



Study of phase transitions in a bent-core liquid crystal probed by infrared spectroscopy



Swapnil Singh^a, Harshita Singh^a, Anubha Srivastava^a, Poonam Tandon^{a,*}, Rahul Deb^b, Somen Debnath^b, N.V.S. Rao^b, A.P. Ayala^c

^a Department of Physics, University of Lucknow, Lucknow 226007, India

^b Chemistry Department, Assam University, Silchar 788011, Assam, India

^c Departamento de Física, Universidade Federal do Ceará, C.P. 6030, 60.455-900 Fortaleza, CE, Brazil

ARTICLE INFO

Article history:

Received 29 December 2015

Received in revised form 28 April 2016

Accepted 26 May 2016

Available online 27 May 2016

Keywords:

Bent-core liquid crystal

Smectic C and nematic phase

DSC

POM

TD-FTIR

Conformational analysis

ABSTRACT

A new four ring bent-core liquid crystal (4'-*n*-octylphenylazo)-phenyl-4-yl-3-[N-(4'-*n*-dodecyloxy-2-hydroxybenzylidene) amino]-2-methyl benzoate has been synthesized and investigated using differential scanning calorimetry (DSC), polarized optical microscopy (POM) and temperature-dependent Fourier transform infrared (TD-FTIR) spectroscopy. DSC and POM were used to detect transition temperatures and identify mesophases. TD-FTIR spectroscopic technique was utilized as a probe to analyze the dynamics of the liquid crystal molecules during the phase transition. The quantum chemical density functional theory (DFT) was used to predict the most stable conformation and the correct vibrational assignment of different modes. Combined theoretical and experimental techniques provided a clear picture of the structural modifications and dynamics of mesophases during the phase transitions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Temperature dependent Fourier transform infrared (TD-FTIR) spectroscopy is a precise and sensitive tool for monitoring the structural, rotational and conformational (torsional) changes in molecules during phase transitions [1,2]. The combination of vibrational spectroscopy and quantum chemical approach has been widely used to understand the mechanism of phase transitions in liquid crystals at molecular level [3–5]. The crystal → mesophase → isotropic transitions and vice-versa result in a change in molecular orientation (that causes a change in inter/intramolecular interactions) and thereby a change in dipole moment of the molecule. Therefore, infrared spectroscopy became a sensitive detection technique for the investigation of phase transitions. The fingerprint region is very informative regarding the structural changes and provides the specific information about the core (phenyl rings) and linking groups (azo, ester, imine) or functional groups (hydroxyl or H-bonding) of liquid crystals. The peak position, peak height and peak width are temperature

sensitive therefore, very useful (especially for the liquid crystals) to investigate the dynamics of the molecule during the phase transition. The bent-core liquid crystals (BCLC) exhibits smectic phase [6] as well as nematic phase [7,8].

In the present work, a four ring bent-core liquid crystal [(4'-*n*-octylphenylazo)-phenyl-4-yl-3-[N-(4'-*n*-dodecyloxy-2-hydroxybenzylidene) amino]-2-methyl benzoate] abbreviated as 12O(OH) 2MA8 possessing four phenyl rings linked through azo-ester-imine linkages was designed and synthesized. The central core of two phenyl rings are connected by an ester linkage followed by the extension with an azo linkage on one side and an imine linkage on the other side to connect the phenyl rings on either side of the central core. The imine linkage is stabilized by hydrogen bonding due to the presence of *o*-hydroxyl group. The presence of ortho hydroxyl group in benzylidene moiety enhances the stability of the imines through intramolecular hydrogen bonding to overcome the hydrolytic instability of the molecules towards moisture and also enhances the transverse dipole-moment. The resorcyldene core is more stable towards to atmospheric hydrolysis. The liquid crystalline phases (smectic to nematic or nematic to isotropic) exhibited by these materials possessing a photochromic azo group can be induced by the trans-to-cis isomerization under the influence of UV irradiation [9]. The azo group in the molecule also provides delocalization of π electrons between donor and

* Corresponding author

E-mail addresses: poonam_tandon@yahoo.co.uk, poonam_tandon@hotmail.com (P. Tandon).

acceptor groups. This delocalization enhances the nonlinear optical properties of the liquid crystals that results in a second-harmonic generation [10]. The Schiff base exhibits E/Z isomerization that results into the conformational change during the phase transitions. The ester group also plays an important role and is involved in the conformational changes during the phase transition. Therefore, all these linking groups provide flexibility to the molecule during the phase transition while phenyl rings provide rigidity to the molecule.

In the present communication, we focused on the design and synthesis of four-ring bent core compound exhibiting liquid crystalline phases followed by the identification of phases of 12O(OH)2MA8 by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The combination of both the techniques provides a clear picture about the mesophases of BCLC. TD-FTIR technique was used to analyze the mechanism of phase transitions and the associated changes at molecular level. Computational approaches following density functional theory (DFT) for conformational and vibrational analysis of the titled molecule. Herein, the focus is on the study of all the three phase transitions as they reflect clear and sharp signature in the TD-FTIR spectroscopy. This is the first time when both spectroscopy and DFT are coupled to study the dynamics of phase transitions in BCLC (such a huge system).

2. Experimental section

2.1. Synthesis

The schematic representation of the synthesis of the titled molecule is shown in Scheme 1. The present four ring system consists of three different types of linkage units (azo $-\text{N}=\text{N}-$, ester $-\text{COO}-$ and salicylidene $-\text{CH}(\text{C}(\text{OH})=\text{N}-)$) bridging the phenyl rings to each other. The compound exhibits broad mesomorphic range with clearing temperatures below 140°C .

(4'-n-octylphenylazo)-phenyl-4-yl-3-[N-(4'-n-dodecyloxy-2-hydroxybenzylidene) amino]-2-methyl benzoate, 12O(OH)2MA8:

Appropriate quantity of 3-(N-(4'-n-dodecyloxy-2-hydroxybenzylidene)-amino)-2-methylbenzoic acid (0.44 g; 10 mmol) was dissolved in dichloromethane stirred with a teflon coated magnetic stirrer and the catalytic amount of N,N'-dimethylaminopyridine (DMAP 2 mg, 0.01 mmol) was added to the solution. Further a solution of 4-(4'-n-octylphenyl-azo) phenol (0.31 ml, 10 mmol) dissolved in dichloromethane was slowly added to the reaction

mixture. To the resulting solution equimolar amount of N,N'-dicyclohexylcarbodiimide (DCC) (0.21 g, 10 mmol) was added and the mixture was stirred for 48 h under inert atmosphere at room temperature. After the completion of stirring, the N,N'-dicyclohexylurea precipitate thus formed in the reaction mixture was filtered off. Evaporation of the solvent gave the crude product which was then recrystallized several times with ethanol to obtain the pure product as orange solid. Yield = 0.44 g, (72%). M. P. 131°C . FTIR ν_{max} in cm^{-1} : 1608 ($\nu_{\text{CH}=\text{N}}$, imine); 1736 ($\nu_{\text{C}=\text{O}}$, ester), 3439 ($\nu_{\text{O}-\text{H}}$, H-bonded); ^1H NMR (CDCl_3 , 500 MHz): δ = 13.42 (s, 1H, $-\text{OH}$); 8.37 (s, 1H, $-\text{CH}=\text{N}-$); 7.96 (d, 1H, $J = 8.0$ Hz, ArH); 7.93 (d, 2H, $J = 8.8$ Hz, ArH); 7.78 (d, 2H, $J = 8.8$ Hz, ArH); 7.33 (d, 2H, ArH); 7.31 (d, 2H, $J = 8.8$ Hz, ArH); 7.30 (t, 1H, $J = 8.8$ Hz, ArH); 7.24 (d, 2H, $J = 7.8$, ArH); 6.44 (dd, 2H, $J = 2.4$ Hz, 7.6 Hz, ArH); 3.95 (t, 2H, $J = 6.0$ Hz, $-\text{O}-\text{CH}_2-$); 2.63 (t, 2H, $J = 7.8$, Ar- CH_2); 2.61 (s, 3H, Ar- CH_3); 1.59-1.60 (q, 4H, $-\text{CH}_2-\text{CH}_2-$); 1.59-1.17 (m, 26H, $-(\text{CH}_2)_{26}-$); 0.87 (t, 6H, $-\text{CH}_3$). Elemental analysis calculated for $\text{C}_{47}\text{H}_{61}\text{N}_3\text{O}_4$: C = 77.12%; H = 8.40%; N = 5.74% Found C = 77.09%; H = 8.43%; N = 5.70%.

2.2. Measurements

2.2.1. Differential scanning calorimetry

Differential scanning calorimetry (DSC) has been performed on a DSC 821e (Mettler Toledo, Switzerland) operating with version 5.1 of Star software. The sample was heated from 25 to 149°C with the scanning rate of $5^\circ\text{C}/\text{min}$.

2.2.2. Polarizing optical microscope

POM (Nikon Optiphot-2-pol, from INSTEC Inc. USA) and heating plate with covered slip were used to record the mesophases of the titled molecule.

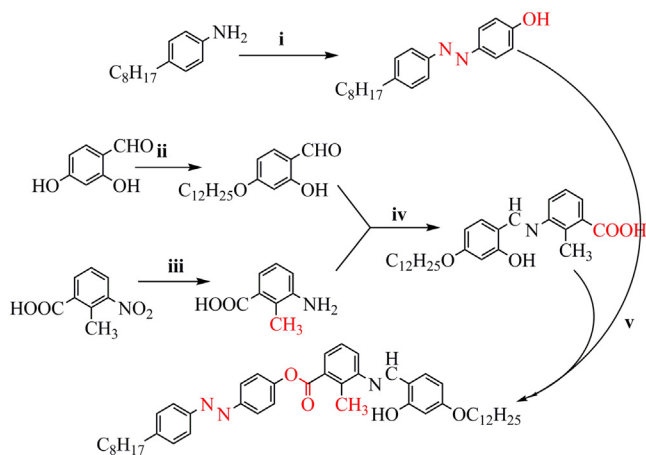
2.2.3. Fourier transformed infrared spectroscopy

Infrared spectrometer (Vertex 70, Bruker, Ettlingen, Germany) was used to record the spectra in different temperature range. A liquid nitrogen cryostat (Janis Research, Wilmington, USA) was employed to record FTIR spectra as a function of temperature. The pellets were prepared from the mixture of KBr and the sample in a 400:1 ratio using a hydraulic pressure machine. Attenuated total reflectance and diffuse reflectance sampling techniques provided similar spectra.

3. Computational methodology

Conformational study and geometry optimization of the title molecule has been performed using DFT approach employing Becke-Lee-Yang-Parr hybrid functional (B3LYP) [11–13] and 6-31G(d) basis set. All the calculations were carried out using Gaussian 09 program [14] employing 6-31G(d) basis set augmented by 'd' diffuse functions on heavy atoms [15,16]. GaussView 05 [17] and ChemCraft [18] softwares were used for visualization of molecular structures and vibrations.

The optimised energy and geometrical parameters (bond length, bond angle, and dihedral angle) of the most stable conformation were calculated at the same level of theory. The normal-mode calculations for each of the internal coordinates were done utilizing potential energy distribution (PED). For 115 atoms; a complete set of 339 internal coordinates was defined using Pulay's recommendations [19,20]. The vibrational assignments of the normal modes were accomplished on the basis of the PED calculated using the program Gar2Ped [21]. Infrared spectra were simulated using a pure Lorentzian band profile ($\text{FWHM} = 8 \text{ cm}^{-1}$) utilizing the indigenously developed software. PeakFitv4.1 software was used for analysis of the observed TD-FTIR spectra.



Scheme 1. Synthetic details of the compound, Reagents, and conditions: i), HCl, H_2O , NaNO_2 , $0-5^\circ\text{C}$, Phenol, NaOH ; ii), dry acetone, dry KHCO_3 , KI , $\text{C}_{12}\text{H}_{25}\text{Br}$, Δ , 24 h; iii), dry EtOAc, Pd/C 10%, iv) Abs EtOH, AcOH, Δ , 6 h; v), DCC, DMAP, dry DCM, Stirring 48 h, 25°C .

Download English Version:

<https://daneshyari.com/en/article/1249499>

Download Persian Version:

<https://daneshyari.com/article/1249499>

[Daneshyari.com](https://daneshyari.com)