum (Fig. 8).

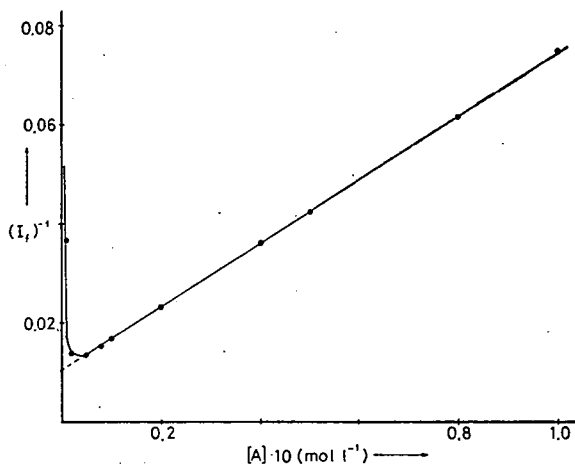


Fig. 2. Relative fluorescence intensity as a function of concentration (anthracene in benzene)

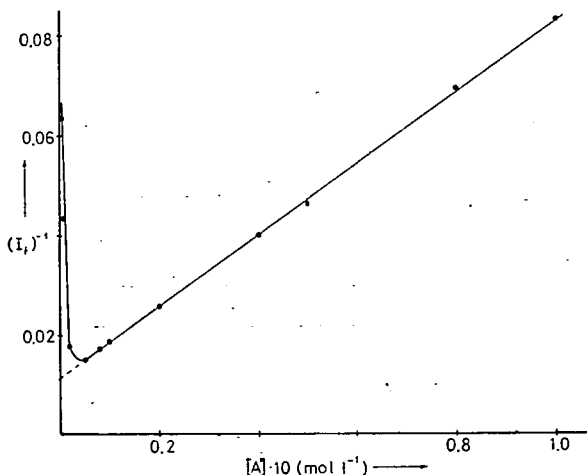


Fig. 3. Relative fluorescence intensity as a function of concentration (2-methylanthracene in benzene)

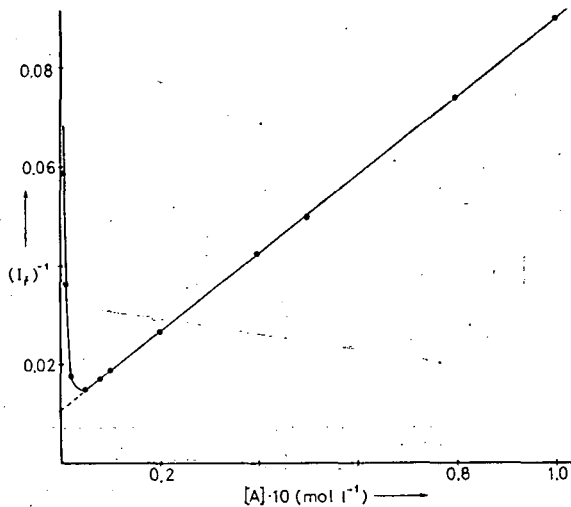


Fig. 4. Relative fluorescence intensity as a function of concentration (9-methylanthracene in benzene)

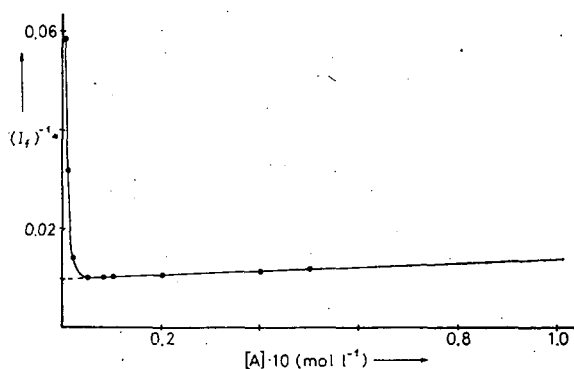


Fig. 5. Relative fluorescence intensity as a function of concentration (9-phenylanthracene in benzene)

The fluorescence quantum yield $\phi_{f,0}^A$ (Table I) can be assigned to the relative fluorescence intensity $I_{f,0}^A$ obtained by extrapolation. The resultant fluorescence quantum yields ϕ_f^A are collected as a function of concentration in Table II. The lifetimes τ_f^A for the fluorophors *Az* and *BQ* were calculated from the fluorescence decay times (Table II). The Stern-Volmer plots according to (2) obtained from these concentration-dependent lifetimes, yield straight lines (Fig. 9). From the slope of these lines the quenching rate constants were calculated (see in Table III).

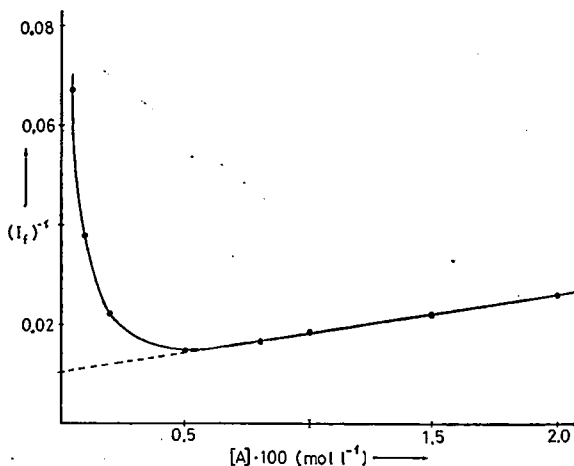


Fig. 6. Relative fluorescence intensity as a function of concentration (acridizinium ion in methanol)

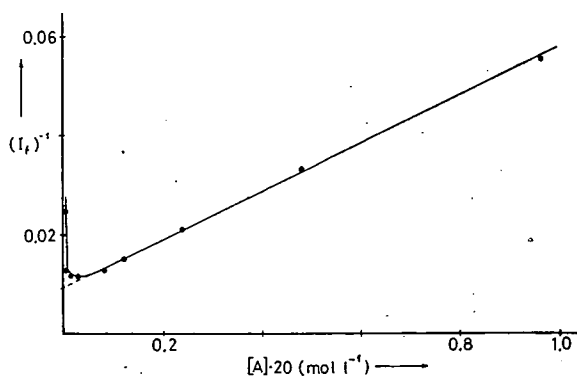


Fig. 7. Relative fluorescence intensity as a function of concentration (6,7-benzoquinoline in ethanol)

Further the fluorescence lifetimes at different fluorophor concentrations by quenching with an external quencher Q were determined (9).

$$\frac{I_{f,0}}{I_f} = 1 + k_s^A Q \tau_f^{w,A} [Q]. \quad (9)$$

For *An*, *2-Me-An*, *9-Me-An* and *9-Ph-An* methyl iodide was used as quencher, for which case the mechanism (10) holds [23].

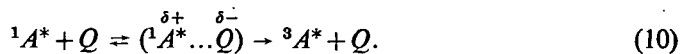


Table II

Fluorescence quantum yields and fluorescence lifetimes (in ns) at different concentrations

[A] [mol l ⁻¹]	An		2-Me-An		9-Me-An		9-Ph-An		BQ		Az	
	φ_f	$\tau_f^{w^a)}$	φ_f	$\tau_f^{w^a)}$	φ_f	$\tau_f^{w^a)}$	φ_f	$\tau_f^{w^a)}$	φ_f	$\tau_f^{w^b)}$	φ_f	τ_f^w
												Ia)· IIb)
1 · 10 ⁻⁴	0.26	4.3	0.30	4.8	0.33	5.2	0.53	5.1	0.61	11.5	0.52	4.4 4.4
1 · 10 ⁻³	0.25	4.0	0.28	4.5	0.31	4.9	0.53	5.1	0.57	10.7	0.48	4.1 4.0
2 · 10 ⁻³	0.23	3.8	0.27	4.2	0.29	4.6	0.53	5.0	0.53	9.8	0.45	3.8 3.8
5 · 10 ⁻³	0.20	3.3	0.23	3.6	0.24	3.8	0.52	5.0	0.43	7.9	0.38	3.2 3.3
8 · 10 ⁻³	0.18	2.9	0.20	3.1	0.21	3.3	0.51	4.9	0.35	6.6	0.33	2.8 2.8
1 · 10 ⁻²	0.16	2.6	0.18	2.9	0.19	3.0	0.51	4.9	0.33	6.2	0.30	2.5 2.5
1.5 · 10 ⁻²	0.14		0.15		0.16		0.50		0.26		0.25	2.1 2.1
2 · 10 ⁻²	0.12	1.9	0.13	2.0	0.14	2.1	0.49	4.6	0.22	4.2	0.21	1.8 1.8
4 · 10 ⁻²	0.08	1.2	0.09	1.3	0.09	1.4	0.46	4.2	0.14	2.6		
5 · 10 ⁻²	0.06	1.0	0.07	1.1	0.07	1.1	0.44	4.1	0.11	2.1		
8 · 10 ⁻²	0.04		0.05		0.05		0.40					
1 · 10 ⁻¹	0.04		0.04		0.04		0.38					
5 · 10 ⁻¹									0.01	0.2		

a) Calculated from the fluorescence quenching results.

b) Decay times.

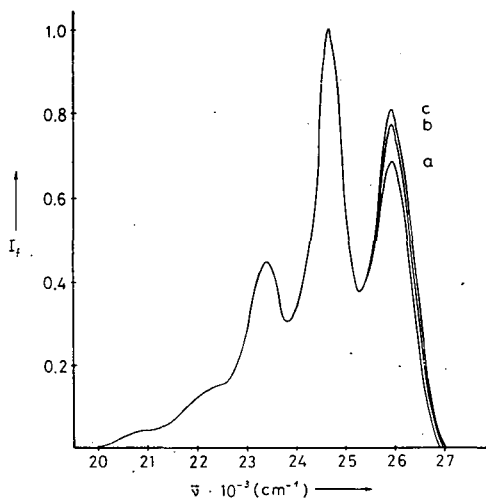


Fig. 8. Fluorescence spectra of anthracene at different concentrations (frontal fluorescence excitation)
 a = $5 \cdot 10^{-3}$ mol l⁻¹, b = $2 \cdot 10^{-3}$ mol l⁻¹,
 c = $1 \cdot 10^{-0}$ mol l⁻¹

Table III

Rate constants of fluorescence self-quenching k_q^{AA} for the investigated fluorophors and rate constants of diffusion (all in $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$)

Fluorophor	Solvent	k_q^{AA}			$k_{diff}^{d)}$
		I ^{a)}	II ^{b)}	III ^{c)}	
An	benzene	14.1		14.6	16.0
2-Me-An	benzene	13.0		14.0	16.0
9-Me-An	benzene	13.6		13.7	16.0
9-Ph-An	benzene	0.8		1.0	16.0
Az	methanol	16.8	16.5	16.5	18.0
BQ	ethanol	8.9	8.1		9.2

a) Calculated by the fluorescence quantum yields.

b) Calculated by fluorescence decay times.

c) Calculated by fluorescence lifetimes result from quenching investigations.

d) [21].

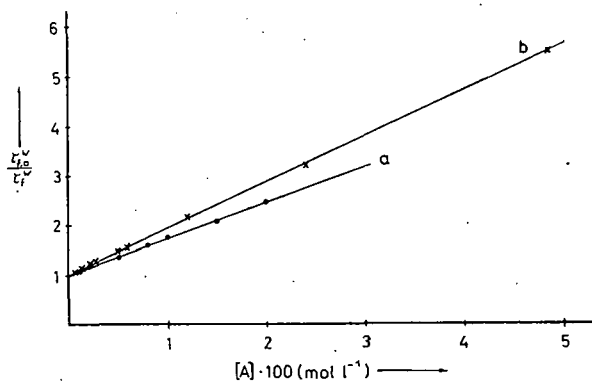
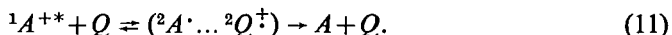


Fig. 9. Stern—Volmer plots of fluorescence lifetimes as obtained from fluorescence decay measurements; for Az in methanol (a) and for BQ in ethanol (b)

The fluorescence of the acridinium ion was quenched by naphthalene (11) [5, 22].



The values of k_q^{AQ} required for interpretation, were determined by means of fluorescence quenching at $[A] \leq 1 \cdot 10^{-5} \text{ mol l}^{-1}$ with reference to $\tau_{f,0}^y$ (Table I) and summarized in Table IV.

The Stern—Volmer plots using the τ_f^y -values found by external quenching are shown in Fig. 10. The resultant quenching rate constants k_q^{AA} , using (2), are likewise included in Table III.

Table IV

Rate constants of fluorescence quenching $k_q^{A^Q}$ for the investigated fluorophor/quencher pairs (in $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$)

Fluorophor	Solvent	Quencher	$k_q^{A^Q}$
An	benzene	methyl iodide	6.2
2-Me-An	benzene	methyl iodide	6.1
9-Me-An	benzene	methyl iodide	5.9
9-Ph-An	benzene	methyl iodide	4.1
Az	methanol	naphthalene	16.1 ^{a)}

^{a)} [22].

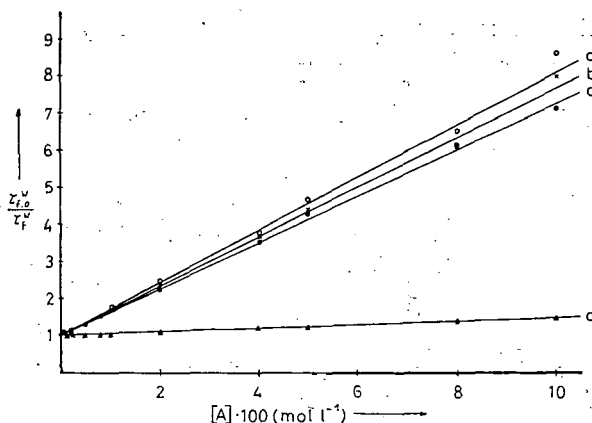


Fig. 10. Stern—Volmer plots of fluorescence lifetimes, obtained from external fluorescence quenching; for An (●, a), 2-Me-An (x, b), 9-Me-An (○, c) and 9-Ph-An (▼, d) in benzene

Discussion

The linear dependencies obtained between $(I_f)^{-1}$ and $[A]$ for $[A] > [A]_t$ (Figs. 2–7) confirm the validity of (8). This result and the fact that the $k_q^{A^Q}$ -values are identical within the experimental accuracy with those determined from fluorescence lifetimes (Table III) prove the applicability of the approach by which self-quenching with frontal excitation is studied by means of the fluorescence quantum yield.

As stated previously, frontal excitation requires a minimum concentration $[A]_t$. Hence self-quenching can be studied only in the concentration range (12), which will be relatively narrow (Fig. 6) with sparingly soluble fluorophors ($[A]_{\text{saturated}}$ low).

$$[A]_{\text{saturated}} \cong [A] > [A]_t \quad (12)$$

As a result, the evaluation will be difficult, especially extrapolation $[A] \rightarrow 0$ for (8). By contrast, concentration range (13) can be utilised when evaluating the fluorescence lifetime.

$$[A]_{\text{saturated}} \cong [A] > 0 \quad (13)$$

Table III shows that there is good agreement for the values of k_q^{AA} obtained by the three methods outlined above. It may be concluded that self-quenching of fluorescence is in all cases a dynamic process. Diffusion control is observed in all cases, apart from *9-Ph-An*, as shown by comparing k_q^{AA} with k_{diff} of the solvents studied (Table III). Hence it may be followed that for the compounds *An*, *2-Me-An*, *9-Me-An*, *Az* and *BQ*, deactivation of the excimer proceeds at a considerably faster rate than the back-reaction k_{EM} , that is to say, it holds (5). In the case of *9-Ph-An* very weak fluorescence self-quenching is observed which implies that (6) holds here. The relationship $k_{EM} \gg k_f^{*,E}$ may be explained either by steric hindrance of complex formation because of the twisted phenyl substituent or by the slower deactivation rate of the excimer as compared to the other fluorophors¹⁾. Investigations which studied the potential ability to form π - π -molecular complexes [24] have shown a comparatively small association constant to be typical of the *9-Ph-An* in this case. Hence it may be assumed that steric hindrance of excimer formation caused by twisting of the phenyl ring relative to the π -plane of the anthracene [28] accounts for the weak tendency toward excimer formation and concomitant self-quenching. This steric effect is not observed in methylanthracene. This group, which takes up little space, has no effect because of the relatively large intermolecular distances in the excimer (0.3... 0.5 nm [2])²⁾.

Endocyclic substitutions (*Az*, *BQ*) are observed to have no noticeable influence on the rate constant k_q^{AA} . Hence it is concluded that the expected destabilization of the excimer by repulsion (free electron pairs, positive charges) is compensated by an improved ability of forming excimers or a very rapid deactivation (formation of photo-dimers, for instance) of the excimer. The favourable position of the endocyclic substitution is of great importance in this context as it does not cause the meso-positions to be blocked like in N-methylacridinium ion or acridine. This problem will be discussed in a report to be published later.

* * *

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¹⁾ Unlike *An*, *9-Me-An* [1-4], *2-Me-An* [25], *Az* [26] and *BQ* [27], where this reaction contributes substantially to a rapid excimer deactivation ($k_f^{*,E}$), *9-Ph-An* does not photodimerise (in the absence of an energy transferring agent) [29].

²⁾ This statement concerns only the formation of excimers and does not apply to photo-dimers [24].

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ПУТИ ДЕЗАКТИВАЦИИ АРЕНОВ И ГЕТЕРОАРЕНОВ, XVI.
 САМОТУШЕНИЕ ФЛУОРЕСЦЕНЦИИ СОЕДИНЕНИЙ ТИПА АНТРАЦЕНА
 ПРИ ОБРАЗОВАНИИ ЭКСИМЕРОВ

Ю. Бендиг, Б. Хенкель, Д. Крейзиг

В случае высокой концентрации флуоресцирующего вещества можно определить квантовые выходы флуоресценции при полном поглощении. Таким образом возможно определения констант скорости самотушения флуоресценции. Соответствующая методика представлен, в данной работе и успешно испытана на примере антрацена и его производных (2-Ме-, 9-Ме-9-Р-), иона акридиния и 6,7-бензхинолина. Полученные таким образом соотношения Штерна-Фольмера совпадают в пределах ошибки с кривыми из зависимости времени жизни от концентрации (определяемые из кривых затухания флуоресценции и тушения посторонними тушителями). Следовательно, можно предположить динамический механизм самотушения.

Константа скорости самотушения 9-фенилантрацена в отличие от других изученных веществ намного меньше константы скорости диффузии, что объясняется стерическими затруднениями при образовании эксимеров.