

Novel Syntheses of Naphthoquinone Methide Near-infrared Dyes

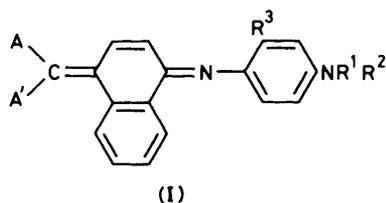
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A novel type of naphthoquinone methide near-i.r. dye has been synthesized by condensing 1-naphthylmalononitrile or 1-naphthylcyanoacetamide with *p*-*N,N*-dialkylaminoanilines in the presence of an oxidizing agent under alkali conditions. These dyes can absorb near-i.r. light at 722–761 nm. A dye film of 4-(4-diethylamino-2-methylphenylimino)-1,4-dihydronaphthylidenemalononitrile showed a λ_{\max} value of 785 nm and reflected 23.3% of the incident light intensity at 830 nm; these properties make the compound a potential diode-laser optical storage medium.

Near-i.r. absorbing dyes have been developed for use as optical information recording media for gallium-aluminium-arsenic (GaAlAs) diode-lasers.¹ Since the latter emit near-i.r. light at 800–830 nm, the dyes used for optical recording have to absorb in this range. Although a small number of chromophoric systems have been prepared to absorb near-i.r. light,² naphthoquinone methide dyes have, until now, not been among them.

Earlier,³ we suggested that the novel deep-coloured naphthoquinone methide dyes (**1**), the first absorption band for



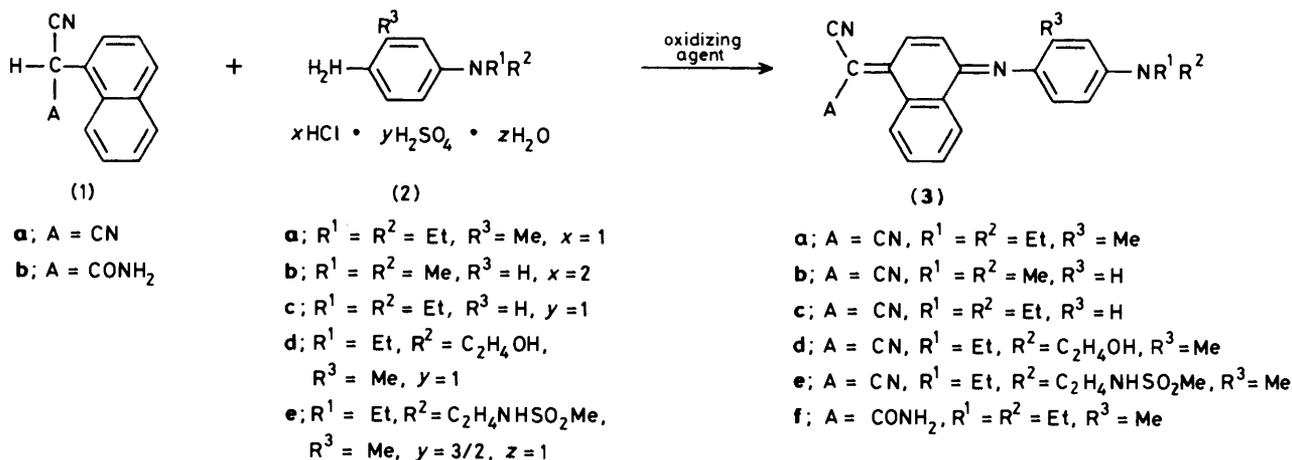
which is caused by the intramolecular charge-transfer character of the transition, would, upon introduction of an electron-accepting group (A,A') such as cyano group in the methylene segment and electron-donating group such as alkylamino group in the phenyl ring, undergo a bathochromic shift and thence absorb the near-i.r. light.

Here, we report the syntheses of such systems by condensing 1-naphthylmalononitrile (**1a**)⁴ or 1-naphthylcyanoacetamide

(**1b**)⁵ with *p*-*N,N*-dialkylaminoaniline (**2**) in the presence of an oxidizing agent under alkaline conditions. The film properties of one of these dyes has been examined for use in diode-laser optical storage.

Results and Discussion

Novel syntheses of 4-(4-diethylamino-2-methylphenylimino)-1,4-dihydronaphthylidenemalononitrile (**3a**) by condensing 1-naphthylmalononitrile (**1a**) with 2-methyl-4-diethylaminoaniline hydrochloride (**2a**) in the presence of an oxidizing agent under alkaline conditions at room temperature for 10 min are summarized in Table 1 (runs 1–6). The reaction was promoted by the following oxidizing agents in the order: sodium hypochlorite > potassium dichromate \geq ammonium peroxydisulphate > potassium ferricyanide (runs 3–6). The yield of (**3a**) also depended on the amount of (**2a**) and on the oxidizing agent (runs 1–3). A 51% yield of (**3a**) was obtained in the case of run 3. Reaction of (**1a**) with *p*-*N,N*-dimethylaminoaniline dihydrochloride (**2b**) under similar conditions and in the presence of sodium hypochlorite gave the naphthylidenemalononitrile (**3b**) in 23% yield (run 7). Use of potassium ferricyanide as the oxidizing agent gave an increased (46%) yield of (**3b**) (run 8). From these results, the reaction is considered to proceed by oxidation of the *p*-*N,N*-dialkylaminoaniline, *via* a semiquinone ion, the ease of formation of which is dependent upon the nature of the oxidizing agent and aniline. Similarly, the derivatives, (**3c**), (**3d**), and (**3e**) were obtained in 27, 29, and 16% yields respectively (runs 9–11). The amide analogue (**3f**)



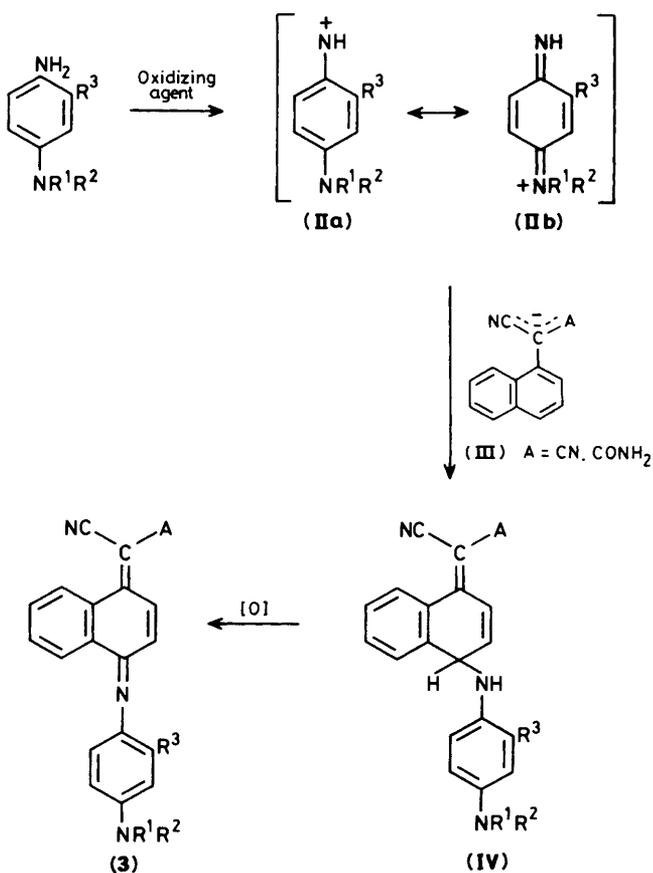
Scheme 1. Reaction of 1-Naphthylmalononitrile (**1a**) or 1-naphthylcyanoacetamide (**1b**) with *p*-*N,N*-dialkylaminoanilines

Table 1. Syntheses of naphthoquinone methide derivatives (3)^a

Run	Substrate	Aniline (mol) ^b	Oxidizing agent (mol) ^c	Product	Yield (%) ^d
1	(1a)	(2a)	1 NaOCl	2 (3a)	17
2	(1a)	(2a)	2 NaOCl	2 (3a)	29
3	(1a)	(2a)	2 NaOCl	5 (3a)	51
4	(1a)	(2a)	2 K ₂ Cr ₂ O ₇	5 (3a)	36
5	(1a)	(2a)	2 K ₃ Fe(CN) ₆	5 (3a)	23
6	(1a)	(2a)	2 (NH ₄) ₂ S ₂ O ₈	5 (3a)	34
7	(1a)	(2b)	2 NaOCl	5 (3b)	23
8	(1a)	(2b)	2 K ₃ Fe(CN) ₆	5 (3b)	46
9	(1a)	(2c)	2 NaOCl	5 (3c)	27
10	(1a)	(2d)	2 NaOCl	5 (3d)	29
11	(1a)	(2e)	2 NaOCl	5 (3e)	16
12	(1b)	(2a)	1 NaOCl	2 (3f)	3

^a Reactions were carried out under room temperature for 10 min. ^b Molar ratio: [2]/[1]. ^c Molar ratio: [Oxidizing agent]/[1]. ^d Yield of isolated material after purification.

synthesized by the reaction of (1b) with (2a) was obtained in very low yield (run 12), many side products being produced which made the isolation of the pure dye difficult.

**Scheme 2.**

Scheme 2 illustrates a possible reaction path. First, oxidation of the *p*-*N,N*-dialkylaminoaniline (I) produces a semiquinone ion which, stabilized by the resonance (IIa) \longleftrightarrow (IIb), reacts with the carbanion of substrate (III) to give the leuco dye (IV); this is then oxidized to yield (3). The low reactivity of 1-naphthylcyanoacetamide (1b) in the dye-forming reaction

Table 2. Light absorption properties of (3)

Dye	$\lambda_{\max.}/\text{nm}$ (CHCl ₃)	$\epsilon_{\max.}/\text{l mol}^{-1} \text{cm}^{-1}$ (CHCl ₃)
(3a)	761	30 800
(3b)	722	25 500
(3c)	738	30 800
(3d)	743	24 200
(3e)	728	28 900
(3f)	754	29 400

Table 3. Effect of solvents on the absorption maxima of (3)

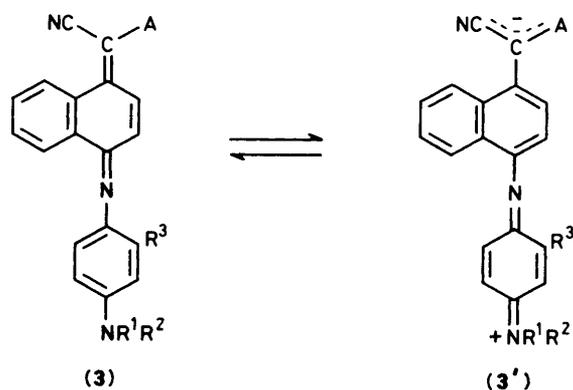
Solvent	$\lambda_{\max.}/\text{nm}$					
	(3a)	(3b)	(3c)	(3d)	(3e)	(3f)
Hexane	707	666	683	<i>a</i>	<i>a</i>	<i>a</i>
Cyclohexane	714	675	691	703	698	<i>a</i>
Benzene	732	695	710	722	706	719
Ethyl acetate	742	700	716	743	727	719
Chloroform	761	722	738	743	728	759
Ethanol	762	729	750	766	753	756
Dimethylformamide	779	731	751	778	762	752

^a Too insoluble.

may be explained in terms of the instability of the amide entity, which underwent many side reactions.

Absorption Spectra of the Dyes (3).—The absorption spectra of these dyes (3) were measured in chloroform (see Table 2). The dye (3a) is green, absorbs near-i.r. light at 761 nm ($\epsilon_{\max.}$ 30 800) in chloroform, and produces a large bathochromic shift of 145 nm in comparison with the $\lambda_{\max.}$ of the corresponding indoaniline dye 4-(4-diethylamino-2-methylphenylimino)-1,4-naphthoquinone.⁶ Introduction of the dicyano groups as an electron acceptor into the methylene segment causes a large bathochromic shift of the absorption band. As shown in Table 2, the first absorption band of each dye is also dependent on the strength of the electron-donating power of the aminophenyl ring. In particular, the introduction of a 2-methyl group into (3c) produced a 23 nm red shift [dye (3a)]. In contrast, the corresponding amide derivative (3f) absorbs near-i.r. light at 754 nm ($\epsilon_{\max.}$ 29 400) in chloroform and produced a 7 nm hypsochromic shift in comparison with the $\lambda_{\max.}$ of (3a). All these dyes (3) showed intense absorption bands in the near-i.r. region.

The effect of solvents on the absorption maxima of (3) are listed in Table 3. The absorption maxima of the dyes (3) shifted

**Scheme 3.**

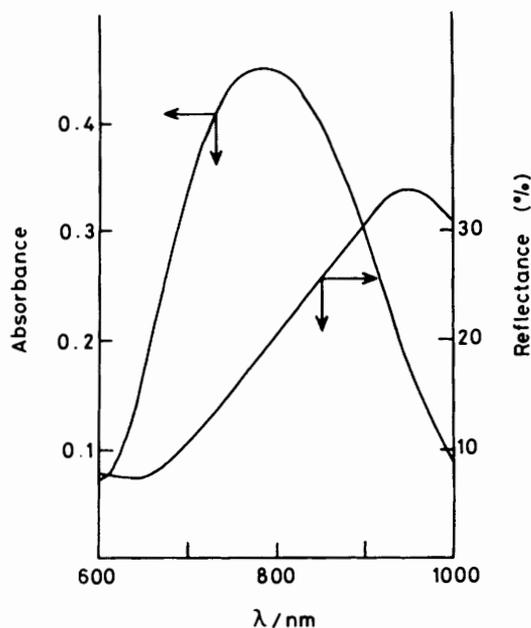


Figure. Absorption and reflection spectra for a 60 nm-thick film of (3a)

to longer wavelength with an increase in solvent polarity. For example, the dye (3a) showed a λ_{\max} value of 707 nm in hexane. A bathochromic shift of 72 nm, positive solvatochromism, was observed for the dye (3a) in going from hexane to dimethylformamide. From these results, it was recognized that the dyes (3) have significant polar structure, (3'), in the excited state (Scheme 3). In the case of (3f), however, the small negative solvatochromism observed in going from chloroform to dimethylformamide, may be explained in terms of stabilization of (3f) by polar solvents in the ground state.

Preparation of a Film of the Dye (3).—Since these dyes have potential for use in diode-laser optical storage, we investigated their film properties. In the spin-coating process used to prepare a dye film, it is necessary, in order to obtain a smooth homogeneous layer, that the dye should have a good solubility in the solvent used. As shown in Table 3, in general, the dyes (3) have better solubility in the following order: (3a—c) > (3d—e) > (3f). A film of (3a) was thought likely to be best for investigating film properties, and the Figure shows absorption and reflection spectra for such a 60 nm-thick dye film prepared by solvent coating onto poly(methylmethacrylate). The absorption spectrum of the film of (3a) exhibited a broad peak at a wavelength of 600—1 000 nm and a λ_{\max} value of 785 nm which produced a bathochromic shift of 24 nm in comparison with that of (3a) in chloroform. The film reflected 23.3% of incident light intensity at 830 nm. These properties suggest that it has potential as a diode-laser optical storage medium.

Experimental

M.p.s are uncorrected. Absorption spectra were measured using a Hitachi 220A spectrophotometer. ^1H N.m.r. spectra were taken on a Hitachi R-90H spectrometer. Mass spectra were run on a Hitachi M-80B spectrometer, and elemental analyses were obtained using a Perkin-Elmer 240C C,H,N, analyser.

Materials.—The following compounds were synthesized by the method described in the literature: 1-naphthylmalononitrile (1a) (74%), m.p. 167—168 °C (lit.,⁴ 166—167 °C); $\delta_{\text{H}}[\text{CDCl}_3-$

$(\text{CD}_3)_2\text{SO}]$ 6.62 (1 H, s, CH) and 7.35—8.02 (7 H, m, ArH); 1-naphthylcyanoacetamide (1b) (64%), m.p. 193—194 °C (lit.,⁵ 193—194 °C). *p*-*N,N*-Dialkylaminoanilines were reagent grade and were used without further purification.

General Procedure for the Preparation of the Substituted Naphthylidene Nitriles (3a—f).—An aqueous solution of an oxidizing agent (4 or 10 mmol) at room temperature was added dropwise to an aqueous NaOH solution of (1a) (2 mmol) and (2) (2 mmol or 4 mmol). The mixture was stirred for 10 min at room temperature after which the product was filtered off, dried, and chromatographed on silica gel (Wacogel C-300) using chloroform or hexane-ethyl acetate mixture as an eluant. The dyes (3a—e) were recrystallized from ethanol.

The reaction of (1b) and (2a) was carried out in the same manner. The reaction mixture was chromatographed on alumina activated (Wako ca. 300 mesh) using chloroform as an eluant and recrystallized from benzene. Details of the actual conditions used are given in Table 1.

4-(4-Diethylamino-2-methylphenylimino)-1,4-dihydro-naphthylidenemalononitrile (3a), m.p. 135—136 °C; $\lambda_{\max}(\text{CHCl}_3)$ 761 nm (ϵ_{\max} 30 800 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.24 (6 H, t, $2 \times \text{CH}_3$), 2.43 (3 H, s, CH_3), 3.44 (4 H, q, $2 \times \text{CH}_2$), 6.62—6.71 (3 H, m, ArH), 7.28 (1 H, d, *J* 9.8 Hz, quinonoid H), 7.51 (1 H, d, *J* 9.8 Hz, quinonoid H), 7.60—7.69 (2 H, m, ArH), and 8.67—8.90 (2 H, m, ArH); *m/z* 366 (M^+) and 351 ($M^+ - 15$) (Found: C, 78.9; H, 5.8; N, 15.4. $\text{C}_{24}\text{H}_{22}\text{N}_4$ requires C, 78.7; H, 6.05; N, 15.3%).

4-(4-Dimethylaminophenylimino)-1,4-dihydronaphthylidenemalononitrile (3b), m.p. 181—183 °C; $\lambda_{\max}(\text{CHCl}_3)$ 722 nm (ϵ_{\max} 25 500 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.06 (6 H, s, $2 \times \text{CH}_3$), 6.75 (2 H, d, *J* 9.0 Hz, ArH), 7.05 (2 H, d, *J* 9.0 Hz, ArH), 7.21 (1 H, d, *J* 9.8 Hz, quinonoid H), 7.42 (1 H, d, *J* 9.8 Hz, quinonoid H), 7.52—7.62 (2 H, m, ArH), and 8.54—8.79 (2 H, m, ArH); *m/z* 324 (M^+), 309 ($M^+ - 15$), and 280 ($M^+ - 44$) (Found: C, 77.8; H, 5.0; N, 17.3. $\text{C}_{21}\text{H}_{16}\text{N}_4$ requires C, 77.25; H, 4.5; N, 17.4%).

4-(4-Diethylaminophenylimino)-1,4-dihydronaphthylidenemalononitrile (3c), m.p. 140—141 °C; $\lambda_{\max}(\text{CHCl}_3)$ 738 nm (ϵ_{\max} 30 800 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\delta_{\text{H}}[\text{CDCl}_3 + (\text{CD}_3)_2\text{SO}]$ 1.25 (6 H, t, $2 \times \text{CH}_3$), 3.47 (4 H, q, $2 \times \text{CH}_2$), 6.75 (2 H, d, *J* 9.2 Hz, ArH), 7.10 (2 H, d, *J* 9.2 Hz, ArH), 7.26 (1 H, d, *J* 10.1 Hz, quinonoid H), 7.52 (1 H, d, *J* 10.1 Hz, quinonoid H), 7.63—7.73 (2 H, m, ArH), and 8.65—8.91 (2 H, m, ArH) (Found: C, 78.0; H, 5.8; N, 15.4%; M^+ , 353. $\text{C}_{23}\text{H}_{20}\text{N}_4$ requires C, 78.4; H, 5.7; N, 15.9%; *M*, 353).

4-{4'-[Ethyl-(2-hydroxyethyl)amino]-2-methylphenylimino}-1,4-dihydronaphthylidenemalononitrile (3d), m.p. 182—183 °C; $\lambda_{\max}(\text{CHCl}_3)$ 743 nm (ϵ_{\max} 24 200 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\delta_{\text{H}}[\text{CDCl}_3 + (\text{CD}_3)_2\text{SO}]$ 1.235 (3 H, t, CH_3), 2.42 (3 H, s, CH_3), 3.41—3.98 (7 H, m), 6.62—6.78 (3 H, m, ArH), 7.23 (1 H, d, *J* 10.1 Hz, quinonoid H), 7.52 (1 H, d, *J* 10.1 Hz, quinonoid H), 7.61—7.75 (2 H, m, ArH), and 8.67—8.90 (2 H, m, ArH) (Found: C, 74.9; H, 5.9; N, 14.4%; M^+ , 383. $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}$ requires C, 75.4; H, 5.8; N, 14.7%; *M*, 383).

4-{4'-[Ethyl-(2-mesyloxyethyl)amino]-2-methylphenylimino}-1,4-dihydronaphthylidenemalononitrile (3e), m.p. 174—175 °C; $\lambda_{\max}(\text{CHCl}_3)$ 728 nm (ϵ_{\max} 28 900 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\delta_{\text{H}}[\text{CDCl}_3 + (\text{CD}_3)_2\text{SO}]$ 1.23 (3 H, t, CH_3), 2.40 (3 H, s, CH_3), 2.95 (3 H, s, SO_2CH_3), 3.26—3.58 (6 H, m), 6.25 (1 H, s, NH), 6.66—6.76 (3 H, m, ArH), 7.20 (1 H, d, *J* 10.1 Hz, quinonoid H), 7.52 (1 H, d, *J* 10.1 Hz, quinonoid H), 7.61—7.74 (2 H, m, ArH), and 8.66—8.89 (2 H, m, ArH) (Found: C, 65.3; H, 5.6; N, 15.0%; M^+ , 459. $\text{C}_{25}\text{H}_{25}\text{N}_3\text{SO}_2$ requires C, 65.4; H, 5.45; N, 15.25%; *M*, 459).

4-(4-Diethylamino-2-methylphenylimino)-1,4-dihydronaphthylidene(carbamoyl)acetoneitrile (3f), m.p. 232—233 °C;

$\lambda_{\max.}(\text{CHCl}_3)$ 754 nm ($\epsilon_{\max.}$ 29 400 dm³ mol⁻¹ cm⁻¹) (Found: C, 73.0; H, 5.6; N, 13.9; M^+ , 384. C₂₄H₂₄N₄O requires C, 75.0; H, 6.3; N, 14.6%; M , 384).

Preparation of 4-(4-Diethylamino-2-methylphenylimino)-1,4-naphthoquinone.—The known title compound was synthesized by condensing 1-naphthol with 4-diethylamino-2-methylaniline hydrochloride; it had m.p. 114–115 °C (lit.,⁶ 114 °C); $\lambda_{\max.}(\text{CHCl}_3)$ 616 nm ($\epsilon_{\max.}$ 16 500 dm³ mol⁻¹ cm⁻¹); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.20 (6 H, t, 2 × CH₃), 2.37 (3 H, s, CH₃), 3.42 (4 H, q, 2 × CH₂), 6.37–6.58 (3 H, m, ArH), 6.54 (1 H, d, J 10.5 Hz, quinonoid H), 7.36 (1 H, d, J 10.2 Hz, quinonoid H), 7.43–7.64 (2 H, m, ArH), 8.02 (1 H, dd, J 6.8 and 2.3 Hz, ArH), and 8.40 (1 H, dd, J 6.2 and 2.1 Hz, ArH).

Preparation of the Film of the Dye (3a).—The dye (3a) (7.0 mg) was dissolved in tetrachloroethane (700 mg), and the solution filtered through a 0.22 μm filter. The filtrate was dropped onto a poly(methyl methacrylate) (PMMA) substrate, and coated by a spinner method at a rotational speed of 800 revolution min⁻¹. The coating layer was dried at 60 °C for ca. 5 min to give an approximately 60 nm-thick dye film of (3a). The absorption and the reflection spectra of this dye film were recorded on a 323 Hitachi Recording Spectrophotometer.

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