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Influence of Substituents on the Spectroscopic and Photochemical Properties of Naphthalimide Derivatives

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ABSTRACT

The spectroscopic and photochemical properties of seven derivatives of 1·8-naphthalimide have been studied. The influence of the substituents on light absorption, fluorescence and photostability were evaluated. The best results were obtained when the substituent is an amino group on the 4-position of the naphthalimide nucleus. Copyright © 1996 Elsevier Science Ltd

1 INTRODUCTION

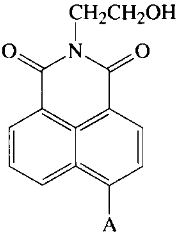
Polyatomic molecules represent a complex quantum chemical system which may be treated as a set of interacting sub-systems, excitation resulting in the formation of different orbital nature and multiplicity. The orbital nature of the electronic states is determined not only by the orbital structure of the sub-system, but also by their mutual positions in the molecule, thus determining the spectral and photochemical properties of the compounds. Study of the spectral luminescence and the photochemical characteristics of the molecular system is of considerable significance for the prediction of some important parameters, which could then enable products with defined spectral and photochemical properties to be synthesised.

Derivatives of 1,8-naphthalimide have been reported as fluorescent dyes for synthetic polymers and textiles materials,[1–3] in fluorescent sun collectors,[4] as liquid-crystal additives,[5] as fluorescent markers in medicine and biology[6] and in laser technology.[7]

We have previously reported the synthesis and properties of a range of naphthalimide dyes.[2,8,9]

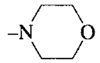
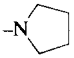
In this work we present results concerning the absorption, luminescence and photochemical properties of naphthalimide dyes having the general formula **I** and an evaluation of the effect of substituents in the 4-position of the naphthalimide moiety.

Compounds **I·2–7** (Table 1) were synthesized by condensation of 4-bromo-1,8-naphthalic anhydride and monoethanolamine, and subsequent replacement of the bromo substituent by the appropriate amine.[10]



I

TABLE 1
Naphthalimide Derivatives

Compound	I.1	I.2	I.3	I.4	I.5	I.6	I.7
A	Br	$-NH_2$	$-NHCH_3$	$-N(CH_3)_2$	$-NHCH_2CH_2Ph$		

2 RESULTS AND DISCUSSION

2.1 Spectral properties

The absorption spectra of the dyes were recorded on a Perkin-Elmer 554 spectrophotometer and fluorescence spectra on a Jobin-Yvon JY3D spectrofluorimeter, using methanol as solvent.

The compounds may be treated as a combination of two sub-systems; viz. the naphthalene moiety and a fragment including the two C=O groups linked through the NCH_2CH_2OH group.

Replacement of the bromo substituent in dye **I·1** by a secondary or a tertiary amino group causes a considerable change in the spectroscopic properties, due to interaction resulting from the electron-donating character of the amino group and the electron-accepting character of the carbonyl group. The main perturbation is due to the amino group;[11] there is a red shift of 86–141 nm and absorption now occurs in the visible within the range 388–443 nm for dyes **I·2–I·7**.

TABLE 2
Spectroscopic Properties of the Naphthalimides

Compounds	*I·1*	*I·2*	*I·3*	*I·4*	*I·5*	*I·6*	*I·7*
λabs (nm)	302	430	432	412	432	388	443
ϵ (l mol^{-1} cm^{-1})	9800	10900	13600	10700	15000	17300	19500
λfl (nm)	370	526	526	526	528	530	528
$\Delta\nu$ (cm^{-1})	6085	4239	4137	5260	4209	6906	3634
E (S1) (kJ mol^{-1})	354	244	246	247	244	255	242
ϕ fl		0·59	0·80	0·05	0·90	0·05	0·09
ϕ d.10^3		7·2	1·6	1·4	3·4	2·1	2·9

A considerable bathochromic shift is also observed in the fluorescence spectra relative to **I·1**, the maxima being in the range 526–528 nm (Table 2). Whilst substitution of only one hydrogen atom of the amino group does not significantly change the absorption and the fluorescence maxima (dyes **I·3** and **I·5**), the presence of a tertiary amino group results in a hypsochromic shift of 18 nm in **I·4** compared to **I·2**.

The low value of the fluorescence quantum yield of **I·4** is due to the decrease in coplanarity of the molecule, originating from steric factors.

For derivatives **I·6** and **I·7**, the resonance effect of the 4-substituent leads to a red shift and increased intensity of the band, which is polarized in the direction of extended conjugation.

2.2 Photochemistry of the dyes

The photoreactivity of the compounds in ethanol solution was investigated using a monochromatic radiation at 254 nm. The change of concentration of the dyes was followed by liquid chromatography (HPLC). The column was a C18 reverse phase column and the mobile phase was methanol–water 90/10.

The quantum yield was calculated using the formula:

$$\phi = \frac{k \cdot V}{2{\cdot}3 \cdot \epsilon_{254} \cdot l \cdot P_0}$$

ϕ = quantum yield
k = rate constant (s^{-1})
V = volume of irradiated solution (1·5 . 10^{-3} litre)
ϵ = molar extinction coefficient at 254 nm
l = radius of the reactor
P_0 = intensity of the emitted light from the UV lamp (Einstein/s)

With the exception of compound **I·2**, the degradation quantum yield was approximately the same for all the compounds, and varied between $1 \cdot 10^{-3}$ and $7 \cdot 10^{-3}$.

3 CONCLUSIONS

When the present results are compared with those previously obtained with other derivatives of 1·8-naphthalimide in which the substituent on the nitrogen atom was $CH_2CH{=}CH_2$ or $CH_2CH_2NH_2$,[2,12] the following observations can be made:

- the compounds have good photostability;
- the photostability does not depend on the nature of the substituents;
- the best values for the fluorescence quantum yield are always obtained when the 4-substituent is an unsubstituted or monosubstituted amino group.

In this present study, the compounds **I·3** and **I·5** were those which had the best properties for their use as dyes for textile or polymeric materials.

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