PHOTOCHEMISTRY OF 3,4,9,10-PERYLENETETRACARBOXYLIC DIANHYDRIDE DYES: VISIBLE ABSORPTION AND FLUORESCENCE SPECTRA AND FLUORESCENCE QUANTUM YIELDS OF THE MONO(*n*-OCTYL)IMIDE DERIVATIVE IN AQUEOUS AND NON-AQUEOUS SOLUTIONS

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Summary

This study characterizes the visible absorption and fluorescence spectra and fluorescence quantum yields of the dicarboxylate, dicarboxylic acid and anhydride forms of the mono(*n*-octyl)imide derivative of 3,4,9,10-perylene-tetracarboxylic dianhydride in aqueous micellar and organic solvent media. All three forms of the mono(*n*-octyl)imide dye have primary visible absorption maxima in the range 495 - 530 nm, with extinction coefficients of $(3 - 8) \times 10^4$ M^{-1} cm^{-1} and fluorescence maxima in the range 520 - 600 nm, with quantum yields of 0.5 - 1.0. Vibrational structure in the absorption and fluorescence spectra increases and the Stokes loss decreases in the sequence dicarboxylate > dicarboxylic acid > anhydride. The dicarboxylic acid form of the dye dehydrates and cyclizes smoothly to the anhydride form in sodium dodecylsulfate micellar solutions with first-order kinetics and a half-time of 7×10^{-5} s^{-1} (24 °C).

1. Introduction

There is a growing need to develop stable, efficient and inexpensive photosensitizers for use in artificial photosynthetic devices. The role of the photosensitizer is to absorb sunlight and catalyze either energy or electron transfer reactions that, in conjunction with auxiliary catalysts, lead to the decomposition of water [1 - 6]. In this context, the monoimide and diimide derivatives of 3,4,9,10-perylenetetracarboxylic dianhydride deserve attention. These are readily prepared dyes that have excellent stability to heat and light, absorb well in the visible spectrum ($\epsilon = 10^4 - 10^5$ M^{-1} cm^{-1}) and have high fluorescence yields (0.5 - 1.0) [7 - 14]. Many new derivatives of 3,4,9,10-perylenetetracarboxylic dianhydride have been synthesized and studied in recent years [9 - 14], but relatively few of the photochemical and redox properties that are often used to characterize photosensitizing dyes

[1, 15 - 20] are yet known for them. This paper examines the visible absorption and fluorescence spectra and fluorescence quantum yields of the mono-(n-octyl)imide derivative of 3,4,9,10-perylenetetracarboxylic dianhydride. This particular derivative, which was first prepared by Nagao and Misono [10], was selected because the molecule is amphiphilic in neutral and basic aqueous media, when the anhydride end of the molecule is hydrolyzed and negatively charged. Amphiphilic molecules like this are readily incorporated into colloidal aqueous systems such as detergent micelles, lipid bilayer vesicles and microemulsions, which can make artificial photosynthetic processes more efficient than in homogeneous solutions by spacially organizing the molecular components and utilizing interfacial electrostatic potentials [2 - 6, 21 - 26].

The mono(n-octyl)imide derivative can exist as the fully ionized dicarboxylate (1), the fully protonated dicarboxylic acid (2) and the anhydride (3) forms shown in Fig. 1. The purpose of this paper is to characterize the spectral properties of these three forms of the dye in various solvent systems, including aqueous detergent micelles. (No attempt will be made here to characterize the singly protonated intermediate in between 1 and 2.) These characteristics can be useful in identifying the state of the dye in other solvents, especially in colloidal systems, where the microenvironment of the dye may be uncertain [23 - 25]. The present study further substantiates the high fluorescence yields and photochemical stabilities of dyes derived from 3,4,9,10-perylenetetracarboxylic dianhydride in aqueous and non-aqueous media.
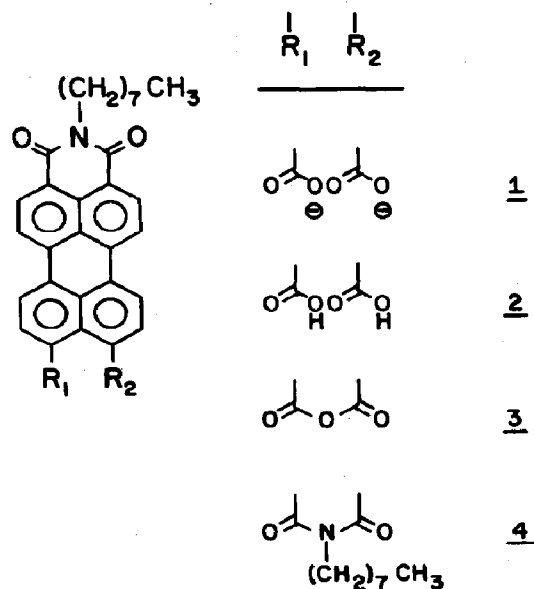

Fig. 1. Structural formulae of the dicarboxylate (1), dicarboxylic acid (2) and anhydride (3) forms of the mono(n-octyl)imide derivative of 3,4,9,10-perylenetetracarboxylic dianhydride and its di(n-octyl)imide derivative (4).

2. Experimental details

2.1. Materials

3,4,9,10-Perylenetetracarboxylic dianhydride (from Aldrich), n-octyl-amine (from Sigma), Rhodamine 6G chloride (Rhodamine 590 chloride, from Exciton), tetrabutylammonium hydrogen sulfate (from Aldrich) and Triton X-100 (TX-100) (from Aldrich) were used as received. Sodium dodecylsulfate (SDS) (from Eastman) was recrystallized twice from ethanol (EtOH), and hexadecyltrimethylammonium bromide (CTAB) (from Eastman) was recrystallized from EtOAc—EtOH (Ac ≡ acetyl). Water was treated with a Millipore—Milli-Q purification system. All other chemical reagents and solvents were of the highest purity commercially available.

The mono(n-octyl)imide derivative and the di(n-octyl)imide derivative (4) of 3,4,9,10-perylenetetracarboxylic dianhydride were prepared by reacting the dianhydride with n-octylamine in the molar ratio of 10:1 in refluxing methanol (MeOH) for 10 h. The precipitate in the reaction mixture was collected by filtration, washed with MeOH and dried. The precipitate was next suspended in hot glacial acetic acid until its color changed from yellow-brown to red-brown, and then it was collected again by filtration, washed with MeOH and dried. This material contained the original dianhydride and 4 (see Fig. 1) but was predominantly 3 (IR (KBr pellet): 1766, 1726 cm^{-1} (C=O, anhydride); 1697, 1657 cm^{-1} (C=O, imide) [9 - 12]). 3 was converted to the potassium salt by suspending it in refluxing MeOH containing an excess of KOH for 3 h. The resultant precipitate was collected by filtration, washed with MeOH and dried. Extraction of the solid with a minimum of 50vol.%EtOH—50vol.%H$_2$O yielded a stock solution of the mono(n-octyl)imide derivative (potassium salt). Drying the remaining solid and extracting it with CHCl$_3$ yielded 4 (see Fig. 1). 3 slowly precipi-tated from the stock solutions of the mono(n-octyl)imide (potassium salt). 3 was periodically removed from the stock solution either by filtration or by centrifugation, and the concentration of dye remaining in solution was deter-mined spectrophotometrically after drying an aliquot of the solution and redissolving it in concentrated sulfuric acid (see below).

The visible absorption spectra of solutions of 3,4,9,10-perylenetetra-carboxylic dianhydride and its derivatives in concentrated sulfuric acid proved to be sensitive indicators of purity [10]. Solutions of the pure dianhydride, mono(n-octyl)imide derivatives (1 - 3) and di(n-octyl)imide (4) had main and satellite absorption maxima at 546 and 509 nm, 580 and 542 nm, and 598 and 553 nm respectively. Mixtures of these derivatives had maxima at intermediate wavelengths. The absorbance ratios of the main and satellite peaks were particularly sensitive to purity. The ratio for the dianhydride starting material was 0.61 ($\epsilon_{509}/\epsilon_{546}$). The corresponding ratios for the mono(n-octyl)imide and di(n-octyl)imide derivatives prepared and investigated in this study were 0.64 ($\epsilon_{542}/\epsilon_{580}$) and 0.61 ($\epsilon_{553}/\epsilon_{598}$) respectively. The extinction coefficient at 580 nm for the mono(n-octyl)imide derivative was determined to be $(6.7 \pm 0.6) \times 10^4$ M^{-1} cm^{-1}, and the coefficient at 598 nm for 4 was $(9.2 \pm 0.9) \times 10^4$ M^{-1} cm^{-1}. Extinction coefficients for

these derivatives in other solvent systems reported below were based on these values.

2.2. Methods

All measurements were carried out at ambient temperature (24 ± 1 °C) using 1.0×1.0 cm quartz cuvettes. Unless noted otherwise, the solutions were saturated with air. Deaeration of samples was achieved by successively evacuating the samples and equilibrating them with argon. The concentrations of dye in the samples ranged from 5×10^{-7} to 5×10^{-6} M. Absorption spectra were recorded using a Cary 219 spectrophotometer (1 nm bandpass). Corrected fluorescence emission and excitation spectra were obtained using an SLM 8000 photon-counting spectrofluorometer (SPC 823–SMC 220). The excitation (4 nm bandpass) and detection (2 nm bandpass) were at right angles to one another. The spectra were measured in the ratio mode using a solution of Rhodamine B perchlorate in ethylene glycol (5.7 g l^{-1}) as the quantum counter. The photomultiplier tube for the sample emission was an EMI type 9635 QA and the photomultiplier tube for the quantum counter emission was a Hamamatsu type R928. Fluorescence quantum yields were measured using the optically dilute relative method [27 - 30] with samples having optical densities of less than 0.04 cm^{-1} at the excitation wavelengths. The areas under the corrected fluorescence spectra were measured with a planimeter and used to calculate fluorescence quantum yields relative to a standard solution of Rhodamine 6G chloride in EtOH. The refractive indices of the solvents used in the quantum yield calculation were measured with an Abbe-type refractometer (Bausch and Lomb) with compensating prisms to isolate the sodium D line (589 nm) [31]. Relative quantum yields were converted to absolute values (Φ_F) based on the value $\Phi_F = 0.95$ [29, 32, 33] for the standard solution. The values of Φ_F reported here were the averages of values obtained at three excitation wavelengths in the range 470 - 500 nm.

Most of the solutions containing the mono(n-octyl)imide (1, 2 and 3) were prepared by diluting the stock solution of the potassium salt (about 10^{-3} M) with the solvent. Aqueous solutions of the dye were made either basic (10^{-3} M OH^{-}) or acidic (10^{-3} M HSO$_4{}^{-}$) by adding either aqueous 0.5 M NaOH or 0.5 M NaHSO$_4$ respectively. For non-aqueous solutions, either 0.5 M KOH in MeOH or 0.4 M tetrabutylammonium hydrogen sulfate in CH$_3$CN were added. Solutions containing 3 were obtained either by the spontaneous conversion of solutions of 2 to 3 or else by dissolving solid 3 in CHCl$_3$, followed by dilution with either CHCl$_3$ or CH$_3$CN. The former solutions contained 10^{-3} M HSO$_4{}^{-}$ while the latter did not, but the subsequent addition of 10^{-3} M HSO$_4{}^{-}$ to the latter samples did not affect their spectral properties.

3. Results

3.1. Absorption and fluorescence

The mono(n-octyl)imide derivative of 3,4,9,10-perylenetetracarboxylic dianhydride can exist as 1, 2 and 3 (Fig. 1). The visible absorption and

fluorescence excitation and emission spectral characteristics of these three forms are summarized in Table 1, and representative excitation and emission spectra are shown in Figs. 2 - 4. Data for **4** are also included in Table 1.

Spectrophotometric titrations of the mono(*n*-octyl)imide derivative in SDS solutions indicated that **1** exists at pHs above 9 and **2** exists at pHs
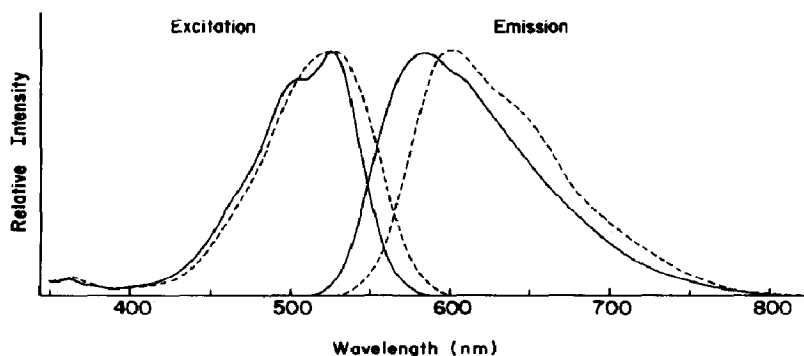

Fig. 2. Normalized fluorescence excitation and emission spectra of 1 (24 °C): ———, aqueous 0.05 M CTAB–0.05 M Na_2SO_4 solution containing 10^{-3} M NaOH; – – –, 50vol.%-EtOH–50vol.%H_2O containing 10^{-3} M NaOH.
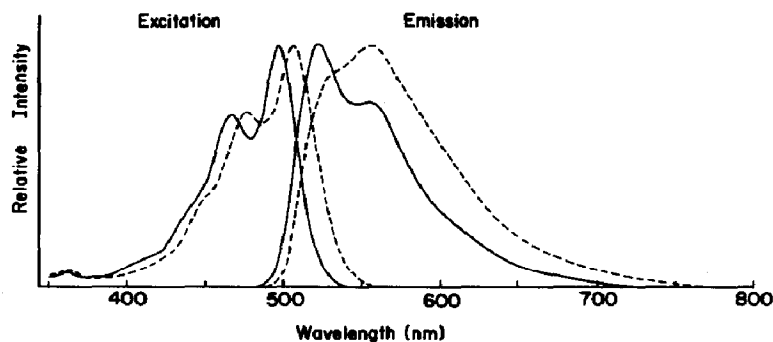

Fig. 3. Normalized fluorescence excitation and emission spectra of 2 (24 °C): – – –, aqueous 0.05 M CTAB–0.05 M Na_2SO_4 solution containing 10^{-3} M $NaHSO_4$; ———, CH_3CN solution containing 10^{-3} M tetrabutylammonium hydrogen sulfate.
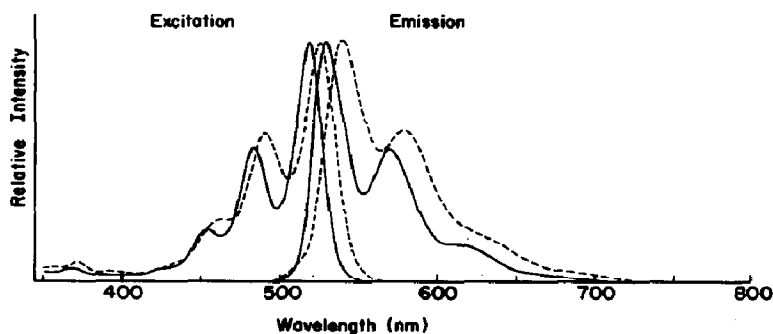

Fig. 4. Normalized fluorescence excitation and emission spectra of 3 (24 °C): ———, 82vol.%CH_3CN–18vol.%$CHCl_3$ solution; – – –, aqueous 0.10 M SDS–0.10 M Na_2SO_4 solution containing 10^{-3} M $NaHSO_4$ (spectra recorded 28 h after adding $NaHSO_4$).

TABLE 1

Visible absorption and fluorescence excitation and emission spectral data and fluorescence quantum yields of solutions of the mono(n-octyl)imide and di(n-octyl)imide derivatives of 3,4,9,10-perylenetetracarboxylic dianhydride[a,b]

Dye	Solvent[c]	Absorption			Excitation		Emission		
		λ_1	λ_2	$\epsilon \times 10^{-4}$	λ_1	λ_2	λ_1	λ_2	Φ_F
1	CTAB	500	524	3.9	505	527	583	610	0.65
		0.95	1.00		0.89	1.00	1.00	sh	
1	TX-100	505	524	3.7	510	528	585	615	0.58
		sh	1.00		sh	1.00	1.00	sh	
1	SDS	495	514	3.8	500	519	588	620	0.57
		sh	1.00		sh	1.00	1.00	sh	
1	50vol.%EtOH–50vol.%H$_2$O	[d]	517	3.7	505	527	600	635	0.65
			1.00		sh	1.00	1.00	sh	
2	CH$_3$CN	466	496	4.5	467	498	523	556	0.87
		0.75	1.00		0.72	1.00	1.00	0.76	
2	SDS[e]	470	501	4.6	475	503	525	548	0.88
		0.70	1.00		0.70	1.00	1.00	0.99	
2	TX-100	474	505	4.3	478	508	527	561	0.22
		0.77	1.00		0.74	1.00	1.00	0.98	
2	CTAB	475	504	4.4	476	507	535	556	0.83
		0.76	1.00		0.73	1.00	sh	1.00	
2	MeOH	472	499	4.5	473	501	544	570	0.75
		0.79	1.00		0.74	1.00	1.00	sh	
3	CH$_3$CN	480	515	6.8	482	517	528	568	0.99
		0.63	1.00		0.57	1.00	1.00	0.62	
3	82vol.%CH$_3$CN–18vol.%CHCl$_3$	482	517	7.2	483	518	529	570	0.87
		0.63	1.00		0.57	1.00	1.00	0.56	
3	CHCl$_3$	485	521	7.7	488	523	531	573	0.94
		0.61	1.00		0.56	1.00	1.00	0.52	
3	SDS	488	523	5.6	489	525	539	579	0.84
		0.69	1.00		0.63	1.00	1.00	0.63	
4	CHCl$_3$	488	525	9.2	490	527	535	577	0.95
		0.60	1.00		0.55	1.00	1.00	0.50	

[a]Conditions: air-saturated solutions; $T = 24 \pm 1$ °C.

[b]Spectral characteristics: the λ (nm) are the peak positions of the main (λ_2) and satellite bands (λ_1) whose relative intensities are listed underneath these values (sh, shoulder). The ϵ (M^{-1} cm^{-1}) are the molar extinction coefficients of the main (λ_2) absorption bands. The spectral resolution is ± 1 nm for absorption, ± 2 nm for excitation and ± 1 nm for emission. The estimated uncertainties are $\pm 10\%$ for the absolute values of ϵ and Φ_F and $\pm 5\%$ for the relative values of ϵ.

[c]Solutions of 1 contained 10^{-3} M OH$^-$ (sodium counterion). Solutions of 2 contained 10^{-3} M HSO$_4^-$ (sodium or tetrabutylammonium counterion). Solutions of 3 were prepared via in situ conversion of 2 (contained 10^{-3} M HSO$_4^-$) or by dissolution of solid 3. SDS solutions contained 0.10 M SDS and 0.10 M Na$_2$SO$_4$. CTAB solutions contained

below 4. The spectra of **1** were obtained in solvents containing 10^{-3} M OH$^-$ to assure complete ionization of the carboxyl groups. These solvents were limited to aqueous systems owing to the insolubility of **1** in purely organic solvents. The spectra of **1** were shifted and had more vibrational structure in the presence of detergent (SDS, CTAB or TX-100) than in water alone (not shown), so it was evident that the dye was predominantly dissolved in the detergent micelles in these systems. The concentrations of the detergents used were well above their critical micelle concentrations [34] so that multiple occupation of individual micelles by the dye was unlikely. The spectra of **2** were obtained in solvents containing 10^{-3} M HSO$_4^-$ to assure complete protonation of the carboxyl groups. The dicarboxylic acid was generated *in situ* by adding HSO$_4^-$ to solutions of the carboxylate, owing to the tendency of the acid form to dehydrate and cyclize to **3** (see below). The absorption and fluorescence excitation spectra paralleled each other except that the vibrational structure in the excitation spectra was generally better resolved and the band maxima were red shifted by about 1 - 4 nm (Table 1). Fluorescence quenching by O$_2$ (air) was not evident (less than 1%) in any of the samples examined, nor was there any evidence of photodecomposition during these measurements.

The following generalizations could be made about the absorption and fluorescence properties that served to distinguish between the three different forms of the mono(*n*-octyl)imide derivative (**1**, **2** and **3**) in solution (Table 1).

(1) **1** had a visible absorption maximum in the range 510 - 530 nm with an extinction coefficient of $(3.7 - 3.9) \times 10^4$ M^{-1} cm^{-1}. The fluorescence had a maximum in the range 580 - 600 nm and a quantum yield of 0.5 - 0.7.

(2) **2** had a visible absorption maximum in the range 495 - 510 nm with an extinction coefficient of $(4.3 - 4.6) \times 10^4$ M^{-1} cm^{-1}. The fluorescence had a maximum in the range 520 - 560 nm and, with the exception of TX-100 solution, the fluorescence quantum yield was in the range 0.7 - 0.9. Quenching of the fluorescence of **2** in the TX-100 solution was presumably either by the phenoxy (electron donating) group or else by a peroxide impurity in the TX-100 molecule. The spectra of the SDS solution, especially the fluorescence excitation and emission spectra, were subject to uncertainty owing to the relatively rapid conversion of **2** into **3** during the measurements (see below).

(3) **3** had a visible absorption maximum in the range 515 - 525 nm with an extinction coefficient of $(5 - 8) \times 10^4$ M^{-1} cm^{-1}. The fluorescence had a maximum in the range 525 - 540 nm with a quantum yield of 0.8 - 1.0. The spectra of **3** resembled those of **4** (Table 1).

0.05 M CTAB and 0.05 M Na$_2$SO$_4$. TX-100 solutions contained 2% (v/v) TX-100 and 0.10 M Na$_2$SO$_4$.

[d]No distinct shoulder present.

[e]Values for **2** in SDS are subject to uncertainty due to time-dependent changes.

(4) Resolution of the vibrational structure in the visible absorption and fluorescence spectra increased in the sequence dicarboxylate < dicarboxylic acid < anhydride. The frequency differences between the maxima of the vibrational components of the absorption (and excitation) spectra were in the range 7000 - 9000 cm^{-1} for 1, 11 500 - 13 500 cm^{-1} for 2 and 13 500 - 14 500 cm^{-1} for 3. The Stokes loss, approximated as the difference in energy between the absorption (excitation) and fluorescence primary maxima, decreased in the sequence dicarboxylate > dicarboxylic acid > anhydride.

3.2. Kinetics of anhydride formation

The spectra of 2, which was produced upon acidification of solutions of 1, exhibited varying degrees of stability to time-dependent changes. The most rapid changes occurred in the aqueous SDS solutions, while the spectra of the CTAB solutions were the most stable. Absorption spectral changes in the SDS system are shown in Fig. 5. These changes indicated the smooth conversion of 2 into 3. There were isosbestic points in the absorption spectra at 479, 493 and 510 nm (Fig. 5), and there were related changes in the fluorescence spectra with isosbestic points at 529, 555, 568 and about 615 nm (not shown). The conversion of 2 into 3 was complete within 24 h, and no further spectral changes were observed within 48 h, but a dye-containing precipitate eventually appeared. Based on the initial and final absorption spectra obtained, the fraction of the unconverted 2 was calculated at the
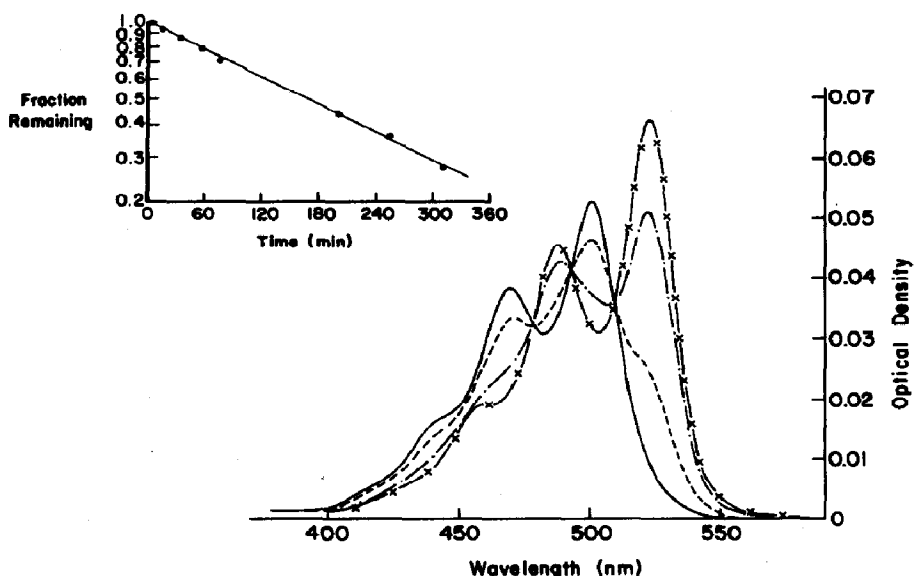

Fig. 5. Visible absorption spectrum of the mono(n-octyl)imide derivative of 3,4,9,10-perylenetetracarboxylic dianhydride in aqueous 0.10 M SDS–0.10 M Na$_2$SO$_4$ solution containing 10^{-3} M NaHSO$_4$, showing the spontaneous conversion of 2 into 3. The spectra shown were recorded at 5 min (———), 76 min (– – –), 310 min (— · —) and 1610 min (—×—) after adding NaHSO$_4$ to the solution (24 °C). Inset: semilogarithmic plot of the fraction of dicarboxylic acid form remaining as a function of time after adding NaHSO$_4$ to the solution.

intermediate times. The kinetics of the conversion of 2 into 3 were first order with a rate constant of $(6.9 \pm 0.7) \times 10^{-5} \text{ s}^{-1}$ at room temperature (Fig. 5, inset). 1 was regenerated quantitatively within seconds after the solutions of 3 were made basic (10^{-3} M OH^-).

The conversion of 2 into 3 occurred in CH_3CN at about one-tenth the rate observed in SDS, and the rate of conversion in MeOH was even slower. Analysis of these changes was complicated by the eventual precipitation of the dye. Spectral changes that could be associated with the conversion of 2 into 3 in TX-100 solutions were accompanied by the formation of a product with an absorption maximum in the range 555 - 560 nm.

4. Discussion

4.1. Absorption and fluorescence

It is evident that the mono(*n*-octyl)imide derivative of 3,4,9,10-perylenetetracarboxylic dianhydride has solubility and spectrophotometric properties that depend on the degree of hydration and protonation of the anhydride end of the molecule. These properties help to distinguish between 1, 2 and 3 (Fig. 1).

The visible absorption and fluorescence spectra of 3 and 4 are similar (Table 1). The red shift and intensification of the primary absorption band in the spectrum of 4 compared with 3 is in accord with the results of Lukac and Langhals [12], who examined related dyes. The prominent vibrational spacing of about 1400 cm^{-1} and the approximate mirror-image relation between the absorption and fluorescence spectra of 3 (Fig. 4) and 4 are present in the spectra of perylene itself [35 - 37]. These features, which are typical of rigid polycyclic aromatic molecules, are indicative of relatively small differences between the geometries and the solvation of the ground and excited singlet states of the dye molecules [35 - 37]. The dyes 3 and 4 have maxima that are about 3800 cm^{-1} lower in energy compared with perylene ($\lambda_{\max} \approx 435$ nm) as a result of conjugation between the π electrons of the carbonyl groups and the π-electron system of the perylene chromophore [38 - 42]. Conjugation is possible because the anhydride and imide bonds in 3 and 4 allow the carbonyl groups to be coplanar with the perylene skeleton.

Hydrolysis of the anhydride end of 3 to produce 2 makes it sterically impossible for both carboxyl groups to be coplanar with the perylene ring system. Although complete coplanarity is not essential for a significant resonance interaction to occur [38 - 42], the extent of conjugation in 2 is expected to be less than in 3. This difference may account for the shift in the absorption (and excitation) band maxima of 2 by about 800 cm^{-1} to higher energies relative to 3 (Table 1). Two factors may contribute to the poorer resolution of vibrational structure in the spectra of 2 compared with 3 (Figs. 3 and 4). One factor is that rotation of the carboxyl groups in 2 makes it possible for several configurations to contribute to the spectra of

this compound. The loss of resolution may also reflect enhanced solvent–dye interactions in the case of 2, as a result of its greater hydrogen-bonding capability compared with 3. These factors apply to both the ground and the first excited singlet states of the dyes since their absorption and fluorescence patterns are approximately mirror images of one another.

As with 2, the extent of conjugation between the π electrons of the carbonyl and perylene groups is expected to be less in 1 than in 3 owing to a loss of planarity. Nevertheless, it is observed that the peak position of the lowest energy absorption (and excitation) band of 1 is lower than the value for 2 by about 800 cm^{-1} (Table 1). A possible explanation of the lower energy of the excited state transition in 1 relative to 2 is that ionization of the carboxylic acid groups makes it possible for intramolecular charge transfer from the carboxylate (donor) end of 1 to the imide (acceptor) end to contribute to the resonance hybrid constituting the first excited singlet state of 1. Ionization of the carboxylic acid groups of the structurally analogous naphthalene dye likewise causes its absorption spectrum to red shift [38]. The more diffuse vibrational structure in the spectra of 1 compared with 2 and 3 (Figs. 2 - 4) presumably reflects a greater sensitivity of the electronic structure of 1 to perturbation by solvent molecules as a result of its ionic character. The greater Stokes loss in 1 compared with 2 and 3 is consistent with this interpretation since the Stokes loss reflects the amount of excited state energy that is lost by the dye to the solvent between the absorption and emission processes.

4.2. Kinetics of anhydride formation

The distinct spectral properties of the different forms of the mono-(n-octyl)imide derivative (1, 2 and 3) make it easy to monitor their interconversions spectrophotometrically. The dehydration and cyclization of 2 into 3 occurs spontaneously in SDS micellar solutions, and the reaction appears to go to completion (Fig. 5). The kinetics of the reaction are first order, as expected for a unimolecular process. One driving force for anhydride formation is that the formation of the six-membered ring in 3 relieves steric tension between the carboxylic acid groups in 2 [38]. Another factor favoring 3 over 2 is the resultant increase in conjugation between the π electrons of the carbonyl groups and those of the perylene chromophore mentioned above. A third factor that has to be considered, however, is that the degrees of solvation of 2 and 3 are likely to be different and could favor either form. The fact that the conversion of 2 into 3 occurs much more rapidly (more than 10^2 times) in SDS than in CTAB micellar solutions is striking. The formation of cyclic anhydrides from dicarboxylic acids is catalyzed by nucleophilic anions [43] as well as by the acidic sites of zeolites [44]. Therefore, the fact that the conversion of 2 into 3 occurs much more rapidly in SDS solutions than in CTAB solutions could be due to catalysis by the sulfate headgroup of the SDS molecule or else by protons which are concentrated near the surface of the SDS micelle [34]. In general, the conversion of 2 into 3 appears to be thermodynamically favorable. For a related

series of 1,8-naphthalenedicarboxylic acid derivatives, the relative stabilities of the dicarboxylic acid and anhydride forms depend on the nature of the substituents in the 4,5-positions [45].

5. Conclusions

The stabilities of the imide derivatives of 3,4,9,10-perylenetetracarboxylic dianhydride and their high fluorescence quantum yields in solution have been well documented in the literature. This study has shown that these characteristics also apply to the mono(n-octyl)imide derivative in acidic and basic aqueous solutions. 1 is readily incorporated into detergent micelles. The tendency of 2 to convert into 3, which is a poorly soluble form of the dye, may limit the practical use of the mono(n-octyl)imide derivative to neutral and basic aqueous solutions. In view of the fact that the diimide derivatives of 3,4,9,10-perylenetetracarboxylic dianhydride, including 4, have high fluorescence quantum yields but are not subject to such pH-dependent changes, it should be worthwhile to extend this investigation to amphiphilic diimide derivatives obtained by further reacting 3 with polar amines (*e.g.* glycine). Further evaluation of these dyes as photosensitizers will require the determination of their one-electron oxidation–reduction potentials and the energies and lifetimes of their singlet and triplet excited states.

Acknowledgment

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