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

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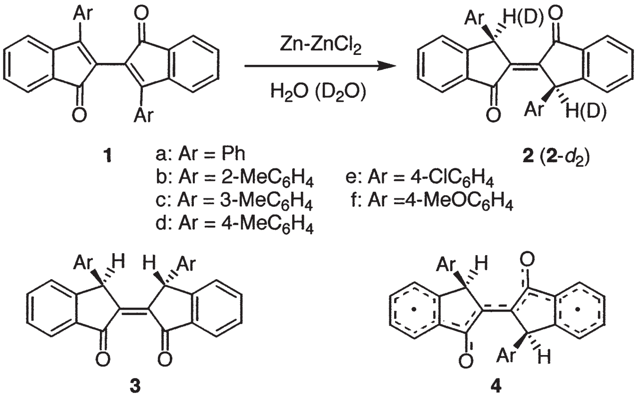
A remarkable deuterium isotope effect on the photochromism of 3,3′-diaryl-3*H*,3′*H*-[2,2′]biindenylidene-1,1′-dione (**2**) in the solid state has been found. The yellow crystals of **2** and **2**-d_2 were immediately changed to reddish purple crystals upon photoirradiation in the solid state. The reddish purple crystals of **2**-d_2 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.[1] Several types of organic photochromic compounds such as naphthopyrans, spiropyrans, fulgides, salicylideneanilines and diarylethenes have been discovered and their properties investigated.[2] Recently, we have reported a new type of photochromic compound, *trans*-3,3′-diaryl-3*H*,3′*H*-[2,2′]biindenylidene-1,1′-dione (**2**) which shows photochromism in the crystalline phase.[3] The yellow crystals of **2** turn 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 CH_2Cl_2 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-3*D*,3′*D*-[2,2′]biindenylidene-1,1′-dione (**2**-d_2) prepared by treatment of **1** with Zn–$ZnCl_2$ in THF–D_2O shows more stable photochromism than **2** in the solid state.

Reduction of biindenones (**1a**) with Zn–$ZnCl_2$ in THF–D_2O gave the corresponding *trans*-3,3′-diaryl-3*D*,3′*D*-[2,2′]biindenylidene-1,1′-dione (**2a**-d_2) as yellow crystals. ^1H NMR peak due to the C–H proton (at δ 5.83 ppm in $CDCl_3$ for **2a**) disappeared by the conversion to the C–D in **2a**-d_2. Similarly, **2b**-d_2–**2f**-d_2 were obtained as pale yellow to yellow crystals. The yellow color of the crystals of **2a** was immediately changed to reddish-purple even under room light for several minutes. (Figure 1) The reddish-purple color faded and back to the original yellow under dark for 2 h at room temperature (Figure 2). Interestingly, however, the reddish-purple color of **2a**-d_2 was more stable than that of **2a** and the color bleached in 72 h under the same conditions. Similarly, the red colors of **2b**-d_2, **2c**-d_2, **2d**-d_2, and **2f**-d_2 were more stable than those of **2b**, **2c**, **2d**, and **2f**, although the compounds **2e** and **2e**-d_2 did not show any photocoloration upon photoirradiation (Table 1).



Scheme 1.

Single crystal X-ray diffraction analyses of the representative compounds **2c** and **2c**-d_2 were performed to confirm the proposed molecular structures and to establish whether there were any differences in their crystal structures. The plate-like crystal morphologies were the same and the unit cell dimensions determined at room temperature (294 K) were the same within experimental error, suggesting isostructurality, which is not unexpected for the replacement of H by D at two sites. For intensity data-collection both crystals were cooled to 203(2) K in a stream of nitrogen vapor to optimize diffraction data quality. No phase change was detected on cooling either

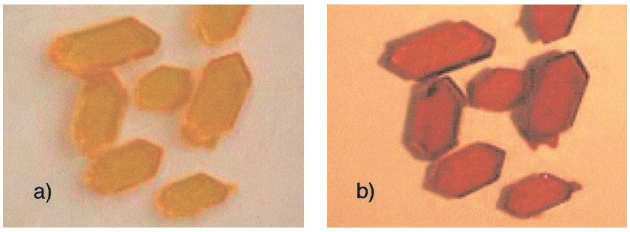


Figure 1. Photographs of the single crystal of **2a** a) before and b) after photoirradiation.

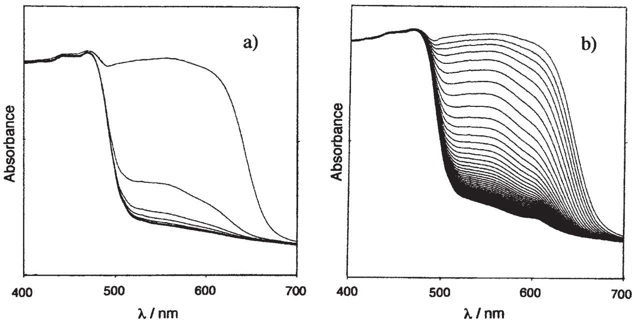


Figure 2. UV spectral changes of a) **2a** and b) **2a**-d_2 in the solid state. Measurement was successively every a) 30 min and b) 60 min from the top (after irradiation) to the bottom.

Table 1. Photochromism of *trans*-biindenylidendiones **2** and **2**-d_2

	2		**2**-d_2	
Ar	mp/°C	bleaching time/h	mp/°C	bleaching time/h
Ph	215–217	2	221–223	72
2-MeC_6H_4	223–225	2	228–230	10
3-MeC_6H_4	221–223	3	220–222	68
4-MeC_6H_4	216–218	3	218–220	8
4-ClC_6H_4	245–247	—a	254–256	—
4-$MeOC_6H_4$	168–170	4	179–181	10

a: no photochromic

crystal from 294 K. ORTEP-views of the molecules are shown in Figure 3.[4]

Comparison of bond distances, angles and torsion angles showed that the level of molecular isostructurality is remarkably high. This is even reflected in the magnitudes and orientations of the thermal ellipsoids in Fig. 3. Using molecular graphics, the crystal structures were likewise shown to superimpose to a remarkable degree, and **2c** and **2c**-d_2 may thus be considered to be indistinguishable by X-ray diffraction. The observed significant difference in the stability of photochromism can therefore be directly attributed to the isotopic change alone. Unit cell dimensions were also measured on the diffractometer for each crystal in its brightly colored state after exposure to sunlight for 10 min. These dimensions matched those reported below.[5]

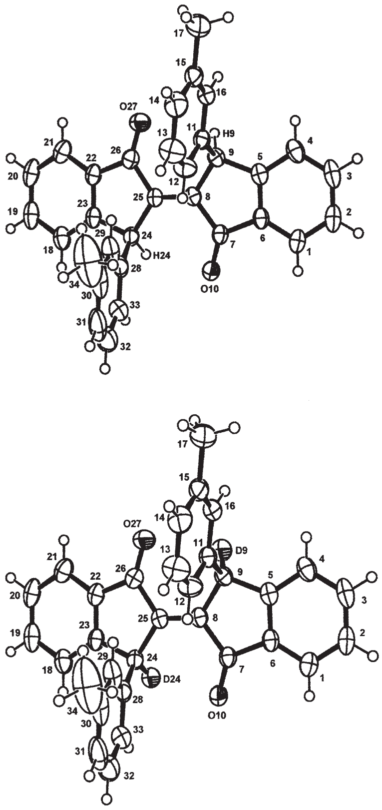


Figure 3. Molecular structures of **2c** (top) and **2c**-d_2 (bottom) with thermal ellipsoids drawn at the 50% probability level.

In the molecules of **2c** and **2c**-d_2 the indenylidenedione ring systems are individually planar to within ca. 0.05 Å but twisted slightly with respect to one another around the C8–C25 bond (1.342(2) Å in both molecules) This twist is reflected in the torsion angles C9–C8–C25–C26 [9.3(3), 9.5(3)°] and C7–C8–C25–C24 [8.4(3), 8.5(3)°], the first value in parentheses referring to **2c** and the second to **2c**-d_2. The orientations of the 3-MeC_6H_4-substituents relative to the bi-indenylidenedione system are given by the torsion angles C5–C9–C11–C16 [93.7(2), 93.6(2)°] and C23–C24–C28–C33 [98.3(2), 98.0(2)°]. Analysis of intermolecular interactions revealed only one C–H···O interaction in each crystal, namely C1–H1···O27^a ($a = 1 - x,\ -1/2 + y,\ 1/2 - z$) with C···O 3.263(2) Å in both structures.

We have discovered a remarkable deuterium isotope effect on the photochromism of *trans*-biindenylidendiones **2**-d_2 in the solid state, although the mechanism has not yet been clarified. A variety of similar systems are under investigation to determine the origin of the effect.

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References and Notes

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4 Intensity data were measured on a Nonius Kappa CCD diffractometer with Mo Kα-radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All H and D atoms were located. All were placed in idealized positions in a riding model except H9, H24, D9 and D24, which were allowed free refinement.

5 Crystal data for **2c**: $C_{32}H_{24}O_2$, $M_r = 440.51$, monoclinic, space group $P2_1/c$, $T = 203(2)$ K, $a = 11.3869(2)$, $b = 14.4134(3)$, $c = 15.1387(3)$ Å, $\beta = 111.152(1)°$, $V = 2317.22(8)$ Å^3, $Z = 4$, $D_{calcd} = 1.263$ Mg m^{-3}, 10937 reflections measured, 5719 unique and used in the refinement, $R1 = 0.0591$ for 3438 data with $I > 2\sigma(I)$, $wR2 = 0.1615$ for all data. Crystal data for **2c**-d_2: $C_{32}H_{22}D_2O_2$, $M_r = 442.52$, monoclinic, space group $P2_1/c$, $T = 203(2)$ K, $a = 11.3857(2)$, $b = 14.4099(4)$, $c = 15.1401(4)$ Å, $\beta = 111.182(1)°$, $V = 2316.2(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.269$ Mg m^{-3}, 9525 reflections measured, 5697 unique and used in the refinement, $R1 = 0.0591$ for 3130 data with $I > 2\sigma(I)$, $wR2 = 0.1636$ for all data.

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