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Syntheses and Characteristics of Naphthoquinone Methide Near Infrared Dyes for Optical Storage Media

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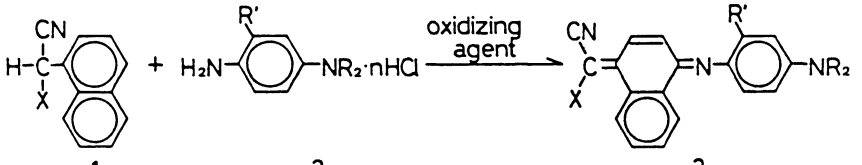
New type of naphthoquinone methide near infrared dyes have been synthesized by condensing 1-naphthylmalononitrile or 1-naphthylcyanoacetamide with p-N,N-dialkylaminoaniline hydrochlorides in the presence of oxidizing agents. These dyes can absorb near infrared light at 722 - 761 nm in chloroform and have excellent characteristics for the practical use as diode-laser optical storage media.

Near infrared absorbing dyes have been developed for optical information recording medium for a gallium-aluminium-arsenic(Ga-Al-As) diode-laser.[1] As the diode-laser emits near infrared light at 800 - 830 nm, the dyes which are used for optical recording have to absorb the near infrared light. Many chromophoric systems which absorb near infrared light have been summarized,[2] however, naphthoquinone methide dyes have not been known yet.

In this paper, we wish to report the novel syntheses of naphthoquinone methide near infrared dyes by condensing 1-naphthylmalononitrile (1a)[3] or 1-naphthylcyanoacetamide (1b)[4] with p-N,N-dialkylaminoaniline hydrochlorides (2) in the presence of an oxidizing agent. The characteristics of these new dyes for the practical use as optical storage media were also examined. In a typical run of synthesis, to an aqueous NaOH solution of 1a (2 mmol) and 2a (4 mmol), was added dropwise an aqueous solution of sodium hypochlorite (10 mmol) at room temperature. The mixture was stirred for 10 min at room temperature to give 4-(2'-methyl-4'-diethylaminophenylimino)-9,9-dicyano-1,4-naphthoquinone methide (3a)[5] in 51% yield. The dye (3a) is green in color and absorbs light at 761 nm(εmax 30800) in chloroform. The similar reaction of 1a with 2b gave the corresponding product (3b). The dye (3b) absorbs near infrared light at 722 nm(εmax 25500) in chloroform, whose wavelength is



1 2 3

			$\lambda_{max}^{chloroform}$	(εmax)
a;X=CN	a;R=Et, R'=Me	a;X=CN, R=Et, R'=Me	761 nm	(30800)
b;X=CONH$_2$	b;R=Me, R'=H	b;X=CN, R=Me, R'=H	722 nm	(25500)
		c;X=CONH$_2$, R=Et, R'=Me	754 nm	(29400)

Table 1. Reaction of 1 with anilines[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 (5)	3a (51)
3	1a	2a (2)	$K_2Cr_2O_7$ (5)	3a (36)
4	1a	2b (2)	NaOCl (5)	3b (23)
5	1b	2a (1)	NaOCl (2)	3c (3)

a) Reactions were carried out under room temperature for 10 min.
b) Molar ratio of [2]/[1]. c) Molar ratio of [oxidizing agent]/[1].
d) Isolated yields after column chromatography.

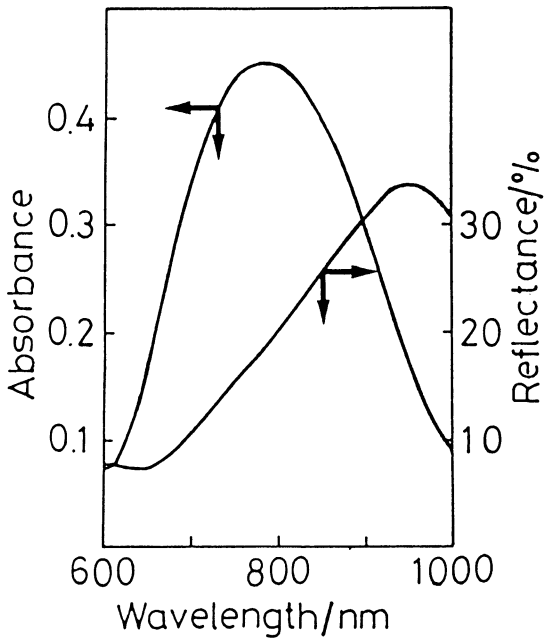


Fig. 1. The absorption and reflection spectra of 60 nm - thick film of 3a.

shorter than that of 3a by 39 nm. The amide analogue, 4-(2'-methyl-4'-diethylamino-phenylimino)-9-cyano-9-amide-1,4-naphtho-quinone methide (3c) which absorbs near infrared light at 754 nm(εmax 29400) in chloroform, can be synthesized by the reaction of 1b with 2a. The results are summarized in Table 1.

Some properties of these new dyes for the practical use as optical storage media were examined. The dye films were prepared by solvent coating onto a polymethyl methacrylate(PMMA). Figure 1 shows absorption and reflection spectra for a 60 nm-thick dye film of 3a in visible and near infrared wavelength regions. The absorption spectrum exhibited a broad peak at wavelength of 600 - 1000 nm and the λmax value of 785 nm. The film reflected 23.3% of incident light intensity at 830 nm. Optical writing on this film with a semiconductor laser(wavelength 830 nm, power 4 mW) proved that the dye film exhibited excellent pit forming characteristics and that rims formed surrounding the pits were quite smooth. The details of these characteristics will be reported elsewhere.

References

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2) M. Matsuoka, Senryo To Yakuhin, 30, 308 (1985).
3) J. K. Williams, E. L. Martin,and W. A. Sheppard, J. Org. Chem., 31, 919 (1966).
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5) 3a: mp 135 - 136 °C; UV λmax (nm)($CHCl_3$),(εmax): 761 (30800); H^1NMR($CDCl_3$) δ= 1.24(6H, t, CH_3x2), 2.43(3H, s, CH_3), 3.44(4H, q, CH_2x2), 6.62 - 6.71(3H, m, aromatic), 7.28(1H, d, J=9.8 Hz, quinonoid proton), 7.51(1H, d, J=9.8 Hz, quinonoid proton), 7.60 - 7.69(2H, m, aromatic), and 8.67 - 8.90(2H, m, aromatic); MS, m/z 366(M^+), 351(M^+-15); Anal Found: C, 78.91; H, 5.77; N, 15.38%. calcd for $C_{24}H_{22}N_4$: C, 78.72; H, 6.05; N, 15.28%.

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