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CALORIMETRIC DETERMINATION OF THE 9,10-DIPHENYLANTHRACENE FLUORESCENCE QUANTUM YIELD

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Summary

A modified calorimetric fluorescence quantum yield method which allows yield determinations on optically dilute samples has been used to determine fluorescence quantum yields of 9,10-diphenylanthracene (DPA) in cyclohexane ($\varphi_f = 0.95_5$) and in ethanol ($\varphi_f = 0.88_5$) and of 2-2′-(1,4-phenylene)bis[5-phenyloxazole] (POPOP) in cyclohexane ($\varphi_f = 0.97_5$) and in ethanol ($\varphi_f = 0.91$). It has also been demonstrated that the DPA fluorescence quantum yields and lifetimes vary significantly from one solvent to another.

Introduction

The search for reliable reference substances for relative fluorescence quantum yield determinations has led many different workers to investigate the luminescence properties of 9,10-diphenylanthracene (DPA). Despite many efforts to obtain a reliable value for the DPA fluorescence quantum yield (φ_f), no agreed upon number has emerged (for a summary of the literature see ref. 1); even in very recent work values ranging from 0.83 [2] to 1.00 [1] have been obtained, and one of the most recent careful fluorimetric determinations has yielded a value of 1.06 ± 0.05 for DPA in cyclohexane [3].

One reason which has been advanced to account for these discrepancies is reabsorption–re-emission in concentrated solutions which could result in anomalously high results [2], but this has not been universally accepted [4]. Another contributing factor to the discrepancies is refractive index corrections, which involve n^2 for point source emitters but which have recently been shown to vary substantially when finite viewing slits are employed [5]. Yet another cause of variations that has only recently been appreciated [1, 4,5] is the dependence of the DPA quantum yield on the solvent used.

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In view of the need for reliable fluorescence quantum yield standard substances [6] and of the continuing uncertainty over the true values of φ_f for DPA, we felt that further investigation of this compound, utilizing an approach which would avoid the need for both reabsorption–re-emission and refractive index corrections, would be useful. We have therefore modified a calorimetric technique for determining fluorescence yields [7] so that it can be applied to optically dilute samples and we report here results obtained by this technique. Some additional data on the fluorescence of DPA in various solvents are also included in order to demonstrate the degree of variation which this compound exhibits.

Experiments and results

One of the most critical factors involved in accurate quantum yield determinations is the achievement of adequate purity both of solvents and substrates. We have found that DPA undergoes significant thermal decomposition, even under vacuum conditions, when heated close to its melting point; it also shows signs of thermal degradation when heated in solution. Purification techniques involving heating, such as recrystallization from hot solvent mixtures, vacuum sublimation and zone refining, are thus unsatisfactory purification methods*. For our work, DPA prepared according to the method of Willemart [9] was finally purified by recrystallizing twice from benzene–ethanol mixtures followed by chromatography on alumina grade I using 30% benzene in petroleum ether as the eluant. The solvent was subsequently evaporated without heating, yielding pale yellow crystals of melting point 248 °C.

All solvents used in this work were fractionally distilled before use and showed no detectable fluorescent impurities. Merck pro analysis grade Rhodamin-B of concentration 3 g l^{-1} in ethylene glycol was used as a quantum counter. Pharmaceutical grade quinine sulfate, 1 g l^{-1} or less in chlorine-free 1.0 N H_2SO_4, was used as a fluorescence standard for those measurements of a relative nature.

Calorimetric method

Determination of absolute fluorescence quantum yields by calorimetric means is a technique that has been developed by Seybold *et al.* [7] utilizing solvent thermal expansion to sense temperature changes. In order to achieve greater sensitivity and to permit measurements on dilute solutions, we have constructed an apparatus using a thermistor probe–Wheatstone bridge combination (Sargent, maximum sensitivity 8 mV K^{-1}) as a temperature sensor.

A schematic diagram of the apparatus is shown in Fig. 1. A special Dewar cell was constructed of Pyrex square cross section tubing with inner

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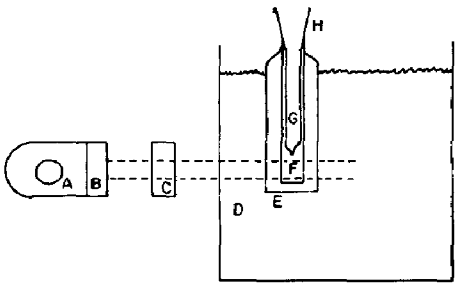
*Since completion of our work we have learned that DPA can be successfully zone refined under sufficiently rigorous conditions [8].



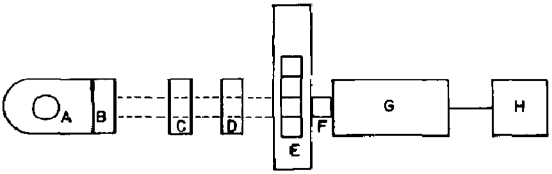


Fig. 1. A schematic diagram of the calorimetric fluorescence quantum yield apparatus: A, 75 W medium pressure Hg lamp; B, collimating lens; C, Corning 7-37 filter; D, thermostated water bath; E, square-walled Dewar cell; F, 1 cm × 1 cm sample area; G, thermistor probe; H, ground-glass joint.

Fig. 2. A schematic diagram of the apparatus for matching solution absorbances: A, 75 W medium pressure Hg lamp; B, collimating lens; C, Corning 7-37 filter; D, neutral density filter; E, Beckman DU spectrophotometer cell compartment; F, Rhodamin-B quantum counter solution; G, photomultiplier tube; H, Hewlett–Packard model 419A d.c. null voltmeter equipped with bucking potential.

dimension of 1 cm. This Dewar cell was equipped with a ground-glass joint into which the thermistor probe was inserted such that the light path passed through the cell just below the thermistor tip. The Dewar cell minimized the rate of heat losses from sample to environment, and stabilization of environmental temperature was achieved by immersing the cell in a water bath thermostated at 298 K.

In order to obtain accurate quantum yield results it is necessary to have solutions of the reference compound ($\varphi_f = 0$) and of the sample whose total absorbances of the 366 nm Hg line are the same. Because the finite width (about 8 nm (0.6 kK) FWHM) of the medium pressure "line" meant that solutions whose absorbances were matched at 366 nm might not have matched total (integrated) absorbances, a special apparatus, shown in Fig. 2, was constructed which allowed comparison of the total absorbances of two different solutions. Sample and reference solutions of nearly matched optical densities of around 0.1 were prepared and were placed in 1 cm cuvettes in the Beckman cell compartment, and the difference in transmitted light intensity was determined by comparing voltmeter readings for the two solutions. Accuracy of better than 1% was achieved by opposing most of the signal and increasing the voltmeter sensitivity one decade. Reference solution concentrations were then adjusted by dilution until exact matching of the transmitted light signal was achieved.

The procedure for calorimetric quantum yield measurements was as follows. 1.50 ml of solution which had been previously thermally equilibrated with the water bath was pipetted into the Dewar cell and the thermistor probe introduced. Further equilibration was allowed to take place until the solution temperature, as monitored by the thermistor (via a Sargent–Wheatstone bridge and 1 mV strip-chart recorder) was stable ($\Delta T/\Delta t < 10^{-2}$ K min^{-1}). The light beam was then unblocked and the solution was irradiated for a time of 2 - 5 min while the temperature rise (of the order of 10^{-2} K min^{-1})

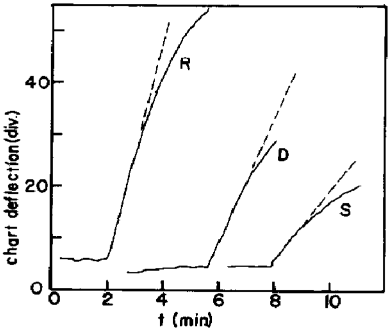


Fig. 3. Representative heating curves for calorimetric quantum yield determinations: R, reference compound (benzophenone); D, 9,10-diphenylanthracene; S, solvent (cyclohexane).

was continually monitored on the recorder. The same procedure was repeated for identical volumes of pure solvent, reference solution and sample solution, with repetition of at least one determination to check lamp stability. Data were then analyzed following the method of Seybold *et al.* [7] by taking the initial slopes of the heating curves and substituting them into the equation

$$\varphi_f = \frac{\bar{\nu}_a}{\bar{\nu}_f}\,\frac{K_r - K_f}{K_r - K_s} \tag{1}$$

where K_r, K_f and K_s are initial heating rates of reference, sample and solvent respectively. A typical set of data is shown in Fig. 3.

The average wavenumber of absorbed light ($\bar{\nu}_a$) was taken to be that of the 366 nm mercury line. The lamp–filter combination was verified as giving symmetric emission about this wavelength and negligible contributions at other wavelengths by measuring its output with a Jarrell–Ash $\frac{1}{4}$ m monochromator equipped with a Rhodamin-B quantum counter and a photomultiplier tube. The same set-up was used to record the corrected emission spectra of the solutions used for the calorimetric runs. From these corrected emission spectra the average wavenumber $\bar{\nu}_f$ of the emitted light was determined by cutting and weighing 10 nm wavelength intervals of the recorded spectra.

Air-saturated samples were used in these calorimetric experiments in order to avoid complications arising from loss of solvent as a result of inert gas bubbling (freeze–pump–thaw degassing was not feasible for the calorimetric cell). Observed quantum yields had therefore to be corrected for the effect of oxygen quenching in air-saturated solutions. These correction factors were measured as described previously [10]. Quenching values thus obtained are included in Table 1.

Calorimetric determinations were carried out in ethanol and in cyclohexane. In ethanol, malachite green was used as a reference of zero quantum yield, while in cyclohexane, benzophenone served as the reference. Besides DPA, we have also calorimetrically determined the yield of 2,2′-(1,4-phenylene) bis[5-phenyloxazole] (POPOP) which is similarly highly fluorescent to DPA. Three different matched-absorbance solution pairs were prepared for each compound in each solvent, and duplicate runs were carried out in some

TABLE 1

Calorimetric values of fluorescence quantum yields

Compound	Solvent	Reference	ν_f (kK × 10^4)	φ_f (air saturated)	Quenching (±0.02)	φ_f (unquenched) (±0.03)
DPA	Cyclohexane	Benzophenone	2.32	0.74_5	1.28	0.95_5
DPA	Ethanol	Malachite green	2.29	0.65	1.37	0.89
POPOP	Cyclohexane	Benzophenone	2.37	0.94	1.04	0.97_5
POPOP	Ethanol	Malachite green	2.29	0.85	1.07	0.91

cases to check reproducibility and instrumental stability. Results of these determinations are collected in Table 1.

Solvent variations

Comparative fluorescence quantum yield determinations were carried out utilizing a FICA MK-II recording spectrofluorimeter. DPA solutions of optical density $\leqslant 0.1$ were loaded into quartz cuvettes, degassed by repeated freeze–pump–thaw cycling and then sealed off under vacuum. Their absorbance spectra were then taken on a Cary 17 spectrophotometer, and quinine bisulfate solutions were prepared to give exact matches of absorbance at two different wavelengths between 340 and 380 nm. Emission spectra as a function of wavenumber were then recorded on the FICA, utilizing excitation bandwidths of 1 or 2.5 nm at the wavelength of matched absorbance. Total integrated emission intensities were determined by the cut and weigh technique.

In order to avoid errors due to uncertainties in the fluorescence yield of quinine bisulfate and in the calibration of the emission monochromator–photomultiplier combination, the emission intensities obtained in this fashion were not used to obtain absolute quantum yield values. Instead, quantum yield ratios for DPA in various solvents were computed, applying the necessary refractive index (n^2) correction factor. These ratios were then normalized to the calorimetrically determined fluorescence yield for DPA in cyclohexane. The results of these determinations are collected in Table 2.

It has been suggested that yield determinations based on oscillator strengths and lifetime measurements may be more reliable than are intensity measurements [5]. In order to test this possibility absorbance and lifetime measurements were also carried out in various solvents, the latter by means of a nitrogen laser as described previously [12]. These data are also presented in Table 2.

Discussion

Accuracy

The calorimetric quantum yield method used in this work possesses certain intrinsic advantages over optical techniques: no refractive index effect,

TABLE 2

Fluorescence parameters of DPA in different solvents

Solvent (n)	φ_f (±0.05)	τ_f (ns) (±0.1)	ϵ_{max} (M^{-1} cm^{-1} × 10^4)	k_r (calc.)[a] (s^{-1} × 10^8)
Tetralin (1.54)	0.98_5	7.6	1.125	1.20
Benzene (1.50)	0.83[b]	7.0[c]	1.20	1.21
Methylcyclohexane (1.43)	$0,83_5$	8.9[d]	1.26_5	1.12
Cyclohexane (1.427)	0.95_5[e]	7.9[f]	1.24	1.10
Ethanol (1.356)	0.88_5	8.8	1.17	0.94
Isopentane (1.351)	0.91_5	8.8	1.39	1.05

[a] Calculated from integrated absorption spectrum using the Strickler–Berg formula [11].
[b] From ref. 2.
[c] From ref. 4.
[d] Measured by single photon counting (H. Staerk, personal communication).
[e] Other values normalized to this calorimetric result.
[f] Measured both by single-photon counting and individual laser flash decay.

no polarization effects, no need to calibrate optical components and no need for an accurately known reference yield (other than a reference of zero yield). Possible sources of error which must be considered are absorbance match, lamp stability, determination of slopes, oxygen quenching, reabsorbance, $\bar{\nu}$ values and reference compound.

Of these, we believe that the absorbance match is the most critical, contributing the bulk of the uncertainty in our reported results. We have checked the contributions of lamp instability and slope uncertainty by duplicate measurements on samples of the same matched solutions, consistently obtaining values that agree to better than 1%. Reabsorbance effects for solutions of optical density less than 0.1 are negligible, especially for high quantum yield materials for which the bulk of reabsorbed photons will again be re-emitted. Values of $\bar{\nu}$ can be quite accurately determined from corrected spectra and are in any case not particularly sensitive to small shifts in spectra (a discrepancy of 5 nm in the apparent average wavelength represents an error of only 1%). Concerning the reference compounds, malachite green is known to have fluorescence [13] and photochemical [14] quantum yields less than 10^{-2}. Benzophenone in cyclohexane requires closer consideration, since although its fluorescence is negligible [15] it undergoes significant photoreduction in degassed cyclohexane solution [16] which raises the possibility of energy losses or gains due to photochemistry. For air-saturated solutions, however, we estimate contributions of photochemistry to have less than 1% effect on the heating rate, based on the following.

(a) In the presence of oxygen competition between quenching of the triplet state ($[O_2] = 10^{-3}$ M, $k_q \approx 3 \times 10^9$ l mol^{-1} s^{-1}) [17] and H abstraction ([solvent] ≈ 10 M, $k_h \approx 4 \times 10^4$ l mol^{-1} s^{-1}) [16, 18] results in a maximum photochemical yield of 0.07.

(b) In the presence of oxygen abstraction is followed by regeneration of benzophenone and production of HO_2 [19].

(c) Thermochemical considerations show that the net exothermicity of the most probable net photochemical reaction $2\ c\text{-}C_6H_{12} + O_2 \rightarrow (C_6H_{11})_2 + H_2O_2$ is only about 12 kcal (4.2 kK).

At most, therefore, photochemical energy release of the order $0.07 \times 4.2 = 0.28$ kK, or about 1% of the energy absorbed, will result. This conclusion is supported by the fact that our ratio of fluorescence quantum yields for cyclohexane and ethanol is the same calorimetrically as fluorimetrically.

The accuracy of our oxygen quenching factors we believe to be within 2%, based on (a) determination of the quenching factor under oxygen saturation, where the effect is fivefold greater than under air saturation, (b) agreement of values obtained under repetitive bubbling, indicating negligible solvent evaporation losses and (c) strict Stern–Volmer agreement for quenching of air-saturated and oxygen-saturated solutions, indicating both consistency and absence of static quenching.

Adequacy of the absorbance match for reference and sample pairs is less easy to assess. Our method of matching integrated absorbances experimentally, with scale expansion to allow maximum precision of transmitted light intensity differences, was designed to yield maximum accuracy of match; yet, matching of absorbances that are smaller than 0.1 is none the less difficult. The fact that quantum yield results for separate matched solution pairs showed more scatter than repetitive results on different samples of the same matched solutions indicates that this factor is one of the major sources of uncertainty. Our ability to achieve matched transmitted intensities to within 1 - 2%, together with the fact that results on different matched samples differed by less than ±0.04, indicates that the average calorimetric yield values are accurate probably to within ±0.03.

Similar accuracy considerations exist for our comparative yield values in different solvents since they have all been normalized to the calorimetric results. In addition, the relative values are subject to uncertainties arising from the adequacy of the matches of absorbance between DPA samples and quinine bisulfate reference solutions; this we estimate to contribute an additional ±0.02 in the reported yield values. Quantum yield ratios between different solvent pairs should, however, be accurate to about 3%.

DPA as a standard

The results reported here, in conjunction with results reported by others, indicate the following conclusions concerning DPA: (1) its fluorescence quantum yield, though high, is definitely less than 1.0 (with the possible exception of tetralin solutions); (2) the yield is significantly solvent dependent; (3) there is no discernible wavelength dependence of the yield [20]; (4) best values for the fluorescence quantum yield in various solvents are 0.83 ± 0.01 in benzene [2, 5, 21 - 23], 0.91 ± 0.03 in ethanol [1, 5, 24 - 27, this work] and 0.92 ± 0.02 in isopentane [5, this work]. For DPA in cyclohexane solvent, over which there has been substantial controversy [28, 29], some uncertainty persists.

Our calorimetrically determined quantum yield of 0.95_5 is in reasonable agreement with Birch and Imhof's [4] cyclohexane/benzene yield ratio of 1.13, which gives a yield in cyclohexane of 0.94 if the benzene yield is 0.83. Heinrich *et al.* [1] have reported for DPA in cyclohexane no evidence of triplet–triplet absorption (which implies a triplet yield of less than 0.03), an air-saturated quantum yield of 0.77 (which gives an unquenched yield of 0.98 using an air quenching factor of 1.28) and a yield of 1.0 in degassed solution. Ware and Rothman [3] report a yield of 1.06 ± 5.6% using an integrating sphere technique. In contrast, Morris *et al.* [5], while observing a yield of 0.95 when the n^2 refractive index factor is applied to their data, favor a value of 0.86 based on their observation that their viewing geometry makes the n^2 correction inappropriate. Gelernt *et al.* [30] have also reported a lower value, 0.84, determined using a calorimetric method. Notwithstanding these last values, we believe that the most reliable quantum yield value for DPA in cyclohexane is 0.96 ± 0.04, inasmuch as four independent and different measuring techniques give values in this range.

The above values must be used with care, however, since they are only valid for carefully degassed solutions of concentration 10^{-5} M or less; moreover, comparisons with other solvents should be undertaken with care in view of the observed solvent variations and possible errors in refractive index corrections.

Concerning the possibility of estimating fluorescence quantum yields from absorbance and lifetime measurements, our data indicate this to be no easier to accomplish experimentally than are intensity determinations. Whereas Morris *et al.* [5] found no significant variation in oscillator strengths for DPA in four different solvents, we observe variations of the order of 10% (Table 2). Our lifetime determinations, which were carried out on thoroughly degassed low optical density samples of highly pure material, give consistently longer lifetimes at room temperature than those reported by Morris *et al.* [5], although measurements with the same apparatus at low temperature [12] agree more closely with their 77 K lifetimes for DPA in ethanol and isopentane. The disagreement in these two sets of carefully determined lifetimes indicates that lifetime measurements are fraught with difficulties similar to those attendant on intensity measurements; hence, our feeling is that quantum yield determinations based on calorimetric measurements such as those reported here are the most reliable that are currently available.

Our calorimetric yield measurements on POPOP can be compared with the scanty data available in the literature where fluorescence yields of 0.86 (benzene solvent) [31] and 0.93 (cyclohexane solvent) [32] have been reported. The latter value disagrees somewhat with our determination of 0.97_5, but since it is based on a concentrated solution of DPA as a standard, its reliability is questionable. POPOP appears to show similar solvent variations in its fluorescence yield as does DPA, indicating that substantial additional study is needed before it could be utilized as a reliable reference compound. Its lower susceptibility to oxygen quenching and the possibility that it might show a concentration independent yield to higher concentrations than does DPA suggests that such further investigation might prove worthwhile.

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