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The Synthesis, Application and Prediction of Stokes Shift in Fluorescent Dyes Derived from 1,8-Naphthalic Anhydride

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ABSTRACT

Eight fluorescent dyes derived from 4-amino-1,8-naphthalic anhydride were synthesized and the effect of amine nucleophilicity on the condensation reaction was studied. The fluorescence properties of the dyes were recorded and their Stokes shifts were calculated using the PPP–SCF (β, γ) method. The potential of the compounds for dyeing polyester and for use as fluorescence solar collectors were also investigated.

1 INTRODUCTION

Many derivatives of 1,8-naphthalic anhydride have been described as fluorescent dyes and fluorescent whitening agents and investigations into the synthesis of benzo[*k*,*l*]thioxanthene and cyclic secondary amino derivatives of 1,8-naphthalic anhydride have been reported.[1–3] In this present paper, we describe the synthesis of some 4-amino-substituted 1,8-naphthalimides (**Ia–Id**) and 7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones (**IIa–IId**) and an evaluation of some potential applications of these compounds.

2 RESULTS AND DISCUSSION

The general synthetic route to the dyes is outlined in Scheme 1.

Using 4-chloro-1,8-naphthalic anhydride as raw material,[4] dyes **Ia–Id**

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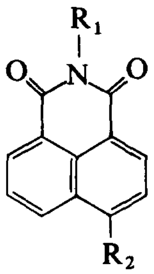
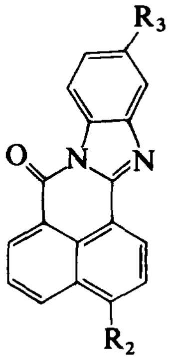
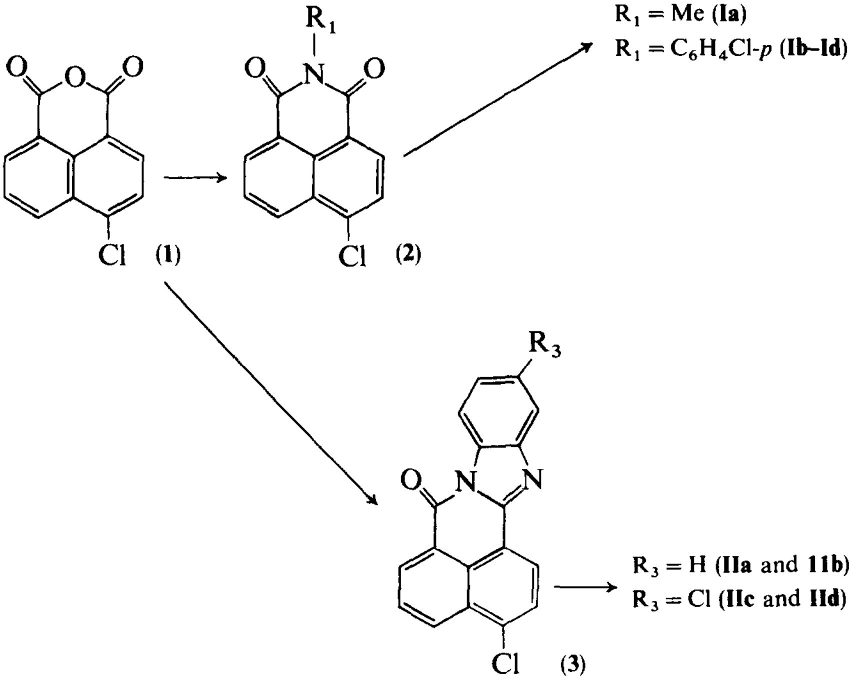


Ia: $R_1 = Me$, $R = NHMe$
Ib: $R_1 = C_6H_4Cl$-*p*, $R_2 = NHCH_2CH_2OH$
Ic: $R_1 = C_6H_4Cl$-*p*, $R_2 = NHCH_2CH_2NH_2$
Id: $R_1 = C_6H_4Cl$-*p*, $R_2 = NMe_2$



IIa: $R_3 = H$, $R_2 = NHCH_2CH_2OH$
IIb: $R_3 = H$, $R_2 = NHCH_2CH_2NH_2$
IIc: $R_3 = Cl$, $R_2 = NHCH_2CH_2OH$
IId: $R_3 = Cl$, $R_2 = NHCH_2CH_2NH_2$

were synthesized by imidation in acetic acid followed by condensation in 2-methoxyethanol or DMF with amines. Dyes **IIa–IId** were synthesized by reaction with *o*-phenylenediamine or with 2-nitro-4-chloroaniline under reductive conditions with iron powder and acetic acid, followed by condensation with amines in 2-methoxyethanol.



Scheme 1

TABLE 1
Fluorescence Properties of Dyes (in DMF)

Dye	*Emission wavelength (nm)*	*Quantum yield*[a]
Ia	520·3	0·3166
Ib	527·9	0·6141
Ic	528·0	0·3821
Id	521·0	0·3602
IIa	510·9	0·8110
IIb	513·2	0·4474
IIc	526·0	0·3192
IId	519·0	0·2227

[a] The standard was Rhodamine B.

In the condensation reaction, a little hydrated copper sulphate was used as catalyst and a large excess of amine was required. In DMF solution, dyes **Ia–Id** were yellow with a green fluorescence , and dyes **IIa–IId** were orange with a green fluorescence. It was found that the fluorescence quantum yield of the —$NHCH_2CH_2OH$ derivative was larger than that of the —$NHCH_2CH_2NH_2$ derivative (see Table 1).

Compounds **2** and **3** condensed readily with alkylamines, but in the condensation with aromatic amines such as aniline, 4-methylaniline and *N*-methylaniline, the reaction was more difficult and, under conditions in which alkylamines reacted easily, very little reaction took place with arylamines.

The condensation reaction is one of nucleophilic replacement and the differences in reactivity are relatable to the different nucleophilicity of the amines; cf. pK_b values (25°C): $NH_2CH_2CH_2OH$, 4·500; $NH_2CH_2CH_2NH_2$, 3·939; $NHMe_2$, 3·280; NH_2Me, 3·360; but $C_6H_5NH_2$, 9·420; $C_6H_4MeNH_2$-*p*, 9·879; C_6H_5NHMe, 9·106.[5]

In aniline, calculations by the PPF–SCF method show that 0·1778 unit of negative charge is delocalized to the phenyl ring (Fig. 1).

Dyes **Ia–Id** and dyes **IIa–IId** coloured polyester fibres in greenish–yellow hues and greenish–orange hues respectively, showing excellent build-up to deep shades. The sublimation fastness of dyes **Ib** and **Ic** was good, but the dyes generally did not have good potential value as textile dyes in view of the low lightfastness (see Table 3).

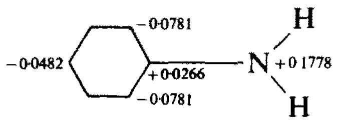


Fig. 1

The Stokes shift is a parameter which indicates the differences in properties and structure of the dyes between the ground state and the first excited state. From the data in Table 2, it can be seen that dyes **Ia–Id** show the largest Stokes shift and dyes **IIa–IId** show smaller values.

In a previous paper,[6] the fluorescence maxima of some dyes were calculated using the PPP–SCF (β, γ) method by correction of bond lengths, β-integrals and γ-integrals in the first excited singlet state. In this present paper, the Stokes shift of the dyes derived from 1,8-naphthalic anhydride were calculated using the same method. It was found that there was good correlation between Stokes shifts (Vs) and (ΔE_{uv}–ΔE_{fl}), the difference between excitation energy and fluorescence emission energy. The results of the calculations are shown in Table 2.

TABLE 2
The Observed and Calculated Values of Stokes Shift
(correlation coefficient $r = 0{\cdot}9629$)

Dye	*Observed value (kcm⁻¹)*	*Calculated value (kcm⁻¹)*
Ia	3·61	3·43
Ib	3·80	3·80
Ic	3·72	3·80
Id	4·28	3·92
IIa	2·09	2·26
IIb	2·11	2·26
IIc	2·54	2·29
IId	2·29	2·29

Fluorescent solar collectors (FSC),[7] which do not require seasonal tracking and can collect incident sunlight to energize the solar cells, usually consist of a transparent plate which contains fluorescent centres. In this study, poly(methyl methacrylate) was used as transparent material and the 1,8-naphthalic anhydride derivatives were used as fluorescing centres.

The collector efficiency of the fluorescent dye in the FSC is the total electrical power output of the FSC divided by that of an FSC of equal size but which does not contain fluorescing centres. It was found that the collector efficiency of the dyes derived from 1,8-naphthalic anydride was higher than that of coumarin laser dyes,[8] but lower than that of Rhodamine B.[8] The dyes with 4-amino substituents did absorb the sunlight which enters the upper face of the FSC and emitted fluorescence effectively, part of the fluorescence being trapped into edge-mounted solar cells by total internal reflection. The results determined are shown in Table 3.

TABLE 3
Properties of Dyes for Dyeing and FSC

Dye	*Lightfastness (2%)*	*Sublimation (180°C)*	*Collector efficiency of FSC*
Ia	3	3–4	2·20
Ib	2	5	2·33
Ic	2	5	2·18
Id	2–3	2–3	2·98
IIa	3	3	2·20
IIb	2–3	4	2·00
IIc	3	3	2·62
IId	3	4	2·35

3 EXPERIMENTAL

3.1 4-Methylamino-*N*-methyl-1,8-naphthalimide (Ia)

A mixture of 4-chloro-1,8-naphthalic anhydride (2·0 g), 33% aq. methylamine (10 ml) and $CuSO_4 . 5H_2O$ (0·2 g) was refluxed in 2-methoxyethanol (40 ml) for 3 h. The liquor was poured into water to give 86·8% of **Ia**, which on crystallization from chlorobenzene gave yellow needles, m.p. 265–266°C; $\lambda_{max}(\log \varepsilon)$: 438 nm (3·83); IR: 3380 cm^{-1} (N—H), 2940 cm^{-1} (CH_2), 1675, 1640 cm^{-1} (C═O). $C_{14}H_{12}N_2O_2$ requires: C, 70·0%; H, 5·0%; N, 11·7%. Found: C, 69·8%; H, 5·1%; N, 11·5%.

3.2 4-(2-hydroxyethyl)amino-*N*-4-chlorophenyl-1,8-naphthalimide (Ib)

4-Chloro-1,8-naphthalic anhydride (10 g) and 4-chloroaniline (6·5 g) were refluxed for 3·5 h in glacial acetic acid (120 ml). The liquor was poured into water to give 99·3% of *N*-(4-chlorophenyl)-4-chloro-1,8-nathphalimide, which was recrystallised from acetic acid as yellowish–white needles, m.p. 284–285°C. IR: 1710, 1670 cm^{-1} (C═O), 740 cm^{-1} (C—Cl). $C_{18}H_9NO_2Cl_2$ requires: C, 63·3%; H, 2·6%; N, 4·1%. Found: C, 62·9%; H, 2·7%; N, 4·3%.

The above product (2·0 g), 2-aminoethanol (5 ml) and $CuSO_4 . 5H_2O$ (0·5 g) were refluxed in 2-methoxyethanol (50 ml) for 1 h, and the liquor poured into water to give 93·3% dye **Ib**, which was recrystallized from chlorobenzene in yellow needles, m.p. 267–268°C; $\lambda_{max}(\log \varepsilon)$: 439·6 nm (4·18); IR: 3350 cm^{-1} (—OH), 2900 cm^{-1} ($>CH_2$), 1700, 1660 cm^{-1} (C═O). $C_{20}H_{15}N_2O_3Cl$ requires: C, 65·1%; H, 4·6%; N, 7·6%. Found: C, 65·5%; H, 4·4%; N, 7·9%.

3.3 4-(2-Aminoethyl)amino-*N*-4-chlorophenyl-1,8-naphthalimide (Ic)

Replacing 2-aminoethanol in the above by ethylenediamine (5 ml) gave 56·1% of dye **Ic**, yellow needles, m.p. 236–237°C. λ_{max}(log ε): 441·4 nm (4·17). IR: 3500 cm^{-1} (—NH_2), 2900 cm^{-1} ($>CH_2$), 1690, 1650 cm^{-1} (C=O). $C_{20}H_{16}N_3O_2Cl$ requires: C, 65·7; H, 4·4; N, 11·5%. Found: C, 65·6%; H, 4·5%; N, 11·0%.

3.4 4-(*N*,*N*-Dimethylamino)-*N*-4-chlorophenyl-1,8-naphthalimide (Id)

Replacing 2-aminoethanol in the above by 33% aq. dimethyldiamine (10 ml) and refluxing in DMF (40 ml) gave 97·6% of dye **Id**, yellow needles, m.p. 269–270°C; λ_{max}(log ε): 426·0 nm (3·96); IR: 2830 cm^{-1} (N—CH_3), 1690, 1650 cm^{-1} (C=O), 770 cm^{-1} (C—Cl). $C_{20}H_{15}N_2O_2Cl$ requires: C, 68·5; H, 4·3; N, 8·0%. Found: C, 68·7; H, 4·5; N, 7·7%.

3.5 3-(and 4-)(2-Hydroxyethyl)amino-7*H*-benzimidazo(2,1-*a*)benz(*d*,*e*)isoquinolin-7-one (IIa)

4-Chloro-1,8-naphthalic anhydride (10 g) and *o*-phenylenediamine (6 g) were refluxed in glacial acetic acid (120 ml) for 7 h and the liquor poured into water to give 99·26% of 3-(and 4-)chloro-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*] isoquinolin-7-ones. Recrystallization from acetic acid gave yellow needles, m.p. 215–216°C; λ_{max}(log ε): 391 nm (4·14). IR: 1700 cm^{-1} (C=O), 750 cm^{-1} (C—Cl). $C_{18}H_9N_2OCl$ requires: C, 70·4; H, 3·1; N, 9·2%. Found: C, 70·9; H, 3·0; N, 9·2%.

A mixture of the above product (1·6 g), 2-aminoethanol (5 ml) and $CuSO_4 . 5H_2O$ (0·2 g) was refluxed in 2-methoxyethanol (50 ml) for 1 h. The liquor was poured into water to give 98·3% of dye **IIa**, which recrystallized from chlorobenzene in orange needles, m.p. 258–259°C; λ_{max}(log ε): 461·6 nm (4·26); IR: 3350 cm^{-1} (—NH—), 2900 cm^{-1} ($>CH_2$), 1660 cm^{-1} (C=O). $C_{20}H_{15}N_3O_2$ requires: C, 72·95; H, 4·6; N, 12·8%. Found: C, 73·0; H, 4·35; N, 12·7%.

3.6 3-(and 4-)(2-Aminoethylamino)-7*H*-benzimidazo(2,1-*a*)benz(*d*,*e*)isoquinolin-7-ones (IIb)

Replacing 2-aminoethanol in the above by ethylenediamine (5 ml) gave 92·8% of dye **IIb**, orange needles, m.p. 207–208°C; λ_{max}(log ε): 463·0 nm (4·34); IR: 3500 cm^{-1} (—NH_2), 2940 cm^{-1} ($>CH_2$), 1660 cm^{-1} (C=O). $C_{20}H_{16}N_4O$ requires: C, 73·2; H, 4·9; N, 17·1%. Found: C, 73·35; H, 5·1; N, 16·6%.

3.7 3-(and 4-)(2-Hydroxyethyl)amino-10-(and 11-)chloro-7*H*-benzimidazo-(2,1-*a*)benz(*d*,*e*)isoquinolin-7-ones (IIc)

A mixture of 4-chloro-1,8-naphthalic anhydride (5 g), 2-nitro-4-chloroaniline (3·5 g) and iron powder (1·0 g) was refluxed in glacial acetic acid for 5 h, and the liquor then poured into water to give 78% of the isomer mixture of 3-(and 4-)chloro-10-(and 11-)chloro-7*H*-benzimidazo [2,1-*a*]benz[*d*,*e*]-isoquinolin-7-ones, which were recrystallized from chlorobenzene as yellow needles, m.p. 258–259°C; $\lambda_{max}(\log \varepsilon)$: 391·0 nm (4·13); IR: 1710 cm^{-1} (C=O), 780 cm^{-1} (C—Cl). $C_{18}H_8N_2OCl_2$ requires: C, 63·7; H, 2·95; N, 8·3%. Found: C, 63·9; H, 2·6; N, 8·1%.

A mixture of the above product (3·0 g), 2-aminoethanol (5 ml) and $CuSO_4 . 5H_2O$ (0·1 g) was refluxed in 2-methoxyethanol (50 ml) for 1 h. The liquor was poured into water to give 47% of **IIc**, which on recrystallization from chlorobenzene gave orange needles, m.p. 204–205°C; $\lambda_{max}(\log \varepsilon)$: 464·0 nm (4·3193); IR: 3400 cm^{-1} (—OH), 1690 cm^{-1} (C=O), 1580 cm^{-1} (C=N), 770 cm (C—Cl). $C_{20}H_{14}N_3O_2Cl$ requires: N, 11·55%. Found: N, 11·2%. *M*/*e*: 363·5.

3.8 3-(and 4-)(2-Aminoethyl)amino-10-(and 11-)chloro-7*H*-benzimidazo-(2,1-*d*)benz(*d*,*e*)isoquinolin-7-ones (IId)

Replacing 2-aminoethanol in the above by ethylenediamine (5 ml) gave 53% of **IId**, orange needles, m.p. 257–258°C; $\lambda_{max}(\log \varepsilon)$: 464 nm (4·24); IR: 3320 cm^{-1} (—NH$_2$), 2940, 2870 cm^{-1} ($>CH_2$), 1680 cm^{-1} (C=O), 770 cm^{-1} (C—Cl). $C_{20}H_{15}N_4OCl$ requires: N, 15·45%. Found: N, 15·0%. *M*/*e* 362·5.

3.9 Preparation of FSC

Methyl methacrylate (70 ml) from which the polymerization retarder (*p*-dihydroxybenzene) had been removed with 5% aq. NaOH and the appropriate dye and polymerization initiator (60 mg) were heated at 65°C for 24 h to give poly(methyl methacrylate) containing the fluorescent dye. This was milled to give an FSC plate (length 30 mm, width 6 mm and height 10 mm) and its four faces were plated with aluminium. The results of the FSC evaluation are shown in Table 3.

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