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ChemComm www.rsc.org/chemcomm

Photoinduced ground-state singlet biradical—novel insight into the photochromic compounds of biindenylidenediones

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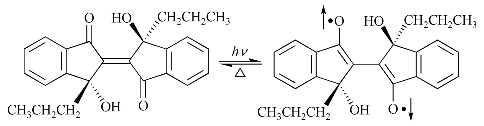
Received (in Cambridge, UK) 15th July 2002, Accepted 28th August 2002

First published as an Advance Article on the web 16th September 2002

The biindenylidenedione derivative (A) developed a biradical accompanied by the simultaneous photocolor development on UV or sunlight irradiation; the former of which showed antiferromagnetic behavior on account of the singlet ground state and a thermally accessible triplet state.

Photochromic compounds continue to attract considerable attention in view of their general applicability as optical information storage materials or switching devices.[1] Among many types of photochromic compounds, the biindenylidene derivatives, first investigated by Toda *et al.* in 1992, are unusual in that they simultaneously undergo photochromism in the crystalline state as well as the generation of radicals.[2] More recently, we designed and synthesized a series of biindenylidenedione derivatives, and reported the photochromic and photomagnetic properties of [2,2′-bi-1*H*-indene]-1,1′-dione-3,3′-dihydroxy-3,3′-diethyl in the solid state.[3] In this paper, we discuss the properties of [2,2′-bi-1*H*-indene]-1,1′-dione-3,3′-dihydroxy-3,3′-dipropyl (**A**), which provides a stepwise insight to the mechanism of photochromism and photomagnetism in this kind of compound.

Toda reported that *trans-syn*-3,3′-diaryl-2,2′-biindenylidene-1,1′-diones underwent photochromism based on the formation of a triplet biradical.[4] Whereas, our recent studies revealed biradical **B**, derived from the irradiation of **A**, was not a triplet biradical but a singlet biradical, which displayed reversible temperature-dependent ESR signals. In addition, biradical **B** exhibited antiferromagnetic interaction in the solid state (see Scheme 1) which is the first observation of magnetic interaction on the photochromic system of biindenylidene.



A **B**

Scheme 1

Compound **A**, which was obtained from the reaction of propylmagnesium bromide to 2,2′-biindanylidene-1,1′,3,3′-tetraone and air oxidation, crystallized from dichloromethane as bright yellow crystals.[5]† The yellow crystals turned to red crystals **B** when exposed to the sunlight for a few minutes either in an air or a nitrogen atmosphere, with the simultaneous generation of a biradical. Also, **B** was thermally labile and returned to **A** upon heating at 70°. The photocolor reaction was monitored by UV-Vis spectra(Fig. 1). No structural change was detected by single or powder crystal X-ray diffraction before and after irradiation.

At room temperature, ESR measurement was carried out in air on the polycrystalline phase of **B** as shown in Fig. 2. The signal indicated the existence of biradical **B** with anisotropic parameter D = 47.06 G and g = 2.005. In addition, the ESR signal intensity showed characteristic temperature dependence: it decayed with the decrease of temperature, and disappeared completely on cooling down to liquid nitrogen temperature; the singal was regenerated gradually with increase of temperature, and restored its original shape at room temperature as shown in Fig. 2. These results are consistent with a ground singlet state and thermally accessible triplet state of the biradical. In contrast to biradical **B**, the unirradiated sample of **A** did not show ESR signals at room temperature. Irradiation of a homolog having ethyl substituents also gave a radical showing a temperature-dependent ESR signal, though the signal shape was very different.[3] This discrepancy may be due to the difference in their crystal packings.

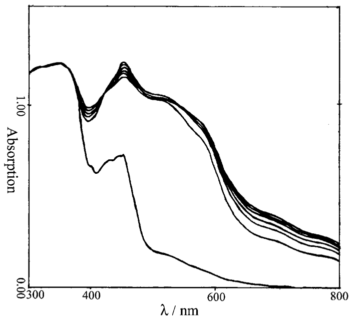


Fig. 1 UV spectral changes of **A** in the solid state on irradiation. Measurement was made every 5 min from the bottom to the top.

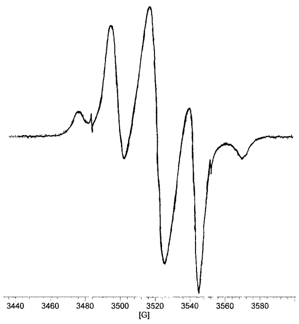


Fig. 2 ESR spectrum of **B** in the solid state at room temperature. Measurement conditions: center field, 3513.75 G; sweep width, 200.00 G; modulation, 100.00 KHz; Amplitude, 0.2 G.

To determine whether biradical **B** behaved as an exchange coupled system, magnetic behaviour was examined on a vibrating sample magnetometer in the temperature range 80–300 K with an applied field of 5000 kOe. The effective magnetic moments (μ_{eff}) *vs.* temperature (T) plot (Fig. 3) qualitatively reveals the existence of antiferromagnetic interactions. The diamagntic correction was calculated from the slope of a plot of M *vs.* H for **A** and was found to be -1.72×10^{-4} emu K mol^{-1}. Considering the unknown yield of this photoreaction, the experimental data were not fitted to any theoretical law. It should be pointed out that different yields only shift the position of the plot along the y axis direction in Fig. 3. The smaller the yield, the higher the plot. Further studies on the yield of this photoreaction are underway to provide a quantitative interpretion.

The description above allows us to propose a plausible mechanism of photomagnetism as shown in Scheme 2.

DOI: 10.1039/b206876a

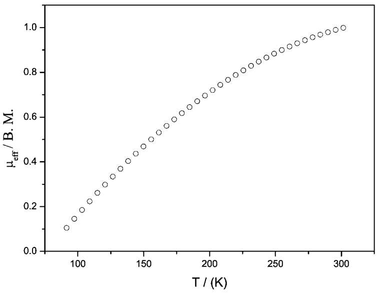
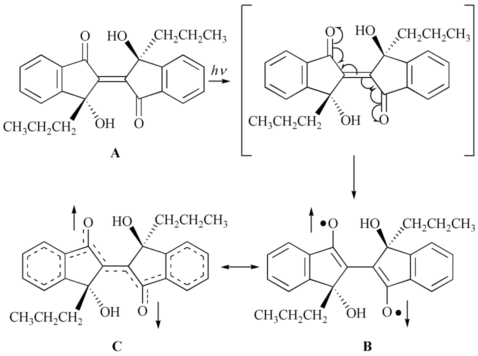
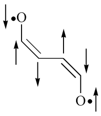


Fig. 3 Experimental temperature dependence of the pseudo-effective moment plot for polycrystalline samples of biradical **B**.



Scheme 2

Irradiation resulted in the reorganization of electron distribution in **A** to generate two unpaired radicals in **B** with antiparallel orientation; The singlet biradical **B** was stablized by conjugation to the whole molecular system as **C** while the oxygen atoms of carbonyls contributed a lot to the spin density distribution. According to the well-known spin polarization rule, the adjacent π electronic spins of conjugated alternate alkene or aromatic rings should be arranged in terms of antiparallel pattern,[6,7] which well describes the observed antiferromagnetic coupling in biradical **B** (Scheme 3).



Scheme 3

The explanation to account for photomagnetism nicely coincided with the photochromism from yellow to red. As the irradiation of the solid state gave rise to an extended conjugated system, the absorption spectrum must display drastic changes, just as shown in Fig. 1. This proposal was also supported by the change in ^{1}H NMR spectra of **A**, wherein the peak shape at δ_H 6.62 ppm lost its sharpness after irradiation. This phenomenon was consistent with the decrease of the H-bonding strength because of the generation of a radical on the oxygen atoms of carbonyls. The H-bond in **A** had been determined by X-ray analysis to be 1.987Å (O2A–H2A…O1) and 149.71° (Fig. 4).

The crystal packing of **A** shows that the distance of the adjacent molecular carbonyl oxygen atoms is 3.982 Å, the optimal distance for radical interaction. Taking the packing of **A** as the model for the transient crystal structure of **B**, we believe that the intramolecular antiferromagentic interaction can be transmitted to the other molecule in a zigzag chain pattern when a biradical is generated (Fig. 5), since the dihedral angle between plane I and II or plane III and IV is calculated to be 61.53°. The antiferromagnetic chain comprises repeated 1,4-dienoloxy units as demonstrated in Scheme 3.

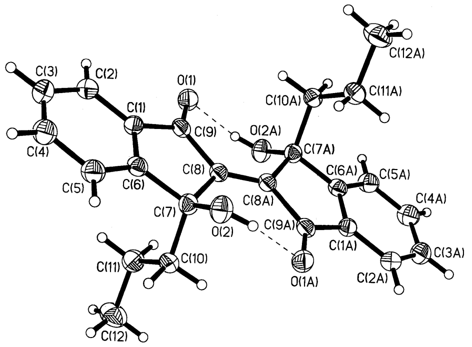


Fig. 4 The structure of compound **A**.

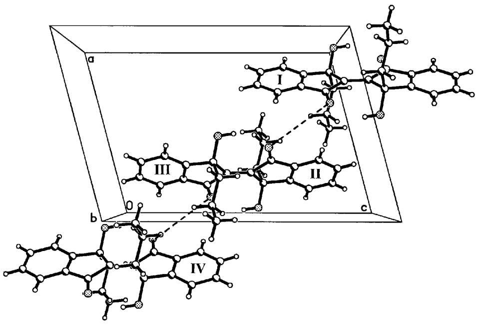


Fig. 5 Stacking of compound **A** in the direction of interaction. The dashed lines link two oxygen atoms up to indicate the intermolecular interaction.

In conclusion, it has been established that irradiation of **A** in the solid state led to the formation of a biradical accompanied by the simultaneous photocolor development from yellow to red. The photogenerated biradicals exhibited antiferromagnetic interaction, which could be attributed to the spin polarization. The temperature dependence of ESR signal intensity was consistent with a singlet ground state and thermally populated triplet state of the biradical. Intramolecular antiferromagnetic interaction was transmitted to give an zigzag antiferromagnetic chain. From both theoretical and practical points of view, we believe the above results are of great significance, since many interpolated phenomena are induced by excitation and can find valuable applications in multifunctional materials.

This work was supported by the grant from the National Natural Science Foundation of China (NSFC). The authors gratefully acknowledge Professor Lingjun Bai for helpful suggestions in ESR measurements in this research work.

Notes and references

† *Crystal data for **A***: $C_{24}H_{24}O_4$, M = 376.43, monoclinic, space group $C2/c$, a = 10.398(3), b = 12.481(4), c = 15.371(4) Å, β = 105.041(5)°, V = 1926.8 Å^3, Z = 4, D_c = 1.298 g cm^{-3}, T = 293(2) K, μ(Mo-Kα) = 0.087 mm^{-1}, 4885 reflections measured, 1712 unique (R_{int} = 0.0633) which were used in all calculations. The final R_1 = 0.0489, wR_2 = 0.1064 and for all data R_1 = 0.1117, wR_2 = 0.1254. CCDC 190058. See http://www.rsc.org/suppdata/cc/b2/b206876a/

*Physical data for **A***: yellow prism crystal. ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.79–7.87 (m, 6H, Ar-H), 7.54–7.58 (m, 2H, Ar-H), 6.62 (s, 2H, −OH), 2.07–2.23 (m, 4H, -CH$_2$), 0.64–0.74 (m, 10H, -CH$_2$CH$_3$). Anal. Calcd. for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.22; H, 6.68%.

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