Molecular Structures of the Coloring Species of a Leuco Dye with Phenolic Color Developers

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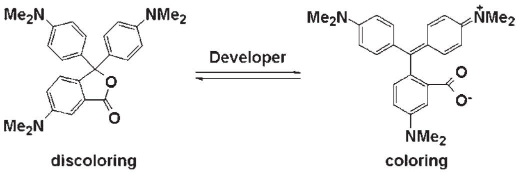
We have isolated the coloring species of a leuco dye colored by three phenolic color developers and have revealed their molecular structures by X-ray crystallographic analysis for the first time: one leuco dye molecule combined with one developer molecule by the hydrogen bonds between the carboxylate anion of a leuco dye and the OH groups of a color developer.

A recording system consisting of leuco dyes and weak acidic color developers has been employed in practical applications, e.g., thermal paper and rewritable paper, owing to its coloring-to-discoloring thermochromism.[1] Recently, we have applied it to a discolorable toner, e-blue.[2] Printed images by the toner can be discolored by moderate heating, and the same paper can be used repeatedly. LCA (Life Cycle Assessment) has demonstrated that CO_2 emission was sharply reduced by using discolorable toner in comparison with conventional toner.[3] However, compared with conventional toner, the color density of discolorable toner has been insufficient until now, which prevents the widespread use of this technology.

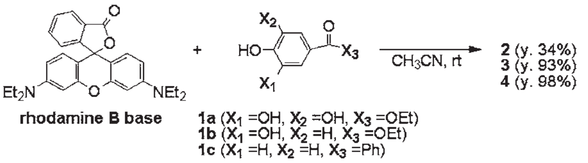
The recording system consisting of leuco dyes and color developers is based on the change in the molecular structure of the leuco dye brought about by the color developer: electron-donating leuco dye reacts with electron-accepting color developer, yielding a zwitterionic coloring species, as shown in eq 1. We assumed that the same reversible reaction as eq 1 was achieved in the production process of discolorable toner and was dominated by discoloring state, causing insufficient color density.



(1)

Though there have been several studies on the reversible reaction of the leuco dye and the weak acidic color developer,[4] no direct evidence on the molecular structure of the coloring species had been reported, which has prevented us from discussing the mechanism of previous findings in detail. We report herein the first successful isolation and determination of the molecular structures of the coloring species **2**–**4**, colored by three phenolic color developers **1a**–**1c**, respectively. In each case, one leuco dye molecule combined with one developer molecule by the hydrogen bond between the carboxylate anion of a leuco dye and the phenolic OH group of a developer. The number of hydrogen bonds and the interaction between coloring species were different among **2**–**4**, owing to the number of OH groups of their color developers.

Coloring species **2**–**4** were obtained as air-stable red crystals by the reaction of rhodamine B base and phenolic color developers **1a**–**1c** in acetonitrile at room temperature, respectively (eq 2).[5] We have selected rhodamine B base as a leuco dye because the metal complexes and salts of its coloring state model, rhodamine B, have been stably isolated.[6]



(2)

The molecular structures of **2**–**4** were determined by X-ray crystallography and Figure 1 shows the molecular structure of **2** (For **3** and **4**, see Supporting Information).[5] The lactone ring of a leuco dye was opened and the benzene ring was almost perpendicular to the xanthene moiety. Bond lengths of C–NEt_2 of **2**, 1.352(4) and 1.357(4) Å, were shorter than that of a single bond. That is, bond lengths of C–NEt_2 of **2** were intermediate between the typical length of a C_{aryl}–NR_2 (C_{aryl}: aromatic carbon atom, R: alkyl group) single bond (1.371 Å) and that of a $C_{aryl} = NR$ double bond (1.346 Å).[7] Also, C–C bond lengths in the xanthene moiety, 1.355–1.430 Å, are considerably shorter than the 1.53 Å bonds typical of alkanes.[7] From these results, it is assumed that the double bonds in the xanthene moiety are conjugated, as shown in Chart 1. The same results were obtained in **3** and **4**.

Table 1 shows O(H)–O distances and O–H–O angles consisting of carboxylate moiety of a leuco dye and phenolic OH groups of a color developer in coloring species **2**. Each value

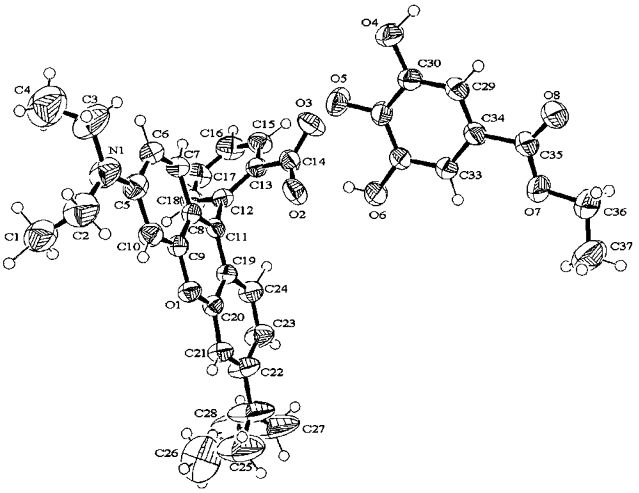
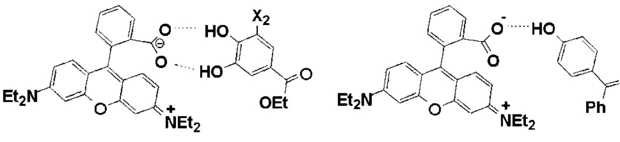


Figure 1. Molecular structure of the coloring species **2**. Crystal data for **2** (293 K): triclinic; $P\bar{1}$ (no. 2), $Z = 2$, $R = 8.34\%$, $wR_2 = 15.15\%$.



2 (X_2 = OH)
3 (X_2 = H)

4

Chart 1.

Table 1. Structural parameters of coloring species **2**

Position	O(H)–O distances/Å	O–H–O angles/degree
O3(H)O5	2.581(3)	164.66
O2(H)O6	2.603(3)	147.40

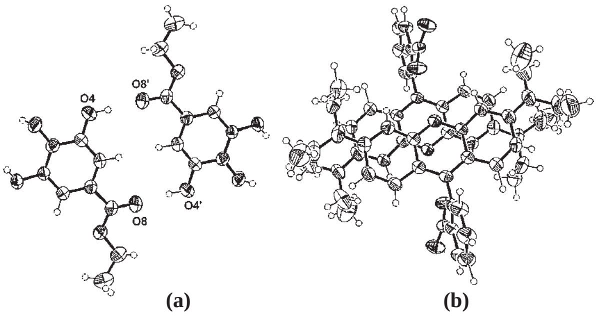


Figure 2. Interaction between developers and xanthene moieties in the coloring species **2**: (a) the hydrogen bond between developers, (b) the π–π stacking interaction between xanthene moieties.

in Table 1 was classified as that of typical hydrogen bond.[8] Thus, it has been revealed that a leuco dye and a phenolic color developer interact with each other by the hydrogen bond between the carboxylate moiety of a leuco dye and the OH groups of a developer. In **2** and **3**, in which developers have more than two OH groups, such hydrogen bonds were formed at two oxygen atoms, presumably for effective stabilization of the entire molecule by electron delocalization. On the other hand, in the coloring species **4**, in which the developer has one OH group, such hydrogen bond was formed at only one oxygen atom. The C–O bond length of **4** which does not combine with developer, 1.229(2) Å, is the same value as that of a typical $C_{aryl}C{=}O(OH)$ double bond (1.226 Å), though the other is 1.262(2) Å.[7] From these results, the coloring species **4** is presumed to be a carboxylic acid form, as shown in Chart 1.

Also two types of interaction between coloring species were observed. One is the hydrogen bond between developers. Figure 2a shows the neighboring developer molecules in the coloring species **2**. Both O4(H)–O8′ distance and O4–H–O8′ angle of 2.806(4) Å and 176.50° were classified as those of typical hydrogen bond.[8] From these results, it has been revealed that two molecules of **2** interact with each other by the hydrogen bond between developers and form a dimer as shown in Figure 3. In **3** and **4**, in which developers have less than two phenolic OH groups, such interaction between developers has not been observed. The other is π–π stacking interaction between xanthene moieties. Figure 2b shows the neighboring xanthene moieties in the coloring species **2**. The xanthene moieties overlapped parallel to each other across an inversion center. The same results were obtained in coloring species **3** and **4**, and reported by other workers, concerning the metal complexes of rhodamine B,[6] but not rhodamine B base itself.[9] These results also show the extension of the electron conjugation in the coloring species **2**–**4**.

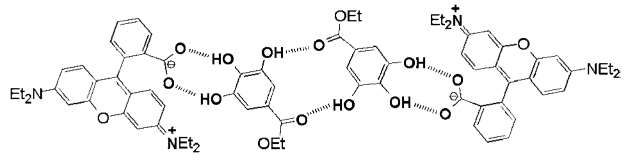


Figure 3. A dimer structure of coloring species **2**.

This study has provided the first direct evidence on the structure of the coloring species consisting of a leuco dye and a phenolic color developer. Further work is in progress.

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References and Notes

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5 Synthesis and isolation of **2**: Rhodamine B base was purchased from Sigma-Aldrich Corp. and purified by recrystallization from toluene. Ethyl-3,4,5-trihydroxybenzoate was purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Rhodamine B base (45.7 mg, 0.10 mmol) and ethyl-3,4,5-trihydroxybenzoate (20.0 mg, 0.10 mmol) were placed in a screw vial (20 cm^3) and acetonitrile (1 cm^3) was added. The mixture was shaken for a few minutes, and dark red solution was immediately obtained. The solution was kept for an hour with the solvent removed under ambient temperature and red blocks were precipitated. The precipitates were separated by decantation and the solvent was removed completely in vacuo, giving red crystals of **2** (22.0 mg, 0.034 mmol, 34% yield). For syntheses and isolation of **3** and **4**, see Supporting Information which is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html.

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