

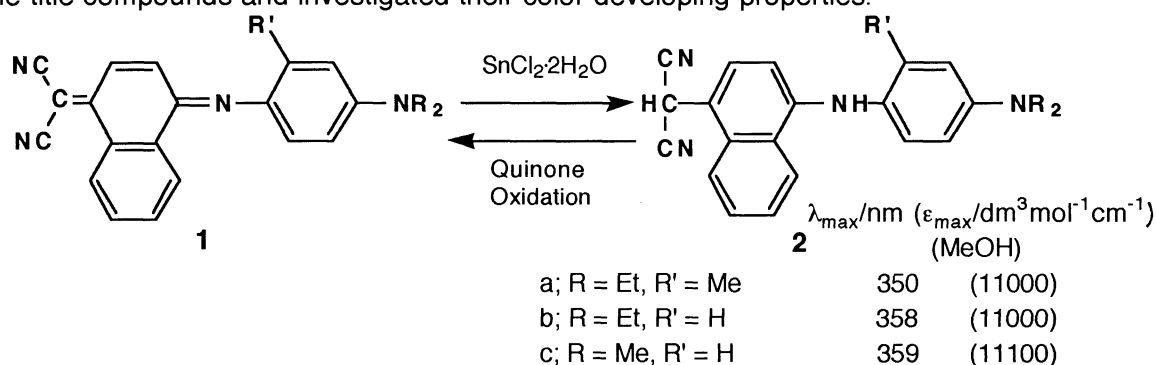
Syntheses of Naphthoquinone Methide-type Near-IR Color Formers

Yuji KUBO,* Kyoichi KOTANI, and Katsuhira YOSHIDA

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

New naphthoquinone methide-type near-IR color formers have been synthesized, which immediately exhibited intense absorption in the near-IR region on oxidation. The color development has been investigated using the stopped-flow technique.

Near-IR color formers are of considerable interest as heat- and pressure-sensitive dyes with electro-optical application utilizing diode-laser technology.¹⁾ To date, triphenylmethane lactone-type near-IR color formers are the best known compounds in this field. The use of leuco-quinones has been little studied because of the instability of the leuco-quinone dyes. However, recently, we found that several types of quinone dyes having metal complexation properties gave rise to stable leuco-dyes and that these produced intense absorption band in the near-IR region in the presence of metal salts.²⁾ To develop other types of Near-IR color formers, we have attempted to synthesize the title compounds and investigated their color developing properties.



Reduction of 4-(4-dialkylaminophenylimino)-1,4-dihydronaphthylidenemalononitrile (**1**)³⁾ with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ under acidic conditions produced the leuco-dyes (**2**)⁴⁾ in 64 - 74% yield, which have weak absorption maxima at 350 - 359 nm in MeOH. Interestingly, **2** could be isolated as stable yellow compounds. With the aim of developing **2** as a new type of color formers, we investigated the oxidation behavior in the presence of quinone oxidant. As shown in Fig. 1, addition of 10 equiv. of *p*-benzoquinone (BQ) to a MeOH solution of **2a** immediately produced new absorption at ca. 760 nm, the character of which was consistent with the presence of **1a**, formed by oxidation of **2a**. From the functional color-formers viewpoint, it is notable that the production of intense absorption band in the near-IR region occurs very rapidly. The spectral characteristics were investigated using the stopped-flow technique. Figure 2 shows the time dependence of the increase in absorbance at 762 nm observed in the case of a $1 \times 10^{-4} \text{ mol dm}^{-3}$ solution of **2a** in MeOH [1:1 v/v; final concentration

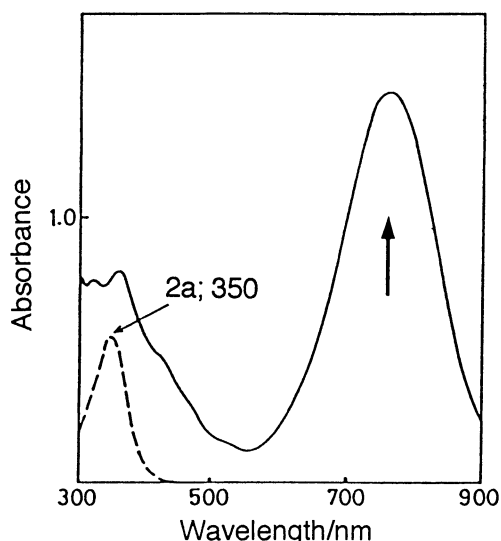


Fig. 1. Spectral changes upon addition of BQ to a MeOH solution of **2a** (---): $[BQ]/[2a] = 10$, $[2a] = 5 \times 10^{-5} \text{ mol dm}^{-3}$.

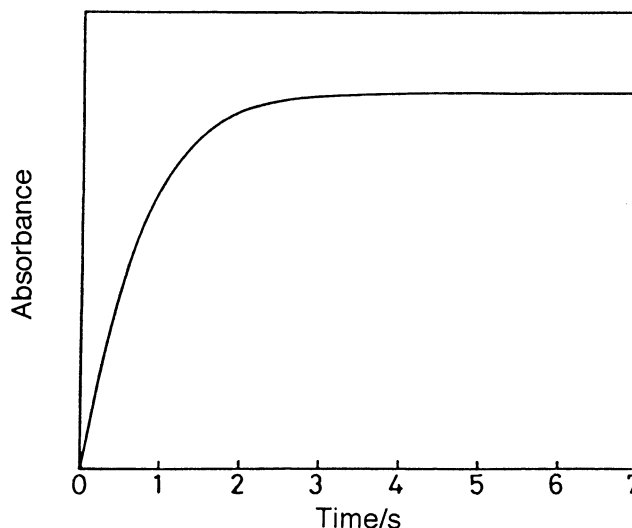


Fig. 2. Formation of **1a** in MeOH at 25 °C: The plot of the absorbance at 762 nm vs. time: $[BQ]/[2a] = 10$, $[2a] = 5 \times 10^{-5} \text{ mol dm}^{-3}$.

Table 1. Half-value period for color development in MeOH at 25 °C^{a)}

Leuco-dye ^{b)}	Near-IR dye ($\lambda_{\text{max}}/\text{nm}$)	$T_{1/2}/\text{s}^{\text{c)}$
2a	1a ; 762	0.55
2b	1b ; 735	0.63
2c	1c ; 718	0.43

a) In the presence of 10 equiv. of BQ ($5 \times 10^{-4} \text{ mol dm}^{-3}$). b) $[\text{Leuco-dye}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$. c) Time for A/A_{∞} ; A is absorbance at λ_{max} of **1**.

of **2a** is $5 \times 10^{-5} \text{ mol dm}^{-3}$. After ca. 2 sec., the absorbance at 762 nm was observed to be saturated. Similar color development was also observed in the case of **2b** and **2c**. In order to estimate the apparent rate of color development, we used the half-value period [$T_{1/2}$: time for $A/A_{\infty} = 0.5$; A is the absorbance of λ_{max} of **1**]. In the presence of 10 equiv. of BQ, $T_{1/2}$ values of 0.43 - 0.63 sec. were obtained (see Table 1). These values are almost consistent with that of 5-(4-dimethylaminoanilino)quinolin-8-ol in the presence of 100 equiv. of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.^{2a)} From these results, the leuco-dyes (**2**) could have potential for use as a suitable near-IR color former.

References

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- 4) **2a**: Mp 172 - 174 °C; ^1H NMR (CDCl_3) 1.20 (6H, t), 2.18 (3H, s), 3.38 (4H, q), 5.39 (1H, s), 6.045 (1H, brd.), 6.43 (1H, d, $J = 8.13 \text{ Hz}$), 6.52 - 6.63 (2H, m), 7.00 - 7.10 (1H, m), 7.44 (1H, d, $J = 8.35 \text{ Hz}$), 7.51 - 7.78 (2H, m), 7.83 - 7.935 (1H, m), 8.035 - 8.14 (1H, m); MS (m/z) 368 (M^+); Anal Found: C, 77.70; H, 6.64; N, 14.80%. Calcd for $\text{C}_{24}\text{H}_{24}\text{N}_4$: C, 78.23; H, 6.56; N, 15.20%.

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