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# Synthesis and characterization of supramolecular optically active bisamides derived from amino acids

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### ABSTRACT

The synthesis and phase transitional behaviour of three pairs of enantiomeric supramolecular hexacatenar liquid crystals (LCs) derived from natural  $\alpha$ -amino acids such as L/D-alanine, L/D-leucine and L/D-valine are described. Their preparation with high enantiomeric purity was accomplished by condensing optically active (amino acid residue containing) trialkoxy amines with a 3,4,5-trialkoxy cinnamic acid core using a peptide coupling reagent namely, 2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyl-uronium hexafluorophosphate (HBTU). The mesomorphic behaviour of these self-complementing mesogens was ascertained by polarising optical microscopy, differential scanning calorimetry and X-ray diffraction. The compounds exhibit columnar (Col) phase over a wide thermal range. Particularly, a pair of enantiomers derived from L/D-leucine residues notably stabilize hexagonal Col (Col<sub>h</sub>) phase over a wide temperature range of  $-5 \,^{\circ}$ C to 180  $^{\circ}$ C. Circular dichroism (CD) and FTIR studies suggest the chiral (helical) organization of mesogens within the columns through intermolecular hydrogen bonding; thus, these enantiomers represent one of the rarely reported examples of LCs exhibiting supramolecular Col<sub>h</sub> phase at room temperature. The gelation studies reveal the ability of these bisamides to form stable supramolecular gels in ethanol caused through H-bonding interactions.

# 1. Introduction

The past two decades have witnessed a remarkable development in supramolecular chemistry where the properties of chemical species, resulting from the noncovalent interactions among simple molecules or supramolecules (self-complementing motifs) or supermolecules, are rationally investigated to demonstrate their significance in materials and biological sciences.<sup>1–5</sup> The studies encompassing molecular engineering and synthesis of novel materials have particularly established that noncovalent interactions, such as hydrogen (H) bonding, electrostastic interactions,  $\pi - \pi$  stacking interactions and van der Waals or dispersive or hydrophobic forces, greatly facilitate the generation of novel structures featuring a high degree of complexity and function.<sup>2</sup> Among these, the H-bond interaction is proven to be very effective in generating numerous interesting structures such as dimers, multimers, ionophores, capsules (molecular containers), chiral capsules, liquid crystal (LC) phases, self-assembled nanotubes and macromolecular assemblies.<sup>1–16</sup> The ability of H-bonds

enforcing the self-assembly of complementary mesogenic/nonmesogenic molecules in generating a range of LC phases, called supramolecular LCs, is especially noteworthy. Supramolecular Hbonded LCs, primarily being anisotropic fluids, are attracting enormous attention as they additionally possess a unique combination of properties as a consequence of the presence of H-bonds, such as moderate bonding energy, directionality, selectivity and reversibility.<sup>2,11–13,16</sup> In fact, significant advances have been made in developing multifunctional columnar (Col) LC phases where the H-bonding plays an important role.<sup>2,8–14,16–36</sup> As is well-known, Col phases, which are generated by the spontaneous self-assembly of disk-like (discotic)  $\pi$ -conjugated molecules into fluid columnar stacks, are highly anisotropic and ordered structures with extensive  $\pi$ -orbital overlap leading to high degree of uniaxial charge-carrier mobilities.<sup>37</sup> Thus, Col phases hold immense promise in electronic devices such as photovoltaic cells,<sup>38</sup> field effect transistors<sup>39</sup> and organic light emitting devices (OLEDs).<sup>40</sup> In recent times it has also been demonstrated that by the rational design and synthesis of H-bonded supramolecular materials, especially nondiscoid (nonconventional) motifs, many other important functional features-attractive from the view points of both life-science and technology-can be incorporated in Col LC phases.<sup>16-36,41-43</sup>

One area of interest that we have been focussing on for some time is the design and synthesis of nondiscoid materials such as hexacatenars, in which naturally occurring  $\alpha$ -amino acids are used





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6529

as one of the important building blocks.<sup>41–43</sup> Precisely, we have realized several chiral supramolecules, which can be regarded as intermediates between the polycatenars and taper-shaped amphiphiles as they possess two lipophilic (half-disk shaped) segments interlinked through a central linking segment derived from one<sup>42</sup> or two<sup>41</sup> amino acid residues. These compounds exhibit a range of important properties such as macroscopic chirality,<sup>41,42</sup> ferroelectric behaviour<sup>41</sup> and gelating ability.<sup>41–43</sup> For example, these self-complementing motifs with multiple H-donating and Haccepting sites self-organize into the chiral Col phase through the intermolecular H-bond interaction; this means that the molecular chirality of the materials is very well manifested in the fluid columns. Furthermore, the nature of the central linking segment in the molecules appears to dictate their packing, which in turn reflects on the magnitude of out-of-plane fluctuation of the lattice plane of 2D (Col) structure. Besides, they form stable organogels in ethanol<sup>41-43</sup> and our investigations reveal the occurrence of 3D network comprising helical fibres in the gel.<sup>41</sup> Most importantly, some of these compounds, especially the dipeptides derived from L–L-/D–D-alanine combinations, exhibit a polar (ferroelectric) oblique columnar (Colob) phase with a high spontaneous polarization value<sup>41</sup> and are thus the first examples of supramolecular columnar LCs showing ferroelectric switching characteristics. These observations motivated us to prepare the variants of abovementioned supramolecular hexacatenars comprising a new functional moiety. In the molecular design suitable for our objectives, we opted to replace one of the taper-shaped units with other lipophilic core featuring extended  $\pi$ -conjugation. We especially chose to incorporate a lipophilic (half-disc like) core derived from 3,4,5-tris(dodecyloxy)cinnamic acid as it not only reduces the symmetry of the resulting hexacatenars but also accounts for electronic properties.<sup>44,45</sup> In fact, it is well documented that cinnamic acid or its derivatives (cinnamates) comprising flexible tails exhibit a range of smectic and/or nematic mesophases.<sup>45</sup> Further, owing to the presence of a trans double bond in conjugation with benzene ring and carbonyl group, the cinnamoyl moiety imparts photophysical properties as well as a particular geometry (shape) to the systems.

Herein, we present the synthesis and characterization of hexacatenar bisamides in which 3,4,5-tris(dodecyloxy)cinnamic acid and 3,4,5-tris(dodecyloxy)aniline cores are interlinked through an amide spacer derived from amino acids such as L/D-alanine, L/Dleucine and L/D-valine. The general molecular structure of the synthesized bisamides, hereafter referred to as **CHBA** series (where **CHBA** stands for **C**innamoyl-based **H**exacatenar **B**is**A**mides), is shown in Scheme 1.

# 2. Experimental

#### 2.1. Synthesis

The synthetic pathway for preparing the target hexacatenar molecules is depicted in Scheme 1. Ethyl (3,4,5-tris-dodecyloxy) benzoate (1) was prepared by esterification of gallic acid with ethanol followed by O-alkylation using Williamson's ether synthesis protocol. This material was then subjected to reduction using LAH in dry THF to obtain 3,4,5-tris(dodecyloxy) benzylalcohol (2) in 98% yield; the oxidation of this primary alcohol using PCC-silica in dry CH<sub>2</sub>Cl<sub>2</sub> yielded 3,4,5-tris(dodecyloxy)benzaldehyde (3). The Knoevenagel condensation of benzaldehyde 3 with malonic acid using catalytic amount of piperidine in pyridine delivered the key intermediate 3,4,5-tris(dodecyloxy)cinnamic acid (4) in 81% yield. 1,2,3-Tris-dodecyloxy-5-nitrobenzene (5), prepared by nitrating 1,2,3-tris-dodecyl-oxybenzene using fuming HNO<sub>3</sub> in the presence of NaNO<sub>2</sub>, was subjected to catalytic hydrogenation to obtain 3,4,5tri(dodecyloxy)aniline (6).<sup>24</sup> Upon treating, readily available, appropriate  $N^{\alpha}$ -Fmoc-amino acids with aniline **6** in the presence of NMM and IBC-Cl gave protected amines **7a–b**, **8a–b** and **9a–b**; deprotection of these compounds using a mixture of  $(C_2H_5)_2NH$  and  $CH_2Cl_2$  furnished the key amines **10a–b**, **11a–b** and **12a–b**.<sup>41</sup> Finally, the target bisamides, the **CHBA** series of compounds, were obtained in 60–65% yield by coupling cinnamic acid **4** with these amines (**10a–b**, **11a–b** and **12a–b**) using HBTU in dry THF. All the synthesized hexacaternars and their intermediates were characterized by spectroscopic methods and elemental analysis (see Supplementary data for details).

# 2.2. Evaluation of liquid crystal behaviour

The mesomorphic behaviour of the synthesized hexacatenars, **CHBA-1** to **CHBA-6**, was investigated by three complementary experimental techniques of polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The results of these investigations are summarized in Table 1 and discussed in detail in the following sections.

The enantiomeric pairs CHBA-1/CHBA-2, CHBA-3/CHBA-4 and CHBA-5/CHBA-6, respectively, derived from L-/D-alanine, L-/D-leucine and L-/D-valine display identical mesomorphic property exhibiting enantiotropic columnar behaviour with an excellent thermal stability as ascertained by optical and calorimetric studies. Notably, the enantiomeric bisamides CHBA-3 and CHBA-4 stabilize the Col phase well below and above the room temperature (rt). In fact, the occurrence of Col phase at rt was immediately apparent as they were isolated, after purification, as sticky mass, which could be readily spread by mechanical shearing. When viewed under microscope, the spread thin films showed a fluid, highly birefringent nonspecific textural pattern. However, sandwiched between a clean glass slide and a coverslip, and on slow cooling from the isotropic liquid, the compounds exhibit birefringent dendritic textural pattern (Fig. 1a) emanating from the dark background of isotropic liquid. This pattern is well-known to be an important signature and conclusive evidence for the occurrence of Col phase. On lowering the samples temperature further, neither any other textural change (Fig. 1b) nor crystallization was seen till rt implying that the Col phase once formed upon cooling from the isotropic phase, crystallizes by no means instead it remains unaltered. These phase transitions were found to be reproducible for any number of heating-cooling cycles.

As shown in Fig. 2, the DSC thermograms obtained during the first and second heating-cooling cycles, corroborate the optical observation. That is, as can be seen in Fig. 2, no exothermic or endothermic peaks exist between the temperature range 0-180 °C and thus, supporting the optical observation that Col phase exists over a wide thermal range covering rt. The other two pairs of enantiomers **CHBA-1/CHBA-2** and **CHBA-5/CHBA-6** derived from L-/p-alanine and L-/p-valine, respectively, exhibit analogous behaviour with the exception that they show Col mesomorphism at elevated temperatures (see Table 1).

In order to ascertain the structure of the mesophase formed by bisamides **CHBA-3** and **CHBA-4**, X-ray diffraction (XRD) measurements were carried out on powder (unaligned) samples. These experiments were performed using Cu K $\alpha$  radiations ( $\lambda$ =1.5418 Å) from a fine focus sealed-tube generator (Enraf Nonius FR590), in conjunction with double mirror focussing optics. The detector employed was an image plate detector (MAC Science, Japan; Model DIP 1030). The mesogens **CHBA-3** and **CHBA-4** were filled in a Lindemann capillary (1 mm diameter) tube in the isotropic phase and both the ends of tube were flame sealed. The diffraction patterns obtained at two different temperatures viz., rt (25 °C) and high temperature (HT) (170 °C), were collected in the cooling mode. The XRD patterns obtained for both the compounds at rt and HT were found to be virtually indistinguishable, as expected. As



**CHAB-1** :  $R_1 = (S)$ -Methyl **CHAB-3** :  $R_1 = (S)$ -Isobutyl **CHAB-5** :  $R_1 = (S)$ -Isopropyl **CHAB-2** :  $R_1 = (R)$ -Methyl **CHAB-4** :  $R_1 = (R)$ -Isobutyl **CHAB-6** :  $R_1 = (R)$ -Isopropyl

Scheme 1. Reagents and conditions. (i) LAH, THF, 0 °C, 2 h (98%); (ii) PCC, DCM, rt, 1 h (85%); (iii) Malonic acid, pyridine, piperidine (catalyst), reflux, 10 h (81%); (iv) H<sub>2</sub> (1 atm, balloon), 10% Pd–C, THF, rt, 4 h (88%); (v) Fmoc-t/D-laurine or Fmoc-t/D-leucine or Fmoc-t/D-valine, *N*-methylmorpholine, isobutoxycarbonyl chloride, THF, 0 °C to rt, 10 h, (74–78%); (vi) diethylamine–dichloromethane (1/1), rt, 2 h (not isolated); (vii) 2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyl-uroniumhexafluorophosphate (HBTU), THF, *N*-ethyldiisopropyl-amine (DIEA), rt, 10 h (60–65%).

representative cases, the 1D intensity versus  $2\theta$  profiles deduced from the powder 2D patterns of the sample **CHBA-3** is shown in Fig. 3. The results of indexing these profiles of the phases are summarized in Table 2.As seen in Fig. 3, the wide angle region of both HT and rt profiles comprises a diffuse reflection with a spacing (*d*) of about 5 Å (Table 2), that can be attributed to the average distance between the molecules within column. In the low angle region ( $0 < 2\theta < 5^{\circ}$ ) of the diffractograms, two sharp reflections were observed; the spacings (*d*) being 24 Å and 14.3 Å at HT, and 23.5 Å, and 13.7 Å at rt. These two reflections of Col phase with the spacing ratio of  $1:\sqrt{3}$  can be assigned to (10) and (11) reflections from a quasi 2D hexagonal lattice with a lattice dimension 27.8 Å at HT and 27.1 Å for rt. Thus, the textural observation coupled with XRD data suggests that these two compounds stabilize a fluid columnar phase possessing  $D_{6h}$  (hexagonal) symmetry; that is, they exhibit columnar hexagonal (Col<sub>h</sub>) phase. It may be recalled here that all

Table 1 Phase transition temperatures  $(^{\circ}C)^{a}$  and enthalpies  $[k] \mod^{-1}]^{b}$  of hexacatenars

Compound	Phase sequence					
	Heating	Cooling				
CHBA-1	Cr 67 [61.2] Col <sup>c</sup> 184 I	I 183 Col <sup>c</sup> 55 [–12.5] Cr				
CHBA-2	Cr 66 [57.4] Col <sup>c</sup> 183 I	I 182 Col <sup>c</sup> 54 [-10.3] Cr				
CHBA-3	Cr –5 [30] Col <sub>h</sub> 184 [6.6] I	I 183 [-6.4] Col <sub>h</sub> -11 [-26.4] Cr				
CHBA-4	Cr –5 [25.6] Col <sub>h</sub> 185 [5.9] I	I 184 [-5.8] Col <sub>h</sub> -10 [-17.7] Cr				
CHBA-5	Cr 66 [70.6] Col <sup>c</sup> 180 I	I 178 Col <sup>c</sup> 51 [-7.4] Cr				
CHBA-6	Cr 65 [73.7] Col <sup>c</sup> 180 I	I 178 Col <sup>c</sup> 68 [-4.6] Cr				

Abbreviations: Col<sub>h</sub>=hexagonal columnar phase; I=isotropic phase; Cr=crystal. <sup>a</sup> Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at 5 °C/min.

<sup>b</sup> Transition enthalpies were obtained from the DSC thermograms.

<sup>c</sup> The Col–I or I–Col phase transition was observed under optical polarizing microscope and too weak [<0.01 kJ mol<sup>-1</sup>] to get recognized in DSC. the six hexacatenars synthesized exhibit a textural pattern, that is, indistinguishable from that for **CHBA-3** and **CHBA-4** and therefore, it is reasonable to assume that the Col phase stabilized by other four compounds, **CHBA-1**, **CHBA-2**, **CHBA-5** and **CHBA-6**, as well possess hexagonal lattice. In fact, the mesophase of **CHBA-3** and **CHBA-4** could be well-mixed with the LC phase formed by other four compounds, clearly indicating that all of them show an identical mesophase.

#### 2.3. Determination of hydrogen bonding

As is well-known, molecular interactions and conformations have a remarkable effect on the wavenumber, intensity and shape of the infrared (IR) absorption bands.<sup>46</sup> Likewise, H-bonding is one of the best-known factors that alters such parameters of IR bands.



Fig. 1. Microphotograph of the optical texture seen for the Col<sub>h</sub> phase of compounds (a) CHBA-3 at 179 °C. (b) CHBA-4 at 30 °C.



**Fig. 2.** DSC traces of the first and second heating-cooling cycles recorded at a rate of 5  $^{\circ}$ C/min. for the compound **CHBA-3**. Notice that the thermograms of both heating and cooling cycles are identical suggesting the high thermal stability of the compound.

Thus, FTIR technique is being employed as an important tool to characterize H-bonding, especially in mesomorphic amides.<sup>32,33,36</sup> To ascertain the self-assembly through intermolecular H-bonding leading to the formation Col phase, all the six compounds synthesized were investigated with the help of FTIR study. They displayed very similar IR spectral patterns, as expected, which ascertained the presence of H-bonding in the Col phase. However, we discuss the experimental details and results of the hexacatenars CHBA-3, as a representative case. Compound CHBA-3 sandwiched between a pair of KBr plates, was cooled from the isotropic phase to rt, and the FTIR spectra were recorded as a function of decreasing temperature. Two important regions of the spectra are shown in Fig. 4. The occurrence of bands due to stretching vibrations of N-H and C=O groups at around  $3270 \text{ cm}^{-1}$  and  $1615 \text{ cm}^{-1}$ , respectively, indicate the presence of H-bonded amide groups in the mesophase. Indeed, the observed band values are less than 3440 cm<sup>-1</sup> and 1680 cm<sup>-1</sup> usually observed for the free N–H and C=O groups, respectively. As can be seen in Fig. 4, the bands due to NH and C=O stretching vibrations become stronger (increase in the intensity)



Fig. 3. 1D intensity versus  $2\theta$  profiles obtained for the Col<sub>h</sub> phase (a) at 170 °C (b) at 25 °C for the compound CHBA-3.

#### Table 2

The result of indexation of XRD profiles of **CHBA-3** and **CHBA-4** at a given temperature  $(T/^{\circ}C)$  of mesophase

Compound	Phase	T/°C	d Observed (Å)	d Calculated (Å)	Miller index, hk	Lattice parameters (Å)
CHBA-3	Col <sub>h</sub>	170	24	24	10	a=27.8
			14.3	13.9	11	
			4.8			
		25	23.5	23.5	10	a=27.1
			13.7	13.5	11	
			4.5			
CHBA-4	Col <sub>h</sub>	170	24.1	24.1	10	a=27.7
			14.4	13.9	11	
			4.8			
		25	23.4	23.4	10	a=27.1
			13.7	13.6	11	
			4.5			

Abbreviation: Col<sub>h</sub>=Hexagonal columnar phase.



Fig. 4. The regions of the FTIR spectra recorded at different temperature intervals during cooling the sample CHBA-3 from the isotropic phase.

and get pronounced near rt, as expected. These features clearly indicate the correlation between NH and CO groups through intermolecular H-bonds.<sup>32,33,36</sup> In addition, the disordering of *n*-alkoxy tails present on either side of the hexacatenar was evidenced based on the observation of bands of asymmetric and symmetric C–H stretching at 2937 cm<sup>-1</sup> and 2858 cm<sup>-1</sup>, respectively.<sup>32,33,36</sup>

## 2.4. UV-visible and circular dichroism (CD) studies

The photophysical properties of these compounds were investigated with the aid of UV—vis absorption and CD spectroscopic studies. The dichloromethane solution UV—vis spectra of all the hexacatenar bisamides exhibit almost identical pattern with absorption maxima centred around 310 nm; as representative cases the spectra obtained for bisamides **CHBA-3** and **CHBA-4** are shown in Fig. 5a and b, respectively. In fact, identical UV spectral patterns were obtained when thin films of the mesophase were studied

using sample cells prepared for CD measurements (see below for details). It may be noted here that the absorption maxima of these compounds shift dramatically to higher wavelength when compared to other hexacatenar reported earlier;<sup>41</sup> needless to say, this shift can be attributed to the presence of extended  $\pi$ -conjugation in cinnamoyl moiety.

It is well documented that circular dichroism (CD) spectroscopy is employed as one important optical techniques to examine if the molecular chirality of the mesogens (discotics) has facilitated molecular organization in chiral (helical) fashion in the columnar and isotropic phases.<sup>47</sup> The appearance of exciton-split Cotton effect in the CD spectrum of the samples especially indicates the manifestations of molecular chirality of discotics into the fluid columnar structure featuring handedness; here, the constituent molecules within the column are twisted with respect to each other and it is the precession of the twist that gives rise to the macroscopic helical structure. It may be noted here that the CD activity of the Col phase may also arise if the optically active discotics are stacked on top of each other randomly and thus, molecules are not correlated. However, if the CD signals (intensities) are strong enough, it may be reasonable to infer that the constituent mesogens are arranged in a helical fashion within the column.<sup>41,47</sup> In order to find out whether the molecular chirality of the molecules, has caused such effects in the Col<sub>h</sub> phase, all the three pairs of enantiomers were probed for chiroptical properties with the aid of CD spectroscopic studies.

Samples held between two quartz plates were heated to their isotropic liquid state using programmable hot stage, which gives an accuracy of about  $\pm 0.6$  °C variations and cooled slowly. The heating-cooling cycle along with the mechanical shearing was performed repeatedly to spread the sample uniformly. It must be mentioned here that very thin films of samples (mesophase) were required for the experiment to work within the upper limits of measurement. Consequently, usage of prefabricated cells with the known thickness was precluded; thus, our experiments are rather gualitative. The CD spectra were recorded carefully<sup>48</sup> as a function of decreasing temperature from isotropic liquid state to rt, covering the entire thermal range of Col phase. None of the samples showed CD activity in isotropic state whereas the mesophases (Col<sub>h</sub> phases) occurring just below the isotropic phase produce signals indicating chiral induction at the isotropic liquid–Col<sub>h</sub> phase transition. This observation clearly suggests that the optical activity of these hexacatenars does not originate from the presence molecular chirality but from the chiral induction in the columnar structure. Most importantly, each of the enantiomeric pairs exhibited mirror image CD curves, as expected. The intensity of CD signals increases with decrease in temperature implying that the supramolecular order, handedness, caused by cooling into Col<sub>h</sub> phase, enhances CD signals remarkably. These features, for example, can be seen in Fig. 6a and b where enantiomers CHBA-3 and CHBA-4 exhibit mirror image cotton effect. That is, enantiomers CHBA-3 and CHBA-4 display



Fig. 5. UV-vis spectra of bisamides CHBA-3 (a) and CHBA-4 (b) dissolved in CH<sub>2</sub>Cl<sub>2</sub>.



Fig. 6. The CD spectra obtained in the Col phases as a function of temperature for the enantiomeric pairs (a) CHBA-3 and (b) CHBA-4. Notice that they exhibit mirror image CD curves in the mesophase.

a negative and a positive exciton splittings, respectively (Table S1), centred at the wavelength of the  $\pi$ - $\pi$ \* transition (350–360 nm).

In fact, the exciton coupling process is an outcome of throughspace interaction between two or more chromophores exhibiting bands due to the  $\pi$ - $\pi$ \* transition. This interaction through-space divides the excited state into two energy levels. For the occurrence of exciton-splitting phenomenon, interacting electric transition moments should not be parallel as it is a vectorial product.<sup>47b,e</sup> The occurrence of exciton splittings in the CD spectra of the Col<sub>h</sub> phase of the present compounds, should be resulting from the twisted (nonparallel) organization of the hexacatenars within the columns. In essence, Cotton effect observed in the CD spectra of the samples indicates the expression of chirality of the molecules into the helical conformation of the columns.

These molecules are arranged in a helical fashion through intermolecular hydrogen bonding as evidenced by CD and IR studies. Perhaps, the substituent (viz., methyl, isobutyl and isopropyl groups) present in the supramolecular central spacer enforces the molecules to twist with respect to each other within the column.

Such an arrangement of molecules causes a dramatic reduction of the steric repulsions while maintaining the intermolecular H-bonding through NH and C=O groups. Based on these facts, a model for the Col<sub>h</sub> phase where the molecules within the columns are arranged in helical manner is shown in Fig. 7.



**Fig. 7.** Schematic representation of hexagonal macroscopic columnar structure formed by self-assembly of individual columns organized in a helical fashion through hydrogen bonding.

These chiral bisamides were examined for their electrical switching behaviour. Samples placed between ITO coated glass plates were cooled slowly from the isotropic phase to the Col phase and a low frequency AC triangular wave electric field was applied and increased gradually. Even with large voltages (200 Vpp), there was no response from the Col phase indicating the absence of polarity. On the other hand, these kinds of bisamides have tendency to gel with various solvents, hence a representative sample tested for gelation property. Compound **CHBA-3** forms gel with 5% ethanol as confirmed by test tube inversion method (Fig. S1a) and IR investigation shows peak at  $v_{N-H}=3269 \text{ cm}^{-1}$ ,  $v_{C-H(as)}=2920 \text{ cm}^{-1}$ ;  $v_{C-H(s)}=2853 \text{ cm}^{-1}$ ,  $v_{CO}=1633 \text{ cm}^{-1}$  indicating H-bonding in the gel. Scanning electron microscopy (SEM) images showed the presence of entangled networks (Fig. S1b–d) at different parts of the sample.

# 3. Summary

Summarizing, optically active cinnamoyl-based bisamides comprising an amino acid residue such as L/D-alanine or L/D-leucine or L/D-valine have been synthesized and characterized. All the compounds display enantiotropic columnar mesophase; XRD study establishes hexagonal ( $D_{6h}$ ) symmetry for the columnar lattice. Notably, bisamides derived from leucine exhibit Col phase over a wide thermal range through rt. The occurrence of CD signals perhaps indicates the chiral organization of the molecules within the column facilitated by intermolecular H-bonding.

# Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.05.070.

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- 48. CD spectra of liquid crystal phases are often accompanied by artifacts due to linear dichroism (LD). Therefore, the occurrence of CD signals in the Col<sub>h</sub> phase of all the compounds was ascertained by recording the spectra at three different temperatures by rotating (in-plane) the sample cells by 90°. The spectra were found to be quite similar to those obtained in the original orientation of the samples. In fact, the instrument used is capable of detecting the LD signal directly: in the measurements no LD signal was found within the instrument limits. These results clearly rule out the possibility that the signal seen in spectra is due to LD of the sample.