

STUDIES ON THE FLUORESCENCE PROPERTIES OF MESO-SUBSTITUTED AMIDOANTHRACENES

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Summary

The fluorescence energy, the shape of the fluorescence spectrum and the fluorescence efficiency of 9-anthramide (9-CONH₂) and *N,N*-diethyl-9-anthramide (9-CONEt₂) have been investigated as a function of solvent. For 9-CONH₂, the average first excited singlet state (S₁) energy decreases and the fluorescence becomes structureless at the polar and non-polar extremes of the solvent scale. This unusual fluorescence behavior for 9-CONH₂ is explained by a solvent-dependent geometry change subsequent to excitation, whereby the exocyclic group rotates about the anthracene ring. In contrast, 9-CONEt₂ shows solvent-independent behavior. The average S₁ energy remains nearly constant and the fluorescence spectra show well-defined vibrational structure in a wide variety of solvents. Thus, the diethyl substitution causes a dramatic change in the fluorescence properties compared with those of the unsubstituted amide. This difference appears to correlate with the increased bulkiness and electron donating ability of the ethyl groups which impede the excited state rotation. Limited fluorescence quantum yield data suggest that the fluorescence efficiency of the amides is intermediate between that of meso-substituted anthryl ketones and esters of 9-anthroic acid.

1. Introduction

Over the past decade, considerable interest has been expressed in the fluorescence properties of carbonyl-substituted anthracenes. In particular, meso-substituted derivatives have received the most attention because of a geometry change that occurs subsequent to excitation [1 - 6]. This change converts the molecular geometry from one in which the carbonyl group and ring are nearly perpendicular to each other in the ground state to one in which they are more nearly coplanar in the excited state [1 - 6].

The nature of the carbonyl substituent at the meso position does have a substantial effect on the fluorescence properties. If the carbonyl-containing group is a ketone or aldehyde the fluorescence quantum yield is often very

low or even negligible at room temperature [5, 7]. However, if the carbonyl functionality is a carboxylic acid or ester the room temperature quantum yield can be about 0.8 in non-polar solvents [4, 8]. In addition, the solvent dependence of the quantum yield and the fluorescence energy can be quite unusual for esters such as methyl-9-anthroate (9-COOME) [3, 4].

Only limited spectral studies have been performed on amidoanthracenes, where the carbonyl now contains an NR_2 group. Nonetheless, the NR_2 group has the potential to provide unique modification of carbonyl-anthracene fluorescence, especially when compared with esters such as 9-COOME. First, unlike 9-COOME, the unsubstituted amide has the ability to interact with hydrogen-bond donor or acceptor solvents. Second, amides disubstituted on the nitrogen atom provide a greater barrier for the excited state rotation than do the esters. Finally, the NR_2 group has greater electron donating ability toward the carbonyl than the OR group of an ester. This, in turn, should modify the extent of ring-carbonyl conjugative interaction in the amide compared with that in an ester. It is this interaction that is primarily responsible for the excited state geometry change [1 - 4].

We report here the results of our spectral investigations on 9-anthramide (9- CONH_2) and *N,N*-diethyl-9-anthramide (9- CONEt_2). Brief studies of 9- CONH_2 have previously been reported [5, 9, 10]; however, we are aware of no literature references to spectral investigations of 9- CONEt_2 .

2. Experimental details

All solvents used for spectral measurements except ethanol and tetrahydrofuran were Matheson Coleman and Bell, Omnisolv, or Aldrich spectro-quality solvents. Ethanol from U.S. Industrial Chemicals was distilled from CaH_2 before use. Tetrahydrofuran from Mallinckrodt was refluxed over CuCl and then distilled from CaH_2 before use.

The 9- CONH_2 was prepared by the method of May and Moseitig [11] beginning with 9-cyanoanthracene (Aldrich Chemical Co.). Thin-layer chromatography using both ethanol and ethyl acetate as solvents indicated the presence of a single product in the reaction mixture. The product was identified as 9- CONH_2 by IR spectroscopy and by comparison of the observed melting point (221 - 222 °C) with the value reported in the literature (219.5 °C [10]).

The method of Koelsch was employed to prepare 9- CONEt_2 [12]. Its melting point (109.5 - 111 °C) could not be used for identification since values could not be found in the literature. However, proton nuclear magnetic resonance (NMR) and IR spectra provide sufficient proof for the structure. The IR spectra show aliphatic and aromatic C-H stretching, a strong amide carbonyl band and the absence of N-H stretching. The NMR spectra contain two separate methyl and methylene resonances which is consistent with restricted rotation about the C-N bond of the amide group.

In addition, integration data confirm the proposed structure of the reaction product.

9-COOME was synthesized and purified as described previously [8].

UV-visible absorption measurements were obtained using a Cary 118c, a Beckman DU or a Perkin-Elmer Lambda 3 spectrophotometer.

Fluorescence spectra were obtained using a Perkin-Elmer MPF-2A spectrofluorometer with excitation and emission band passes of 7 nm and 3 nm respectively. The MPF-2A is interfaced to an Apple II+ computer to correct emission spectra for instrument response, determine areas under corrected emission spectra, calculate fluorescence quantum yields, convert corrected emission spectra from a wavelength to a wavenumber axis and to determine the mean wavenumber of fluorescence (see Section 3).

Fluorescence quantum yields were determined as described previously [8].

3. Results

The UV-visible absorption spectra of 9-CONH₂ and 9-CONEt₂ in ethanol are shown in Fig. 1. Both molecules have similar-structured anthracene-like absorption spectra in all solvents used in this work. Esters of 9-anthric acid and other meso-substituted carbonyl anthracenes also exhibit anthracene-like absorption spectra [1 - 5].

The wavenumbers ν_a of the 0-0 absorption band for the two amides in a series of solvents are given in Tables 1 and 2. These absorption maxima for both amides show little solvent dependence and no correlation with solvent polarity as determined by the empirical $E_T(30)$ scale (see Tables 1 and 2). This is also consistent with the reported behavior of other meso-substituted carbonyl anthracenes [1, 2].

By contrast, the shape and position of the corrected fluorescence spectra of 9-CONH₂ in hexane, dioxane, water and trifluoroethanol, shown

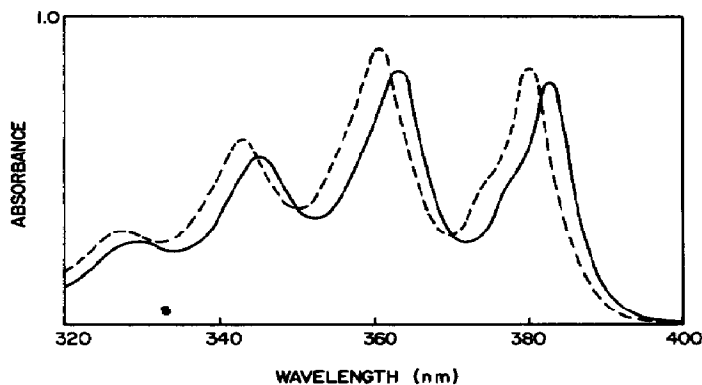


Fig. 1. Absorption spectra of 9-CONH₂ (---) and 9-CONEt₂ (—) in ethanol (concentration, 1×10^{-4} M).

TABLE 1

Solvent dependence of the absorption, fluorescence emission and Stokes shift for 9-CONH₂

<i>Solvent</i>	$E_T(30)^a$ (kcal mol ⁻¹)	$\nu_a \times 10^{-4}{}^b$ (cm ⁻¹)	$\nu_m \times 10^{-4}{}^c$ (cm ⁻¹)	$(\nu_a - \nu_m) \times 10^{-3}{}^d$ (cm ⁻¹)
Hexane	31	2.63	2.34	2.9
Cyclohexane	33	2.62	2.33	2.9
Dioxane	36	2.61	2.39	2.2
Acetonitrile	46	2.62	2.36	2.6
Ethanol	52	2.63	2.34	2.9
Methanol	56	2.63	2.34	2.9
Trifluoroethanol	61	2.64	2.17	4.7
Water	63	2.62	2.25	3.7

^aFrom ref. 13.^b0-0 absorption band.^cMean wavenumber of fluorescence.^dStokes shift.

TABLE 2

Solvent dependence of the absorption, fluorescence emission and Stokes shift for 9-CONEt₂

<i>Solvent</i>	$E_T(30)^a$ (kcal mol ⁻¹)	$\nu_a \times 10^{-4}{}^b$ (cm ⁻¹)	$\nu_m \times 10^{-4}{}^c$ (cm ⁻¹)	$(\nu_a - \nu_m) \times 10^{-3}{}^d$ (cm ⁻¹)
Hexane	31	2.61	2.43	1.8
Cyclohexane	33	2.60	2.41	1.9
Dioxane	36	2.60	2.40	2.0
Tetrahydrofuran	37	2.60	2.39	2.1
Ethyl acetate	38	2.61	2.42	1.9
Dimethylformamide	44	2.59	2.40	1.9
Dimethyl sulfoxide	45	2.58	2.39	1.9
Acetonitrile	46	2.61	2.41	2.0
Ethanol	52	2.61	2.41	2.0
Methanol	56	2.62	2.42	2.0
Trifluoroethanol	61	2.62	2.41	2.1
Water	63	2.61	2.39	2.2

^aFrom ref. 13.^b0-0 absorption band.^cMean wavenumber of fluorescence.^dStokes shift.

in Fig. 2, are quite solvent dependent. It should be noted that the fluorescence spectrum is most structured in the solvent of intermediate polarity, *i.e.* dioxane. Similar anthracene-like structure is observed in acetonitrile, another solvent of intermediate polarity. Conversely, the spectra in cyclohexane and methanol more closely resemble the less-structured spectra in hexane. Shon *et al.* [10] have previously reported the emission spectrum of

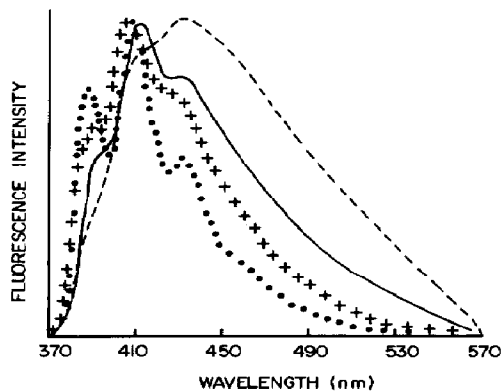


Fig. 2. Fluorescence spectra of 9-CONH₂ in hexane (+ + +), dioxane (···), water (—) and trifluoroethanol (---). The spectra are normalized to the same maximum intensity.

9-CONH₂ to be more structured in tetrahydrofuran than in benzene, while Sturgeon and Schulman [9] have presented emission spectra of the amide showing a more anthracene-like appearance in water than in hexane.

Since the shape of these fluorescence spectra is so solvent dependent, we have chosen the mean wavenumber ν_m of fluorescence as a measure of the excited singlet state energy in a given solvent. ν_m is defined as

$$\frac{1}{2} \int_{\nu_1}^{\nu_f} F(\nu) d\nu = \int_{\nu_1}^{\nu_m} F(\nu) d\nu \quad (1)$$

where ν_1 is the initial wavenumber of fluorescence, ν_f is the final wavenumber of fluorescence and $F(\nu)$ is the corrected fluorescence intensity at a given wavenumber [15]. Thus ν_m is an effective average energy of the excited singlet state in a given solvent and reflects solvent-induced changes in the shape as well as in the position of the fluorescence band. The value of ν_m for 9-CONH₂ in a given solvent and the Stokes shift ($\nu_a - \nu_m$) in that solvent are listed in Table 1.

The shape and position of the fluorescence emission spectrum of 9-CONH₂ in water are unchanged by the presence of 5 M NaClO₄ or 1.5 M MgSO₄. NaClO₄ is a known water-structure breaker while MgSO₄ is a known water-structure former [16].

The fluorescence excitation spectra of 9-CONH₂ were obtained by monitoring the fluorescence at both the blue end and the red end of the emission spectrum in both water (411, 480 nm) and hexane (407, 490 nm). In each solvent the excitation spectra were identical at both wavelengths.

The corrected fluorescence emission spectra of 9-CONEt₂ in hexane and trifluoroethanol, shown in Fig. 3, imply a remarkable solvent independence in sharp contrast with the solvent dependence of the 9-CONH₂ emission spectra in Fig. 2. In support of this, the mean wavenumber of fluorescence and the Stokes shift, listed in Table 2, show much less variation with solvent than observed for 9-CONH₂ in Table 1. Moreover, the shape of

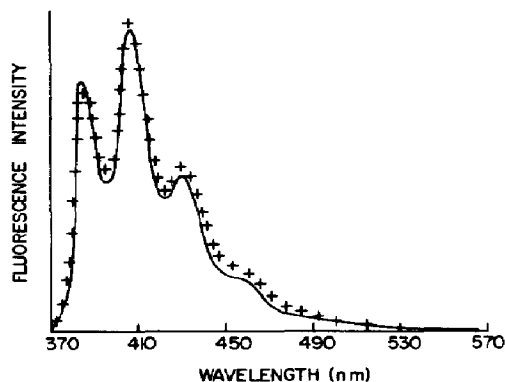


Fig. 3. Fluorescence spectra of 9-CONEt₂ in hexane (—) and trifluoroethanol (+ + +). The spectra are normalized to the same maximum intensity.

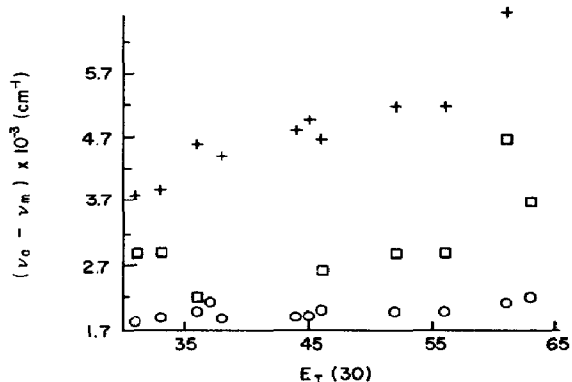


Fig. 4. Stokes shift as a function of the solvent $E_T(30)$ value for 9-COOME (+ + +), 9-CONH₂ (□ □ □) and 9-CONEt₂ (○ ○ ○). The data for 9-COOME are from refs. 4 and 8.

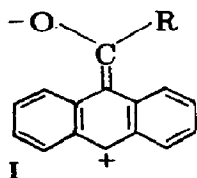
the 9-CONEt₂ spectra is highly structured and anthracene-like in all solvents studied.

The Stokes shifts of the two amides as a function of solvent polarity (the $E_T(30)$ value) are compared with those of 9-COOME in Fig. 4. The $(\nu_a - \nu_m)$ values show a general increase with increasing solvent polarity for 9-COOME and are always larger in a given solvent than for either of the amides. For 9-CONH₂ the $(\nu_a - \nu_m)$ values are relatively large in the most non-polar solvents, where the spectral structure is markedly diffuse. However, they sharply decrease in solvents of intermediate polarity as a result of the blue shift in the spectrum that accompanies the enhanced spectral structure in these solvents. Further increase in solvent polarity results in a return to a more diffuse spectrum and larger Stokes shifts. The largest Stokes shift, and the most diffuse spectrum, is observed for trifluoroethanol, an exceptionally strong hydrogen-bond donor solvent. By comparison, the Stokes shift for 9-CONEt₂ is unusually solvent independent, more similar to that expected for the parent anthracene than observed for 9-COOME or 9-CONH₂.

4. Discussion

The geometry of carbonyl-substituted anthracenes in a given electronic state is determined by a balance between the opposing effects of ring-carbonyl group conjugation and steric hindrance between the carbonyl group and the ring hydrogens [1]. In the ground state (S_0) of meso-substituted carbonyl anthracenes, steric hindrance dominates, resulting in a nearly perpendicular carbonyl-to-ring configuration [18, 19]. As a result, the absorption spectra of these derivatives are quite similar to that of the parent anthracene. However, on excitation of these derivatives to the first excited

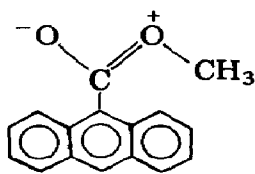
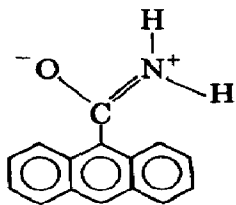
singlet state (S_1) the conjugative interaction becomes more competitive as a result of the magnitude and direction of the transition moment that accompanies excitation [1, 2]. The excited state thereby becomes more planar and more polar than S_0 , as indicated by the contributing resonance form I



and the resulting fluorescence spectrum becomes quite diffuse and red shifted from that of the parent anthracene [1, 2]. This blurring of the fluorescence relative to the absorption probably results from a combination of factors which include differences in the equilibrium geometries of S_0 and S_1 , the greater polarity of S_1 and the availability of a greater range of conformations in the "looser" S_1 .

The dominance of the drive for S_1 coplanarity is apparent in the temperature dependence of the fluorescence spectra of 9-anthracic acid esters. These spectra take on an anthracene-like appearance only for the more bulky esters at low temperatures (less than 100 K) in protic solvents [19].

However, our data herein suggest the desire for coplanarity and the opposing steric effects are more subtly balanced in S_1 of the amidoanthracene 9- CONH_2 . For example, the emission spectra of 9- CONH_2 in Fig. 2, all obtained at room temperature, indicate that the excited state carbonyl rotation is favored in solvents of low or high polarity but inhibited in solvents of intermediate polarity. The lack of any dependence of the fluorescence excitation spectra on emission wavelength even in solvents at the polarity extremes suggests that the diffuse emission has an excited rather than ground state origin. Moreover, the S_1 energy of the amide in solvents where the rotation is observed is always higher than that of 9-COOME in these same solvents. This indicates that the conjugative interaction between the ring and the carbonyl group in S_1 is inherently stronger for 9-COOME than for 9- CONH_2 . An explanation for this is found in the relative abilities of structures II and III



to compete with structure I, thereby reducing carbonyl–ring interaction. The lower IR stretching frequency of the amide carbonyl compared with that of an ester carbonyl implies that structure II is a stronger competitor than structure III.

Sturgeon and Schulman [9] have previously reported a diffuse fluorescence spectrum for 9-CONH₂ in hexane. Apparently, ground state solvation of the amide group and steric hindrance to rotation do not provide a sufficient barrier to formation of a coplanar S₁ in this solvent.

The more structured emission in dioxane in Fig. 2 must mean that enhanced ground state solvation in combination with steric effects is now sufficient to block the rotation in this solvent. Presumably, the major solvation interaction involves hydrogen bond formation between the hydrogens on the amide and oxygens on dioxane. However, a structured emission spectrum is also observed in acetonitrile, a polar solvent with lesser hydrogen-bond accepting ability and modest hydrogen bond donor ability [20].

Sturgeon and Schulman [9] were the first to report a solvent dependence of the excited state rotation for 9-CONH₂. Their spectral data show considerably more structure for the emission of the amide in water than in hexane compared with our spectra in Fig. 2. They concluded that the rotation is inhibited in water as a result of the existence of a bulky solvent cage which results from strong hydrogen bonding between water and the amide group nitrogen [9].

In contrast, our data are more consistent with an enhancing rather than an inhibiting effect of water on the excited state rotation. The water spectrum in Fig. 2 is more red shifted and diffuse than those in hexane or in dioxane, implying a more favored rotation in water. The reason for this, we believe, is that water can effectively tie up the electrons on the amide nitrogen, thereby reducing the ability of structure II to inhibit ring–carbonyl group conjugative interaction (structure I). There is evidence to support this view. First, the emission spectrum of 9-CONH₂ is the most red shifted and diffuse in trifluoroethanol (see Fig. 2), a solvent with strong hydrogen-bond donor ability but weak hydrogen-bond acceptor and solvent structuring abilities [21]. Second, protonation of the amide nitrogen results in a virtually structureless emission spectrum for 9-CONH₂ [9]. Thus, reduced availability of the electrons of the amide nitrogen for resonance with the carbonyl clearly promotes the rotation.

The lack of any effect on the shape or position of the emission spectra in water by structure breaking or making salts such as NaClO₄ or MgSO₄ indicates that only short-range solvent interactions affect the fluorescence properties of 9-CONH₂.

The data in Fig. 3 and Table 2 show that the carbonyl rotation in S₁ is completely inhibited for 9-CONEt₂ in all solvents. The amide ethyl groups can impede the rotation both electronically and sterically. Their electron donating ability enhances the competitive effect of the amide–carbonyl conjugation (structure II) over that of ring–carbonyl conjugation (structure I). Support for this is seen in the lower carbonyl stretching frequency ob-

served in the IR spectrum of 9-CONEt₂ (1620 cm⁻¹) than that observed for 9-CONH₂ (1650 cm⁻¹). Thus, the conjugative "benefit" derived from a coplanar S₁ decreases in the order 9-COOMe > 9-CONH₂ > 9-CONEt₂. More importantly, however, is the fact that two alkyl groups on the amide nitrogen provide a more substantial barrier to rotation than exists for 9-COOMe or 9-CONH₂, as molecular models clearly demonstrate. The observed anthracene-like fluorescence spectrum of 9-CONEt₂ in trifluoroethanol also shows the relative importance of steric blockage. The ability of this solvent to tie up the electrons of the amide nitrogen and thereby favoring the rotation, seen for 9-CONH₂, is not observed for 9-CONEt₂, presumably as a result of the greater steric barrier for 9-CONEt₂.

In summary, the relative importance of extended conjugation from rotation and steric hindrance to rotation varies greatly among 9-COOMe, 9-CONH₂ and 9-CONEt₂. As a result, the room temperature equilibrium geometry of S₁ changes from nearly coplanar (9-COOMe) to nearly perpendicular (9-CONEt₂) to either of these conformations depending on the solvent (9-CONH₂).

The fluorescence quantum yields ϕ_f of 9-CONH₂ in dioxane and dimethyl sulfoxide are 0.055 and 0.19 respectively, while for 9-CONEt₂ the ϕ_f values are 0.13 and 0.36 in these same solvents. Thus, the amides are more efficient than meso-substituted anthryl ketones [5] but less efficient than meso-substituted anthroic acid esters [8].

Meso-substituted anthryl ketones are virtually non-fluorescent at room temperature in aprotic solvents presumably as a result of a suitably placed n, π^* triplet level which enhances intersystem crossing [6]. The amide carbonyl, like that of an ester carbonyl, will have its n, π^* too high in energy to affect S₁ decay [5, 8]. Consequently, intersystem crossing to a nearby upper triplet state (T_x) is a probable major competition to fluorescence decay from S₁, just as it is for anthroic acid esters [4].

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