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Synthesis and mesomorphic properties of 7-acyloxy-3-(4-acyloxyphenyl)-4H-1-benzopyran-4-one

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A new homologous series of 7-acyloxy-3-(4-acyloxyphenyl)-4H-1-benzopyran-4-ones was synthesized and characterized by elemental analysis and spectroscopic techniques along with thermal behaviour study using differential scanning calorimetry. Texture observation was performed under the polarizing optical microscope from which the derivatives were found to exhibit different molecular organizations as exemplified by various mesophases. Whilst the compounds containing butanoyloxy and hexanoyloxy groups behave as nematogens, the other compounds with heptanoyloxy and longer side chains show a SmC phase. The octadecanoyloxy derivative was the only member showing a monotropic SmC phase. The difference in phase behaviour is discussed based on the molecular structure and the presence of a lateral dipole which can be associated with the intermolecular interaction within the mesophase.

1. Introduction

It has been well documented that the study of liquid crystalline compounds is very important for the continual development and understanding of the field of molecular engineering. Research focused on modifying existing molecules, particularly natural products, has shown to be a viable approach leading to new compounds showing liquid crystalline properties [1, 2]. Part of our present interest in developing new mesomorphic compounds has been focused on isoflavone derivatives [3–5]. Isoflavone derivatives constitute the largest number of compounds among the natural isoflavonoids [6]. Like many natural products containing heterocycles in their structures, such as flavone and coumarin derivatives, isoflavone compounds in biological systems can show liquid crystalline behaviour [1]. To date, the liquid crystalline behaviour of isoflavone derivatives containing one or two terminal chains has been studied and reported [2, 3, 5]. In our present work, we describe the synthesis and characterization of liquid crystalline properties of a homologous series of isoflavone compounds with the classical calamitic structure: two flexible terminal alkyl chains attached to a rigid central core via ester linkages. The phase transition behaviour as well as the associated mesomorphic textures have been investigated along with the structural elucidation. In addition, the results from an investigation of the relationship between chemical structure and polarizability are also reported.

2. Experimental

Resorcinol was obtained from Aldrich, USA. Methanesulphonyl chloride and boron trifluoride were purchased from Merck, Germany. 4-Hydroxyphenylacetic acid and acid chlorides (butanoyl, hexanoyl, octanoyl, decanoyl, dodecanoyl, tetradecanoyl, hexadecanoyl and octadecanoyl chlorides) were obtained from Acros Organics, Belgium.

Thin layer chromatography analyses were performed using aluminium-backed silica gel plates (Merck 60

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F254), with examination under UV light. Column chromatography was performed under gravity using Merck 60 mesh silica gel.

The molecular formulae for the target compounds were determined by elemental analysis. Molecular structures in the solid state were characterized by FTIR. ^{1}H and ^{13}C NMR techniques were employed in elucidating structures in solution. Reported chemicals shifts for isoflavone, including the ^{1}H–^{13}C correlation spectra, were used as reference [5, 7–9] when making assignment related to the chemical shifts of the synthesized compounds.

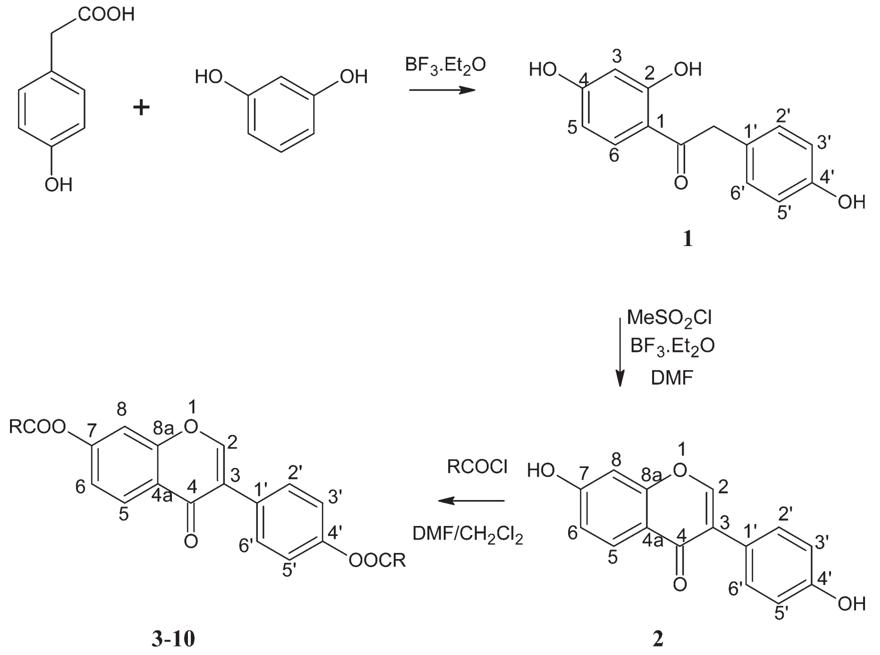
The mesomorphic textures were studied using a polarizing optical microscope (POM) fitted with a Linkam LST350 hot stage in the Liquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia. The heating and cooling temperatures were monitored by a Linkam TMS94 temperature controller. Phase transition temperatures and enthalpies were determined with a Shimadzu DSC-50 differential scanning calorimeter with heating and cooling rates of 5°C min^{-1}.

Molecular modelling was carried out using ACD/ Chemsketch Version 4.5. Geometrical optimization or energy minimization of the molecules was performed in order to study the molecular shape and geometry. The final conformation was then used in calculating the polarizabilities for all the title compounds.

2.1. *Synthesis*

The syntheses of the intermediate **2** and the target compounds **3**–**10** were carried out using the experimental procedure illustrated in scheme 1. Representative syntheses are described below.

2.1.1. Synthesis of 1-(2,4-Dihydroxyphenyl)-2-(4-hydroxyphenyl)ethanone, 1. A mixture containing 10.0 g of 4-hydroxyphenylacetic acid and 7.3 g of resorcinol in 82.0 ml $BF_3.Et_2O$ was heated for 4 h at



Compound	R
3	C_3H_7
4	C_5H_{11}
5	C_7H_{15}
6	C_9H_{19}
7	$C_{11}H_{23}$
8	$C_{13}H_{27}$
9	$C_{15}H_{31}$
10	$C_{17}H_{35}$

Scheme 1. Synthetic routes for the intermediates **1**, **2** and target compounds **3**–**10**.

70–75°C under nitrogen [8]. The mixture was then poured into a bath containing ice-water. The yellow solid was filtered and purified using chloroform; yield 64%. Anal: calcd for $C_{14}H_{12}O_4$, C 68.85, H 4.95; found, C 68.87, H 4.92%. IR (KBr) ν_{max} 3221 (OH), 2914 (CH_2 aliphatic), 1635 cm^{-1} (C=O). ^1H NMR (DMSO-d_6) δ 7.93 (1H,d, J=8.9, H-6), 7.08 (2H, d, J=8.5, H-2’,6’), 6.7 (2H,d, J=8.5 H-3’,5’), 6.38 (1H, dd, J_{56}=8.8, J_{58}=2.3, H-5), 6.25 (1H, d, J=2.3, H-3) ppm. ^{13}C NMR (DMSO-d_6) δ 203.34 (CO), 166.24 (C-4), 165.08 (C-2), 156.08 (C-4’), 133.82 (C-6), 130.75 (C-2’,6’), 126.24 (C-1’), 115.68 (C-3’,5’), 112.96 (C-1), 108.29 (C-5), 103.13 (C-3), 43.79 (CH_2) ppm.

2.1.2. Synthesis of 7-Hydroxy-3-(4-hydroxyphenyl)-4H-1-benzopyran-4-one, 2. 5.0 g of compound **1** in dry DMF was treated cautiously with 4 equiv. $BF_3.Et_2O$. To this mixture, 3 equiv. $MeSO_2Cl$ was added at 50°C. The mixture was heated under nitrogen for 1.5 h at 75–80°C [10, 11]. This mixture was poured with rapid stirring into an ice-water bath. The product was recrystallized from methanol; yield 35%. Anal: calcd for $C_{15}H_{10}O_4$, C 70.87, H 3.96; found, C 70.75, H 3.94%. IR (KBr) ν_{max} 3229 (OH), 1633 (C=O), 1606 (C=C aromatic) cm^{-1}. ^1H NMR (DMSO-d_6) δ 12.79 (1H, s, OH-7), 10.91 (1H, s, OH-4’), 8.27 (1H, s, H-2), 7.96 (1H, d, J_{56}=8.8, H-5), 7.37 (2H, d, J=8.6, H-2’,6’), 6.93 (1H, dd, J_{65}=8.7, J_{68}=2.2, H-6), 6.81 (2H, d, J=8.7, H-3’,5’), 6.72 (1H, d, J=2.2, H-8) ppm. ^{13}C NMR (DMSO-d_6) δ 153.71 (C-2), 124.33 (C-3), 175.70 (CO), 128.15 (C-5), 116.03 (C-6), 163.34 (C-7), 102.94 (C-8), 123.38 (C-1’), 130.96 (C-2’,6’), 115.83 (C-3’,5’), 117.42 (C-4a), 157.95 (C-8a), 158.29 (C-4’) ppm.

2.1.3. 7-Butanoyloxy-3-(4-butanoyloxyphenyl)-4H-1-benzopyran-4-one, 3. 3.4 mmol of butanoyl chloride was added to a mixture of 0.3 g of compound **2** in DMF/CH_2Cl_2 and 0.2 ml of triethylamine, the mixture was stirred at room temperature for 6 h. The solvent was removed and diethyl ether was added to the residue. Triethylammonium chloride was filtered off and the product was purified using column chromatography with chloroform/ethyl acetate (9/1) as eluant. The subsequent members of the homologous series were prepared and purified using the same method; yield 36%. Anal: calcd for $C_{21}H_{22}O_6$, C 70.04, H 5.62; found, C 70.00, H 5.57%. IR (KBr) ν_{max} 2959, 2929, 2878 (CH_2 aliphatic), 1757 (CO ester), 1638 (C=O), 1618 (C=C aromatic) cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.36 (1H, d, J_{56}=8.8, H-5), 8.04 (1H, s, H-2), 7.62 (2H,d, J=8.5, H-2’,6’), 7.35 (1H, d, J=1.9, H-8), 7.15-7.19 (3H, overlapped peaks of H-3’,5’ and H-6), 2.58–2.66 (4H, CH_2COO), 1.83–1.87 (4H, m, CH_2), 1.13 (6H, t, CH_3) ppm. ^{13}C NMR ($CDCl_3$) δ 175.88 (C-4), 157.06 (C-4’), 155.06 (C-7), 153.58 (C-8a), 151.19 (C-2), 130.41 (C-2’,6’), 129.47 (C-5), 128.20 (C-1’), 125.17 (C-3), 122.59 (C-4a), 122.15 (C-3’,5’), 120.06 (C-6), 111.35 (C-8), 171.68, 172.52 (COO), 36.60, 36.65 (CH_2CO), 18.79 (CH_2), 14.14 (CH_3) ppm.

2.1.4. 7-Dodecanoyloxy-3-(4-dodecanoyloxyphenyl)-4H-1-benzopyran-4-one, 7. Yield 41%. Anal: calcd for $C_{37}H_{54}O_6$, C 75.69, H 8.80; found, C 75.60, H 8.80%. IR (KBr) ν_{max} 2922, 2848 (CH_2 aliphatic) 1752 (CO ester), 1645 (C=O), 1623 (C=C aromatic) cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.34 (1H, d, J_{56}=8.7, H-5), 8.02 (1H, s, H-2), 7.60 (2H,d, J=8.6, H-2’,6’), 7.32 (1H, d, J=2.1, H-8), 7.17–7.19 (3H, overlapped peaks of H-3’,5’ and H-6), 2.57–2.65 (4H, CH_2COO), 1.77–1.80 (4H, m, CH_2), 1.30–1.45 [36H, m, $(–CH_2)_{18}$], 0.91 (6H, t, CH_3) ppm. ^{13}C NMR ($CDCl_3$) δ 175.88 (C-4), 157.06 (C-4’), 155.08 (C-7), 153.56 (C-8a), 151.22 (C-2), 130.42 (C-2’,6’), 129.47 (C-5), 128.22 (C-1’), 125.19 (C-3), 122.60 (C-4a), 122.15 (C-3’,5’), 120.06 (C-6), 111.35 (C-8), 171.88, 172.72 (COO), 34.80, 34.84 (CH_2CO), 23.11–32.30 (CH_2), 14.55 (CH_3) ppm.

3. Results and discussion

3.1. *Thermal behaviour and texture observation*

The phase transition temperatures for the title compounds **3**–**10** are shown in table 1. It can be seen from the data listed in table 1 that there is a drop in the clearing temperatures of compounds when ascending from compound **3** to **4**. However, isotropization occurred at a higher temperature on moving from **4** to **5** for which the chains are moderately long. There is a gradual decrease in clearing points for the molecules with much longer carbon chains (compounds **6**–**10**). This observation agrees with the previously reported homologous series of *N*,*N′*-bis(3-methoxy-4-alkoxybenzylidene)-1,4-phenylenediamine in which the longest chain homologue possessed the lowest thermal stability [12]. This suggests that as the terminal chain length increases, the long molecular axis no longer remains fully stretched and the molecular shape is not linear. This may also be explained in terms of the flexibility of the long terminal chains which tend to coil with increasing length [13].

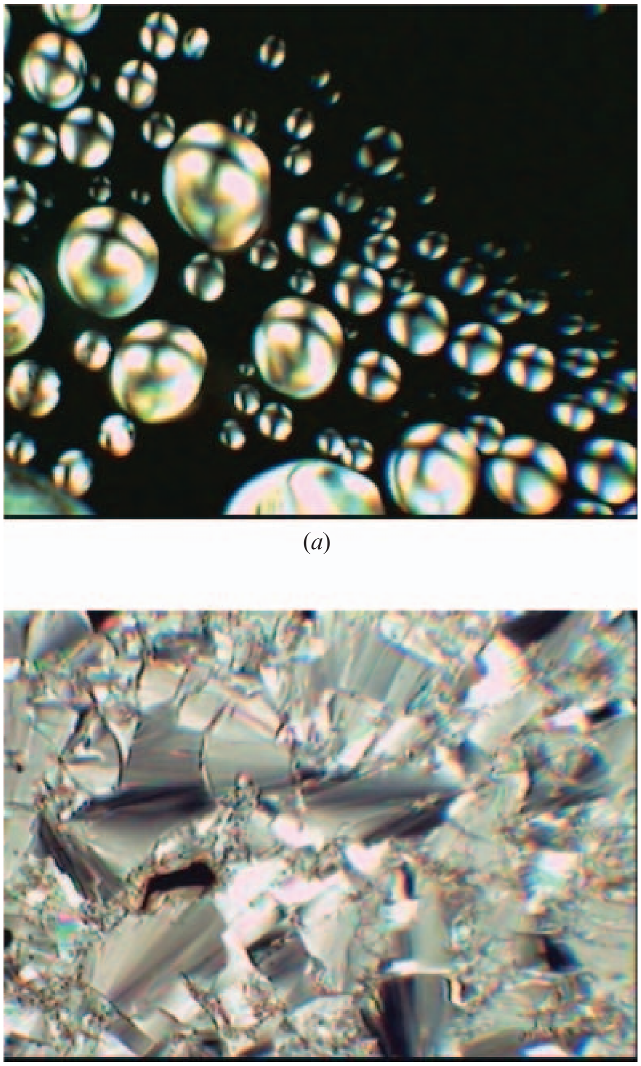
Types of mesophases are assigned according to the textures observed under POM and compared with those reported in the literature [14]. For the title compounds containing two carbonyl groups, nematic and SmC phases are seen. Nematic droplets and schlieren texture are observed for compounds **3** and **4**, resembling the texture observed for molecular orientation under

Table 1. Phase transition temperature (°C) and enthalpies (kJ mol^{-1}) in parentheses for compounds **3**–**10**.

Compound	Heating Cooling
3	Cr 115.2 (22.4) N 166.4(0.6) I I 165.1(0.8) N 85.0(21.5) Cr
4	Cr 108.6(19.7) N 154.6(1.0) I I 153.8(1.2) N 77.0(17.4) Cr
5	Cr 100.5(21.4) SmC 155.7(7.4) I I 154.1(6.6) SmC 77.0(19.2) Cr
6	Cr 89.9(24.8) SmC 155.5(9.5) I I 158.0(8.8) SmC 70.5(20.5) Cr
7	Cr_1 63.4(20.5) Cr_2 93.2(24.3) SmC 152.4(9.1) I I 149.1(10.1) SmC 59.0(21.3) Cr
8	Cr_1 70.4(27.1) Cr_2 99.0(35.7) SmC 147.6(10.4) I I 147.6(11.0) SmC 67.7(45.7) Cr
9	Cr_1 72.5(23.9) Cr_2 102.6(46.5) SmC 145.9(15.4) I I 148.9(12.3) SmC 91.4(15.8) Cr_2 77.4(18.5) Cr_1
10	Cr_1 95.4(31.0) Cr_2 106.1(46.8) SmC 142.3(13.5) I I 140.2(14.0) SmC 95.7(22.8) Cr_1

homogeneous alignment. Figure 1 (*a*) shows an optical photomicrograph of compound **4**, which exhibits nematic droplets when it approaches the clearing point. In compounds **3** and **4**, the central cores are longer relative to the overall molecular length; therefore, this facilitates the formation of the nematic phase [15]. The nematic phases for compounds **3** and **4** are thermally stable with high N–I transition temperatures. However, the nematic phase is not seen in compounds **5**–**10**.

In general, compounds **5**–**10**, with long terminal alkyl chains, exhibit a smectic phase which can be characterized by the formation of bâtonnets that coalesce to form a SmC schlieren texture. A typical morphology of these compounds can be seen for compound **10**, in which the molecular orientation is inclined to a texture with some fan-shaped domains. However, the seemingly fan-shaped texture becomes less crisp in appearance on cooling, figure 1 (*b*). This observation may be attributed to the presence of longer terminal alkyl chains which become interwined, leading to tilted and disordered lamellar packing as commonly found in the SmC phase [13, 16]. Furthermore, the flexibility of the long terminal chains tends to disrupt molecular packing, which promotes the formation of a nematic phase. These conditions, when coupled with enhanced intermolecular lateral forces of attraction associated with both the ester linkages of the terminal alkyl chains as well as the heterocyclic cores, facilitates molecular tilting and stabilizes the SmC phase formation [16]. The molecules are thus assumed to be able to pack effectively in a lamellar manner and in space leading to higher sustainability of the SmC phase. This is indicated by a rather large thermal mesomorphic range, with an average of about 50°C. High clearing points (>100°C) are also seen for all derivatives of the title compounds. This may be due to the planarity and enhanced polarity of the heterocyclic oxygen atoms within their central cores.



(*a*)

(*b*)

Figure 1. (*a*) Optical photomicrograph for compound **4** which exhibits nematic droplets; (*b*) optical photomicrograph of compound **10** displaying less crisp fan-shaped texture upon cooling directly from isotropic liquid.

3.2. *Influence of structural changes on thermal stability*

It has been shown that the temperature associated with the crystal–mesophase (Cr–M) transition within a homologous series varies depending on the molar mass, and the molecule with a lower mass possesses a lower

Table 2. Polarizability (calculated values) for compounds **3**–**10**.

Compound	Polarizability ($\alpha \pm 0.5 \times 10^{-24}$)cm^{-3}
3	41.79
4	49.13
5	56.48
6	63.83
7	71.17
8	78.52
9	85.87
10	93.21

Cr–M transition temperature in comparison with a member of higher mass. In general, the Cr–M transition temperature will increase when the polarizability of the compounds within the same series increases. However, the trend exhibited by the title compounds deviates from this common rule. The Cr–M transition temperatures initially show a decrease on passing from compound **3** to **4**, **5** and then **6**. However, this temperature increases on going from compound **7** to **8**, **9** and finally **10**. The unusual feature shown by compounds **3**–**6** may be rationalized in terms of the rigidity of the molecular long axis which will often be reduced owing to the increase of flexibility of the terminal alkyl chains, which suppress the anisotropic shape of the molecules [13]. As for compounds **7**–**10** in which the chains are much longer, the temperature associated with the Cr–M transition seemed to be increased. This may be explained in terms of the change in the molecular length (L) with little or no change at all in the width (W). One of the probable reasons contributing to the increase of the L/W ratio is that the molecules are closely packed with each other via the van der Waals intermolecular forces of attraction. Thus, the polarizability values for compounds **7**–**10** are expected to increase. This has been confirmed by the polarizability values which follows the order of compound **7** [$(71.17 \pm 0.5) \times 10^{-24}$ cm^{-3}]<compound **8** [$(78.52 \pm 0.5) \times 10^{-24}$ cm^{-3}]<compound **9** [$(85.87 \pm 0.5) \times 10^{-24}$ cm^{-3}]<compound **10** [$(93.21 \pm 0.5) \times 10^{-24}$ cm^{-3}] (table 2). Therefore, a compromise in chain length is required for a low Cr–M transition temperature, which is in accordance with those reported in alkylcyanobiphenyl homologues [15].

3.3. *Physical characterization*

Spectroscopic methods such as FTIR and NMR (^{1}H and ^{13}C) were employed to elucidate the structures of compounds **3**–**10**. The FTIR spectra of compounds **3**–**10** exhibit absorption bands that can be assigned to the stretching of aliphatic C–H within the frequency range 2959–2878 cm^{-1}. The band which appears at the frequency 1618–1623 cm^{-1} can be attributed to the stretching of C=C of benzene ring. The appearance of two C=O bands at 1747–1757 and 1638–1647 cm^{-1} can be ascribed to the stretching of C=O of both the ester linking groups and the carbonyl group of pyranone, respectively.

High resolution ^{1}H and ^{13}C NMR spectroscopic techniques were used further to substantiate the molecular structure of compounds **3**–**10**. The NMR spectra obtained indicate that all members of the homologous series exhibit similar trend in ^{1}H–^{1}H splitting and chemical shifts. The NMR resonances with respect to the diagnostic peaks are discussed based on the representative compound **4**.

A complete ^{1}H NMR assignment of compound **4** has been carried out with the aid of a two-dimensional ^{1}H–^{1}H COSY experiment. The presence of a singlet at δ=8.03 ppm is attributable to the vinyllic proton of the hetero oxygen atom within the central core. The five different types of aromatic protons are observed as doublets or double doublet within the range δ=7.17–8.34 ppm. A triplet at δ=0.96 ppm can be assigned to the methyl protons of both terminal alkyl chains. The two subsequent sets of methylene protons at each terminal alkyl chain give rise to two separate sets of multiplets within the range δ=1.40–1.82 ppm. Two peaks attributable to the presence of methylene protons attached to the ester linking groups (CH_2–COO) are observed within the range δ=2.58–2.65 ppm.

The ^{13}C NMR spectrum of compound **4** indicates that the aromatic carbons give rise to different peaks in the rang δ=111.32–175.88 ppm. The observation of peaks at δ=171.84–172.68 ppm can be assigned to carbons of both ester linking groups (COO). A peak due to the methyl carbons of both terminal alkyl chains is observed at δ=14.30 ppm. The methylene carbons of terminal alkyl chains are observed at δ=22.70–31.64 ppm. The peaks assignable to the two methylene carbons attached to the ester linkages are observed at 34.79 and 34.75 ppm.

The molecular structures and formulations of the compounds are supported by elemental analysis data in which the found percentages of C and H are in good agreement with theoretical values.

4. Conclusion

A series of new mesogenic compounds comprising a main core isoflavone system linked with dual flexible terminal aliphatic chains via ester linkages have been synthesized and well characterized in which the results showed that they are mesomorphic in nature. Whilst compounds possessing shorter terminal carbon chains were found to be nematogens, the others with longer alkanoyloxy side chains showed the SmC phase. Through this study the effect of elongation of the molecule by increasing the terminal chain carbon number upon a high clearing temperature is also revealed. The anisotropic properties of the molecules have also been correlated with their polarizability values, which the corresponded with the occurrence of intermolecular interaction within the mesophase.

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