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Richard Leslie Dubs
Union College - Schenectady, NY

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SYNTHESES AND FLUORESCENCE PROPERTIES

OF STERICALLY-HINDERED ESTERS OF

9-ANTHROIC ACID

by

Richard Leslie Dubs

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Submitted in partial fulfillment
of the requirements for
Honors in the Department of Chemistry

UNION COLLEGE

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ABSTRACT

DUBS, RICHARD   Syntheses and Fluorescence Properties
of Sterically-hindered Esters of 9-Anthroic Acid.
Department of Chemistry, March 1983.

For over a decade, Professor Thomas C. Werner and his students have been studying the unusual fluorescence properties of methyl-9-anthroate. In the ground state of this ester, the carboxyl group lies perpendicular to the anthracene rings due to steric inhibition by the peri hydrogens. Werner has postulated that, upon excitation, the carboxyl group rotates to form a planar configuration with the anthracene rings, and that this rotation is the cause of the unusual spectral properties. In our work, we have attempted to prove or disprove this hypothesis.

We have chosen to synthesize analogues of methyl-9-anthroate in which carboxyl group rotation is sterically hindered. Ideally, replacing one or both of the peri hydrogens by a chlorine or methyl group would hinder carboxyl group rotation most effectively. However, after a long effort, we have been unable to synthesize one of these molecules. We have, however, synthesized two esters in which the ester groups are bulky, namely, cyclohexyl-9-anthroate and t-butyl-9-anthroate. The quantum yield of these esters in solvents of various polarity has been investigated. While our results do not shed any further light on the question of carboxyl group rotation, the data do support a hypothesis set forth by Werner and Hoffman attributing the decrease in quantum yield with increasing solvent polarity to increasing internal conversion due to excited state solute-solvent interactions.

ACKNOWLEDGEMENTS

" If God gives you a separation, take advantage of it."

John Sowa
Union College
Organic III Lab
1982

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CHAPTER 1: INTRODUCTION

For the past 13 years, Professor T. C. Werner and his students have been studying the fluorescence properties of 9- Anthroic Acid and its esters (See Figure 1). These molecules are very interesting to study because the fluorescence properties exhibited are unique. However, before an understanding of these unusual properties is possible, an understanding of normal fluorescence properties is essential. For this reason, the first part of this introduction will present a very qualicative picture of the fluorescence phenomenon.

During absorption, a molecule interacts with a photon of light, causing the molecule to change from a lower (ground) state to an excited state. Fluorescence is simply the opposite of absorption; during fluorescence, a molecule _emits_ a photon of light and simultaneously changes from an excited state to the ground state. The frequency of light involved in both absorption and fluorescence is proportional to the energy difference between states ($\Delta E = h\nu$). However, if the frequencies of absorption and fluorescence between "two" states of a given molecule are compared, the fluorescence frequency is usually found to be lower than that of absorption.[1] This difference in frequency occurs because absorption actually involves two distinct states from those of fluorescence.[1]

Consider a molecule in its ground state. The atoms in the molecule are in a nuclear configuration of minimum energy for the ground state electron distribution. When a photon of light is absorbed by the molecule, only the electron distrib-
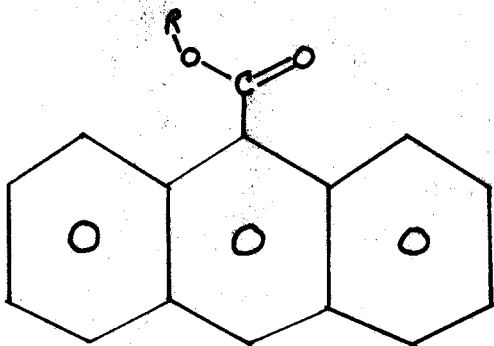
R=H, 9-Anthroic Acid
R=CH$_3$, Methyl-9-Anthroate

Figure 1- Structure of 9-Anthroic Acid
and its Methyl Ester

ution of the molecule changes at first, because electronic transitions occur much more rapidly (10^{-15} sec) than nuclear configurational changes (10^{-11}-10^{-13} sec). For a short time, then, the excited molecule has a new electronic configuration but the same nuclear configuration as the ground state. The molecule in this state, called the Franck-Condon excited state, is, thus, energetically unstable. Finally, however, the nuclei shift to minimize the energy of the excited molecule.[1]

During fluorescence, the reverse process occurs. A photon of light is emitted as the electronic distribution of the excited state changes to that of the ground state. However, at first, the nuclear configuration remains that of the excited state. This state, called the Franck-Condon ground state, is energetically unstable relative to the original ground state which existed before absorption. Shortly after the electronic transition, however, the nuclei do shift back to the equilibrium ground state configuration.[1]

This new description of absorption and fluorescence is summarized in Figure 2 (only for transitions between lowest electronic bands - i.e. the 0-0 transitions). Notice that the energy difference, ΔE, between S_0 and S_1' is larger than that between S_1 and S_0'. The smaller ΔE for fluorescence is consistant with the observation that fluorescence frequencies are usually lower than those of absorption for transitions between "two" states.
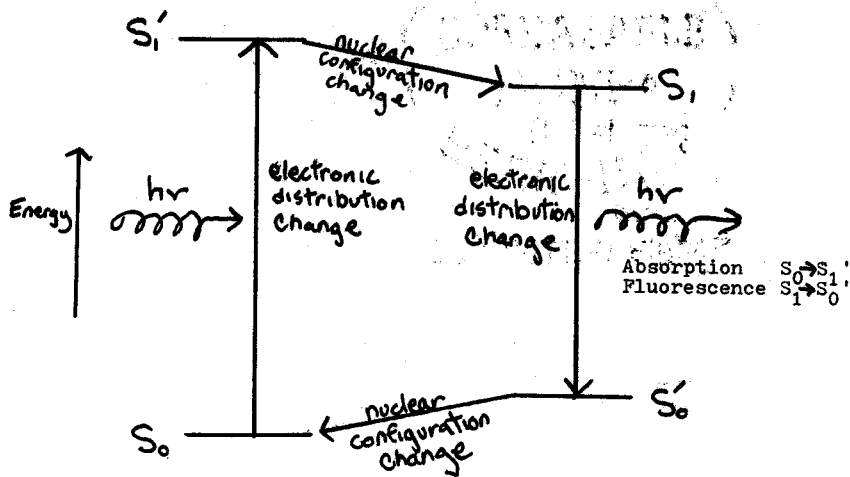
Figure 2- Energy Diagram of the Absorption
and Fluorescence Phenomena

If the absorption and fluorescence spectra of anthracene are examined, the difference in frequencies corresponding to the $S_0 \rightarrow S_1'$ and $S_1 \rightarrow S_0'$ transitions (for the 0-0 transitions) is found to be very small.[1] This small difference indicates that the geometries and solvation of the ground state and excited state are very similar. However, if the absorption and fluorescence spectra for methyl-9-anthroate are examined, a large difference in frequencies corresponding to the transitions is found.[2] This large frequency difference suggests that the geometries (and/or solvation) of the ground state and excited state are drastically different.

In addition to the frequency shifts in absorption and fluorescence spectra, structural differences in the spectra can contain information about molecular geometry. In general, the more planar a molecule is in a particular state, the more structured will be the spectrum which corresponds to a transition originating from that state. Thus, if a molecule in its ground state is planar, the absorption spectrum will be more structured than one for a non-planar molecule. Similarly, if a molecule in an excited state is planar, its fluorescence spectrum will be, in general, more structured than one for a non-planar molecule. While the reason for these observations will not be explained fully in this Introduction, note that planar molecules, in general, have a more restricted geometry range than non-planar molecules, and, therefore, less vibrational states from which a transition can

originate. The fewer number of transitions leads to a more structured, less overlapped spectrum.[4]

If the absorption and fluorescence spectra of anthracene are examined again, both spectra are found to be very structured[4]. This observation is consistant with the fact that anthracene is a planar molecule which undergoes little geometry change upon excitation. Another clue that the geometry change is minimal is that the absorption and fluorescence spectra are mirror images of each other.[4] However, the absorption and fluorescence spectra of methyl-9-anthroate, on the other hand, are very different; although the absorption spectrum is very structured and anthracene-like, the fluorescence spectrum is diffuse.[2] Based on the previous discussion of what causes a more structured spectrum, the conclusion drawn might be that methyl-9-anthroate is more planar in the ground state than in the excited state; in fact, the opposite has been found to be true.[3] The reason for this unexpected behavior is due to the effect of the polar substituents on absorption and fluorescence spectra. In general, when a polar substituent interacts with a molecule through resonance, the substituent causes spectra due to transitions originating from the resonating state to be very diffuse. This diffuseness is due to both solvent interaction with the polar substituents and charge transfer between the polar substituent and the rest of the molecule. In methyl-9-anthroate, the carboxyl group is actually perpendicular to the anthracene rings in the ground

state; very little conjugation occurs between the group and
the rings, and thus, the molecule retains its structured,
anthracene-like absorption spectrum. In the excited state,
the carboxyl group becomes planar with the anthracene rings;
strong orbital interaction is now possible, and the fluores-
cence spectrum is diffuse.[3]

Why is the carboxyl group perpendicular to the anthra-
cene rings in the ground state and planar with the rings in
the excited state? In the ground state, the hydrogens in the
1 and 8, or peri, positions of the ester sterically interfere
with the carboxyl group and prevent it from becoming coplanar
with the anthracene ring.[3] In the excited state, however, the
carbon-carbon bond between the carboxyl group and the ring
acquires more double bond character than in the ground state,
enough extra bond character to overcome some of the peri hydro-
gen interference.[3] In the excited state, then, the carboxyl
group adopts a more coplanar configuration with the anthracene
rings.

If rotation of the carboxyl group is, indeed, the cause
of the observed absorption and fluorescence behavior, a pre-
diction of what will happen to this behavior if carboxyl rota-
tion is inhibited should be possible. The goal of our research
was: 1) to synthesize 9-anthroic acid derivatives which have
sterically-hindered carboxyl groups and, therefore, prevented
rotation, and 2) to study the absorption and fluorescence
properties of these molecules. If the carboxyl group can be

"locked" into a position perpendicular to the anthracene rings, even in the excited state, the fluorescence spectra should be less diffuse than when the carboxyl group is planar with the rings because conjugation between the polar group and the rings will be minimized. In fact, a mirror image relationship between the absorption and fluorescence spectra might then exist.

Carboxyl group rotation might be inhibited in one of two ways: 1) by synthesizing 9-anthroic acid derivatives in which the peri hydrogens are replaced by bigger groups such as chlorine or methyl, or 2) by synthesizing molecules with bulky ester groups. After much effort, we have been unsuccessful at syntheses via this first route. This result is not surprising; space-filling models indicate peri-substituted 9-anthroic acids are extremely crowded. Nevertheless, these molecules have been reported in the literature, and we are continuing our effort toward synthesizing one of them. We have, however, synthesized compounds with bulky ester groups, namely, cyclohexyl-9-anthroate and t-butyl-9-anthroate. The effect of solvent polarity on the quantum yields of these compounds has been examined.

CHAPTER 2: SYNTHETIC SCHEME

We have synthesized 1-chloro-9-anthroic acid by the
method of Tret'yakova, et. al. (Figure 3).[4] We do
not understand why bromination occurs in the 9-position as
opposed to the 10-position; steric hinderance certainly favors
the latter position. The authors offer only a melting point
as structural proof for the carboxylic acid, and previous work
has not clearly determined the position of the group.[5] (The
structural proof is a difficult one - one which we have chosen
to pursue no further.)

Because we are not satisfied that the carboxylic acid
obtained is the one in which we are interested, we are pre-
sently synthesizing a carboxylic acid in which the 9 and 10
positions are indistiguishable (Figure 4).[5] Using 1,5-dichloro-
anthracene assures us that the carboxyl group will be peri to
a chlorine atom. The extra chlorine atom in the 5-position
will have little effect on the fluorescence properties of the
esters.

The esters of the carboxylic acids are prepared by the
method of Parish and Stock.[6] This method results in excellent
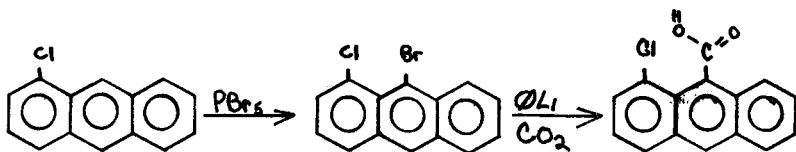yields for sterically-hindered anthroates.

Figure 3- Synthetic Scheme for the
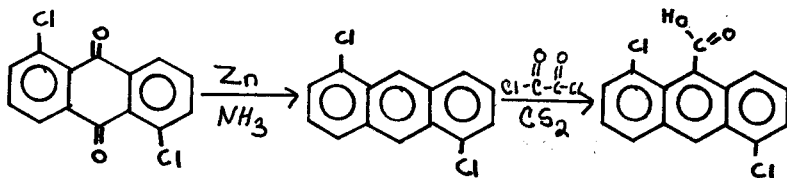Preparation of 1-Chloro-
9-Anthroic Acid

Figure 4- Synthetic Scheme for the
Preparation of 1,5-Dichloro-
9-Anthroic Acid

CHAPTER 3: EXPERIMENTAL WORK

Spectral grade ethanol was obtained from U. S. Industrial Chemicals. Cyclohexane (spectrophotometric) and 2,2,2-trifluoroethanol were Aldrich solvents. Fischer Certified Grade ethylene glycol and Burdick and Jackson Laboratories UV Grade acetonitrile were used. Spectroquality N,N-dimethylformamide was obtained from Matheson Coleman and Bell.

Absorbance spectra were recorded on a Cary Model 118 spectrophotometer.

Fluorescence spectra were recorded on a Perkin-Elmer Hitachi MPF-2A spectrofluorometer which was uncorrected for spectral response. The emission and excitation bandpasses were 3 and 7 nm respectively, and the excitation wavelength was 361-364 nm.

The fluorescence quantum yield (ϕ_f) in a given solvent for cyclohexyl-9-anthroate and t-butyl-9-anthroate was determined using the following formula:

$$\phi_u = \phi_r \ \frac{A_r}{A_u} \ \frac{F_u}{F_r} \ \frac{D_u}{D_r}$$

where r and u stand for reference and unknown, respectively, A is the solution absorbance at the exciting wavelength ($\sim$.02 in 1 cm cells), F is the area under the emission spectrum obtained by the cut and weigh method, and D is the deoxygenation factor. Deoxygenation was performed by bubbling solutions with pure nitrogen gas for 5 minutes. The reference quantum yield, ϕ_r, was the known quantum yield of methyl-9-anthroate in the given solvent. Fluorescence spectra were

uncorrected for spectral response. All reported ϕ_f values
are the average of three independent determinations with the
exception being that for cyclohexyl-9-anthroate in ethylene
glycol which is the average of two determinations.

The esters were synthesized by the method of Parish and
Stock.[6] Structures were confirmed by NMR and comparison of
melting points with literature values.

Cyclohexyl-9-anthroate, mp 124°C

Syntheses:

(Reference 7)
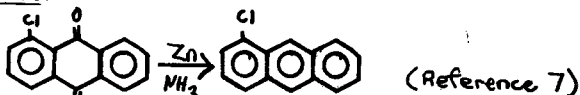
All attempts at this reduction resulted in a mixture of 1-chloro-
anthracene and anthracene (as determined by UV) which could not
be separated by TLC. For this reason, 1-chloroanthracene was
purchased from Aldrich Chemicals (UV max.(cyclohexane) 382,
362,344 nm).

(Reference 4)
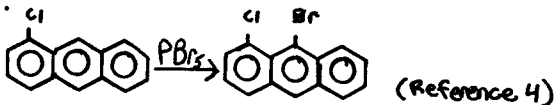
To .3ml Br_2 in 20ml cold ligroin is added .55ml PBr_3 dropwise.
A yellow precipitate immediately forms. Ligroin is decanted
off, the yellow PBr_5 is washed once with ligroin, and 20ml
benzene and 1 gram 1-chloroanthracene are added. The solution
is stirred for 20 minutes at room temperature and then filtered
and washed with MeOH until the washings are clear. Product is
olive white in color. Yield 1.03 grams. mp 141-2°C (lit. 145°C),
Uv max. (95% EtOH) 394,374,355 nm.

. (Reference 4)
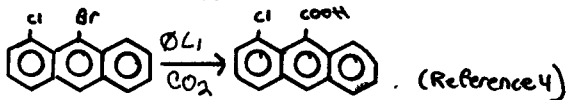
NOTE- This reaction is unsuccessful without a N_2 atmosphere.
To 10ml anhydrous ether is added .11 grams Li metal. Slight
bubbling on Li surface indicates ether is not truly anhydrous.
Bromobenzene (.5ml) is then added. Li metal is broken up with
a stirring rod - reaction begins and flask gets warm - solution
turns cloudy. Li is broken up again with a stirring rod to

expose fresh surface, and more bromobenzene (.2ml) is added.
The solution is stirred 1 hour, after which most Li is chewed
up. To the reaction mixture is then added .5 grams 9-bromo-
1-chloroanthracene. Solution bubbles violently upon addition.
Solution turns brown - compound goes right into solution.
Stirred 20 minutes - cooled momentarily in $N_{2(1)}$, then $CO_{2(g)}$
bubbled through solution. Solution extracted with 1M NaOH -
product precipitated with conc. HCL. Filtered, dried in a
dessicator overnight. Yield 0.22 grams, mp 230°C (lit 255°C),
UV max. (neutral 95% EtOH) 386,366,348 nm, (basic 95% EtOH)
390,370,351 nm.

CHAPTER 4:   RESULTS AND DISCUSSION

The Absorption and Fluorescence λmax for the three esters in six solvents are given in Table 1.

TABLE 1: λ max of Absorption and Fluorescence
for the Three Esters in Pure Solvents

Solvent	$E_T(30)$	Absorption λ max/nm all esters	Fluorescence λmax/nm methyl	λmax/nm hexyl	λmax/nm t-butyl
Cyclohexane	31.2	361	440	438	438
DMF	43.8	364	456	455	450
Acetonitrile	46	362	455	452	450
Ethanol	51.9	361	462	462	456
Ethylene Glycol	56.3	364	470	468	464
trifluoroethanol	61.1	360	482	480	468

As solvent polarity increases, as indicated by Dimroth $E_T(30)$ values, the λmax for fluorescence generally increases for all three esters. This result indicates that the more polar solvents tend to stabilize the relatively polar excited state, reducing the energy of the fluorescence transition (Remember - Energy $1/\lambda$max). A slight increase in fluorescence energy is observed for a given solvent in the order methyl<cyclohexyl≤ t-butyl ester. These bulky ester groups appear to interfere slightly with the stabilization of the excited state by the solvent. A clear trend in solvent stabilization of the ground state is not observable in the λmax of absorption. In a given solvent, the λmax for absorption is the same for all three esters.

The ratios of quantum yields of the cyclohexyl and t-butyl esters to that of the methyl ester are given in Table 2. The relative quantum yields for the cyclohexyl and t-butyl esters are sig-

nificantly greater than that of the methyl ester in all solvents except cyclohexane, in which the quantum yields are significantly less. These ratios are plotted in Figure 5 versus $E_T(30)$ values.

TABLE 2: Quantum Yields of the Three Esters in Pure Solvents

Solvent	Øf methyl	Øf hexyl	Øf t-butyl	Øf hexyl / Øf methyl	Øf t-butyl / Øf methyl
Cyclohexane	.76	.67±.01	.58±.01	.883±.015	.765±.014
DMF	.70	.84±.03	.88±.03	1.20±.04	1.26±.05
Acetonitrile	.39	.53±.03	.55±.02	1.37±.07	1.42±.06
Ethanol	.17	.21±.01	.21±.01	1.25±.04	1.23±.04
Ethylene Glycol				1.28±.05	1.34±.06
trifluoroethanol	.02	.02±.00	.02±.00	1.26±.01	1.10±.01

The absolute quantum yields of the cyclohexyl and t-butyl esters were obtained by multiplying the quantum yield ratios in Table 2 by the literature values of the quantum yield for the methyl ester.[9] These values are also listed in Table 2. (No value for Øf in ethylene glycol was available.) The absolute quantum yields for all three esters versus $E_T(30)$ values are shown graphically in Figure 6. Except for the values in cyclohexane, the quantum yields of all three esters decrease with increasing solvent polarity. Werner and Hoffman have explained this decrease for the methyl ester in terms of increasing internal conversion due to greater solute-solvent interactions with increasing solvent polarity.[10] In the protic solvents, this internal conversion might be due partly to hydrogen bonding effects.[10] The quantum yield data for the cyclohexyl and t-butyl esters support this explanation. Starting
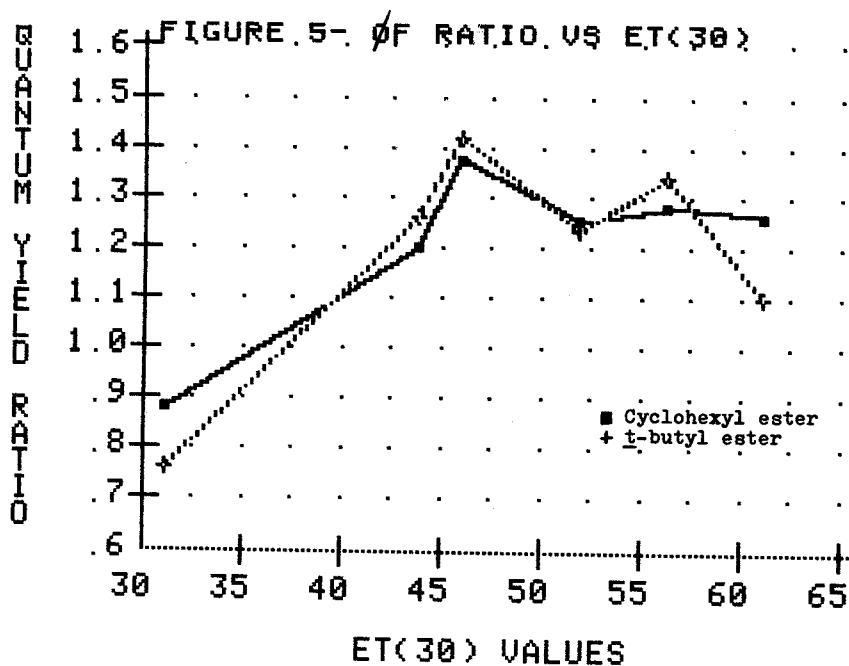
Figure 5- Graph of Quantum Yield
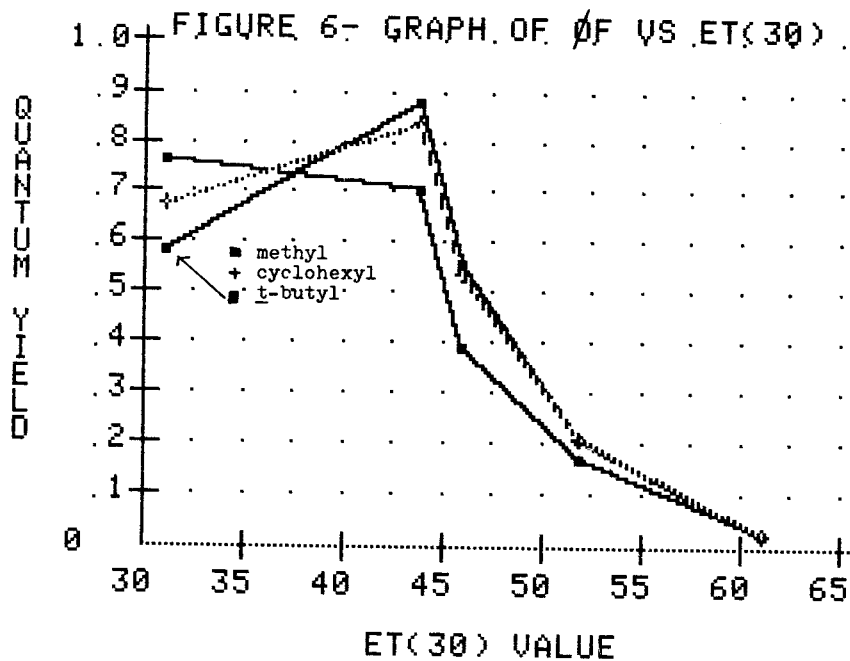Ratios versus $E_T(30)$ Values

Figure 6- Graph of Quantum Yield
versus $E_T(30)$ Values

with the quantum yields in DMF, the cyclohexyl and $\underline{t}$-butyl esters have significantly higher yields than the methyl ester. This result can be rationalized by steric hinderance of the solute-solvent interactions inducing internal conversion by the bulky cyclohexyl and $\underline{t}$-butyl ester groups. As solvent polarity increases, however, the steric hindrance becomes less and less important, and the quantum yields of the three esters approach the same value.[*]

The reason for the lower quantum yields in cyclohexane is not clear. Werner and Lyon have found that in cyclohexane, the activation energy for nonradiative decay is unusually low (2.67 kcal/mole) compared to values in other solvents (For EtOH, DMF, and CH_3CN, $E_a > 4.0$).[9] Perhaps in cyclohexane, this low activation energy indicates that the S_1 state and an accepting upper triplet are close enough in energy for efficient intersystem crossing, causing the lower quantum yield. If the activation energies for all three esters are very low, the relative rates of intersystem crossing will be very sensitive to subtle differences in solute-solvent interactions. This speculation might explain why the quantum yields for the $\underline{t}$-butyl and cyclohexyl esters are significantly less than that for the methyl ester.

[*] This explanation assumes that the radiative rate constants for all three esters in a given solvent are similar.

CHAPTER 5: FUTURE WORK

While the results presented in Tables 1 and 2 and in Figures 5 and 6 support results obtained in earlier studies of the esters of 9-anthroic acid, the results do not shed any further light on the hypothesis concerning carboxyl group rotation in the excited state of these esters. Werner and Hercules found that both the cyclohexyl and t-butyl esters have a much more structured fluorescence spectrum than the methyl ester at 77K in EPA, indicating hindered rotation.[3] However, we have found no significant difference due to the bulky esters in spectra taken at room temperature. For this reason, one of our first goals for future work consists of studying the fluorescence spectra at room temperature in very viscous, nonpolar solvents, such as n-hexadecane to see if carboxyl group rotation can be slowed to an observable rate. A second goal of our future work will be to gain a better understanding of the quantum yield behavior of the three esters in cyclohexane. Quantum yield determinations will be done in other solvents with $E_T(30)$ values between 30 and 45, such as hexane (30.9), ether (34.6), ethyl acetate (38.1), and acetone (42.2). Of course, our most important goal for future work is the synthesis of 1,5-dichloro-9-anthroic acid and its esters. This molecule should give us a definitive answer concerning carboxyl group rotation.

REFERENCES

[1] Thomas C. Werner, "Use of Fluorescence to Study Structural Changes and Solvation Phenomena in Electronically Excited Molecules," Modern Fluorescence Spectroscopy, Vol. 2, ed. E. L. Wehry (New York: Plenum Press, 1976), pp.278-80.

[2] Thomas C. Werner, et.al., The Journal of Physical Chemistry, 80, 535 (1976).

[3] Thomas C. Werner and David M. Hercules, The Journal of Physical Chemistry, 73, 2005-11 (1969).

[4] G. S. Tret'yakova, et.al., Ukrainskii Khimicheskii Zhurnal, 33, No. 3, 301-2 (1967).

[5] D. Betuscu, Berichte der Deutschen Chemischen Gesellschaft, 45, 1213-7 (1912).

[6] Roger G. Parish and Leon M. Stock, The Journal of Organic Chemistry, 30, 927 (1965).

[7] Otto Fischer and Hugo Ziegler, Journal fur Praktishe Chemie, 86, 293 (1912).

[8] K. Dimroth, et.al., Justus Liebigs Ann. Chem., 661, 1 (1963).

[9] Thomas C. Werner and David B. Lyon, Journal of Photo-Chemistry, 18, 355-64 (1982).

[10] Thomas C. Werner and Ronald M. Hoffman, The Journal of Physical Chemistry, 77, 1611-5 (1973).

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