Novel Syntheses of Di-iminonaphthalene Type Near-I.R. Dyes

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

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

New di-iminonaphthalene type near-i.r. dyes are conveniently synthesized by condensing 1-naphthylcyanamide with *p*-*N*,*N*-dialkylaminoanilines in the presence of an oxidising agent; their absorption properties are discussed.

In recent years, near-i.r. dyes which show absorption maxima beyond *ca.* 700 nm have attracted considerable attention for many applications in such areas as diode-laser optical storage, laser printing, optical filters, *etc.* Earlier,[1] we reported that new deep coloured naphthoquinone methide dyes (**1**) which absorb near-i.r. light at 722—761 nm in chloroform have good film properties for use as a diode-laser optical storage medium. Further progress requires the synthesis of related compounds. Aumüller and Hünig have prepared a new class of quinonoid acceptors, the bis-cyanoimino compounds (**2**),[2] whose properties with respect to potentially conductive charge-transfer complexes were investigated. However, deep coloured di-imino dyes including such an acceptor segment are as yet unknown, and so we have designed a new type of dye, the di-iminonaphthalenes (**3**).

The near-i.r. dyes (**3**) were synthesized by condensing 1-naphthylcyanamide (**4**)[3] with *p*-*N*,*N*-dialkylaminoanilines (Scheme 1) using an oxidizing agent. The results are summarized in Table 1. In a typical preparation, to an aqueous NaOH solution of (**4**) (0.59 mmol) at 5 °C were added dropwise simultaneously aqueous solutions of (**5a**) (2.97 mmol) and $(NH_4)_2S_2O_8$ (2.97 mmol). The mixture was stirred for 30 min at 5 °C to give the di-imine (**3a**)† in 97% yield (run 1). The reaction was promoted by oxidizing agents in the following order: $(NH_4)_2S_2O_8$ > NaOCl > $K_3[Fe(CN)_6]$ > $K_2Cr_2O_7$ (runs 1—4). Other derivatives (**3b**—**e**) were prepared similarly: yields 61—96% (runs 5—8).

A possible reaction path is as follows: *p*-*N*,*N*-dialkylaminoaniline is first oxidized to a semiquinone ion which

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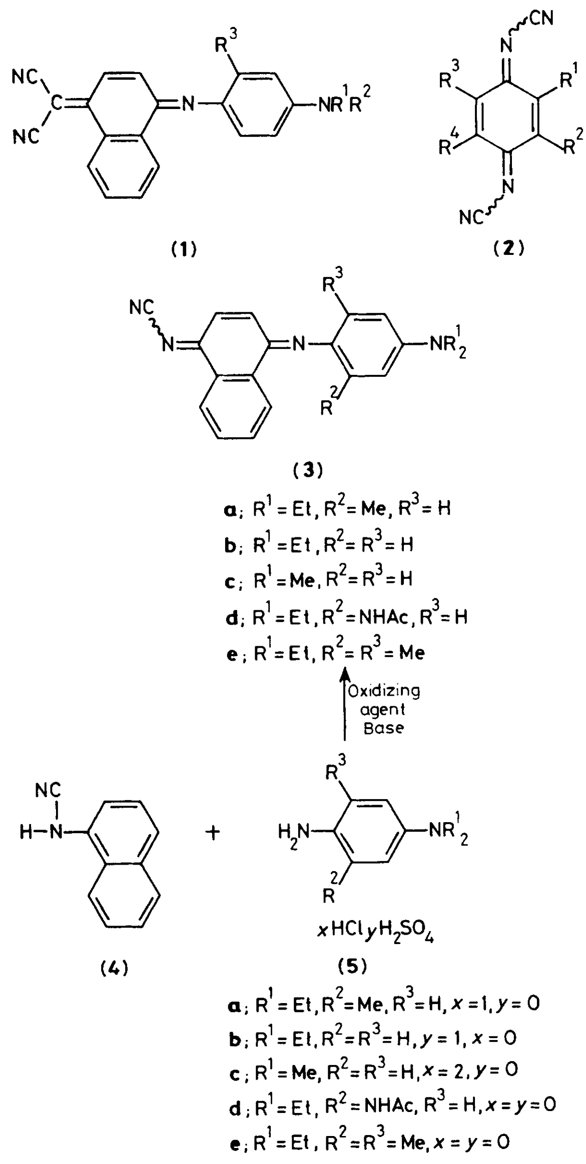
† (**3a**): m.p. 138—139 °C; δ_H ($CDCl_3$) 1.24 (6H, t, 2 × Me), 2.43 (3H, s, Me), 3.45 (4H, q, 2 × CH_2), 6.48—6.75 (3H, m), 7.38—7.80 (4H, m), 8.31—8.63 (m, 2H); *m*/*z* 342 (M^+) and 327 ($M^+ - 15$); i.r. (KBr), 2168 cm^{-1}; satisfactory elemental analyses were obtained.

Table 1. Syntheses of the di-imino dyes (**3**).

Run	Aniline[a]	Oxidizing agent	(mol)[b]	Base	Solvent	Product[c]	Yield (%)[d]
1	(**5a**)	$(NH_4)_2S_2O_8$	5	NaOH	H_2O	(**3a**)	97
2	(**5a**)	NaOCl	5	NaOH	H_2O	(**3a**)	87
3	(**5a**)	$K_3[Fe(CN)_6]$	10	NaOH	H_2O	(**3a**)	69
4	(**5a**)	$K_2Cr_2O_7$	1.67	NaOH	H_2O	(**3a**)	56
5	(**5b**)	$(NH_4)_2S_2O_8$	5	NaOH	H_2O	(**3b**)	61
6	(**5c**)	$(NH_4)_2S_2O_8$	5	NaOH	H_2O	(**3c**)	72
7	(**5d**)	$(NH_4)_2S_2O_8$	5	NH_3	Me_2CO/H_2O	(**3d**)	96
8	(**5e**)	$(NH_4)_2S_2O_8$	5	NH_3	Me_2CO/H_2O	(**3e**)	92

[a] Molar ratio: [aniline]/[(**4**)] = 5. [b] Molar ratio: [oxidizing agent]/[(**4**)]. [c] All new compounds gave satisfactory analytical data. [d] Isolated yield after column chromatography.



Scheme 1

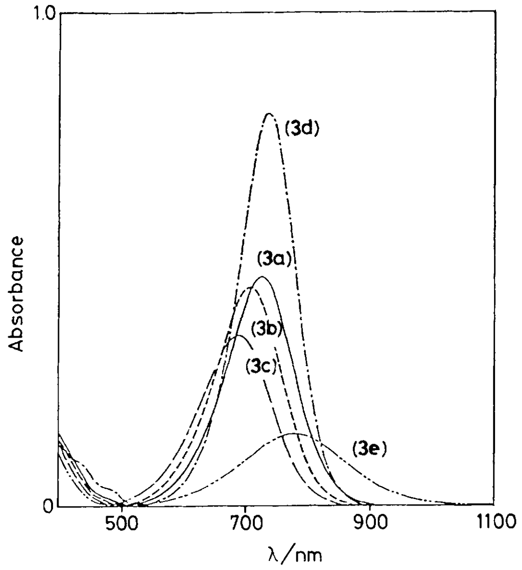


Figure 1. Absorption spectra of the dyes (**3**) (1.5 × 10^{-5} M) in chloroform.

reacts with the anion of (**4**) to give the leuco dye; this is then oxidized to yield (**3**).

The absorption spectra of these dyes were measured in several solvents (Table 2), and Figure 1 shows the absorption bands of (**3**) in chloroform. The dye (**3a**) is green in colour and absorbs near-i.r. light at 725 nm (ε_{max} 31 000) in chloroform; this wavelength is shorter by 36 nm than that of the corresponding naphthoquinone methide dye (**1a**, $R^1 = R^2$ = Et, R^3 = Me).[1] This result suggests that the electron accepting power of the quinoid segment was decreased by replacing the $=C(CN)_2$ group with the =N–CN group.

The first absorption bands for the dyes (**3**) are dependent on the electron-donating power of the phenyl ring (Table 2). However, as shown in Figure 1 the dyes (**3d**) and (**3e**) show specific spectral features. In the case of (**3d**) the introduction of an acetylamino group into the 2′-position of (**3b**) produces a 31 nm bathochromic shift with an increase in molecular extinction coefficient. These properties are considered to be caused by both electronic and steric factors of the acetylamino group. In particular, the large increase in ε suggests that the steric torsion between the di-imine segment (acceptor) and the phenyl ring (donor) is decreased by intramolecular hydrogen bonding 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[4] (**1b**, $R^1 = R^2$ = Et, R^3 = NHAc). The dye (**3e**) shows $\lambda_{max.}$ 779 nm and a broad absorption band in the range *ca.* 500—1100 nm in chloroform. A pronounced bathochromic shift (74 nm) is apparent on comparing (**3e**) with

Table 2. Light absorption properties of the dyes (**3**).

Dye	$\lambda_{max.}$/nm (CHCl$_3$)	$\varepsilon_{max.}$/mol^{-1} dm^3 cm^{-1} (CHCl$_3$)	$\lambda_{max.}$/nm (n-Hexane)	$\lambda_{max.}$/nm (DMF[a])	$\Delta\lambda$[b]
(**3a**)	725	31 000	667	744	77
(**3b**)	705	29 100	646	722	76
(**3c**)	686	23 100	631	706	75
(**3d**)	736	53 000	692	752	60
(**3e**)	779	9 800	721	794	73

[a] Dimethylformamide. [b] $\Delta\lambda = \lambda_{max.}$ (DMF) − $\lambda_{max.}$ (n-hexane).

(**3b**), 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 (**1**), and interpreted by using semiempirical M.O. INDO/S and AM 1 calculations.[5]

The effect of solvents on the absorption maxima of (**3**) has been examined (Table 2). The absorption maxima of (**3**) shifted to longer wavelength with increase in solvent polarity. A bathochromic shift of 60—77 nm, positive solvatochromism, was observed for the dye (**3**) in going from n-hexane to dimethylformamide, whcih suggests that the dyes (**3**) have significant polar character in the excited state.

These new dyes (**3**) have the prospect of many applications as new functional organic materials. In addition, 1-naphthylcyanamide reacting with oxidized *p*-*N*,*N*-dialkylaminoanilines to yield (**3**) may be used as a cyan coupler in current colour reversal print systems.

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