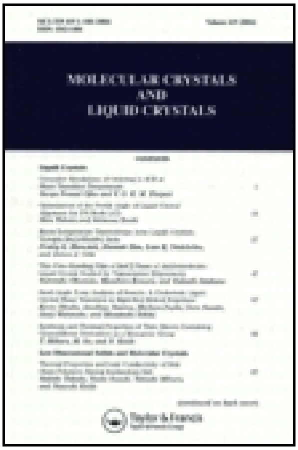

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Synthesis and Radiation Sensitivity of Phenoxazine Type Color Formers Including Thiol Ester Protective Group

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Synthesis and Radiation Sensitivity of Phenoxazine Type Color Formers Including Thiol Ester Protective Group

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*3,7-Bis(N,N-diethylamino)-10-(phenylthio)carbonylphenoxazine (***1a***) and its analogs (***1b–f***) were synthesized and the color change after* γ *irradiation was investigated. The color change of acetonitrile solutions of* **1a** *(*$[\mathbf{1a}]_0 = 1.0 \times 10^{-3}$ *M) after* γ *irradiation was identified by naked eyes at the dose of 20 Gy. Phenylthio-substituted compound* **1a** *showed more significant absorbance increase than phenoxy-substituted compound, 3,7-bis(N,N-diethylamino)-10-phenoxycarbonylphenoxazine (***2a***). The C–S cleavage in* **1a** *by* γ *irradiation was revealed to occur more easily than the C–O cleavage in* **2a***. The sensitivity of the color formers (***1a–f***) to* γ *rays was correlated with the stability of the thiyl radicals generated in the reaction.*

Keywords: γ rays; color former; dosimetry system; phenoxazine dyes; substituent effect

INTRODUCTION

γ rays are useful in various fields such as radiometric analysis, food hygiene or medical treatment, but they can ruin our health and cause cancer and even death. We cannot detect γ rays by any of our senses. The visualization of γ rays using leuco dyes [1,2], which change their color by γ irradiation, must be important to study.

The C–S cleavage by γ irradiation would occur more easily than that of C–O bonds [3,4]. In out previous study [5], tris(4-*N,N*-dimethylaminophenyl)methanethiol could produce the colored form ($\lambda_{\max} = 587.5$ nm) by C–S cleavage initiated by γ rays, and the absorbance change at

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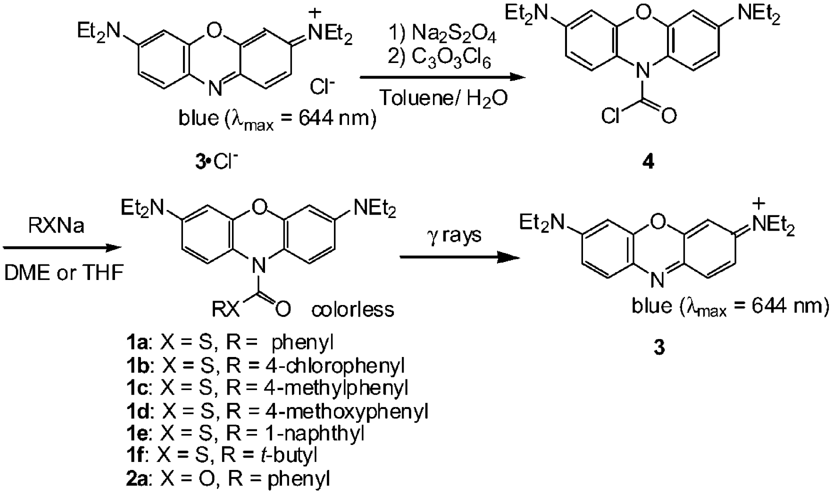
587.5 nm after γ irradiation of 10 Gy was about 100 times larger than that of a C—O analog, tris(4-*N,N*-dimethylaminophenyl)methanol. The introduction of a C—S bond into a cleavage position by γ irradiation will be a key concept to improve the sensitivity to γ rays. The leuco phenoxazine color formers, which consisted of a precursor of phenoxazine dye and a protective group, were revealed to give the colored form **3** ($\gamma_{max} = 644$ nm) by γ irradiation in our previous study [6]. As leuco phenoxazine type color formers are more stable to heat or light than triarylmethane type color formers, the leuco phenoxazine type color formers with a C—S bond at a cleavage position will be an excellent component of γ rays detection system.

In this paper, synthesis and sensitivity to γ rays of phenoxazine type color formers including a thiol ester protective group (**1a–f**), and their substituent effect on the sensitivity to γ rays will be reported.

RESULTS AND DISCUSSION

Phenoxazine type color formers including a thiol ester protective group (**1a–f**) were prepared by the analogous method with our previous paper [7] as shown in Scheme 1. 3,7-Bis(diethylamino)-10-chloroformylphenoxazine (**4**) was obtained by reduction of basic blue 3 (**3**•Cl$^-$) using sodium dithionite, followed by addition of toluene solution of triphosgen. Sodium thiolates (RSNa) were prepared from



SCHEME 1

sodium and corresponding thiols. Reaction between the chloroformylphenoxazine (**4**) and the sodium thiolates gave the compounds **1a–f** as white or pale yellow crystals. The yields were improved by using dimethoxyethane (DME) instead of tetrahydrofurane (THF) as solvent for the preparation of **1a–f** [8,9].

γ rays were irradiated to dry acetonitrile solutions of leuco dyes (1.0×10^{-3} M) with a dose rate of 600 Gy/h using ^{60}Co source. The electronic spectra of the solutions after γ irradiation were recorded on a spectrometer. The absorbance at 644 nm increased gradually as the irradiated dose increased. As the peak at the first absorption band of basic blue 3 was at 644 nm, generation of colored form **3** after γ irradiation was obvious. This color change to blue can be recognized by naked eyes after γ irradiation of 20 Gy.

The absorbance change observed in **1a** was compared with that of phenoxy compound **2a** (Fig. 1). The absorbances at 644 nm obtained for **1a** were larger than those for **2a** after irradiation from 10 Gy to 1100 Gy and the absorbance after irradiation of 1100 Gy was about 1.4 times larger than that for **2a**. Introduction of a sulfur atom into a cleavage position was effective to increase the sensitivity to γ rays of leuco phenoxazine type color formers. However, the introduction of a sulfur atom was less effective to increase the sensitivity to γ rays of leuco phenoxazine type color formers than we expected. By

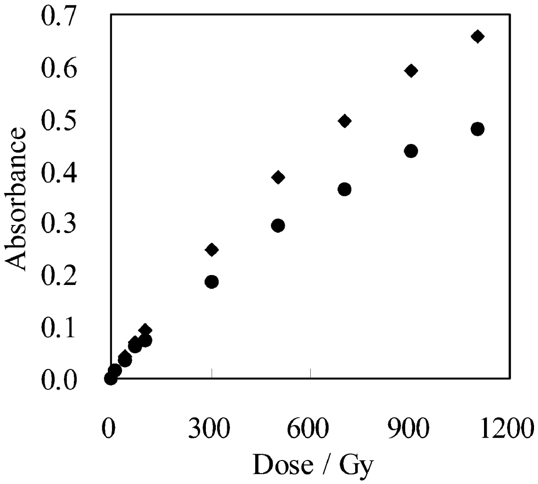


FIGURE 1 Absorbance changes at 644 nm observed in acetonitrile solutions of **1a** (◆) or **2a** (●) to give 3 ($\lambda_{max} = 644$ nm) after γ irradiation, $[\mathbf{1a}]_0 = [\mathbf{2a}]_0 = 1.0 \times 10^{-3}$ M.

the effect of the neighboring carbonyl group, the bond order of C–S bond in the thiol ester became larger than C–S bond [10,11], and the C–S cleavage must become more difficult than that in the triarylmethanethiol type color formers.

The effect of the substituents was investigated using phenylthio derivative (**1a**), 1-naphthylthio derivative (**1e**), and *t*-butylthio derivative (**1f**). The absorbance change at 644 nm observed for **1a, 1e** or **1f** after γ irradiation is shown in Figure 2 (A). The order of the sensitivity to γ rays was **1e** > **1a** > **1f**. The order was explained by the stability of the thiyl radicals generated by γ irradiation (Fig. 3 (A)). A free electron is stabilized by the delocalization in the conjugated system. The order of the stability of the thiyl radicals was **5e** > **5a** > **5f**, judging from the extent of conjugation. This order coincided with that of the sensitivity to γ rays of the leuco dyes. Generation of the thiyl radicals by γ irradiation would be made certain by MS spectra. Fragment peaks at the same mass number position with the corresponding thiyl radicals were detected in MS spectra of the color formers.

The effect of the substituent at *p*-position of the phenyl group in leuco dyes was investigated using **1a–d**. The absorbance change at 644 nm observed for **1a–d** is shown in Figure 2 (B). The order of the sensitivity to γ rays of **1a–d** was **1b** > **1a** > **1c** > **1d**. This order could be explained by the same consideration as mentioned above for **1a**, **1e**, and **1f**. The order was same with the electron withdrawing ability of

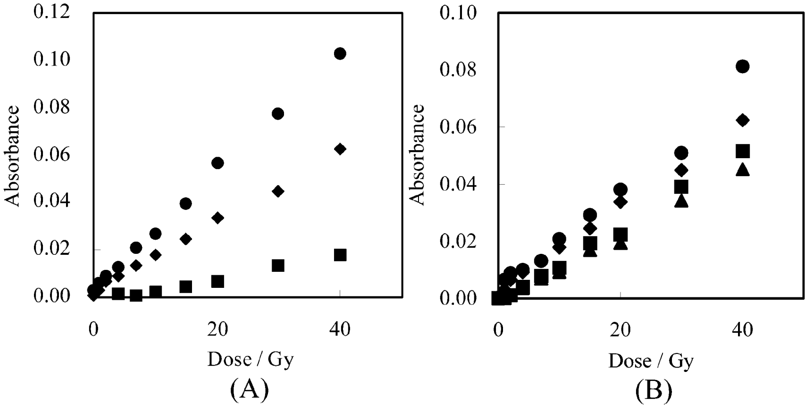


FIGURE 2 (A) Absorbance changes at 644 nm observed in acetonitrile solution of **1a** (◆), **1e** (●) or **1f** (■) to give 3 ($\lambda_{max} = 644$ nm) after γ irradiation, $[\mathbf{1a}]_0 = [\mathbf{1e}]_0 = [\mathbf{1f}]_0 = 1.0 \times 10^{-3}$ M; (B) Absorbance changes at 644 nm observed in acetonitrile solution of **1a** (◆), **1b** (●), **1c** (■) or **1d** (▲) to give 3 ($\lambda_{max} = 644$ nm) after γ irradiation, $[\mathbf{1a–d}]_0 = 1.0 \times 10^{-3}$ M.

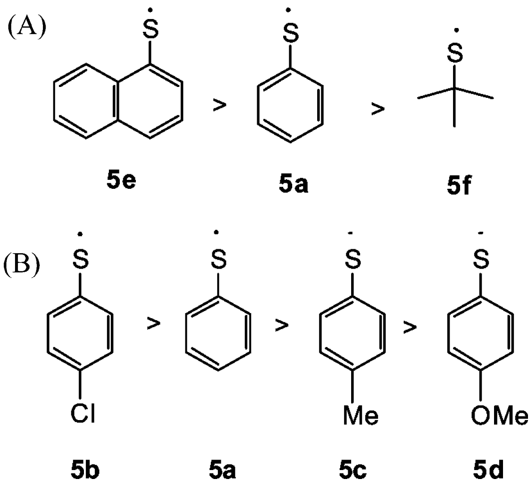


FIGURE 3 Structures and orders of stability of the thiyl radicals (**5a–f**).

the substituent at *p*-position of the phenyl group. The delocalization of a free radical to the phenyl ring increases as the electron withdrawing ability of the substituents on the phenyl ring increases. Thus, the order of the stability of the thiyl radicals was **5b** > **5a** > **5c** > **5d** (Fig. 3 (B)). This order coincided with that of the sensitivity to γ rays of the leuco dyes.

The correlation between the absorbances at 644 nm observed in the solution of **1a–d** after γ irradiation of 15 and 40 Gy and Hammett sigma constants at *para* position is shown in Figure 4. The absorbances and Hammett sigma constants showed a linear relationship and the correlation constants (R^2) were above 0.99 in both case. These correlations indicated that the sensitivity to γ rays of the color formers concerned with the stability of the thiyl radicals.

CONCLUSION

3,7-Bis(*N,N*-diethylamino)-10-(phenylthio)carbonylphenoxazine (**1a**) and its analogs (**1b–f**) were synthesized and the color changes after γ irradiation were investigated. The γ irradiation to acetonitrile solutions of **1a** ($[\mathbf{1a}]_0 = 1.0 \times 10^{-3}$ M) was identified by color change at the dose of 20 Gy. Phenylthio substituted compound **1a** showed more significant absorbance increase than phenoxy substituted compound, 3,7-bis(*N,N*-diethylamino)-10-phenoxycarbonylphenoxazine (**2a**). The absorbance change at 644 nm for **1a** was about 1.4 times larger than

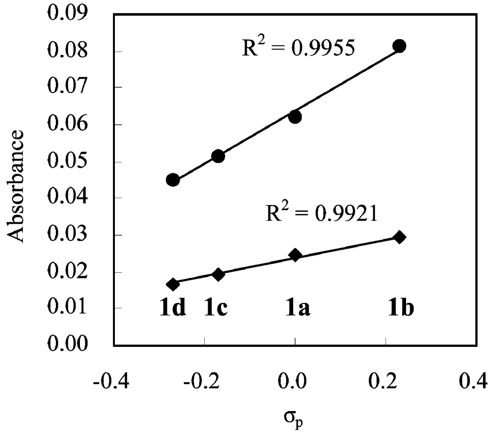


FIGURE 4 Correlation between absorbance at 644 nm observed in acetonitrile solutions of **1a–d** after γ irradiation (◆: 15 Gy, ●: 40 Gy) and Hammett sigma constants for substituents at *p*-position of phenyl ring in **1a–d**.

that for **2a** after irradiation of 1100 Gy. The sensitivity of the color formers (**1a–f**) to γ rays was correlated with the stability of the thiyl radicals (**5a–f**) generated in the reaction.

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