A Remarkable Isotope Effect on the Photochromism of trans-Biindenylidenedione in the Solid State

YAMAMOTO, Yohei, TANAKA, Hideyuki, Mino R, Caira, TANAKA, Koichi

Chemistry Letters, 32(8): 680-681

2003

http://hdl.handle.net/10112/5621

Journal Article

publisher
A Remarkable Isotope Effect on the Photochromism of trans-Biindenylidenedione in the Solid State

Koichi Tanaka,* Yohei Yamamoto, Hideyuki Takano, and Mino R. Caira

1Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790-8577
2Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa

(Received May 9, 2003; CL-030401)

A remarkable deuterium isotope effect on the photochromism of 3,3′-diaryl-3H,3′H-[2,2′]biindenylidene-1,1′-dione (2) in the solid state has been found. The yellow crystals of 2 and 2-d₂ were immediately changed to reddish purple crystals upon photoirradiation in the solid state. This color-change is reproducible and no decomposition of crystals was observed. We have now found that 2-d₂ returned back to the original yellow crystals under dark for 72 h, whereas that of 2 faded within 2 h.

Organic photochromic compounds have received considerable attention in recent years because of their potential applications such as information storage, electronic display systems, optical switching devices, ophthalmic glasses, and so on. Several types of organic photochromic compounds such as naphthopyrans, spiropyran, fulgides, salicylideneanilines and diarylethenes have been discovered and their properties investigated. Recently, we have reported a new type of photochromic compound, trans-3,3′-diaryl-3H,3′H-[2,2′]biindenylidene-1,1′-dione (2) which shows photochromism in the crystalline phase. The yellow crystals of 2 turned reddish-purple when exposed to sunlight for a few minutes, and the reddish-purple crystals return slowly to yellow in the dark. However, irradiation of 2 in CH₂Cl₂ solution gives its cis-isomer 3, irreversibly. The reddish-purple crystals show EPR signals of triplet biradicals such as 4 formed by twisting the central C=C bond of 2 upon photoirradiation in the solid state. This color-change is reproducible and no decomposition of crystals was observed. We have now found that trans-3,3′-diaryl-3D,3′D-[2,2′]biindenylidene-1,1′-dione (2-d₂) prepared by treatment of 1 with Zn–ZnCl₂ in THF–D₂O shows more stable photochromism than 2 in the solid state.

Reduction of biindenones (1a) with Zn–ZnCl₂ in THF–D₂O gave the corresponding trans-3,3′-diaryl-3D,3′D-[2,2′]biindenylidene-1,1′-dione (2a-d₂) as yellow crystals.

![Scheme 1.](image)

**Figure 1.** Photographs of the single crystal of 2a a) before and b) after photoirradiation.

**Figure 2.** UV spectral changes of a) 2a and b) 2a-d₂ in the solid state. Measurement was successively every a) 30 min and b) 60 min from the top (after irradiation) to the bottom.

Copyright © 2003 The Chemical Society of Japan
the crystal structures were likewise shown to superimpose to
of the thermal ellipsoids in Fig. 3. Using molecular graphics,
high. This is even reflected in the magnitudes and orientations
showed that the level of molecular isostructurality is remarkably
variety of similar systems are under investigation to determine
the origin of the effect.

Financial support from The Matsuda Foundation to K. T. is
gratefully acknowledged. M. R. C. thanks the University of
Cape Town for financial assistance.

References and Notes
1 B. V. Gemert, in “Organic Photochromic and Thermochromic
Compounds,” ed. by J. C. Crano and R. J. Guggelmetti, Plenum Press,
Kobatake, K. Uchida, E. Tsushima, and M. Irie, Chem. Commun.,
Nishikiori, Chem. Lett., 2000, 142. g) M. Nanasawa, M. Miwa, M.
B. L. Houze, C. Bochu, Y. Teral, M. Campredon, and G.
Eichen, J.-M. Lehn, M. Scherli, D. Haarer, J. Fischer, A. DeCian,
A. Corval, and P. Trommsdorff, Angew. Chem., Int. Ed. Engl., 34,
2530 (1995). o) H. Koyama, T. Kawato, H. Nishikiori, H. Kanatomi,
Soc., 121, 10937 (1999). p) S. Delbaere, B. L. Houze, C. Bochu,
Delbaere, B. L. Houze, C. Bochu, Y. Teral, M. Campredon, and G.
Delbaere, B. L. Houze, C. Bochu, Y. Teral, M. Campredon, and G.