Accepted Manuscript

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PII: S1658-3655(15)00187-9
DOI: http://dx.doi.org/doi:10.1016/j.jtusci.2015.12.004
Reference: JTUSCI 267

To appear in:

Received date: 19-11-2015
Revised date: 14-12-2015
Accepted date: 15-12-2015


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Synthesis and Mesomorphic Properties of New Heterocyclic Liquid Crystals with Ester-Chalcone Central Linkages

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Abstract

A series of new calamitic liquid crystals, 4-[3-(pyridin-4-yl)prop-2-enoyl]phenyl 4-alkyloxybenzoates comprising a pyridyl core, ester-chalcone central linkage and terminal alkyloxy chain were synthesized and characterized. This series consists of four members wherein the members differ by the length of alkyloxy chain (C\textsubscript{n}H\textsubscript{2n+1}O-, where n = 10, 12, 14, 16). The structures of the title compounds were elucidated using spectroscopic techniques, such as FT-IR, NMR (\textsuperscript{1}H & \textsuperscript{13}C) and EI-MS. Their mesomorphic properties were studied by using differential scanning calorimetry and optical polarizing microscopy. Decyloxy member was found non-mesogenic, whilst n-dodecyloxy to n-hexadecyloxy exhibited enantiotropic smectic A phase with fan-shaped texture. From the structure-property relationship study, it was proposed that the number of carbons in the alkyloxy chain must be at least 12 (n \geq 12) in order to generate the smectic phase in the analogous substituted ArCOOArCOCH=CHC\textsubscript{5}H\textsubscript{4}N compounds.

Keywords: pyridyl; chalcone; smectic A; mesomorphic
1. Introduction

Study of electronic conducting behaviours of liquid crystals (LCs) have received overwhelming attention ever since the discovery of high hole mobility in the hexagonal columnar phase of hexapenthyloxy-triphenylene [1-5]. Lately, calamitic LCs turn out to be another potential material for applications in electronic devices due to the presence of some ordered mesophases such as SmA, SmC, SmB, SmE, etc. The two-dimensional arrangement (layers) in smectics is more tolerant with regard to defects than the one-dimensional ordered discotic columns resulting in an enhanced performance [6]. The electronic conducting behaviours of calamitic liquid crystals were first investigated in the SmA phase of a 2-phenylbenzothiazole derivatives. The presence of layer structure in all smectic liquid crystalline materials induces a π-π stacking interactions which can facilitate the hopping of charge carrier mobility [7-9].

Our previous works focus on the synthesis of a few homologues series of smectic LCs containing benzothiazole moiety [10-13]. Incorporation of benzothiazole ring into calamitic liquid crystals as mesogenic core enabled them to exhibit mesophase easily due to the more polarizable nature of those heteroatoms, sulfur and nitrogen [14]. In this paper, we report another new homologues series of heterocyclic liquid crystals comprising pyridyl unit (Scheme 1). Introduction of a nitrogen atom into the aromatic core results in a more complex mesomorphic behavior. In a few cases, the higher ordered smectic phases (e.g. G, H) are observed at or near room temperature which would be of interest should such materials possess useful charge mobilities and can be applied in real devices.
Liquid crystals with a chalcone central linkage are relatively rare. In the literature there are several reports of mesogenic compounds having chalcone linkage. However, many years ago Chudgar and Shah [15] and Yeap et al. [16] have reported homologous series of containing ester-chalcone linkages. Recently, Thaker et al. [17] have also synthesized mesomorphic compounds containing Schiff base-chalcone linkage. The emergent scientific interest in the synthesis of heterocyclic-based liquid crystals and outstanding behavior of chalcone has prompted us to synthesize a series of mixed pyridyl-chalcone liquid crystals. The present molecules consist of three core units (one pyridyl and two phenyl rings) connected via enone and ester linkers which can increase the molecular broadness and anisotropy.

2. Experimental

2.1 Characterization

Infrared spectroscopy was performed on a Perkin-Elmer System 2000 FT-IR Spectrometer. All compounds were analyzed using KBr discs with a measurement range of 4000-400 cm⁻¹. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in CDCl₃ using a JEOL LA-400 MHz NMR spectrometer with tetramethyl as the internal standard. EI-MS (70 eV) were measured with a Mass Spectrometer Finnigan MAT95XL-T at a source temperature of 200 °C.

Phase-transition temperatures and associated enthalpy changes were measured using a Differential Scanning Calorimeter Mettler Toledo DSC823 at heating and cooling rates of 10 °C/min and -10 °C/min, respectively. A polarizing optical microscope (Carl Zeiss) equipped with a Linkam hotstage was used for temperature dependent studies of the liquid crystal textures. A video camera
(Video Master coomo20P) installed on the microscope was attached to a video capture card (Video Master coomo600), allowing real-time video capture and image saving. Textures exhibited by the compounds were observed using polarized light with crossed polarizers. Samples were prepared as thin films sandwiched between a glass slide and a cover slip. Phase identification was made by comparing the observed textures with those reported in the literature [18,19].

2.2 Synthesis

All solvents and reagents were purchased commercially and used without any further purification. 4-Dimethylaminopyridine (DMAP), 4-hydroxyacetophenone, pyridine-4-carbaldehyde, 1-bromoalkane (C_nH_{2n+1}Br where n = 10, 12, 14, 16), potassium hydroxide and potassium carbonate were obtained from Merck (Germany). Ethyl 4-hydroxybenzoate and N,N'-dicyclohexylcarbodiimide (DCC) were purchased from Acros Organics (USA).

The synthetic route towards formation of the title compounds, 4-[3-(pyridin-4-yl)prop-2-enoyl]phenyl 4-alkyloxybenzoates (PPPABCn, where n = 10, 12, 14, 16) is illustrated in Scheme 1. Intermediate compounds, 1-(4-hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one and 4-alkyloxybenzoic acid were prepared according to method described by Ha and Low [20] and Kadkin et al. [21], respectively.

2.2.1 Synthesis of mixed pyridyl-chalcone liquid crystals
1-(4-Hydroxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one (2 mmol, 0.45 g), appropriate 4-alkyloxybenzoic acid (2 mmol) and DMAP (1 mmol, 0.12 g) were dissolved in 10 mL mixture of DCM and DMF, and the solution was stirred at 0 °C. DCC (2 mmol, 0.41 g) dissolved in 10 mL of DCM was added into the mixture dropwise and the solution was continuously stirred for an hour at 0 °C. The mixture was then stirred at room temperature for forty eight hours. Finally, the mixture was filtered and the solvent was removed by evaporation. All the crude products were purified upon repeated recrystallization using 2:1 ratio of methanol and chloroform until constant melting points were obtained. The purity of all compounds was checked by thin layer chromatography (Merck 60 F254) and visualized under short-wave UV light.

The IR, NMR (1H and 13C) and mass spectral data for the representative compound, PPPABC12, are summarized as follows.

4-[3-(pyridin-4-yl)prop-2-enoyl]phenyl 4-dodecyloxybenzoates (PPPABC12): IR νmax (KBr, cm⁻¹): 2922, 2852 (C-H aliphatic); 1728 (C=O ester); 1662 (C=O keto), 1273 (C-O, aromatic ether). 1H NMR (400 MHz, CDCl₃, δppm): 0.9 (t, 3H, CH₃-), 1.3-1.5 (m, 18H, CH₃-(CH₂)₀-(CH₂)₂-O-), 1.8 (p, 2H, -CH₂-CH₂-O-), 4.0 (t, 2H, -CH₂-O-), 7.0 (d, 1H, olefinic-H), 7.4 (d, 2H, Ar-H), 7.5 (d, 1H, olefinic), 7.6-7.7 (m, 4H, Ar-H), 8.1-8.2 (m, 4H, Ar-H), 8.7 (d, 2H, Ar-H). 13C NMR (100 MHz, CDCl₃, δppm): 14.23 (CH₃-), 22.79, 26.06, 29.44, 29.68, 32.01 for methylene carbons (CH₃-(CH₂)₁₀-), 64.49 (-CH₂O-), 122.38, 141.77 for olefinic carbons, 114.52, 120.94, 122.13, 125.94, 130.37, 132.52, 134.96, 142.11, 150.75, 155.21, 163.95 for aromatic carbons, 164.45 (-COO-), 188.71 (C=O keto). EI-MS m/z (rel. int. %): 513 (<1) [M⁺], 289 (100).
3. Results and discussion

3.1 Synthesis and Spectroscopic Studies

The synthetic route used for the preparation of PPPABCn is shown in Scheme 1. Claisen-Schmidt condensation method was used in the reaction of 4-hydroxyacetophene and pyridine 4-carbaldehyde to yield intermediate A. Etherification of ethyl-4-hydroxybenzoate in acetone with appropriate 1-bromoalkane and acidification using concentrated hydrochloric acid produce intermediate B. Intermediates A and B were then subjected to Steglich esterification in the presence of DCC and DMAP to yield title compounds PPPABCn.

The structure of the title compound was elucidated using EI-MS, IR and NMR spectroscopic techniques. Figure 1 show EI-MS spectrum of representative compound PPPABC12. The prominent molecular ion peak at 513 m/z in the mass spectrum established its molecular formula as \( C_{33}H_{39}NO_4 \), supporting the proposed structure.

Infrared data of PPPABC12 show the absorption bands assignable to the stretching of aliphatic C-H at the frequency range of 2852-2946 cm\(^{-1}\). The band appears at the 1728 cm\(^{-1}\) can be ascribed to the stretching of C=O bond belonged to the ester group. Another C=O bond can be observed at lower frequency, 1662 cm\(^{-1}\); it is attributed to the keto group. Aromatic ether bond (C-O-Ar) was confirmed based on the absorption band at 1273 cm\(^{-1}\).

Figures 2 and 3 show the \(^1\)H and \(^13\)C NMR spectra for the representative compound PPPABC12. \(^1\)H NMR data of PPPABC12 shows two triplets assignable to the methyl (CH\(_3\)) group of ether linkage and methylene protons which attached to the ether oxygen (–
CH₂-O-) at δ 0.9 and δ 4.0, respectively. The triplet splitting was observed due to the presence of two neighbor protons in both cases. The other methylene protons of CH₃(CH₂)₉(CH₂)₂-O- group in the alkyl chain were confirmed by the presence of multiplet signal at δ = 1.3-1.5. A pentet signal assignable to the methylene protons of CH₂CH₃CH₂O- group is resonated at δ 1.8. The presence of two olefinic protons is confirmed with the presence doublet signal at the respective chemical shift of δ 7.0 and δ 7.4. The resonance owing to the eight aromatic and four pyridyl protons were observed with the range of δ 7.4 and 8.7.

The molecular structure of PPPABC12 was further substantiated by ¹³C NMR spectroscopy. The presence of the C=O ester group can be substantiated by the ¹³C signal observed at δ 164.45. The most downfield signal at δ 188.71 is assigned to the C=O keto of the enone group. Signals belonged to the olefinic carbons can be found δ 122.38 and 141.77. The peaks belonged to the aromatic and pyridyl carbons showed ¹³C signals between δ 114.52 and δ 163.95. Methylene carbon which attached to the ether oxygen (-CH₂O-) possessed the highest chemical shift (δ 64.49) among the methylene carbons. The remaining carbons due to the alkyl chain exhibited signals between δ 14.23 and δ 32.01.

3.2 Mesomorphic Behaviour

The mesophases of all the compounds were observed under an optical polarizing microscope during heating and cooling cycles. The optical photomicrographs of PPPABC12 and PPPABC14 are depicted in Figure 4 as a representative illustration. Upon cooling from isotropic liquid, the co-existence of fan-shaped and homeotropic (dark area) textures of smectic A (SmA) phase was observed for PPPABC12 (Fig. 4a) and PPPABC14 (Fig. 4b). All observed liquid crystalline textures are typical according to literature [18,19].
The phase transition temperatures and corresponding enthalpy changes of compounds PPPAB\(\text{Cn}\) were determined using a differential scanning calorimeter. The data obtained from the DSC analysis are summarized in Table 1. DSC thermogram (Fig. 5) of PPPAB\(\text{C14}\) shows two endotherms upon heating which can be attributed to the isotropic-mesophase and mesophase-crystal transitions. Such transitions were also supported by the enthalpy values of the respective compounds. From Table 1, it is clearly noticed that the PPPAB\(\text{C14}\) and PPPAB\(\text{C16}\) showing enantiotropic properties as the mesophase were observed during heating and cooling cycles. All the compounds exhibited smectic A (SmA) phase except \(n\)-decyloxy derivative.

Linking group is one of the factors influencing the target compounds in exhibiting the smectic phase instead of a nematic phase. The ester linking group favour the lamellar packing due to the dipole-dipole interaction which ultimately generated the smectic phase [22]. Then, a conjugative interaction over the entire molecule is better achieved between the enone linking group and pyridyl core system, and led to smectic property in PPPAB\(\text{Cn}\). This suggests that heteroatom of pyridyl group at the terminal position has substantial effect on influencing certain phase. It has been reported that inclusion of heteroatom can change significantly the polarity, polarisability and occasionally the geometric shape of the molecule, thus influencing the type of mesophase, the phase transition temperatures, dielectric and other properties of the mesogens [14]. Owing to the presence of nitrogen in the pyridyl ring at the terminal position, these compounds may also serve as new type of donor group for hydrogen bonding studies (-COOH–N-) with acceptor molecules (for example, 4-alkyloxybenzoic acids) to form new binary liquid crystals [23-26].

With the increasing length of terminal chain, the phase changed from non-mesogenic to enantiotropic smectic A phase. The smectic character was absent in lower member, PPPAB\(\text{C10}\) but present in higher member (PPPAB\(\text{C12, 14, 16}\)). The molecule of \(n\)-
decyloxy derivative is too rigid for it to be mesogenic. It can be understood that longer terminal alkyloxy chain may favour the lamellar arrangement in smectic layer structure due to higher Van der Waals interactions and possibilities of intertwining between alkoxy chains. It can therefore be proposed that in order to generate the smectic phase in the analogous substituted ArCOOArCOCH=CHC\textsubscript{5}H\textsubscript{4}N compounds, the number of carbons in the alkyloxy chain (C\textsubscript{n}H\textsubscript{2n+1}O-) must be at least 12 (n \geq 12). Lastly, the SmA phase range (\Delta\text{SmA}) was reduced as the chain length increasing from C12 to C16. It could be due to the dilution of mesogenic core [27,28].

4. Conclusion

In this paper, we described the synthesis and mesomorphic behavior of a new homologous series of 4-[3-(pyridin-4-yl)prop-2-enoyl]phenyl 4-alkyloxybenzoates comprising ester-chalcone central linkage and pyridyl core system. Higher members of the homologous series, C12, C14 and C16 members exhibited liquid crystal behaviour in which SmA phase was observed. Therefore, it can be concluded the current core system requires a specific alkyloxy chain length (n \geq 12) in order to produce smectic phase. The length of the terminal alkyloxy chain affects the melting, clearing temperatures and mesophase ranges. In our future work, molecular modifications will be carried out on this homologues series in order to yield liquid crystal compounds with high thermal stability and wider mesophase range.

Acknowledgements
The authors would like to thank Universiti Tunku Abdul Rahman for the research facilities and financial support through UTAR Research Fund (Project No. IPSR/RMC/UTARRF/2014-C1/H01 with the Vote No. 6200/H21).

References


<table>
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<tr>
<th>Compound</th>
<th>Phase transition, °C (corresponding enthalpy changes, kJ mol⁻¹)</th>
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<tbody>
<tr>
<td>PPPABC10</td>
<td>Heating: Cr 115.8 (49.9) I</td>
</tr>
<tr>
<td></td>
<td>Cooling: Cr 108.7 (49.6) I</td>
</tr>
<tr>
<td>PPPABC12</td>
<td>Heating: Cr₁ 110.9 (44.1) Cr₂ 118.8 (23.1) I</td>
</tr>
<tr>
<td></td>
<td>Cooling: Cr 94.6 (57.8) SmA 111.5 (3.5) I</td>
</tr>
<tr>
<td>PPPABC14</td>
<td>Heating: Cr 109.8 (64.4) SmA 117.1 (4.6) I</td>
</tr>
<tr>
<td></td>
<td>Cooling: Cr 98.2 (59.5) SmA 116.0 (2.5) I</td>
</tr>
<tr>
<td>PPPABC16</td>
<td>Heating: Cr 111.4 (41.8) SmA 118.1 (2.9) I</td>
</tr>
<tr>
<td></td>
<td>Cooling: Cr 89.7 (41.6) SmA 115.8 (2.7) I</td>
</tr>
</tbody>
</table>

Note: Cr = crystal; SmA = Smectic A; I = isotropic. Value in the bracket is enthalpy change.
Scheme 1. Synthetic route for the target compounds. (i) KOH dissolved in EtOH:H₂O (1:1), 2M HCl (ii) CₙH₂n₊₁Br, K₂CO₃, CH₃COCH₃ (iii) H₂O:EtOH (1:1), KOH, conc. HCl (iv) DCC, DMAP, DCM, DMF.
Fig. 1. EI-MS spectrum of PPPABC12
Fig. 2. $^1$H NMR spectrum of PPPABC12
Fig. 3. $^{13}$C NMR spectrum of PPPABC12
Fig. 4. Optical photomicrographs (100x) of (a) PPPABC12 and (b) PPPABC14 exhibiting smectic A phase with fan-shaped and homeotropic textures.
Fig. 5. DSC thermogram of PPPABC14 upon heating and cooling