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Intramolecular deactivation of photoexcited anthracenes by aromatic ketones

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Abstract

The excited state properties of anthracenes non-conjugatively linked to various types of aromatic ketone were investigated in non-polar solution by determination of the quantum yields of fluorescence and intersystem crossing. In a series of substituted bichromophoric ω-(9-anthryl)propiophenones, the degree of intramolecular fluorescence quenching by the ketone was found to be associated with an increase in the quantum yield of anthracene triplet state formation. Excitation of 4'-piperazinoacetophenone tethered to anthracene resulted in deactivation within the acetophenone chromophore, rather than singlet energy transfer to anthracene. For photoexcited anthracene linked to 2-amido-substituted fluorenone, intramolecular exothermic transfer of the singlet excitation energy to the fluorenone chromophore was found to proceed with high efficiency.
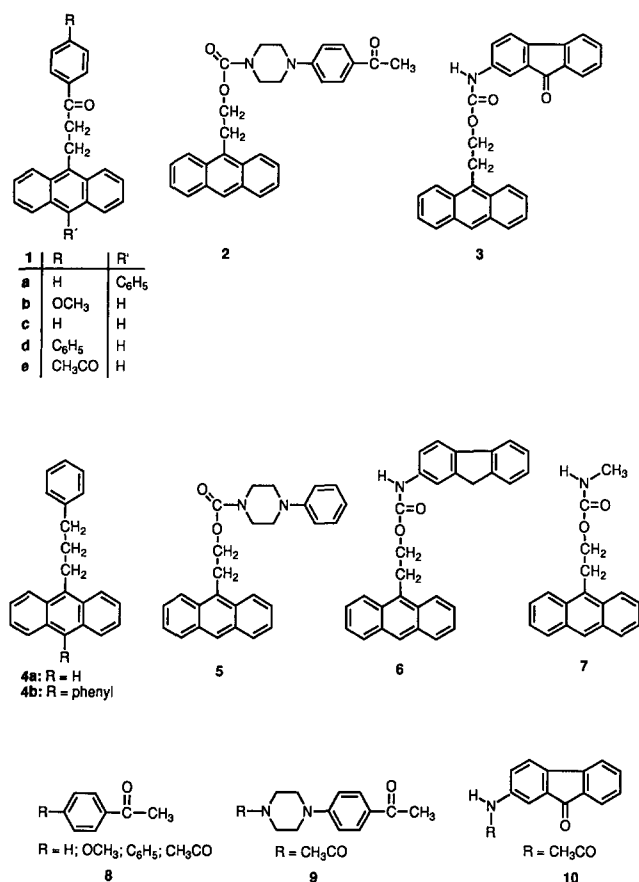
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1. Introduction

In conjunction with exploratory studies on the relationship between the molecular topology and excited state properties of π-chromophorically-substituted anthracenes, the fluorescence quantum yields (Φ_F) of anthracenes tethered to aromatic ketones were found to be affected markedly by the substitution of aromatic π-systems [1]. In non-polar solvents, an increase in Φ_F was induced by substitution of the anthracene chromophore, which resulted in a decrease in its excited singlet (S_1) energy level. By contrast, Φ_F decreased on substitution of the aromatic ketone moiety, which led to a decrease in the energy of the S_1 level of the carbonyl chromophore. Since the decrease in the fluorescence quantum yield seemingly parallels the narrowing of the energy gap between the S_1 states of anthracene and the aromatic ketone, deactivation of the fluorescent state has been suggested to involve the initial intramolecular endothermic transfer of singlet energy from the photoexcited anthracene to the ketone, and subsequent efficient intersystem crossing within the ketone π-system. It is not known whether deactivation to the ground state proceeds within the ketone chromophore, by intramolecular triplet energy transfer from the ketone to the lowest excited triplet state (T_1) of the anthracene

moiety or by other ketone-induced, non-radiative processes.

We have addressed this question in an investigation of the emission and transient absorption spectroscopy of the bichromophoric compounds 1–3, in which the anthracene π-system is non-conjugatively linked to three different kinds of aromatic ketone (see Scheme 1). The bichromophoric compounds 1a–1e are ω-(9-anthryl)propiophenones, in which the S_1 state of the ketone is either of n–π^* or π–π^* in nature and its energy is only slightly higher than that of the S_1 state of anthracene. In bichromophore 2, anthracene is tethered to 4'-piperazinoacetophenone, i.e. an aromatic ketone whose absorption spectrum is characterized by a charge transfer (CT) transition which lies considerably above, and well separated from, the S_1 state of anthracene. Finally, in bichromophore 3, the anthracene π-system is linked to the 2-amido-9-fluorenone chromophore, whose lowest excited state also has CT character, but is lower in energy than the S_1 state of anthracene. The relative positions of the excited state energy levels of the various ketone chromophores with respect to those of anthracene in compounds 1–3 are depicted schematically in Fig. 1.

The excited state properties in methylcyclohexane (MCH) and toluene solution were studied by measuring

1	R	R'
a	H	C₆H₅
b	OCH₃	H
c	H	H
d	C₆H₅	H
e	CH₃CO	H

4a: R = H
4b: R = phenyl

R = H; OCH₃; C₆H₅; CH₃CO
8

R = CH₃CO
9

R = CH₃CO
10

Scheme 1.

the quantum yields and lifetimes of fluorescence (Φ_F; τ_F) and the quantum yields of intersystem crossing (Φ_{ISC}). For reference purposes, model compounds 4–7,

lacking the ketone function, and aromatic ketones 8–10 (see Scheme 1) were included.

2. Experimental details

2.1. Spectroscopy

UV–visible absorption spectra were obtained on a Shimadzu UV-240 instrument. Fluorescence spectra were measured with a Perkin–Elmer MPF-44E spectrofluorometer connected to a personal computer for data processing and quantum correction. Transient absorption spectroscopy was carried out with a laser flash apparatus described previously [2,3]. For measurements in the temperature range 163–352 K, a liquid nitrogen cryostat (DN 1704, Oxford Instruments) was used. Fluorescence lifetimes were determined with a time-correlated, single-photon-counting apparatus described elsewhere [4]. Spectroscopic grade MCH and toluene (Aldrich) were used as received. Fluorescence quantum yields were determined relative to anthracene in cyclohexane (0.30) [5], tetracene in benzene (0.17) [5] and quinine bisulphate in 1 N aqueous sulphuric acid (0.55) [6]. Absolute values of the triplet extinction coefficients (ϵ_T) and quantum yields of intersystem crossing were determined by energy transfer and reference excitation methods [7]. Anthracene was taken as reference ($\Phi_{ISC} = 0.70$, $\epsilon_T = 62\,000$ M⁻¹ cm⁻¹ in cyclohexane; $\Phi_{ISC} = 0.70$, $\epsilon_T = 42\,000$ M⁻¹ cm⁻¹ in toluene) [5,7,8]. Triplet lifetimes (τ_T) were typically about 1 ms for anthracene, 0.15–0.6 ms for bichromophores 1a–1e (in MCH), 0.2 ms for 2 (in MCH) and 1.6 ms for 3 (in toluene).
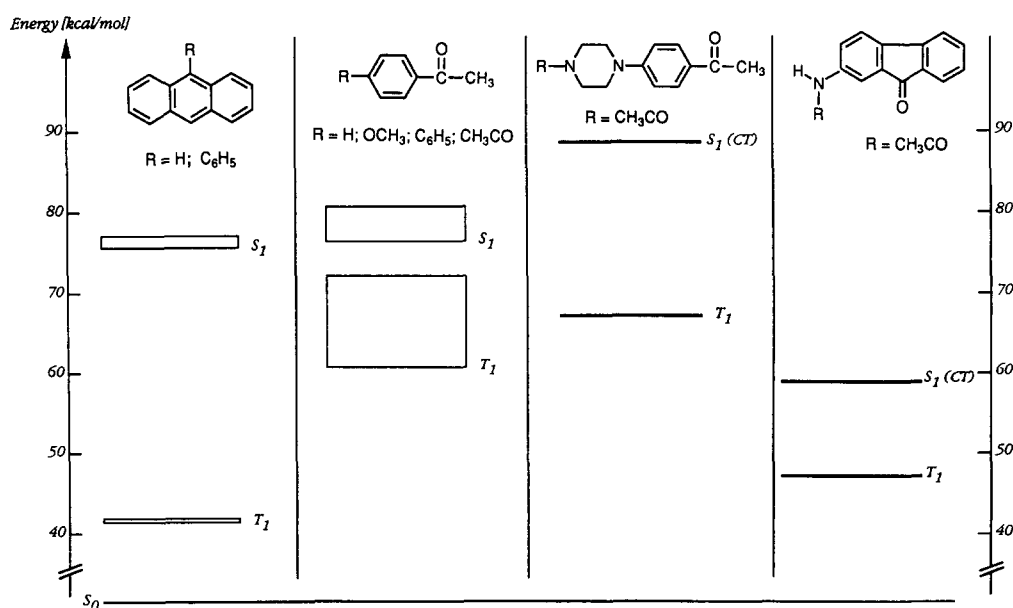
Fig. 1. Schematic representation of the lowest excited singlet and triplet energy levels of the π-systems in the bichromophoric compounds 1–3. (The boxes depict energy ranges due to chromophore substitution.)

2.2. Materials

The syntheses of the bichromophoric compounds 1–6 are outlined in Scheme 2. Thus trans-1-(9-anthryl)-2-benzoylethylenes were prepared by hydrogen-chloride-catalysed condensation of the corresponding 9-anthral-dehydes with acetophenones in ethyl acetate as described in the literature for trans-1-(9-anthryl)-2-benzoylethylene [9]. The melting points (m.p.) were as follows: trans-1-(10-phenyl-9-anthryl)-2-benzoylethylene, 198–201 °C; trans-1-(9-anthryl)-2-(4-methoxybenzoyl)ethylene, 127–129 °C; trans-1-(9-anthryl)-2-(4-phenylbenzoyl)ethylene, 212–214 °C; trans-1-(9-anthryl)-2-(4-acetylbenzoyl)ethylene, 173–175 °C. The catalytic hydrogenation of trans-1-(9-anthryl)-2-benzoylethylenes in ethyl acetate in the presence of Pd on calcium carbonate (10%) afforded the ω-(9-anthryl)propiophenones 1a–1e. Purification in all cases involved column chromatography on silica gel using dichloromethane as eluent. Recrystallization from dichloromethane solution by precipitation with hexane gave ω-(9-anthryl)propiophenones 1 as pale greenish-yellow crystalline substances which had melting points as follows: ω-(10-phenyl-9-anthryl)propiophenone (1a), 167–169 °C; ω-(9-anthryl)-4'-methoxypropiophenone (1b), 137–140 °C; ω-(9-anthryl)propiophenone (1c), 126–128 °C (116–117 °C [10]); ω-(9-anthryl)-4'-phenylpropiophenone (1d), 192–194 °C; ω-(9-anthryl)-4'-acetylpropiophenone (1e), 182–184 °C.
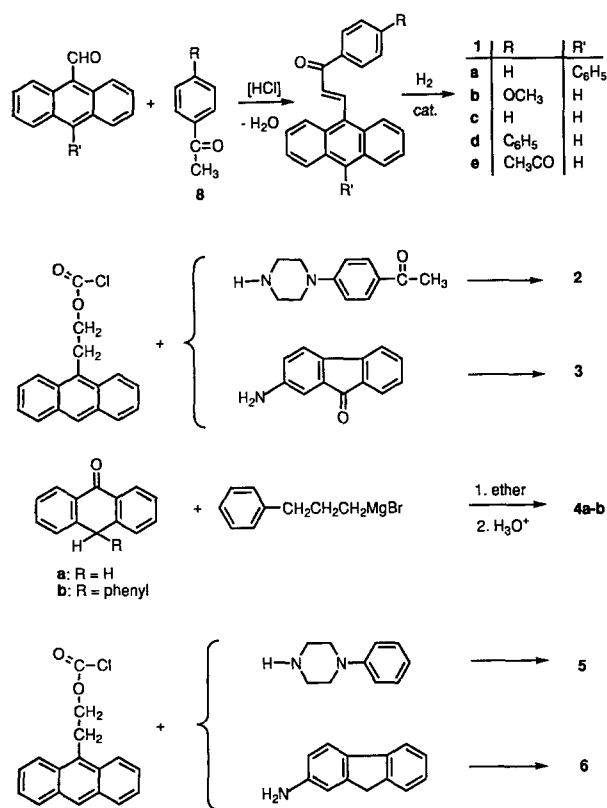
Scheme 2.

The bichromophoric anthracenes 2–6 were synthesized in straightforward fashion (see Scheme 2). Thus 1-[β-(9-anthryl)ethyloxycarbonyl]-4-(p-acetylphenyl)-piperazine (2) was obtained by reaction of β-(9-anthryl)ethyl chloroformate with 4'-piperazinoacetophenone in tetrahydrofuran in the presence of pyridine. Purification by column chromatography on silica gel/ethyl acetate gave 2 as greenish-yellow crystals, m.p. 173–175 °C. N-[β-(9-Anthryl)ethyloxycarbonyl]-2-aminofluorenone (3) was prepared from β-(9-anthryl)ethyl chloroformate and 2-aminofluorenone in the same manner as described for 2. Purification by column chromatography on silica gel/dichloromethane gave bright yellow, needle-shaped crystals, m.p. 252–254 °C. 1-(9-Anthryl)-3-phenylpropane (4a), m.p. 79–80 °C [10] (colourless needles), was prepared by Grignard reaction of 3-phenylpropylmagnesium bromide with 9-anthrone, followed by HCl-catalysed dehydration in acetic acid. 1-(10-Phenyl-9-anthryl)-3-phenylpropane (4b) (pale greenish-yellow crystals, m.p. 96–99 °C) was prepared in the same fashion as 4a from 10-phenyl-9-anthrone. 1-[β-(9-Anthryl)ethyloxycarbonyl]-4-phenylpiperazine (5), prepared from β-(9-anthryl)ethyl chloroformate and 1-phenylpiperazine, formed colourless, needle-shaped crystals, m.p. 110–112 °C. N-[β-(9-Anthryl)-ethyloxycarbonyl]-2-aminofluorene (6) (colourless, needle-shaped crystals, m.p. 224–225 °C) was prepared from β-(9-anthryl)ethyl chloroformate and 2-aminofluorene in tetrahydrofuran in the presence of pyridine. The anthracene derivative 7, m.p. 164–165 °C, was prepared by reaction of β-(9-anthryl)ethyl chloroformate with methylamine. The substituted acetophenones 8 were commercially available, and were purified by column chromatography (silica gel/dichloromethane). Acetophenone 9 (colourless crystals, m.p. 154–155 °C) and fluorenone 10 (red, needle-shaped crystals, m.p. 227–228 °C [11,12]) were prepared by reaction of acetic anhydride with 4'-piperazinoacetophenone and 2-aminofluorenone respectively. Purification of 9 involved column chromatography on silica gel using ethyl acetate as eluent. Fluorenone 10 was purified by column chromatography on silica gel/dichloromethane.

The purity of all the compounds was established by satisfactory elemental analyses and 270 MHz and 400 MHz proton nuclear magnetic resonance (^{1}H NMR) spectra. The molecular structure of 1a was established by X-ray diffraction.

3. Results and discussion

3.1. ω-(9-Anthryl)propiophenones 1

It is apparent from a comparison with the electronic absorption spectra of the corresponding model chro-

mophores **4** and **8** that the spectra of ω- (9-an-thryl)propiophenones **1** are superpositions of the anthracene and aryl ketone absorptions (see Figs. 2 and 3). Moreover, the absorption spectra of the acetophenones **8** reveal that the low-intensity n–π* transition of the phenyl ketone chromophore in ω-(9-anthryl)propiophenones **1a–1e** is higher in energy than the S₁ state of anthracene. Substitution of the anthracene and aromatic ketone moieties alters the relative positions of the singlet excited state energy levels of the anthracene and ketone π-systems (see Fig. 1). As shown in Fig. 3, the onset of absorption in the electronic spectra of the acetophenones shifts towards higher energy in the order p-acetylacetophenone <p-phenylacetophenone acetophenone <p-methoxyacetophenone. The absorption spectra of p-phenylacetophenone and p-acetylacetophenone indicate that the lowest excited singlet states of both of these aromatic ketones may have considerable π–π* character. Evidence for the π–π* nature of the lowest excited triplet state of p-methoxyacetophenone has been obtained previously by phosphorescence measurements in an

ether–ethanol–toluene mixture [13].

The excited state properties of the bichromophoric hydrocarbon **4a** ($\Phi_F = 0.48$; $\Phi_{ISC} = 0.51$) are typical of a 9-alkylanthracene, i.e. deactivation of S₁ by internal conversion is negligible. By contrast, the 9-phenylanthracene derivative **4b** is characterized by a fluorescence quantum yield of 0.75, and Φ_{ISC} was found to be as small as 0.06. It is worth noting that strikingly similar excited state properties ($\Phi_F = 0.72$; $\Phi_{ISC} \leqslant 0.07$) were found to characterize 9-methyl-10-phenylanthracene. Apparently, internal conversion may contribute significantly to the deactivation of photoexcited 9-alkyl-10-phenyl-substituted anthracenes.

By comparison with the excited state properties of the hydrocarbons **4**, the presence of the phenyl ketone moiety in ω-(9-anthryl)propiophenones **1** is demonstrated by the decreased fluorescence quantum yields, which range from 0.40 for **1a** to less than 0.003 for **1e**. The corresponding quantum yields of intersystem crossing increase from 0.17 for **1a** to unity for **1e** (see Table 1). For all compounds in Table 1, the fluorescence decay in MCH is monoexponential. It is evident from the characteristic shape and energy of the triplet–triplet absorption spectra obtained on laser excitation of ω-(9-anthryl)propiophenones **1** that intersystem crossing leads to the population of the T₁ state of the anthracene chromophore. The spectral shapes and the different absolute $\varepsilon_T(\lambda_{max})$ values observed for **1a** and **1c** (see Fig. 4) are virtually identical to the triplet absorption spectra of anthracene [7] and 9-phenylanthracene [14] respectively.

The high quantum yields of triplet formation found for the ω-(9-anthryl)propiophenones **1d** and **1e** show that intersystem crossing to the anthracene chromophore is highly efficient. However, as summarized in Table 1, for the ω-(9- anthryl)propiophenones **1a–1c**, the sum of the fluorescence quantum yield and quantum yield of intersystem crossing is noticeably smaller than unity, indicating the occurrence of some kind of non-radiative deactivation. Radiationless deactivation of the S₁ state
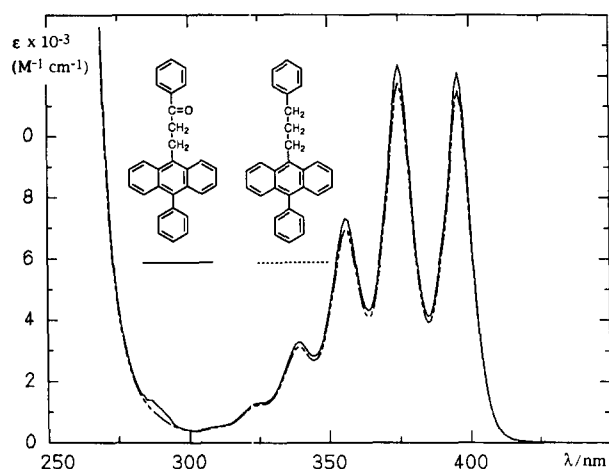

Fig. 2. Absorption spectra of ω-(10-phenyl-9-anthryl)propiophenone (**1a**; full curve) and hydrocarbon **4b** (broken curve) in MCH.
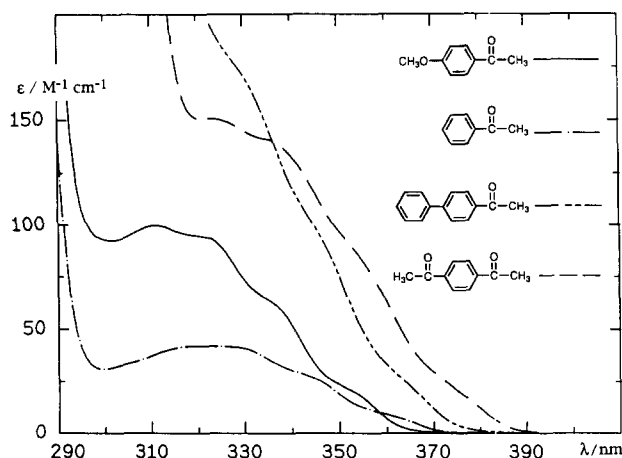

Fig. 3. Absorption (n–π*) of substituted acetophenones **8** in MCH.

Table 1
Excited state properties of ω-(9-anthryl)propiophenones (**1**) and bichromophoric hydrocarbons (**4**) in methylcyclohexane (293 K)

Compound	R	R'	λ_{max}[a] (nm)	Φ_F[b]	τ_F[c] (ns)	Φ_{ISC}	$\Phi_F + \Phi_{ISC}$
1a	H	C₆H₅	396	0.40	4.93	0.17	0.57
1b	OCH₃	H	388	0.25	3.09	0.54	0.79
1c	H	H	388	0.10	1.46	0.72	0.82
1d	C₆H₅	H	388	0.04	≈0.5	0.98	1
1e	CH₃CO	H	388	<0.003	–	1.00	1
4a			388	0.48	7.0	0.51	1
4b			396	0.75	8.92	0.06	0.81

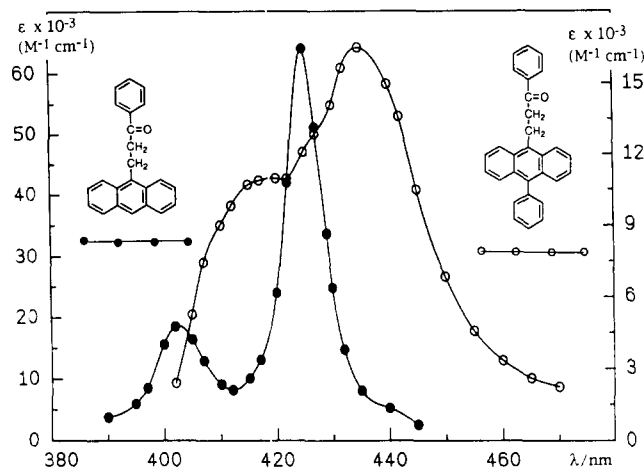[a] λ_{max} refers to the longest wavelength absorption maximum.
[b] ±10%.
[c] ±0.1 ns.

Fig. 4. Triplet absorption spectra of ω-(9-anthryl)propiophenones 1a and 1c in MCH at room temperature.
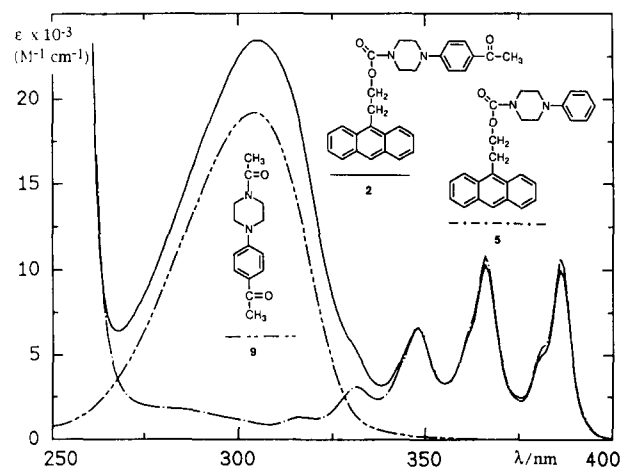

Fig. 5. Absorption spectra of bichromophore 2 and model compounds 5 and 9 in MCH.

by internal conversion has previously been noted to be an important feature of photoexcited 9-anthryl ketones such as 9-benzoylanthracene [15].

3.2. [β- (9-Anthryl)ethyloxycarbonyl]-4-(p-acetylphenyl)piperazine (2)

The electronic absorption spectrum of 2 is a superposition of the electronic spectra of model compounds 5 and 9 (see Fig. 5). The strong absorption around 308 nm in the spectrum of 2, attributable to the CT character of the lowest excited state of the 4'-piperazinoacetophenone chromophore, makes it experimentally possible to excite selectively both the anthracene and the energetically higher situated 4'-piperazinoacetophenone chromophore. (The presence of weak n–π* transitions in the spectral region of the CT transition can be neglected). Thus we have found that excitation of the anthracene chromophore in 2 at both 376 and 255 nm gives rise to characteristic anthracene fluorescence with $\Phi_F = 0.24$ ($\tau_F = 4.1$ ns). Significantly, the

quantum yield of fluorescence decreases to 0.03 when the excitation involves the CT absorption of the 4'-piperazinoacetophenone chromophore at 308 nm. The absence of the CT absorption band in the excitation spectrum of 2 is worth noting. This suggests that the electronically excited CT state in 2 deactivates within the ketone moiety, rather than by singlet energy transfer to the anthracene chromophore. However, the quantum yields of intersystem crossing involving excitation of 2 at 376 nm ($\Phi_{ISC} = 0.70$) and 308 nm ($\Phi_{ISC} = 0.38$) indicate that triplet energy transfer from piperazinoacetophenone to the anthracene chromophore does take place. We have ascertained that the fluorescence quantum yield of the piperazino-tethered anthracene 5 lacking the aromatic keto group is independent of the wavelength of excitation (see Table 2). The triplet absorption spectra of both 2 and 5 ($\epsilon_T \approx 70\,000$ M^{-1} cm^{-1} at 424 nm) show the spectral shape typical of 9-alkylanthracenes. In the case of 5, the quantum yields of fluorescence and intersystem crossing do not add up to unity. It is conceivable that a non-radiative deactivation path in photoexcited 5 involves intramolecular charge transfer interactions between the photoexcited anthracene and the N,N-dialkylanilino chromophore [16].

3.3. N-[β- (9-Anthryl)ethyloxycarbonyl]-2-aminofluorenone (3)

The presence of the 2-acetamidofluorenone chromophore is demonstrated in the electronic absorption spectrum of 3 by the broad absorption around 430 nm (see Fig. 6). Moreover, the photoexcited acetamidofluorenone π-system differs from those of the aromatic ketones 8 and 9 in so far as deactivation at room temperature by fluorescence is clearly detectable. Thus the photoexcitation of 2-acetamido-9-fluorenone (10) in toluene solution at room temperature gives rise to emission at $\lambda_{max} = 530$ nm ($\Phi_F = 0.03$), and excitation of the acetamido-9-fluorenone chromophore in 3 ($\lambda_{exc} = 430$ nm) also gives rise to emission from the locally excited state.

Evidence for intramolecular singlet energy transfer in bichromophoric 3 was obtained by selective excitation of the anthracene chromophore ($\lambda_{exc} = 368$ nm in toluene) which resulted in emission from the locally excited

Table 2
Quantum yields of fluorescence (Φ_F) and intersystem crossing (Φ_{ISC}) for 2 and 5 in methylcyclohexane at 293 K

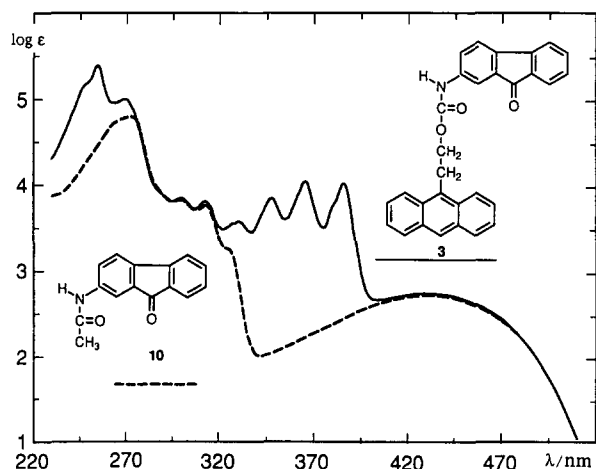| λ_{exc} (nm)	2		5	
	Φ_F	Φ_{ISC}	Φ_F	Φ_{ISC}
376	0.24	0.70	0.25	0.62
308	0.03	0.38	0.25	–
255	0.24	–	0.25	–

Fig. 6. Absorption spectra of bichromophore 3 and 2-acetamido-9-fluorenone (10) in toluene solution.
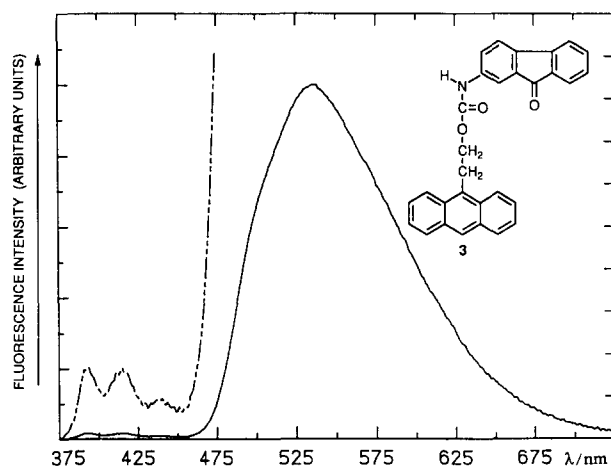

Fig. 7. Fluorescence spectrum ($\lambda_{exc} = 368$ nm) of bichromophore 3 in toluene solution. The emission from anthracene, indicated by the broken curve, was recorded at enhanced spectral amplitude.

Table 3
Photophyscial properties of N-[β-(9-anthryl)ethoxycarbonyl]-2-aminofluorenone (3) and model compounds 6, 7 and 10

Compound	Φ_F (λ_{em} (nm))	τ_F (ns)	Φ_{ISC}	τ_T (M^{-1} cm^{-1}) (λ_{max} (nm))
3	0.03 (530)		0.10	42000 (430)
	0.0004 (391)			
6	0.62 (391)	8.03	0.36	41300 (430)
7	0.60 (391)	7.95	0.37	40700 (430)
10	0.03 (530)	10.0	0.15	10400 (480)

state with only low quantum efficiency (0.0004; see Fig. 7 and Table 3). The quantum yield of emission from the acetamido-substituted 9-fluorenone at 530 nm was found to be 0.03, indicating efficient exothermic intramolecular energy transfer from anthracene to the 2-acetamido-9-fluorenone moiety. Intersystem crossing in 3 leads to population of the T_1 state of anthracene with a quantum yield of 0.10. As for the photophysical

properties of the relevant model compounds 6 and 7 lacking the ketone chromophore, their fluorescence quantum yields at room temperature in toluene solution are about 60%, and the quantum yields of intersystem crossing to the T_1 state of anthracene are nearly 40% (see Table 3). By contrast, high quantum yields of internal conversion ($\Phi_{IC} > 0.8$) characterize the photophysical properties of bichromophore 3 and acetamidofluorenone 10.

4. Conclusions

The intramolecular deactivation of photoexcited anthracenes by non-conjugatively linked aromatic ketones, leading to the triplet state of anthracene, has been established for ω-(9-anthryl)propiophenones. Photoexcited anthracene tethered to 2-acetamidofluorenone deactivates mainly by exothermic intramolecular singlet energy transfer to the 2-amidofluorenone π-system. By contrast, no evidence was found for the occurrence of exothermic intramolecular singlet energy transfer to anthracene from the photoexcited 4'-piperazinoacetophenone chromophore.

The intramolecular deactivation modes of photoexcited anthracenes by aromatic ketones discussed above are those applying to solutions in non-polar solvents. Preliminary studies have shown that polar solvents, such as dichloromethane or chloroform, markedly enhance the electron acceptor properties of the arylcarbonyl moiety, as demonstrated by the fluorescence quenching of the locally excited state of anthracene and the formation of luminescent intramolecular exciplexes [1,17].

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