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Spectroscopic properties of aromatic dicarboximides
Part 3: Substituent effect on the photophysical properties of *N*-phenyl-2,3-naphthalimides

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Abstract

In the present article we describe the effect of the substitution on the photolysis properties of a series of *N*-phenyl-2,3-naphthalimides. It is found that the decrease in the electron-donating character of the substituent on the *N*-phenyl ring changes the fluorescence emission from a weak, broad and short-lived long-wavelength (LW) emission into a structured and long-lived fluorescence localized at the short wavelengths (SW) which behaves like that of the unsubstituted 2,3-naphthalimide. Both SW and LW emissions can be observed in some cases.

The different results can be explained on the basis of a three-level scheme where the vibrationally relaxed Franck–Condon state populates two different excited states, the one (SW) emitting at short wavelengths, and the other (LW) emitting at long wavelengths. The substitution on the phenyl ring influences mainly the energy of the LW excited state. The nature of the substituent on the *N*-phenyl ring has a determining influence also on the internal conversion process by virtue of the solvent- and rotation-induced pseudo-Jahn–Teller coupling of the two excited states.

Keywords: *N*-Phenyl-2,3-naphthalimides; Fluorine derivatives; Hammett's correlation; Dual fluorescence

1. Introduction

In a previous article [1] concerned with various naphthalimides, it was shown that the substitution of the hydrogen bound to the nitrogen atom by a methyl group hardly changes the spectroscopic properties of the molecule. For example, 2,3-naphthalimide (N-H) and *N*-methyl-2,3-naphthalimide (N-Me) have similar absorption and fluorescence maxima at 355 nm and 390 nm respectively in acetonitrile solution and their fluorescence quantum yield and lifetime are 0.25 and 8.0 ns respectively.

Substitution of the hydrogen in N-H by a phenyl group leads to a dramatic change in the spectroscopic properties. In the case of the *N*-phenyl-2,3-naphthalimide (N-Ph), a dual emission is observed [2]. In acetonitrile, the emission found at short wavelength (SW) appears at the same location as the emission of N-H, but it is weak ($\Phi_f \approx 10^{-4}$) and short lived ($\tau < 50$ ps) while the emission at long wavelength (LW) is broad and centred at 495 nm, stronger ($\Phi_f \approx 0.005$) and longer lived ($\tau \approx 1.3$ ns) than the SW emission. Both emissions are only slightly sensitive to the solvent polarity: for instance, the LW state exhibits only a 3.4 D change in its dipole moment when a non-polar solvent is substituted by a polar solvent. The LW excited state has been demonstrated to have a geometry in which the *N*-phenyl and the naphthalimide moieties are coplanar [2]. Kinetic analysis showed that the SW excited state is not the precursor of the LW excited state, and that they both originate from the Franck–Condon excited state. We have proposed [2,3] that the vibrationally relaxed Franck–Condon excited state undergoes solvent and geometrical relaxation yielding two singlet excited states, the one emitting at SW and the other emitting at LW. The N atom may be partially pyramidalized in the SW excited state which is expected to lie close in energy to the relaxed Franck–Condon state. The planar geometry of the LW state enables an extended conjugation which lowers the energy of this excited state.

The aim of the present paper is to show that the same substituent on the *N*-phenyl ring of N-Ph may induce different effects depending on its position (i.e. *ortho*, *meta* or *para*). For this purpose, the phenyl ring bound to the nitrogen atom of the 2,3-naphthalimide skeleton has been substituted at various positions by fluorine atoms. Furthermore, these effects on the spectroscopic properties of *N*-phenyl-2,3-

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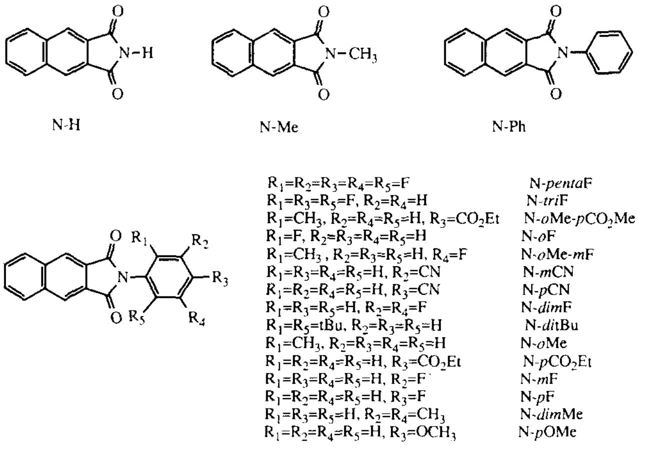
naphthalimides will be compared with the predictions of the model developed [3] for explaining the photophysical properties of N-Ph. In addition, the weak charge transfer character of the LW excited state is expected to be strongly enhanced by electron donating groups attached to the *N*-phenyl substituent by virtue of the electron-accepting property of the naphthalimide moiety.

2. Experimental details

Ethyl acetate (Prolabo, HPLC grade) and triacetin (Prolabo, RP) were used as received. The preparation, purification and characterization of 1*H*-benz[*f*]isoindole-1,3(2H)-dione (N-H) [4], 2-methyl-1*H*-benz[*f*]isoindole-1,3(2H)-dione (N-Me) [5], 2-phenyl-1*H*-benz[*f*]isoindole-1,3(2H)-dione (N-Ph) [6], 2-(2′-methyl-phenyl)-1*H*-benz[*f*]isoindole-1,3(2H)-dione (N-oMe) [3b], and 2-(2′,5′-di-*tert*-butyl-phenyl)-1*H*-benz[*f*]isoindole-1,3(2H)-dione (N-ditBu) [2] have been already described.

The other substituted *N*-phenyl-2,3-naphthalimides were prepared using the following general procedure. One equivalent of 2,3-naphthalenedicarboxylic acid (Aldrich) was intimately mixed with five equivalents of the appropriate substituted aniline (Aldrich), and the mixture was heated for 2 h at 180–200 °C. After cooling, the solid reaction mixture was ground down, added to an aqueous HCl solution (1 M) and kept at 60 °C for 0.5 h. The solid phase was then separated by filtration, washed with water, and kept at 60 °C for 0.5 h in an aqueous $NaHCO_3$ solution. After separation, the solid was purified by column chromatography over silica gel (elution with CH_2Cl_2), and the product was recrystallized from ethyl acetate. The different compounds were characterized by IR and nuclear magnetic resonance analysis.

The UV–visible absorption spectra were obtained with a Varian–Cary model 219 apparatus. Fluorescence spectra were recorded with a SLM–Aminco model 8000 apparatus. Fluorescence quantum yields of N-pentaF, N-oF, N-mF and N-Ph (Scheme 1) in oxygen–free solution of ethyl acetate were determined by comparison with the emission of N-H in an oxygen-free solution of acetonitrile, for which the value $\Phi_f = 0.27$ had been taken [1]. The emissions of the above four products have been recorded with the same experimental conditions, using a series of calibrated neutral density filters. These four compounds were taken as standards for measuring the fluorescence quantum yields of the other derivatives in the different range of quantum yields.



$R_1=R_2=R_3=R_4=R_5=F$	N-*penta*F
$R_1=R_3=R_5=F$, $R_2=R_4=H$	N-*tri*F
$R_1=CH_3$, $R_2=R_4=R_5=H$, $R_3=CO_2Et$	N-*o*Me-*p*CO_2Me
$R_1=F$, $R_2=R_3=R_4=R_5=H$	N-*o*F
$R_1=CH_3$, $R_2=R_3=R_5=H$, $R_4=F$	N-*o*Me-*m*F
$R_1=R_3=R_4=R_5=H$, $R_2=CN$	N-*m*CN
$R_1=R_2=R_4=R_5=H$, $R_3=CN$	N-*p*CN
$R_1=R_3=R_5=H$, $R_2=R_4=F$	N-*dim*F
$R_1=R_5=tBu$, $R_2=R_3=R_5=H$	N-*di*tBu
$R_1=CH_3$, $R_2=R_3=R_4=R_5=H$	N-*o*Me
$R_1=R_2=R_4=R_5=H$, $R_3=CO_2Et$	N-*p*CO_2Et
$R_1=R_3=R_4=R_5=H$, $R_2=F$	N-*m*F
$R_1=R_2=R_4=R_5=H$, $R_3=F$	N-*p*F
$R_1=R_3=R_5=H$, $R_2=R_4=CH_3$	N-*dim*Me
$R_1=R_2=R_4=R_5=H$, $R_3=OCH_3$	N-*p*OMe

Scheme 1.

Singlet lifetimes were measured by excitation with a frequency-tripled pulsed YAG laser (from B.M. Industries) with a 30 ps full width at half-maximum (FWHM), using the experimental set-up already described [2].

Variable-temperature measurements were carried out using a home-made temperature-regulated cell holder equipped with an external circulating bath. The temperature of the sample was measured directly inside the cell.

3. Results

Formula of the studied compounds are given in Scheme 1 and the photophysical data obtained in ethyl acetate are reported in Table 1.

3.1. Absorption

All the UV spectra of the studied compounds are structured in the 330–370 nm range and several of them are shown in Fig. 1. Locations of the absorption maxima are given in Table 1. Substitution of the hydrogen in N-H by a methyl group, or by a phenyl group, leads to a slight red shift of the absorption maximum: 353 nm for N-H compared with 354.5 nm for N-Me and 356 nm for N-Ph. Practically no change is observed in the absorption if the *N*-phenyl is substituted with an electron-donating group, such as methoxy (355.5 nm for N-pOMe). A minor bathochromic shift is observed when the phenyl ring is substituted with an electron-withdrawing group: 357 nm for N-pCO_2Et and 358 nm for N-pCN.

In addition to the moderate effect on the absorption maximum, the substituents also modify the shape of the absorption spectra in the 285–340 nm range. Thus, N-Ph has a more intense absorption than N-Me in this wavelength range (Fig. 1(a)) but *ortho* methyl substitution on the phenyl ring decreases the absorption; for instance, N-oMe and N-Me have almost the same absorption spectra. The presence of either an electron-donating group (N-pOMe) or an electron-withdrawing group (N-pCN) in the *para* position of the phenyl ring increases the absorption in the 285–340 nm range compared with that of N-Ph (Fig. 1(b)). On the contrary, the absorption spectra of N-mCN and N-Ph are nearly the same, while N-pentaF has an absorption very similar to that of N-Me.

3.2. Fluorescence

Fluorescence spectra of five *N*-(fluorophenyl)-2,3-naphthalimides in ethyl acetate are given in Fig. 2. The com-

Table 1
Spectroscopic data of the substituted 2,3-naphthalimides in ethyl acetate solution

Compound	σ	λ_{abs} (nm)	λ_f (nm)	Φ_f^{SW}	Φ_f^{LW}	τ ($\times 10^{-9}$ s)	Φ_f^{SW}/τ_{SW} ($\times 10^7$ s^{-1})	Φ_f^{LW}/τ_{LW} ($\times 10^7$ s^{-1})
N-H		353	380	0.23		7.8	2.9	
N-Me		354.5	381	0.18		7.5	2.4	
N-pentaF	+1.09 [a]	359	388	0.34		8.4	4.0	
N-triF	+0.41 [a]	357.5	385	0.31		7.7	4.0	
N-oMe-pCO$_2$Me	+0.35 [a]	356	384	0.13		3.7	3.5	
N-oF	+0.24 [b]	356	383	0.054		1.8	3.0	
N-oMe-mF	+0.17 [a]	356	384	0.066		2.4	2.8	
N-mCN	+0.68 [c]	357.5	389	0.070		3.0	2.3	
N-pCN	+0.63 [c]	358	389	0.040		2.2	1.8	
N-dimF	+0.68 [a]	357.5	388	0.0324		2.7	1.2	
			452		0.0076			
N-ditBu		355.5	382	0.0024	[d]	<0.75	>0.32	
N-oMe	−0.17 [b]	355.5	382	0.0078		0.9	0.87	
			472		0.0014			
N-pCO$_2$Et	+0.52 [c]	357	388	0.0041		1.65	0.25	
			465		0.0062	1.65		0.38
N-mF	+0.34 [c]	357	388	0.0018		1.9	0.09	
			480		0.0082	1.9		0.43
N-Ph	0	356	387	[d]		<0.05		
			495		0.0064	1.6		0.40
N-pF	−0.07 [e]	355.5	502		0.0056	1.4		0.40
N-dimMe	−0.14 [a]	355.5	507		0.0041	1.4		0.29
N-pOMe	−0.78 [e]	355.5	573		0.0006	0.21		0.28

[a] See text.
[b] Data from Taft [7].
[c] Data from Jaffé [8].
[d] Too weak to be quantified.
[e] Data from Brown and Okamoto [9].

plexity of the effect induced by the fluorine substituent on the phenyl group is visualized easily by the spectroscopic properties of the various fluorinated derivatives. In some cases, one observes only the SW emission band in the 370–420 nm range with a strong vibrational structure; in other cases only the broad and structureless LW band is found in the 420 and 600 nm range. A few compounds present both the SW and LW emissions.

The shape and the maximum of the emission spectra strongly depend on the number and the position of the fluorine atoms on the phenyl group. For instance, N-pF exhibits a broad emission centred at 502 nm and practically no SW emission can be detected. This LW emission at 502 nm is blue shifted to 480 nm in the case of N-mF which also has a weak SW fluorescence. In case of the 3,5-difluorophenyl derivative (N-dimF) the relative intensities of the SW and LW emissions are inverted: the SW emission has become predominant, and the LW emission is weak.

Compounds *ortho* substituted on the phenyl nucleus exhibit principally the SW fluorescence as already reported for N-ditBu [2]. Thus, N-oF presents a moderate SW fluorescence which is blue shifted by 5 nm to 383 nm by comparison with the emission of N-dimF; no LW emission could be detected in this case. Increasing the number of fluorine atoms on the *N*-phenyl substituent increases the efficiency of the SW emission and suppresses the LW emission: this is well demonstrated by the 0.31 and 0.34 fluorescence quantum yields determined for N-triF and N-pentaF respectively, as can be seen in Table 1. These values are even higher than those obtained for N-H and N-Me.

The location of the fluorescence given in Table 1 corresponds either to the second maximum of the SW emission or to the maximum of the broad LW emission. Accurate data for both the SW and LW emissions could be obtained for N-mF and N-pCO$_2$Et; approximate values of the LW emission were deduced for N-oMe and N-dimF; for the other compounds, only one of the two emissions could be characterized with sufficient accuracy.

The SW fluorescence spectra are structured and their shapes are mirror images of the absorption spectra. The different derivatives exhibit an SW emission slightly red shifted by 2–9 nm compared with that of N-H. With increasing electron-withdrawing character of the substituent the maximum of the fluorescence spectrum moves from 383 nm for N-oF to 385 nm for N-triF and to 388 nm for N-pentaF. Substitution with an *ortho*-methyl group induces a blue shift of the SW maximum, for instance from 388 nm for N-mF to 384 nm for N-oMe-mF.

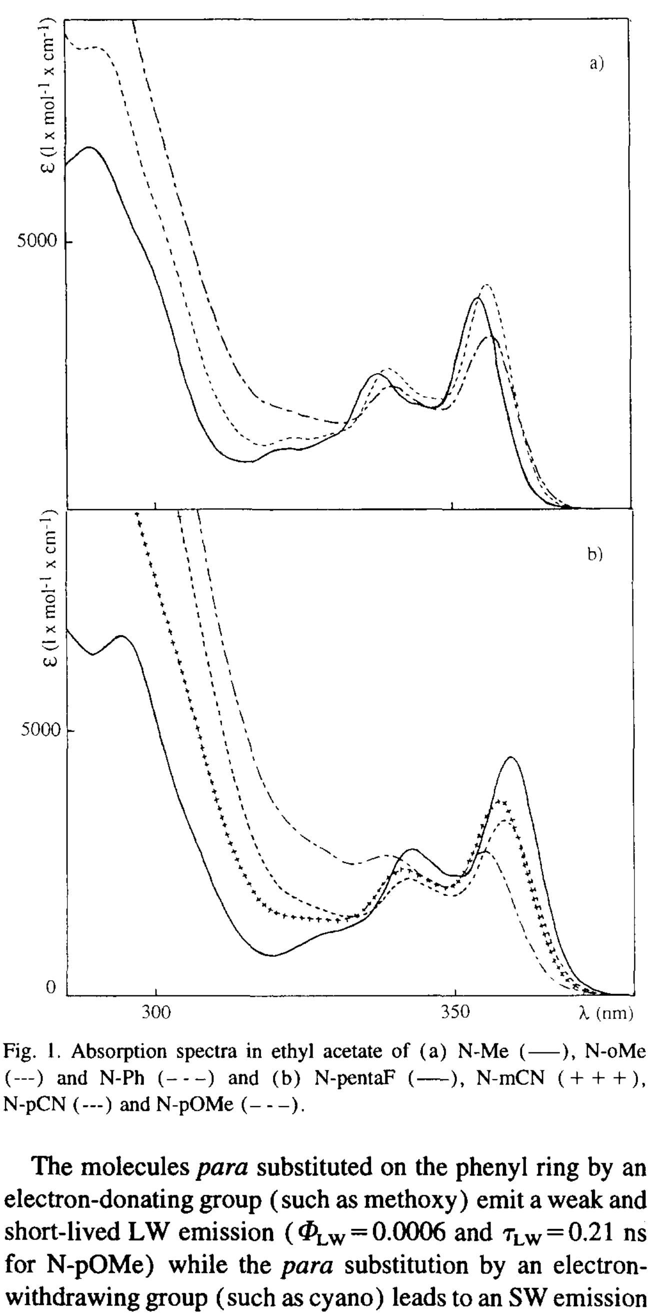


Fig. 1. Absorption spectra in ethyl acetate of (a) N-Me (——), N-oMe (---) and N-Ph (- - -) and (b) N-pentaF (——), N-mCN (+ + +), N-pCN (---) and N-pOMe (- - -).

The molecules *para* substituted on the phenyl ring by an electron-donating group (such as methoxy) emit a weak and short-lived LW emission ($\Phi_{LW}=0.0006$ and $\tau_{LW}=0.21$ ns for N-pOMe) while the *para* substitution by an electron-withdrawing group (such as cyano) leads to an SW emission with moderate fluorescence quantum yield and with a lifetime in the nanosecond time range ($\Phi_{SW}=0.04$ and $\tau_{SW}=2.2$ ns for N-pCN).

The influence of the viscosity was studied for N-mF in ethyl acetate and triacetin. Both solvents have similar polarities at room temperature, so that all the observed spectroscopic differences could be attributed to the effect of viscosity. Furthermore, the viscosity of triacetin can be increased considerably by a small decrease in the temperature, and in this temperature range the change in the rate of the activation-controlled processes can be neglected. Fig. 3 shows the spectra of N-mF in the 295 K–273 K temperature range for which the viscosity has increased from 25 cP to 140 cP [10]. During this temperature decrease, the SW emission increases by almost a factor of 2 while the LW emission grows by only 20%. Their fluorescence quantum yields at 295 K are 0.0034 and 0.010 respectively. On the contrary, the lifetimes of the two SW and LW emissions are identical and increase slightly from 2.05 ns at 295 K to 2.3 ns at 273 K.

4. Discussion

4.1. Absorption

The structured LW absorption band of the naphthalimides is associated with a $\pi\rightarrow\pi^*$ transition. In accordance with Hückel calculations [3] on the highest occupied molecular orbital (HOMO) → lowest unoccupied molecular orbital (LUMO) (π,π^*) transition, the *N*-phenyl group exerts little influence on the absorption associated with the naphthalimide moiety. The slight bathochromic shift of the absorption maximum observed for N-Ph as compared with N-H (or N-Me) reflects the weak interaction between the naphthalimide moiety and the *N*-phenyl ring, an interaction which is enhanced when the *N*-phenyl is substituted by electron-withdrawing groups; thus, this maximum is found at 353 nm for N-H, 356 nm for N-Ph, 357 nm for N-mF, 357.5 nm for N-dimF and N-triF, and 359 nm for N-pentaF. However, this interaction also depends on the dihedral angle between the plane of the naphthalimide part and the plane of the phenyl ring. X-ray analysis of N-Ph indicates that, in the solid state, the nitrogen is in the plane defined by the naphthalene ring and the carbonyl groups, and that the plane of the phenyl group makes a 59° angle with that of the naphthalimide moiety [11]. Any *ortho* substituent induces a steric hindrance, which increases this angle, and therefore reduces the overlap between the orbitals of the two moieties of the molecule. Thus, an *ortho* methyl group induces a weak hypsochromic effect as observed when comparing N-oMe-mF and N-mF which absorb at 356 nm and 357 nm respectively.

Transitions corresponding to the absorption in the SW range (i.e. 285–340 nm) are more sensitive to the substitution on the phenyl ring than those corresponding to the absorption at LWs. This is shown by the absorption spectra (Fig. 1) and by the results of Hückel calculations (Table 2) which indicate that the lowest (HOMO → LUMO) transition with (π,π^*) character is practically independent of the substituent, while the next (HOMO − 1 → LUMO) transition is an (n,π^*) state with definite charge transfer character. The UV absorption band corresponding to this $S_0\rightarrow S_2$ transition is expected to lie close to that of the $S_0\rightarrow S_1$ transition. A well-resolved absorption band attributed to this $S_0\rightarrow S_2$ transition was observed for *N*-phenyl-1,2-naphthalimide [3a]. In the case of *N*-phenyl-2,3-naphthalimides the overlap with other transitions makes difficult the identification of this $S_0\rightarrow S_2$ transition. However, such a band could be visualized by the change in the absorption spectra below 340 nm (Fig. 1). The importance of this transition with charge transfer character increases with the electron-donating ability of the phenyl

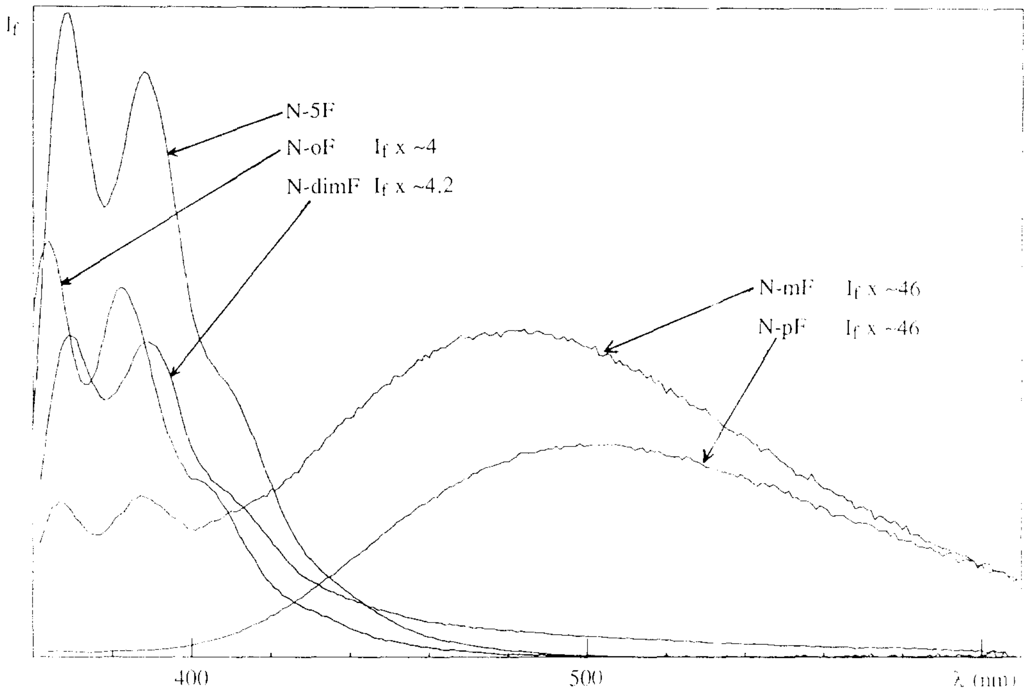


Fig. 2. Fluorescence spectra at room temperature of N-pentaF, N-oF, N-dimF, N-mF and N-pF in ethyl acetate.

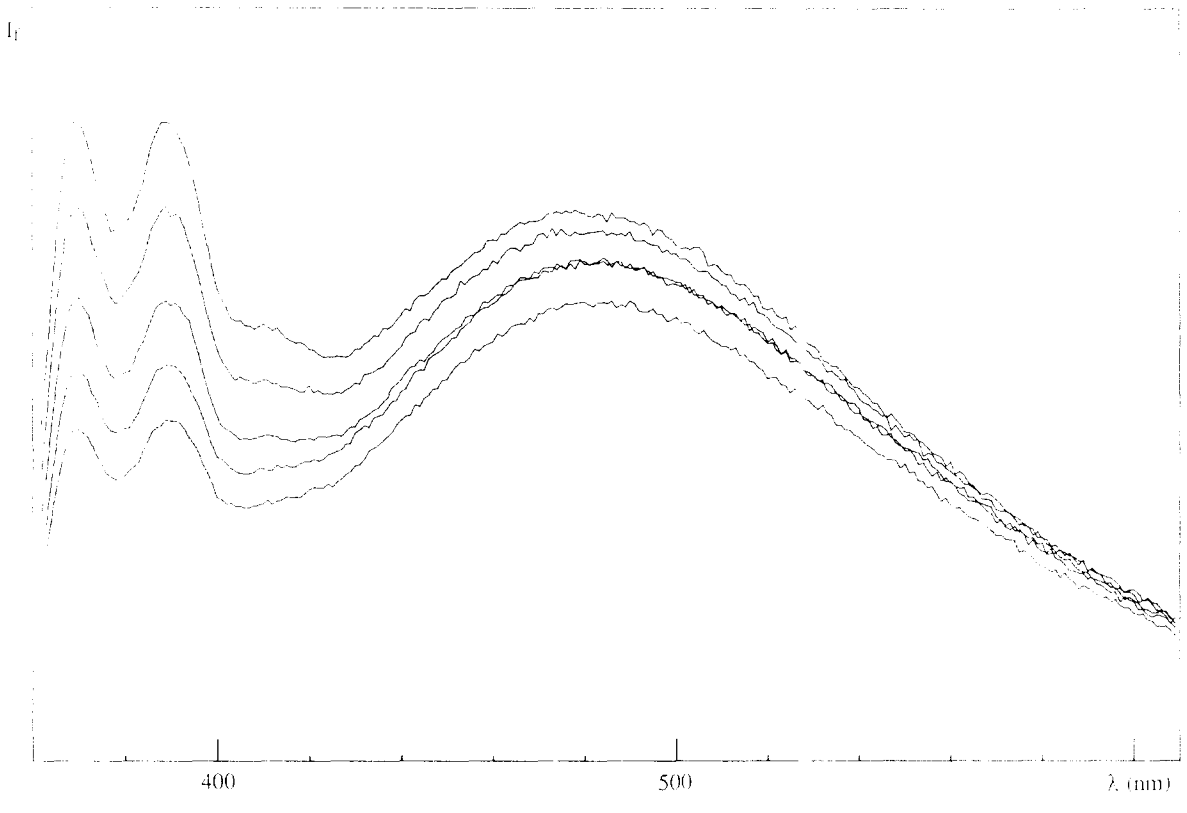


Fig. 3. Fluorescence spectra of N-mF in triacetin at 273 K, 277 K, 281 K, 289 K and 295 K.

substituent, and this can be seen by comparing the absorption spectra of N-Ph and N-pOMe. Concurrently, the Hückel calculations show that electron-donating substituents, for instance a methoxy group, lower the energy of the charge transfer (n,π^*) state below that of the (π,π^*) state (Table 2). With electron-withdrawing substituents the effect is the opposite and it slightly increases the energy of this state. For the fluorinated derivatives, a small gradual increase of the

Table 2
Energy in β units of the frontier molecular orbitals for several studied compounds

	N-H	N-Ph	N-pCN	N-pOMe	N-pF	N-mF	N-dimF	N-pentaF
LUMO+1	−0.4749	−0.4647	−0.4259	−0.4658	−0.4630	−0.4646	−0.4645	−0.4598
LUMO	−0.1511	−0.1511	−0.1511	−0.1511	−0.1511	−0.1511	−0.1511	−0.1511
HOMO	0.6629	0.6629	0.6629	0.6314	0.6629	0.6629	0.6629	0.6629
HOMO−1	1.0000	0.8106	0.7445	0.6629	0.8269	0.8131	0.8160	0.8426
HOMO−2	1.2119	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

HOMO − 1 energy can be observed with increasing the number of the fluorine atoms on the phenyl ring.

4.2. Fluorescence

The full characterization of the scheme in which the Franck–Condon excited state forms two other SW and LW excited states requires not only the knowledge of the quantum yield Φ_f and lifetime τ of both SW and LW emissions but also the estimation of the quantum yield Φ_{form} of formation of these two states from the Franck–Condon state. The fluorescence quantum yield of the two states can be expressed as $\Phi_f = \Phi_{form} k_f \tau$, where k_f is the radiative rate constant, k_f^{SW} and k_f^{LW} for SW and LW respectively. The fluorescence rate constants k_f^{SW} and k_f^{LW} can be taken as constant (but not necessarily identical) from one phenyl derivative to the other, and the ratio Φ_f/τ (Table 1) will vary in the same direction as the formation quantum yield Φ_{form} of the SW and LW states. However, the lifetime τ reflects the stability of the excited SW and LW states; any variation in τ will correspond to a modification of the rate of the different non-radiative deactivation processes, for instance the rotation of the phenyl group or the electronic inductive effect of the substituents.

The electron-donating and electron-withdrawing character of the substituents attached to a phenyl ring has been evaluated by several researchers and is generally characterized by the Hammett constants σ. Values of these constants are listed in Table 1. Discrepancies are found in the literature about the effect of some substituents: for the substituents studied here, the main diversity is observed when the fluorine atom is in the *para* position; in such a position, it has been claimed to act as an electron donor (the parameter σ is then given to be -0.07 [9]) as well as an electron-withdrawing entity (in which case σ is evaluated to be $+0.06$ [8]). However, it can be seen from these values that the electronic effect is small in both approximations. The fluorine atom in *N-para*-fluorophenyl-2,3-naphthalimide behaves here as an electron-donating species (vide infra). Fluorine atoms in the *ortho* and *meta* positions are reported, as expected, to act as electron-withdrawing groups. In case of the polysubstituted derivatives (N-dimF, N-triF, N-pentaF, N-oMe-mF and N-oMe-pCO_2Me) we have assumed that the effects of the substituents were additive.

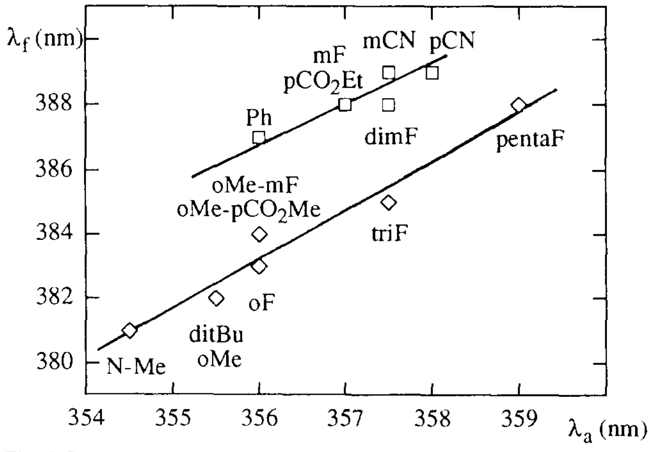


Fig. 4. Plot of fluorescence maximum vs. the absorption maximum of substituted *N*-phenyl-2,3-naphthalimides.

As already noticed for the absorption spectra, the different substituents on the phenyl ring slightly influence the SW spectra. Fig. 4, which gives the fluorescence maxima of different compounds as a function of the absorption maxima, shows that the compounds can be divided into two groups: one, which includes N-Me and the compounds substituted in the *ortho* position of the *N*-phenyl ring, exhibits a Stokes shift of about 2000 cm^{-1}; the other, which includes N-Ph and the compounds with no *ortho* substituent, has a Stokes' shift around 2200 cm^{-1}. The Stokes shift is usually related to the solvent and to the structural relaxation of the excited molecule. In the present case, the lowest Stokes shift value is obtained with the compounds substituted in the *ortho* position of the phenyl ring; this could be attributed to the steric hindrance induced by the substituent which hinders the rotation of the phenyl group and decreases the interaction between the naphthalimide moiety and the phenyl ring in the excited state.

4.2.1. *Ortho substitution on the N-phenyl ring: short-wavelength emission*

Ortho substitution may have two effects on the photophysical properties. First, as it hinders the rotation of the phenyl and prevents the molecule from reaching a planar structure, it makes the formation of the LW state difficult. Second, the substitution brings an electronic effect which may influence the relative importance of the formation of the SW and LW states and change the branching ratios of the primary processes. For instance, N-mF which has a free rotating *meta*-fluorophenyl substituent on the nitrogen atom emits at both SW and LW, while N-oMe-mF exhibits a fluorescence at only the SWs owing to the steric hindrance brought about by the *ortho*-methyl substituent. The electronic effect induced by the substituents will be developed subsequently.

The lifetime of the SW emission was found to be less than 50 ps at room temperature in the case of the unsubstituted N-Ph molecule. It was shown for methyl-substituted *N*-phenyl-1,2-naphthalimides [3a], and more recently for the three types of naphthalimides [3b], that an S_2 (n,π^*) state with strong charge transfer character lies close in energy to the lowest S_1 (π,π^*) excited state. The strong vibronic coupling which exists between these two excited states induced by solvent and geometrical relaxation leads to an efficient non-radiative deactivation process as it has been shown in other cases [12]. The presence of an *ortho* substituent on the *N*-phenyl ring limits its rotation and increases markedly the lifetime of the SW excited state: from less than 50 ps for N-Ph to 0.9 ns and 1.8 ns when the phenyl ring is *ortho* substituted by a methyl group or a fluorine atom respectively. The same trend is observed in the case of N-mF which exhibits an increase in lifetime from 1.9 ns to 2.4 ns caused by an additional *ortho*-methyl group on the phenyl ring (compound N-oMe-mF) and in the case of N-pCO_2Et for which the SW lifetime increases from 1.65 ns to 3.7 ns by adding an *ortho*-methyl group on the phenyl ring (compound N-oMe-pCO_2Me). The effect of the *ortho* substituent is also reflected in the increase of the fluorescence quantum yield.

4.2.2. *Electron-withdrawing groups on the N-phenyl ring*

Electron-withdrawing substituents on the phenyl ring increase markedly the lifetime and the formation quantum yield of the SW excited state. Thus, compounds with no rotational hindrance and substituted on the *N*-phenyl ring by electron-withdrawing groups (N-dimF, N-pCN, N-mCN) have SW lifetimes longer than 2.2 ns (Table 1). Electron-withdrawing substituents on the phenyl ring increase the energy gap between S_1 and S_2 which, consequently, decreases the interaction between these two states and limits the non-radiative deactivation processes. This is also illustrated with N-trif and N-pentaF which have lifetimes of the same order of magnitude (ca. 8 ns) as N-H, but more than four times longer than that of N-oF of somewhat similar steric hindrance. Thus, the electronic effect of the substituent is important in the deactivation process of the SW emitting state.

With compounds substituted in the *ortho* position by a methyl group, the addition of an electron-withdrawing substituent, for instance a fluorine atom in the *meta* position ($\sigma = +0.34$ [8]) or a carboethoxy group in the *para* position ($\sigma = +0.52$ [8]), as is the case with N-oMe-mF and N-oMe-pCO_2Me respectively, the Φ_f^{SW}/τ_{SW} value increases by a factor of 3 compared with that of N-oMe. A 33% increase in Φ_f^{SW}/τ_{SW} is also noticed for N-triF and N-pentaF as compared with N-oF, the former compounds exhibiting the highest values of the SW excited state formation. Such high values of the SW excited state formation reflect a decrease in the efficiency of the non-radiative deactivation processes from the Franck–Condon excited state for the compounds substituted by electron–withdrawing groups; thus, the electronic effect of the substituent is also important in the deactivation process of the Franck–Condon state. Strong vibronic interactions between S_2 and S_1 should also be responsible for the efficient internal conversion from the Franck–Condon excited state to the ground state as found for the SW internal conversion process.

The SW state formation quantum yield of N-pCN ($\sigma = +0.63$ [8]) and N-dimF (for which σ can be taken roughly as ca. 2×0.34 [8]), determined by the Φ_f^{SW}/τ_{SW} ratio, is found to be lower than that of N-oF ($\sigma = +0.24$ [7]) in spite of the strong electron-withdrawing character of the cyano and fluorine substituents. This unexpected result could be attributed to the steric effect of the *ortho* fluorine atom which prevents the molecule from becoming planar and favours the formation of the SW excited state at the expense of the LW excited state.

4.2.3. *Long-wavelength emission: electron-donating groups on the N-phenyl ring*

The broad LW emission centred around 495 nm for N-Ph originates from a configuration of the excited state in which the naphthalimide moiety and the phenyl ring are coplanar [2]. This excited state has a dipole moment which differs by only 3.4 D from that of the ground state. This value is ca. 50% higher than the corresponding value for the SW state. However, contrary to the SW state which belongs to a transition from the naphthalene to the π orbital of the carbonyl group, the LW state is assumed to have a net charge transfer character from the aniline moiety to the π^* orbital of the carbonyl group [3]. The dipole moment of this state has a direction opposite to those of the ground state and the SW excited state. Increasing the electron-donating character of the substituent on the phenyl ring results in a red shift of the LW emission and, at the same time, in the increase in the dipole moment $\Delta\mu$ between the ground state and the LW excited state [13] from 3.4 D for N-Ph to 11 D for N-pOMe. A blue shift of the maximum of the LW emission is observed (Table 1) when electron-withdrawing substituents are on the phenyl ring. This effect is illustrated in Fig. 5 where a straight line is obtained when plotting the fluorescence maximum of

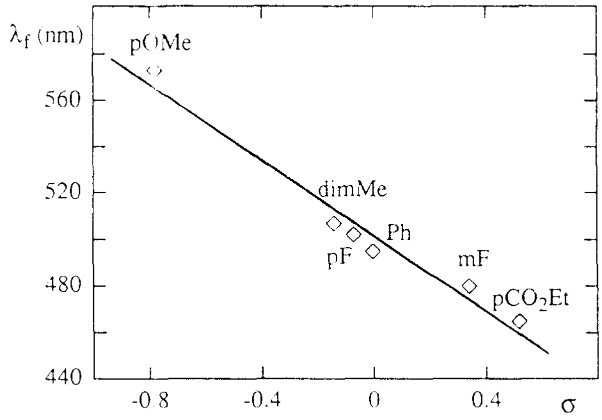


Fig. 5. Correlation between the LW fluorescence maximum and Hammett σ constant for substituted *N*-phenyl-2,3-naphthalimides.

the LW emission as a function of the characteristic Hammett σ constants of the electron-withdrawing or electron-donating property of the phenyl substituents. Such correlation between the LW emission and the inductive effect of the substituent on the phenyl ring makes a clear indication of the charge transfer character which involves the aniline part and the naphthalimide moiety (by the π^* orbital of the carbonyl group) of the corresponding transition.

The Φ_f^{LW}/τ_{LW} ratio appears to be only slightly influenced by the substitution on the phenyl ring. Thus, changing the electron-donating character of the *para* substituent of N-Ph from H ($\sigma = 0$) to OMe ($\sigma = -0.78$ [9]) causes a decrease in the Φ_f^{LW}/τ_{LW} ratio by only a factor of 1.4. With the other compounds of Table 1, for which Φ_f^{LW} can be measured, the formation of the LW state, as visualized by Φ_f^{LW}/τ_{LW}, decreases slightly when increasing the electron-withdrawing character of the substituent on the phenyl ring. According to the work of Strickler and Berg [14] and of Birks and Dyson [15], the fluorescence rate constant k_f is expected to depend on the wavelength of the absorption and emission. Since the position of the SW fluorescence practically does not vary from one compound to the other, its rate constant k_f^{SW} remains the same. On the contrary, k_f^{LW} could change considerably with the substitution since the position of the emission, in ethyl acetate solution, varies from 465 nm to 573 nm for the series of the studied compounds. Correction of the Φ_f^{LW}/τ_{LW} ratio with the calculated variation in k_f^{LW} is not satisfactory since it does not agree with the experimental results for all the compounds; thus, if the decrease in Φ_f^{LW}/τ_{LW} for N-pOMe compared with N-Ph could be due to the k_f^{LW} variation, this is not the case for N-dimMe.

Contrary to the Φ_f^{LW}/τ_{LW} ratio, the lifetime of the LW state depends on the type of substituent and its position on the ring. For instance, in ethyl acetate solution, τ_{LW} decreases from 1.9 ns for N-Ph to 0.21 ns for N-pOMe. However, the lifetime of N-pOMe is also sensitive to the solvent polarity and decreases from 0.41 ns ($\lambda_f = 540$ nm) in diethyl ether to 0.21 ns ($\lambda_f = 573$ nm) in ethyl acetate and to 0.095 ns ($\lambda_f = 598$ nm) in acetonitrile. These changes in the LW lifetime can be attributed to the decrease in the energy gap between the polar excited state and the ground state (compare the corresponding λ_f values), leading to larger Franck–Condon factors, that is to say to higher internal conversion rates and, consequently, to shorter lifetimes and smaller Φ_f^{LW} values (energy gap law [16,17]).

The effect of the electron-donating or electron-withdrawing substituent on the photophysical properties of the LW state can be explained on the basis of the Hückel calculations which show that the electronic system of the phenyl group is involved in the HOMO-1 → LUMO transition but only weakly in the HOMO → LUMO transition. A donor substituent in the *para* position of the phenyl group enhances the charge transfer from the aniline moiety to the π^* orbital of the carbonyl group and therefore reinforces the charge transfer character of the LW state. As a consequence, it decreases the energy of the LW state as compared with the non-substituted molecule and induces simultaneously a red shift of the emission and a decrease in the fluorescence quantum yield. The reverse is expected with electron-accepting substituents.

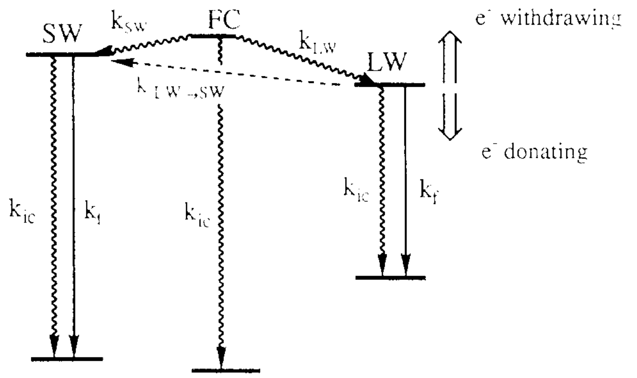
4.2.4. Dual short-wavelength and long-wavelength fluorescence emission

Several of the compounds studied here present dual emission in ethyl acetate. For N-ditBu and N-oMe the LW emission is weak owing to the *ortho* substitution on the phenyl ring (vide supra). In the case of N-Ph, it was found [2] that the lifetimes of the SW and LW fluorescence emissions were different from each other by three orders of magnitude (Table 1). A different behaviour is observed for the SW and LW emissions of N-pCO$_2$Et and N-mF which have the same lifetime at room temperature; this feature occurs in other solvents too. There are two possibilities which can explain such phenomena: (i) an equilibrium exists between the SW and LW excited states; (ii) an irreversible transition occurs from one state to the other and the latter decays with a rate constant greater than the rate constant of its formation from the precursor.

Increasing the viscosity of the medium by using triacetin as solvent increases, in the case of N-mF, the formation of both SW and LW excited states, although differently, at the expense of the Franck–Condon non-radiative deactivation processes. Thus, the ratio Φ_f^{SW}/τ_{SW} increases from 0.9×10^6 s^{-1} in ethyl acetate to 1.7×10^6 s^{-1} in triacetin, while Φ_f^{LW}/τ_{LW} varies only slightly (from 4.3×10^6 to 4.9×10^6 s^{-1}) from one solvent to the other.

The results are different from those obtained by similar experiments with N-Ph in glycerol–ethanol solutions [2]: when the viscosity increased, both the SW fluorescence quantum yield and its lifetime increased. The increase in the lifetime is due to the reduced internal conversion rate of the SW state; however, the quantum yield of formation of the two states remained approximately constant.

Temperature-dependent measurements were carried out in triacetin with N-mF in order to elucidate the relationship existing between the LW and SW excited states. Decreasing the temperature from 295 K to 273 K changes the viscosity of the triacetin solution from 25 to 140 cP and increases the SW and LW states fluorescence quantum yields. However, during the same measurements, one finds that Φ_{form}^{LW} remains constant while Φ_{form}^{SW} increases by a factor of 1.6. Similar experiments carried out in the same temperature range, but in ethyl acetate solution, do not change the formation quantum yields of the SW and LW states, indicating that the results obtained in triacetin can be attributed to the change in the solvent viscosity. At room temperature, both the SW and the LW excited states decay monoexponentially with the same lifetime. When the viscosity of the solvent is increased, the decay of the LW state fluorescence remains monoexponential. This is not the case with SW, the fluorescence of which decays now biexponentially with a long-lived component identical to that found for the LW state, and a short-lived component shorter than the lower limit (less than 0.2 ns) of



Scheme 2.

our instrumentation. A similar dual fluorescence with a short-lived component could be observed also but at low temperature ($T \leqslant 220$ K) with both N-mF and N-pCO_2Et in butyronitrile and diethyl ether solution. This behaviour indicates that the long component of the SW emission originates from the partial repopulation of SW by the LW excited state. For this process to occur, the SW and LW levels must be close in energy (thermodynamic condition) and the solvatation energy must be small (kinetic condition).

The energy diagram presented in Scheme 2 is similar to that proposed [2] previously, in that the vibrationally relaxed Franck–Condon excited state populates both SW and LW with the difference that, in the case of N-Ph, the two SW and LW excited states are not kinetically connected. According to the molecules studied here, the energy of the LW excited state is sensitive to the substitution on the phenyl ring and can be lowered or raised by electron-donating or electron-attracting substituents respectively. Thus, electron-withdrawing substituents such as a *meta*-fluoro or a *para*-carbethoxy group do raise the energy level of the LW state and bring it close to that of the SW state, thus enhancing the LW to SW transition since the process has become energetically more favourable. Further increase in the electron-withdrawing character of the substituent, which occurs for instance in the case of *para*-cyano substitution or on putting additional fluorine atoms on the phenyl ring, increases gradually the energy of the LW state (to become eventually even higher than that of the Franck–Condon state), because the electronic effect of the substituent is quite the contrary of the electron transfer required in the formation of the LW state. This causes *N*-phenyl naphthalimides substituted with groups of strong electron-withdrawing character to exhibit no LW emission. On the contrary, increasing the electron-donating character of the substituent on the phenyl ring lowers the energy of the LW state and decreases the quantum yield of its formation.

5. Conclusion

The spectroscopic properties of *N*-phenyl-2,3-naphthalimides substituted on the phenyl ring can be explained with a three-level scheme in which two SW and LW excited states are populated from the vibrationally relaxed Franck–Condon state. The internal conversion processes of the three excited states strongly depend on the electronic properties of the substituent on the phenyl ring: strong electron-withdrawing groups decrease the efficiency of these processes and increase the SW fluorescence efficiency of the molecule; in contrast, strong electron-donating groups lead to a single broad but weak charge transfer LW emission. The substitution also modifies the energy of the excited LW state and, for substituents with moderate electron-attracting character, the LW and SW excited states become close in energy and the molecule exhibits a dual fluorescence.

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