

The deexcitation of the S_1 state of aminoanthraquinones: A steady-state and time-resolved study

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Abstract. The non-radiative processes of deactivation from the lowest singlet excited state of aminoanthraquinones have been studied using steady-state and time-resolved methods. The fluorescence decay rate constant, k_f , correlates well with the solvent polarity parameter, $E_T(30)$, in nonhydrogen bonding solvents. Large deuterium isotope effects in fluorescence lifetimes (τ_f) and quantum yields (ϕ_f) are observed in the case of 1-amino (AAQ) and 1-methylaminoanthraquinones (MAQ), where the S_1 state is mainly deactivated through internal conversion to the ground state. The temperature-dependence of the fluorescence quantum yields of various aminoanthraquinones was also investigated. The ϕ_f and τ_f exhibited strong temperature-dependence in the case of 1-acetylaminoanthraquinone (ACAQ). In the case of ACAQ, the intersystem crossing to the triplet state is a major deactivation channel from the S_1 and in this derivative a close-lying T_2 state seems to be responsible for the high k_{isc} rate.

The fluorescence properties of 1,5-diaminoanthraquinone (DAQ) are affected by intermolecular hydrogen bonding with alcohols. Increasing n -alkyl chain length in the case of 1-(n -alkyl)aminoanthraquinones from methyl to butyl does not produce any change in the fluorescence properties, whereas a hydroxypropyl substitution results in a small decrease of ϕ_f and τ_f in these compounds, indicating an interaction of the hydroxyl group with the carbonyl group of the aminoanthraquinones.

Keywords. Photochemistry of aminoanthraquinones; isotope effect; fluorescence lifetimes; fluorescence quenching; excited singlet state of aminoanthraquinones.

1. Introduction

The non-radiative processes of deactivation from the lowest singlet state of several aminoanthraquinones have been studied using steady-state and time-resolved methods: 1-aminoanthraquinone (AAQ), 1-methylaminoanthraquinone (MAQ), 1-acetylaminoanthraquinone (ACAQ) and 1,5-diaminoanthraquinone (DAQ) were studied in detail. Beside MAQ, the 1-alkyl substituted anthraquinones, 1-propylamino- (PAQ), 1-butylamino- (BAQ) and 1-N-hydroxypropylamino-anthraquinones were investigated to study the effect of the nature of the n -alkyl group.

For measurement of fluorescence quantum yield, Rhodamine B ($\phi_f = 0.72$) was used as a fluorescent standard and a Shimadzu RF-540 spectrofluorimeter was used. Fluorescent lifetimes were measured on a picosecond fluorescence spectrometer using the time-correlated single photon counting (TCSPC) technique (Bankar *et al* 1989). A

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microchannel plate photomultiplier (Hamamatsu R2809) having a fast response was employed. The triplet quantum yields for AAQ, MAQ and DAQ are known (Ritter *et al* 1988) and the triplet quantum yield for ACAQ was determined in CCl_4 using 9-fluorenone as standard. Triplet quantum yields were determined relative to the value in CCl_4 .

2. Results and discussion

Anthraquinone derivatives have four $\pi\pi^*$ bands in the wavelength region between 220 to 350 nm. Also, there is a weak $n\pi^*$ band near 400 nm (Yoshida and Takabayashi 1968). When an electron donating substituent such as amino or hydroxyl is introduced in the ring, a new band appears in the visible region, which has been assigned to the intermolecular charge-transfer (CT) band (Yoshida and Takabayashi 1968). Aminoanthraquinones used in this study have CT bands in the region between 400 to 520 nm, the band position depending on the electron-donating character of the substituents. Emissions from these compounds were observed in the region 500 to 650 nm.

From fluorescence quantum yields (ϕ_f), triplet quantum yields (ϕ_T) and fluorescence lifetimes (τ_f), various rate constants are evaluated using the following expressions:

$$k_r = \phi_f / \tau_f \text{ (radiative rate constant),} \quad (1)$$

$$k_{nr} = (1 - \phi_f) / \tau_f \text{ (nonradiative rate constant),} \quad (2)$$

$$k_{isc} = \phi_T / \tau_f \text{ (rate constant for intersystem crossing),} \quad (3)$$

$$k_{ic} = k_{nr} - k_{isc} \text{ (rate constant for internal conversion),} \quad (4)$$

$$\tau_f = [k_{isc} + k_r + k_{ic}]^{-1} \text{ (fluorescence lifetime).} \quad (5)$$

Table 1 gives a summary of fluorescence lifetimes and quantum yields of various derivatives. Tables 2–5 list the absorption maxima ($\lambda_{\text{max}}^{\text{abs}}$), emission maxima ($\lambda_{\text{max}}^{\text{em}}$), ϕ_f , τ_f , k_f and k_{nr} for AAQ, MAQ, ACAQ and DAQ in various solvents.

Table 1. Fluorescence quantum yields and lifetimes of several aminoanthraquinones in CCl_4 . ($\lambda_{\text{ex}} = 300 \text{ nm}$).

Compound	$\phi_f (\times 100)$	$\tau_f (\text{ps})$
1-NH ₂ (AAQ)	7.15	2100
1-NHCH ₃ (MAQ)	1.36	486
1-NHCOCH ₃ (ACAQ)	0.54	140
1-NHC ₃ H ₇ (PAQ)	1.3	486
1-NHC ₄ H ₉ (BAQ)	1.3	481
1-NH(CH ₂) ₃ OH(HPAQ)	1.1	460
1,5-NH ₂ (DAQ)	1.9	485 [†]

[†]In toluene. Solubility of DAQ is low in CCl_4 .

Table 2. Emission properties of 1-aminoanthraquinone.

Solvent	$\lambda_{\max}^{\text{abs}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	ϕ_f ($\times 100$)	τ_f^\dagger (ps)	k_r ($\times 10^7 \text{ s}^{-1}$)	k_{nr} ($\times 10^8 \text{ s}^{-1}$)
CCl_4	453	532	7.15	2100	3.4	4.4
$\text{CCl}_4/\text{D}_2\text{O}$	453	532	25.7	7420	3.5	1.0
Hexane	450	530	6.0	1770	3.4	5.3
			7.0 ^a			
Cyclohexane	450	530	6.6	1800	3.6	5.2
Toluene	460	560	4.7	1600	2.9	6.0
			6.5 ^c	1750 ben. ^b		
Toluene/ D_2O	460	560	20.7	6460	3.2	1.2
Chloroform	460	565	3.1	1350	2.3	7.2
Dioxane	460	570	3.6	1210	3.0	8.0
Acetonitrile	468	590	0.94	936	1.0	10.6
			1.0 ^b	660 ^b		
Ethanol	470	595	0.66	550	1.2	18.1
			0.82 ^b	460 ^b		
Ethanol-O-d	470	595	3.0	2750	1.1	3.5
			5.0 ^b	3030 ^b		
Methanol	470	595	0.42	430	1.0	23

[†]The excitation wavelength was 300 nm. The error in τ_f is less than 20 ps. ben = benzene. ^aAllen *et al* (1976); ^bInoue *et al* (1982); ^cRitter *et al* (1988).

Table 3. Emission properties of 1-methylaminoanthraquinone.

Solvent	$\lambda_{\max}^{\text{abs}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	ϕ_f ($\times 100$)	τ_f^\dagger (ps)	k_r ($\times 10^7 \text{ s}^{-1}$)	k_{nr} ($\times 10^8 \text{ s}^{-1}$)
Hexane	486	560	1.2	455 [‡]	2.6	2.2
Cyclohexane	486	560	1.3	460 [‡]	2.8	2.2
CCl_4	492	578	1.3	484 [‡]	2.7	2.0
$\text{CCl}_4/\text{D}_2\text{O}$	492	578	6.9	2840 [‡]	2.4	0.33
Toluene	497	590	0.81	373 [‡]	2.2	2.7
			0.8 ^a			
Toluene/ D_2O	497	590	4.0	2100 [‡]	1.9	0.46
Benzene	497	590	0.8	352	2.3	2.8
			0.76 ^b	330 ^b		
Dioxane	494	595	0.51	262	2.0	3.8
Chloroform	500	595	0.66	325	2.0	3.1
Acetonitrile	500	640	0.16	187	0.9	5.3
			0.16 ^b	190 ^b		
Ethanol	500	640	0.14	137	1.0	7.3
			0.14 ^b	94 ^b		
Ethanol-O-d	500	640	0.48	543	0.9	1.8
Methanol	500	640	0.13	116	1.1	8.6

[†]The excitation wavelength was 578 nm, unless indicated otherwise. The error in the lifetime measurements is less than 20 ps. [‡]Excitation wavelength was 300 nm.

^aRitter *et al* (1988); ^bInoue *et al* (1982).

Table 4. Emission properties of 1-acetylaminoanthraquinone.

Solvent	$\lambda_{\max}^{\text{abs}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	ϕ_f ($\times 1000$)	τ_f^\dagger (ps)	k_r ($\times 10^7 \text{s}^{-1}$)	k_{nr} ($\times 10^9 \text{s}^{-1}$)
Hexane	420	500	2.1	70	3.0	14.3
Cyclohexane	420	500	2.1	68	3.0	14.3
Freon	420	500	3.4	94	3.6	10.6
CCl ₄	420	505	5.4	140	3.9	7.1
CCl ₄ /D ₂ O	420	505	5.4	137	3.9	7.1
Toluene	420	520	18.0	490	3.7	2.0
Toluene/D ₂ O	420	520	18.0	527	3.4	1.9
Chloroform	420	520	20.0	469	4.3	2.1
Dioxane	420	520	16.0	427	3.8	2.3
Acetonitrile	400	530	9.1	377	2.4	2.7
			8.1	320 ^a		
Ethanol	395	530	3.8	157	2.4	6.3
Methanol	395	530	3.4	140	2.4	7.1

[†]The excitation wavelength was 300 nm and the error in lifetimes is less than 20 ps. ^a Inoue *et al* (1982).

Table 5. Emission properties of 1,5-diaminoanthraquinone.

Solvent	$\lambda_{\max}^{\text{abs}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	ϕ_f ($\times 100$)	τ_f^\dagger (ps)	k_r ($\times 10^7 \text{s}^{-1}$)	k_{nr} ($\times 10^9 \text{s}^{-1}$)
Toluene	468	545	1.9	485	3.9	2.0
			2.5 ^a	500 ^b		
Toluene/D ₂ O	468	545	2.3	610	3.8	1.6
Dioxane	474	555	2.4	523	4.6	1.87
Acetonitrile	476	580	2.0	595	3.4	1.65
				625 ^b		
Methanol	486	584	1.6	470	3.4	2.1
Ethanol	490	576	1.65	500	3.3	2.0
				450 ^b		
Ethanol-O-d	490	576	2.6	770	3.4	1.26
Butanol	490	576	1.74	484 [†]	3.6	2.0
Hexanol	490	576	1.82	490 [†]	3.7	2.0
Glycerol	490	576	1.9	450	4.2	2.2

[†]578 nm excitation and others 300 nm excitation. The error in lifetimes is less than 20 ps. ^aRitter *et al* (1988); ^bFlom and Barbara (1985).

2.1 Solvent polarity effects

Fluorescence quantum yields (ϕ_f) and lifetimes (τ_f) of aminoanthraquinones are strongly dependent on the solvent polarity. ϕ_f and τ_f decrease with increasing solvent polarity. We have found that the solvent polarity parameter, $E_T(30)$, proposed by Dimroth *et al* (1963) correlates well with the polarity effects found in these systems. $E_T(30)$ parameters are based on the transition energies of the intramolecular charge-transfer band of pyridinium phenol betaine and hence are expected to correlate better with the polarity effects found in the absorption and emission properties of

anthraquinones whose longest wavelength absorption band is a $\pi\pi^*$ charge-transfer band. Figure 1 shows the correlation of the normalized fluorescence quantum yields, $\phi_f(n)$ [defined as $\phi_f/\phi_f(\max)$, where $\phi_f(\max)$ is the maximum ϕ_f observed in one of the solvents] of ACAQ, AAQ, MAQ with $E_T(30)$ values for 8 solvents. While in AAQ and MAQ, the ϕ_f decreases gradually on going from CCl_4 to more polar solvents, such a trend in ACAQ starts only for solvents more polar than chloroform. For DAQ, which is symmetric with zero dipole moment in the ground state, the effect of solvent polarity is minimal.

Table 6 compares the values of k_r , k_{ic} and k_{isc} for AAQ, MAQ, ACAQ and DAQ in toluene and methanol. It is clear that k_{isc} increases considerably in a polar solvent, if the aminoquinone has a dipole moment in the ground state. The small increase of k_{ic} in methanol as compared to toluene for DAQ may be attributable to intermolecular hydrogen bonding effects as indicated by the deuterium studies discussed below.

2.2 Deuterium isotope effect

The aminoanthraquinones with near-complete deuteration of the exchangeable protons (NH_2 and OH) are easily prepared by shaking a solution of the quinone in toluene (or CCl_4) with D_2O . The deuteration of these sites is complete in a few hours.

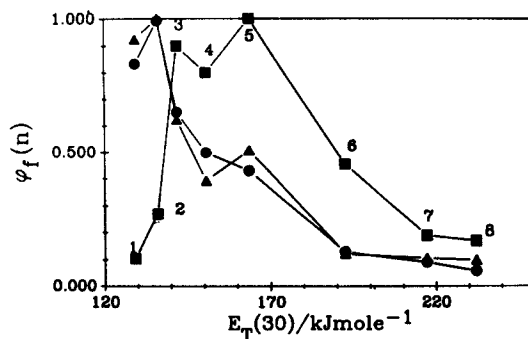


Figure 1. Plot of the normalized quantum yield $\phi_f(n)$ vs $E_T(30)$ values for ACAQ (■), AAQ (●) and MAQ (▲) in 8 solvents: hexane (1), CCl_4 (2), toluene (3), dioxane (4), chloroform (5), acetonitrile (6), ethanol (7) and methanol (8).

Table 6. Various rate constants for aminoanthraquinones.

Compound	Rate constants ($\times 10^7 \text{ s}^{-1}$)						R_1	R_2	R_3
	Toluene			Methanol					
	k_r	k_{ic}	k_{isc}	k_r	k_{ic}	k_{isc}			
AAQ	2.9	53	6.3	1.0	230	3.0	0.34	4.3	0.5
MAQ	2.7	260	5.4	1.1	850	6.9	0.41	3.3	1.3
DAQ	3.9	110	93	3.4	140	64	0.87	1.3	0.7
ACAQ	3.7	60	140	2.4	630	85	0.65	10.5	0.6

Triplet quantum yields for AAQ, MAQ and DAQ are taken from Ritter *et al* (1988); R_1 , R_2 and R_3 are the ratios of the k_r , k_{ic} and k_{isc} values in methanol and toluene.

Table 7. The deuterium isotope effect on τ_f .

Compound	Solvent	ϕ_f ($\times 100$)	τ_f (ps)	Solvent	ϕ_f ($\times 100$)	τ_f (ps)	$k_f(\text{H})$ $k_f(\text{D})$
1-NH ₂ (AAQ)	CCl ₄	7.15	2100	CCl ₄ /D ₂ O	25.7	7420	3.5
	Toluene	4.7	1600	Toluene/D ₂ O	20.7	6460	4.0
1-NHCH ₃ (MAQ)	CCl ₄	1.3	484	CCl ₄ /D ₂ O	6.9	2840	5.9
	Toluene	0.81	373	Toluene/D ₂ O	4.0	2100	5.6
1-NHCOCH ₃ (ACAQ)	CCl ₄	8.4	140	CCl ₄ /D ₂ O	5.4	137	1.0
	Toluene	18.0	490	Toluene/D ₂ O	18.0	530	1.08
1,5-NH ₂ (DAQ)	Toluene	1.9	485	Toluene/D ₂ O	2.3	610	1.26

$k_f(\text{H})/k_f(\text{D})$ is the ratio of the fluorescence decay rate constants for the undeuterated and the deuterated derivatives.

Experiments of this kind are referred to in the tables as toluene/D₂O or CCl₄/D₂O. The fluorescence quantum yields and fluorescence lifetimes of these deuterated derivatives show significant change only for AAQ and MAQ (see table 7).

The radiative rate constant, k_r , does not change on deuteration for the derivatives studied in the present work (see tables 2–5). Among the two contributions to k_{nr} , it is expected that k_{isc} will not change much on deuteration of the amino protons since the spin-orbit coupling cannot vary substantially on deuteration. This is confirmed by the finding that in DAQ and ACAQ, where the k_{isc} is larger than in AAQ and MAQ, the ratio of the fluorescence decay rate constants of the deuterated and undeuterated species is found to be in close agreement with the ratio of the triplet quantum yields (Srivatsavoy 1990). In the case of AAQ and MAQ, where k_{isc} is very much smaller than k_{ic} for the undeuterated species, we assume that k_{isc} is not affected by deuteration. k_{ic} is then determined for the deuterated [$k_{ic}(\text{D})$] and undeuterated species [$k_{ic}(\text{H})$] with the equation:

$$k_{ic}(\text{H}, \text{D}) = k_f(\text{H}, \text{D}) - k_{isc} - k_r$$

where the $k_f(\text{H}, \text{D})$ are the corresponding fluorescence decay rate constants for the undeuterated and deuterated derivatives respectively. The rate constants for the internal conversion are listed in table 8. For DAQ the isotope effect is much smaller and for ACAQ there is almost no observable effect. From these results we conclude that in these compounds it is mainly k_{ic} which is changed on deuteration and the isotope effect on fluorescence lifetimes is observable only when $k_{ic} \ll k_{isc}$.

2.3 Effect of temperature on ϕ_f and τ_f

Fluorescence quantum yields and fluorescence lifetimes in toluene were determined between 300 and 350 K. Only in ACAQ, the change of ϕ_f and τ_f with temperature is dramatic. This is attributed to a thermally accessible low-lying T_2 state in ACAQ.

2.4 Effect of N-alkyl substitution in DAQ

The alkyl substitution at the amino group affects the fluorescence lifetimes and quantum yields (table 1). However, increase of the alkyl group does not change the values significantly except for the hydroxypropyl derivative, where there is a small

Table 8. k_{ic} values for AAQ, MAQ, DAQ and ACAQ.

Compound	Solvent*	$k_{ic}(H)$	$k_{ic}(D)$	k_{isc}	k_r	$\frac{k_{ic}(H)}{k_{ic}(D)}$
		$(\times 10^7 \text{ s}^{-1})$				
AAQ	T, TD	53.4	6.4	6.25	2.9	8.3
MAQ	T, TD	260	40	5.36	2.2	6.5
DAQ	T, TD	109	67	93	3.9	1.6
ACAQ	T, TD	60	46	140	3.7	1.3

*T = toluene, TD = toluene/D₂O; H, D represent the undeuterated and deuterated molecules.

change. A molecular model shows that in the hydroxypropyl derivative, the hydroxyl group can come close to the carbonyl of the quinone and the resulting interaction may cause an enhancement of k_f .

3. Conclusions

It is observed that in the N-substituted derivatives of 1-aminoanthraquinones, efficient non-radiative processes of deactivation lead to a decrease of fluorescence quantum yields and lifetimes, as compared to the unsubstituted compounds. Both ϕ_f and τ_f are sensitive to solvent polarity and intermolecular hydrogen bonding. The results indicated that k_{ic} is most affected by these factors. Deuterium substitution of aminoprotons again leads to an enhancement of k_{ic} and the isotope effect is noted only when $k_{ic} > k_{isc}$. When k_{isc} is dominant as in ACAQ, the temperature dependence of ϕ_f and τ_f in this compound indicates a low-lying T_2 state which participates in thermally assisted intersystem crossing.

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