

Photochromism and crystal structure of 3,3'-dimethyl-3,3'-dihydroxy-5,5'-dimethyl-2,2'-bi-1H-indanylidene-1,1'-dione

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A novel photochromic compound, 3,3'-dimethyl-3,3'-dihydroxy-5,5'-dimethyl-2,2'-bi-1H-indanylidene-1,1'-dione (**I**), was synthesised and its structure was determined by X-ray crystallography. The compound exhibited reversible photochromism, and a stable organic radical was generated which was detected by electron spin resonance spectroscopy.

Keywords: biindenylidene derivatives, photochromism, radical, crystal structure

Organic photochromic compounds have attracted attention in the past because of their potential applications. A large number of photochromic compounds have been reported, and quite a few are photochromic in the crystalline state. Photochromic organic crystals are interesting as novel materials for optical data processing and storage.^{1–2} Typical examples include N-salicylideneanilines, nitrobenzylpyridines, triarylimidazole dimers, diarylethenes and biindenylidene derivatives.^{3–7} Among these, the biindenylidene derivatives are the most promising materials for single-crystalline photochromism, as well as for the generation of stable organic radicals.^{8–11}

In this paper, we report the preparation, crystal structure and crystalline state photochemical properties of 3,3'-dimethyl-3,3'-dihydroxy-5,5'-dimethyl-2,2'-bi-1H-indanylidene-1,1'-dione. The synthesis route of the compound **I** for this work is shown in Scheme 1.

Compound **I** was synthesised by the reaction of methyl magnesium bromide with 5,5'-bimethyl-2,2'-biindanylidene-1,1',3,3'-tetraone under an argon atmosphere as shown in Scheme 1. In order to confirm the structure, the product was subjected to spectroscopic analysis using IR, ¹H NMR and elemental analysis. Crystals of a suitable quality for single crystal X-ray diffraction were obtained by slow evaporation from CH₂Cl₂ solutions. The molecular structure of **I** is shown in Fig. 1.

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 C3=C3ⁱ bond [symmetry code: (i) 1–x, 2–y, 2–z]. The C3=C3ⁱ bond distance of 1.332 (6) Å confirms its double-bond character. The cyclopentenone ring adopts a flattened envelope conformation, with atom C3 at the flap.

Two rings of indanone are almost perfectly parallel, which produces little distortion of the double bond. The two methyl groups are located on different sides of the double bond with *trans*-configuration referring to the indanone planes.

Results and discussion

Photochromic properties in the solid state

The yellow crystal of **I** turned to red brown when exposed to the sunlight for a few minutes. The colour change could be seen easily by the naked eye. Measurement of the colour change was also conducted by UV spectra in the solid state, which was shown in Fig. 2. The UV absorption band around 450–650 nm appeared after photoirradiation in the solid state and resulted in the photochromism. The irradiated sample was stable at room temperature in air or in a nitrogen atmosphere. The red brown changed slowly back to yellow in the dark.

ESR spectra

The ESR measurement was carried out in air at room temperature. Measurement conditions were as follows: centre

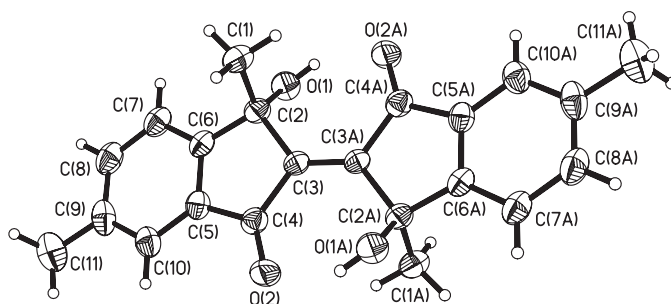
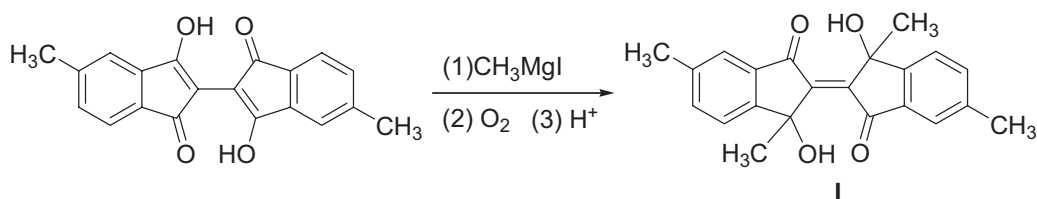


Fig. 1 Molecular structure of **I** with atom numbering.



Scheme 1

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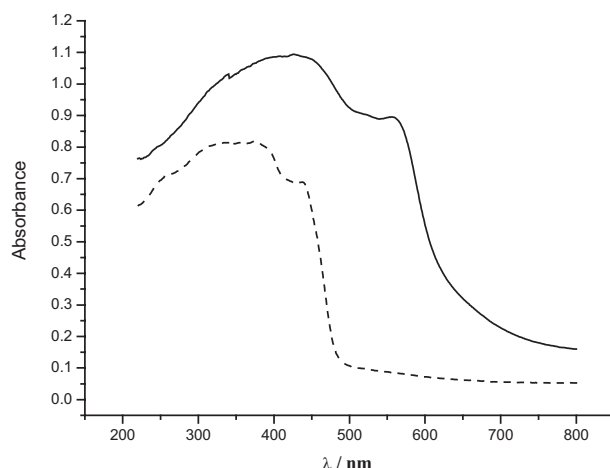


Fig. 2 UV spectral changes of **I** (...) before and (—) after irradiation in the solid.

field, 3510 G; sweep width, 100 G; modulation, 100.00kHz; amplitude, 0.2G. The unirradiated yellow compound **I** did not show any ESR signals at room temperature, while the corresponding irradiated red brown compound showed distinct ESR signals. The ESR spectrum of the irradiated compound **I** was shown in Fig. 3. The radical species were also stable at room temperature since its ESR signal could be observed after three months in the solid state. When **I** was dissolved in dichloromethane, the ESR signals disappeared.

Experimental

All chemicals were purchased from commercial sources, and the 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 data collection was performed on a Bruker SMART APEX II diffractometer with Mo $K\alpha$ radiation. The structure was solved by direct methods (SHELXS-97) and non-H atoms were refined by full-matrix least-squares method with anisotropic temperature factors (SHELXL-97). (Programs by G.H. Sheldrick, University of Gottingen, Germany, 1997).

Synthesis of 3,3'-dimethyl-3,3'-dihydroxy-5,5'-dimethyl-2,2'-bi-1H-indanylidene-1,1'-dione (I): Magnesium (2.4 g, 0.10 mol) and anhydrous THF (15 ml) were 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, under N_2 atmosphere. A solution of CH_3I (0.10 mol) in anhydrous ether (60 ml) was added to this suspension from pressure-equalising funnel. After the addition was complete, the mixture was stirred under reflux for additional 0.5 h. The pressure-equalising funnel was then recharged with 5,5'-bimethyl-2,2'-biindanylidene-1,1',3,3'-tetraone (3.18 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

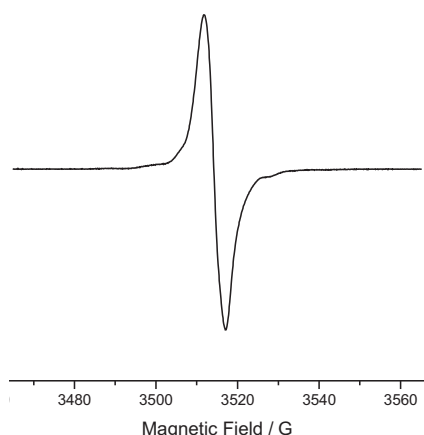


Fig. 3 ESR spectrum of **I** in the solid state at room temperature.

the reaction was quenched with saturated NH_4Cl aqueous solution to give immiscible liquid phases. The crude desired compound **I** precipitated as insoluble powder between the organic and aqueous phases. Filtration afforded crude product, which was purified by column chromatography on silica gel. Yield: 15.6%. yellow crystals: m.p. 121–122°C. 1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.77–7.37 (m, 6H, $6 \times -ArH$), 6.59–6.53 (m, 2H, $2 \times -OH$), 2.48 (s, 6H, $2 \times ArCH_3$), 1.77 (s, 6H, $2 \times -CH_3$). Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79; Found: C, 75.94; H, 6.03%. IR (KBr) $\nu_{max}(cm^{-1})$: 3334($-OH$), 1675 ($-C=O$) cm^{-1} . Crystal data for **I**. $C_{22}H_{20}O_4$, $M = 348.38$, Monoclinic, $a = 17.666(2)$, $b = 7.6579(10)$, $c = 14.6778(19)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 117.007(2)^\circ$, $V = 1769.1(4)$ Å³, $T = 293(2)$ K, space group $C2/c$, $Z = 4$, $d = 1.308$ Mg/m³, $\mu(Mo-K\alpha) = 0.089$ mm⁻¹, 4667 reflections measured, 1571 unique ($R_{int} = 0.0233$), which were used in calculations. CCDC-678428

The data have been deposited at the Cambridge Crystallographic Data Centre as CCDC-678428

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