C. R. Chimie xxx (2016) 1–10

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

# Benzoate liquid crystals with direct isotropic–smectic transition and antipathogenic activity

Daniela Ailincai [a], Luminita Marin [a, *], Sergiu Shova [a], Cristina Tuchilus [b]

[a] "Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy, Grigore Ghica Voda Alley, No. 41A, 700487, Iasi, Romania
[b] "Grigore T. Popa" University of Medicine & Pharmacy, Pharmacy Faculty, Universitatii Street, No. 16, 700115, Iasi, Romania

ARTICLE INFO

*Article history:*
Received 30 October 2015
Accepted 21 January 2016
Available online xxxx

*Keywords:*
Ester
Smectic liquid crystal
Wettability
Antipathogen

ABSTRACT

A smectogen liquid crystal based on benzoate units has been synthesized and structurally characterized by FTIR and $^{1}$H NMR spectroscopy. Besides, its structure and supramolecular arrangement in the crystalline state was demonstrated by single crystal X-ray diffraction measurements. The thermotropic behaviour, monitored by differential scanning calorimetry and polarized light microscopy, consists in the formation of an enantiotropic smectic mesophase with a direct first order transition from the isotropic to smectic mesophase, and with its thermal stability range superposed on human body temperature. The smectogen liquid crystal has moderate wettability – suitable for biocompatible materials and presents good antipathogenic activity against gram positive and gram negative bacteria and fungus.

All these properties recommend the understudied liquid crystal to be used in biochemical and biological applications.



## 1. Introduction

Liquid crystals (LC) based on ester units are an interesting class of compounds which combine the anisotropic properties of the liquid crystals with the biological characteristics of the esters, promising to be a new class of biological relevant materials for surface functionalization [1], drug delivery systems [2], protein sorption/desorption [3], biological sensors [4], wound healing [5] membranes [6], gene therapy [7] and so on. A significant number of ester based liquid crystals have been mainly synthesized with the aim of being applied in optoelectronics and photonics as LC displays [8], field effect transistors [9], organic light emitting diodes [10], optical data storage devices [11], or photovoltaic cells [12]. Their application field is further enlarged by incorporating them into a polymeric matrix when systems known as polymer dispersed liquid crystals (PDLCs) are obtained [13]. The PDLC systems combine valuable properties of the two components and are designed for a wide range of applications, those in high performance biomedical field being especially envisaged in the last years, as artificial iris [14], blood sensors or sperm testers [15], smart packaging, and so on [16]. To be applied in such biological applications, liquid crystals must have the mesophase stability range at low temperature, eventually superposed on human body temperature. Moreover, speaking about the particular case of smectic liquid crystals, a direct isotropic–smectic transition is required, in order to reach a monomorphic stable mesophase capable of bistability [17].

Having all these in mind, we designed an ester based liquid crystal with a benzoate core and two aliphatic end groups which bring the benefits of the low temperature mesophase stability and of the direct isotropic–smectic transition. Besides, the ester groups provide the advantage of a potential biologically friendly compound, with real possibilities to be used in biochemistry and biological applications.

* Corresponding author.
*E-mail address:* lmarin@icmpp.ro (L. Marin).

http://dx.doi.org/10.1016/j.crci.2016.01.008
1631-0748/

## 2. Experimental

### 2.1. Reagents

4-Hydroxybenzoic acid ≥99%, butyl 4-hydroxybenzoate ≥99%, 1-bromooctane 99%, thionyl chloride 99%, anhydrous pyridine 99.8%, potassium hydroxide >85% were purchased from Aldrich and used as received. All the solvents of high purity were purchased from Carl Roth and used without any other purification.

### 2.2. Synthesis

The smectic liquid crystal has been synthesized using an input from published procedures [18] and optimized to the best yield, as can be seen in Scheme 1.

#### 2.2.1. p-Octyloxy-benzoic acid (**2**)

In a round bottom flask, solutions of 4-hydroxybenzoic acid (1.1 g, 8 mmol) in 15 mL dry ethanol, and KOH (0.89 g, 16 mmol) in 5 mL dry ethanol were introduced, and over the resulted mixture *n*-bromooctyl (1 mL, 8 mmol) reagent was added drop wise, under vigorous stirring. The reaction mixture was refluxed for 14 h under nitrogen atmosphere, and then allowed to reach room temperature. The solid inorganic salts were removed by filtration and the pH of the resulted solution was adjusted to 2 by adding diluted HCl (0.1M). The crude product was filtered off, washed with water and recrystallized from acetic acid and then toluene, to give a white powder with a yield of 67%.

#### 2.2.2. p-n-Octyloxy benzoyl chloride (**3**)

Thionyl chloride (1.5 g, 25 mmol) was added dropwise, at room temperature, to a solution of *p*-octyloxybenzoic acid (2.2 g, 13 mmol) in dimethylchloride (25 mL) with few drops of dimethylformamide, and the resulted mixture was stirred for 2 h. After that, the solvent was removed by distillation to give an ochre powder which was further used without any purification.

#### 2.2.3. Butyl-p-[p′-n-octyloxy benzoyloxy]benzoate (***BBO***)

The final product butyl-*p*-[*p*′-*n*-octyloxy benzoyloxy] benzoate (**BBO**) was obtained by reaction of the *p*-*n*-octyloxy benzoyl chloride (**3**) with the commercial *p*-hydroxy butyl benzoate (**4**). The crude product has been recrystallized from ethyl acetate when fine white single crystals suitable for crystallographic measurements were obtained.

**$^1$H NMR** (400.13 MHz, DMSO-$d_6$, ppm) $\delta$ = 8.12, 8.10 (d, 2H, H3,H5); 8.09, 8.07 (d, 2H, H20,H22); 7.47, 7.45 (d, 2H, H19,H23); 7.16, 7.14 (d, 2H, H2,H6); 4.34, 4.32, 4.30 (t, 2H, H27); 4.13, 4.11, 4.10 (t, 2H, H8); 1.79, 1.77, 1.75, 1.74, 1.71 (m, 4H, H9,H28); 1.49, 1.47, 1.45, 1.44, 1.42 (m, 4H, H10,H29); 1.40–1.24 (overlapped peaks, 8H, H11,H12,H13,H14); 0.99, 0.97, 0.95 (t, 3H, H30); 0.91, 0.89, 0.87 (t, 3H, H15)

**FTIR** (KBr, cm$^{-1}$): 2954, 2921, 2855 ($\nu_{CH3}$, $\nu_{CH2}$), 1720 ($\nu_{C=O}$), 1602 ($\nu_{C=Caromatic}$), 1252 ($\nu_{C-O-C}$), 845, 760 ($\delta_{CHaromatic}$).

**Crystal data** $C_{52}H_{68}O_{10}$ ($M_r$ = 853.06 g mol$^{-1}$), triclinic, $a$ = 5.7447(6) Å, $b$ = 14.5648(14) Å, $c$ = 28.725(2) Å, $\alpha$ = 98.673(7)°, $\beta$ = 94.343(7)°, $\gamma$ = 91.478(8)°; $V$ = 2367.4(4) Å$^3$, $T$ = 160 K, space group $P-1$, $Z$ = 2, 1652 coll. refl., 8053 indep. ($R_{int}$ = 0.0779), $G_{of}$ = 1.000, $R_1$ = 0.0935, $wR(F^2)$ = 0.2132.

### 2.3. Equipment

*Infrared* (*IR*) spectrum of the solid **BBO** was recorded on a FTIR Bruker Vertex 70 Spectrophotometer in the transmission mode, by using KBr pellets.

*$^1$H-NMR spectrum* was recorded on a BRUKER Avance DRX 400 MHz spectrometer, equipped with a 5 mm direct detection QNP probe with *z*-gradients. The chemical shifts are reported as $\delta$ (ppm) relative to the residual peak of the DMSO solvent.

Crystallographic measurements on the **BBO** single crystal were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer using graphite-monochromatic MoK$\alpha$ radiation, under the conditions described in the literature [19]. Crystallographic data for BBO have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publications No. CCDC-1416309. Copies of the data can be obtained free of charge from CCDC (12 Union Road, Cambridge CB2 1EZ, UK; Tel.: +44 1223 336 408; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk; www:http://ccdc.cam.ac.uk).

The textures of the **BBO** liquid crystal were investigated by polarized light microscopy, with an Olympus BH-2 microscope equipped with a Linkam THMS 600/HSF9I heating stage and a TMS91 control unit. The samples were observed during a heating/cooling/heating scan, at a heating/cooling rate of 5 °C min$^{-1}$.

Differential scanning calorimetric (DSC) measurements were performed on a DSC 200 F3 Maia device (Netzsch, Germany), under nitrogen purge (nitrogen flow 50 mL/min). The device temperature and sensitivity was