Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
ELSEVIER
Tetrahedron 63 (2007) 4319–4327

Synthesis, crystal structures, and photochromic properties of 6,6′ or 7,7′ or 6,7′-dimethyl-[2,2′-bi-1*H*-indene]-3,3′-diethyl-3,3′-dihydroxy-1,1′-diones

Yong Chen, Mei-Li Pang,* Kai-Ge Cheng, Ying Wang, Jie Han, Zheng-Jie He and Ji-Ben Meng*

Department of Chemistry, Nankai University, Tianjin 300071, PR China

Received 27 November 2006; revised 2 March 2007; accepted 5 March 2007
Available online 12 March 2007

Abstract—New photochromic title compounds **1**, **2**, and **3** have been prepared starting from 4-methylphthalic anhydride. Compounds **3a** and **3b** are a pair of enantiomers and were obtained as a racemic mixture (numbered as **3**). Compounds **1**, **2**, and **3** were successfully separated from the isomeric mixture product through fractional crystallization, and their structures are confirmed by X-ray crystallographic analysis. UV–vis absorption and photochromic properties of **1**, **2**, and **3** have also been investigated. Results reveal that the substituents, even like the simple methyl, on the benzene rings of biindenylidenedione could considerably affect the photochromic property, as well as other properties of this kind of compounds.

1. Introduction

Solid-state organic photochromic molecules have attracted much attention due to their potential applications in various optoelectronic devices such as optical memory, optical switch, electronic display, information storage, and so on.[1–8] Typical examples include *N*-salicylideneanilines,[9,10] dinitrobenzylpyridines,[11,12] diphenylmaleonitriles,[13] triarylimidazole dimers,[14,15] aziridines,[16] diarylperfluorocyclopentenes,[17] diarylethenes,[18] and biindenylidenedione derivatives.[19] Among them, the biindenylidenedione derivatives are a class of unique photochromic compounds, which simultaneously generate stable radicals and undergo photochromism in the crystalline state.[20–26] This property is particularly promising for their potential utility in optoelectronic devices. In order to explore the relationship between the structure and physical properties such as photochromic and photomagnetic ones, we have continuously made modifications on biindenylidenedione backbone, and prepared a series of biindenylidenedione derivatives.[22–26] Most of the structural modifications have been carried out on the five-membered rings of the biindenylidenedione, and results showed that such modifications have considerable effect on both photochromic and photomagnetic properties of this kind of molecules in the solid state.[23–26] Rare attempts have been made to introduce other substituents rather than hydrogen on the benzene rings in the biindenylidenediones, since such substituents unavoidably result in an increasing number of product stereoisomers in the preparation due to the rigidity of the biindenylidenedione backbone. As part of our research efforts on biindenylidenedione derivatives, herein we report the synthesis of new methyl substituted biindenylidenedione derivatives on the benzene rings dimethyl-[2,2′-bi-1*H*-indene]-3,3′-diethyl-3,3′-dihydroxy-1,1′-dione from 4-methylphthalic anhydride. As expected, four stereoisomers were obtained as the final products, which were successfully isolated by fractional crystallization into two diastereomers **1** and **2**, and a racemic mixture of two enantiomers **3a** and **3b**. Their structures were determined by X-ray crystallography. Their UV–vis absorption and photochromism were also investigated. Also, one more purpose for this study is to explore a feasible route to introduce some functional groups to the benzene rings derived from methyl groups to develop novel organic multi-functionality compounds.[27]

2. Results and discussion

2.1. Synthesis

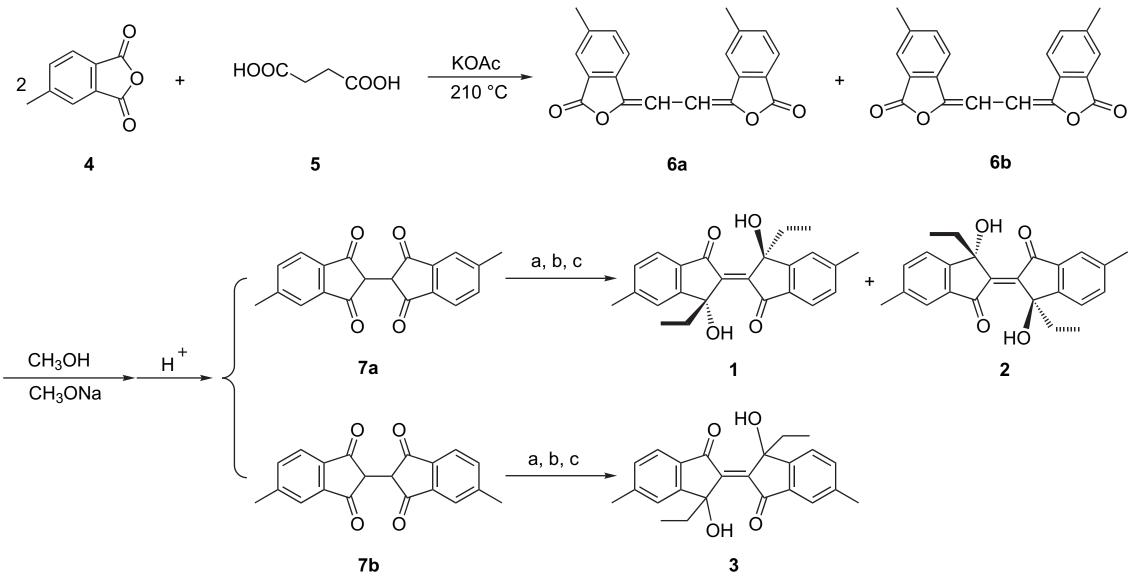
The synthetic route for title compounds **1**, **2**, and **3** is shown in Scheme 1. As expected, the emergence of increasing isomers in the final products from the introduction of methyl on the benzene ring takes place upon the treatment of the tetraone **7** or its enol-form **8** with Grignard reagent ethylmagnesium bromide. Three isomeric products **1–3** were obtained from the reaction of biindanyltetraone **7** with ethylmagnesium bromide. After many unsuccessful attempts,

---

Keywords: Dimethyl-[2,2′-bi-1*H*-indene]-diethyl-3,3′-dihydroxy-1,1′-diones; Synthesis; Crystal structure; Photochromism; Organic solid material.

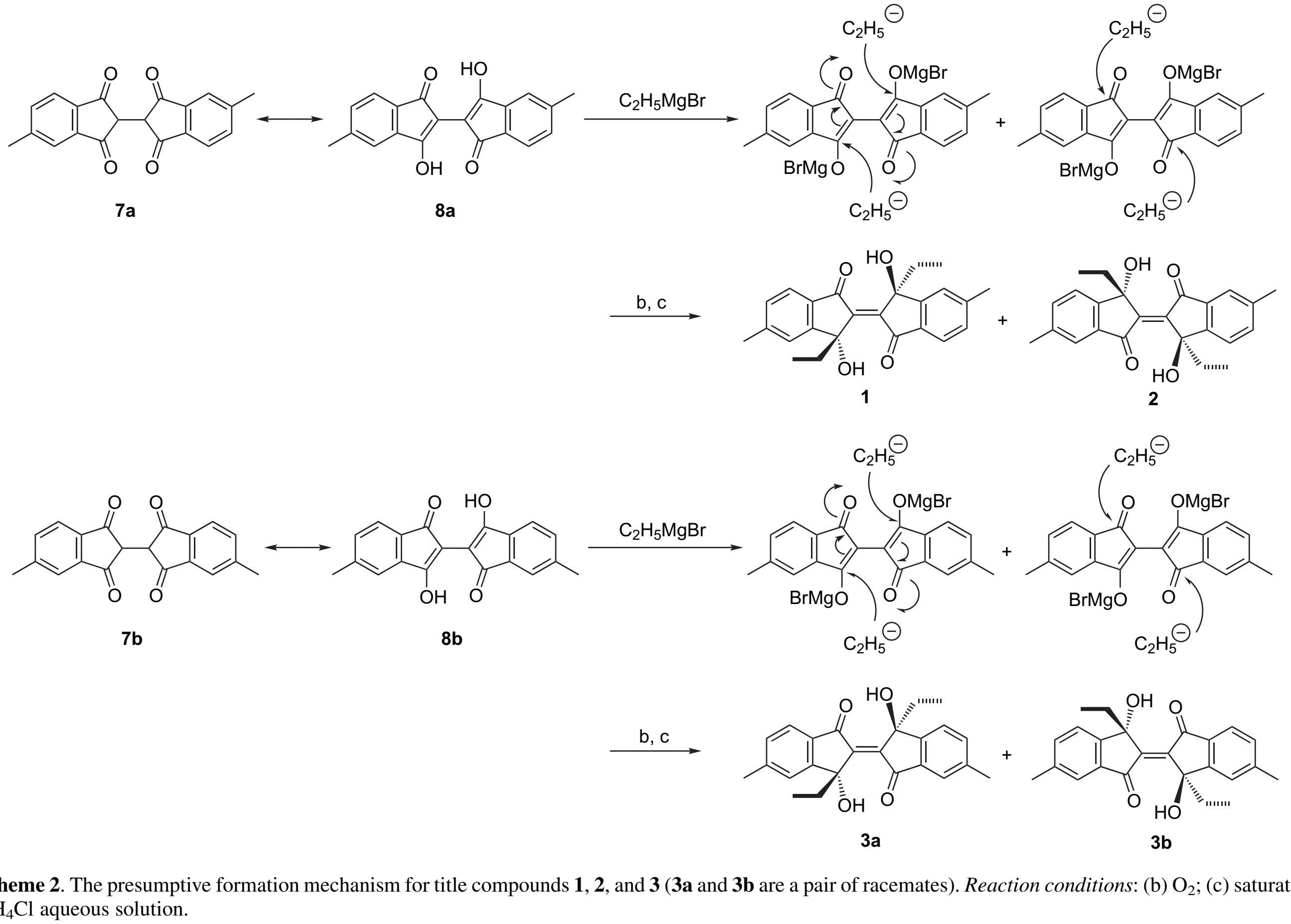
* Corresponding authors. Tel.: +86 2223 509 933; fax: +86 2223 502 230; e-mail addresses: pangmeili@nankai.edu.cn; mengjiben@nankai.edu.cn

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.03.030



Scheme 1. Synthetic route for title compounds **1**, **2**, and **3**. *Reaction conditions*: (a) C_2H_5MgBr; (b) O_2; (c) saturated NH_4Cl aqueous solution.

fractional crystallization proves most effective in the separation of these isomers. Thus, the yellow solid crude product (10 g) was dissolved in a solvent mixture (C_2H_5OH–CH_2Cl_2 3:1, v/v) under heating. Slow evaporation of the solution consecutively gave three crystalline fractions: the first fraction as yellow powder (2.2 g), mp 269–271 °C; the second as yellow sheet crystalline (4.2 g), mp 173–178 °C; the third as yellow granular solid (2.1 g), mp 203–205 °C. End-point of crystallization can be estimated by the solid appearance, and if necessary a little impurity can be removed through recrystallization again. Spectroscopic data (^1H NMR, ESI-MS) and elemental analysis indicated that they are isomeric. X-ray diffraction results provided unambiguous evidence, and confirmed that the first and third fractions are compounds **1** and **2**, respectively, and the second fraction is the racemate **3**.



Scheme 2. The presumptive formation mechanism for title compounds **1**, **2**, and **3** (**3a** and **3b** are a pair of racemates). *Reaction conditions*: (b) O_2; (c) saturated NH_4Cl aqueous solution.

Table 1. The featured ^{1}H NMR assignments for intermediate **8**

Compound	δ (OH)	δ (Ar–CH_3)
8 (**8a**+**8b**)	14.68 (0.5H), 14.58 (1H), 14.52 (0.5H)	2.35 (s, 4.5H), 1.54 (s, 1.5H)
8a	14.58 (1H)	2.35 (s, 3H)
8b	14.68 (0.5H), 14.52 (0.5H)	2.35 (s, 1.5H), 1.54 (s, 1.5H)

According to the known formation mechanism of biindenylidenediones,[23] a proposed mechanism for formation of isomeric **1**–**3** is shown in Scheme 2. ^{1}H NMR data of the intermediate tetraone **7** confirmed that the tetraone exists in a 1:1 mixture of its enolic forms **8a** and **8b**. The signals from enolic hydroxyls at 14.68 (s), 14.58 (s), and 14.52 (s) ppm with 1:2:1 ratio of their integrals, and from methyls on the benzenes at 2.35 (s) and 1.54 (s) ppm with 3:1 ratio of the integrals provide diagnostic evidence: for enolic form **8a**, two hydroxyls (14.58 ppm) and two methyls (2.35 ppm) are equivalent, respectively; for **8b**, hydroxyls (14.68 and 14.52 ppm) and methyls (2.35 and 1.54 ppm) are inequivalent, and one signal (2.35 ppm) from one methyl group in **8b** overlaps with that of methyls in **8a**. The featured ^{1}H NMR assignments are listed in Table 1. As shown in Scheme 2, hydroxyls at 6.79 (s) ppm and methyls on the benzene rings at 2.54 (s) ppm in **1** are equivalent, respectively; hydroxyls at 6.66 (s) ppm and methyls at 2.48 (s) ppm in **2** are also equivalent. On the other hand, the corresponding hydroxyls at 6.71 (br s) ppm and methyls at 2.54 (s) and 2.48 (s) ppm in enantiomer **3a** or **3b** are inequivalent, respectively. In the ^{1}H NMR spectrum of the crude product containing **1**–**3** before fractional crystallization, there are three singlets from hydroxyls at 6.79, 6.71, and 6.66 ppm with 1:2:1 ratio of integrals and two singlets from methyls on the benzene rings at 2.54 and 2.48 ppm with 1:1 ratio of integrals. After comparison with the NMR data of individual compounds **1**–**3**, these ^{1}H NMR data for crude product clearly indicated that compounds **1**, **2**, and **3** were formed in 1:1:2 molar ratio from the synthetic reaction, namely, the four isomers **1**, **2**, and a pair of enantiomers **3a** and **3b** were unbiasedly formed in this reaction.

2.2. Crystal structure analysis

The single crystals of compound **1** were obtained from slow evaporation of its CH_2Cl_2 solution at room temperature. One suitable crystal was picked and subjected to X-ray diffraction analysis. Its crystal parameters are listed in the reference,[34] and selected crystal data are given in Table 2. Crystallographic data clearly confirm that the two indanone moieties are linked by a double bond (the bond distance between C8 and C8A is 1.354 Å), and two hydroxyl groups are located in *anti* positions along the molecular backbone plane (Fig. 1). In crystals of **1**, molecules are arranged parallel

Table 2. Selected bond lengths (Å), angles (°), and torsion angles (°) for **1**

Bond lengths	Bond angles	Torsion angles
O1–C7=1.426(3)	C1–C6–C5=120.4(2)	C9–C1–C2–C3=−179.1(2)
O2–C9=1.222(3)	C1–C6–C7=112.00(18)	C2–C3–C4–C10=178.3(2)
C4–C10=1.503(3)	O1–C7–C11=111.49(18)	C2–C3–C4–C10=178.3(2)
C8–C8A=1.354(4)	O1–C7–C8=112.64(17)	C2–C1–C6–C7=179.8(2)
C7–C8=1.537(3)	C6–C7–C8=102.29(16)	C4–C5–C6–C7=179.5(5)
C8–C9=1.510(3)	C8A–C8–C9=125.1(2)	C1–C6–C7–C8=7.5(2)
	C8A–C8–C7=127.5(2)	C6–C7–C8–C8A=167.7(3)
	O2–C9–C8=127.5(2)	C2–C1–C9–O2=−7.7(4)
		C2–C1–C9–C8=172.7(2)
		C8A–C8–C9–C1=167.6(3)

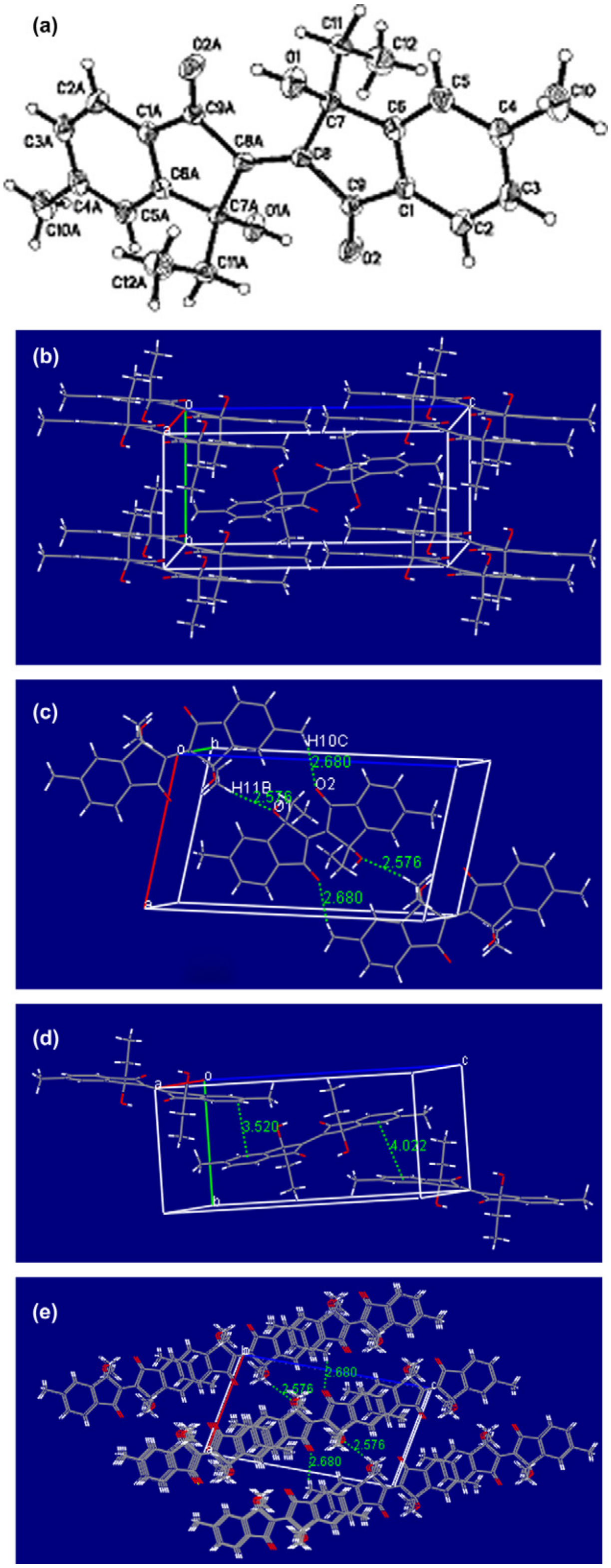


Figure 1. (a) Molecular structure and atom numbering scheme for **1**; (b) single crystal structure of **1**; (c) display of H-bonding interactions; (d) view along the *b*-axis; (e) expanded crystal packing diagram for **1**.

with *ac*-plane of crystal cell forming a chain along the diagonal direction of *ac*-plane. Chains connect with each other through intermolecular H-bonding forming 2D layer network (the H-bond lengths: HO1···H11B–C11, 2.576 Å; C10–H10···O2═C9, 2.679 Å)[28–30] (Fig. 1c). Along the *b*-axis direction, benzene rings from adjacent molecule layers take parallel positions in an offset face-to-face manner[31,32] (Fig. 1e). The shortest distance between the edge of benzene ring of one molecule layer and the center of benzene ring of another molecule layer is 3.520 Å (Fig. 1d). This distance is close enough for π–π stacking interaction between the benzene rings.

The single crystals of compound **2**, suitable for X-ray diffraction, were collected from slow evaporation of a solution of compound **2** in a mixture of ethanol–acetone (1:1, v/v). The crystal parameters are given in the reference.[34] Selected bond lengths and angles are listed in Table 3. Compared with compound **1**, compound **2** has a very similar structure, except that the relative position of methyl group on benzene ring is different from that of compound **1** with reference to carbonyl group (Fig. 2). To our surprise, the double bond (C9–C9A) length (1.303 Å) and the single bond (C4–C5) length (1.412 Å) in **2** are considerably shorter than the corresponding ones (1.354 Å and 1.503 Å, respectively) of **1**. In crystal **2**, as well as in crystal **1**, H-bonding interaction among molecules exists (Fig. 2b and d), but the shortest distance between the benzene rings of the neighboring molecules of **2** is about 6.688 Å (Fig. 2c), which is too long for any possible intermolecular π–π stacking interaction. The lower melting point (203–205 °C) of **2** may be attributable to the lack of π–π stacking interaction when compared to compound **1** (269–271 °C). Different perspectives for crystal structure of compound **2** are shown in Figure 2.

The single crystals from the racemic mixture of **3a** and **3b** were obtained from slow evaporation of the racemate solution in a mixture of ethanol–acetone (2:1, v/v). At the first glance, we were surprised that the X-ray crystallography revealed a molecular structure as compound **3** with four methyls on the benzene rings (Fig. 3a). According to the synthetic route, there is no rational chemistry to support the formation of **3**. Therefore, such a proposed molecular structure must result from the net reflection of a pair of isomers **3a** and **3b**. Isomers **3a** and **3b** are mainly superposable except methyls on the benzene rings. It is known that in the crystallization of a racemic mixture, one enantiomer sometimes has a greater affinity for its counterpart than itself. Thus, each enantiomer prefers to stack with its counterpart, and crystallizes with the exact 1:1 ratio of two enantiomers.[33] Selected crystal structure data for the racemate of **3a** and **3b** are given in Table 4. Crystal packing feature of **3** is similar to that of **2**. But in crystal **3**, among the molecules exists neither intermolecular H-bonding interaction nor π–π stacking interaction (Fig. 3b and c). Its melting point is lower (173–178 °C) compared with those of **1** and **2**.

2.3. UV–vis absorption and photochromic properties

All title compounds **1**, **2**, and **3** (the racemate of **3a** and **3b**) have UV–vis absorption in CH_2Cl_2 with two major absorption peaks in the wavelength ranges of 226–229 nm and 312–340 nm (Fig. 4). For **2** and **3**, their UV–vis spectra are very similar. It is interesting to note that maximum absorption of **1** for the second peak is at 340.8 nm, which is about 16 nm longer than those for **2** and **3** (Table 5). This wavelength difference should result from the substituent effect on the UV absorption. For **2**, two methyl groups on the benzene ring occupy *meta* positions to carbonyl; for **3**, at least one methyl group on the benzene ring occupies *meta* position to carbonyl group; but for **1**, both the methyl groups are located at *para* positions to carbonyl. This situation is more favored for methyl group to make contribution to the π-conjugated system of the whole molecule, resulting in the red shift of UV absorption.

As expected, compounds **1**, **2**, and **3** all undergo photochromism in the solid state (crystalline or powder) upon irradiation with sunlight or high-pressure mercury lamp for about 10 min, and distinct color changes were observed after photoirradiation (Fig. 5). Figure 5 clearly shows the obvious color changes after irradiation with sunlight. It is noteworthy that either before or after irradiation, the color of compound **1** has a remarkable difference from those of compounds **2** and **3**. Both compounds **2** and **3** have very similar color. This color difference should be attributed to the difference in molecular structures, namely, the methyl groups on benzene rings occupying different positions in compounds **1**, **2**, and **3**. Furthermore, we previously reported that a yellow compound without any non-hydrogen substituent, [2,2′-bi-1*H*-indene]-3,3′-diethyl-3,3′-dihydroxy-1,1′-dione, turns green when exposed to the sunlight.[22] These results indicate that the substituent, even like a simple methyl, and its position on the benzene ring of biindenylidenedione significantly affect the photochromic properties of this class of compounds.

The photochemical reactions of **1**, **2**, and **3** were monitored by UV–vis spectra in the solid state (see Fig. 6). Figure 6 shows the changes of UV–vis absorption spectra of **1**, **2**,

Table 3. Selected bond lengths (Å), angles (°), and torsion angles (°) for **2**

Bond lengths	Bond angles	Torsion angles
O1–C8=1.20(8)	O1–C8–C9=127.4(6)	C10–C1–C2–C3=177.9(8)
O2–C10=1.446(9)	C9A–C9–C10=128.9(8)	C2–C3–C4–C5=176.0(10)
C4–C5=1.412(15)	C9A–C9–C8=124.6(8)	C5–C4–C6–C7=180.0(10)
C8–C9=1.542(10)	C10–C9–C8=106.4(6)	C10–C1–C7–C6=179.2(7)
C9–C9A=1.303(12)	C1–C10–C11=110.8(6)	C2–C1–C7–C8=179.7(7)
C9–C10=1.535(9)		C6–C7–C8–O1=9.4(14)
		C1–C7–C8–C9=6.4(8)
		C7–C8–C9–C9A=166.2(10)
		C9A–C9–C10–C1=165.6(10)

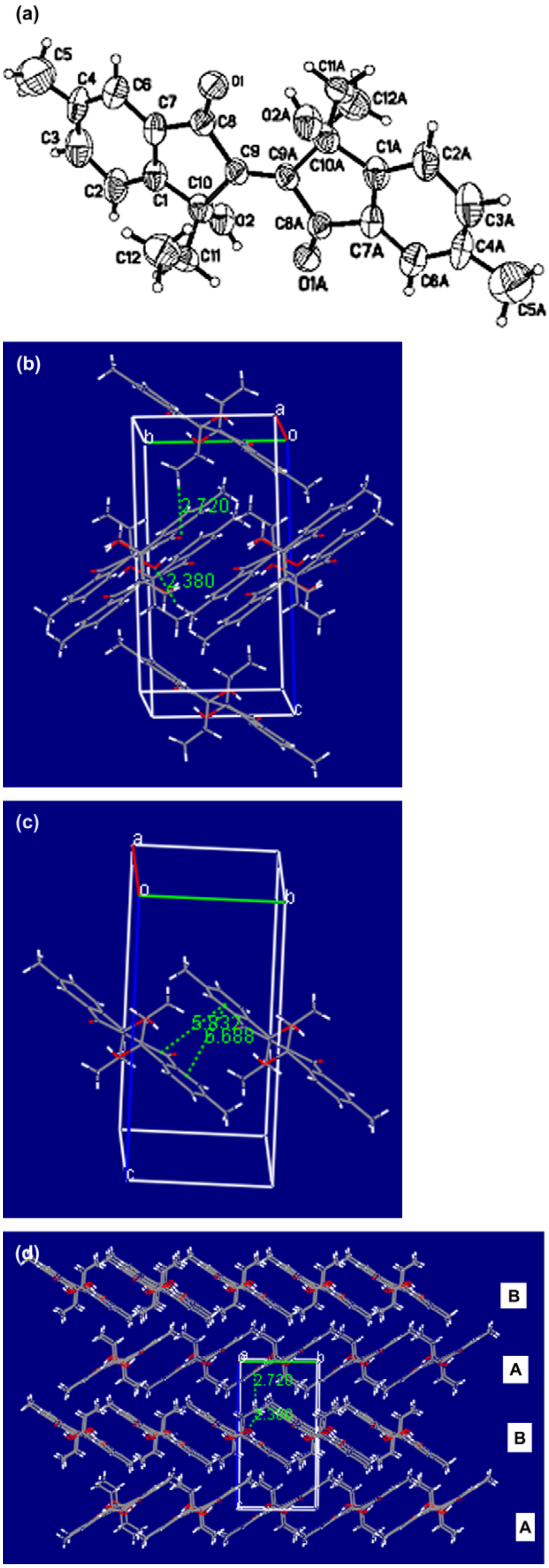


Figure 2. (a) Molecular structure and atom numbering scheme for **2**; (b) single crystal structure of **2**; (c) the distance of centroid–centroid between the benzene rings of neighboring molecules; (d) expanded crystal packing diagram for **2**.

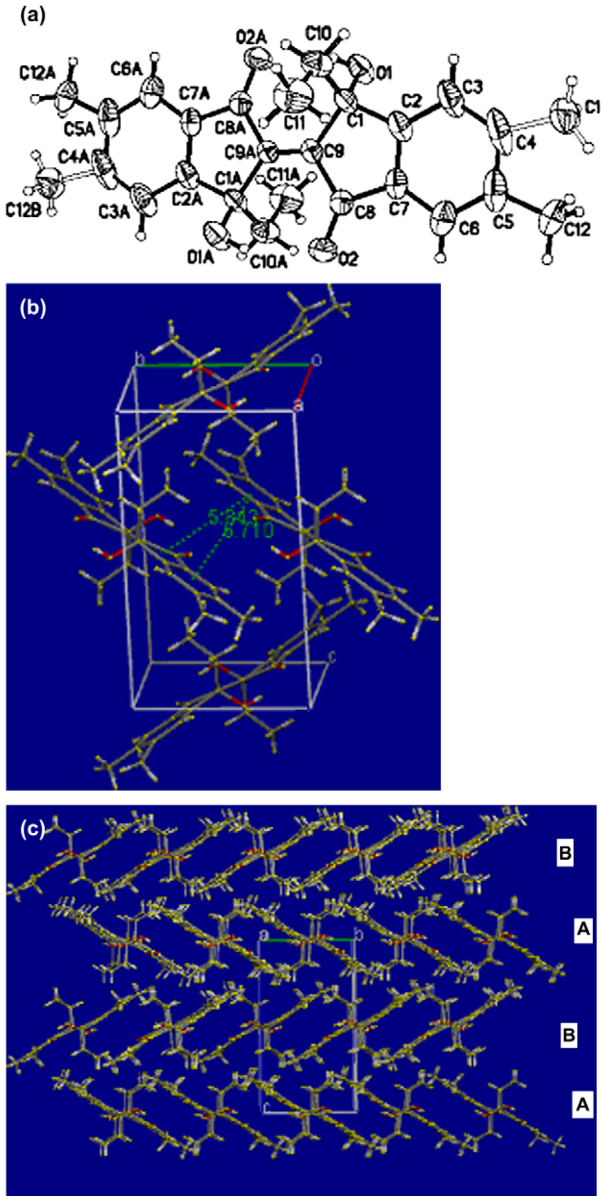


Figure 3. (a) Molecular structure and atom numbering scheme for **3**; (b) single crystal structure of **3**; (c) expanded crystal packing diagram for **3**.

and **3** after irradiation with sunlight. Before photoirradiation, the UV–vis absorptions of the three samples appear in the wavelength range of 250–500 nm with the maximum absorption at about 450 nm. After photoirradiation, the absorptions increase in the range of 500–800 nm with the

Table 4. Selected bond lengths (Å), angles (°), and torsion angles (°) for **3**

Bond lengths	Bond angles	Torsion angles
O1–C1=1.435(5)	C9A–C9–C8=125.4(5)	C9A–C9–C1–C2=166.8(6)
O2–C8=1.223(5)	C9A–C9–C1=127.9(5)	C8–C9–C1–C2=12.0(4)
C9–C9A=1.336(8)	C8–C9–C1=106.7(3)	C1–C2–C7–C8=1.9(6)
C9–C1=1.544(5)	O1–C1–C10=110.7(4)	C8–C7–C6–C5=178.1(5)
C4–C12=1.529(8)	C5–C4–C12′=108.0(8)	C1–C2–C3–C4=179.0(5)
C5–C12=1.467(7)	C4–C5–C12=110.9(7)	C2–C3–C4–C12′=165.6(9)
	C6–C5–C12=127.7(8)	C12′–C4–C5–C6=168.4(7)
		C3–C4–C5–C12=177.2(7)
		C12′–C4–C5–C12=12.0(10)
		C7–C6–C5–C12=178.7(7)

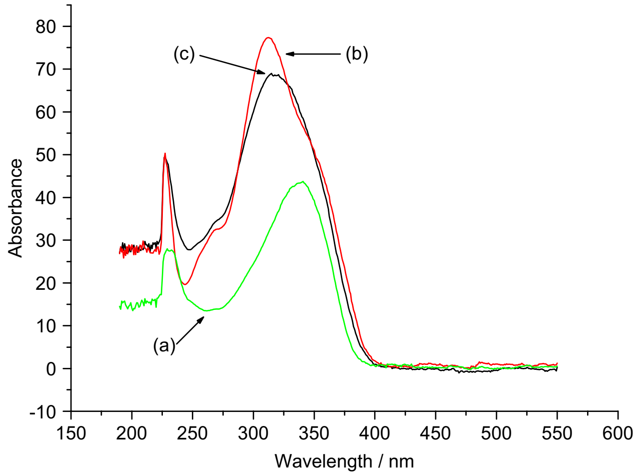


Figure 4. UV–vis absorption spectra of title compounds in CH_2Cl_2 solution. (a) **1** (1.5×10^{-5} M); (b) **2** (3.2×10^{-5} M); (c) **3** (2.7×10^{-5} M).

Table 5. UV–vis absorption and coefficients of **1**, **2**, **3** in CH_2Cl_2

Compound	λ_{max} (nm) (ε)	c (M)
1	229.2 (18,496), 340.8 (28,885)	1.5×10^{-5}
2	227.5 (15,608), 312.5 (23,996)	3.2×10^{-5}
3	226.7 (18,427), 315 (25,772)	2.7×10^{-5}

maximum absorption around 570 nm. After photochromism, the colors of **1**, **2**, and **3** could be stable at room temperature for a substantially long time, and could be reversed to the initial colors upon heating under nitrogen atmosphere.

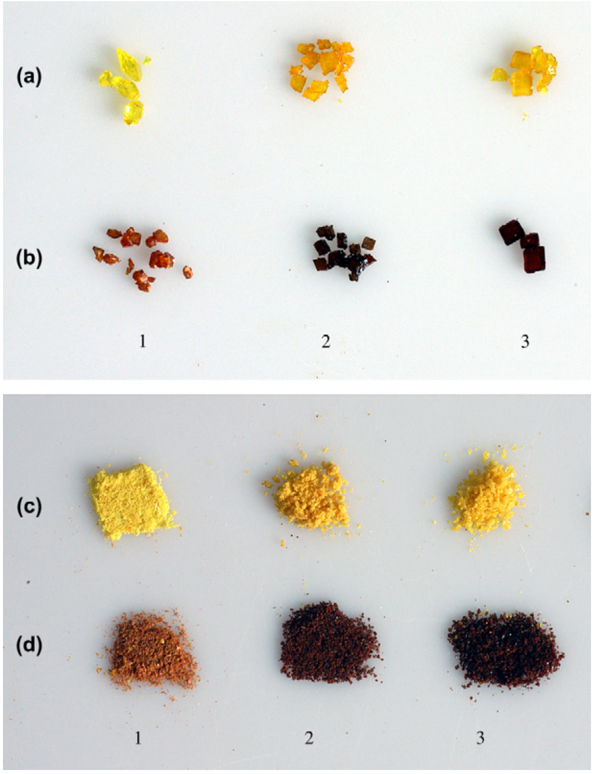


Figure 5. The color changes of compounds **1**, **2**, and **3** before and after irradiation with sunlight in the solid state. (a) Crystal, before irradiation with sunlight; (b) crystal, after irradiation with sunlight; (c) powder, before irradiation with sunlight; (d) powder, after irradiation with sunlight.

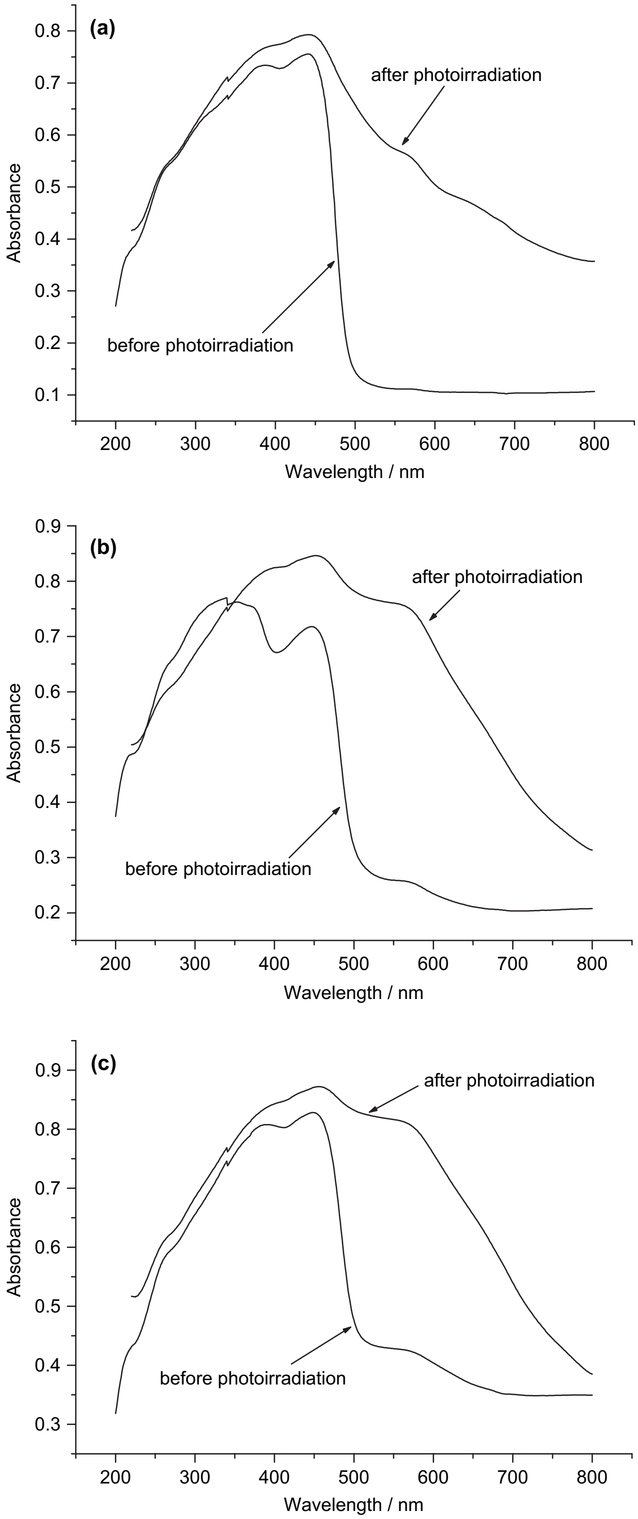


Figure 6. The changes of UV–vis spectra of compounds **1**, **2**, and **3** before and after irradiation with sunlight in the solid state. (a) Compound **1**; (b) compound **2**; (c) 'racemic compound' **3**.

Solid samples of **1**, **2**, and **3** were measured by electron spin resonance spectroscopy. Before irradiation, no ESR signal was detected. Conversely, clear ESR signal was observed for each of the samples after irradiation (Fig. 7a, b, and c). The g values for **1**, **2**, and **3** are 1.999, 2.003, and 2.001, respectively. These results are in agreement with the

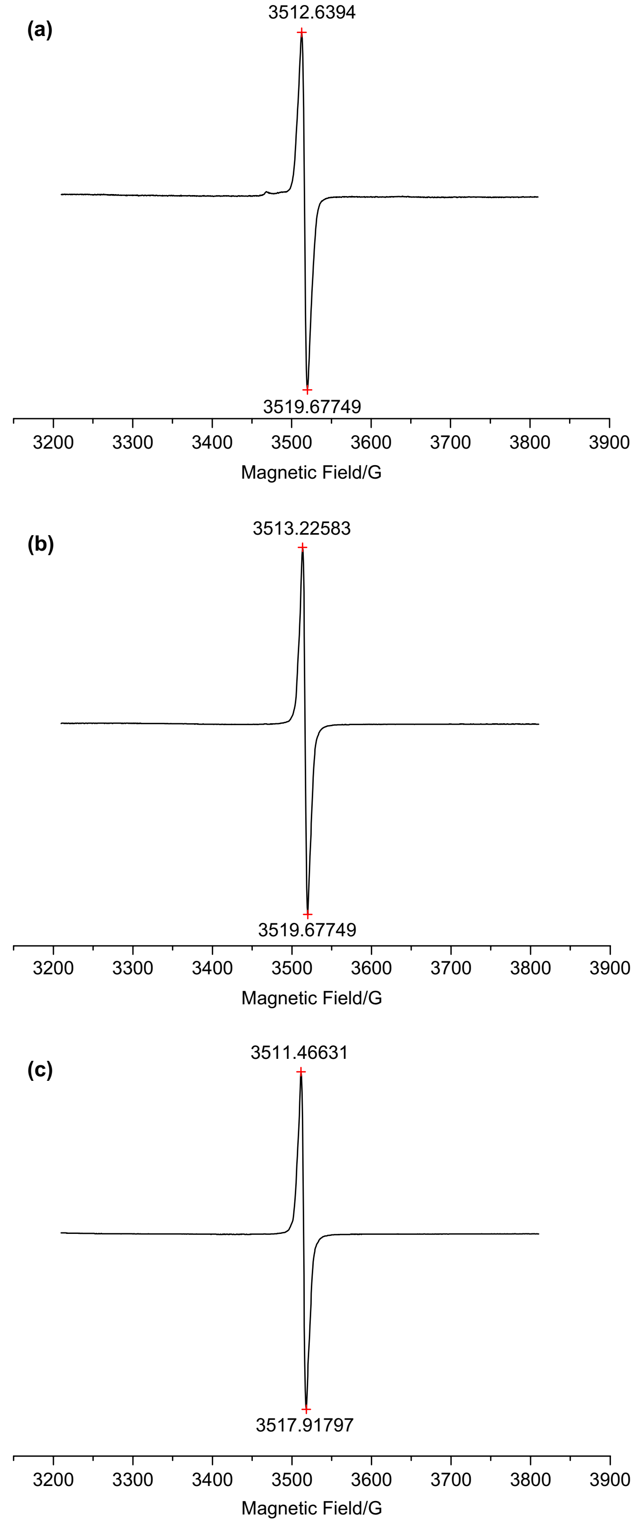
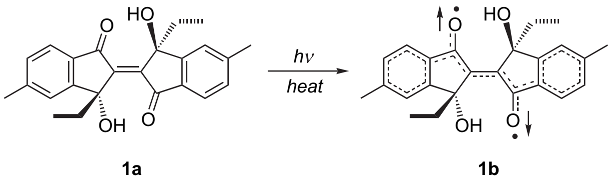


Figure 7. ESR spectra of **1**, **2**, and **3**, upon sunlight irradiation in the solid state at room temperature. (a) **1**; (b) **2**; (c) **3** (working frequency: 9.85 GHz).

previously proposed photochromism mechanism for biindenylidenedione derivatives.[24] Upon photoirradiation, each compound is supposed to generate two unpaired radicals in the molecule with oppositely parallel orientation. These singlet biradicals could be stabilized by the conjugation of the whole molecule while the oxygen atoms of carbonyls greatly contribute to the spin density distribution (Scheme 3).



Scheme 3. Photochromic reaction of **1**.

3. Conclusions

New photochromic biindenylidenedione compounds **1**, **2**, and a racemate of **3a**, **3b** have been successfully synthesized. Their structures have been well determined and the physical properties including UV–vis absorption and photochromism have been investigated. Results reveal that the substituents, even like the simple methyl, on the benzene rings of biindenylidenedione could considerably influence the photochromic property, as well as other properties of this kind of compounds.

4. Experimental

4.1. Materials and apparatuses

All chemicals were purchased from commercial sources, and solvents were dried by refluxing over an appropriate drying agent and distilled prior to use. Melting points were determined with Yanagimoto MP-35 melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on BRUKER AC-P300. UV–vis spectra were recorded on Shimadzu UV-2101PC UV–vis spectrophotometer. The mass spectra were recorded on Thermo Finnigan LCQ Advantage spectrometer in ESI mode-I with spray voltage 4.8 kV. A Yamaco CHN corder MT-3 apparatus was used for elemental analysis. The X-ray diffraction data were collected using Mo Kα radiation (λ=0.71073 Å) on a BRUKER SMART 1000 diffractometer.

4.1.1. Intermediate (6). 4-Methylphthalic anhydride (10 g, 62 mmol) and butanedioic acid (10 g, 83 mmol) were mixed and heated to melt with stirring. Then anhydrous KOAc was added. The resulting mixture was refluxed with vigorous stirring for 2 h. Upon cooling, red solid intermediate **6** (7.6 g) was collected, and directly used for next step.

4.1.2. 5,5′-Dimethyl-[2,2′-biindanylidene]-1,1′,3,3′-tetraone(7). To a suspension of intermediate **6** (7.6 g) in CH_3OH (40 mL) was rapidly added a solution of CH_3ONa (made from 1.6 g of Na metal) in CH_3OH (30 mL), and the reaction was then stirred under reflux for 1 h. After cooling to room temperature and filtration, a dark precipitate was obtained. The precipitate was taken in CH_3OH (100 mL) and boiled for 0.5 h, and then filtered to give a dark-brown solution, which was neutralized with dilute hydrochloric acid affording a purple precipitate. This purple precipitate was then recrystallized from nitrobenzene to give a dark needle-like crystalline solid **7** (2.2 g) in 23% yield, mp 271–273 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.54 (s, 1.5H, Ar–CH_3), 2.35 (s, 4.5H, Ar–CH_3), 7.10–7.26 (m, 6H, –Ar), 14.52 (s, 0.5H, *OH* of enol), 14.58 (s, 1H, *OH* of enol), 14.68 (s, 0.5H, *OH* of enol). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 191.971, 188.085, 187.430, 183.320, 143.860, 143.251, 138.238, 137.255, 133.969, 133.027, 131.993, 131.472, 121.883, 121.600, 120.980, 120.655, 103.775, 103.693, 22.127, 22.083. MS (ESI, *m/z*): 319.26 $[M+1]^+$. Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46, H, 4.43. Found: C, 75.53, H, 4.40.

4.1.3. 6,6′ or 7,7′ or 6,7′-dimethyl-[2,2′-bi-1*H*-indene]-3,3′-diethyl-3,3′-dihydroxy-1,1′-dione (1, 2, 3). To a solution of ethylmagnesium bromide prepared from bromoethane (2.7 g, 25 mmol) and magnesium (0.5 g, 21 mmol) in anhydrous ether (5 mL), a suspension of **7** (1.6 g, 5 mmol) in dry benzene (30 mL) was added over a period of 10 min. The dark green reaction mixture was stirred for 12 h under nitrogen atmosphere, and then exposed to air for additional 3 h. The reaction mixture then had a dark purple color, and was quenched with saturated NH_4Cl aqueous solution. The organic phase was collected and dried over anhydrous $MgSO_4$. After filtration and evaporation of solvent, the residue was washed with acetone to give yellow powder (0.7 g, 39%) as the crude product. The crude product (10 g) was accumulated, which was then dissolved in a solvent mixture (C_2H_5OH–CH_2Cl_2 3:1, v/v) under heating. Fractional crystallization gave in turn three kinds of crystalline solids: yellow powder **1** (2.2 g), yellow sheet **3** (a racemate of **3a** and **3b**, 4.2 g), and yellow grain **2** (2.1 g).

Compound 1: mp: 269–271 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.52–0.57 (t, 6H, $-CH_2CH_3$, $^3J_{HH}$=15 Hz), 2.12–2.34 (m, 4H, $-CH_2CH_3$), 2.54 (s, 6H, Ar–CH_3), 6.79 (s, 2H, –OH), 7.35–7.77 (m, 6H, –Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.3, 155.3, 150.8, 149.6, 135.8, 131.2, 125.0, 123.8, 79.4, 33.9, 22.9, 9.8. MS (ESI, *m/z*): 377.27 $[M+1]^+$. IR (cm^{-1}): 3371, 3050, 2964, 1664, 1607. Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57, H, 6.43. Found: C, 76.61, H, 6.35.

Compound 2: mp: 203–205 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.52–0.57 (t, 6H, $-CH_2CH_3$, $^3J_{HH}$=15 Hz), 2.12–2.28 (m, 4H, $-CH_2CH_3$), 2.48 (s, 6H, Ar–CH_3), 6.66 (s, 2H, –OH), 7.35–7.77 (m, 6H, –Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.7, 152.4, 150.8, 140.1, 139.0, 131.2, 124.7, 123.6, 79.4, 33.8, 22.9, 9.8. MS (ESI, *m/z*): 377.27 $[M+1]^+$. IR (cm^{-1}): 3336, 3052, 2971, 1660, 1607. Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57, H, 6.43. Found: C, 76.49, H, 6.54.

‘Racemic compound’ 3: mp: 173–178 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.52–0.57 (t, 6H, $-CH_2CH_3$, $^3J_{HH}$=15 Hz), 2.12–2.29 (m, 4H, $-CH_2CH_3$), 2.48 (s, 3H, Ar–CH_3), 2.54 (s, 3H, Ar–CH_3), 6.71 (s, 2H, –OH), 7.34–7.77 (m, 6H, –Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.0, 196.2, 155.2, 152.5, 150.8, 149.6, 140.1, 139.0, 138.0, 135.8, 131.2, 125.0, 124.7, 124.5, 123.8, 123.6, 79.4, 33.8, 22.9, 21.6, 9.85, 9.79. MS (ESI, *m/z*): 377.27 $[M+1]^+$. IR (cm^{-1}): 3339, 3053, 2969, 1661, 1607. Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57, H, 6.43. Found: C, 76.52, H, 6.38.

4.2. Supporting information

Crystal structure data for **1**, **2**, and **3** are available from the Cambridge Crystallographic Data Center, CCDC nos. 627736–627738.

Acknowledgements

We thank the National Natural Science Foundation of China (20490210, 20602020) and N&T Joint Academy of China for financial support.

References and notes

1. Irie, M. *Chem. Rev.* **2000**, *100*, 5.
2. Masttsud, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 383.
3. Masttsud, K.; Matsuda, M.; Mizoguti, S. *J. Phys. Chem. B* **2002**, *106*, 11218.
4. Bénard, S.; Riviére, E.; Yu, P. *Chem. Mater.* **2001**, *13*, 159.
5. Matsuda, K.; Irie, M. *Chem.—Eur. J.* **2001**, *7*, 3466.
6. Takayama, K.; Matsuda, K.; Irie, M. *Chem.—Eur. J.* **2003**, *9*, 5605.
7. Matsuda, K.; Matsuo, M.; Irie, M. *J. Org. Chem.* **2001**, *66*, 8799.
8. Tanifuji, M.; Irie, M.; Matsuda, K. *J. Am. Chem. Soc.* **2005**, *127*, 13344.
9. Hadjoudis, E.; Vitiorakis, M.; Mouskakeli, M. I. *Tetrahedron* **1987**, *43*, 1345.
10. Harada, J.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 5809.
11. Sixl, H.; Wara, R. *Chem. Phys.* **1985**, *94*, 147.
12. Shinohara, S.; Takeda, J.; Ooike, T.; Kurita, S. *J. Phys. Soc. Jpn.* **1999**, *68*, 1423.
13. Ichimura, K.; Watanabe, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2220.
14. Maeda, K.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 429.
15. Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 8106.
16. Trozzolo, A. M.; Lesli, T. M.; Sarpotdar, A. S.; Small, R. D.; Ferraudi, G. J.; DoMinh, T.; Hartless, R. L. *Pure Appl. Chem.* **1979**, *51*, 261.
17. Kobatake, S.; Yamada, M.; Yamada, T.; Irie, M. *J. Am. Chem. Soc.* **1999**, *121*, 8450.
18. Kobatake, S.; Yamada, T.; Uchida, K.; Kato, N.; Irie, M. *J. Am. Chem. Soc.* **1999**, *121*, 2380.
19. Tanaka, K.; Toda, F. *J. Chem. Soc., Perkin Trans. 1* **2000**, 873.
20. Tanaka, K.; Toda, F.; Higuchi, T. *Mol. Cryst. Liq. Cryst.* **1992**, *219*, 135.
21. Tanaka, K.; Yamamoto, Y.; Ohba, S. *Chem. Commun.* **2003**, 1866.
22. Xu, L. L.; Meng, J. B.; Wang, H.; Sugiyama, T.; Wang, Y. M.; Matsuura, T. *Mol. Cryst. Liq. Cryst.* **2002**, *389*, 33.
23. Xu, L. L.; Huang, H. M.; Song, Z. Y.; Meng, J. B.; Matsuura, T. *Tetrahedron Lett.* **2002**, *43*, 7435.
24. Xu, L. L.; Sugiyama, T.; Meng, J. B.; Matsuura, T. *Chem. Commun.* **2002**, 2328.
25. Li, X.; Song, Z. Y.; Chen, Y.; Meng, J. B. *J. Mol. Struct.* **2005**, *748*, 161.
26. Li, X.; Xu, L. L.; Han, J.; Pang, M. L.; Ma, H.; Meng, J. B. *Tetrahedron* **2005**, *61*, 5373.
27. Nakatsuji, S. *Adv. Mater.* **2001**, *13*, 1719.
28. Mark, S.; Alexander, V.; Vladimir, K. *J. Org. Chem.* **2005**, *70*, 92.
29. Said, F. F.; Ong, T. G.; Bazinet, P. *Cryst. Growth Des.* **2006**, *6*, 1848.
30. Singh, F. S.; Kumar, R.; Sharon, A. *J. Mol. Struct.* **2006**, *782*, 55.

31. Tang, H. D.; Gao, J. P.; Xiong, Y. *Cryst. Growth Des.* **2006**, *6*, 1559.
32. Plans, J. G.; Mohamed, G. G. *J. Mol. Struct.* **2006**, *787*, 121.
33. Mitchell, A. G. *J. Pharm. Pharm. Sci.* **1998**, *1*, 8.
34. *X-ray crystal and molecular structure analysis.* Data for **1**, **2**, **3** were collected using Mo Kα radiation (λ=0.71073 Å) at 294(2) K. (a) *Crystal data for 1*: empirical formula $C_{24}H_{24}O_4$, formula weight=376.43, monoclinic, space group $P2(1)/n$, a=8.571(4) Å, b=7.472(3) Å, c=15.531(6) Å, α=90°, β=100.566(6)°, γ=90°, V=977.8(7) Å^3, Z=2, d (calcd)=1.279 g cm^{-3}, reflection collected/unique 5034/2014 [R (int)=0.0552], final R indices [$I>2\sigma(I)$] $R1$=0.0538, $wR2$=0.1327, R indices (all data) $R1$=0.1067, wR=0.1584, GOF=1.004, CCDC 627737; (b) *Crystal data for 2*: empirical formula $C_{48}H_{48}O_8$, formula weight=752.86, monoclinic, space group $P2(1)/n$, a=9.577(5) Å, b=7.548(4) Å, c=14.708(8) Å, α=90°, β=107.290(9)°, γ=90°, V=1015.2(9) Å^3, Z=2, d (calcd)=1.231 g cm^{-3}, reflection collected/unique 4774/1790 [R (int)=0.0720], final R indices [$I>2\sigma(I)$] $R1$=0.144, $wR2$=0.3816, R indices (all data) $R1$=0.2355, wR=0.4357, GOF=1.275, CCDC 627738; (c) *Crystal data for 3*: empirical formula $C_{12}H_{12}O_2$, formula weight=188.22, monoclinic, space group $P2/n$, a=9.613(4) Å, b=7.581(3) Å, c=14.978(5) Å, α=90°, β=110.38(2)°, γ=90°, V=1023.2(7) Å^3, Z=2, d (calcd)=1.222 g cm^{-3}, reflection collected/unique 4679/1774 [R (int)=0.0720], final R indices [$I>2\sigma(I)$] $R1$=0.0897, $wR2$=0.2195, R indices (all data) $R1$=0.1247, wR=0.2496, GOF=1.019, CCDC 627736.