

## Novel Syntheses of Near-infrared-absorbing Di-iminonaphthalene Dyes Based on Cyanoimino Derivatives of Indoaniline<sup>1</sup>

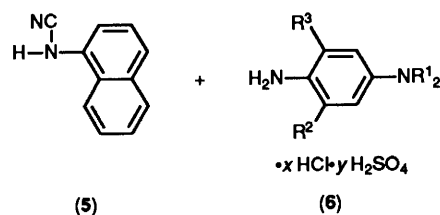
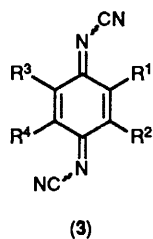
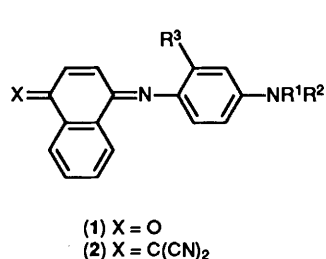
Yuji Kubo,\* Minoru Kuwana, Ken Okamoto, and Katsuhira Yoshida

Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780, Japan

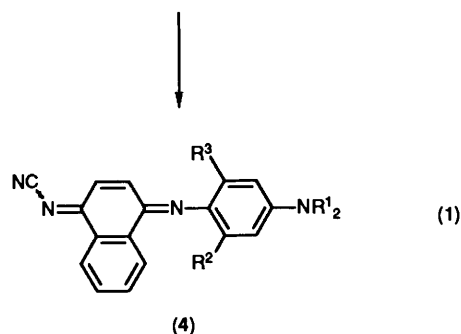
New types of di-iminonaphthalene-type near-IR dyes have been conveniently synthesized by the condensation of 1-naphthylcyanamide with *p*-(*N,N*-dialkylamino)anilines in the presence of an oxidizing agent. The dyes show  $\lambda_{\max}$  686–779 nm in chloroform, the absorption properties of which are discussed in detail. An intramolecular ring-closure reaction of the acetylamino analogue, *N*-(2'-acetyl-amino-4'-diethylaminophenyl)-*N'*-cyano-1,4-naphthoquinone di-imine, under alkaline conditions gave a new benzophenazine dye.

Much more attention has been recently paid to non-textile dyes which absorb light in the near-infra-red (IR) region. Various new applications, such as the use of organic dyes as materials for optical storage by diode-laser,<sup>2</sup> as photosemiconductor layers for laser printers,<sup>3</sup> as absorbers in laser filters,<sup>4</sup> *etc.* led to the syntheses of new near-IR dyes. However, the number of compounds available for such applications is still limited.

The indoaniline dyes (1)<sup>5</sup> are blue in colour, and typical donor-acceptor chromogens. Replacement of the carbonyl group in compounds (1) by the more powerful acceptor dicyanovinyl group gave the naphthoquinone methide dyes (2),<sup>6</sup> whose absorption maxima shifted to longer wavelength than that for compounds (1). Consequently, the dyes (2) absorb near-IR light at 722–761 nm in chloroform. The donor-



- a; R<sup>1</sup> = Et, R<sup>2</sup> = Me, R<sup>3</sup> = H, x = 1, y = 0  
 b; R<sup>1</sup> = Et, R<sup>2</sup> = R<sup>3</sup> = H, x = 0, y = 1  
 c; R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H, x = 2, y = 0  
 d; R<sup>1</sup> = Et, R<sup>2</sup> = NHAc, R<sup>3</sup> = H, x = y = 0  
 e; R<sup>1</sup> = Et, R<sup>2</sup> = R<sup>3</sup> = Me, x = y = 0



- a; R<sup>1</sup> = Et, R<sup>2</sup> = Me, R<sup>3</sup> = H  
 b; R<sup>1</sup> = Et, R<sup>2</sup> = R<sup>3</sup> = H  
 c; R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H  
 d; R<sup>1</sup> = Et, R<sup>2</sup> = NHAc, R<sup>3</sup> = H  
 e; R<sup>1</sup> = Et, R<sup>2</sup> = R<sup>3</sup> = Me

Reagents: Oxidizing agent, base.

acceptor character of compounds (1) suggests that a pronounced bathochromic shift should be produced by the introduction of a new powerful acceptor group in the quinonoid segment.

On the other hand, Aumüller and Hünig have prepared a new class of quinonoid acceptor, the bis-cyanoimino compounds (3),<sup>7</sup> whose properties with respect to potentially conductive charge-transfer complexes were investigated. However, deeply coloured di-imino dyes possessing such an acceptor moiety are as yet unknown, and so we have designed a new type of dye, the di-iminonaphthalenes (4).

Here, we report the syntheses of such systems by condensation of 1-naphthylcyanamide (5)<sup>8</sup> with 4-dialkylaminoanilines (6) in the presence of an oxidizing agent [equation (1)]. The absorption properties of the dyes are also discussed in detail.

### Results and Discussion

**Syntheses of Di-iminonaphthalene Dyes (4).**—We considered that the syntheses of the dyes (4) by condensation of 1-naphthylcyanamide (5) with 4-dialkylaminoanilines (6) would

be the most convenient. Compound (5) as the starting material could be quantitatively prepared by desulphurization of 1-(1-naphthyl)thiourea in the presence of Pb(OAc)<sub>2</sub>. Novel syntheses of *N*-cyano-*N'*-(4'-diethylamino-2'-methylphenyl)-1,4-naphthoquinone di-imine (4a) by reaction of compound (5) with 4-diethylamino-2-methylaniline hydrochloride (6a) in the presence of an oxidizing agent under alkaline conditions at 5 °C for 30 min are summarized in Table 1. The reaction was promoted by oxidizing agents in the following order: (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> > NaOCl > K<sub>3</sub>[Fe(CN)<sub>6</sub>] > K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (runs 1–4). Finally, a 97% yield of compound (4a) was obtained in the case of run 1. Other derivatives (4b–e) were prepared similarly: yield 61–96% (runs 5–8).

**Table 1.** Syntheses of di-imino dyes (4).

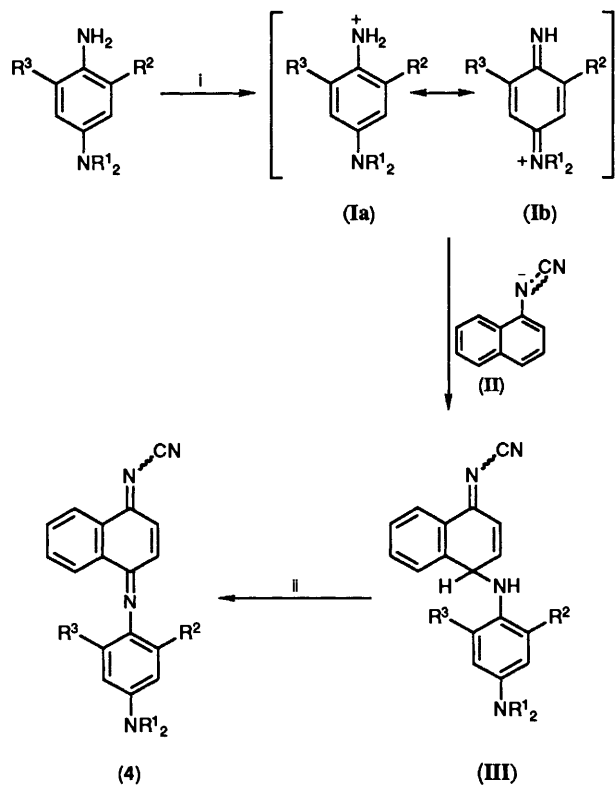
Run	Aniline <sup>a</sup>	Oxidizing agent		Base	Solvent	Product	Yield (%) <sup>c</sup>
			(mol) <sup>b</sup>				
1	(6a)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	5	NaOH	Water	(4a)	97
2	(6a)	NaOCl	5	NaOH	Water	(4a)	87
3	(6a)	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	10	NaOH	Water	(4a)	69
4	(6a)	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	1.67	NaOH	Water	(4a)	56
5	(6b)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	5	NaOH	Water	(4b)	61
6	(6c)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	5	NaOH	Water	(4c)	72
7	(6d)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	5	NH <sub>3</sub>	Me <sub>2</sub> CO-water	(4d)	96
8	(6e)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	5	NH <sub>3</sub>	Me <sub>2</sub> CO-water	(4e)	92

<sup>a</sup> Molar ratio [aniline]:[(5)] 5:1. <sup>b</sup> Molar quotient [oxidizing agent]/[(5)]. <sup>c</sup> Isolated yield after column chromatography.

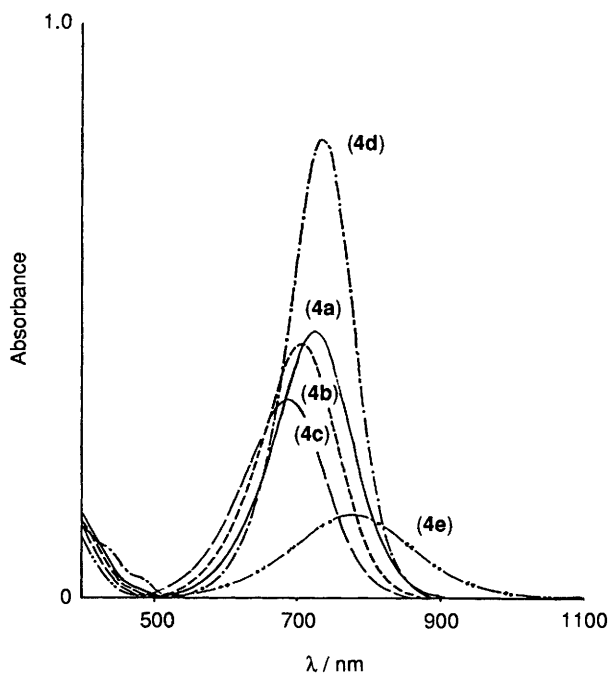
**Table 2.** Light-absorption properties of the dyes (1a), (2a), and (4).

Dye	$\lambda_{\max}/\text{nm}$ (CHCl <sub>3</sub> )	$\epsilon_{\max}/\text{dm}^3$ $\text{mol}^{-1}$ $\text{cm}^{-1}$ (CHCl <sub>3</sub> )	$\lambda_{\max}/\text{nm}$ (hexane)	$\lambda_{\max}/\text{nm}$ (DMF <sup>a</sup> )	$\Delta\lambda$ <sup>b</sup>
(2a) <sup>d</sup>	761	30 800	707	779	72
(4a)	725	31 000	667	744	77
(4b)	705	29 100	646	722	76
(4c)	686	23 100	631	706	75
(4d)	736	53 000	692	752	60
(4e)	779	9 800	721	794	73

<sup>a</sup> Dimethylformamide. <sup>b</sup>  $\Delta\lambda = \lambda_{\max}(\text{DMF}) - \lambda_{\max}(\text{hexane})$ . <sup>c,d</sup> R<sup>1</sup> = R<sup>2</sup> = Et, R<sup>3</sup> = Me.

**Scheme 1.** Reagents and conditions: i, oxidizing agent; ii, *in situ* oxidation.

Scheme 1 illustrates a possible synthetic pathway; 4-dialkylaminoaniline is first oxidized to a mono cation, which was

**Figure 1.** Absorption spectra of the dyes (4) ( $1.5 \times 10^{-5}$  M) in chloroform.

stabilized by the resonance (Ia)  $\longleftrightarrow$  (Ib), and which reacts with the anion of substrate (II) to give the leuco dye (III); this is then oxidized to yield the dyes (4).

**Absorption Spectra of the Dyes (4).**—The absorption spectra of these dyes (4) were measured in several solvents (see Table 2), and Figure 1 shows the absorption bands of compounds (4) in chloroform. The dye (4a) is green in colour and absorbs near-IR light at 725 nm ( $\epsilon_{\max}$  31 000) in chloroform; this wavelength is much longer (by 109 nm) than the  $\lambda_{\max}$  of the corresponding indoaniline dye (1a), and has increased absorption intensity, but the wavelength is shorter by 36 nm than  $\lambda_{\max}$  of the corresponding naphthoquinone methide dye (2a). This result suggests that the electron-accepting power of the quinonoid segment was increased by substitution at C-1 in the naphthalene ring in the following order:  $=\text{C}(\text{CN})_2 > =\text{N}(\text{CN}) \gg =\text{O}$ .

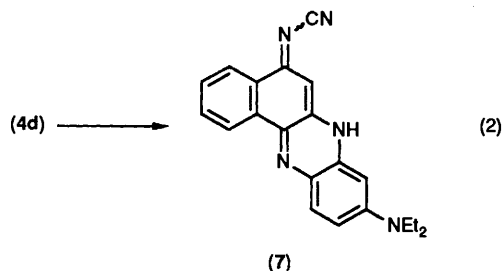
The first absorption bands for the dyes (4) are also dependent on the electron-donating power of the phenyl ring (see Table 2). However, as shown in Figure 1 the dyes (4d) and (4e) show specific spectral features. In the case of compound (4d), the introduction of an acetamino group into a position *ortho* to the nitrogen bridge produces a 31 nm bathochromic shift with an increase in molecular extinction coefficient ( $\epsilon$ ) in comparison with that of compound (4b). These properties are considered to

be caused by both electronic and steric factors of the acetylamino group. In particular, the large increase in  $\epsilon$  suggests that the steric torsion between the di-imine segment (acceptor) and the phenyl ring (donor) is decreased by an intramolecular hydrogen bond between the peptide segment of the acetylamino group and the imino nitrogen. Similar hydrogen bonding was observed in the X-ray structure of the corresponding naphthoquinone methide dye (**2b**;  $R^1 = R^2 = \text{Et}$ ,  $R^3 = \text{NAHc}$ ).<sup>9</sup> The dye (**4e**) shows  $\lambda_{\text{max}}$  779 nm and a broad absorption band in the range of ca. 500–1100 nm. A pronounced bathochromic shift (74 nm) is apparent on comparing spectra for compounds (**4e**) and (**4b**), which is probably caused by further steric torsion between the di-imine and phenyl segments by the introduction of the 2',6'-dimethyl groups into the phenyl ring. This steric effect was also observed in the corresponding analogue (**2**), and was interpreted by using semiempirical MO INDO/S and AM1 calculations.<sup>10</sup>

The effect of solvents on the absorption maxima of dyes (**4**) was examined (see Table 2). The absorption maximum of compounds (**4**) shifts to longer wavelength with increasing solvent polarity. For example, the dye (**4a**) shows a  $\lambda_{\text{max}}$ -value of 667 nm in hexane. A bathochromic shift of 77 nm, positive solvatochromism, was observed for the dye (**4a**) on going from hexane to dimethylformamide (DMF). The value of the bathochromic shift,  $\Delta\lambda = \lambda_{\text{max}}(\text{DMF}) - \lambda_{\text{max}}(\text{hexane})$ , is comparable to that of the naphthoquinone methide dye (**2a**), and is more pronounced than that of the indoaniline dye (**1a**). These results suggest that the dyes have significant polar structure in the excited state, and the degree of stabilization of the excited structure for dyes (**2**) and (**4**) in going from the non-polar solvent to the polar one is larger than that for compounds (**1**).

The dyes (**4**) have potential for many applications as new functional organic materials. In addition, the reaction of 1-naphthylcyanamide with oxidized *p*-(*N,N*-dialkylamino)-anilines to yield dyes (**4**) may be of use for cyan coupling in current reversal print systems.

**The Intramolecular Ring-closure Reaction of Dye (4d).**—The dye (**4d**) having an acetylamino group as a functional group at the 2'-position in the phenyl ring would be a new compound. We therefore examined the hydrolysis of the acetylamino group. In the KOH-EtOH system, the intramolecular ring-closure reaction of compound (**4d**) proceeded to give the new benzophenazine dye (**7**) in 75% yield [equation (2)]. On the



Reagents: KOH-EtOH.

other hand, hydrolysis on addition of an acid catalyst, such as HCl, gave many products which could not be identified.

The dye (**7**) has an intense absorption band at 577 nm ( $\epsilon_{\text{max}}$  55 400), whose wavelength is shorter than that of compound (**4b**) by 128 nm, probably because the bridging nitrogen atom acts as a donor on the quinoneimine moiety. However, the  $\epsilon_{\text{max}}$  of compound (**7**) was almost twice that of the dye (**4b**), suggesting that the conjugation between the quinone-di-imine and phenyl segments is strengthened by the nitrogen bridging.

The large hypsochromic shift by ring-closure from the near-IR to the visible wavelength region should have applications in the design of new functional dyes.

## Experimental

M.p.s were measured on a SIBATA melting-point apparatus and are uncorrected. Absorption spectra were measured using a JASCO U best-30 UV/VIS spectrophotometer. <sup>1</sup>H NMR spectra were taken on a Hitachi R-90H spectrometer. IR spectra were obtained by using a JASCO FT/IR 5000 spectrometer on KBr pellets. Mass spectra were run on a Hitachi M-80A spectrometer, and elemental analyses were obtained using a Perkin-Elmer 240 C,H,N analyser.

**Materials.**—The indoaniline dye 4-(4'-diethylamino-2'-methylphenylimino)naphthalen-1(4*H*)-one (**1a**;  $R^1 = R^2 = \text{Et}$ ,  $R^3 = \text{Me}$ ), was prepared by the standard method with  $\text{K}_3\text{Fe}(\text{CN})_6$  as an oxidant;<sup>11</sup> m.p. 111–112.5 °C (lit.,<sup>5</sup> 114 °C) (Found: C, 79.2; H, 6.95; N, 8.8.  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}$  requires C, 79.2; H, 7.0; N, 8.8%). 1-Naphthylcyanamide (**5**) was synthesized by the literature method; m.p. 124–125 °C (lit.,<sup>8</sup> 124–128 °C);  $\nu_{\text{max}}(\text{KBr})$  2 238  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ). 4-Dialkylaminoanilines, except 2-acetylamino-4-diethylaminoaniline (**6d**) and 4-diethylamino-2,6-dimethylaniline (**6e**), were reagent grade and were used without further purification. Compounds (**6d**) and (**6e**) were synthesized from 3-acetylamino-*N,N*-diethylaniline and 3,5-xylidine, respectively.

**General Procedure for the Preparation of the Substituted Di-iminonaphthalene Dyes (4a–e).**—To an aq. NaOH solution of compound (**5**) (0.59 mmol) at 5 °C were added dropwise simultaneously aq. solutions of a diamine (**6a–c**) (2.97 mmol) and an oxidizing agent. After the mixture had been stirred for 30 min at 5 °C, the product was filtered off, washed with water, dried, and chromatographed on silica gel (Wakogel C-300) with  $\text{CHCl}_3$  as eluant. The di-imino dyes (**4a–c**) were recrystallized from MeOH.

The dyes (**4d**) and (**4e**) were synthesized as follows: To an acetone-conc.  $\text{NH}_3$  solution of compound (**5**) (0.988 mmol) at 5 °C were added dropwise a solution of the aniline (**6d**) or (**6e**) (4.94 mmol) and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (4.94 mmol). After the mixture had been stirred for 30 min at 5 °C, the acetone was removed under reduced pressure. The product was filtered off, washed with water, dried, and chromatographed on silica gel (Wakogel C-300) with  $\text{CH}_2\text{Cl}_2$  as eluant. The dyes (**4d**) and (**4e**) were purified by recrystallization from hexane- $\text{CHCl}_3$  and from MeOH, respectively. Details of the actual conditions are given in Table 1.

**N-Cyano-*N'*-(4'-diethylamino-2'-methylphenyl)-1,4-naphthoquinone di-imine (4a)**, m.p. 138–139 °C;  $\lambda_{\text{max}}(\text{CHCl}_3)$  725 nm ( $\epsilon_{\text{max}}$  31 000  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ );  $\delta_{\text{H}}(\text{CDCl}_3)$  1.24 (6 H, t), 2.43 (3 H, s), 3.45 (4 H, q), 6.48–6.75 (3 H, m), 7.38–7.80 (4 H, m), and 8.31–8.63 (2 H, m);  $m/z$  342 ( $M^+$ ) and 327 ( $M^+ - 15$ );  $\nu_{\text{max}}(\text{KBr})$  2 168  $\text{cm}^{-1}$  (Found: C, 77.2; H, 6.5; N, 16.3.  $\text{C}_{22}\text{H}_{22}\text{N}_4$  requires C, 77.2; H, 6.5; N, 16.4%).

**N-Cyano-*N'*-(4'-diethylaminophenyl)-1,4-naphthoquinone di-imine (4b)**, m.p. 128–129 °C;  $\lambda_{\text{max}}(\text{CHCl}_3)$  705 nm ( $\epsilon_{\text{max}}$  29 100);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.24 (6 H, t), 3.45 (4 H, q), 6.75 (2 H, d,  $J$  9.23 Hz), 7.075 (2 H, d,  $J$  9.23 Hz), 7.34–7.81 (4 H, m), and 8.29–8.59 (2 H, m);  $\nu_{\text{max}}(\text{KBr})$  2 170  $\text{cm}^{-1}$  (Found: C, 76.8; H, 6.3; N, 16.5%;  $M^+$ , 328.  $\text{C}_{21}\text{H}_{20}\text{N}_4$  requires C, 76.8; H, 6.1; N, 17.1%;  $M$ , 328).

**N-Cyano-*N'*-(4'-dimethylaminophenyl)-1,4-naphthoquinone di-imine (4c)**, m.p. 181–182 °C;  $\lambda_{\text{max}}(\text{CHCl}_3)$  686 nm ( $\epsilon_{\text{max}}$  23 100);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.07 (6 H, s), 6.76 (2 H, d,  $J$  9.23 Hz), 7.05 (2 H, d,  $J$  9.23 Hz), 7.35–7.83 (4 H, m), and 8.28–8.58 (2 H, m);  $\nu_{\text{max}}(\text{KBr})$  2 127  $\text{cm}^{-1}$ ;  $m/z$  300 ( $M^+$ ) and 285 ( $M^+ - 15$ ) (Found: C, 76.0; H, 5.4; N, 18.4.  $\text{C}_{19}\text{H}_{16}\text{N}_4$  requires C, 76.0; H, 5.4; N, 18.65%).

*N'*-(2'-Acetylamino-4'-diethylaminophenyl)-*N*-cyano-1,4-naphthoquinone di-imine (**4d**), m.p. 174–175 °C;  $\lambda_{\max}(\text{CHCl}_3)$  736 nm ( $\epsilon_{\max}$  53 000);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.29 (6 H, t), 2.27 (3 H, s), 3.51 (4 H, q), 6.45 (1 H, dd,  $J$  2.86, 9.23 Hz), 6.88 (1 H, d,  $J$  9.23 Hz), 7.23–7.82 (4 H, m), 8.14 (1 H, d,  $J$  2.86 Hz), 8.28–8.46 (2 H, m), and 8.84 (1 H, br s),  $\nu_{\max}(\text{KBr})$  3 314 and 2 166  $\text{cm}^{-1}$  (Found: C, 71.6; H, 5.7; N, 18.2.  $\text{C}_{23}\text{H}_{23}\text{N}_5\text{O}$  requires C, 71.7; H, 6.0; N, 18.2%).

*N*-Cyano-*N'*-(4'-diethylamino-2',6'-dimethylphenyl)-1,4-naphthoquinone di-imine (**4e**), m.p. 146–147 °C;  $\lambda_{\max}(\text{CHCl}_3)$  779 nm ( $\epsilon_{\max}$  9 800);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.20 (6 H, t), 2.04 (6 H, s), 3.38 (4 H, q), 6.47 (2 H, s), 6.88 (1 H, d,  $J$  10.11 Hz), 7.32 (1 H, d,  $J$  10.11 Hz), 7.52–7.85 (2 H, m), and 8.30–8.66 (2 H, m);  $\nu_{\max}(\text{KBr})$  2 176  $\text{cm}^{-1}$ ;  $m/z$  356 ( $M^+$ ) and 341 ( $M^+ - 15$ ) (Found: C, 77.5; H, 6.8; N, 15.7.  $\text{C}_{23}\text{H}_{24}\text{N}_4$  requires C, 77.5; H, 6.8; N, 15.7%).

*Preparation of 5-(N-Cyanoimino)-9-diethylamino-5,7-dihydrobenzo[a]phenazine (7)*.—*N'*-(2'-Acetylamino-4'-diethylaminophenyl)-*N*-cyano-1,4-naphthoquinone di-imine (**4d**) (0.65 mmol) was added to an ethanolic solution (30 ml) of KOH (6.5 mmol). After the mixture had been stirred for 10 min at room temperature, it was neutralized with AcOH. The product was collected and purified by being washed successively with EtOH and dil. HCl. The dye 5-(*N*-cyanoimino)-9-diethylamino-5,7-dihydrobenzo[a]phenazine (**7**) was obtained in 75% yield, m.p. 242–243 °C;  $\lambda_{\max}(\text{CHCl}_3)$  577 ( $\epsilon_{\max}$  55 400) and 543 nm (41 900);  $m/z$  341 ( $M^+$ ) and 326 ( $M^+ - 15$ ) (Found: C, 74.0; H, 5.7; N, 20.4.  $\text{C}_{21}\text{H}_{19}\text{N}_5$  requires C, 73.9; H, 5.6; N, 20.5%).

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