

Fluorescence Quantum Yield Determinations. 9,10-Diphenylanthracene as a Reference Standard in Different Solvents

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A controversy has arisen regarding the photophysical properties of 9,10-diphenylanthracene (DPA), a popular emission quantum yield standard. In order to elucidate the causes of the disagreement in the literature, fluorescence quantum yields, lifetimes, and oscillator strengths were measured for DPA in ethanol, 3-methylpentane, cyclohexane, and benzene solutions. The effects of high concentrations and self-absorption were dramatized by determining the measured lifetime for a series of concentrations of DPA in cyclohexane, demonstrating that the optical density in the 0-0 band must be kept below 0.05/cm in DPA to avoid reabsorption. It is proposed that these effects constitute a partial explanation for the discrepancies in the literature. In addition, the universal application in quantum yield measurements of the correction factor n_s^2/n_r^2 for differences between the index of refraction of the sample n_s and the reference n_r is questioned. By means of a variable slit arrangement, we have shown that the proper correction is a strong function of the geometry of the sample compartment. This effect suggests that wide utilization of the standard correction term may also provide a source of error. Taking these deficiencies into consideration the following fluorescence quantum yields and lifetimes of DPA at 293 K were determined: 0.95, 8.19 ns in ethanol; 0.93, 7.88 ns in 3-methylpentane; 0.86, 7.58 ns in cyclohexane; 0.82, 7.34 ns in benzene.

Introduction

Most emission quantum yield determinations found in the literature are relative measurements vs. a standard whose quantum efficiency has been accurately determined by absolute methods or is otherwise generally agreed upon. As a consequence of the difficult and time consuming nature of absolute methods, only a very small number of compounds have been investigated in this manner.^{1,2} The most popular of these substances for use as a standard is quinine bisulfate in aqueous 1.0 or 0.1 N H₂SO₄.^{3,4} Additionally, anthracene in ethanol is accepted as a standard because of the constancy of the results obtained by different authors.^{2,3,5} 9,10-Diphenylanthracene (DPA) has also been employed by several researchers,⁶⁻¹⁰ although it has several disadvantages with regard to its use as a fluorescence standard including a long lifetime (susceptibility to oxygen quenching), a large 0-0 band overlap (possibility of self-absorption), and a structured absorption spectrum. In spite of these drawbacks, its continued use is maintained largely due to its high quantum yield, the presence in the literature of values in a large number of solvents, and because it is one of the few emission standards available for work at 77 K. Unfortunately, a controversy has arisen between certain authors^{11,12} about the values themselves. In the time since the airing of this dispute in the literature, a pair of articles have appeared in an attempt to clear it up. Gusten and co-workers¹³ have compiled a large collection of literature values as well as presenting their own determinations. Birch and Imhof¹⁴ reported lifetimes of DPA in cyclohexane and benzene and observed that a solvent dependence is manifest in DPA which the disputants had not hitherto remarked upon. However, this difference was not sufficient to account for the discrepancies in the literature. These authors suggested high concentrations and resulting reabsorption as a possible explanation for the disparity.

The dramatic increase in apparent intensity which results from self-absorption with a solute such as DPA with both high fluorescence yield and strong overlap between ab-

sorption and emission has already been demonstrated by Melhuish.¹⁵ Still, some researchers prefer to work under conditions which allow all exciting light to be absorbed, obviating the necessity of correcting for differences in absorbance between sample and reference. Certain authors are under the impression that by observing front-face, they have eliminated any problem with reabsorption.¹² This is most definitely not the case, as Melhuish pointed out, stating that ca. 85% of the emission passes back into the solution where a part may be absorbed.¹⁵

The only additional major source of error involves the differences between the refractive index of the sample and reference solutions. Losses or amplifications, depending on the viewing geometry, in the observed intensity due to internal reflections are exacerbated as the index of refraction n increases. When comparing solutions with different refractive indices, very few authors account for the resultant differences in reflection errors. More important, however, is the correction for the spreading of the emission upon leaving the sample cell. The well-known n^2 factor has been recognized for a quarter century^{16,17} and is commonly used by most researchers, but many fail to report whether or not it has been applied. Moreover, some workers may have ignored the admonition by Hermans and Levinson¹⁷ to employ small slits when applying the n^2 correction term. Large slits and large viewing angles can lead to errors in the application of this factor, which might provide an explanation for some anomalies observed by Demas and Crosby.³ When these authors corrected quantum yield values found in the literature prior to the initial acceptance of the refractive index term, many of the results proved to be greater than unity. The possibility suggests itself that in these cases, the viewing geometry may not have been compatible with the n^2 correction factor.

We began this study in an attempt to determine the causes of the dispute as well as possibly settling it. To this end, we have measured the fluorescence quantum yields and lifetimes of DPA in the three main solvents in which literature values are reported (ethanol, cyclohexane, and

benzene) and in 3-methylpentane, because of the importance of this solvent in temperature dependent studies. In addition, the oscillator strengths were determined from the absorption spectra in each of these solvents to verify the correlation between the rate constants found from the ratio of quantum yields and lifetimes and those calculated from the oscillator strengths.

Experimental Section

Materials. Quinine bisulfate (Mallinckrodt Co.), anthracene (Merck, Schuchardt), and 9,10-diphenylanthracene (Aldrich) were purified by multiple recrystallizations (from water in the case of quinine bisulfate and from ethanol for anthracene and 9,10-diphenylanthracene). The melting points of these substances after purification were as follows: quinine bisulfate, 235 °C (lit. 235.2 °C¹⁸); anthracene, 216.2–216.4 °C (lit. 216.2 °C¹⁹); 9,10-diphenylanthracene, 250.6 °C (lit. 245–247 °C²⁰). Both benzene (Uvasol, fluorescence grade, Merck) and 3-methylpentane (purum, Fluka) contained traces of absorbing impurities. These were removed by frontal analysis chromatography employing a basic aluminum oxide column (activity level I, Merck).

Cyclohexane (Uvasol, fluorescence grade, Merck), absolute ethanol (analysis grade Merck), and aqueous 0.1 N H₂SO₄ (fluorescence grade, Merck) were used as received.

Apparatus and Techniques. A fully computerized spectrofluorimeter with a photon counting detection system which has been described elsewhere²¹ was utilized for most emission spectra; in addition, a series of measurements of DPA in ethanol has also been performed at Northeastern University with a system which has been previously described.²² A Cary 17 recording spectrometer was employed for all absorption measurements. The observed emission spectra were corrected for spectral response of the emission monochromator and photomultiplier. The sensitivity curve for this correction was derived by use of a 200-W standard tungsten-iodide lamp (ES-732, Eppley Laboratory, Newport, R.I.) which had been calibrated against U.S. National Bureau of Standards QM-111, QM-112, and EPI-1469 reference standards. The resulting correction function was checked by comparison of the spectra of several compounds with their published spectra.²³

The room temperature quantum yields of DPA were determined relative to fluorescent standards, with the possibility of correcting for differences between the refractive index of the reference n_r , and the sample solutions n_s using the expression

$$\phi_f(s) = \phi_f(r) \frac{\int I_s(\tilde{\nu}) d\tilde{\nu} D_r n_s^2}{\int I_r(\tilde{\nu}) d\tilde{\nu} D_s n_r^2} \quad (1)$$

Here the indices s and r , respectively, denote sample and reference. The integrals over I represent areas of the corrected emission spectra, and D is the optical density at the wavelength of excitation. Anthracene in ethanol ($\phi_f = 0.28$)^{3,5} and quinine bisulfate in aqueous 0.1 N H₂SO₄ ($\phi_f = 0.55$)^{3,4} were standards for DPA in ethanol. DPA in both benzene and 3-methylpentane was measured against DPA in ethanol using our value of 0.95 as well as against quinine bisulfate, whereas DPA in cyclohexane had only DPA in ethanol as a standard. Over 20 measurements were involved in determining each quantum yield. The excitation wavelengths (nm) employed in each case were 331.7, 343.8, 347.5, 358.8, 370.0 in ethanol; 357, 360, 370, 380 in 3-methylpentane; 342.5, 362.5, 364, 382 in cyclohexane; and 346.5, 363, 367.8, 368.3, 370, 372.5, 384 in benzene. The spectral

bandpass of the excitation monochromator was ~ 1 nm in each case. In order to minimize reabsorption effects, the solutions for both quantum yield and lifetime measurements were prepared such that the optical density was generally about 0.02 at the 0–0 band maximum, but was never higher than 0.05 for our 1-cm path length. Because it was deemed necessary to determine the effect on the quantum yield measurements of the slit geometry at the emission face of the sample cell, the sample holder shown in Figure 1 was employed for a separate series of experiments. To arrive at the results given in Table I, a very similar arrangement with fixed apertures of 5 mm width and 10 mm height on both excitation and emission faces of the cell holder was used in place of the central portion of the apparatus in Figure 1. In the experiments using the pictured sample holder, DPA in benzene, cyclohexane, and ethanol were compared with quinine bisulfate for a range of slit widths from 5 to 0.1 mm. This series of measurements was performed with the same wavelengths for all three solvents. The fluorescence lifetime measurements were carried out on an Ortec 9200 single-photon counting system equipped with an Ortec 462 time calibrator. Excitation was provided by a free-running air lamp and isolated by a bandpass filter (300–400 nm). The emission, after passing through a Spex 1670 Minimate focal length 220 mm, $f/4$ analyzing monochromator, was monitored by either an RCA 8850 photomultiplier tube or an RCA C31034 cooled photomultiplier tube. Samples for both lifetime and quantum yield measurements were normally deoxygenated by bubbling nitrogen through the solution for 20 min before being stoppered; this procedure was held to be sufficient after comparison with several degassed solutions. Lamp decay curves were determined by using a mixture of fluorescence-free glycerin (Merck) and aluminum oxide in a 2-cm quartz cell as a scatterer. This method of acquiring the lamp function $I(t)$ was found to fit the criteria for apparent optical density and optical path which must be met in order that the convoluted function²⁴

$$F'(t) = \int_0^t I(t-t')e^{-t'/\tau} dt' \quad (2)$$

yields a good fit when compared with the measured function $F(t)$. The goodness of fit was determined by minimizing the weighted sum of squares of residuals for the measured and calculated decay functions.²⁵

Oscillator strengths were obtained by integrating absorption spectra measured with a Cary 17 spectrometer, using a Hewlett-Packard 9820A calculator equipped with a 9864A digitizer unit. The short wavelength limit of integration was chosen as 310 nm for spectra in all four solvents.

Results

Quantum Yields. For reasons discussed below, we have presented the quantum yield results both with and without the correction for refractive index (n_s^2/n_r^2 ; cf. eq 1). The quantum yield values for DPA in the four different solvents are listed in Table I. When the correction is applied (parameters labeled with superscript n), the quantum yield of DPA appears to remain constant in different solvents. Although Gusten reports a quantum yield value of unity in cyclohexane, his room temperature values in both benzene ($\phi_f = 0.96$) and ethanol ($\phi_f = 0.94$) are in excellent agreement with ours.^{13,26} The quantum yield of 0.93 in 95% ethanol from the work of Lentz et al.²⁹ also agree quite well with our value. In addition, our ethanol result is consistent

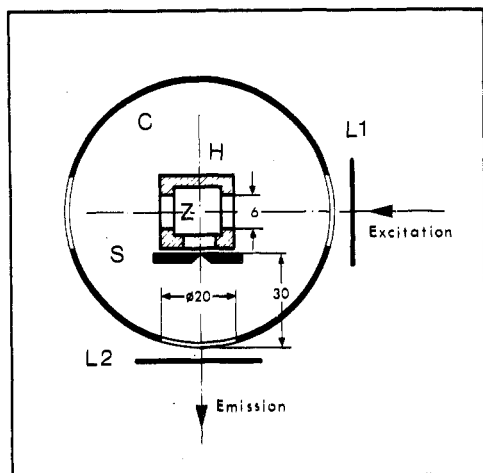


Figure 1. Cylindrical "can" C containing sample holder H with variable slit S on the emission face. Variable slit on excitation face (not shown here) was kept constant at 4 mm in these experiments. Sample cell (1 cm) is positioned at Z. Lenses L1 (focal length 76.1 mm) and L2 (focal length 63.4 mm) are each part of a two-lens collimating system between the excitation or emission monochromator slits and the sample holder.

TABLE I: Fluorescence Quantum Yields ϕ_f , Fluorescence Lifetimes τ_f , Oscillator Strengths f , and Radiative Rate Constants k_f^0 for 9,10-Diphenylanthracene in Solution at Room Temperature^a

	Ethanol	3-Methyl-pentane	Cyclo-hexane	Benzene
ϕ_f	0.95	0.93	0.86	0.82
τ_f , ns	8.19(7.95)	7.88(7.90)	7.58	7.34
f	0.175	0.178	0.176	0.175
k_f^0 , 10^8 s ⁻¹ b	1.16	1.18	1.13	1.12
$\phi_f^{(n)}$	0.95	0.95	0.95	0.96
$k_f^{0(n)}$, 10^8 s ⁻¹ b	1.16	1.21	1.25	1.30

^a Values in parentheses were determined at 77 K. Super-script n denotes application of the standard refractive index correction (eq 1). ^b $k_f^0 = \phi_f/\tau_f$.

with the triplet efficiency of 0.03 in ethanol published by Parker and Joyce³⁰ which they measured by delayed fluorescence. Aside from these quantum yields, the remaining values found in the literature tend to lie between two extremes, unity and ~ 0.8 . Several authors have reported fluorescence quantum yields of unity or greater for DPA in various solvents. Some of these higher quantum yields can be attributed to reabsorption effects. Bowen and Sahu used "concentrations necessary to give practically total light absorption";³¹ Berلمان²³ reported using 0.32 g/l. (giving an optical density at the 0-0 band of ~ 12). Due to the lack of published information, the concentrations used by Eastman³² are unknown. Other researchers^{15,33,34} have observed lower quantum yields than ours, generally centering around 0.84. Given universal application of the refractive index correction, we have no explanation for this discrepancy.

If, however, the refractive index correction is neglected,

an interesting correlation appears (cf. Table I). The quantum yields determined in this manner parallel the behavior of the fluorescence lifetimes, yielding values for the radiative rate constant of fluorescence k_f^0 which are practically independent of solvent. Comparison of these quantum yields with those of Melhuish,¹⁵ Birks and Dyson,³³ and Medinger and Wilkinson³⁴ reveals a reasonable agreement among the values in benzene solution. The failure to correspond with the values given in ethanol is simply presented noting that some older values of the lifetime of DPA in ethanol are also too low.³⁵

Omission of the refractive index in the determination of quantum yields is justified only for an integrating sphere technique, although for some viewing geometries the correction factor may lie between 1 and n^2 .¹⁷ To ascertain the role played by differences between the index of refraction of the sample and of the reference in our measurements, the quantum yield determinations were repeated with the sample holder shown in Figure 1. In these experiments, the emission slit was varied from 5 to 0.1 mm as quinine bisulfate in aqueous 0.1 N H₂SO₄ and DPA in benzene were compared. As a result, a continuous dependence of the quantum yield of DPA upon slit width was found when the n^2 factor was universally applied, ranging from the 0.95 value for wide slits to 0.84 for 0.5-mm slits (cf. Table II). No further decrease was found for narrower slits. A similar effect was observed when DPA in cyclohexane was measured against quinine bisulfate, whereas no discernable dependence was found for DPA in ethanol.

Lifetimes. Our data presented in Table I and literature values of the fluorescence lifetime of DPA demonstrate a distinct solvent dependence which has been little noted to date. The data of Gusten and co-workers¹³ essentially agrees with our work, with the exception of benzene solution. In addition, we match the value in cyclohexane of Birch and Imhof¹⁴ but again we differ with their value for benzene. Our measured lifetime in benzene solution does agree quite well with the values of Ware and Baldwin³⁶ and of Birks and Dyson.³³ In contrast to this grouping of relatively consistent data, a few strongly divergent values are to be found. The long lifetime of Berلمان²³ in cyclohexane and that of Amata et al.,³⁷ whom he quotes as support, can be explained on the basis of the high concentrations used and the resulting reabsorption effects.

Possible effects of water in the ethanol were investigated by adding distilled water dropwise to absolute ethanol solutions of DPA and measuring the lifetime after rebubbling with nitrogen. No significant difference was found for up to 10% water. Reabsorption effects resulting from high concentrations combined with high quantum yield are well known.¹⁵ To confirm and graphically demonstrate this effect, fluorescence lifetimes were determined for a series of concentrations in cyclohexane. These results are presented in Figure 2. This curve was not extended to the upper limit of total reabsorption found by Melhuish because of the difficulty encountered in dissolving the necessary quantities of DPA.

Oscillator Strengths. The oscillator strengths were derived by means of the relationship³⁸

$$f = 4.32 \times 10^{-9} \int \epsilon d\nu \quad (3)$$

As these results are presented in Table I, they appear independent of solvent indicating a solvent independent radiative rate constant.

TABLE II: Variation in the Measured Quantum Yield of Fluorescence ϕ_f for 9,10-Diphenylanthracene in Benzene and Ethanol as Determined against Quinine Bisulfate in Aqueous 0.1 N H₂SO₄ as a Function of Emission Slit Width (cf. Figure 1) with Application of Refractive Index Correction (Eq 1)

Slit width, mm	ϕ_f (benzene)	ϕ_f (ethanol)
5	0.96	0.95
4	0.94	0.95
3	0.92	
2	0.90	
1	0.86	0.95
0.5	0.84	0.95
0.1	0.84	0.95

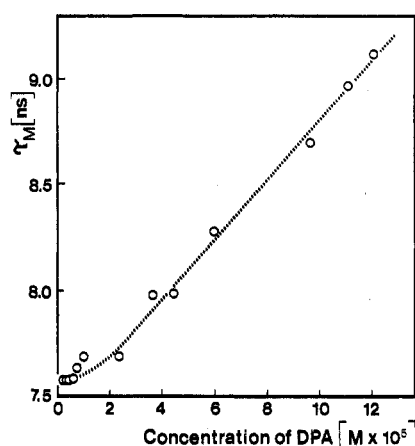


Figure 2. Measured lifetime τ_M , as determined by convolution (eq 2) with the lamp function, vs. concentration of DPA in cyclohexane.

Discussion

High concentrations and consequent reabsorption effects appear to account for at least some of the discrepancies in the literature, generally resulting in quantum yields which are too high and lifetimes which are too long. Of course, if the standard employed strongly reabsorbs, it is quite possible that quantum yields measured against it will be too low. Reabsorption and reemission can take place at concentrations much lower than 10^{-3} M, depending on the amount of overlap between absorption and emission. As has been noted above, Melhuish has previously treated this subject from the standpoint of the effect on quantum yields and has presented an integral expression for the intensity of fluorescence from a concentrated solution.¹⁵ Although portions of the expression are specific for his front-face viewing geometry, we have not attempted to rewrite these parts to fit our right-angle setup, since the description of the solid angle of observation will be individual to the instrument. However, the effect of reabsorption on the emission lifetime can be expressed independently of viewing geometry because the measurement is not based on absolute intensity. The observed decay curve for a single exponential in the absence of reabsorption may be expressed by the convolution integral²⁴

$$F(t) = \int_0^t I(t-t')e^{-t'/\tau} dt' \quad (4)$$

where $F(t)$ is the observed decay, $I(t)$ is the lamp function, and τ is the single-exponential decay time. When a portion

of this light is reabsorbed, the reemitted light will follow an exponential decay convoluted not with the lamp function, but with the first decay, thus

$$F'(t) = \int_0^t F(t-t')e^{-t'/\tau} dt' \quad (5)$$

Subsequent reabsorption of this light will result in a function $F''(t)$ which is a convolution with $F'(t)$, and so forth. Each of these observed decay functions is additive, with the proper normalization factor for their relative intensities. The lamp intensity is the strongest, with a factor

$$L = \int_0^\infty \int_0^l I(\tilde{\nu})(1 - e^{-2.3\epsilon(\tilde{\nu})cz}) d\tilde{\nu} dz \quad (6)$$

where $\epsilon(\tilde{\nu})$ is the extinction coefficient as a function of wave number, c the concentration, l the path length in the z direction, and $I(\tilde{\nu})$ is the frequency distribution of the excitation. Here we have neglected the cross sectional area of the exciting light, leaving only one dimension. This function is of course normalized such that $\int_0^\infty I(\tilde{\nu}) d\tilde{\nu} = 1$. The less intense reemission curves are multiplied by factors similar to Melhuish's K integrals¹⁵

$$A = \phi_f \int_0^\infty \int_v f(\tilde{\nu})(1 - e^{-2.3\epsilon(\tilde{\nu})cl(r)}) dr d\tilde{\nu} \quad (7)$$

where r indicates integration over all coordinates of the cell, and the fluorescence distribution function is normalized such that $\int_0^\infty f(\tilde{\nu}) d\tilde{\nu} = 1$. The observed decay function in the presence of reabsorption is consequently

$$F^*(t) = L F(t) + A F'(t) + A^2 F''(t) + \dots \quad (8)$$

This resultant functional form of the decay, when treated by normal deconvolution procedures or even a simple least-squares analysis, will yield a measured lifetime τ_M longer than the intrinsic fluorescence lifetime τ_f which would be found in the absence of reabsorption effects. Elimination of all reabsorption terms leaves only the simple convolution integral $F(t)$ times a constant, reducing τ_M to τ_f . Note that the viewing geometry of the detecting system does not enter this expression, since only the relative amounts of emission and reemission are important for the determination of the final decay function. The dimensions of the cell are the only geometrical factors necessary to define the amount of reabsorption. Given the difficulty of calculating the integrals involved in this formula and the expression of Melhuish, it is advised to keep the optical density of the 0-0 band below 0.05/cm for solutes which strongly self-absorb.

It appears that another possible source of error in quantum yield determinations lies in too broad an application of the standard n^2 correction term for the index of refraction (cf. eq 1). Hermans and Levinson derived this factor with the admonition that it was appropriate for systems of small slits.¹⁷ For example, these authors determined a relative error of 8% arising from a system of two slits between the sample and detector where the angle δ in the horizontal plane viewed by the detector is 0.1 radians, considered typical for their instrument. This approximation is of course reasonable only when $\sin \delta \sim \delta$. If one considers the "can" illustrated in Figure 1 as the limiting optics of the instrument, one finds δ to be beyond the range of this approximation, which probably indicates a large error in the refractive index correction. The results of varying the emission slit seem to confirm that errors can result from larger slit widths. The probability that these results are simply an ar-

tifact is reduced by the fact that, although a decrease is observed with narrower slit width for both benzene and cyclohexane, no measurable effect is observed for ethanol, which has an index of refraction very similar to that of the standard solution. This finding would seem to indicate that the dependence on slit width is a function of solvent. This dependence suggests that the normal correction for the difference in refractive index between the sample and the reference is best applied when the emission approximates a point source. As the slits are widened, the viewing geometry approaches a sphere, with a consequent decrease in the proper refractive index correction factor from n^2 to 1. The possibility that this effect can manifest itself at much smaller slit widths than is commonly thought (5 mm and smaller) may provide one explanation for the wide range of quantum yield values found in the literature. Since nearly all determinations are performed with guanine bisulfate in either aqueous 1.0 or 0.1 N H_2SO_4 or anthracene in ethanol as a standard, measurements made in solvents with refractive indices much different from 1.35 such as benzene and cyclohexane can be expected to show peculiarities of viewing geometry. It is therefore important that the individual system be tested to ascertain the true dependence upon index of refraction for its limiting optics.

Accepting the universal application of the n^2 form of the refractive index correction term, one is forced to explain the occurrence of solvent independence of the quantum yield together with solvent dependence of the fluorescence lifetime. As observed in Table I, this would indicate that the radiative rate constant k_f^0 would be a function of the solvent medium. If an actual dependence exists, it should also be reflected in the oscillator strengths. Immediately we find ourselves confronted with yet another question involving the index of refraction. Although throughout much of the literature³⁸ any factor involving the refractive index n in the oscillator strength calculation is neglected, a large number of possibilities for such a correction for the solvent medium exist in the literature. The more common ones range from the $1/n$ factor of Birks,³⁹ derived from the slowdown of light upon passage through condensed media, to the direct proportionality of Mataga and Kubota,⁴⁰ based on the formulations of Förster⁴¹ for the transition probabilities. However, Förster's expression for the oscillator strength does not involve refractive index. Berlman⁴² also presents a factor of n in his expression for f , but his constant is a factor of 3 larger than the accepted one. No explanation is given for this difference. Scheibe and co-workers⁴³ have extracted an interesting refractive index correction term from the work of Onsager⁴⁴ on electric dipole moments. They have applied their correction factor of $n\{(2n^2 + 1)/3n^2\}^{1/2}$ (which might be approximated as $\sim 0.7n$ for the solvents used here) to oscillator strengths on the basis that the electric transition dipole is acted upon in a manner similar to a static dipole. A correction factor which has been quoted by several authors is the Lorentz-Lorenz term derived by Chako⁴⁵ in the form $9/(n^2 + 2)^2$. This expression is often found in the literature as $9n/(n^2 + 2)^2$.^{46,47} However, Chako compared this factor and others by means of experimentally measured quantities and found that it alone could not account for solvent dependences, and that there was not enough variation to decide among the possibilities. Also, Bayliss and Hulme,⁴⁸ in their study of solvent shifts in the absorption spectra of benzene and its derivatives, found no effect of solvent upon the oscillator strength except for highly interactive solvents such as the chlorinat-

ed methanes. Though theoretical justifications for considering the index of refraction in the oscillator strength calculation can be advanced, the resulting correction factor depends on the model used. The possibility that more than one of these models may be valid, and that the resulting correction terms could cancel each other out, must be considered. Nevertheless, the experimental findings indicate that this correction is quite small. We have thus neglected any factor involving n in the f values shown in Table I. The solvent independence of the oscillator strengths would favor the corollary solvent independence of the radiative rate constants k_f^0 . This statement in turn supports the contention that the quantum yield of fluorescence should follow the lifetime in its behavior upon change of medium. Because of the greater number of experimental errors intrinsic to quantum yield measurements, and because the agreement in the literature is more widespread for the lifetimes, we tend to favor the latter quantities among our data. A constant k_f^0 in conjunction with a solvent dependent ϕ_f and τ_f requires that a nonradiative channel be enhanced in DPA by the solvent medium. It can be recognized from the red shift ($\sim 500 \text{ cm}^{-1}$) in the absorption spectrum of DPA in benzene relative to the other three solvents that there is slight alteration of the electronic wavefunctions of the ground state, the first excited state, or both. What role this change might play in stimulating a radiationless channel is not obvious. It is known that intersystem crossing is the only significant deactivation other than fluorescence in the singlet manifold of large aromatic hydrocarbons.³⁴ There does appear to be some solvent dependence of the triplet yield, as indicated by the value of 0.03 in ethanol of Parker and Joyce,³⁰ and the value of 0.12 in liquid paraffin found by Medinger and Wilkinson.³⁴ The shifts observed in the singlet absorption spectrum can result in a stronger interaction with an intermediate triplet state. In the work of Kearvell and Wilkinson on substituted anthracenes, although the k_f^0 values given were slightly solvent dependent (see above), the bulk of the solvent and temperature dependence lay in the intersystem crossing rate constant k_{ISC} .⁴⁹ Considering this fact, a small shift in electronic energy levels due to the solvent medium will certainly have a greater effect on the intersystem crossing process involving a narrow energy gap than on a radiative channel covering well over $20\,000 \text{ cm}^{-1}$, particularly since the upper states are well separated from the lowest excited singlet. Thus we conclude that k_f^0 should be solvent independent, and so the quantum yield values should follow the behavior of the fluorescence lifetimes. Bearing this in mind, we are inclined to believe that the values of ϕ_f presented in Table I without the superscript n represent the true quantum yields of DPA in the various solvents.

The controversy^{11,12} about the photophysical properties of DPA appears to have arisen partly from the failure to recognize the solvent dependence, and partly from the use of high concentrations by certain authors. In addition, many researchers may be introducing errors into their data through their failure to recognize that the correction for differences in index of refraction between sample and reference may deviate from n^2 (cf. eq 1). In order to correctly apply this factor, the angle δ viewed by the detector (see above) must be kept small. It is obvious that with sufficiently small slit widths the sample will appear to the detector as a point source, allowing the n^2 term to be used in accordance with Snell's law. Whether complete neglect of this correction factor is permitted for systems of larger slit

short of a complete integrating sphere is not entirely clear and demands further study.

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Inter- and Intramolecular Quenching of Indole Fluorescence by Carbonyl Compounds

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Indole fluorescence was found to be quenched by a variety of carbonyl compounds. In the case of carboxylic acids the quenching rates were proportional to the K_a of the acid. The acid proton was not essential for quenching, however, as the ester derivatives were found to retain their quenching ability to a great degree. Quenching is interpreted as resulting through formation of an excited state charge-transfer complex in which the photoexcited indole acts as the donor. A simple molecular orbital scheme is presented which correlates these results with complimentary studies in which carbonyl fluorescence is quenched by aromatics and other π -electron systems. Intramolecular quenching by indole-3-carboxylic acids may take place through a complex stabilized by a σ interaction between photoexcited indole and the carbonyl carbon.

Introduction

The fluorescence yield of the indole ring system is sensitive to additives in solution as well as to groups attached to the ring itself.¹ The hydronium ion is an excellent quench-

er^{1a} as are other potential proton-donating groups, particularly the $-\text{NH}_3^+$ moiety when attached to the ring as in the case of tryptophan.² In addition, studies have revealed the importance of the carboxyl group as a quenching center of indole fluorescence.³ Several mechanisms have been sug-