A new type of banana shape bifunctional monomer of ester chalcones

Zainab Ngaini*, Chua Mei Chee and Lim Lian Chin

Department of Chemistry, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

*Corresponding Author: nzainab@frst.unimas.my (Z. Ngaini)

Article history:
Received 21 March 2013
Revised 1 July 2013
Accepted 19 July 2013
Available online 1 September 2013

ABSTRACT

A synthesis of a new type of chalcone analogue banana-shaped liquid crystals compounds is described. The approach involved the reaction of hydroxyl chalcones with isophthaloyl dichloride to form benzene-1,3-dicarbonyl-bis-1-(4-alkoxyphenyl)-3-(4-hydroxylphenyl)prop-2-en-1-one (7a-c and 8a-c) having two chalcone units via esterification reaction. The hydroxyl chalcones, which differ in the length of alkyl group, CnH2n+1, where n= 10, 12 and 14 were synthesised via Claisen Schmidt condensation prior to the reaction with isophthaloyl dichloride. The reaction was a catalyst dependence. No sign of product was formed by employing NaH (60%). It was only occurred in the presence of NaH (95%) to afford banana shape bi-functional monomer of ester chalcone 7a-c and 8a-c. The synthesized compound was characterized by 1H and 13C Nuclear Magnetic Resonance (NMR), and Fourier Transform Infrared (FTIR).

Keywords: Chalcones, banana shape liquid crystals, alkyl chains, ester

1. INTRODUCTION

Liquid crystal technology has been widely applied in device technology. Both fluidity and crystalline properties of liquid crystal facilitate better control over alignment when applied to device. The advantages of liquid crystals for these applications such as faster switching times, a wider viewing angle, continuous gray level, improved transmittance of the clear state, approximately no threshold voltage and low power consumption [1]. Series of linear shape of mesogens based on chalcone has been studied for their liquid crystal behavior [2,3]. Chalcone derivatives were reported for excellent nonlinear optic property [4] and liquid crystal displays [5,6]. Chalcones has been used in promoting light transmittance [7] and crystalliability [8].

In recent years, banana-shaped liquid crystals have been given much attention in various aspects such as fast polarization reorientation, ferroelectricity and antiferroelectricity, and small threshold voltage when applied to liquid crystal display mode [9]. Banana-shaped liquid crystals have also been identified as interesting compounds due to their unexpected electro-optical properties, polarity and chirality [10].

In this paper, we describe the preparation of a new type banana shape compound of benzene-1,3-dicarbonyl-bis-1-(4-alkoxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one 5a-c possessing alkyl chains of varying length from C10 to C14 which potentially used for liquid crystal studies.
177.0°C. v max (KBr / cm⁻¹) 3140 (-OH), 1646(C=O), 980(trans CH=CH) and 823(para disub benzene). δ H (500 MHz, CDCl₃) 8.10 (d, J 8.6, 2H, H₁-3), 7.85 (d, J 15, 1H, H₁-a), 7.81-7.83 (m, 3H, H₁-3'& 4'), 7.75 (d, J 15, 1H, H₁-b), 7.43 (d, J 6.9, 2H, H₁-2), 6.96 (d, J 8.05, 2H, H₁-2').

2.3 Synthesis of benzene-1,3-dicarbonyl-bis-4-chalcone (2)

Attempted Strategy 1

4-hydroxychalcone (0.11 g, 0.50 mmol) and tetrahydrofuran (THF) (30 mL) was added to sodium hydride (NaH) (0.01 g, 0.50 mmol, 60 %) and stirred for 1 h at room temperature. Benzene-1,3-dicarbonyl dichloride (0.05 g, 0.25 mmol) in THF (20 mL) was added to the mixture and stirred for 6 h at room temperature. The mixture was refluxed for 8 h. The mixture was cooled to room temperature, filtered, and washed with distilled water and methanol. Dichloromethane (DCM) and distilled water were used to extract the organic layer. The organic layer was washed, and dried. The crude was recrystallized from hexane:ethanol (7:1) to give 3a-c. The crude was filtered, and concentrated in vacuo. The crude was recrystallized from ethanol to give 3a–3c. 1-(4-Decyloxyphenyl)-ethanone (3a)

2.4 Synthesis of alkylxyophenyl-ethanone (3a–3c)

General procedure

Bromoalkane (72 mmol), 4-hydroxyacetophenone (72 mmol), K₂CO₃ (72 mmol), and TBAI (6 mmol) in MEK (200 mL) were heated at reflux for 5 h. The mixture was filtered and cooled to room temperature. Water (30 mL) was added to the filtrate, and the layers separated. The aqueous layer was extracted with dichloromethane (2 x 30 mL). The combined layers were washed with water (2 x 20 mL), dried (MgSO₄), and concentrated in vacuo. The crude was recrystallized from ethanol to give 3a–3c. 1-(4-Decyloxyphenyl)-ethanone (3a)

2.5 Synthesis of (E)-1-[4-(alkyloxy)phenyl]-3-[4-hydroxyphenyl]prop-2-en-1-one (4a-4c)

General procedure

A mixture of 4-hydroxybenzaldehyde (12.5 mmol) and 3a-c (12.5 mmol) in 35 mL of methanol was added under stirring to a solution of KOH (2.52 g) in methanol (10 mL). The mixture was heated at reflux for 10 h. The reaction was cooled to room temperature and acidified with cold dilute HCl (2 N). The resulting precipitate was filtered, washed, and dried. The crude was recrystallized from hexane:ethanol (7:1) to give 4a-4c. ((E)-1-(4-decyloxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one (4a))

Compounds 4a was obtained as yellow crystals (5.74 mL, 20 mmol). Yield (2.66 g, 35%). FTIR and NMR data were consistent with the reported literature [11].

(E)-1-[4-(Dodecyloxy)phenyl]-3-[4-hydroxyphenyl]prop-2-en-1-one (4b)

Compounds 4b was obtained as yellow crystals. Yield: 44%. FTIR and NMR data were consistent with the reported literature [11].

(E)-1-[4-(Tetradecyloxy)phenyl]-3-[4-hydroxyphenyl]prop-2-en-1-one (4c)

Compounds 4c was obtained as yellow crystals. Yield: 39%. FTIR and NMR data were consistent with the reported literature [11].

2.6 Synthesis of alkylxybenzaldehyde (5a–5c)

General procedure

Bromoalkane (60 mmol), 4-hydroxybenzaldehyde (60 mmol), K₂CO₃ (60 mmol), and TBAI (6 mmol) in MEK (200 mL) were heated at reflux for 5 h. The mixture was filtered and cooled to room temperature. Water (30 mL) was added to the filtrate, and the layers separated. The aqueous layer was extracted with dichloromethane (2 x 30 mL). The combined layers were washed with water (2 x 20 mL), dried (MgSO₄), and concentrated in vacuo. The crude product was purified by column chromatography (eluting
with 1:20 ethyl acetate:petroleum ether). The same general procedure gave compounds 5a–c.

### 4-Decyloxybenzaldehyde (5a)

Bromododecane (12.40 mL, 60 mmol). Yield: 8.69 g, 66%. FTIR and NMR data were consistent with the reported literature [12].

### 4-Decyloxybenzaldehyde (5b)

Bromododecane (14.38 mL, 60 mmol). Yield: 13.03 g, 90%. The FTIR and NMR data were consistent with the reported literature [12].

### 4-Decyloxybenzaldehyde (5c)

Bromotetradecane (16.31 mL, 60 mmol). Yield: 11.78 g, 74%. The FTIR and NMR data were consistent with the reported literature [12].

### General procedure

A mixture of 4-hydroxyacetophenone (30 mmol) and 6a-c (30 mmol) in 90 mL of methanol was added under stirring to a solution of KOH (6.06 g, 108 mmol) in methanol (10 mL). The mixture was heated at reflux for 10 h. The reaction was cooled to room temperature and acidified with cold diluted HCl (2 N). The resulting precipitate was filtered, washed, and dried. The crude was recrystallized from hexane:ethanol (7:1) to give 6a–6c.

### 2.7 Synthesis of (E)-3-(4-alkyloxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (6a–6c)

#### General procedure

A mixture of 4-hydroxyacetophenone (30 mmol) and 6a-c (30 mmol) in 90 mL of methanol was added under stirring to a solution of KOH (6.06 g, 108 mmol) in methanol (10 mL). The mixture was heated at reflux for 10 h. The reaction was cooled to room temperature and acidified with cold diluted HCl (2 N). The resulting precipitate was filtered, washed, and dried. The crude was recrystallized from hexane:ethanol (7:1) to give 6a–6c.

#### (E)-3-(4-Decyloxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (6a) Yield: 8.32 g, 52%. The FTIR and NMR data were consistent with the reported literature [12].

#### (E)-3-(4-Decyloxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (6b) Yield: 8.32 g, 52%. The FTIR and NMR data were consistent with the reported literature [12].

#### (E)-3-(4-Decyloxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (6c) Yield: 8.32 g, 52%. The FTIR and NMR data were consistent with the reported literature [12].

### 2.8 Synthesis of bifunctional monomer of ester chalcones (7a–7c) and (8a–8c)

#### Benzene-1,3-dicarbonyl-bis-1-(4-dodecyloxyphenyl)-3(4-hydroxyphenyl)prop-2-en-1-one (7b)

Yield: (0.08 g, 17%) as sticky yellow oil. The same general procedure to afford compound 7a (0.07 g, 15%) as sticky yellow oil.

### Benzene-1,3-dicarbonyl-bis-1-(4-dodecyloxyphenyl)-3(4-hydroxyphenyl)prop-2-en-1-one (7c)

Yield: (0.41 g, 1 mmol). Yield: (0.09 g, 18%) as sticky yellow oil. 

#### Benzene-1,3-dicarbonyl-bis-1-(4-tetradecyloxyphenyl)-3(4-hydroxyphenyl)prop-2-en-1-one (7d)

Yield: (0.21 g, 8.67%) as a pale yellow oil.

### Benzene-1,3-dicarbonyl-bis-1-(4-dodecyloxyphenyl)-3(4-hydroxyphenyl)prop-2-en-1-one (8a)

Yield: (0.10 g, 11.6%) as a pale yellow oil.

### Benzene-1,3-dicarbonyl-bis-1-(4-tetradecyloxyphenyl)-3(4-hydroxyphenyl)prop-2-en-1-one (8b)

Yield: (0.21 g, 8.67%) as a pale yellow oil.

### Benzene-1,3-dicarbonyl-bis-1-(4-cyanoxyphenyl)-3(4-hydroxyphenyl)prop-2-en-1-one (8c)

Yield: (0.21 g, 8.67%) as a pale yellow oil.

### Benzene-1,3-dicarbonyl-bis-1-(4-(4-hydroxyphenyl)prop-2-en-1-one (8d)

Yield: (0.21 g, 8.67%) as a pale yellow oil.

### Benzene-1,3-dicarbonyl-bis-1-(4-(4-hydroxyphenyl)prop-2-en-1-one (8e)

Yield: (0.21 g, 8.67%) as a pale yellow oil.
0.86 (t, 6H, H3-12”), 1.26-1.71 (m, 40H, H2-2”-11”), 3.97 (t, 4H, H2-1”), 6.88-6.92 (m, 4H, H1-2”), 7.39-7.40 (t, 1H, H1-4), 7.45 (d, J 15.45, 1H, H1-b), 7.55-7.57 (m, 4H, H1-2), 7.77 (d, J 16.60, 2H, H1-a), 7.87-7.90 (d, 4H, H1-3), 7.94, 7.98 (dd, 8H, H1-3” & 2”), 8.07 (s, 1H, H1-1).

Benzene-1,3-dicarbonyl-bis-3-(4-tetradecyloxyphenyl)-1-(hydroxyphenyl) prop-2-ene-1-one (8c)

6c (0.44 g, 1 mmol). Yield: (0.20 g, 21.5%) as a pale yellowish oil.

νmax (KBr / cm⁻¹) 2917(-CH2), 2849(-CH3), 1729(C=O ester), 1655(C=O carbonyl), 1259(C-O-C), 1021(C=C), 799(para disub benzene).

δH (500 MHz, CDCl3) 0.86 (t, 6H, H3-14”), 1.24-1.78 (m, 48H, H2-2”-13”), 3.99 (t, 4H, H2-1”), 6.89-6.92 (m, 4H, H1-2”), 7.35-7.37 (t, 1H, H1-4), 7.37 (d, J 15.45, 2H, H1-b), 7.57-7.61 (m, 4H, H1-3”), 7.78 (d, J 15.45, 2H, H1-a), 8.09-8.11 (d, 4H, H1-3), 8.31, 8.38 (dd, 8H, H1-3” & 2”), 8.86 (s, 1H, H1-1).

3. RESULTS & DISCUSSION

Initial study on the preparation of 2 was performed following typical procedure, where earlier synthesized 4-hydroxychalcone, 1, in tetrahydrofuran (THF) was added into sodium hydride (NaH) (60 %) and stirred for 1 h at room temperature. Benzene-1,3-dicarbonyl dichloride in THF was added to the mixture and stirred at room temperature. TLC analysis, however, showed no sign of product formed after 24 h.

Several attempts were made with slight modifications on the reaction condition (solvent, time, temperature), however no evidence for formation of the desired product.

NaH (95%) was chosen over NaH (60%) as a catalyst and successfully afforded 2 with 50% yield. The preparation of 2 is depicted in Scheme 1.

The chemical structure of 2 was found to be consistent with FT-IR and 1H NMR spectroscopic methods and showed the peaks corresponded to the structures.

The IR spectrum of 2 is shown in Fig. 1. The IR spectrum showed the disappearance of -OH peak at 3140 cm⁻¹ and the appearance of absorption band at 1727 cm⁻¹, which were attributed to the formation of ester bond. The structure of 2 were further confirmed by 1H NMR spectrum (Fig. 2), which showed peaks attributed to trans vinylic proton at δ 6.96 and 7.89, with a coupling constant, J 15 Hz. New peak attributed to center aromatic H1 appeared as singlet at δ 8.49. The peaks corresponded to H3&4 were appeared at δ 7.57-8.08. This proton resonates more downfield from other resonances due to the attachment with two chalcones moieties.

![IR Spectrum of compound (2) using NaH (95%)](image)

Several methods have been employed in the synthesis of chalcones due to ease of chalcone structure itself to be substituted [13, 14]. A series of chalcone derivatives (E)-1-[4-(alkyloxy)phenyl]-3-[4-hydroxyphenyl] prop-2-en-1-one (4a-4c) and (E)-3-[4-alkyloxyphenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one (6a-6c) were prepared via Claisen-Schmidt condensation by the route depicted in Scheme 2.

Compound 3a-c and 5a-c were reacted with 4-hydroxybenzaldehyde and 4-hydroxyacetophenone, respectively, under refluxing methanol to afford hydroxylated chalcones 4a-c and 6a-c as yellow crystals. IR
spectra showed the presence of $v_{\text{OH}}$ at 3262 cm$^{-1}$, while $v_{\text{CH}_2}$ and $v_{\text{CH}_3}$ bands were observed at 2922 and 2851 cm$^{-1}$ respectively.

K$_2$CO$_3$, TBAI

MEK

MeOH, reflux

KOH (3.6 equiv)

$4a$, $R = \text{C}10\text{H}21$

$4b$, $R = \text{C}12\text{H}25$

$4c$, $R = \text{C}14\text{H}29$

$6a$, $R = \text{C}10\text{H}21$

$6b$, $R = \text{C}12\text{H}25$

$6c$, $R = \text{C}14\text{H}29$

$3a$, $R = \text{C}10\text{H}21$

$3b$, $R = \text{C}12\text{H}25$

$3c$, $R = \text{C}14\text{H}29$

$5a$, $R = \text{C}10\text{H}21$

$5b$, $R = \text{C}12\text{H}25$

$5c$, $R = \text{C}14\text{H}29$

Scheme 2 Synthesis of chalcone derivatives $4a$-$c$ and $6a$-$c$

Scheme 3 Synthesis of banana-shaped chalcones ester $7a$-$c$ and $8a$-$c$

The IR spectrum of $7a$ (Fig 3) showed the presence of $v_{\text{c=O}}$ for ester at 1746 cm$^{-1}$ and $v_{\text{c-o-c}}$ attributed to alkyl aryl ether at 1245 cm$^{-1}$. The $1\text{H}$ NMR spectrum of $7a$ (Fig. 4) showed peaks attributed to CH$_3$ and CH$_2$ at $\delta$ 0.85 and 1.24-1.63, while peak attributed to OCH$_2$ at $\delta$ 3.97. The trans vinylic proton $\alpha$ and $\beta$ were assigned at $\delta$ 7.60 and 7.78 with $J_{\text{ab}}$ 15.45 Hz. The attachment of two chalcone units onto the benzene ring was supported by the appearance of a resonance as a triplet and a singlet at $\delta$ 7.37 and 8.85 respectively.

4. CONCLUSION

We have synthesised new homologues series of banana-shaped compounds $7a$-$c$ and $8a$-$c$ comprising bifunctional chalcone units in the presence of NaH (95%). The low yield of $7a$-$c$ and $8a$-$c$ might due to the steric effect of hydroxylated chalcone $4a$-$c$ bearing long alkyl chains. Compounds $7a$-$c$ and $8a$-$c$ could be useful in the study of banana shaped liquid crystals properties.

ACKNOWLEDGEMENTS

The authors wish to thank Universiti Malaysia Sarawak and Ministry of Science, Technology, and Innovation (MOSTI) for the financial support through FRGS/01(14)/743/2010 (29).
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