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Photochemistry of Some 1,8-naphthalic Anhydride Derivatives

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ABSTRACT

Derivatives of 1,8-naphthalic anhydride have been synthesized and their spectroscopic and photochemical properties studied. Whilst these compounds have a good photostability, only derivatives with a primary or secondary amino group, had a good fluorescence quantum yield. © 1997 Elsevier Science Ltd

Keywords: Photochemistry, naphthalic anhydride derivatives.

INTRODUCTION

Derivatives of 1,8-naphthalimide have been described in the context of applications in dyeing synthetic polymers and textile materials [1,2], in sun energy collectors [3], as fluorescent tags for use in molecular biology [4], for potential photosensitising biological activity [5], and in liquid crystal displays [6]. The presence of an unsaturated polymerisable double bond in such compounds, enables them to be used in copolymerization processes with vinyl monomers forming a covalent bond in the polymer molecule [7–9].

This paper reports the synthesis and spectroscopic properties of three 4-allylamino-*N*-substituted 1,8-naphthalimides.

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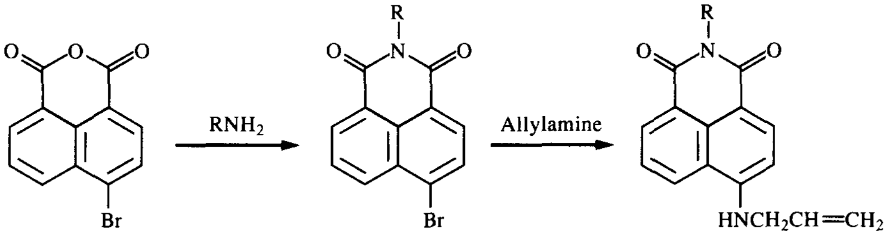
RESULTS AND DISCUSSION

Synthesis

The routes adopted for the synthesis of compounds **2** and **3** are given in the scheme



Compound 1 Compound 2 Compound 3

	R
2a and 3a	CH_3
2b and 3b	CH_2CH_3
2c and 3c	$C_6H_4CH_3$-*p*

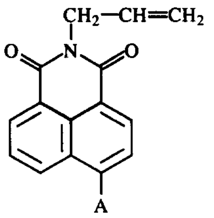
4-Bromo-1,8-naphthalic anhydride (**1**), synthesized as previously described [10], was reacted with an equimolar quantity of amine RNH_2 in boiling absolute ethanol for 5-6 h; under these conditions RNH_2 reacts mainly with the anhydride group. The subsequent step of the reaction was performed in 2-methoxyethanol, the reaction between the 4-bromo-*N*-substituted naphthalimide and allylamine was catalysed by $Cu_2SO_4 \cdot 5H_2O$ with addition of ethanolamine to remove HBr.

Three new naphthalimide derivatives containing an allylamino group at the 4 position, and with different substituents on the imide nitrogen atom, were prepared. Reaction yield and characterisation data of the dyes (compounds *3a–c*) and their bromo precursors (*2a–c*) are given in Tables 1 and 2.

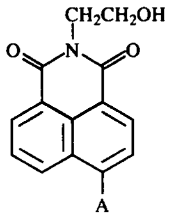
Spectral data

These compounds, as do all naphthalimide derivatives [11], present a combination of two sub-systems, namely, the naphthalene moiety and a fragment including the two C=O groups linked through the N—R group (Table 3).

It is of interest to note the influence of substituents R (on the nitrogen atom) and A on the naphthalene moiety. Table 4 shows the results obtained with groups I and II.



Group I



Group II

TABLE 1
Characterisation Data for Dyes **2** and **3**

Dye	*Yield (%)*	*Mp (°C)*	R_f^a	*Elemental analysis (%)*			
					C	*H*	*N*
2a	72	176–177	0.78	Calc:	53.79	2.75	4.82
				Found:	53.50	2.68	4.69
2b	78	157–158	0.62	Calc:	55.26	2.96	4.60
				Found:	55.11	2.90	4.49
2c	66	180–182	0.66	Calc:	62.29	3.27	3.82
				Found:	63.13	3.21	3.74
3a	62	108–110	0.53	Calc:	72.18	5.26	10.52
				Found:	72.10	5.21	10.34
3b	60	138–149	0.48	Calc:	72.85	5.71	10.00
				Found:	72.71	5.64	9.87
3c	58	106–107	0.38	Calc:	72.19	5.26	8.18
				Found:	77.08	5.20	8.10

[a] Using *n*-heptane–acetone (1:1).

TABLE 2
FT-IR and ^1H NMR Data for Dye **3**

FB	*FT-IR (KBr) cm*$^{-1}$	^1H *NMR δ (ppm) (CDCl*$_3$*)*
3a	3340 [ν(—NH)]	3.53 (*s*, 1H, CH_3)
	1670 [ν(C=O)]	4.00 (*s*, 1H, NH)
	1621 [ν(CH_2= =)]	5.10–5.50 (*m*, 2H, NCH_2)
	1382 [ν(CH_3)]	5.75–6.20 (*m*, 2H, CH_2=)
	1352 [ν(C—N imide)]	6.50–6.70 (*m*, 1H, CH=)
	702 [δ(CH—Ar)]	7.50–8.80 (*m*, 5H, arom)
3b	3310 [ν(—NH)]	1.15–1.40 (*t*, 3H, CH_3)
	1678 [ν(C=O)]	4.05 (*s*, 1H, NH)
	1619 [ν(CH_2)]	4.15–4.35 (*q*, 2H, CH_2—CH_3)
	1379 [ν(CH_3)]	5.20–5.60 (*m*, 2H, NCH_2CH=)
	1362 [ν(C—N imide)]	5.90–6.15 (*m*, 2H, CH_2=)
	704 [δ(CH—Ar)]	7.45–8.30 (*m*, 5H, arom)
3c	3296 [ν(—NH)]	1.67 (*s*, 1H, CH_3)
	1664 [ν(C=O)]	4.07 (*s*, 1H, NH)
	1614 [ν(CH_2=)]	4.70–4.85 (*m*, 2H, NCH_2)
	1375 [ν(CH_3)]	5.10–5.40 (*m*, 2H, CH_2=)
	1359 [ν(C—N imide)]	5.85–6.15 (*m*, 1H, CH=)
	701 [δ(CH—Ar)]	7.10–8.25 (*m*, 10H, Arom)

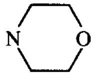
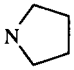
Comparison of the results in Tables 3 and 4 shows that the influence of the R substituent is negligible, particularly with respect to the important dye parameters, namely, absorption field, photodegradation, fluorescence quantum yield.

With respect to the absorption, the spectra of naphthalene derivatives indicate that the electronic transition corresponds to a polarisation along the short axis of the naphthalene moiety. Enhancement of this leads to an increase of the molecular absorption coefficient and shift of the absorption maximum to longer wavelength.

The extent of these two effects depends on the conjugation of the chromophore with the aromatic nucleus. Deviation from coplanarity decreases the interaction, with consequent displacement of the absorption maxima and decrease in intensity.

To determine the photostability of the compounds, we calculated the photodegradation quantum yield ϕ_D at low absorbance for actinic light, using an irradiation wavelength of 254 nm.

TABLE 3
Influence of the A Substituent on Spectroscopic and Photochemical Properties

	NH_2		$NHCH_3$		$N(CH_3)_2$					
Substituents	*I*	*II*	*I*	*II*	*I*	*II*	*I*	*II*	*I*	*II*
λ_{abs} (nm)	430	430	432	432	416	412	390	388	444	443
ϵ ($l\,cm^{-1}\,mol^{-1}$)	10 600	9800	13 200	13 600	9800	10 700	12 600	17 300	15 800	19 500
λ_{fluo} (nm)	518	526	522	526	520	526	522	530	525	528
ϕ_{fluo}	≈ 1	0.6	0.99	0.8	0.04	0.05	0.11	0.05	0.05	0.09
$\phi_D \times 10^3$	1	7	2.5	1.6	1.4	1.6	2.1	1	2.9	0.5

λ_{abs} = wavelength of absorption maximum; ϵ = molecular extinction coefficient; ϕ_{fluo} = fluorescence quantum yield; ϕ_D = photodegradation quantum yield.

TABLE 4
Absorption and Fluorescence Characteristics of Dyes **3** in Ethanol

	3a	*3b*	*3c*
λ_{abs} (nm)	434	434	428
ϵ_{max} ($l\,cm^{-1}\,mol^{-1}$)	9200	9100	10 100
λ_{fl} (nm)	526	524	526
E_{s1} ($kJ\,mol^{-1}$)	246.0	246.0	245.0
Stoke shift (cm^{-1})	4029	3957	4353
Φ_{fluo}	0.74	0.94	0.81
$\phi_D \times 10^3$	3.8	3.9	2.9

See Table 3 for key to symbols.

$$\phi_D = \frac{kV}{2.3\varepsilon_{254} l P_0}$$

where 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^{-1}). All the compounds showed good stability to light, and the variation of the quantum yield was not significant.

With respect to fluorescence, differences were very significant and only derivatives which had a primary or secondary amino group were of potential interest as dyes for textile or polymeric materials. The high values of the fluorescence quantum yield are relatable to the conjugation parameters noted above with respect to absorption.

Copolymerization of dyes with styrene

Mass copolymerization of styrene with compound 3 was investigated according to the previously described method: [12] 0.1 wt% AIBN was used as an initiator of radical polymerization. Polymerization was carried out at 80°C for 10 h and the amount of dye was 0.2 wt%. Transparent polymers showing a yellow-green fluorescence were obtained. It was observed that the absorption curves in toluene had identical absorption maxima, which indicated that no structural changes pertaining to the chromophoric system appeared during the polymerization. This makes possible the use of the standard curve method in determining the percentage of the dye chemically bound to the polymer chain. It was found that over 90% of the initially introduced dyes were chemically bound.

EXPERIMENTAL

IR spectra were recorded on Perkin-Elmer 1600 spectrophotometer, UV spectra on a Kontron model Uvikon 930 and fluorescence spectra on a Kontron model SFM 25.

For HPLC analysis we used a C_{18} column reverse phase and the solvent was a mixture of methanol–water and acetonitrile.

General method for synthesis of 4-bromo-*n*-substituted-1,8-naphthalimides (2)

A mixture of 4-bromo-1,8-naphthalic anhydride (0.01 mole) and amine RNH_2 (0.01 mole) was dissolved in 60 ml ethanol. The solution was refluxed for 6 h and after cooling to room temperature the liquor was poured into 250 ml water. The resulting crystals were filtered and dried.

General method for synthesis of 4-allylamino-*n*-substitutent-1,8-naphthalimides (3)

A mixture of 0.01 mole of dye **2**, 0.015 M allylamine, 0.01 mole triethylamine and 0.1 g $CuSO_4 \cdot 5H_2O$ was dissolved in 100 ml 2-methoxyethanol. The mixture was heated at 90°C for 5 h and then cooled to room temperature. The solid residue was filtered, washed with water and recrystallized from *o*-dichlorobenzene.

Polymerization

Styrene (10 g), the dye (0.02 g) and azoisobothironitrile (AIBN) (0.01 g) were heated in a nitrogen-purged glass ampoule for 10 h at 80°C. The resulting polymers were dissolved in toluene and precipitated with ethanol; this procedure was repeated several times and the polymers were finally dried under vacuum at 40°C.

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