



Three armed star mesogens based on 1,3,5-benzenetricarboxylic acid: Synthesis and mesophase characterization



A. Shanavas^{a,*}, T. Narasimhaswamy^{b,*}, E. Rotimi Sadiku^a

^aChemical, Metallurgical and Material Engineering, Polymer Technology Division, Tshwane University of Technology, Pretoria, South Africa

^bPolymer Laboratory, CSIR – Central Leather Research Institute, Adyar, Chennai 600020, India

HIGHLIGHTS

- Star mesogens containing 1,3,5-benzenetricarboxylic acid central unit, two phenyl ring side arm core, ester and azomethine linking groups and terminal alkoxy groups were synthesised.
- The structural changes made in the mesogens such as increasing the terminal chain length causes significant effect in the mesophase sequence.
- The increase of arm length stabilizes the smectic phases.
- Smectic polymorphism was observed on cooling.

ARTICLE INFO

Article history:

Received 31 July 2013

Received in revised form 11 September 2013

Accepted 18 September 2013

Available online 25 September 2013

Keywords:

Thermotropic liquid crystals

1,3,5-Benzene tricarboxylic acid

Three armed mesogens

Nematic

Smectic

ABSTRACT

A series of star mesogens based on 1,3,5-benzenetricarboxylic acid central core, side arms containing two phenyl rings, linked through azomethine groups and hexamethylene spacers, which connect the central core and side arms were synthesised via divergent approach. The mesogens synthesised and their intermediates were structurally well characterized, using FT-IR, ¹H NMR, ¹³C NMR spectroscopy and elemental analysis techniques. The mesophase characterization was carried out using a hot stage-polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques. Enantiotropic mesophases were observed for all the mesogens synthesised. An increase in the terminal chain length stabilized the smectic phase. Nematic phase was observed for the mesogens with short terminal chain length, whereas smectic polymorphism was observed on increasing the terminal chain length. XRD results suggested a tripod-like assembly of molecules in the mesophase.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The contemporary concept of designing thermotropic liquid crystals emphasizes on; shape anisometry, nanosegregation and non-linear core units [1]. Conventionally, liquid crystals were designed with rod [2–4] or disc [5,6] shaped cores. The challenge posed by banana or bent-core mesogens has in turn motivated researchers to focus on non-conventional mesogens, deviating from linear core, typical for calamitic mesogens [7]. Thus, topologically, different molecular shapes, such as; bent-core [8], multiarm or stars [9], cones [10], shuttles [11], rings [12], dendrimers [13] etc., have made inroad in liquid crystal research. These non-linear mesogens resulted in new mesophase morphologies which have paved the way for novel applications. In view of the major developments in the area of dendrons and dendrimers (multi-arm), star mesogens are gaining popularity. It is important to note

that, the open chain oligomers have been shown to exhibit interesting mesophase sequence and also serve as model compounds for liquid crystalline polymers [14]. Thus, star mesogens based on tri-functional groups, such as 1,3,5-benzenetricarboxylic acid, are classified as cyclic trimers [15]. Recently, Lehmann [16] named these cyclic trimers as 'Hekates'.

From the literature [17,18], it is found that studies on mesogens, based on 1,3,5-benzenetricarboxylic acid are relatively less and they are suitable examples of star mesogens. Aggregation behavior, charge carrier mobility and nanoscale properties of 1,3,5-benzenetricarboxylic acid core, based star mesogens with C₃ symmetry, have been reported recently [19–21]. The flexible spacers used to connect the central core and side arms would make the molecule to assemble in different ways in liquid crystalline phases, which causes the appearance of the different mesophase sequences. Yet, the studies on the spacer-containing arms are less reported. In this context, a series of spacer-containing star mesogens, are hereby reported, following their synthesis with a view to investigate the structure-property relationships.

* Corresponding authors.

E-mail address: shanavaslc@gmail.com (A. Shanavas).

2. Experimental

2.1. Materials

1,3,5-Benzenetricarbonyltrichloride, 4-hydroxybenzaldehyde, 4-butoxybenzaldehyde, 4-hexyloxybenzaldehyde, 4-nitrophenol, 6-chlorohexanol, n-bromooctane, n-bromodecane, n-bromododecane, n-bromotetradecane, n-bromohexadecane and palladium on charcoal (Pd/C, 10%) were purchased from Aldrich and used without further purification. N,N'-Dimethylformamide, tetrahydrofuran, ethanol and methanol (all obtained from SD Fine chemicals) were purified by standard procedures. Dichloromethane, ethyl acetate, diethyl ether, n-hexane, 2-butanone, acetone, potassium hydroxide (pellets), Celite-540, anhydrous potassium carbonate, anhydrous sodium sulphate were obtained from Merck (India) and used as such. Triethylamine (SD Fine chemicals) was distilled before use.

2.2. Measurements

The FT-IR spectra of samples were recorded on a Thermo-Mattson FT-IR spectrometer by the KBr pellet method. ¹H NMR and ¹³C NMR spectra of the compounds were recorded using JEOL GSX 500 NMR spectrometer; the samples were dissolved in CDCl₃ and TMS was used as an internal standard. Elemental analyses of the samples were recorded using Elemental Analyzer for CHNS, Model-Euro EA 3000, Euro Vector S.P.A.

Optical polarizing microphotographs were taken using Olympus BX50 polarizing microscope equipped with a Linkam THMS heating stage and a TMS 94 temperature programmer with a C7070 digital camera. The samples were placed between two 12 mm diameter cover slips and were heated with a programmed heating rate.

Differential scanning calorimetry calibrated for enthalpy and temperature was performed using TA Instruments Q-10 series. The experiments were carried out in nitrogen atmosphere at a heating rate of 10 °C/min. Each sample (~5 mg) was subjected to two heating and two cooling cycles and data obtained from the 2nd heating and 2nd cooling cycles were considered for discussion. Samples were crimped in aluminium pans in order to ensure good thermal contact between the sample and the pan.

Small-angle X-ray scattering spectra were measured with an evacuated high performance SAXS instrument "SAXSess" (Anton Paar KG, Graz, Austria). The "SAXSess" was attached to a conventional X-ray generator (Philips, Holland) equipped with a sealed X-ray tube (a Cu anode target type, producing Cu K α X-ray radiation with a wavelength of 0.154 nm), operating at 40 kV and 50 mA. The samples were measured as past cell method. The scattered X-ray intensities were detected with a 2D-imaging plate detection system Cyclone (Packard, A Packard Bioscience Company) with a spatial resolution of 50 \times 50 μ m per pixel and at sample-to-detector distance of 265 mm. A measuring time of 30 s yielded sufficient measuring statistics. Scattering data that were read off from the imaging plate and were first corrected for the absorption of the X-rays in the sample and later transformed to the *q*-scale ($q = 4\pi/\lambda \cdot \sin \theta/2$; program SAXS Quant; Anton Paar KG, Graz, Austria). The SAXS measurements were further corrected for the empty cell.

2.3. Synthesis

2.3.1. 6-(4-Nitrophenoxy)hexan-1-ol (1)

In a 500 mL two necked flask, 12.5 g (90 mmol) of K₂CO₃ and 11.8 g (85 mmol) of 4-nitrophenol were measured and dissolved in 200 mL of DMF. The solution was stirred and heated to 90 °C,

followed by the drop-wise addition of 100 mL DMF solution containing 12.3 g (90 mmol) of 6-chlorohexanol. The temperature of the mixture was maintained at 90 °C for 4 h. Then, the reaction mixture was allowed to cool to room temperature and subsequently poured into 1 L of distilled water in order to obtain a precipitate. The precipitate was filtered, washed with distilled water and dried under vacuum. The product was recrystallised in 1:3 ratio of ethyl acetate-hexane mixed solvent. The solid product was pale yellow in color.

Yield: 74%. Melting point: 66–67 °C. IR (KBr, cm⁻¹): 3522 (–OH_{str}), 2950 and 2860 (–CH_{2str}), 1596 and 1504 (C=C_{str} aromatic), 1463 (–CH_{ben}), 1336 (–NO_{2str}), 1260 and 1108 (C–O–C_{str}). ¹H NMR ppm (CDCl₃): δ 8.13 (d, 2H), 6.89 (d, 2H), 4.00 (t, 2H), 3.63 (t, 2H), 1.90 (bs, –OH), 1.79 (m, 2H), 1.56 (m, 2H), 1.45 (m, 4H). ¹³C NMR ppm (CDCl₃): δ 164.30, 141.32, 125.95, 114.47, 68.82, 62.74, 32.63, 28.99, 25.81, 25.55. Elemental analysis: calcd. (%) for C₁₂H₁₇NO₄: C 60.23, H 7.16, N 5.85; found: C 60.01, H 6.97, N 5.63.

2.3.2. Tris[(4-nitrophenoxy)hexyl]benzene-1,3,5-tricarboxylate (2)

55 mmol (1) and 5.5 g (55 mmol) of triethylamine were dissolved in 200 mL of 2-butanone. To this solution, a 100 mL of 2-butanone solution containing 4.8 g (18.3 mmol) of 1,3,5-benzenetricarbonyltrichloride was added drop wise at 0 °C and the reaction mixture was stirred for 3 h at room temperature. Then the triethylamine salt was filtered off and then the solvent was evaporated. The solid product obtained was recrystallized in 1:3 ratio of acetone-methanol mixed solvent. The solid product obtained was pale yellow in color.

Yield: 55%. m.p.: 71–73 °C. IR (KBr, cm⁻¹): 3064 (CH_{str} aromatic), 2954 and 2874 (–CH_{2str}), 1724 (C=O_{str} ester), 1597 and 1504 (C=C_{str} aromatic), 1448 (–CH_{ben}), 1340 (–NO_{2str}), 1260 and 1109 (C–O–C_{str} of ester). ¹H NMR ppm (CDCl₃): δ 8.81 (s, 3H), 8.16 (d, 6H), 6.90 (d, 6H), 4.39 (t, 6H), 4.05 (t, 6H), 1.84 (m, 6H), 1.63 (m, 6H), 1.55 (m, 12H). ¹³C NMR ppm (CDCl₃): δ 165.15, 164.20, 141.39, 134.53, 131.48, 126.00, 114.46, 68.68, 65.76, 28.92, 28.63, 25.80, 25.73. Elemental analysis: calcd (%) for C₄₅H₅₁N₃O₁₅: C 61.84, H 5.88, N 4.80; found: C 61.61, H 5.72, N 4.58.

2.3.3. Synthesis of Tris[(4-aminophenoxy)hexyl]benzene-1,3,5-tricarboxylate (3)

9.92 mmol of the compound (2) was reduced under hydrogen atmosphere in the presence of 10% Pd-charcoal catalyst in a 100 mL of 1:1 mixture of ethanol and tetrahydrofuran at room temperature for 48 h. Pd/C catalyst was removed by filtering the reaction mixture through Celite-540 filtering aid and evaporation of the solvents, yielded the product. The product was recrystallised in 1:3 mixture of ethyl acetate and hexane. The solid product was reddish brown in color.

Yield: 92%. m.p.: 78–80 °C. IR (KBr, cm⁻¹): 3467 and 3387 (–NH_{2str} free amine), 2934 and 2860 (–CH_{2str}), 1724 (C=O_{str} ester), 1634 (–NH_{ben}), 1513 (C=C_{str} aromatic), 1472 (–CH_{ben}), 1239 (C–O–C_{str} of ester). ¹H NMR ppm (CDCl₃): δ 8.82 (s, 3H), 6.72 (d, 6H), 6.61 (d, 6H), 4.37 (t, 6H), 3.88 (t, 6H), 1.83 (m, 6H), 1.76 (m, 6H), 1.51 (m, 12H). ¹³C NMR ppm (CDCl₃): δ 165.20, 152.30, 139.82, 134.02, 131.55, 116.51, 115.70, 68.50, 65.80, 29.40, 28.70, 25.88. Elemental analysis: calcd (%) for C₄₅H₅₇N₃O₉: C 68.94, H 7.32, N 5.36; found: C 68.78, H 7.21, N 5.14.

2.3.4. Synthesis of 4-alkoxybenzaldehydes 4(c-g)

Synthetic procedures and analytical data of 4-alkoxybenzaldehydes 4(c-g) are given in supporting information. **4a** and **4b** were purchased from Aldrich, India.

Download English Version:

<https://daneshyari.com/en/article/1405843>

Download Persian Version:

<https://daneshyari.com/article/1405843>

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