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Photophysical characterization of a 1,4,5,8-naphthalenediimide derivative

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Abstract

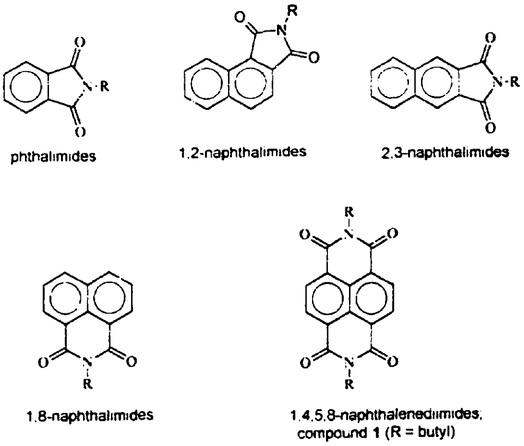
The photophysical properties of *N,N*-dibutyl-1,4,5,8-naphthalenediimide (**1**, Scheme 1) were studied using absorption and fluorescence spectroscopy. The absorption and emission spectra of **1** are mirror images and show resolved vibrational structure, indicating that **1** is a rigid molecule which does not relax substantially from the initially formed Franck–Condon state. The fluorescence of **1** is rather weak (quantum yield, approximately 0.002), supposedly due to fast intersystem crossing to a close-lying triplet level. Diimide **1** aggregates in acetonitrile and in aqueous medium, but aggregation is prevented by the presence of α-cyclodextrin (α-CD) due to complex formation between α-CD and the butyl substituents of **1**. Diimide **1** displays unusual spectral characteristics in aromatic hydrocarbon solvents, which can be attributed to ground state complex formation between **1** and the aromatic compound. The addition of benzene, toluene and *p*-xylene to an acetonitrile solution of **1** was followed by fluorescence spectroscopy, and the data obtained were treated as simple 1 : 1 equilibria. Association constants were calculated for the complexes between **1** and the aromatic compounds. The magnitude of the constants suggests that these ground state complexes are basically of the π-stacking type, with no charge transfer character. In the excited state, however, the complexes show polar character, suggesting that electron transfer occurs following excitation.

Keywords: *N,N*-Dibutyl-1,4,5,8-naphthalenediimide; Photophysical properties

1. Introduction

Renewed interest is being shown in phthalimide and naphthalimide derivatives, including biological (local anaesthetics [1], DNA-cleaving agents [2], tumoricidals [3]) and non-biological (optical brighteners [4], Lucifer dyes [5]) applications. We have systematically studied the photophysics of these compounds, starting from simple phthalimides [6,7], and increasing the complexity of the molecules from a photophysical point of view by enhancing the contribution of the π,π* transition via the introduction of larger aromatic rings vicinal to the imide moiety, as in naphthalimide derivatives [8,9].

Our investigations and the studies of other workers [10] have helped to clarify the origin of the different photophysical behaviour of different phthalimide and naphthalimide derivatives. Thus, for the simple phthalimides (Scheme 1), the lowest singlet excited state has typical n,π* character, which accounts for the low absorption coefficient and very weak fluorescence observed [6,7]. For naphthalimides, however, the lowest excited state is predominantly π,π* in character, although significant differences have been found in the behaviour of the three types of naphthalimide (Scheme 1). Whereas 1,2- and 2,3-naphthalimides fluoresce with high to moderate quantum yields (ϕ_f) in acetonitrile solution



Scheme 1.

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($\phi_f \approx 0.8$ and 0.2 respectively), the fluorescence of 1,8-naphthalimides is quite weak ($\phi_f \approx 0.06$) [8,10]. These trends have been explained by the fast intersystem crossing from the excited π,π^* singlet state to a close-lying n,π^* triplet state, which is particularly efficient in the case of the 1,8-naphthalimides.

In order to improve the current knowledge of the photophysics of naphthalimides, we have investigated the effect of addition of a second imide group to the structure of 1,8-naphthalimides, as in 1,4,5,8-naphthalenediimides (Scheme 1). Reports on the photophysics of such compounds are scarce in the literature [11]. In this report, we present the photophysical characterization of *N,N*-dibutyl-1,4,5,8-naphthalenediimide (compound **1**). Studies on the self-aggregation of **1** in solution are also presented, as well as the formation of molecular complexes between **1** and aromatic hydrocarbons. Only a few reports can be found in the literature describing complex formation between 1,4,5,8-naphthalenediimide derivatives and electron donors [12–14].

There has been increasing interest in 1,4,5,8-naphthalenediimide derivatives in recent years, mainly due to their electron acceptor properties [15,16], which make them suitable for a series of applications, including the formation of Langmuir–Blodgett films [17], the preparation of electrically conducting materials [18,19], π-stacked materials absorbing in the near-IR region [20] and nanotube-like structures [21] and as models for the photosynthetic reaction centre [22]. These novel applications for derivatives of **1** fully justify the investigation of their photophysical properties.

2. Experimental details

2.1. Materials

N,N-Dibutyl-1,4,5,8-naphthalenediimide (**1**) was prepared by the condensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride (Aldrich) with *N*-butylamine (Aldrich), as described in the literature [13]. The product was characterized by elemental analysis and IR, proton nuclear magnetic resonance (^{1}H NMR) and ^{13}C NMR spectroscopy, which were in agreement with the literature values.

All organic solvents employed were of spectroscopic grade. Aqueous solutions were prepared with fresh doubly distilled water. α-Cyclodextrin (α-CD) was purchased from Aldrich.

2.2. Methods

The UV–visible absorption spectra were recorded in a Beckman DU-7 or Hitachi U-2000 spectrophotometer. Fluorescence spectra were obtained in an LS-100 (PTI-Canada) or SPEX-DM-3000F fluorometer (frontal face mode), and were computer corrected using the software provided with the apparatus. All measurements were carried out at 25 ± 1 °C.

Fluorescence quantum yields (ϕ_f) were calculated relative to the area of the corrected emission spectrum of quinine bisulphate in 0.1 N $HClO_4$ ($\phi_f = 0.546$) [23] or *N*-butyl-1,8-naphthalimide in acetonitrile ($\phi_f = 0.065$) [8].

The effect of the addition of aromatic hydrocarbons on the fluorescence of **1** was studied by adding aliquots from a 1×10^{-5} M solution of **1** in the hydrocarbon solvent to an acetonitrile solution of **1** at the same concentration. Association constants (K_s) were determined from Benesi–Hildebrand plots for a 1 : 1 binding model (Eq. (1)) [24]

$$\frac{1}{(I/I_0-1)} = \frac{1}{(\Phi/\Phi_0-1)} + \frac{1}{(\Phi/\Phi_0-1)K_s}\,\frac{1}{[\mathrm{HC}]} \qquad (1)$$

where I/I_0 is the observed fluorescence intensity ratio for diimide **1** in the presence (I) and absence (I_0) of the aromatic hydrocarbon, ϕ/ϕ_0 represents the quantum yield ratio between complexed (ϕ) and free (ϕ_0) diimide, K_s is the association constant for complex formation (M^{-1}) and [HC] is the molar concentration of the hydrocarbon.

In cases in which a non-emissive complex is formed, Eq. (1) is transformed into a simpler Stern–Volmer-like expression for static fluorescence quenching (Eq. (2)) [24], where the terms have the same meaning as in Eq. (1)

$$\frac{I_0}{I} = 1 + K_s[\mathrm{HC}] \qquad (2)$$

3. Results

3.1. Spectral characteristics of 1

The absorption and fluorescence emission spectra of diimide **1** in acetonitrile are shown in Fig. 1. The remarkable

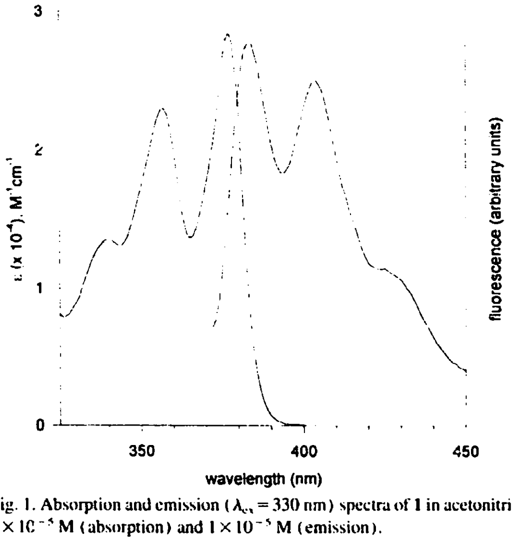


Fig. 1. Absorption and emission ($\lambda_{ex} = 330$ nm) spectra of **1** in acetonitrile: 3×10^{-5} M (absorption) and 1×10^{-5} M (emission).

Table 1
Absorption and fluorescence data for **1** in solvents of different polarity

Solvent	λ_{max}^{abs} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max}^{em} (nm) [a]	$\phi_f \times 10^2$
Water	388	12900 [b]	480	2.0
Methanol	378	27000	391	0.18
Acetonitrile	377	28300	386	0.18
CH_2Cl_2	379	30200	388	0.19
CCl_4	378	28400	–	–
Cyclohexane	376	29600	384	0.08
Benzene	381	22300	436	2.68

[a] λ_{ex} = 330 nm.
[b] Estimated value.

mirror image relationship observed between the spectra should be noted, with a small Stokes shift (620 cm^{-1} in acetonitrile). The absorption spectrum has an intense, short-wavelength band (λ_{max} = 235 nm, not shown) and a structured band at lower energies with three maxima at 377, 357 and 340 nm, with absorption coefficients (ϵ) of 28 300, 23 500 and 13 900 M^{-1} cm^{-1} respectively. The emission spectrum shows three maxima at 429, 407 and 386 nm, with an intensity ratio of 0.4 : 0.9 : 1. The excitation spectrum of **1** (not shown) is identical to the absorption spectrum.

The absorption and fluorescence data of **1** in solvents of different polarity are given in Table 1. The spectra in different solvents are almost identical with that in Fig. 1 for acetonitrile (except for water and aromatic solvents, see below), with three absorption maxima and three emission maxima which are mirror images of each other (only the values for the most intense peaks are given in Table 1). The rather small sensitivity of the absorption and fluorescence maxima of **1** to changes in solvent polarity should be noted. The maxima (not taking into account the values in water and aromatic solvents) vary in the range 376–379 nm (absorption) and 384–391 nm (emission), and the small shifts observed do not seem to have any correlation with the polarity of the solvent. (Compare, for instance, the values in acetonitrile with those in cyclohexane; a very small shift (1–2 nm) is observed, despite the large difference in the polarity of these two solvents.)

The fluorescence of compound **1** is rather weak, as shown by the low quantum yields (Table 1). We were unable to measure the fluorescence lifetime of compound **1**, which is shorter than the resolution of our equipment, but the value reported recently by Green and Fox [11] (τ_f < 20 ps), together with the low quantum yields, indicates a fast deactivation of the S_1 state, probably via intersystem crossing to a close-lying triplet state, as observed with other related 1,8-naphthalimide derivatives (see Section 4).

3.2. Aggregation of 1

The effect of increasing the concentration of diimide **1** in acetonitrile on the emission spectrum is shown in Fig. 2. At concentrations above 2×10^{-5} M, a new structureless band appears, with a maximum near 500 nm, suggesting the formation of excimers of **1**. It should be noted that the lifetime of the singlet excited state (less than 20 ps) is too short for diffusional processes to occur, so that the excimer in this case must be formed by direct excitation of a ground state dimer (or perhaps trimer, etc.). Therefore, we can conclude that diimide **1** self-associates in acetonitrile with a critical concentration of approximately 2×10^{-5} M. It should be added that no spectral effect of this kind was observed with the corresponding monoimide (1,8-*N*-butylnaphthalimide) in acetonitrile, up to its solubility limit.

The emission spectrum of **1** in water is compared with that of an acetonitrile solution in Fig. 3. The structured emission band of monomeric **1** observed in most solvents is replaced by a broad, structureless band in water, displaying a maximum at 480 nm and a shoulder at 430 nm. The maximum is

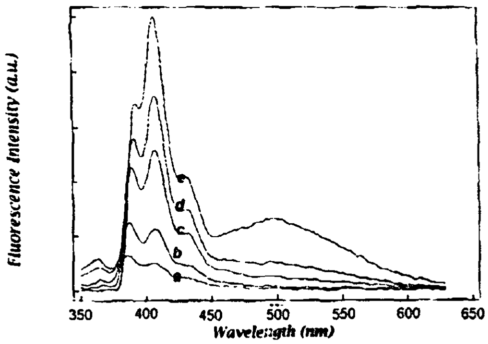


Fig. 2. Emission spectrum of **1** in acetonitrile as a function of the concentration of **1**: (a) 4.6×10^{-6} M; (b) 1.8×10^{-5} M; (c) 4.9×10^{-5} M; (d) 7.7×10^{-5} M; (e) 1.5×10^{-4} M. λ_{ex} = 330 nm.

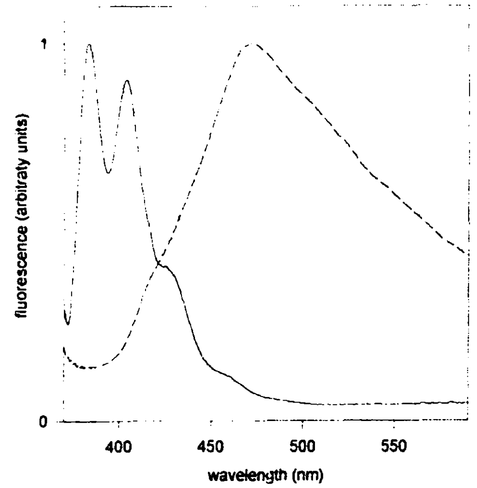


Fig. 3. Emission spectra of **1** in pure water (– – –) and in the presence of 0.05 M α-CD (· · ·). The spectrum in acetonitrile (———) is also shown for comparison. The spectra have been rescaled to the same maximum intensity. [**1**] = 5×10^{-6} M. λ_{ex} = 330 nm.

red shifted by almost 100 nm relative to most of the solvents studied. These results show that, in water, diimide **1** forms ground state aggregates. The shape of the emission spectrum of **1** does not change in the concentration range 1×10^{-6}–1×10^{-5} M, so that a critical concentration lower than 10^{-6} M is inferred.

Additional proof for the aggregation of **1** is provided by the behaviour of the emission spectrum in water containing 0.05 M α-CD. The spectrum (Fig. 3) is basically that of the monomeric diimide, very similar to that observed in acetonitrile. α-CD presumably prevents aggregation by forming an inclusion complex with the butyl substituents of **1**, thus preventing the close approach of two diimide molecules. A detailed study of the complex formation between compound **1** and cyclodextrins will be reported elsewhere [25].

3.3. Complex formation with aromatic hydrocarbons

The emission spectrum of naphthalene diimide **1** in aromatic hydrocarbon solvents shows a broad band red shifted relative to that observed for monomeric **1** (Fig. 4, Table 2), and similar to that observed in water. This exciplex-like emission suggests the formation of ground state complexes of **1** with aromatic hydrocarbons, at least in conditions of low concentration of the aromatic compound, when the short lifetime of singlet **1** does not allow it to diffuse before emission.

Table 2
Fluorescence data for **1** in aromatic hydrocarbon solvents compared with the data in acetonitrile

Solvent	λ_{max}^{em} (nm) [a]	$\phi_f\times10^2$	K_s (M^{-1})
Acetonitrile	386	0.18	–
Benzene	436	2.68	0.80
Toluene	481	2.48	1.4
p-Xylene	522	2.33	1.8

[a] λ_{ex} = 320 nm.

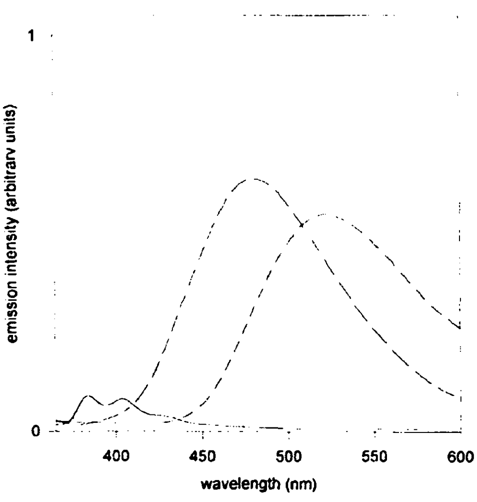


Fig. 4. Emission spectra of **1** in acetonitrile (———), benzene (· · ·), toluene (– – –) and *p*-xylene (– · –). [**1**] = 1×10^{-5} M. λ_{ex} = 330 nm.

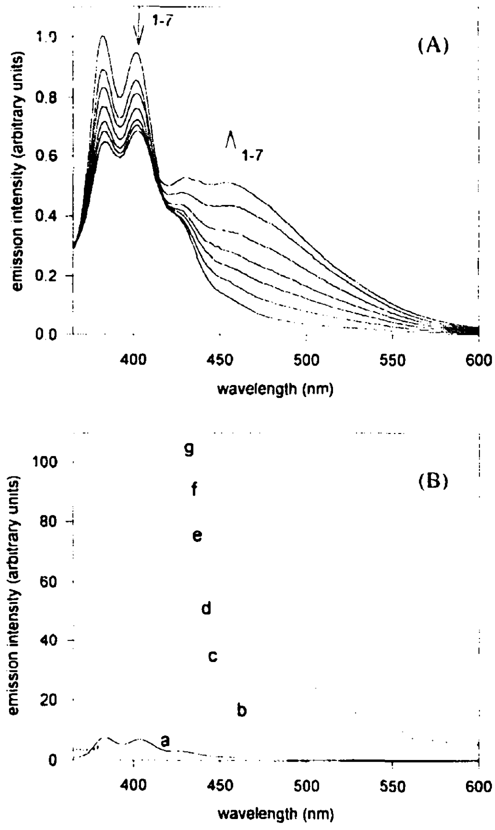


Fig. 5. Effect of the addition of benzene on the fluorescence emission of **1** in acetonitrile solution ([**1**] = 1×10^{-5} M; λ_{ex} = 320 nm). (A) Concentration of benzene: 1, 0 M; 2, 0.11 M; 3, 0.22 M; 4, 0.33 M; 5, 0.43 M; 6, 0.54 M; 7, 0.74 M. (B) Percentage of benzene (v/v): (a) 0%; (b) 75%; (c) 83%; (d) 88%; (e) 93%; (f) 97%; (g) 100%.

The most interesting feature is the behaviour of the emission spectrum when the aromatic compound is added stepwise to an acetonitrile solution of **1**. As shown in Fig. 5(A), the addition of benzene at concentrations up to 1 M (approximately 10% v/v) causes a decrease in the fluorescence due to monomeric **1**, with the concomitant appearance of a new, broad band with a maximum at approximately 460 nm. The pattern of the spectrum suggests a 1 : 1 equilibrium, with an isoemissive point at 418 nm. Treatment of the data according to the Benesi–Hildebrand equation (Eq. (1)) gives a good linear fit, from where the equilibrium constant for ground state complexation (K_s = 0.80 M^{-1}) was obtained (Table 2).

The fluorescence of the band due to **1** complexed to benzene is quite weak in polar solvents such as acetonitrile and benzene–acetonitrile mixtures up to 50% benzene (v/v). In the range 75%–100% benzene, however, a curious phenomenon is observed (Fig. 5(B)): there is a sharp increase in the

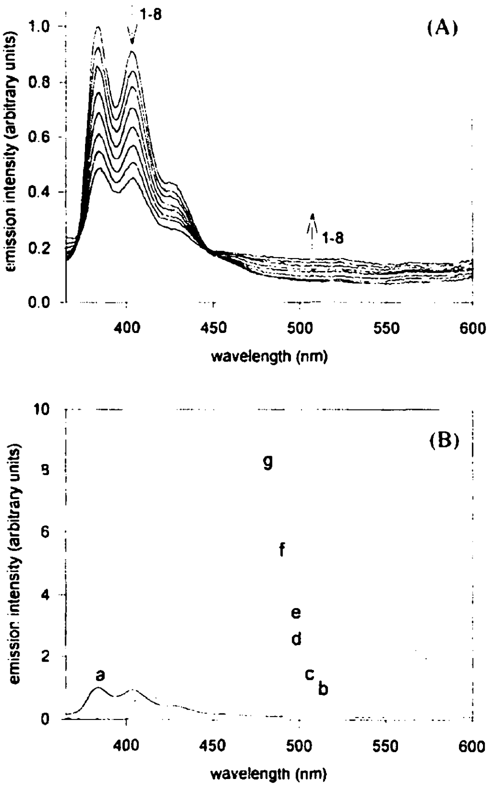


Fig. 6. Effect of the addition of toluene on the fluorescence emission of **1** in acetonitrile solution ([**1**] = 1×10^{-5} M; λ_{ex} = 320 nm). (A) Concentration of toluene: 1, 0 M; 2, 0.075 M; 3, 0.15 M; 4, 0.29 M; 5, 0.43 M; 6, 0.63 M; 7, 0.86 M; 8, 1.2 M. (B) Percentage of toluene (v/v): (a) 0%; (b) 83%; (c) 88%; (d) 92%; (e) 94%; (f) 97%; (g) 100%.

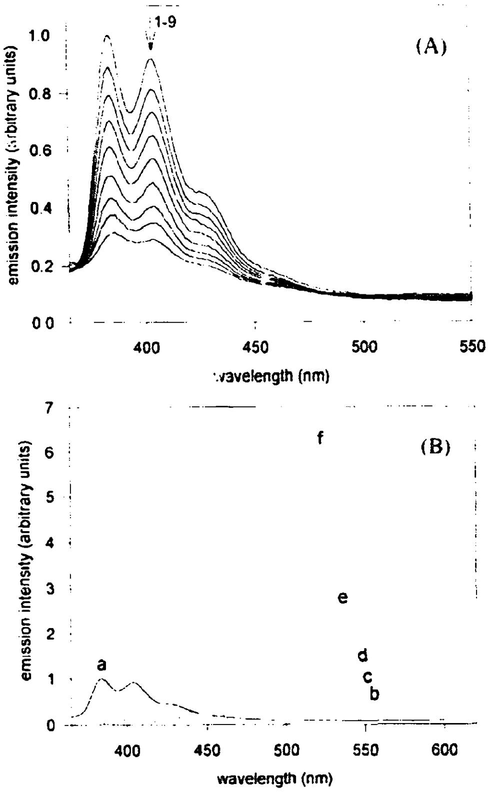


Fig. 7. Effect of the addition of *p*-xylene on the fluorescence emission of **1** in acetonitrile solution ([**1**] = 1×10^{-5} M; λ_{ex} = 320 nm). (A) Concentration of *p*-xylene: 1, 0 M; 2, 0.065 M; 3, 0.13 M; 4, 0.22 M; 5, 0.34 M; 6, 0.52 M; 7, 0.71 M; 8, 0.92 M; 9, 1.4 M. (B) Percentage of *p*-xylene (v/v): (a) 0%; (b) 88%; (c) 92%; (d) 94%; (e) 97%; (f) 100%.

complex fluorescence intensity, the quantum yield varying from $\phi_f \approx 0.002$ at 50% benzene to $\phi_f \approx 0.027$ in pure benzene. At the same time, the emission maximum is blue shifted from 460 nm at low benzene proportions to 436 nm in pure benzene.

The addition of toluene to an acetonitrile solution of **1** follows a similar pattern, as shown in Fig. 6. At toluene concentrations up to 1.2 M (12% toluene v/v), an equilibrium is observed with an isoemissive point at 444 nm (Fig. 6(A)), but the complex emission is much weaker ($\phi_f < 10^{-3}$) than that observed for benzene within this polarity range. The equilibrium constant ($K_s = 1.4$ M^{-1}) was obtained from the Benesi–Hildebrand plot, which is linear in this concentration range.

For amounts of toluene in the range 15%–50% (v/v), only a very faint fluorescence is observed, without a defined maximum; however, at 75% toluene, a broad band due to the complex appears with a maximum at approximately 520 nm. The maximum is gradually blue shifted and the quantum yield increased as the amount of toluene is further increased, reaching 481 nm ($\phi_f = 0.025$) in pure toluene (Fig. 6(B)).

The addition of *p*-xylene to an acetonitrile solution of **1** is shown in Fig. 7. In contrast with the benzene and toluene complexes, the complex between **1** and *p*-xylene does not show any detectable fluorescence in polar medium, but its presence can be deduced from the fluorescence quenching of monomeric **1** by *p*-xylene (Fig. 7(A)) in the concentration range 0–2 M (approximately 25% v/v). In this case, when the new species formed is non-emissive, it is more appropriate to use a simplified form of the Benesi–Hildebrand equation, which leads to a Stern–Volmer-like expression describing static fluorescence quenching (Eq. (2)). A plot of the data in Fig. 7(A) according to Eq. (2) is linear, giving $K_s = 1.8$ M^{-1}.

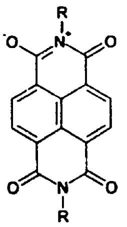
No detectable fluorescence can be seen in the range 30%–75% *p*-xylene (v/v), but above 80% *p*-xylene a broad emission band begins to appear, with a maximum at approximately 560 nm. With a further increase in the amount of *p*-xylene, this band becomes more intense and the maximum is blue shifted to 522 nm ($\phi_f = 0.023$) in pure *p*-xylene.

4. Discussion

4.1. Spectral characteristics of 1

The very good mirror image relationship observed between the absorption and emission spectra in most solvents, and the presence of well-defined vibrational structure in the spectra, show that diimide **1** is a rigid molecule, whose emissive state undergoes only slight changes from the initially formed Franck–Condon state. The small solvent sensitivity shown by **1** provides further evidence for the rigid structure of the molecule, which has no flexibility to undergo conformational changes when the polarity of the environment is altered.

The value of the absorption coefficient of **1**, of the order of 3×10^4 M^{-1} cm^{-1}, allows the assignment of π,π^* character to the $S_0\rightarrow S_1$ transition. The transition energy obtained from the intersection of the absorption and emission spectra is 75 kcal mol^{-1}. This value is lower than that for the analogous compound *N*-butyl-1,8-naphthalimide [8], where the transition energy for the first transition (π,π^*) is 81 kcal mol^{-1}. The decrease in transition energy shows that the addition of a second imide group helps to stabilize the π,π^* state, suggesting a strong π conjugation between the carbonyl groups and the naphthalene ring in **1**. It is probable that resonance structures, such as **I** and **II**, contribute considerably to the S_1 state (and to the ground state to a lesser extent) of **1** giving it pyrenoid character.



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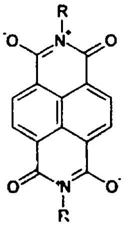

II

The quantum yields given in Table 1 for diimide **1** in most solvents are approximately one order of magnitude lower than the values for *N*-butyl-1,8-naphthalimide [8]. In acetonitrile, for instance, $\phi_f = 0.065$ for the monoimide, but only 0.0018 for the diimide.

With these results, we can conclude that the fluorescence quantum yields for naphthalenic imides decrease in the order 1,2-naphthalimides > 2,3-naphthalimides > 1,8-naphthalimides > 1,4,5,8-naphthalenediimides. The most probable explanation for the low quantum yield of diimide **1** is the fast intersystem crossing to a triplet level, as proposed by Wintgens et al. [10] for 1,8-naphthalimides and by Green and Fox [11] for *N,N*-didodecyl-1,4,5,8-naphthalenediimide, an analogue of **1**.

Wintgens et al. [10] suggested the existence of an upper triplet n,π^* state (T_2) close in energy ($\Delta E\approx 2$ kcal mol^{-1}) to the singlet π,π^* state of 1,8-naphthalimides. Green and Fox [11], on the other hand, could not detect any triplet level close in energy to the singlet state for the dodecyl diimide (they found an S_1–T_1 gap of 27 kcal mol^{-1}), and proposed that the fast intersystem crossing in diimides, such as **1**, could be promoted by vibrational coupling, or by means of an efficient spin–orbit coupling mechanism involving the four carbonyl groups. However, the conclusions of Green and Fox [11] were based on triplet–triplet absorption experiments, and it cannot be ruled out that a $T_1\rightarrow T_n$ absorption (with $n>2$) was observed, with the T_2 level remaining undetected.

In conclusion, our results reinforce the idea that a rapid intersystem crossing process occurs for the deactivation of the singlet excited state of 1,8-naphthalimides and 1,4,5,8-naphthalenediimides. However, the mechanism of this process is not clear at present.

4.2. Aggregation of 1

Because of the very short lifetime found for the singlet state of 1,4,5,8-naphthalenediimides [11], we believe that the excimer-like emission observed with the diimide **1** in water and in concentrated acetonitrile solution is due to the direct excitation of ground state aggregates, although it is not clear whether dimers or higher aggregates are formed. The same phenomenon has been observed for structurally related compounds, such as pyrene [26], which aggregates in aqueous solution, and *N,N'*-bis(2,5-di-tert-butylphenyl)-3,4:9,10-perylenediimide, which aggregates in ethanol with a critical concentration of 2×10^{-4} M [27]. This value is one order of magnitude higher than the critical concentration found for diimide **1** in acetonitrile ($C=2\times10^{-5}$ M), suggesting that naphthalenediimides have a higher tendency to aggregate than the corresponding perylenediimides. Furthermore, the fluorescence quantum yield of aggregated **1** is approximately one order of magnitude higher than that of monomeric **1** (Table 1), whereas the opposite effect has been found for perylenediimides, where molecular aggregation causes a substantial decrease in ϕ_f [27].

Extensive ground state aggregation in water has also been observed by Penneau et al. [20] for the anion radical form of 1,4,5,8-naphthalenediimides similar to **1**. They attributed the phenomenon to intermolecular π-stacking interactions, which are probably also responsible for the ground state association observed for **1** in this paper.

In water, diimide **1** is found in the aggregated form at concentrations as low as 1×10^{-6} M. These aggregates collapse in the presence of excess α-CD, which probably complexes with the substituent butyl groups of diimide **1**, thus preventing the packing of diimide molecules. Complex formation has been observed between α-CD and *N*-butyl-1,8-naphthalimide [28], a result which can be explained only if the butyl group is included in the cyclodextrin cavity, since the naphthalene ring is too bulky for inclusion in the small α-CD cavity.

4.3. Complex formation with aromatic hydrocarbons

The spectral behaviour of diimide **1** in pure aromatic solvents is quite distinct to that in most other solvents (Table 1, Fig. 4), with the presence of a broad, excimer-like emission. The behaviour of the fluorescence spectrum when the aromatic compound is added slowly to an acetonitrile solution of **1** can be divided into three distinct parts (Figs. (5)–(7)). At low concentrations of the aromatic (less than 10% v/v), when the polarity of the medium is essentially that of an acetonitrile solution, the shape of the spectrum suggests an equilibrium between monomeric **1** and a weakly emitting excimer (or non-emitting in the case of *p*-xylene). At intermediate concentrations of the aromatic (10%–75% v/v), only a very weak fluorescence due to the exciplex is observed (or no fluorescence at all in the case of *p*-xylene). At higher concentrations of the aromatic compound (more than 25% v/v), where the polarity of the medium eventually becomes more like that of the aromatic solvent, a new emission band appears, which becomes stronger and is simultaneously blue shifted with a further increase in the proportion of the aromatic, reaching a maximum intensity in the pure aromatic solvent.

The sudden increase in this broad, intense emission band at a high proportion of aromatic hydrocarbon can be explained simply as the effect of the decreasing polarity on the emission of the complex, which is virtually the only species present at high concentrations of the aromatic (more than 75%). The complexes have a low value of ϕ_f in polar environments, with a high proportion of acetonitrile, but become strongly fluorescent in apolar media, with a high proportion of the aromatic solvent.

A similar phenomenon has been observed by Chow and coworkers [29,30] for the fluorescence of dibenzoylmethanatoboron difluoride in the presence of aromatic solvents, a behaviour which was attributed to excited state molecular association with the aromatic compound.

In our case, we believe that the exciplex is generated by direct excitation of a ground state complex, for the following reasons.

1. The lifetime of singlet **1**, as determined by Green and Fox [11] (less than 20 ps), is shorter than the time necessary for the molecules to diffuse towards each other.
2. The fluorescence data for **1** in Fig. 5(A), Fig. 6(A) and Fig. 7(A) give a good linear fit when treated according to the equation for a 1 : 1 equilibrium, showing that a double equilibrium is not involved. Therefore, the trends observed must be either due to a purely static or a purely dynamic process.
3. Charge transfer (CT) complexes have been previously reported between *N,N*-dihexyl-1,4,5,8-naphthalenediimide (a compound very similar to **1**) and a series of electron donors [13]. CT complexes have also been found in the case of polyimides containing the 1,4,5,8-naphthalenediimide nucleus alternated with an electron donor unit [14].

We observed a CT transition, with $\lambda_{max} = 480$ nm and $\epsilon \approx 500$ M^{-1} cm^{-1}, in the absorption spectrum of **1** in acetonitrile in the presence of a 100-fold excess of pyrene (an orange solution is obtained), similar to that reported by Kheifets et al. [13] for the dihexyl derivative of **1**. However, we did not detect any sign of a CT band for **1** in the presence of benzene, toluene or *p*-xylene, indicating that, unlike pyrene and other stronger electron donors, the ground state complexes with these aromatics do not have CT character.

The association constants for the complexes between **1** and the aromatic compounds increase (Table 2) from 0.8 M^{-1} (benzene complexes) to 1.4 M^{-1} (toluene complexes) and 1.8 M^{-1} (*p*-xylene complexes). Although this increase follows the order of increasing electron donor character of the aromatic compound, the differences are small (compare, for instance, the value of 20 M^{-1} reported for the pyrene CT complex with the dihexyl analogue of **1** [13]). The small difference between the values of K_s supports the occurrence of π stacking rather than CT interactions in the ground state of these complexes [31].

When the complexes are excited, electron transfer from the aromatic hydrocarbon to the diimide seems to occur, as judged by the spectral characteristics of the exciplex emission. The exciplex-like bands observed at high proportions of the aromatic compounds undergo a blue shift of 30–40 nm on going from 75% to 100% (v/v) of the aromatic. In addition, the maximum in the pure aromatic solvent is shifted from 436 nm in benzene to 481 nm in toluene and 522 nm in *p*-xylene. This high solvent sensitivity indicates a polar character for the emitting species, which may be due to the relaxation to a CT excited state following excitation, with the transfer of one electron.

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