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Synthesis of some Polymerisable 1,8-Naphthalimide Derivatives for use as Fluorescent Brighteners

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ABSTRACT

Four unsaturated 1,8-naphthalimide derivatives, which are fluorescent brightening agents, were synthesised. Their properties, Cielab colour coordinates, bleaching effect on polyamide fabrics and their ability to copolymerise with styrene have been determined. © *1997 Elsevier Science Ltd. All rights reserved*

Keywords: polymerisable fluorescent brighteners, unsaturated naphthalimide derivatives, chemical bleaching of polymers.

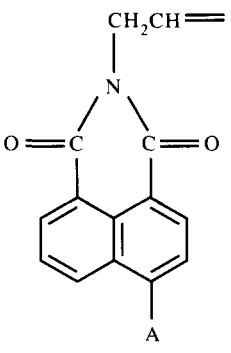
INTRODUCTION

4-Alkoxy and 4-acylamino derivatives of 1,8-naphthalimide are well established as fluorescent brightening agents (FBAs) for polymers with an intensive bluish–green fluorescence.[1–4] They have also been described as semi-products in the synthesis of derivatives with photosensitising or chemiluminescent properties,[5] and for markers in molecular biology.[6]

In previous papers, we reported the synthesis and properties of some 4-amino derivatives of N-allylnaphthalimide as dyes for polymers.[7–9] They possessed an intense yellow–green fluorescence and were able to copolymerise with styrene and acrylonitrile. Polymers thus obtained had resistance to wet treatment and solvents. On the basis that the whitening of the polymers was of importance as well as their coloration, and considering our previous investigations on polymerisable FBA–triazinylstilbene derivatives,[10,11] it was of interest to study the possibility of obtaining polymerisable FBA–naphthalimide derivatives.

RESULTS AND DISCUSSION

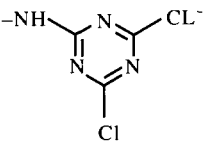
The 1,8-naphthalimide derivatives used in this study were of the general formula **1**, where A is:



(1)

1a = $-OCH_3$
1b = $-OC_2H_5$
1c = $-NHCOCH_2Cl$

1d =

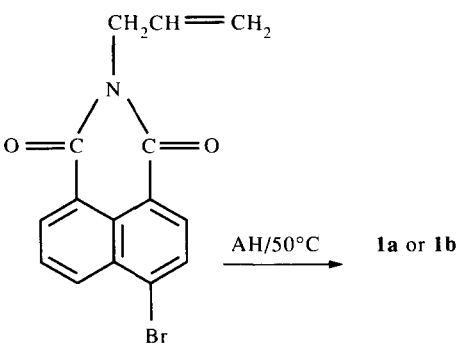


Synthesis of the fluorescent brightening agents

The route employed for compounds **1a** and **1b** is shown in Scheme 1, in which AH for **1a** was CH_3OH, and for **1b** C_2H_5OH.

The synthesis of 4-bromo-N-allylnaphthalimide has been reported previously.[7] The reaction was carried out in solution of the respective alcohol at reflux temperature and controlled by thin-layer chromatography (TLC). After 4 h the products **1a** and **1b**, respectively, were isolated in good yield (94–96%).

The synthesis of **1c** and **1d** was performed following Scheme 2; 4-amino-N-allylnaphthalimide was obtained as previously described.[7]



(1)

Scheme 1

The synthesis of **1c** was effected by reaction of 4-amino-N-allylnaphthalimide with chloroacetic chloride (CAC) in acetic acid at 50°C. The reaction was monitored by TLC and, after 2 h, **1c** was isolated in 90% yield.

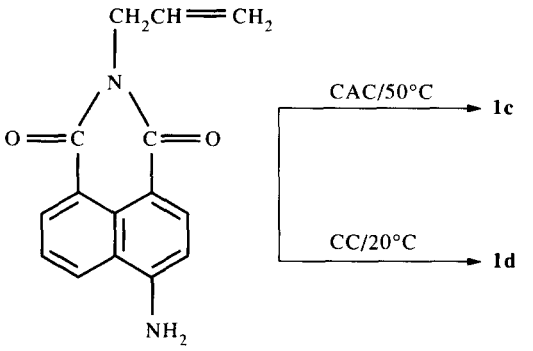
Compound **1d** was synthesised by reaction of 4-amino-N-allylnaphthalimide with cyanuric chloride (CC) in an aqueous acetone suspension at room temperature, the product being isolated after 2 h in 85% yield.

All compounds were characterised and identified by R_f, m.p., elemental analysis, UV/vis, IR and ^{1}H-NMR spectra. They had an intense blue fluorescence in solution. Relevant data are presented in Table 1 and in the Experimental section.

All compounds contained one unsaturated allylamino group, thus making them able to copolymerise with vinyl monomers. On the other hand, compounds **1c** and **1d** have in the 4 position a reactive $ClCH_2CO$– or dichlorotriazine group, thus making them capable of acting as reactive fluorescent whitening agents for textile materials.

Spectrophotometric investigations

The absorption and fluorescence spectra of the compounds were recorded in benzene and the data are presented in Table 2. All compounds had an



Scheme 2

TABLE 1
Characterisation Data for Compounds of Formula **1**

Compound	Yield (%)	M.p. (°C)	R_f[a]
1a	94	119–120	0.54
1b	96	131–133	0.50
1c	90	256–258	0.28
1d	85	145–148	0.34

TABLE 2
Absorption, Fluorescence, Stokes' Shift and Quantum Yield of Compounds of Formula **1**

	1a	**1b**	**1c**	**1d**
λ_{abs} (nm)	360	362	360	362
log ε	4.05	4.02	3.99	4.00
λ_{fl} (nm)	438	440	450	457
E_{s1} (kJ/mol)	296.3	294.8	291.9	290.5
Stokes' shift (cm^{-1})	4947	4897	5555	5742
ϕ_{fl}[a]	0.79	0.74	0.53	0.58

[a] Relative to quantum yield of quinine bisulphate.[12]

intense blue fluorescence with absorption maximum between 340 and 360 nm. In the absorption spectra of the compounds **1c** and **1d** a hypsochromic shift was observed in comparison to the maximum of 4-amino-N-allylnaphthalimide (430 nm).

The fluorescence maximum was between 438 and 440 nm for the 4-alkoxy derivatives and between 450 and 457 nm for the 4-acylamino derivatives. The energy of the excited state E_{s1} and the corresponding λ_{s1} were determined. There was no difference in the E_{s1} for the compounds, irrespective of their structure.

The fluorescence quantum yield was calculated using quinine bisulphate as standard (quantum yield 0.55[12]). The results are presented in Table 2. It can be seen that the 4-alkoxy derivatives have higher quantum yield than the 4-acylamino derivatives.

Colour assessment

Polyamide fabrics were whitened at 1% depth by the traditional method[13] and colour assessment of the materials was made using the "Texflach ACS" equipment in the "Datacolor" laboratory (Sofia). The results are given in Tables 3 and 4, where Cielab co-ordinates, chromaticity, luminance, CIE

TABLE 3
Whiteness, Tint Values for Classment and Yellowing Index Data of Compounds of Formula **1** on Polyamide

Compound	CIE whiteness	Tint classment	Yellowing index
1a	143.0	0.8 G1	−23.47
1b	130.7	−0.1 —	−18.39
1c	137.2	0.9 G1	−22.08
1d	146.0	1.2 G1	−27.41
without	65.1	−0.5 R1	6.25

TABLE 4
Colour Data of Compounds of Formula **1** on Polyamide

Compound	x^a	y^a	Y^b (%)	L^{*c}	a^{*c}	b^{*c}
1a	0.296	0.307	87.68	95.02	2.46	−12.33
1b	0.299	0.311	85.46	94.25	2.43	−9.91
1c	0.293	0.302	80.77	92.03	3.84	−14.22
1d	0.296	0.305	78.54	91.03	3.79	−12.64
without	0.319	0.338	80.47	92.11	0.47	−3.40

[a] x and y, Chromaticity.
[b] Y, Luminance.
[c] L^*, a^* and b^*, Cielab.

whiteness and tint values are presented. It is apparent that the whiteness increased two-fold with a weak greenish nuance (G1), that the luminance was good, and that the values for the yellowing index were satisfactory. From these data it was, however, not possible to make any discussion concerning structure–property relationships within the compounds.

Polymerisation with styrene

The ability of the synthesised FBA to copolymerise with styrene was investigated. The polymerisation was effected in bulk at 80°C in the presence of 0.1 wt.% of dibenzoylperoxide (DBP) as initiator and 0.1 wt.% of the corresponding FBA. The transparent, with blue fluorescence, polymers thus obtained were purified by several-fold precipitation with methanol. The intense fluorescence was retained in the polymers, thus indicating a covalent bond between the FBAs and the polymer. The UV/vis absorption spectra for the precipitated polymers showed the same λ_{max} as the parent FBA. It was established spectrophotometrically, using the standard calibration curve method, that more than 85% of the initial amount of the FBAs in the monomeric mixture was incorporated into the polymer molecule, which was enough to provide a very good whiteness.

EXPERIMENTAL

Materials, analysis and equipment

All melting points were determined on a "Boetius PHMK" apparatus without correction. TLC was performed on silica gel plates (Fluka F_{60} 254, 20×20 cm^2, 0.2 mm) using *n*-heptane:acetone 1:1 as eluent.

UV/vis spectra were recorded in benzene on a Hewlett-Packard 8452, IR spectra (KBr) on a Perkin Elmer 1600 FT-IR, ^{1}H-NMR spectra on a JEOL (100 MHz, $CDCl_3$) spectrophotometer, and fluorescence spectra on a Jobin Yvone spectrofluorimeter.

4-Bromo-N-allylnaphthalimide and 4-amino-N-allylnaphthalimide were synthesised by methods described previously.[7,9]

Synthesis of the compounds

*Synthesis of **1a** and **1b***

A mixture of 3.2 g (0.01 mol) 4-bromo-N-allylnaphthalimide and 0.6 g KOH was dissolved in 50 ml methanol. The solution was refluxed and the reaction was monitored by TLC. After 4 h the liquor was poured into 200 ml water and the resulting crystals were filtered and dried in vacuum.

1a: Yield 94%, elemental analysis calculated N = 5.24%, found N = 5.20%; ^{1}H-NMR spectra [$CDCl_3$]: δ = 3.8–4.0 (s, 3H, OCH_3), 4.4–4.7 (d, 2H, NCH_2), 4.9–5.2 (t, 2H, CH_2), 5.4–6.0 (m, 1H, CH), 6.6–8.3 (m, 5H, ArH); IR [KBr]: ν = 1694 cm^{-1} (CO), 1656 (CH_2), 1582, 1514 (CH), 1097 (C–O–C).

1b: Yield 96%, elemental analysis calculated N = 4.98%, found N = 5.07%; ^{1}H-NMR [$CDCl_3$]: δ = 1.3–1.6 (t, 2H, CH_2CH_3), 4.0–4.3 (q, 3H, CH_2CH_3), 4.5–4.7 (d, 2H, NCH_2), 4.9–5.3 (t, 2H, CH_2), 5.6–6.0 (m, 1H, CH), 6.6–8.4 (m, 5H, ArH); IR [KBr]: ν = 1695 cm^{-1} (CO), 1657 (CH_2), 1591, 1514 (CH), 1077 (C–O–C).

*Synthesis of **1c***

2.5 g (0.01 mol) of 4-amino-N-allylnaphthalimide was dissolved in 50 ml of acetic acid and to this solution at 50°C 2 ml $ClCH_2COCl$ was added dropwise. The mixture was stirred at this temperature and after 2 h (TLC control) the product was isolated by pouring into water, filtering and drying in vacuum.

Yield 90%, elemental analysis calculated N = 8.52%, found N = 8.30%; ^{1}H-NMR [$CDCl_3$]: δ = 3.3 (s, 2H, CH_2CO), 4.3–4.6 (d, 2H, NCH_2), 4.9–5.2 (t, 2H, CH_2), 5.5–6.0 (m, 1H, CH), 7.5–8.6 (m, 5H, ArH), 10.4 (s, 1H, NH); IR [KBr]: ν = 3241 cm^{-1} (NH), 1679 (CO), 1646 (CH_2), 1588, 1521 (CH).

*Synthesis of **1d***

2.5 g (0.01 mol) of 4-amino-N-allylnaphthalimide was suspended in 50 ml acetone:water (1:1) mixture. To this suspension at room temperature was added 1.84 g (0.01 mol) of cyanuric chloride. The mixture was stirred at this temperature and monitored by TLC, the pH being maintained at 6–7 by addition of 30% aq. NaOH. After 4 h the product was isolated and dried in vacuum at 30°C.

Yield 85%; ^{1}H-NMR spectra [$CDCl_3$]: $\delta = 4.4$–4.6 (d, 2H, NCH_2), 4.9–5.2 (t, 2H, CH_2), 5.5–6.0 (m, 1H, CH), 7.4–8.4 (m, 5H, ArH), 11.4 (s, 1H, NH); IR [KBr]: $\nu = 3302$ cm^{-1} (NH), 1682 (CO), 1648 (CH_2), 1580, 1521 (CH).

Polymerisation with styrene

In an ampoule flushed with dry nitrogen, 10 g of purified styrene, 0.01 g of the appropriate compound **1a–1d** and 0.01 g of DBP were mixed. The ampoule was sealed and heated at 80°C in a thermostat for 8 h. The resultant transparent polymers with an intense blue fluorescence were dissolved in toluene and reprecipitated several times with methanol until free of fluorescence under UV light. The polymers were then dried at 35°C in vacuum.

REFERENCES

1. Alexion, M., Tychopolous, V. & Chorbanbin, S., *J. Chem. Soc. Perkin Trans.*, **2** (1990) 837.
2. Qian, X., Jun, T., Janzong, Z. & Julan, Z., *Dyes and Pigments*, **25** (1994) 109.
3. Donze, J., *L'Industrie Textile*, **1177** (1987) 519.
4. *USSR Author Certificate, No. 583128*, 1976.
5. Adam, W., Qian, X. & Saha-Moller, Ch., *Tetrahedron*, **49**(22) (1993) 417.
6. Dubey, K., Singh, R. & Mizra, K., *Indian J. Chem.*, **34B** (1995) 876.
7. Konstantinova, T., Meallier, P. & Grabchev, I., *Dyes and Pigments*, **22** (1993) 191.
8. Grabchev, I., Meallier, P., Konstantinova, T. & Popova, M., *Dyes and Pigments*, **28** (1995) 41.
9. Grabchev, I., Guittonneau, S., Konstantinova, T. & Meallier, P., *Bull. Soc. Chim. France*, **131** (1994) 828.
10. Konstantinova, T., *Bulgarian Author Certificate, No. 25441*, 1977.
11. Konstantinova, T. & Grabchev, I., *Compt. rendus de l'Acad. Bulgarian Sci.*, **44**(10) (1991) 59.
12. Olsbach, J., *J. Chem. Phys.*, **20** (1979) 25.
13. Grabchev, I. & Konstantinova, T., *Melliand Textilberichte*, **2** (1994) 125.