

# A novel photochromism of biindenylidene in crystal form

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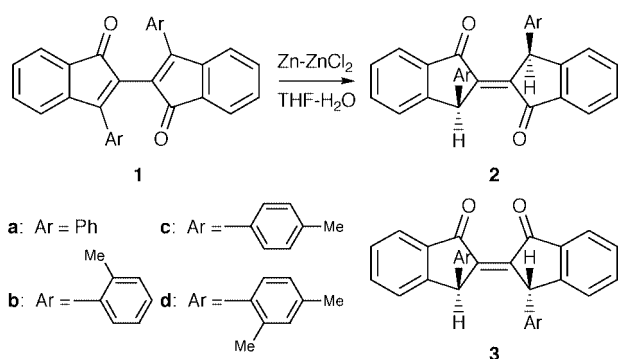
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The yellow crystals of *trans-syn*-3,3'-diaryl-2,2'-biindenylidene-1,1'-diones (**2**) turned to reddish purple crystals when exposed to sunlight, which showed EPR signals of triplet biradicals in the solid state.

Organic photochromic compounds have received considerable attention in recent years because they have potential application in areas such as information storage, switching devices, electric display systems, and so on.<sup>1</sup> Several types of organic photochromic compounds such as spiroyrans, fulgides, anils, hydrazone, stilbene and sydnone have been found and their properties have been investigated.<sup>2</sup> The photochromism in crystals has also been studied for diarylperfluorocyclopentenes,<sup>3</sup> salicylideneanils<sup>4</sup> and diphenylmaleonitrile.<sup>5</sup> We have now found a new type of photochromic compound, *trans-syn*-3,3'-diaryl-2,2'-biindenylidene-1,1'-diones (**2**) which show photochromism in a single crystalline phase. The yellow crystals of **2** turned to reddish purple crystals when exposed to sunlight for a few minutes, and the reddish purple crystals returned slowly to yellow crystals in the dark or quickly upon heating at 60 °C. The reddish purple crystals showed EPR signals of triplet biradicals. This is the first example of photochromism based on the formation of triplet biradicals in the crystal.

Reduction of biindenones (**1a-d**)<sup>6</sup> with Zn-ZnCl<sub>2</sub> reagent<sup>7</sup> gave the corresponding *trans-syn*-3,3'-diaryl-2,2'-biindenylidene-1,1'-diones (**2a-d**) as yellow prisms. For example, treat-



Scheme 1

ment of **1a** with Zn-powder and ZnCl<sub>2</sub> in 10% aqueous THF under stirring for 10 min at room temperature gave **2a** † in 45% yield. Similarly, **2b-2d** were obtained as yellow prisms in the yields listed in Table 1.

The yellow prisms of **2a** turned to reddish purple crystals on exposure to sunlight for a few minutes. In the dark, the reddish purple crystals returned slowly to the yellow crystals. The reaction was monitored by UV spectra in the solid state (Fig. 1). Heating the irradiated sample above 60 °C reverted its color to yellow immediately. The reddish purple crystals of **2a** showed EPR signals which are assignable to triplet biradicals (zero field splitting parameters  $D = 13.78$  G,  $E = 1.377$  G;  $g_{xx} = 2.0026$ ,

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Table 1 Synthesis and properties of *trans*-biindenylidenes **2a-d**

Compound	Ar	Yield (%)	Mp/°C	Photochromism	EPR
<b>2a</b>	Ph	45	203–205	yes	+
<b>2b</b>		33	214–216	yes	+
<b>2c</b>		47	{198–200 (A) 211–215 (B)}	yes yes	+
<b>2d</b>		51	228–230	no	–

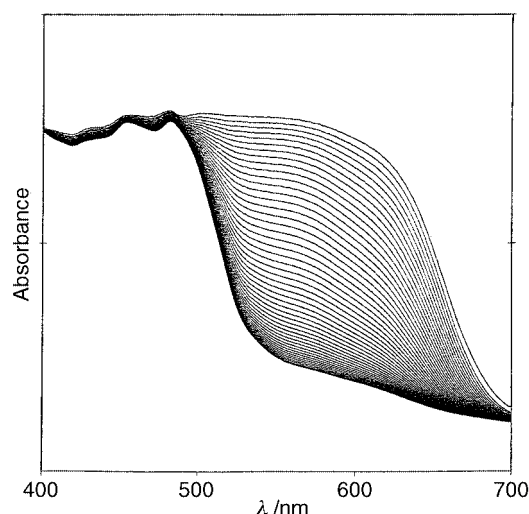


Fig. 1 UV spectral changes of **2c** in the solid state. Measurement was successively every 30 min from the top (after irradiation) to the bottom (after keeping 24 h).

$g_{yy} = 2.0027$ ,  $g_{zz} = 2.0020$ ) (Fig. 2). The biradical is stable with a half-life of about one hour, although it is thermally labile and returned to **2a** immediately upon heating at 60 °C. During the reaction, no detectable changes were observed in the solid state IR spectra, and no decomposition occurred.

Similarly, **2b** and **2c** showed photochromism, and gave the similar reddish purple crystals that showed EPR signals upon photoirradiation in a single crystalline phase. Of the two crystal modifications of **2c**, yellow prisms (A) obtained by recrystallization from toluene showed strong photochromism, while yellow prisms (B) obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> showed weak photochromism in the crystalline state. The photochromic properties of **2a-2c** are probably due to a

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**Table 2** Photoisomerization of *trans*-biindenylidene **2a–d** to *cis*-biindenylidene **3a–d** in CH<sub>2</sub>Cl<sub>2</sub>

Compound	Yield (%)	Mp/°C
<b>3a</b>	90	209–211
<b>3b</b>	88	230–232
<b>3c</b>	85	236–238
<b>3d</b>	91	239–241



**Fig. 2** EPR spectrum of irradiated **2a** in the solid state. Measurement conditions: field, 3360 ± 50 G; modulation, 2 GHz; amplitude, 2.5 × 10.

restricted rotation around the double bond in the crystal, because photoirradiation of **2a–c** in CH<sub>2</sub>Cl<sub>2</sub> solution with a high pressure Hg-lamp gave the corresponding *cis-anti*-isomer (**3a–c**), irreversibly (Table 2). Nevertheless, **2d** did not show photochromic behavior in the solid state, although it gave *cis-anti*-isomer (**3d**) when irradiated in solution. The molecular packing of **2d** would not be suitable for photoexcitation to the corresponding triplet state in the crystal.

Further detailed studies on the relationship between the crystal structures and photochromic properties of **2** are in progress.

## Experimental

### *trans-syn*-3,3'-Diaryl-2,2'-biindenylidene-1,1'-diones (**2a–d**)

Treatment of **1a** (3.0 g, 7.3 mmol) with Zn powder (6 g) and ZnCl<sub>2</sub> (1 g) in 10% aqueous THF (30 ml) under stirring for 10 min at room temperature gave **2a** (1.35 g, 45%) as yellow prisms.

Mp: 203–205 °C (d); IR  $\nu$  C=O 1685 cm<sup>-1</sup>; UV:  $\lambda$ /nm ( $\epsilon$ ) 252 (10000), 303 (16000), 340sh (7800), 443 (260), 468 (230); <sup>1</sup>H NMR:  $\delta$  5.80 (2H, s, CH); Anal: Found: C, 87.53%; H, 4.93%. Calcd. for C<sub>30</sub>H<sub>20</sub>O<sub>2</sub>: C, 87.36%; H, 4.89%. Similarly, **2b–2d** were also prepared by the same synthetic method (Table 1).

### *cis-anti*-3,3'-Diaryl-2,2'-biindenylidene-1,1'-dione (**3a–d**)

A solution of **2a** (1.0 g, 2.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 ml) was irradiated with a 100 W high pressure Hg-lamp for 1 h. The reaction mixture was evaporated *in vacuo* and the crude product was recrystallized from EtOAc to give **3a** (0.9 g, 90%) as yellow prisms. Mp: 209–211 °C; IR:  $\nu$  C=O 1710, 1690 cm<sup>-1</sup>; UV:  $\lambda$ /nm ( $\epsilon$ ) 249 (7100), 302 (22000); <sup>1</sup>H NMR:  $\delta$  4.50 (2H, s, CH); Anal: Found: C, 87.50%; H, 4.91%. Calcd. for C<sub>30</sub>H<sub>20</sub>O<sub>2</sub>: C, 87.36%; H, 4.89%. Similarly, **3b–d** were also prepared by the same synthetic method (Table 2).

## Notes and references

† The structure was elucidated by X-ray crystal structure analysis. The data will be published in the near future.

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