Structure and photochemical properties of biindenylidene derivatives in the solid state

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Two photochromic compounds, *trans*-3,3'-dipentyl-3,3'-dihydroxy-2,2'-bi-1H-indene-1,1'-dione (**I**), and *cis*-3,3'-di (2-methylally)-3,3'-dihydroxy-2,2'-bi-1H-indene-1,1'-dione (**II**), were synthesised and their crystal structures were determined by X-ray crystallography. The photoinduced properties of the compound were studied. The results showed that compound **I** exhibited reversible photochromism, and at the same time a stable organic radical was generated, while compound **II** did not show photochemical properties.

Keywords: biindenylidene derivatives, photochromism, radical, crystal structure

Photochromism is defined as the photochemically reversible transformation of a chemical species between two isomers having different absorption spectra. Many photochromic compounds have been reported, and a few were found to be photochromic in the crystalline state.[1] Photochromic organic crystals are particularly interesting as potential novel materials for optical data processing and storage. It is also expected to be used to afford control over other physical properties in the solid state.[2] Typical examples include N-salicylideneanilines, nitrobenzylpyridines, triarylimidazole dimmers, diarylethenes and biindenylidene derivativies.[3-7] Among them, the biindenylidene derivatives are the most promising materials for single-crystal photochromism, as well as the generation of stable organic radicals.[8-11]

We now report the crystal structures and crystalline state photochemical properties of compounds **I** and **II**. The synthetic route is shown in Scheme 1.

Compounds **I** and **II** were obtained by the Grignard reaction of an alkylmagnesium bromide and 2,2'-biindanylidene-1,1',3,3'-tetraone under an argon atmosphere as shown in Scheme 1.[9] In order to confirm the structures, the products were subjected to spectroscopic analysis using IR, ^{1}H NMR and elemental analysis. Crystals of suitable quality for single crystal X-ray diffraction were obtained by slow evaporation from CH_2Cl_2 solutions. The molecular structure of **I** and **II** are shown in Figs 1 and 2.

Results and discussion

Photochromic properties in the solid state

The red *cis*- compound **II** had no colour change upon exposure to either sunlight or UV light, while the yellow *trans*- compound **I** turned to a reddish brown on irradiation

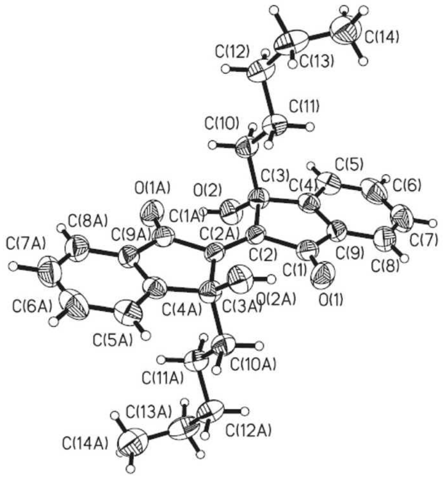


Fig. 1 Molecular structure of **I** with atom numbering scheme.

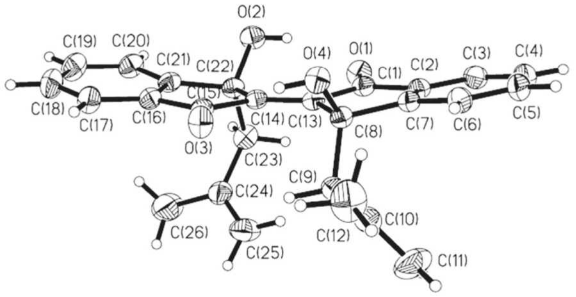
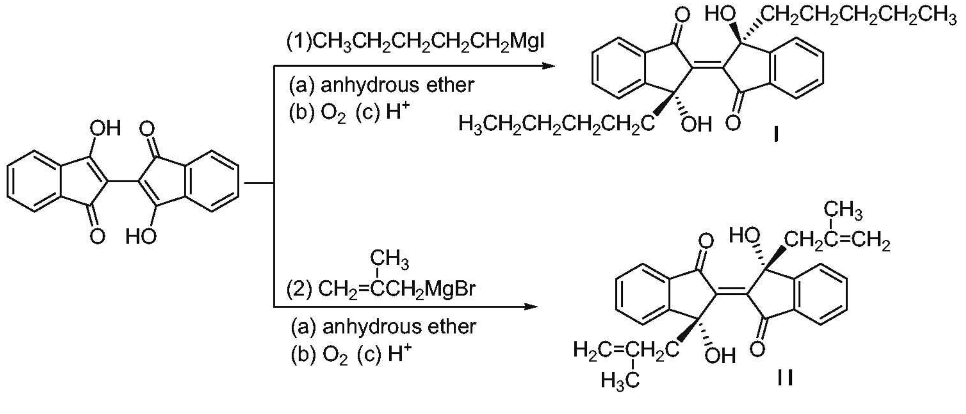


Fig. 2 Molecular structure of **II** with atom numbering scheme.



Scheme 1

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for a few minutes with the visible or ultraviolet light. The colour change in the solid state was monitored by UV VIS spectra (Fig. 3). The UV absorption band around 450–700nm appeared after photoirradiation in the solid state and resulted the photochromism. The irradiated sample **I** was stable at ambient temperature in air or in the nitrogen atmosphere, and the reddish brown **I** returned slowly to yellow in the dark.

ESR spectra

The ESR spectrum was determined at room temperature. Measurement conditions were as follows: centre field, 3505.00G; sweep width, 100.00G; modulation, 100.00KHZ; amplitude, 0.2G. After irradiation for a period of time, the red crystal **II** had no ESR signal, while reddish brown crystal **I** produced distinct ESR signals (Fig. 4).

The relationship between the crystal structure and photochemical properties

The asymmetric unit of **I** contains one half-molecule with the other half generated by a centre of inversion (Fig. 1); the centre of inversion lies at the mid-point of the C(2) =C(2A) bond [symmetry code: –x + 1, –y + 2, –z + 1]. The C(2) =C(2A) bond distance of 1.342 (4) Å confirms its double-bond character. The cyclopentenone ring adopts a flattened envelope conformation, with atom C2 at the flap. The two rings of indanione are almost perfectly parallel, and therefore the double bond is not distorted. The two pentyl groups are located on different sides of the double bond with the *trans*-configuration referring to the indanone planes. This arrangement allowed the formation of an extended π-conjugation over the whole molecular system. The structures of **I** was consistent with the photochromic mechanism of biindenylidene derivatives.[10] Light irradiation of **I** at room temperature resulted in the reorganisation of electron distribution to generate radicals; the radical producing the ESR signals was stabilised by the extended π-conjugation provided by the double bond linking the whole molecular system. Hence **I** showed photochemical properties.

The compound **II** had a similar underlying skeleton to **I**. However, the two 2-methylallyl substituents were located on different sides of the double bond and along *cis*- direction of the indanone planes. The steric effects of the substituents distorted the two indanone planes and the dihedral angle between the two indanone planes was 18.8°. The extended π-conjugation was not possible. Consequently, the radical was not stabilised and photochromism was not observed based the extended conjugation. Hence compound **II** did not show photochemical properties.

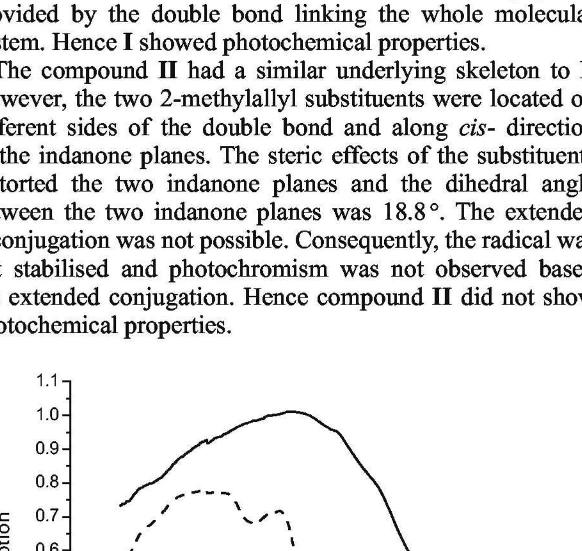

Fig. 3 UV spectral change of **I** (...) before and (—) after irradiation in the solid.

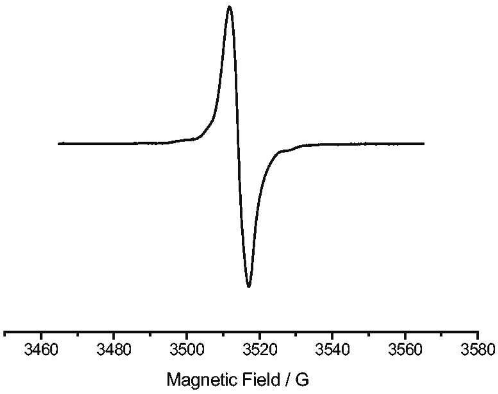

Fig. 4 ESR spectrum of irradiated **I** in the solid state at room temperature.

Experimental

All chemicals were purchased from commercial sources, and solvents were of analytical grade, and were dried by refluxing under N_2 over an appropriate drying agent and distilled before use. Melting points were determined with Yanagimoto MP-35 melting point apparatus. ^1H NMR spectra were recorded at 300 MHz on a Bruker-P300 instrument using TMS as an internal reference. Elemental analysis was performed on a YANACO CHN CORDER MT-3 apparatus. UV spectra were recorded on TU-1901 UV–vis spectrophotometer. ESR measurement was carried out on a Bruker EMX-6/1 EPR spectrometer. X-ray date collection was performed on a Bruker SMART APEX II diffractometer with Mo·Kα radiation. The structure was solved by direct methods (SHELXS-97)[12] and non-H atoms were refined by full-matrix least-squares method with anisotropic temperature factors (SHELXL-97).[12]

Synthesis of trans-3,3'-dipentyl-3,3'-dihydroxy-2,2'-bi-1H-indene-1,1'-dione (**I**): Mg (2.4 g, 0.10 mol), anhydrous ether (15 ml) under N_2 atmosphere was added to a three-necked 250-ml round-bottomed flask containing a stirrer bar, fitted with a pressure-equalising dropping funnel and a reflux condenser. To this suspension a solution of $CH_3CH_2CH_2CH_2CH_2Br$ (0.10 mol) was added in anhydrous ether (60 ml) from pressure-equalising funnel. After the addition was complete, the mixture was stirred under reflux for an additional 0.5 h. The pressure-equalising funnel was then recharged with 2,2'-biindanylidene-1,1',3,3'-tetraone (2.9 g, 0.01 mol) suspended in dry benzene (50 ml). The suspension was added portion-wise over a period of 20 min. The dark green reaction mixture was stirred at room temperature under a nitrogen atmosphere for 12 h, and then exposed to air for another 3 h. Finally, quenching the reaction with saturated NH_4Cl aqueous solution gave immiscible liquid phases. The crude desired compound **I** precipitated as an insoluble powder between the organic and aqueous phases. Filtration afforded the crude product, which was purified by column chromatography on silica gel. Yield: 29.6%. Yellow crystals: m.p. 133–134 °C. ^1H NMR(300 MHz, $CDCl_3$): δ(ppm) 7.71–7.38 (m, 8H, 8 ArH), 6.48 (s, 2H, 2 OH), 2.01–1.95(m, 4H, 2 CH_2–), 0.87–0.67(m, 12H, 2 CH_2–CH_2–CH_2–), 0.54–0.48(m, 6H, 2 CH_3). Anal. Calcd for $C_{28}H_{32}O_4$: C, 77.75; H, 7.46; Found: C, 77.96; H, 7.43%. IR (KBr): 3334 (–OH), 1675 (–C=O)cm^{-1}. Crystal data for **I**. $C_{28}H_{32}O_4$ M = 432.54, Monoclinic, a = 9.174(5) Å, b = 11.108(6) Å, c = 11.455(6) Å, $\alpha = \gamma = 90°$, β = 102.279(11)°, V = 1140.6(11)Å^3, T = 293(2) K, space group p2(1)/c, Z = 2, d = 1.259 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.083 mm^{-1}, 5770 reflections measured, 2234 unique (R_{int} = 0.0881), which were used in calculations. The data have been deposited at the Cambridge Crystallographic Data Centre as CCDC-695294.

Synthesis of cis-3,3'-di(2-methylally)-3,3'-dihydroxy-2,2'-bi-1H-indene-1,1'-dione (**II**)

The procedure was that previously described for compound **I**. The crude product **II** precipitated as an insoluble yellow powder between the organic and aqueous phases. Filtration afforded a crude product, which was purified by column chromatography on silica gel in 36.2% yield. Yellow powder, m.p. 238–240 °C. ^1H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.70–7.37 (m, 8H, ArH), 6.90 (s, 2H, 2 OH), 4.88–4.63 (q, 4H, 2 =CH_2, J = 1.5 Hz), 2.57–2.32 (m, 2 CH_2), 1.71–1.69 (s, 2 CH_3). IR (KBr) ν_{max}(cm^{-1}): 3365(–OH), 1665 (–C=O) cm^{-1}, 1600 (–C=CH_2) cm^{-1}. Ms (ESI): m/z 400.48(M^+). Anal. Calcd for $C_{26}H_{24}O_4$: C 77.98, H 6.04. Found: C 77.71, H 6.17%. Crystal data for I.

$C_{26}H_{24}O_4$, M = 400.45, Triclinic, a = 9.009(2) Å, b = 11.320(3) Å, c = 12.049(3)Å, α = 66.526(4)°, β = 72.121(4)°, γ = 89.706(4)°, V = 1063.0(4)Å^3, T = 293(2)K, space group p-1, Z = 2, d = 1.251 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.084 mm^{-1}, 5463 reflections measured, 3725 unique (R_{int} = 0.0149), which were used in calculations. The data have been deposited at the Cambridge Crystallographic Data Centre as CCDC-695296.

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