Organic photochromic radical compound based on a biindenylidene system

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A novel dual functional biindenylidene derivative (**4**) having nitronyl nitroxide radicals on both sides of the molecules, was synthesised. Its photochromism, as well as magnetic properties were investigated. The compound **4** underwent photochromic reactions by irradiation with UV and visible light. The intermolecular magnetic interactions were measured with a SQUID susceptometer.

Keywords: biindenylidene, radicals, photochromism, magnetic interactions

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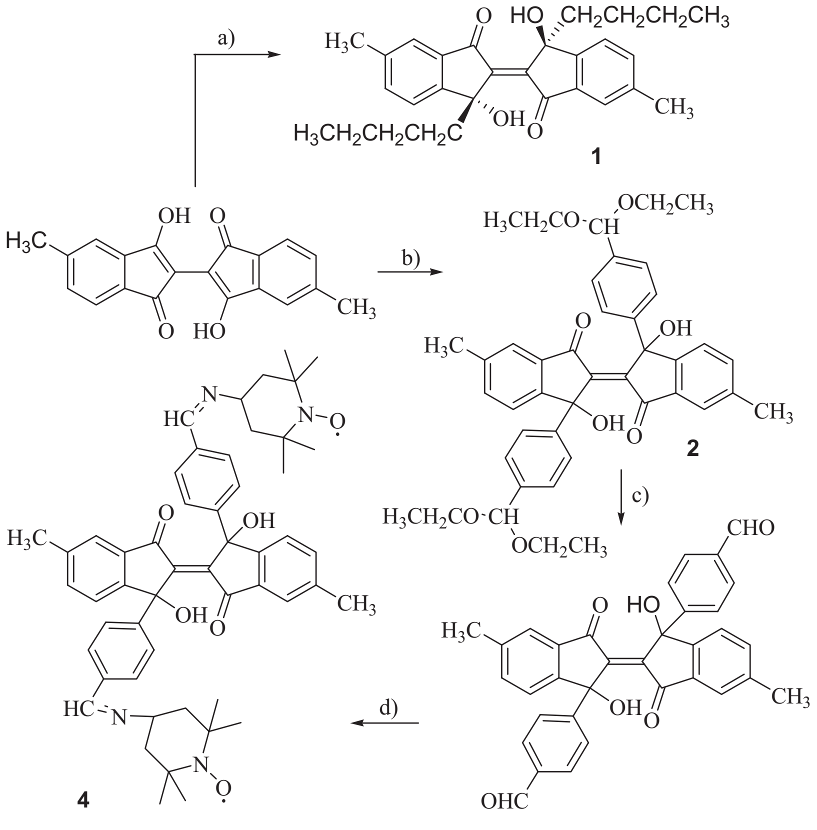
There is interest in the preparation of photomagnetic materials whose magnetic properties may be controlled by using light. From both the scientific and technological point of view, to afford examples of molecular devices as thermal or optical switching systems correlated with spins.[1-2] Several interesting example of organic photochromic and photomagnetic compounds such as azobenzene, diarylethene, spiropyran, terphenoquinone, anthracene, and naphthopyran have been reported, and their properties have been extensively investigated.[3-7] Aminoxyl radical moieties have been widely adopted in those compounds, because of their versatility and good stability in the field of material chemistry as building blocks for molecule-based magnetic materials.[8-10] As disclosed in recent reports,[11-13] the biindenylidene derivatives are a unique class of photochromic organic compounds, which undergo photochromism simultaneously with the formation of radicals in the crystalline state. If the stable aminoxyl radical moiety is incorporated into such a photochromic compound like biindenylidene, a new multifunctional molecule could be designed.

On the basis of this concept, a new dual-functional biindenylidene derivative **4** was designed by introducing two nitroxide radicals to the biindenylidene system (Scheme 1). Its photochromic and magnetic properties were investigated. For the purpose of comparison, the precursors **1, 2** and **3** were investigated accordingly as well. We report here the results from these investigations.

In order to confirm the structure, the products were subjected to spectroscopic analysis using IR, ^{1}H NMR and elemental analysis. A crystal of suitable quality for single crystal X-ray diffraction was obtained by slow evaporation from CH_2Cl_2 solutions. The molecular structure of **1** is shown in the Fig. 1.

The asymmetric unit of **1** 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(9) =C(9A) bond [symmetry code: –x + 1,–y,–z + 2]. The C(9) =C(9A) bond distance of 1.342 (5) Å confirms its double-bond character. The cyclopentenone ring adopts a flattened envelope conformation, with atom C(9) at the flap. Two loops



Scheme 1 (a) *n*-butyl magnesium bromide in dry THF, then air oxidation H+; (b) *p*-benzaldehyde diethyl acetal magnesium bromide in dry THF, then air oxidation H+; (c) *p* -toluenesulfonic acid in chloroform; (d) 4-amino-2,2,6,6-tetramethylpiperidino acetate AcOH in dichloromethane.

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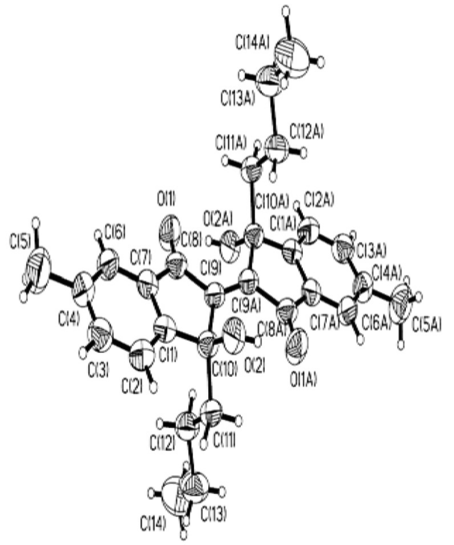

Fig. 1 Molecular structure of **1** with atom numbering scheme.

of indanione are almost perfectly parallel, which makes the double bond have little distortion. The two methyl groups locate at different sides of the double bond with trans-configuration referring to the indanone planes.

Results and discussion

Photochromic properties in the solid state

The colour of **1, 2, 3** and **4** was measured by UV-Vis absorption in the solid state. During the reaction, no remarkable changes were observed in the IR spectra. As expected, the precursor **1, 2, 3** showed photochromic properties. Photoirradiation of the yellow powder **1** with UV light produced by a high pressure Hg-lamp led to the formation of a brown powder, and the brown powder returned slowly to yellow solid in the dark. The new radical compound **4** showed photochromism in a solid state too. The yellow crystals of **4** turn to brown, when exposed to UV light for few minutes. The brown solid fade and return to the original yellow gradually in the dark. The UV absorption of **4** considerably increased in the wavelength range of 500–700 nm after irradiation (Fig. 2).

Magnetic properties

In order to examine the magnetic properties of the photochromic compounds **1, 2, 3** and **4,** their magnetic susceptibilities were measured by a SQUID susceptometer within the temperature range of 2–300K. The data are summarised in Table 1. The magnetic interaction of photo product **1, 2, 3** could not be identified, due to the too weak signal on the magnetometer. While after introducing nitroxide to the biindenylidene system, the significant changes of magnetic properties were observed along with the photochromism in solid state. Antiferromagnetic interactions have been observed for **4.** According to Curie–Weiss law, Curie constants as well as Weiss temperatures favour an antiferromagnetic interaction for **4**.[14-16]

In conclusion, biindenylidene derivative having nitronyl nitroxide radicals at both ends of the molecule was synthesised, and the photochromic and magnetic interactions were investigated. The biindenylidene derived radicals underwent photochromic reactions by irradiation with UV and visible light in the solid state. SQUID susceptometer analysis demonstrated that the intermolecular magnetic interactions were antiferromagnetic interaction. These result showed that incorporation of organic photochromism into magnetic system could not only lead to interesting photochromic behaviour, but also provided a new strategy to develop photomagnetic materials.

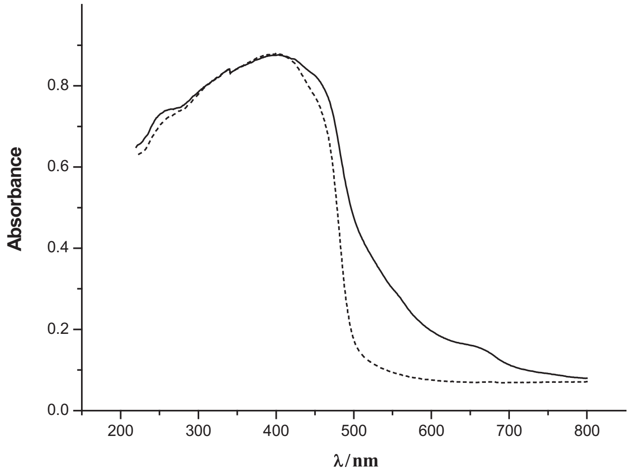

Fig. 2 UV spectral changes of **4** (…) before and (—) after irradiation.

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 tetramethylsilane as an internal reference. Elemental analysis was performed on a YANACO CHN CORDER MT-3 apparatus. UV–Vis spectra were recorded on TU-1901 UV–Vis spectrophotometer. Magnetic susceptibilities were measured by SQUID susceptometer. X-ray data collection was performed on a Bruker SMART 1000 diffractometer with Mo-Kα radiation. The structure was solved by direct methods (SHELXS-97)[17] and non-H atoms were refined by full-matrix least-squares method with anisotropic temperature factors (SHELXL-97).[17]

Synthesis of 3,3'-dibutyl-3,3'-dihydroxy-7,7'-dimethyl-2,2'-bi-1H-indanylidene-1,1'-dione (**1**): To a three-necked 250 ml round-bottomed flask containing a stirrer bar, fitted with a pressure-equalising dropping funnel and a reflux condenser, was added Mg (2.4 g, 0.10 mol), anhydrous THF (15 ml) under N_2 atmosphere. A solution of $CH_3CH_2CH_2CH_2Br$ (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 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

Table 1 Magnetic data of photochromic compound **1, 2, 3** and **4**

Compound	Magnetic interaction[a]	C[b] (emu K mol^{-1})	θ[c] (K)[c]
1	—	—	
2	—	—	
3	—	—	—
4	Antiferromagnetic	0.63(78)	–9.26

[a]Fitting for Curie–Weiss law. [b]Curie constant. Values in parentheses denote the estimated spin concentration. [c]Weiss temperature.

desired compound **I** precipitated as insoluble power between the organic and aqueous phases. Filtration afforded crude product, which was purified by column chromatography on silica gel. Yield: 29.6%. Yellow crystals: m.p. 163–164 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ(ppm) 7.77–7.27 (m, 6H, 6 × –ArH), 6.79–6.68 (m, 2H, 2 × –OH), 2.55(s, 6H, 2 × ArCH$_3$), 2.27–2.09(m, 4H, 2 × –CH$_2$–), 1.13–0.879(m, 14H, 2 × –CH$_2$CH$_2$CH$_3$). Anal. Calcd for $C_{28}H_{32}O_4$: C, 77.75; H, 7.46; Found: C, 77.89; H, 7.48%. IR (KBr): 3334 (–OH), 1675 (–C=O) cm^{-1}. Crystal data for **I**. $C_{28}H_{32}O_4$, M = 432.54, Triclinic, a = 9.704(2), b = 10.822(3), c = 12.743(3) Å, α = 75.290(4)°, γ = 78.439(4)°, β = 73.240(4)°, V = 1769.1(4) Å^3, T = 294(2) K, space group $C2/c$, Z = 2, d = 1.170 Mg/m^3, μ(Mo-K$_\alpha$) = 0.077 mm^{-1}, 6288 reflections measured, 4310 unique (R$_{int}$ = 0.0293), which were used in calculations. CCDC-695295.

Synthesis of 3,3'-di-(4-diethyl acetal benzaldehyde)-3,3'-dihydroxyl-7,7'-dimethyl-[2,2'-bi-1Hindene]-1,1'-dione (**2**): Following the procedure previously described for **1**, the crude desired compound **2** precipitated as insoluble yellow power between the organic and aqueous phases. Filtration afforded crude product, which was purified by column chromatography on silica gel in 43.1% yield. Yellow powder, m.p. 258–260 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ(ppm): 7.59–7.09 (m, 14H, –ArH), 7.04–7.04 (m, 2H, 2×–OH), 5.40 (s, 2H, –CH), 3.58–3.47 (q, –CH$_2$, J = 7.5 Hz), 2.38 (s,–ArCH$_3$),1.21–1.18 (t,–CH$_3$, J = 7.5 Hz). IR (KBr) ν_{max}(cm^{-1}): 3375(–OH), 1675 (–C=O) cm^{-1}. Ms (ESI) Calcd for: m/z 676.30. Found: 676.48(M$^+$). Anal. Calcd for $C_{42}H_{44}O_8$: C 74.54, H 6.55. Found: C 74.61, H 6.57%.

Synthesis of 3,3'-di-(4-benzaldehyde)-3,3'-dihydroxyl-7,7'-dimethyl-[2,2'-bi-1Hindene]-1,1'-dione (**3**): To a solution of **2** (0.648 g, 1 mmol) in chloroform (100 ml) was added a small amount of *p*-toluenesulfonic acid monohydrate, and the solution was refluxed for 4 h. Then, the acid reaction mixture was concentrated to 10 ml volume, and, on cooling, an off-yellow precipitate of crude **3** was collected by filtration, washed with acetone and dried in 86% yield. **3** was pure enough to use without further recrystallisation. Yellow powder, m.p.>300 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ(ppm): 9.95 (s, 2H, –CHO), 7.83–7.26 (m, 14H, –ArH), 6.99–6.94 (d, 2H, –OH), 2.40 (s, –ArCH$_3$). IR (KBr) ν_{max}(cm^{-1}): 3344(–OH), 1698 (–CHO), 1675 (–C=O) cm^{-1}.Ms (ESI) Calcd for: m/z 528.16. Found: 528.37. Anal. Calcd for $C_{34}H_{24}O_6$: C 77.26, H 4.54. Found: C 77.39, H 4.48%.

Synthesis of radical (**4**): A mixture of **3** (0.106 g, 0.2 mmol) and 4-amino-2,2,6,6-tetramethylpiperidinooxy (0.068 g, 0.4 mmol) with a small amount of acetic acid was stirred for 4 h in dichloromethane at ambient temperature. Concentration *in vacuum* gave radical **4** as brown powdery solid that was recrystallised from methanol and dichloromethane in 53% yield. Brown powder, m.p. 266–267 °C. Ms (ESI) Calcd for: m/z 834.44. Found: 834.42. IR (KBr) ν_{max}(cm^{-1}): 3362(–OH), 1673 (–C=O) cm^{-1}. Anal. Calcd for $C_{52}H_{58}N_4O_6$: C 74.79, H 7.00, N 6.71. Found: C 74.82, H 6.74, N 6.63%.

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References

1 S. Nakatsuji, *Adv. Mater*., 2001, **13**, 1719.
2 S. Nakatsuji, *Chem. Soc. Rev*., 2004, **33**, 348.
3 K. Hamachi, K. Matsuda, T. Itoh and H. Iwamura, *Bull. Chem. Soc. Jpn*., 1998, **71,** 2937.
4 K. Matsuda and M. Irie, *J. Am. Chem. Soc*., 2000, **122**, 7195.
5 T. Kaneko, H. Akutsu, J. Yamada and S. Nakatsuji, *Org. Lett*., 2003, **5**, 2127.
6 M. Kawano, T. Sano, J. Abe and Y. Ohashi, *J. Am. Chem. Soc*., 1999, **121**, 8106.
7 H. Kurata, Y. Takehara, T. Kawase and M. Oda, *Chem. Lett*., 2003, 538.
8 N.L. Frank, R. Clerac, J.P. Sutter, N. Daro, O. Kahn, C. Coulon, M.T. Green, S. Golhen and L. Ouahab, *J. Am. Chem. Soc*., 2000, **122**, 2053.
9 S. Nakatsuji, H. Ikemoto, H. Akutsu, J.I. Yamada and A. Mori, *J. Org. Chem*., 2003, **68,** 1708.
10 S. Greve, C. Nather and W. Friedrichsen, *Org. Lett.,* 2000, **2**, 2269.
11 L.L. Xu, T. Sugiyama, H.M. Huang, Z.Y. Song, J.B. Meng and T. Matsuura, *Chem. Commun.,* 2002, 2328.
12 X. Li, L.L. Xu, J. Han, M.L. Pang, H. Ma and J.B. Meng, *Tetrahedron.,* 2005, **61** 5373.
13 X. Li, J. Han, M.L. Pang, Y. Chen, J.X. Zhang, H. Ma, Z.J. He and J.B. Meng, *Tetrahedron Lett*., 2007, **48**, 6044.
14 S. Nakatsuji, T. Ojima, H.Akutsu and J.I. Yamada, *J. Org. Chem*., 2002, **67**, 916;
15 H.M. McConnell, *J. Chem. Phys*. 1963, **39,** 1910.
16 T. Kaneko, H. Akutusu, J.I. Yamada and S. Nakatsuji, *Org. Lett*., 2003, **5**, 2127.
17 G.H. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Germany, 1997.