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Photochromism and Photomagnetism of Biindenylidene-Dione Derivative in a Single Crystalline Phase

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PHOTOCHROMISM AND PHOTOMAGNETISM OF BIINDENYLIDENE-DIONE DERIVATIVE IN A SINGLE CRYSTALLINE PHASE

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[2,2′-Bi-1H-indene]-1,1′-dione-3,3′-dihydroxyl-3,3′-diethyl ***(1)*** *was found to undergo photochromism in a single crystalline phase from yellow to green. And at the same time a stable organic radical was generated which had been detected by electron spin resonance spectroscopy. The structure of* ***1*** *was determined by X-ray crystallographic analysis.*

Keywords: photochromism; free radical; electron spin resonance; paramagnetism; X-ray crystallographic analysis

INTRODUCTION

Organic photochromism and photomagnetism are two remarkable fields of organic functional materials. A large number of scientists have devoted themselves to the study on organic photochromism, which can occur in solution or in solid-state. The solid-state photochromism has attracted newer attentions due to its practical uses in various optoelectronic devices, such as optical memory, photo-optical, display systems, and so on [11]. However, photochromic molecules that show reactivity in the crystalline phase are rather rare. Typical examples are N-salicylideneanilines [2], 2-(2,4-dinitrobenzyl)pyridine [3], diphenyl-maleonitrile [4], triarylimidazole dimer [5], aziridines [6] and diarylper-fluorocyclopentenes [7].

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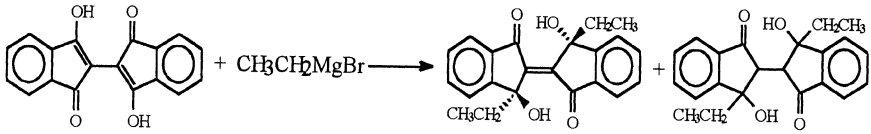
Compared with the research on photochromism, photomagnetism is a fairly new and original topic. Since the theory of ferromagnet based on molecular system was first put forward [8], scientists have done a great deal designing and synthesizing organic compounds with magnetic properties, which have broken the traditional idea that organic materials cannot be ferromagnetic. There has been considerable interest in the magnetic behavior of organic free radicals, and particularly in the development of materials that exhibit spontaneous magnetic order or ferromagnetism. Organic ferromagent shows highly potential applications in electromagnetic shield, magnetic recorded materials such as flexible magnetic disk, optic-magnetic disk, and so on [9].

We found that compound **1** has photochromic and photomagnetic properties mentioned above. It was obtained unexpectedly by the nucleophilic addition reaction of ethylmagnesium bromide with 2,2′-biindan-1,1′,3,3′-tetraone existing in the di-enolic form [10], which had been expected to gave compound **2**. The structure of compound **1** was confirmed by X-ray crystallographic analysis.[†]



1 **2**

Compound **1** has a reversible conversion that can be expressed as follows:

$$\underset{\mathbf{1a}}{\text{yellow crystal}} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \underset{\mathbf{1b}}{\text{green crystal}}$$

The yellow single crystal **1a**, obtained by recrystallization from dichloromethane, turned to deep green crystal **1b** when exposed to UV-VIS light of >300 nm. The green crystal **1b** showed ESR signals in the solid state.

In this paper, we describe the photochromic property of [2,2′-Bi-1H-indene]-1,1′-dione-3,3′-dihydroxyl-3,3′-diethyl (**1**) in the single crystalline phase. The course of color change is monitored by UV spectra and of radical's generation, by ESR spectroscopy.

[†]The data will be published elsewhere.

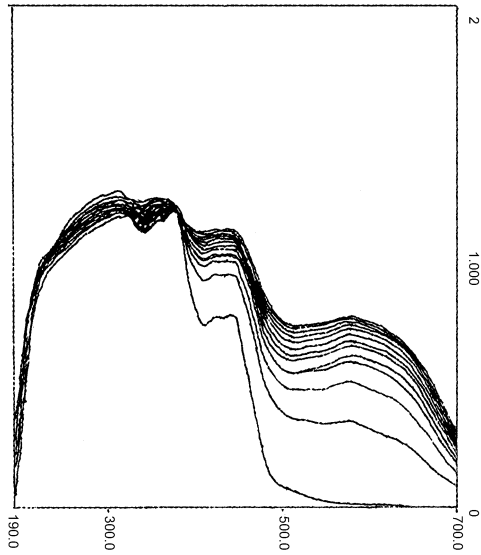


FIGURE 1 UV spectral changes of **1a** in the solid state on irradiation. Measurement was made every 5 min from the top to the bottom.

RESULTS AND DISCUSSION

The UV-VIS Solid Reflection Spectra

Photoirradiation of the yellow single crystal **1a** with UV-VIS light originated by a high pressure Hg-lamp of Pyrex housing leads to the formation of a green single crystal **1b** without change in the crystal shape of **1a**. The measurement of color change was conducted by UV-VIS spectra in the solid state every 5 minutes (Fig. 1). During the reaction, no remarkable changes were observed in the IR spectra.

ESR Spectroscopy Analysis

Magnetic properties of **1a** and **1b** have been investigated with the help of ESR spectroscopy. The yellow state **1a** had no ESR signal, while **1b** produced a distinct ESR signal after irradiation (Fig. 2).

The signal appeared between the Mn-mark of 3 and 4. The g value was 2.004 which was calculated by the known parameters of g_3 and g_4 of Mn-mark.

The radical is stable at ambient temperature and relatively insensitive toward oxygen, for its ESR signal can also be conveniently observed and

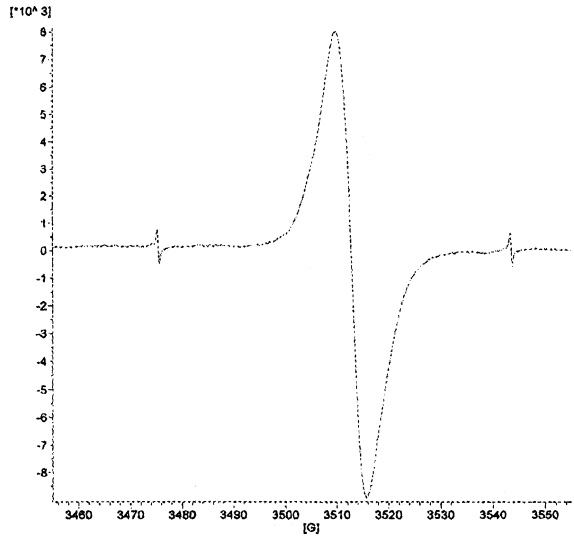


FIGURE 2 ESR spectrum of **1b** in the solid state at room temperature. Measurement conditions: center field, 3505.000 G; sweep width, 100.000 G; modulation, 100.00 KHz; Amplitude, 0.2 G. The ESR test was carried out on a Bruker EMX-6/1 EPR Spectrometer.

identified even after two months. This is an important aspect for potential practical use.

The Relationship between Photochromism and Light-induced Paramagnetism

Tanaka and Toda have reported that several *trans-syn*-3,3′-diaryl-2,2′-biindenyl-idene-1,1′-dione derivatives exhibited photo-chromism due to the formation of triplet biradicals in the crystal [11]. We found that the compound **1** showed photochromic properties also related to the light-induced paramagnetism. Although in one case the yellow crystal of **1** having no ESR signal similarly turned to deep green crystal with the generation of a radical, we have no experimental evidence for interpreting that both cases are mechanistically similar and we should await further experimental and theoretical studies.

CONCLUSION

It has been demonstrated that [2,2′-Bi-1H-indene]-1,1′-dione-3,3′-dihydroxyl-3,3′-diethyl undergoes photochromism and light-induced

paramagnetism in the single crystalline phase. Upon irradiation with UV-VIS light, the yellow colored crystal turned to deep green crystal, and at the same time, an organic radical was generated. It is apparent that the color chang attributes to the generation of the radical. Further investigation should be done to determine how the radical is generated, and the mechanism of photochromism.

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