Mesomorphic behavior of methanesulfonate salts of esters of L-Methionine and their optical properties

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MS received 18 February 2019; revised 2 May 2019; accepted 14 May 2019

Abstract. A set of methanesulfonate salts of esters of (S)-2-Amino-4-(methylthio)butanoic acid [L-Methionine] and fatty alcohols have been synthesized in good yields by a green protocol involving a one-step and solvent-free approach. All derivatives have been evaluated for their liquid crystalline properties using polarizing optical microscopy and differential scanning calorimetry and found to be enantiotropic liquid crystals. Refractive indices were measured for one of the derivatives at different temperatures and wavelengths. It exhibited a high Abbe number and low dispersive power.

Keywords. Abbe number; dispersive power; enantiotropic; liquid crystals; refractive indices.

1. Introduction

Liquid crystals (LCs) are soft materials composed of self-organized molecules, capable of forming ordered and mobile states.¹ At the phase transition from amorphous liquid to liquid crystalline state, the properties become anisotropic, which is an important feature of liquid crystals.² LCs possess long-range orientational or positional ordering in at least one direction. The introduction of order into soft materials induces new dynamic functions. Liquid crystals are useful in low-power-consuming flat-panel displays which have allowed the development of mobile data processing and communication tools.³ They also find potential applications as new functional materials for electron, ion, or molecular transporting, sensory, catalytic, optical, and bioactive materials, sensing, catalysis, templates, and stimuli responsiveness as well as electro-optical displays.⁴

Ionic liquid crystals (ILCs) are a new class of compounds combining the properties of liquid crystals and ionic liquids.⁴ They are formed by a modification of the conventional design of liquid crystals by the introduction of ionic groups into them.⁵ ILCs are most-commonly built-up from long hydrophobic chains

linked to a positively charged organic core and inorganic anions. This favors the formation of smectic structures by microphase segregation of the hydrophobic groups and charged groups.⁶ Another unique feature of ILCs is their spontaneous homeotropic alignment on a glass substrate. This spontaneous self-organization of the ionic mesophase is caused by interactions between cationic head groups and the surface and by an arrangement of hydrophobic tails, thus creating mono-domains of similarly oriented molecules of the ionic mesogens.⁷ ILCs have applications in directed synthesis,⁸ anisotropic tribology,⁹ ion self-assembly,^{10,11} molecular electronics,⁶ dye-sensitized solar cells,¹² fuel cells¹³ and sensors.¹⁴

When compared with the huge library of liquid crystals, there are fewer number of ionic liquid crystals reported. Most of these liquid crystals are derived from heterocyclic cores. Largely popular ones are those derived from imidazolium cores. Some other examples include ionic liquid crystals based on guanidinium, pyrrolidium, viologens, pyrazolium, triazolium, pyrrolidinium, etc.^{4,6,15} Their preparation methods involve multiple steps, use of expensive reactants, tedious purification steps and low yields. They are mostly non-biodegradable, therefore, undergoing bioaccumulation and hence are not very eco-friendly.

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Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s12039-019-1644-3>) contains supplementary material, which is available to authorized users.

In the present work, we report the preparation of ionic liquid crystals in good yields with the cationic part derived from an α -amino acid, that is, (S)-2-amino-4-(methylthio)butanoic acid [L-Methionine] esterified with fatty alcohols and the anionic part obtained from methane sulfonic acid. Amino acids and their derivatives are abundant sources of quaternary nitrogens and also readily available in pure form at low prices. Literature survey suggests that there are only a few reports^{16–19} of amino acids being used to make up the cationic part in ionic liquid crystals. Examples of ionic liquid crystals with protonated amino acid core are hardly known. This is the reason behind choosing an amino acid as the cationic part of this work. Attachment of a mesophase-inducing unit to other moieties is a common and effective strategy to induce LC behavior in a molecule. It helps in imparting the molecular assembly with shape anisotropy that is essential for liquid crystallinity.¹⁵ It is for this reason that fatty alcohols have been chosen as they help in inducing mesomorphism and at the same time provide shape anisotropy. The length of the alkyl chain influences the mesophases and melting points. The alkyl chain volume (i.e., the number and length of alkyl chains) influences the placement of the long alkyl chains (i.e., either all on the same side of the ionic planes, or on opposite sides of the ionic planes), as well as the degree of interdigitation between alkyl chains of neighboring molecules.¹⁵ Methane sulfonic acid has been chosen as the anion as anions with strong organic character have exhibited remarkable properties for thermal stabilities and reduction in the phase transition temperatures (PTTs).⁵ Another advantage is that all the three reactants involved: methane sulfonic acid, amino acid and fatty alcohols are easily available, inexpensive and biodegradable.^{20–22} The procedure employed for the synthesis comprises of a one-pot, solvent-free method with non-tedious workup, easy purification, high atom-economy, high yields of the desired products and is in agreement with the principles of green chemistry. To the best of our knowledge, these are the first reports on the synthesis and refractive indices of ionic liquid crystals derived from L-Methionine.

2. Experimental

2.1 Materials and methods

All reactions were carried out in oven-dried glassware. Materials were obtained from commercial suppliers and used without further purification unless otherwise noted. Elemental Analysis was recorded on Euro Vector EUROEA 3000 Elemental Analyser. ¹H NMR (300 MHz) and ¹³C NMR

(75 MHz) spectra were recorded on Bruker AVANCE spectrometer (Bruker BioSpin AG, Fallanden, Switzerland; 300 MHz) using CDCl₃ or MeOD as a solvent. TMS was used as an internal standard. Infrared (IR) spectra were recorded on a Perkin Elmer (Model–Frontier) spectrometer (Waltham, MA, USA). Mass spectra were recorded on ABSCIEX 3200 QTRAP mass spectrometer. The phase transition temperatures and enthalpy values were measured by Mettler Toledo Differential Scanning Calorimeter at heating and cooling rates of 1 °C min^{–1}, respectively. Transition temperatures were evaluated by Polarizing Optical Microscope using Mettler Toledo FP90 heating stage, containing temperature control unit in conjunction with a Carl Zeiss polarising optical microscope (Carl Zeiss MicroImaging GmbH, Koenigsallee, Goettingen, Germany). The mesophase type was assigned by visual comparison under the microscope with known phase standards. The samples studied by polarizing optical microscopy were prepared in thin films sandwiched between the glass slide and cover. The refractive indices were measured at various temperatures in the visible spectral region using a multiple wavelength Abbe Refractometer (DSR- λ , SCHMIDT + HAENSCH).

2.2 Synthesis of 3a–3b

Compound **1** (0.149g, 1 mmol) and fatty alcohols **2a/2b** (1.1 mmol) were taken in a round bottom flask and heated to 120 °C on a heating mantle equipped with stirring facility. The reaction mixture was stirred at this temperature for about 5 min. To this reaction mixture, methane sulfonic acid (0.115g, 1.2 mmol) was added in a dropwise manner over a period of 5 mins. The reaction was stirred at 130–135 °C for 2 and 1/2 h till the solution became golden brown. After completion of the reaction (as monitored by TLC), the hot golden brown solution was poured cautiously into 50 mL of chilled diethyl ether (dry ice-acetone bath). The resultant suspension was stirred for 2 h at room temperature and filtered to afford a buff coloured solid. It was purified by recrystallization from diethyl ether (30 mL) and dried in air to get pure product in good yields. The synthetic protocol for the preparation of **3a–3b** is outlined in Scheme 1.

(S)-4-(methylthio)-1-(octadecyloxy)-1-oxobutan-2-aminium methane sulfonate (**3a**): as a white solid (0.388g, 78%); IR (neat) $\nu_{\max}$ /cm^{–1}: 3418.22 (br, **N–H** str.), 2915.21, 2848.53, 1745.31 (s, **C=O** str.), 1625.04 (**N–H** bending), 1538.94, 1470.10, 1333.43 (Asymm. **S=O** str.), 1204.26, 1147.83 (Symm. **S=O** str.), 1076.85, 776.49. ¹H-NMR (300MHz, CDCl₃, 25 °C, TMS) δ 8.097 (s, 3H, –CH₂–CH–NH₃⁺), 4.239 (t, *J* = 6.9 Hz, 2H, –CO–OCH₂–), 4.180 (t, *J* = 6.9 Hz, 1H, –CH₂–CH–NH₃⁺), 2.775 (s, 3H, CH₃–SO–), 2.512 (t, *J* = 7.5 Hz, 2H, –S–CH₂–CH₂–), 2.310–2.240 (q, *J* = 6.9 Hz, 2H, –CH₂–CH–NH₃⁺), 2.114 (s, 3H, CH₃–S–CH₂–), 1.683–1.559 (m, 2H, –OCH₂–CH₂–(CH₂)₁₅–CH₃), 1.256 (m, 30H, –OCH₂–CH₂–(CH₂)₁₅–CH₃), 0.880 (t, *J* = 6.9 Hz, 3H, –OCH₂–CH₂–(CH₂)₁₅–CH₃). ¹³C-NMR (75MHz, CDCl₃, 25 °C, TMS) δ 169.539 (**C=O**), 66.748 (–CO–OCH₂–), 52.034 (–CH–NH₃⁺), 39.288 (CH₃–SO–), 31.945, 31.783, 29.737,

29.574, 29.382, 29.284, 25.834, 22.704, 15.032, 14.120. m/z calc. for $\text{C}_{23}\text{H}_{48}\text{NO}_2\text{S} + [\text{M}-\text{CH}_3\text{SO}_3]^{+} = 402.700$, obs. mass $[\text{M}-\text{CH}_3\text{SO}_3]^{+} = 402.200$, $[(\text{M}+\text{H})-\text{CH}_3\text{SO}_3]^{+} = 403.300$. Anal. calcd. for $\text{C}_{24}\text{H}_{51}\text{NO}_5\text{S}_2$ (497.80): C, 57.91; H, 10.33; N, 2.81; S, 12.88; found: C 57.79, H 10.36, N, 2.82; S, 12.92.

(S)-4-(methylthio)-1-(hexadecyloxy)-1-oxobutan-2-aminium methane sulfonate (3b): as a white solid (0.380g, 81%); IR (neat) ν_{max} /cm⁻¹: 3423.36 (br, **N-H** str.), 2952.83, 2914.78, 2847.94, 1745.88 (s, **C=O** str.), 1625.08 (**N-H** bending), 1470.85, 1379.87, 1318.09 (Asymm. **S=O** str.), 1205.63, 1147.24 (Symm. **S=O** str.), 1038.63, 775.02. ¹H-NMR (300MHz, MeOD, 25 °C, TMS) δ 4.252 (t, *J* = 7.2 Hz, 2H, -CO-OCH₂-), 4.143 (t, *J* = 6.6 Hz, 2H, -CH₂-CH-NH₃⁺), 2.776 (s, 3H, CH₃-SO-), 2.675 (t, *J* = 6.6 Hz, 3H, CH₃-S-CH₂-), 2.543 (t, *J* = 7.5 Hz, 2H, -S-CH₂-CH₂-), 2.213–2.143 (q, *J* = 7.2 Hz, 2H; -CH₂-CH₂-CH-NH₃⁺), 1.728–1.570 (m, 4H, -OCH₂-CH₂-CH₂-(CH₂)₁₂-CH₃), 1.269 (m, 24H, -OCH₂-CH₂-CH₂-(CH₂)₁₂-CH₃), 0.863 (t, *J* = 6.9 Hz, 3H; -OCH₂-CH₂-CH₂-(CH₂)₁₂-CH₃). ¹³C-NMR (75MHz, MeOD, 25 °C, TMS) δ 170.480 (**C** = O), 67.752 (-CH₂-CH-NH₃⁺), 52.853 (-CO-OCH₂-), 39.589 (CH₃-SO-), 33.108, 30.824, 30.722, 30.679, 30.510, 30.123, 26.986, 23.774, 15.086, 14.985, 14.536. m/z calc. for C₂₁H₄₄NO₂S⁺ [M-CH₃SO₃]¹⁺ = 374.40 obs. mass [M-CH₃SO₃]¹⁺ = 374.300, [(M+H)-CH₃SO₃]¹⁺ = 375.200. Anal. calcd. for C₂₂H₄₇NO₅S₂ (469.74): C, 56.25; H, 10.08; N, 2.98; S, 13.65; found: C 56.09, H 10.11, N, 2.99; S, 13.69.

3. Results and Discussion

3.1 Synthesis

Esterification of L-Methionine with fatty alcohols [octadecan-1-ol (**2a**), hexadecan-1-ol (**2b**)] along with simultaneous salt formation using methane sulfonic acid

yielded two derivatives: **3a** and **3b** in high yields and pure form. Detailed protocol for the synthesis of the derivatives can be found in the *Experimental* section. Both the derivatives were found to be solids and investigated for their liquid crystalline properties using Differential Scanning Calorimetry (DSC) and Polarizing Optical Microscopy (POM).

3.2 Thermal and phase behaviour

POM images were recorded at a scan rate of 1 °C/min during heating and cooling. Identification of mesophases have been carried out by the comparison of the POM textures exhibited by the compounds (during heating and cooling cycles) with the reported^{23–25} textures. The compounds displayed Smectic C (SmC) phases during the heating and cooling cycles. Compound **3a** displayed SmC phases during both heating and cooling, while compound **3b** showed SmC phase during heating and Schlieren textures of SmC during cooling. Selected POM images of mesophases for the compounds **3a** and **3b** during heating and cooling cycles are displayed in Figure 1 and Figure 2.

The formation of the liquid crystalline phases was further confirmed by Differential Scanning Calorimetry (DSC) analysis of the synthesized derivatives. DSC analysis was carried out at a scan rate of 1 °C/min during heating and cooling. Figure 3 shows the DSC thermograms of compound **3a** and **3b**. Compound **3a** showed transitions from crystalline solid to mesophase at 53.29 °C. On cooling from the isotropic melt, a broad peak at 58.80 °C was observed corresponding to isotropic to liquid crystalline transition with an enthalpy change of 10.49 kJ/mol. Finally, a crystallization peak was observed at 46.50 °C. Compound **3b** exhibited

Figure 1. (a) Thermal optical micrograph of the SmC texture displayed by compound **3a** during heating at 53.1 °C at a scan rate of 1 °C/min (magnification = 10x; scale bar: 1000 μm) (Magnification = 10X; Scale bar: 1000 μm) (b) Thermal optical micrograph of the SmC texture displayed by compound **3b** during heating at 59.9 °C at a scan rate of 1 °C/min (Magnification = 10X; Scale bar: 1000 μm).

Figure 2. (a)-(b) Thermal optical micrograph of the SmC textures displayed by compound **3a** during first and second cooling cycles at 58.6 °C and 57.2 °C at a scan rate of 1 °C/min (magnification = 10x; scale bar: 1000 μm) (Magnification = 10X; Scale bar: 1000 μm) (c)-(d) Thermal optical micrograph of the Schlieren textures of SmC phases displayed by compound **3b** during first and second cooling cycles at 74.5 °C and 75.6 °C at a scan rate of 1 °C/min (Magnification = 10X; Scale bar: 1000 μm).

two endothermic peaks at 62.32 °C and 90.05 °C, with the first peak corresponding to a transition from crystalline solid to liquid crystalline phase and the second peak corresponding to a transition from the mesophase to isotropic liquid. Two exothermic peaks at 74.83 °C and 73.42 °C were observed during the cooling process with enthalpy values of 0.29 kJ/mol and 3.36 kJ/mol respectively, with the first peak corresponding

to a transition from the isotropic melt to liquid crystalline phase and the second peak corresponding to the transition from the mesophase to a crystalline solid (Table 1).

Compounds **3a** and **3b** were analyzed for their thermal stabilities using TG/DTA analysis at a scan rate of 10 °C/min. Figure 4 shows the TG/DTA spectra of compound **3a** and **3b**.

Figure 3. (a) DSC thermogram of compound **3a** at a scan rate of 1°C/min during heating and cooling (b) DSC thermogram of compound **3b** at a scan rate of 1°C/min during heating and cooling.

Table 1. The enthalpies (kJ/mol) and dimensionless entropies associated with the transition for compounds **3a–3b**.

Entry	Compound	R-	Phase transitions/°C (ΔH in kJ/mol)	$\Delta S/R$ (mesophase)	Nature
1	3a	C ₁₈ H ₃₅	$Cr \xrightleftharpoons[46.50^\circ C (16.93)]{53.29^\circ C} SmC \xrightleftharpoons[58.80^\circ C (10.49)]{76.00^\circ C} I$	4.57 3.80	Mesomorphic
2	3b	C ₁₆ H ₃₁	$Cr \xrightleftharpoons[73.42^\circ C (3.36)]{62.32^\circ C (4.69)} SmC \xrightleftharpoons[74.83^\circ C (0.29)]{90.05^\circ C (15.36)} I$	1.68 0.11	Mesomorphic

Note: Cr = crystalline, SmC = smectic C phase, I = isotropic phase, δH = enthalpy change, δS = entropy change, R = gas constant (8.314 J mol⁻¹ K⁻¹).

From Figure 4, it can be seen that both the compounds showed no significant loss in weight between 40 °C to 90 °C which covers the melting point range of the compound. Decomposition was observed from 250 °C to 350 °C.

3.3 Study of refractive indices

In case of a liquid crystalline compound, the polarized light encounters different refractive indices due to

different polarizations of the incident light. Refractive indices are dependent on wavelengths and operating temperatures and are influential in optimizing the performance and device design of applications like thermally induced band-gap tuning, thermally tunable LC photonic crystal fibers, etc.²⁶ They may increase or decrease according to the occurrence of reorientation of the LC molecules. Apart from molecular constituents, the most important parameters affecting the LC refractive indices are, wavelength and temperature.^{27,28}

Figure 4. (a) TG / DTA of Compound **3a** at a scan rate of 10°C/min (b) TG/DTA of Compound **3b** at a scan rate of 10°C/min.

Figure 5. (a) Plot of Refractive Indices v/s Temperature at different wavelengths for Compound **3a** (b) Plot of Refractive Indices v/s Wavelength at 45 °C for Compound **3a**.

The refractive indices of the liquid crystalline compounds are usually measured as a function of the operating temperatures and wavelength of the incident light. In this work, the refractive indices were measured in the visible region using a multiple wavelength Abbe Refractometer (DSR- λ SCHMIDT + HAENSCH) for the wavelengths: 404.7, 435.8, 486.1, 546.1, 587.6, 589.3, 632.8, 656.3 and 706.5 nm. The refractive indices were recorded by varying the temperature from 20 °C to 80 °C at an interval of 5 °C (Supplementary Information). The plots of **Refractive Indices v/s Wavelength** and **Refractive Index v/s Temperature** for compound **3a** are displayed in Figure 5.

This refractometer gives the average of both parallel and perpendicular refractive indices and hence, the refractive indices values are average of the two (equation 1).

$$\langle n \rangle = (n_e + 2n_o) / 3 \dots \dots \dots (1)$$

From Figure 5, it is clear that the refractive indices decrease with an increase in the temperature and wavelength. Thus, it can be noted that the refractive indices increase towards the blue region of the visible spectra as the wavelength decreases. A decline in the refractive indices can be observed in the range of 40–65 °C and this range corresponds to the range in which mesophases were observed during heating and cooling, which further confirms the existence of these intermediate liquid crystalline phases.

A term called ‘Abbe number’ was calculated for better characterization of this behavior. The equation to calculate Abbe number is given below (equation 2):

$$\text{Abbe number} = \frac{n_D - 1}{n_F - n_C} \dots \dots \dots (2)$$

Table 2. Optical parameters calculated from the refractive indices data.

Compound	Abbe number	Dispersive power
3a	45.99	0.0217

where,

n_D is the index for sodium D line, that is, R.I. at 587.6 nm

n_F is the index for hydrogen F line, that is, R.I. at 486.1 nm

n_C is the index for hydrogen C line, that is, R.I. at 656.3 nm

Abbe number is a quantitative measure of a material's dispersion, that is, the degree to which light is dispersed or separated when passing through a lens. When values of Abbe number are high, they indicate low dispersion.²⁹ Abbe numbers are helpful while classifying optical materials like glass in terms of their chromicity. It can be noted that a material with high Abbe number produces less chromatic aberration than the one with a lower Abbe number.²⁷ Higher values are indicative of better peripheral optics. Abbe numbers are important while designing achromatic lenses.

The reciprocal of Abbe number gives the Dispersive Power which is^{27,28} a measure of how much the colours making up of white light are spread out.

The Abbe number and Dispersive Power of compound **3a** are tabulated in Table 2.

Table 2 shows that the Abbe number value of compounds **3a** is quite high and that the dispersive power low. This could be beneficial when it comes to their applications in optics design, tunable lasers, lens design, electrically tunable LC lenses, extra low dispersion glasses, etc. LC lenses exhibit large focal length tunability and low operating voltages.³⁰ Unlike a mechanical zoom lens, the focal length of a LC lens can be tuned electrically.³¹ LC lenses have widespread applications in various fields like pico and holographic projection systems, endoscopic systems, ophthalmic lenses, etc. In imaging systems, LC lenses can help realize optical zoom and auto-focusing systems for portable devices like cellphones, camera, etc.³²

4. Conclusions

Two methane sulfonate salt derivatives of esters of L-Methionine have been successfully synthesized using biodegradable, inexpensive and readily available raw

materials and in good yields by a green, one-step and neat procedure. Both the derivatives have been found to be enantiotropic liquid crystals. They showed mesophases below 100 °C during heating and cooling and thermally stabilities upto a temperature of 250 °C. The refractive indices have exhibited a decrease with an increase in the temperature and wavelength. A decline in the R. I. values in the range in which mesophases were observed during heating and cooling, confirms the existence of the liquid crystalline phases. The Abbe number value was found to be quite high and the dispersive power low, which is beneficial in applications like optical lenses, tunable lasers, electrically tunable LC lenses, extra low dispersion glasses, etc.

Supplementary Information (SI)

Supporting Information containing IR, ¹H-NMR, ¹³C-NMR and Mass spectra of compounds **3a–3b**, DSC thermograms of compounds **3a–3b**, Refractive Indices data of compound **3a** for this article is available at www.ias.ac.in/chemsci.

Acknowledgements

The authors thank the Department of Chemistry, University of Mumbai for financial support and facilities. Sheetal Venkatesh and Pushpa Kumari Yadav also thank UGC, New Delhi for the UGC Non-NET Ph. D Research fellowship.

Compliance with ethical standards

Conflict of interest There are no conflicts of interest to declare.

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