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SUBSTITUENT EFFECTS ON TRIPLET YIELDS IN AMINOANTHRAQUINONES: RADIATIONLESS DEACTIVATION VIA INTERMOLECULAR AND INTRAMOLECULAR HYDROGEN BONDING[†]

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Summary

The dependence of the triplet quantum yields of monosubstituted and disubstituted aminoanthraquinones on the number of substituents and on their position was studied. Using fluorescence lifetimes, fluorescence quantum yields and triplet quantum yields, the rate constants of the inter-system crossing into the triplet state and of the internal conversion into the ground state were evaluated. For monosubstituted aminoanthraquinones the individual contributions of various mechanisms to the internal conversion have been estimated. In quenching the excited singlet state, intermolecular hydrogen bonding to the solvent is more efficient by an order of magnitude than intramolecular hydrogen bonding.

1. Introduction

Some years ago Rembold and Kramer [1, 2] reported on the catalytic fading of yellow azo dyes in the presence of blue, violet or red anthraquinonoid dyes. In this case, catalytic fading means that the light fastness of the yellow azo dyes is lower in admixture with the anthraquinonoid dyes

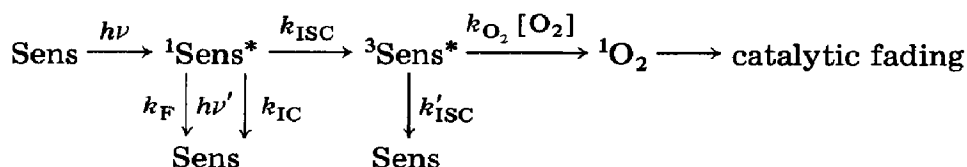
[†]Dedicated to Professor Dr. W. Nultsch on the occasion of his 60th birthday.

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than when applied alone. Although generally various mechanisms might be responsible for the catalytic fading of dye mixtures [3 - 6], in the present case energy transfer processes could be excluded and it was shown that the anthraquinonoid dyes (Sens in Scheme 1) act as triplet sensitizers thus producing singlet molecular oxygen $^1\text{O}_2$ which finally oxidizes the azo dyes (type II photo-oxygenation mechanism [1, 2, 7]). (Whereas Zweig and Henderson [8] assumed that azo dyes produce virtually no singlet oxygen, recently Gruen *et al.* [9] have reported quantum yields of singlet oxygen formation of $(0.03 - 2) \times 10^{-3}$ for *trans*-4-dialkylamino-4'-nitroazobenzenes.)



Scheme 1.

In fact, catalytic fading was only found in mixtures where the triplet yields of the anthraquinonoid dyes used are comparably high [1, 2]. In spite of the technical importance of the anthraquinonoid dyes, little is known about the rates and quantum yields of triplet formation, whereas much data concerning their spectroscopy [10 - 14], fluorescence [15, 16], light fastness [17], fluorescence decay times [18], photochemistry [19 - 21], especially singlet oxygen production [22], and hydrogen bonding [23 - 27] are available.

In the present paper the dependence of the triplet quantum yield of the aminoanthraquinonoid dyes on the number of substituents and on their position will be described. Special attention is paid to the hydrogen bonding which may greatly influence the geometry and the photochemical behaviour [23]. Recent studies have shown that either proton transfer in the excited state or hydrogen bonding is the origin of very effective radiationless deactivation [28, 29]. Similar results have been obtained for UV stabilizers of the 2-(2'-hydroxyphenyl)benzotriazole type [30 - 34]. The quenching of the excited singlet state can be either an intramolecular process including sometimes a rapid keto-enol tautomerization [28 - 35] or an intermolecular process [18, 36]. Intermolecular hydrogen bonding plays an important role in the radiationless deactivation of the excited anthraquinonoid dyes as has been demonstrated by Inoue *et al.* [18] (*cf.* also Drissler *et al.* [37]). Therefore, information about the interactions between dye and solvent may be helpful in finding a quenching mechanism and thus in improving the light fastness of the dye.

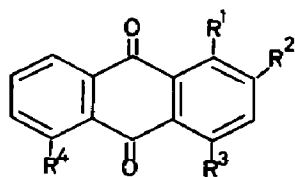
In the present work we focused our attention on the spectroscopy of aminoanthraquinones because for this class of compounds a systematic investigation of the influence of the different types of hydrogen bonding in

relation to the position of the substituent and to the solvent is possible. The radiationless deactivation of the first excited singlet state (S_1) and the triplet formation for some aminoanthraquinones in toluene and methanol were studied using laser flash photolysis and singlet oxygen production (triplet quantum yields), phase fluorometry (fluorescence lifetimes) and emission spectroscopy (fluorescence quantum yields).

2. Experimental details

2.1. Materials

The structures of the anthraquinonoid dyes used (substituted aminoanthraquinones) are given below.



| | |
|--|------------------------------------|
| $R^1 \equiv \text{NH}_2$; $R^2, R^3, R^4 \equiv \text{H}$ | 1-aminoanthraquinone (1-AA) |
| $R^1 \equiv \text{NHCH}_3$; $R^2, R^3, R^4 \equiv \text{H}$ | 1-methylaminoanthraquinone (1-MAA) |
| $R^2 \equiv \text{NH}_2$; $R^1, R^3, R^4 \equiv \text{H}$ | 2-aminoanthraquinone (2-AA) |
| $R^1, R^3 \equiv \text{NH}_2$; $R^2, R^4 \equiv \text{H}$ | 1,4-diaminoanthraquinone (1,4-DAA) |
| $R^1, R^4 \equiv \text{NH}_2$; $R^2, R^3 \equiv \text{H}$ | 1,5-diaminoanthraquinone (1,5-DAA) |

2.1.1. Anthraquinonoid dyes

1-Aminoanthraquinone (1-AA) and 1-methylaminoanthraquinone (1-MAA) were purified by chromatography. For 1-AA the melting point is 252 °C (literature value, 253 - 254 °C [38]); for 1-MAA the melting point is 169 °C (literature value, 170 °C [38]). 2-Aminoanthraquinone was purified by (1) heating *in vacuo* at 150 °C where the volatile impurities disappeared by sublimation, (2) Soxhlet extraction with CCl_4 for about one week where by further impurities were extracted, and finally (3) recrystallizing twice from distilled nitrobenzene; melting point, 304 °C (literature value, 304 °C [38]). The purity was checked by thin-layer chromatography (TLC).

1,4-Diaminoanthraquinone (1,4-DAA) was recrystallized from ethanol-acetone; melting point, 265 °C (literature value, 268 °C [38]); the purity was checked by TLC.

1,5-Diaminoanthraquinone (1,5-DAA) was recrystallized from ethanol; melting point, 313 °C (literature value, 319 °C [38]); the purity was checked by TLC.

2.1.2. Standards of emission

Quinine sulphate (pro analyse, Fluka) and rhodamine 6G (RH 6G) laser dye (Lambda Physik, Göttingen) were used as supplied. Sodium hydroxypyrenetrisulphonate (HOPTS^-) was used as described by Bassler [39].

The solvents used were methanol (pro analyse, Merck), toluene, which was dried over sodium and then distilled, and iodobenzene which was distilled prior to use.

2.2. Fluorescence lifetimes

The fluorescence lifetimes were measured using the phase fluorometer described previously [40 - 42]. A krypton ion laser (Spectra Physics 164) was used for excitation at 473 and 530 nm. In order to eliminate apparatus parameters of the phase fluorometer, only relative phase angles ($\Delta\phi = \phi_{\text{probe}} - \phi_{\text{standard}}$) against known standards were measured (see Klein [42]). The lifetime τ is given by the following equation:

$$\tau = \frac{1}{2\pi\nu} \tan(\phi_{\text{standard}} + \Delta\phi) \quad (1)$$

where ν is the frequency modulating the intensity of the exciting light. HOPTS⁻ (lifetime, 5.4 ns) was used as the standard for 473 nm and rhodamine 6G (lifetime, 4.5 ns) for 530 nm. With HOPTS⁻ as standard the lifetime of 2-AA in toluene (5.0 ns) was measured which was then used as a standard for the dye with the next shorter lifetime and so on in order to make sure that only small phase angle differences have to be measured with high accuracy. A set of anthraquinonoid dyes was used whose lifetimes correspond to those measured here. The results for these other dyes will be published in a forthcoming paper. The modulation frequencies were 12.5, 25, 50 and 100 MHz.

2.3. Fluorescence quantum yields

The fluorescence spectra were recorded with a home-made micro-computerized emission spectrometer [31, 43]. Either a mercury super pressure lamp HBO 500 W (Osram) or a xenon super pressure lamp XBO 900 W (Osram) was used as the exciting light source. The excitation monochromator had a grating (Bausch & Lomb; focal length, 0.5 m) while the emission monochromator (Leiss) was supplied with a flint-glass prism (range, 350 - 850 nm). The emitted light was measured at right angles to the exciting light. The emission signal was detected by a red-sensitive photomultiplier (EMI 9659 B with S 20 extended cathode) and amplified by a lock-in amplifier (dynatrac 3; Ithaco). The amplified signal was processed on a 16-bit microprocessor. To determine the fluorescence quantum yields the emission spectra were measured relative to quinine sulphate as a standard ($\phi_F = 0.54$ in 0.1 N aqueous sulphuric acid) [44] and were corrected for the spectral sensitivity of the photomultiplier. The dye concentrations were maintained from 10^{-5} to 5×10^{-5} M to avoid distortion of the emission spectra owing to reabsorption. The fluorescence yields were independent of the oxygen content of the solutions. The removal of oxygen with a nitrogen gas stream did not affect the fluorescence yield in solution.

2.4. Triplet yields

The triplet quantum yield was determined by the method of Wilkinson and coworkers [45 - 47] using the external heavy atom effect of iodobenzene as a quencher. The increase in the triplet absorbance with increasing concentration of iodobenzene was followed by laser spectroscopy. The laser flash spectrometer has been described in detail by Ulrich [48]. The excitation source was an excimer laser pumped dye laser (EMG 101 Lambda Physik). Stilbene was used as the laser dye for the excitation at 430 nm (laser energy, 4 - 5 mJ), while rhodamine 6G was used for 585 nm (laser energy, about 8 mJ). The absorption of the transients was measured using a pulsed 150 W xenon lamp (Osram) as the spectral light source and the signal was registered by a programmable digitizer (Tektronix 7912 D) and processed by a microcomputer (Kontron PSI 80).

2.5. Continuous illumination apparatus

A 200 W mercury super pressure lamp (Osram) was the excitation source for the continuous illumination apparatus. The mercury lines, 436 and 546 nm, were selected using interference filters (Schott Type PIL: (a) $\lambda_{\max} = 431.8$ nm; $T_{\max} = 0.488$; full width at half-maximum (FWHM), 11.1 nm; (b) $\lambda_{\max} = 544.7$ nm; $T_{\max} = 0.472$; FWHM, 11.6 nm). The measurements were carried out in oxygen-saturated solution which was stirred during illumination. The reaction was followed by monitoring the disappearance of dimethylantracene in toluene as solvent and of 2,5-dimethylfuran in methanol and the reaction yield was determined from the intercept [2] (see Section 3 for the triplet yield by continuous illumination). For actinometric measurements the method of Brauer *et al.* [49] was used at 546 nm and that of Gauglitz and Hubig [50] at 436 nm.

3. Results

3.1. Emission spectra, fluorescence yields and fluorescence lifetimes

Derivatives of anthraquinone show four $\pi\pi^*$ absorption bands in the wavelength region between 220 and 350 nm and an $n\pi^*$ band at about 400 nm [51 - 53]. When electron-donating substituents such as hydroxy or amino groups are introduced into the anthraquinone molecule a new $\pi\pi^*$ band arises in the visible spectral region.

The relative position of this new band results from the conjugation of the $2p_z$ orbital of the nitrogen or oxygen with the π -electron system of the anthraquinone; therefore, this band is called a charge transfer (CT) band [51, 54 - 56]. The anthraquinones studied here show CT bands between 400 and 600 nm depending on the electron-donating capability of the substituents. The fluorescence emissions are recorded in the wavelength region from 450 to 850 nm. The excitation spectra of all derivatives agree with the corresponding absorption spectra (see also ref. 57).

The energies of the $S_0 \rightarrow S_1$ transitions are determined from the intersection of absorption and emission spectra (see Figs. 1 and 2 and Table 1). The fluorescence quantum yields of all the amino derivatives except those of 2-AA in toluene are small (less than 0.1). Therefore it follows that the excited singlet is mainly deactivated by radiationless processes either to S_0 (k_{IC}) or to the triplet (k_{ISC}) (see Table 1 together with values from the literature). The singlet lifetimes as well as the fluorescence quantum yields decrease on changing the solvent from toluene to methanol. From this decrease it may be concluded that intermolecular hydrogen bonding to the solvent makes an essential contribution to the radiationless deactivation.

Compounds having neither intramolecular nor intermolecular hydrogen bonding, such as 2-AA in toluene, show a lower singlet lifetime (5 ns) and a higher fluorescence quantum yield (0.25) than compounds with intramolecular hydrogen bonding (see Table 1). Obviously, the number of intramolecular and intermolecular hydrogen bonds is of decisive importance for the radiationless deactivation (see Section 4).

The fluorescence lifetime as well as the fluorescence quantum yield decrease strongly if a methyl group is attached to the amino group (e.g. 1-MAA). This seems to indicate that a methyl group contributes to the radiationless deactivation to a similar extent as hydrogen bonding.

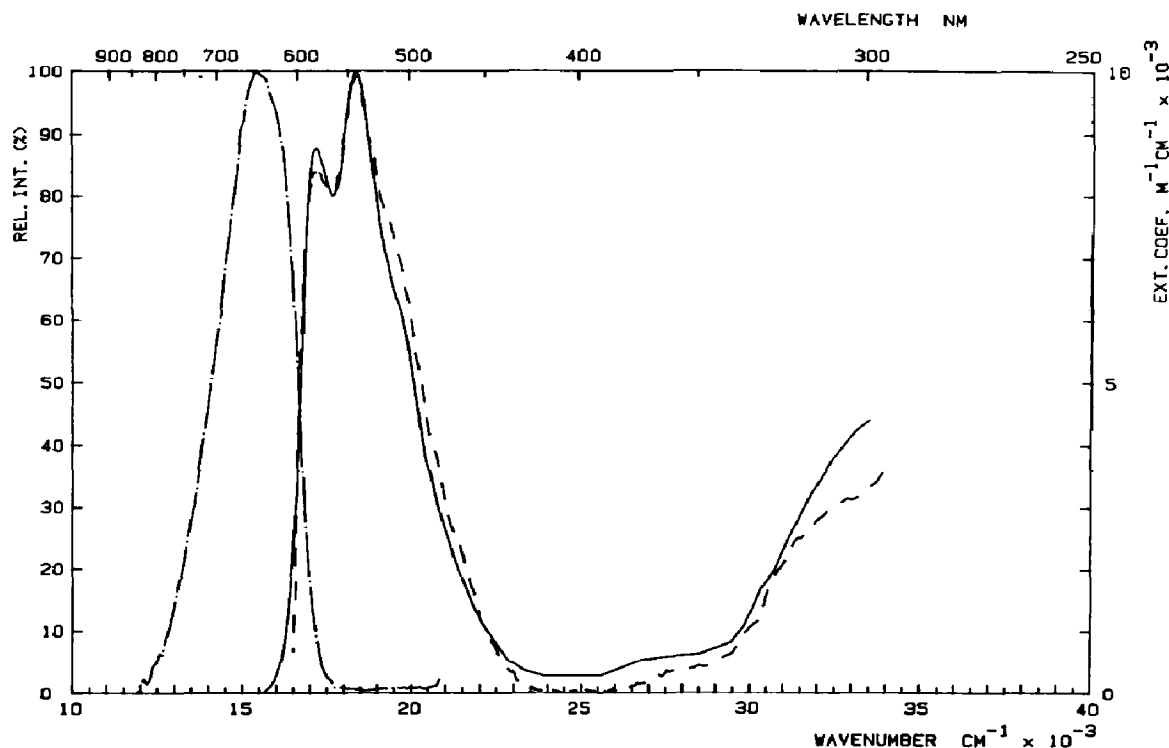


Fig. 1. Absorption (—), fluorescence (— · —) ($\lambda_{exc} = 546$ nm), and fluorescence excitation (---) ($\lambda_{obs} = 650$ nm) spectra of 1,4-DAA ($c = 8 \times 10^{-5}$ M) in toluene. The emission spectrum is normalized to the longest wavelength band of the absorption spectrum ($\phi_F = 0.04$).

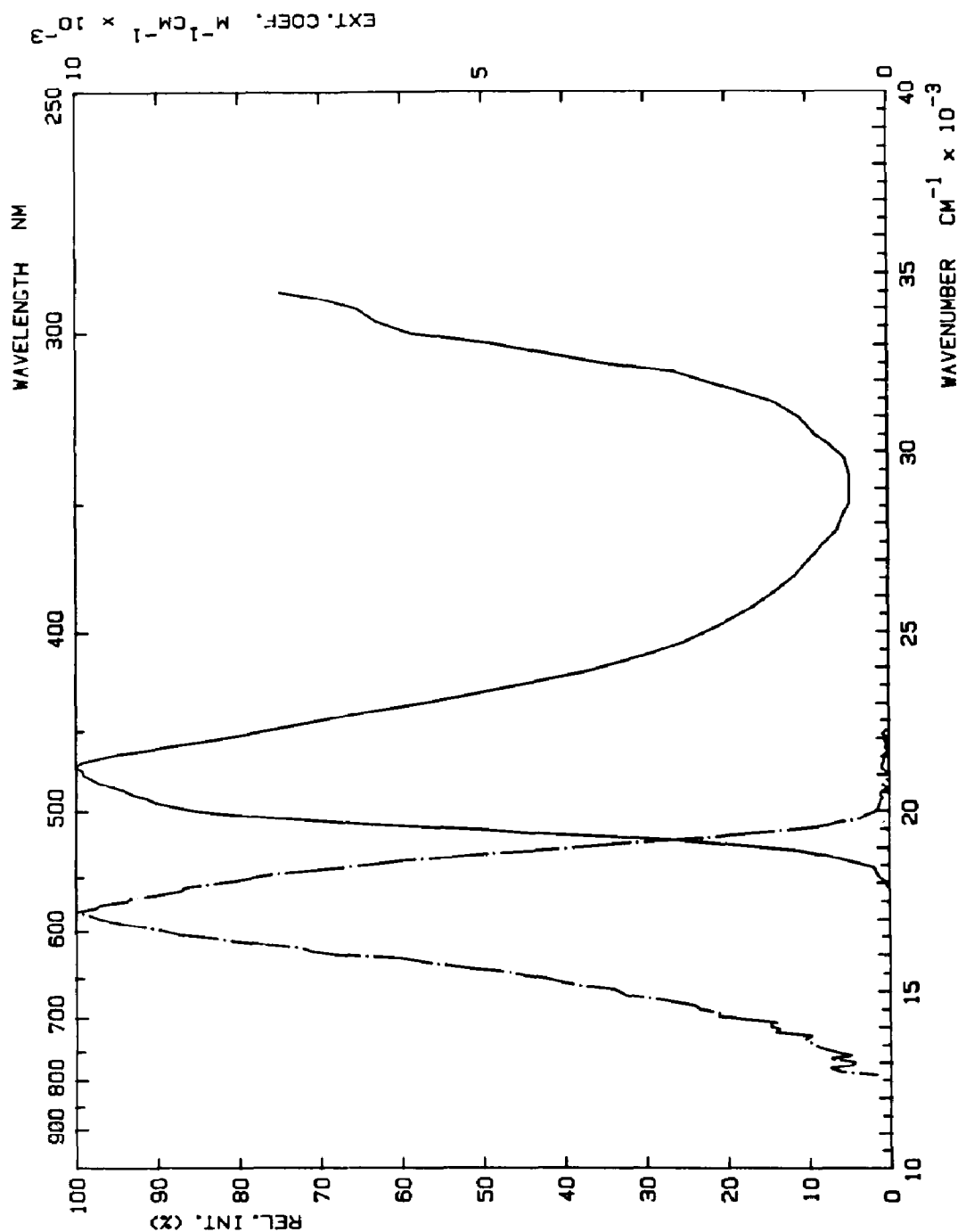


Fig. 2. Absorption (—), fluorescence (---), fluorescence (- · -) ($\lambda_{\text{exc}} = 436 \text{ nm}$) spectra of 1,5-DAA ($c = 4 \times 10^{-5} \text{ M}$) in toluene ($\phi_F = 0.025$). For further details see legend to Fig. 1.

TABLE 1

Fluorescence lifetimes and quantum yields of aminoanthraquinones

| Anthraquinone | Solvent ^a | $S_0 \cdot S_1$ (cm ⁻¹) | $\phi_F \times 10^2$ | | $\tau \times 10^{12}$ (s) | |
|---------------|----------------------|-------------------------------------|----------------------|-------------------------------|---------------------------|------------------|
| | | | Experimental value | Literature value | Experimental value | Literature value |
| 1-AA | MeOH | 18250 | 1.2 | 0.82 [18] (EtOH) ^a | 560 | 460 [18] (EtOH) |
| | Tol | 19400 | 6.5 | 5.8 [18] (B) ^a | 1740 | 1750 [18] (B) |
| 1-MAA | MeOH | 17300 | 0.2 | 0.14 [18] (EtOH) | 280 | 94 [18] (B) |
| | Tol | 17800 | 0.8 | 0.76 [18] (B) | 530 | 330 [18] (B) |
| 2-AA | MeOH | 18750 | 0.2 | 0.059 [18] (EtOH) | 100 | 54 [18] (EtOH) |
| | Tol | 21000 | 25.0 | 21 [18] (B) | 5000 | 6500 [18] (B) |
| 1,4-DAA | MeOH | 16500 | 2.2 | — | 830 | — |
| | Tol | 16750 | 4.0 | — | 960 | — |
| 1,5-DAA | MeOH | 18400 | 2.4 | 0.78 [25] (EtOH) | 550 | 450 [25] (EtOH) |
| | Tol | 19100 | 2.5 | 2.2 [25] (B) | 590 | 500 [25] (B) |

^aSolvents: MeOH = methanol; Tol = toluene; EtOH = ethanol; B = benzene.

TABLE 2

Triplet quantum yields of aminoanthraquinones

| Anthraquinone | Solvent ^a | $\phi_{ISC} \times 10^2$ | | Literature value |
|---------------|----------------------|-------------------------------------|-------------------------|---------------------------|
| | | Laser flash photolysis ^b | Continuous illumination | |
| 1-AA | MeOH | 3 | 1.3 | — |
| | Tol | 10 | 10 | — |
| 1-MAA | MeOH | 0.8 | 0.9 | — |
| | Tol | 2.0 | 4 | — |
| 2-AA | MeOH | 0.4 | 0.04 | — |
| | Tol | 20 | 40 | — |
| 1,4-DAA | MeOH | < 0.1 | 0.7 | < 5 [2] |
| | Tol | 1.5 | 1 | 1.5 [20] (B) ^a |
| 1,5-DAA | MeOH | 30 | 42 | > 50 [2] |
| | Tol | 45 | 80 | 67 [2] (C) ^a |

^aSolvents: MeOH = methanol; Tol = toluene; B = benzene; C = CHCl₃.^bMethod according to Wilkinson and coworkers [45, 46].

3.2. Triplet quantum yields

The triplet quantum yield of the aminoanthraquinone was determined according to the method of Wilkinson and coworkers [45 - 47] and also by the method of Rembold and Kramer [2] (see ref. 7 with the modified evaluation of Borst and Kramer [58]).

Wilkinson and collaborators [45 - 47] demonstrated that the quenching of the fluorescence by a solvent containing heavy atoms is accompanied by a corresponding increase in the triplet population. In our investigation the increase in the triplet population was followed by laser spectroscopy. 1,4-DAA was excited at 585 nm and all the other compounds at 430 nm. In Table 2 the triplet yields of the aminoanthraquinones determined either by the external heavy atom effect [45 - 47] or by the singlet oxygen method [2, 7, 58] are presented together with values from the literature.

The method of Wilkinson and coworkers applied to high monomolecular triplet quantum yields gives values that are low in comparison with those obtained from continuous illumination (see 2-AA and 1,5-DAA in toluene, Table 2). An explanation might be that for high monomolecular triplet quantum yields there is only a small increase in the triplet extinction due to induced triplet formation and therefore the differences cannot be measured with high accuracy.

The continuous illumination [2, 7, 58] for the determination of triplet quantum yields is based on the assumption that the anthraquinone triplet reacts with molecular oxygen in its triplet ground state and thus produces an amount of singlet molecular oxygen which is equivalent to the anthraquinone triplet. Singlet oxygen oxidizes 9,10-dimethylantracene (DMA)

whose disappearance can be followed by UV spectroscopy [7]. Meanwhile, the mathematical procedure was improved by Borst and Kramer [58]. Whereas Rembold and Kramer [2] used the differential form of the equation, evaluating the initial rates $\{d[\text{DMAO}_2]/dt\}_{t \rightarrow 0}$ only, Borst and Kramer [58] could obtain the integrated form of the rate equation so that the complete photokinetic curve can be utilized for the quantum yield determination. The data in the fourth column of Table 2 were calculated according to the method of Borst and Kramer [58].

The triplet quantum yields determined by the two independent methods are of the same order of magnitude. It is interesting to note that for the monoaminoanthraquinones the triplet quantum yields in methanol are much smaller than those in toluene. This elucidates the influence of the intermolecular hydrogen bonding which favours internal conversion (k_{IC}) to the ground state at the expense of intersystem crossing (k_{ISC}) to the triplet state.

The fluorescence lifetimes of the diaminoanthraquinones studied here are only slightly smaller in methanol than in toluene and their fluorescence quantum yields and triplet quantum yields increase only by a factor of 2 when changing from methanol to toluene. From this it may be concluded that intermolecular hydrogen bonding plays a minor role in the deactivation of the S_1 state of the diaminoanthraquinones.

4. Discussion

Since fluorescence is practically of no importance for the deactivation of the excited singlet state, the question arises as to which factors influence the radiationless deactivation processes k_{ISC} and k_{IC} .

4.1. Factors influencing the intersystem crossing

For the aminoanthraquinones the lowest excited singlet state as well as the lowest triplet state have $\pi\pi^*$ character [51, 52, 54, 57, 59, 60]. According to El Sayed [61] an intercombination is favoured between states of different orbital character. Appreciable triplet formation is expected only if the energy difference between the singlet $S_1(\pi\pi^*)$ and the next-lying triplet $T_n(n\pi^*)$ is small.

The energies of the S_1 states are shown in Table 1. The energy of the $S_2(n\pi^*)$ singlet state is taken from the anthraquinone spectrum on the assumption that substituents on the aromatic system do not influence appreciably the $n\pi^*$ transition of the carbonyl group [51, 52, 57, 62, 63]. This assumption is corroborated by the appearance of the $n\pi^*$ band in the absorption spectrum of the 1,4-DAA (Fig. 1) at about 390 nm. (Since the maxima of the $n\pi^*$ transitions of 1,4-DAA and of unsubstituted anthraquinone [51, 52] appear at nearly the same wavelength, the 0,0-transition of the 1,4-DAA is supposed to have the same frequency as that of anthraquinone, namely $23\,300\text{ cm}^{-1}$ [64].) In all other absorption spectra of the

anthraquinones studied here this $n\pi^*$ band is buried under the much more intense CT bands.

The energies of the T_1 states were taken from the literature where they were determined by energy transfer experiments. The triplet energies of 1,4-DAA and of 1,5-DAA are found to be in the range between 123 - 151 kJ mol⁻¹ [65] and 170 - 180 kJ mol⁻¹ [66] respectively. The T_2 level cannot be determined directly by spectroscopic methods. To estimate its energy the $n\pi^*$ triplet of the anthraquinone molecule was taken from the literature [57, 64, 67] and its value is the upper limit in Fig. 3.

Since the direct population of the T_1 state from the S_1 state is slow according to the rule of El Sayed [61], an appreciable triplet formation, as found in the case of 1,5-DAA in toluene ($k_{ISC} = 1.4 \times 10^9$ s⁻¹) is an indication that the reaction proceeds via the higher-lying T_2 state as has already been described for 1-AA and 2-AA derivatives [19, 68, 69] (Tables 2 and 3).

According to Robinson and Frosch [70] (see also Lim *et al.* [71]) the rate of $S_1 \rightarrow T_n$ intersystem crossing is proportional to the vibrational overlap factor whose magnitude increases with decreasing energy gap between the two interacting states. The rate constant of such a transition from the $S_1(\pi\pi^*)$ to the $T_n(n\pi^*)$ state may lie in the range $10^8 - 10^9$ s⁻¹ [61]. For 1,5-DAA in toluene we find k_{ISC} to be 1.4×10^9 s⁻¹. This result suggests that the T_2 state may be thermally accessible from the S_1 state.

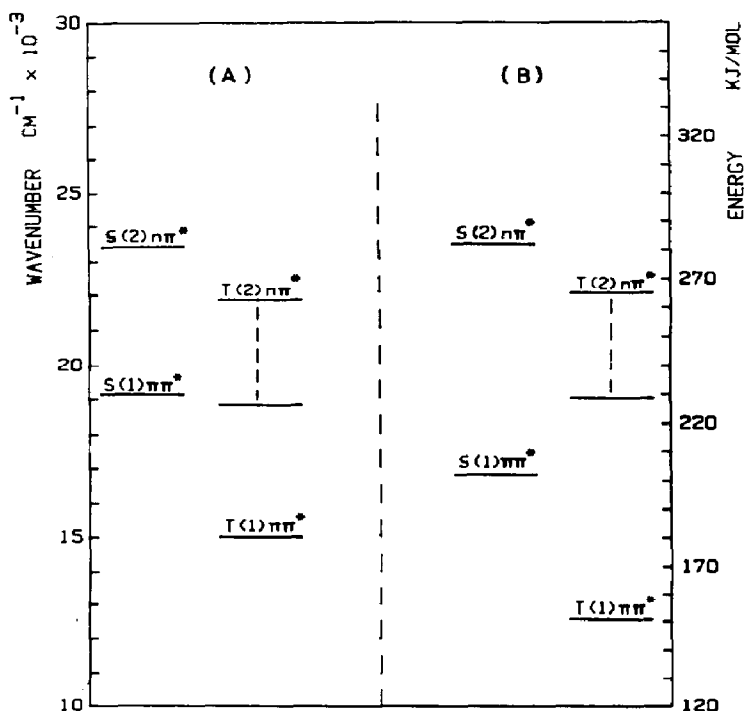


Fig. 3. Energy level diagram of the singlet and triplet states of 1,5-DAA (A) and 1,4-DAA (B) in toluene (see text).

TABLE 3

Rate constants of the radiationless deactivation of aminoanthraquinones

| Anthraquinones | Solvent ^a | k_{ISC}^b (s ⁻¹) | k_{IC}^b (s ⁻¹) |
|----------------|----------------------|--------------------------------|-------------------------------|
| 1-AA | MeOH | 2.3×10^7 | 1.7×10^9 |
| | Tol | 5.7×10^7 | 4.8×10^8 |
| 1-MAA | MeOH | $\approx 3 \times 10^7$ | $\approx 3.5 \times 10^9$ |
| | Tol | 7.5×10^7 | 1.8×10^9 |
| 2-AA | MeOH | $\approx 4 \times 10^6$ | $\approx 1 \times 10^{10}$ |
| | Tol | 8.0×10^7 | 7×10^7 |
| 1,4-DAA | MeOH | 8.4×10^6 | 1.2×10^9 |
| | Tol | 1.0×10^7 | 9.9×10^8 |
| 1,5-DAA | MeOH | 7.6×10^8 | 1.0×10^9 |
| | Tol | 1.4×10^9 | 3.0×10^8 |

^aSolvents: MeOH = methanol; Tol = toluene.^bThe rate constants k_{IC} and k_{ISC} are calculated using the triplet yields determined by continuous illumination (singlet oxygen method).

A further hint for the suggested ISC mechanism ($S_1(\pi\pi^*) \rightarrow T_2(n\pi^*)$) is the fact that k_{ISC} decreases on changing from toluene in methanol as solvent (Table 3) (for 1,4-DAA the decrease is very small). By analogy with the work of Inoue and Hida [68] (see Fig. 2 in ref. 68) we assume that $S_1(\pi\pi^*)$ is lowered and $T_2(n\pi^*)$ is slightly raised on changing from toluene to methanol as solvent. Therefore, the ISC contribution via $S_1(\pi\pi^*) \rightarrow T_2(n\pi^*)$ decreases whereas the direct (but small) ISC contribution via $S_1(\pi\pi^*) \rightarrow T_1(\pi\pi^*)$ remains unchanged (Table 3 and eqn (2)):

$$k_{ISC} = k_{ISC} \{S_1(\pi\pi^*) \rightarrow T_1(\pi\pi^*)\} + k_{ISC}^0 \{S_1(\pi\pi^*) \rightarrow T_2(n\pi^*)\} \\ \times \exp\left(-\frac{\Delta E_{S_1 T_2}}{RT}\right) \quad (2)$$

For 1,4-DAA, however, only a small effect was found for the change of solvents (Table 3). The energy difference between $S_1(\pi\pi^*)$ and $T_2(n\pi^*)$ is too high even in toluene, so that the triplet cannot be populated via this channel (Fig. 3(B)).

In this context the work of Dreeskamp and Pabst [72] should be mentioned. They studied the bimolecular rate constant of fluorescence quenching by haloalkanes for meso-substituted anthracenes. They found a linear correlation with unit slope between the activation energy of intramolecular S_1 decay and the free enthalpy of activation for the heavy atom quenching. This is strong evidence that both processes are based on thermally assisted S_1-T_n crossing via the same higher triplet state T_n .

Summing up, we can say that a mechanism of thermally assisted S_1-T_n intersystem crossing is supported by our k_{ISC} results for the diaminoanthra-

quinones. The observed small triplet quantum yields (0.015 in toluene) for 1,4-DAA correlate with the large energy gap, whereas for 1,5-DAA which has a fairly high triplet quantum yield the energy gap is probably small (Fig. 3).

For the monoaminoanthraquinones the situation is less clear. Triplet quantum yields have also been determined by Borst and Kramer [58] for numerous substituted aminoanthraquinones in addition to those for the derivatives listed in Table 3. However, not all of these results can be understood in the light of the simplified model presented above.

4.2. Factors influencing the internal conversion

According to Inoue *et al.* [18] the S_1 state can undergo an effective radiationless deactivation process by intramolecular hydrogen bonding (probably involving a keto-enol or a ketimine-enamine tautomerism respectively) and also by intermolecular hydrogen bonding. To obtain detailed information about the individual processes contributing to the internal conversion, monosubstituted aminoanthraquinones in methanol and toluene were studied as model systems (see also Inoue *et al.* [18]). The contributions to the internal conversion are indicated in Fig. 4 (see also ref. 73): (A) intermolecular hydrogen bonding between the NH_2 group and the solvent methanol; (B) intramolecular hydrogen bonding; (C) intermolecular hydrogen bonding of the CO group to methanol; (D) contribution from the skeleton of the molecule; (E) contribution of a methyl substituent on the amino group.

The rate constant k_{IC} from Table 3 may be conceived as representing the sum of individual radiationless deactivation processes from S_1 to S_0 . To obtain the five unknown rate constants $k_A - k_E$, five constants (k_{IC}) containing the individual processes in different combinations are needed (see the corresponding combinations of dyes and solvents in Table 4). The following assumptions have to be made for a determination of individual constants.

(i) The individual rate constants $k_A - k_E$ are practically independent of each other and as a consequence they are additive. We are aware that this is only a very rough estimation and the values thus obtained (Table 4) are subject to large uncertainties. However, the assumption that the individual rate constants are practically independent of each other seems to be justi-

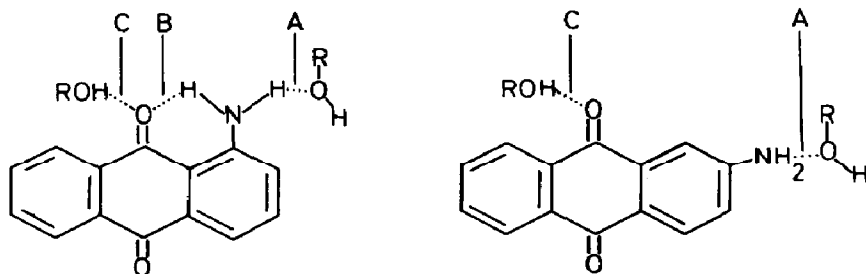


Fig. 4. Contributions to the internal conversion of monosubstituted aminoanthraquinones in the excited singlet state (see text).

TABLE 4

Individual contributions to the internal conversion for monosubstituted aminoanthraquinones

| <i>Anthraquinone</i> | <i>Solvent</i> ^a | <i>Individual contributions to internal conversion</i> ^b |
|----------------------|-----------------------------|---|
| 2-AA | Tol | $k_{IC(1)} = k_D$ |
| 1-AA | Tol | $k_{IC(2)} = k_B + k_D$ |
| 1-MAA | Tol | $k_{IC(3)} = k_B + k_E + k_D$ |
| 1-MAA | MeOH | $k_{IC(4)} = k_B + k_C + k_E + k_D$ |
| 2-AA | MeOH | $k_{IC(5)} = k_A + k_C + k_D$ |

^aSolvents: Tol = toluene; MeOH = methanol.

^bFrom these combinations the following individual contributions to the internal conversion are obtained: $k_A \approx 8 \times 10^9 \text{ s}^{-1}$; $k_B = 4 \times 10^8 \text{ s}^{-1}$; $k_C \approx 2 \times 10^9 \text{ s}^{-1}$; $k_D = 7 \times 10^7 \text{ s}^{-1}$; $k_E = 1.4 \times 10^9 \text{ s}^{-1}$. (The values given here differ slightly from those reported in a previous publication [73].)

fied to some extent by the fact that the individual contributions (*vide infra*) differ by an order of magnitude respectively.

(ii) The k_D values (contribution from the skeleton of the anthraquinone molecule without hydrogen bonding) for 1-AA and for 2-AA have to be of the same order of magnitude.

In Siebrand's [74 - 76] theory of radiationless transitions, the non-radiative rate constant (k_{nr}) is the product of the density-of-states factors, the electronic factors involving the nuclear kinetic energy operator and the Franck-Condon factor, which is the square of the nuclear overlap integral. The density-of-states factor should be the same in the present comparison for both molecular skeletons, provided the involvement of the same type of vibrational modes is assumed. Likewise, the electronic factor is expected to remain constant if the nuclear kinetic energy operator is the same for both compounds, corresponding to common vibrational modes. Finally, the Franck-Condon factor is determined solely by the magnitude of the energy gap between the involved electronic states, here S_1 and S_0 , and by the vibrational modes of the ground state molecule. As the singlet energies of 1-AA and 2-AA differ by only 1600 cm^{-1} in toluene and 500 cm^{-1} in methanol respectively, we shall assume that also the Franck-Condon factors are the same within an order of magnitude. With these assumptions, a k_D value of $7 \times 10^7 \text{ s}^{-1}$ results for the aminoanthraquinone dye skeleton, a value which agrees well with the non-radiative rate constants for internal conversion of aromatic molecules. As an example, tetrazine is quoted as having an estimated k_{nr} of about $(1.6 - 2.0) \times 10^7 \text{ s}^{-1}$ with a comparable energy gap of $21\,200 \text{ cm}^{-1}$ [77].

For these monosubstituted aminoanthraquinones the intermolecular hydrogen bonding either to the oxygen of the CO group ($k_C \approx 2 \times 10^9 \text{ s}^{-1}$) or to the amino hydrogen ($k_A \approx 8 \times 10^9 \text{ s}^{-1}$) gives the highest contributions to the internal conversion.

On excitation of the intramolecularly hydrogen-bonded aminoanthraquinones into their first singlet state (CT state) a reorientation of the surrounding solvent molecules is induced. In the vibrational ground state of S_1 the hydrogen bonding between the CO group of the anthraquinone and the OH group of methanol should be strengthened if we assume that the electron density at the oxygen atom of the carbonyl group increases owing to the intramolecular CT nature of the excited state [18]. Therefore, in the excited state the methanol molecule is closer to the carbonyl oxygen. For this reason a large part of the excitation energy can be deactivated via this intermolecular hydrogen bonding, the vibrational modes of the hydrogen bonding acting as accepting modes for the energy $S_1 \rightarrow S_0$ of the anthraquinone (k_C).

The same argument should apply to the intermolecular hydrogen bonding involving the amino nitrogen.

It is interesting to note that in agreement with the earlier results of Inoue *et al.* [18] the contribution of intramolecular hydrogen bonding ($k_B \approx 4 \times 10^8 \text{ s}^{-1}$) is smaller by a factor of 10 than that of intermolecular hydrogen bonding, whereas the very opposite holds for 2-(2'-hydroxy-5'-methylphenyl)benzotriazole [30, 31, 73]. The explanation of this difference in behaviour may be seen in the fact that the conditions for tautomerization (proton transfer) in the excited state are not as favourable for the aminoanthraquinones as for the hydroxyanthraquinones or hydroxyphenylbenzotriazoles [30 - 34, 73] (see also the discussion in ref. 25).

The anthraquinone skeleton itself makes the smallest contribution ($k_D \approx 7 \times 10^7 \text{ s}^{-1}$) to the internal conversion. From the results presented above we may conclude that hydrogen bonding is very important for the radiationless deactivation of the excited singlet state and thus for its photochemical behaviour.

The contribution of the methylamino group ($k_E \approx 1.4 \times 10^9 \text{ s}^{-1}$) is surprisingly great and lies in the same range as that of the intermolecular hydrogen bonding. Little is known in the literature about this "methyl group effect" and its influence on the photochemical behaviour. The results of Shizuka *et al.* [78] for methyl- and methylene-substituted benzenes cannot be compared directly with our results since in their systems the alkyl groups are bound to the aromatic nucleus.

In a forthcoming paper we shall report on the influence of alkylation of the $\alpha\text{-NH}_2$ and the $\beta\text{-NH}_2$ group in the anthraquinonoid systems and the changes thus obtained in k_{ISC} and ϕ_{ISC} [58].

5. Conclusion

To avoid the problems of catalytic fading by the singlet oxygen mechanism it is recommended that an aminoanthraquinone dye should fulfil the following conditions (see ref. 2).

1. The energy gap between the singlet $S_1(\pi\pi^*)$ and the next-lying triplet $T_n(n\pi^*)$ should be high in order to minimize the triplet quantum yield.

2. From our results obtained in solution we would infer that on textile fibres the dye should be embedded in a chemical environment which allows hydrogen bonding. However, the activity of the hydrogen bonding should be restricted to the acceleration of internal conversion, *i.e.* additional processes such as hydrogen-atom transfer should be avoided.

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