



# Cybotactic nematic phase of achiral unsymmetrical bent-core liquid crystals – Quelling of polar ordering and the influence of terminal substituent moiety

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## ARTICLE INFO

### Article history:

Received 26 October 2017

Received in revised form 13 February 2018

Accepted 21 February 2018

Available online xxx

### Keywords:

Bent-core

Liquid crystals

Cybotactic

Ferronematic

## ABSTRACT

Nematic phase of bent-core liquid crystals (LCs) exhibiting cybotactic clusters ( $N_{C_{yb}}$ ) have gained significant importance owing to its promising ability to demonstrate macroscopic biaxiality and the ferronematic phase. In this context, three achiral unsymmetrical four-ring bent-core LC compounds, bearing a long alkyloxy chain and differing only in the terminal substituent moiety (methyl, chloro, nitro), are designed and synthesized followed by their optical, dielectric, electro-optic and structural investigations. The presence of  $N_{C_{yb}}$  in the methyl and chloro substituted compounds was confirmed via dielectric spectroscopy and X-ray diffraction observations. The absence of ferroelectric behaviour in any of these compounds, even in the cybotactic nematic phase and in presence of polar substituent moieties (chloro and nitro), is attributed to the increased alkyloxy chain length and antiparallel molecular arrangement. The density functional theory (DFT) optimized molecular structure along with the experimental observations further substantiates these findings. The study establishes that cybotactic clusters and polar end moiety, although being a prerequisite for ferroelectric-like nature, do not necessarily result in a ferronematic phase.

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## 1. Introduction

Shape-dependent achiral bent-core liquid crystals (LCs) exhibiting nematic phase have drawn special attention among the researchers in recent years and have been studied extensively due to their unusual shape and reduced symmetry offering widespread applications in electro-optic devices. The distinctive features of the bent-core nematic phase are its polarity [1], chirality [2–4] and biaxiality [5] despite the fact that they are formed by achiral molecules. The nematic phase exhibited by a majority of the bent-core LCs, possessing short range smectic-like cybotactic clusters ( $N_{C_{yb}}$ ), is a hotly debated topic in liquid crystal science. The bent-core LCs possessing  $N_{C_{yb}}$  phase are potential candidates to exhibit macroscopic biaxiality [6–12], the ferroelectric nematic (ferronematic) phase [13–16] (ferroelectric switching), and negative bend-splay elastic anisotropy [17] that have promising applications in faster [12] and energy sustainable next-generation displays. Smectic C type cybotactic clusters in the nematic phase were first identified in 1,2,4-oxadiazole based bent-core LCs [18]. In a similar series of 1,2,4-

oxadiazole derivatives, ferroelectric switching in the nematic phase was reported by Francescangeli et al., which was the first evidence of ferronematic phase in low molar mass thermotropic nematic LCs [13]. They also observed cybotactic clustering in the nematic phase of these LC compounds and the observed polar nature was attributed to the field-induced reorganization of polar cybotactic groups within the nematic phase with local biaxial ordering. Later, Shanker et al. also reported ferroelectric switching in a new series of 1,2,4-oxadiazole based bent-core LCs accompanied by the presence of cybotactic clusters [15]. Further, ferroelectric-like switching was observed by Ghosh et al. in four-ring achiral unsymmetrical bent-core compounds exhibiting nematic phase with cybotactic clusters of smectic C type molecular ordering [16]. Recently, Nafees et al. had reported the effect of replacing the polar substituent by a methoxy moiety in four-ring achiral bent-core compounds, resulting in an absence of polar ordering in the nematic phase although possessing smectic C type cybotactic clusters [19]. Thus, there is no subtle description whether the polar ordering in this class of LCs depends only on the cybotactic clusters or on the presence of polar end moieties and therefore needs a lucid explanation.

The bent-core LCs due to their reduced symmetry and transverse dipole moment, especially in the nematic phase, are strong candidates to

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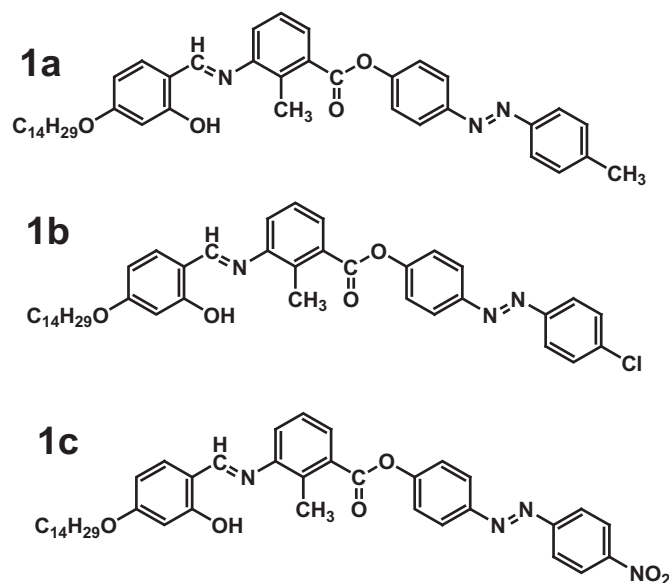
exhibit macroscopic biaxiality [12]. Gleeson et al. had reported such biaxial ordering in bent-core LCs by means of electro-convection patterns [10]. To obtain macroscopic biaxiality in these LCs, a collective ordering must also be present in the system apart from the transverse dipole moment [12,20]. A few studies have demonstrated a strong correlation between the end group moieties and their effects on the molecular assembly as well as the physical properties in oxadiazole based bent-core compounds exhibiting cybotactic nematic phase [14,15]. However, the four-ring bent-core LC compounds are still unexplored and proper correlations are yet to be made to make an understanding of the effects of the end group moieties.

Realization of the nematic phase in achiral unsymmetrical bent-core compounds as such is rare and limited due to the hindered rotation of the molecules around its axis imposed by the bent shape of the molecule. Although it is conceivable that the bent shape do not promote nematic phase, the lengthy alkyl chains as well as modified intermolecular interactions by the introduction of transverse methyl moieties can transform an otherwise layered molecular structure imposed by the bent-shape into a nematic phase with smectic C type molecular ordering and is abbreviated as a cybotactic nematic phase ( $N_{Cybc}$ ). The introduction of a polar moiety viz., chloro or nitro group in a lateral position is one of the methods for decreasing the melting and clearing temperatures and to suppress mesomorphism in calamitic mesogens [21]. The lateral dipole in the bent-molecule promotes the perpendicular component of the dielectric constant and changes the ratio of dielectric anisotropy, both of which find applications in display devices. Further, the nematic phases are realized in five-ring bent-core systems with the introduction of a lateral chloro [22,23] or cyano group [24,25] in the central phenyl ring. However, very few studies are reported on the influence of terminal polar substituents in bent-core compounds [26–31] than lateral substitution. The electronegative chloro or nitro moiety in the lateral position at one end of the molecule is responsible for an enhanced polarization of C–X (X = Cl or  $\text{NO}_2$ ) bond, thereby inducing strong local dipole moment and possibly promoting anti-parallel molecular arrangement which is yet to be established by X-ray and density functional theory (DFT) studies.

In this article, we have made an attempt to establish an enhanced correlation between cybotactic clusters and polar ordering in the nematic phase of achiral unsymmetrical four-ring bent-core LC compounds (Fig. 1). The compounds have been studied using different techniques viz., polarizing optical microscopy (POM), differential scanning calorimetry (DSC), X-ray diffraction (XRD), dielectric spectroscopy, density functional theory (DFT) and electro-optic studies. The liquid crystalline phases were initially characterized using POM studies followed by the determination of phase transition temperatures, associated enthalpies and entropies from DSC investigations. The existence of smectic-like (cybotactic) clusters in the nematic phase of the compounds, extending into the isotropic phase, was investigated via dielectric spectroscopy and X-ray investigations. Further, an indication of field-induced biaxial ordering of the molecular short axes in the nematic phase of chloro substituted compound, owing to its enhanced transverse dipole moment, was reflected in field dependent dielectric studies. Investigation of polar ordering in the compounds was carried out using repolarization current measurement technique under a triangular wave field. The density functional theory (DFT) calculations and the experimental findings along with the earlier reported observations are then collated in an attempt to bridge a correlation between cybotactic clusters and polar ordering in the nematic phase as well as to investigate the predominant effects of the side chain length and nature of the substituent group on cybotaxis, polar ordering and the optical, dielectric and electro-optic properties of bent-core LCs.

## 2. Experimental details

The synthetic scheme details and molecular characterization are presented in the electronic supporting information (ESI). Thermal



**Fig. 1.** Molecular structure of the compounds **1a**: (4'-methylphenylazo)phenyl-4-yl-3-[N-(4'-n-tetradecyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate 14-2M-CH<sub>3</sub>, **1b**: (4'-chlorophenylazo)phenyl-4-yl-3-[N-(4'-n-tetradecyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 14-2M-Cl and **1c**: (4'-nitrophenylazo)phenyl-4-yl-3-[N-(4'-n-tetradecyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 14-2M-NO<sub>2</sub>.

behaviour of the compounds was studied using differential scanning calorimetry (DSC) at a scan rate of 5 °C/min in the second heating and cooling scans. An Indium Tin Oxide (ITO) coated planar cell (Instec.) of thickness 5 μm with antiparallel rubbing was employed for dielectric and electro-optic investigation of the LC compounds. While an ITO coated 3.2 μm homemade cell with antiparallel rubbing was used for electro-optic investigation of the compound **1c**. The sample was introduced into the LC cell using capillary action in its isotropic phase, 5 °C above the clearing temperature. An Instec. HCS302 hot stage attached to an Instec. MK1000 temperature controller was used to maintain the temperature of the LC sample during dielectric and electro-optic measurements. The textures of the LC compounds were recorded using Nikon Eclipse LV100POL polarizing optical microscope provided with a Linkam heating stage (LTS 420) with the crossed polarizers assembly (90° with respect to each other). X-ray diffraction (XRD) studies were carried out on unaligned fluid LC samples using Cu Kα ( $\lambda = 1.54 \text{ \AA}$ ) radiation from GeniX3D micro-source, using Pilatus 200 K detector in Xeuss 2.0 SAXS/WAXS system. Dielectric investigations were carried out using the Agilent E4980A precision LCR meter in the frequency region 20 Hz to 2 MHz and in the voltage range of 0 V to 20 V. A Tektronix AFG3021 function generator, TPS 2024 digital oscilloscope and a homemade high voltage amplifier of gain 10 and operating bandwidth 0–10 kHz were employed for spontaneous polarization measurements using polarization reversal triangular wave method.

## 3. Results and discussion

A set of three four-ring bent-core molecules possessing azo-ester-imine linkages between the phenyl rings, a transverse methyl group to modify the molecular interactions and with different terminal substituents at the longer arm keeping the *n*-tetradecyloxy moiety at the shorter arm fixed, have been engineered (Fig. 1). The principal difference in the chemical structure of the set of three compounds is the different terminal substituent moieties (viz., —CH<sub>3</sub>, —Cl and —NO<sub>2</sub>). The imine linkage, susceptible to moisture, is stabilized by a strong intramolecular hydrogen bonding formed between the imine-N and the *ortho* hydroxyl moiety. The compounds are abbreviated as 14-2M-CH<sub>3</sub> (**1a**), 14-2M-Cl (**1b**) and 14-2M-NO<sub>2</sub> (**1c**). The transition temperatures, entropies and enthalpies associated with the phase transitions of the

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