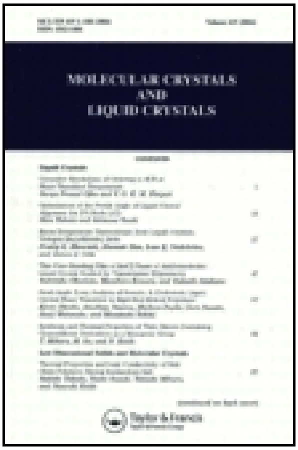

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Application of Photochromic Benzodixanthene Endoperoxide to a Novel Dosimetry System

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Application of Photochromic Benzodixanthene Endoperoxide to a Novel Dosimetry System

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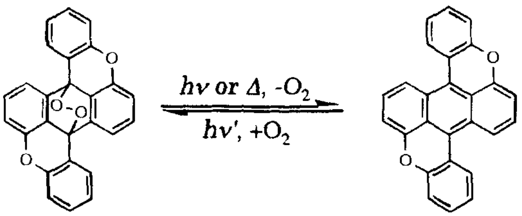
A colorless toluene solution of benzo[1,2,3-*kl*:4,5,6-*k'l'*]dixanthene endoperoxide (BDXepo) **1** slowly changes to red BDX **2**, by refluxing at 110 °C in toluene. However, in the presence of HCl, **2** was formed more rapidly from **1** even at room temperature. A novel dosimetry system was proposed using **1** and acid generating materials such as chlorinated alkanes. A chloroform solution of **1** ([**1**] = 1.0×10^{-3} M) gave red color of **2** after irradiation with γ ray at 73 Gy.

Keywords: Photochromism; Dosimetry system; Benzodixanthene Endoperoxide; Acid catalyst; γ ray

INTRODUCTION

Interest in photochromic behavior of benzo[1,2,3-*kl*:4,5,6-*k'l'*]dixanthene (BDX) **2** was first addressed by Schmidt and coworkers.[1] Photooxidation of the red solution of **2** (λ_{max}: 541 nm) in toluene by visible light produced the colorless **1** (λ_{max}: 301 nm).[1,2] The endoperoxide **1** in toluene has been known to give **2** slowly with the liberation of molecular oxygen by heating above 100 °C.



BDXepo **1** BDX **2**

We found that in the presence of HCl, a toluene solution of BDXepo **1** containing HCl immediately changes its color to red even at room temperature. We expected that HCl generation by the irradiation could lead to an application of the photochromic compound **1** to a novel dosimetry system.

EXPERIMENTAL

UV-Vis Spectra were recorded on a Shimadzu UV-2100 spectrophotometer. IR spectra were obtained on JASCO A-302 and Perkin-Elmer 1600 FT-IR. ^{1}H NMR spectra were recorded on Bruker AC-300 spectrometer, using tetramethylsilane as an internal standard. Thin-layer chromatography (TLC) was performed on plastic sheets (1.0 x 4.0 cm) coated with Merck silica gel $60F_{254}$.

Compound **2** was synthesized according to the procedure of literatures.[1,3]A chloroform solution (400 ml) of **2** (227 mg, 0.774 mmol) was irradiated using a 100 W tungsten lamp with bubbling air for 1.5 h. The solution turned from red to almost clear. After chloroform was removed, recrystallization from chloroform afforded **1** (165 mg, 57 %). Clear powder. Spot of TLC was clear (Rf = 0.6), and turned red by irradiation with UV lamp (254 nm). ^{1}H NMR($CDCl_3$): δ / ppm; 6.95 (dd, 2H), 7.11 (dd, 2H), 7.30 (dd, 2H), 7.35 (dd, 2H), 7.37 (dd, 2H), 7.58 (pseudo-t, 2H), 7.82 (dd, 2H). UV-Vis (λ_{max} / nm (ε / M^{-1} cm^{-1}), toluene): 304 (8500).

Aliquots (10 ml) of $CHCl_3$ solutions of BDXepo **1** (1.0×10^{-3} M) were irradiated with ^{60}Co γ ray at room temperature after having been deoxygenated by flushing the solutions for about 30 min with pure argon gas. Irradiation was performed at the dose rate of 1090 Gy h^{-1}.

RESULTS AND DISCUSSION

Absorption Spectrum Change of the Reaction of BDXepo 1 with HCl

When a toluene solution of HCl ([HCl] = 2.6×10^{-2} M, 1.5 ml) was added into a solution of **1** ([**1**] = 1.0×10^{-3} M, 1.5 ml) at room temperature, a new absorption band assigned to **2** appeared. Namely, the colorless toluene solution containing **1** turned to red, in which the absorption maximum was observed at 541 nm. The new peak was found to increase linearly with the passage of time.

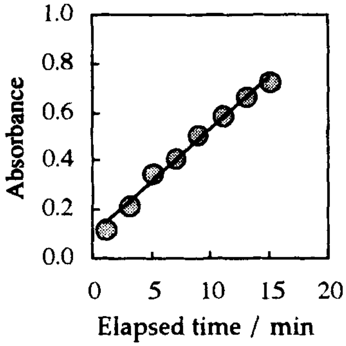


FIGURE 1 Absorbance change (541 nm) upon addition of HCl to toluene solution of **1** at room temperature. [HCl] = 1.3×10^{-2} M, [**1**] = 5.0×10^{-4} M, [HCl]/[**1**] = 26.

Mechanism of the Reaction of BDXepo 1 in Chloroform

It is known that a chain dechlorination reaction takes place in the γ ray irradiation of chloroform, resulting in the formation of HCl[4,5]. As we would expect, HCl generated from $CHCl_3$ by γ irradiation, results in the liberation of oxygen by π electron migration. Actually, HCl from

$CHCl_3$ irradiated with γ ray was detected with neutralization titration ([HCl] = 6.8×10^{-4} M).

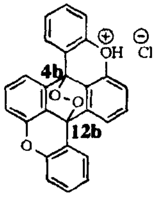
The mechanism, the catalytic effect of **1** by adding HCl, has been supposed to bring about the following equations. In the first step, γ ray irradiation leads chloroform to form a chlorine radical (equation 1)[4,5]. Secondly, the radical reacts with another chloroform molecule to generate HCl (equation 2). The reaction of the resulting trichloromethyl radical with chloroform gives chlorine radical (equation 3). The G value of HCl is reported to 10.2,[6] indicating that these reactions are chain propagating step.

$$CHCl_3 \xrightarrow{\gamma\ ray} \bullet CHCl_2 + \bullet Cl \qquad (1)$$

$$\bullet Cl + CHCl_3 \longrightarrow \bullet CCl_3 + HCl \qquad (2)$$

$$\bullet CCl_3 + CHCl_3 \longrightarrow CCl_3\text{-}CHCl_2 + \bullet Cl \qquad (3)$$

$\mathbf{1} + HCl \rightleftharpoons$



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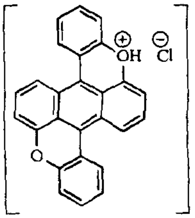
(4)

$\mathbf{3} \xrightarrow{-{}^1O_2}$



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(5)

$$\mathbf{4} \rightleftharpoons \mathbf{2} + HCl \qquad (6)$$

HCl generated by equation (2) reacts with **1** to give salt **3** (equation 4). The attachment of the proton to the ether oxygen gives rise to the increase of electron density at carbon atoms **4b** and **12b**. The bonds between the oxygen and the carbon atoms become weak, and the release of singlet oxygen by the scission of the bonds leads to form salt **4** (equation 5). It is known that a singlet oxygen easily attacks to a condensed aromatic compound by a Diels-Alder type reaction at positions of the largest π electron density of the highest occupied molecular orbital (HOMO). [7,8] Finally, the equilibrium reaction of equation (6) leans toward the right side, and red compound **2** is formed.

Absorption Change with the Passage of Time after γ ray Irradiation

After the colorless solution of **1** in chloroform containing 0.5 % ethanol was irradiated with γ ray up to 182 Gy at room temperature, the absorbance of **2** at 541 nm gradually increased with the passage of time (FIGURE 2).

As a result, the application of γ ray dosimetry can be expected. Although molar extinction coefficient ε (λ_{max} = 541 nm, toluene) of BDX **2** is very high in value,[9] 4.29, the absorption intensity is not enough. This indicates that interaction between **1** and HCl is very weak.

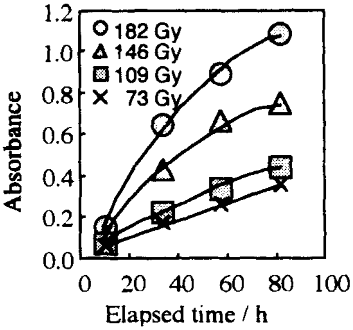

FIGURE 2 Absorbance change of γ irradiated BDXepo **1** in $CHCl_3$ with 0.5 % ethanol at room temperature. [**1**] = 1.0×10^{-3} M

CONCLUSION

In summary, we have presented the result that with toluene solution including HCl, the formation of **1** from **2** was observed; HCl do plays an important role in the mechanism of color form. A wide assortment of color-changing materials may serve as qualitative radiation monitoring labels over fairly wide range of high doses, depending on the material used. Acid generation occurs by irradiation to the acid generator with dissociable hydrogen and subsequent release of a proton, probably followed by the cascade of events of equation 1 to 3. Studies of the interaction between **1** and acid are now in progress, using the products prepared by γ radiation synthesis from related systems. The results will be useful to those developing radiation-dosimeter for applications.

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