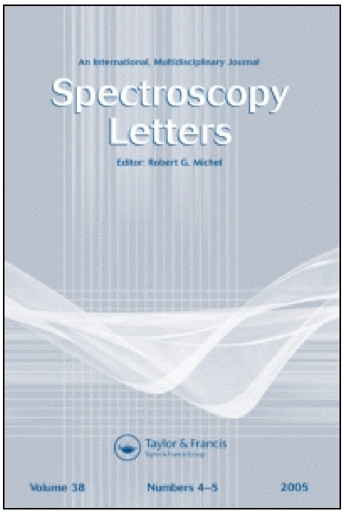

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SPECTRAL STUDIES ON AROMATIC ESTERS OF 9-ANTHROIC ACID

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INTRODUCTION

Substitution of a carboxyl group onto the 9 position of anthracene, as in 9-methyl anthroate (9-COOMe), results in some significant differences in the spectral properties of the ester relative to those of the anthracene parent molecule. For example, the fluorescence quantum yield (ϕ_f) and fluorescence maximum ($\nu_{max.}$) of 9-COOMe become quite solvent dependent due to an excited state geometry change in which the excited singlet takes on significant charge transfer character (1, 2).

During our investigation of the spectral behavior of 9-COOMe, we synthesized several aromatic esters of 9-anthroic acid (9-COOAR). We found that some of these aromatic esters had significantly different spectral properties than the aliphatic ester (9-COOMe). Rather large variations in Stokes shift, ϕ_f values and photoreactivity were noted for the aromatic esters. We report here the results of our investigation.

EXPERIMENTAL

Matheson Coleman and Bell Spectroquality cyclohexane and methanol and U.S. Industrial Chemicals' absolute ethanol were used as spectral solvents

The esters of 9-anthroic acid were prepared by the method of Parrish and Stock (3). Proof of structure was obtained by comparison with known melting points where available and by infrared spectroscopy. p-Nitrophenyl acetate, p-methoxyphenyl acetate and β-naphthyl acetate were synthesized from p-nitrophenol, p-methoxyphenol or β-naphthol and acetic anhydride (4).

Electronic absorption spectra were recorded on a Cary Model 14MS and emission spectra were recorded on a Perkin-Elmer-Hitachi-MPF-2A spectrofluorometer. Emission spectra were corrected for instrument response as described previously (2). Fluorescence quantum yield (ϕ_f) determinations were made as described previously (2) using 9-methyl anthroate as the quantum yield reference ($\phi_f = 0.68$). Since the β-naphthyl (9-COO-β-Naph) and p-methoxy-phenyl (9-COO-p-MeOPh) anthroates proved to be quite photoreactive, solutions of these esters were made up in the dark and used immediately.

RESULTS

The absorption and fluorescence spectra of the aromatic esters are quite similar to those of 9-COOMe (1, 2). The absorption spectra from 320-400 nm all possess a characteristic anthracene vibrational pattern while the fluorescence spectra are structureless and highly Stokes shifted relative to anthracene's emission. Spectral data for the esters are tabulated in Table 1. Data for anthracene are included for comparison purposes. The Stokes shifts ($\nu_a - \nu_f$) listed in Table 1 are from the 0-0 absorption band to the fluorescence maximum since no 0-0 fluorescence band can be picked out for the esters.

ϕ_f data for the esters are also included in Table 1. The β-naphthyl (9-COO-β-Naph) and p-methoxyphenyl (9-COO-p-MeOPh) esters are quite photoreactive. The ϕ_f for the former ester is probably reliable but photodecomposition for the latter ester is so rapid that only an estimate of ϕ_f can be made. No detailed study of the photodecomposition has been made but preliminary evidence indicates that 9-anthroic acid and β-naphthol or

TABLE 1

Spectral Data for Anthracene and Anthroic Acid Esters in Cyclohexane

Compound	ν_a (a)	ν_f (b)	$\Delta\nu$ (c)	ϕ_f
Anthracene	2.66	2.45	2.1	0.30
9-COOMe	2.62	2.21	4.1	0.68
9-COOPh	2.62	2.17	4.5	0.72
9-COO-p-BrPh	2.61	2.16	4.5	0.73
9-COO-p-NO_2Ph	2.61	2.11	5.0	0.17
9-COO-p-MeOPh	2.61	2.17	4.4	< 0.1
9-COO-β-Naph	2.61	2.17	4.4	0.07

(a) 0-0 absorption band, x 10^{-4}cm^{-1}

(b) fluorescence maximum, x 10^{-4}cm^{-1}

(c) $\Delta\nu = \nu_a - \nu_f$, x 10^{-3}cm^{-1}

p-methoxyphenol are two of the break down products.

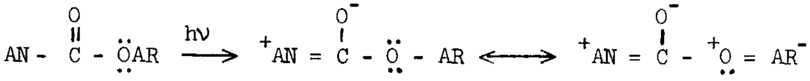
Phosphorescence spectra were recorded for p-methoxyphenyl acetate and β-naphthyl acetate in methanol/ethanol (1:5). The latter ester had a structured spectrum with a 0-0 band ca. 21,200 cm^{-1} while the former's spectrum was structureless with a maximum ca. 22,400 cm^{-1}. No phosphorescence could be measured for p-nitrophenyl acetate.

DISCUSSION

The anthracene-like structure observed in the absorption spectra of the anthroate esters is consistent with the near perpendicularity of the carboxyl group and anthracene ring in the ground and Franck-Condon excited states (1,2). The lack of coplanarity is a result of steric interaction between the carboxyl group and the peri hydrogens (1, 2). Thus, the absorption is primarily the ring localized, short axis polarized $^1A \rightarrow {}^1L_a$ transition (5). In the equilibrium excited singlet state, the carboxyl group and anthracene ring become more coplanar and considerable charge transfer (CT) character is introduced into the excited state due to electron density shifts toward the carboxyl group (1, 2). This excited state geometry change with subsequent introduction of CT character into the excited state results in a broad and structureless fluorescence. Since all of the esters show this diffuse fluorescence the <u>size</u> of the ester group must not affect the excited state rotation. This is substantiated by molecular models which indicate that most of the steric interaction is between the peri hydrogens and the carboxyl group oxygens.

The data in Table 1 show that the Stokes shifts of the aromatic esters (9-COOAR) are significantly larger than that of the methyl ester (9-COOMe). It is clear from Table 1 that this Stokes shift difference arises primarily from a <u>lower</u> excited state energy for the aromatic esters. The excited state for the aromatic anthroates has an electron delocalization pathway not available to an aliphatic ester. This pathway involves delocalization of the electrons on the carboxyl group's "ether type" oxygen into the AR portion of the ester. Scheme I, on the following page, in which the ester excited singlet is represented by its CT component, illustrates this point.

(I)



$$AN-\overset{O}{\overset{\|}{C}}-\underset{\cdot\cdot}{\ddot{O}}AR \xrightarrow{h\nu} {}^{+}AN=\overset{O^{-}}{\overset{|}{C}}-\underset{\cdot\cdot}{\ddot{O}}-AR \longleftrightarrow {}^{+}AN=\overset{O^{-}}{\overset{|}{C}}-{}^{+}\underset{\cdot\cdot}{O}=AR^{-}$$

AN = anthracene AR = aromatic substituent

The net effect of this electron delocalization is to produce a lower energy and more polar aromatic ester excited state than that of 9-COOMe. The effect should be greatest for the p-nitrophenyl ester (9-COO-p-NO_2Ph) where the strongly electron withdrawing NO_2 group in the p position should enhance delocalization. This is confirmed by the data in Table 1 which show 9-COO-p-NO_2Ph to have the lowest excited state energy and the greatest Stokes shift. Also, the increase in the Stokes shift for the nitrophenyl ester on going from cyclohexane to ethanol is ca. 600 cm^{-1} greater than for any other ester.

Based on ϕ_f values and photostability, the aromatic anthroates can be grouped into three categories. In the first category are the phenyl and p-bromophenyl esters whose ϕ_f values are high (ca. 0.7) and within experimental error of ϕ_f for 9-COOMe. When exposed for 30 minutes to radiation from the spectrofluorometer's xenon lamp at the excitation maximum (362 nm), no evidence for photodecomposition of either ester was found. We therefore classify these esters as photostable. The high and virtually identical ϕ_f's for the methyl, phenyl and p-bromophenyl esters implies that the ester portion (-OAR) has no significant effect on the photophysical processes deactivating the lowest excited singlet of these esters. The lowest excited singlet and triplet levels associated with the ester portion of these esters are expected to be at quite higher energies than the lowest excited singlet of the anthroate portion ($AN - \overset{\overset{O}{\|}}{C} -$). Thus the anthroate excited singlet decay is therefore not influenced by electronic states on the ester portion.

A most important implication from the similarity of ϕ_f values for the phenyl and p-bromophenyl ester is the failure of the heavy bromine atom to induce significant spin orbit coupling in the latter ester. In order to induce spin-orbit coupling, the portion of the molecule in which the excitation energy is localized must have orbital overlap with the bromine p orbital (6). The lack of a heavy atom effect for the p-bromophenyl ester means that the excitation is localized primarily on the $AN - \overset{\overset{O}{\|}}{C} -$ "half" of the ester. This can be crudely rationalized by the valence bond structure in Scheme I. In the excited state, the $^{+}AN = \overset{\overset{O^{-}}{|}}{C} -$ and $- O -$ AR parts of the molecule are "insulated" by the C - O bond and consequently are not in <u>direct</u> conjugation. Electron density from the $^{+}AN = \overset{\overset{O^{-}}{|}}{C}$ part can not be delocalized into the -OAR part and the bromine atom is unable to induce significant spin-orbit coupling. A second contributing factor to the absence of a heavy atom effect may arise from the size of the energy gap between the ester excited singlet and the next lower triplet. Several workers have suggested that heavy atom effects are most pronounced when the energy gap $\Delta E_{S_1} - T_x$ is small (7). Werner and Hoffman have explained the large ϕ_f values for these esters in cyclohexane ($\sim$0.7) on the basis of a large $\Delta E_{S_1} - T_x$ energy gap with subsequent inefficient intersystem crossing (2).

The second category includes only the p-nitrophenyl ester (9-COO-p-NO_2Ph). This ester has a low ϕ_f (0.17) but is photostable under the photolysis condition mentioned above. Thus the nitrophenyl group has a dramatic effect on the anthroate ϕ_f value. The lowest singlet state of the p-nitrophenyl portion is still expected to be much higher in energy than the anthroate singlet. However, it was thought that the p-nitrophenyl portion might have a triplet level below that of the anthroate excited singlet. To this end, p-nitrophenyl acetate was synthesized as a model compound for the ester portion and attempts were made to measure the phosphorescence spectrum of this compound at 77° in methanol/ethanol (1:5). No phosphorescence could be measured but, by analogy to nitrobenzene, the triplet level should be ca. 21,000 cm^{-1} (8). This would place a triplet level nearby and slightly lower in energy than the equilibrium excited singlet energy of 9-COO-p-NO_2Ph in cyclohexane (21,100 cm^{-1}). Generally, small singlet-triplet energy gaps lead to enhanced intersystem crossing rates and reduced ϕ_f values (9). For the p-nitrophenyl ester, the intersystem crossing process would therefore couple a singlet state located primarily on the anthroate portion with a triplet level of the p-nitrophenyl part. In lieu of the discussion above on the ability of the C - O bond to "insulate" the two "halves" of these esters, one might expect this process to be considered energy transfer rather than intersystem crossing. However the required energy transfer process ($^1D + {}^1A \rightarrow {}^1D + {}^3A$) is forbidden by both the exchange and dipole-dipole mechanisms since spin is not conserved (10). Moreover, to be considered true energy transfer, the donor and acceptor moities must be completely non-interacting. Although our data do suggest that the carboxyl group effectively insulates the two halves of the ester molecule, it would be naive to expect complete isolation of the two parts. Indeed, electronic interaction between two chromophores has been observed even when the linkage between the chromophores is a methylene group (11). Therefore, we conclude that any quenching which occurs by this process should be considered intersystem crossing.

A second possibility for the low ϕ_f of 9-COO-p-NO_2Ph involves formation of a non-radiative intramolecular exciplex. Although we can not completely rule out this mechanism, we feel it is less likely than the previous one. Space filling models of the planar ester excited state indicate that the p-nitrophenyl ring is nearly perpendicular to and offset from the anthracene ring. Such a relative geometry of the ring systems makes intramolecular exciplex formation unlikely.

The third category includes the p-methoxyphenyl (9-COO-p-MeOPh) and β-naphthyl (9-COO-β-Naph) esters. Both of these esters have low ϕ_f's and are classified as photochemically unstable by the criteria mentioned above. The fluorescence spectrum of a fresh solution of 9-COO-β-Naph in cyclohexane had both a β-naphthyl (-OAR) and an anthroate (AN - $\overset{\text{O}}{\overset{\|}{\text{C}}}$ -) component when excitation was at 280 nm. The ratio of the former to the latter was 0.6 using uncorrected fluorescence maxima for comparison. After 25 minutes exposure to 280 nm excitation in the spectrofluorometer cell compartment, the ratio increased to 2.7. The increased ratio indicates a reduction in the quenching of β-naphthyl fluorescence via singlet-singlet energy transfer to the anthroate portion. This is exactly what is expected if photodecomposition of the ester had occurred. The initial and final anthroate fluorescence spectrum (EX. 362 nm) were both quite diffuse, but the latter had shifted slightly to shorter wavelength. The final spectrum appeared to be a good match to the spectrum of 9-anthroic acid. 9-Anthroic acid was confirmed as a photodecomposition product by running the photolysis in dioxane and then diluting the final dioxane solution 1:10 with water. The fluorescence of the water diluted dioxane solution showed the highly structured and quite characteristic spectrum of the 9-anthroate anion (1). Thus it appears that 9-COO-β-Naph must decompose under U.V. excitation to give 9-anthroic acid and probably β-naphthol. It should be noted that 362 nm radiation, where only the AN - $\overset{\overset{O}{\|}}{C}$ - portion is initially excited, also causes photodecomposition. The initially formed fragments of the photoreaction must react with traces of water in the cyclohexane to give the final products. Some decomposition (ca. 40%) of 9-COO-β-Naph occurs even on standing on the lab bench overnight. Conceivably, some of the reaction may therefore involve ground state pathways but the reaction is significantly faster when U.V. excitation is used. The other ester in this category, 9-COO-p-MeOPh, was even more photoreactive. The ϕ_f value listed in the table for this ester can only be considered as an estimation of the true ϕ_f due to the great photoreactivity.

We do not know what ester electronic state(s) are responsible for the photoreactions. Certainly the lower ϕ_f's for these two esters could be a reflection of competitive photoreactions from their lowest excited singlets. It is also conceivable that the lower ϕ_f's are due to intersystem crossing to triplet levels on the -OAR portion as discussed for 9-COO-p-NO_2Ph. For this reason we measured the phosphorescence spectra of β-naphthyl acetate and p-methoxyphenyl acetate as model compounds for the -OAR portions. The spectrum for the former ester has a 0-0 band ca. 21,200 cm^{-1} which is slightly below the room temperature fluorescence maxima of 9-COO-β-Naph (21,700 cm^{-1}). Thus a favorable arrangement does appear to exist for intersystem crossing in 9-COO-β-Naph. The phosphorescence spectrum for p-methoxyphenyl acetate has a *maximum* ca. 22,400 cm^{-1} which is slightly above the fluorescence *maximum* for 9-COO-p-MeOPh (21,700 cm^{-1}). However both spectra are very broad and it is quite possible that the zero point energy difference for the two states is even smaller. In addition, the phosphorescence was measured at 77°K and the energy of the p-methoxyphenyl acetate triplet at room temperature would probably be lower in energy than at 77°K. Thus it does appear that a triplet level on -OAR would also be available for intersystem crossing from the AN - $\overset{\overset{O}{\|}}{C}$ - excited singlet. We are currently investigating the non-radiative decay modes and the photoreactive excited state(s) of these esters.

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