



Isophthalic acid based mesogenic dimers: Synthesis and structural effects on mesophase properties

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HIGHLIGHTS

- ▶ Mesogenic dimers containing two and three phenyl ring side arm core were synthesized.
- ▶ The structural changes made in the mesogens causes significant effect in the melting and clearing temperatures.
- ▶ The increase of arm length stabilizes the enantiotropic fashion.
- ▶ Smectic polymorphism was observed on cooling.

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ABSTRACT

Two series of mesogens based on isophthalic acid and side arms containing two and three phenyl rings linked through azomethine or ester groups were synthesized via divergent approach. Another type of structurally similar mesogen was synthesized via convergent approach in which the azomethine groups were replaced by ester groups. All the synthesized mesogens and their intermediates were structurally well characterized using FT-IR, ¹H NMR, ¹³C NMR and EI-MASS spectrometry. The mesophase characterization was carried out using hot stage-polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques. The structural changes made in the mesogens i.e. increase of terminal chain length and replacement of azomethine groups with ester groups decreased the transition temperatures whereas the increase of side arm length improves the phase stability to a wide temperature range. Nematic phase was observed for the mesogens with short terminal chain length whereas the smectic polymorphism was observed on increasing the terminal chain length. The structural modification (three ring) on the side arm core stabilizes the mesophases enantiotropically.

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1. Introduction

Thermotropic liquid crystals are important functional materials [1]. The unique combination of order and mobility present in these materials made them as stimuli responsive [2]. Apart from the conventional liquid crystals of rod [3–6] and disc [7,8] shaped molecules, a wide variety of molecular shapes includes V or bent-core [9], T [10], H [11], λ [12], ∈ [13], ψ [14], dimers [15–17], stars [18,19] and dendrimers [20,21] are continuously gaining importance due to the self assembly of these molecules forming the new mesophase structures which are very much interesting for investigation. In recent years, liquid crystalline dimers or dimeso-

gens or twins have attracted much attention not only because of exhibiting variety of mesophases but also they serve as useful model compounds for liquid crystalline polymers [22–24]. Generally, a liquid crystal dimer is designed with two identical or non-identical mesogenic groups linked, often, via a flexible spacer or, more rarely, through a rigid unit. Literature search indicates isophthalic acid [25], 1,3-diaminobenzene [26] and resorcinol [27], etc. are used as rigid central connecting units in liquid crystal dimers and the mesogens based on these molecules exhibiting lamellar, banana, and columnar mesophases. The research works on mesogenic dimers with oxymethylene spacer connecting the central rigid unit and mesogenic unit are less reported [28].

In this context, here we report two series of isophthalic acid-based mesogenic dimers with ester and azomethine linkages and a structurally similar mesogenic dimer without azomethine linkage. In both the series, hexamethylene spacer is used to connect

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the central and mesogenic units. These mesogens are designed in such a manner to investigate the influence of side arm core length, linking unit and terminal chain length on the mesomorphic behavior and mesophase stability. Variation in the side arm core length and in the terminal chain length is found to improve the liquid crystalline property of mesogens.

2. Experimental

2.1. Materials

Bis[(4-aminophenoxy)hexyl]benzene-1,3-dicarboxylate (**1**) was synthesized using the reported procedure [29]. 4-Ethoxybenzaldehyde (**2a**), 4-hexyloxybenzaldehyde (**2b**), 4-hydroxybenzaldehyde, 4-dodecyloxybenzoic acid, 4-octyloxybenzoic acid, 4-ethoxy benzoic acid, 6-Chlorohexanol, *n*-bromododecane, 4-benzyloxyphenol, palladium on charcoal (Pd/C, 10%), *N,N'*-dicyclohexylcarbodiimide (DCC) and *N,N*-dimethylaminopyridine (DMAP) were purchased from Aldrich and used without further purification. *N,N*-Dimethylformamide, tetrahydrofuran, isopropanol, 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 sulfate, silica gel (100–200 mesh) were obtained from Merck (India) and used as such. Triethylamine (SD Fine chemicals) was distilled and used.

2.2. Measurements

The FT-IR spectra of samples were recorded by the KBr pellet method on a Thermo-Mattson FT-IR spectrometer. 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. The EI mass spectra were recorded using a JEOL DX-303 spectrometer. Polarizing optical microphotographs were taken using Olympus BX50 polarizing microscope equipped with a Linkam THMS heating stage, and TMS 94 temperature programmer with a C7070 digital camera. The samples were placed between two 12 mm 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 was subjected to two heating and cooling cycles and the data obtained from second heating and cooling was considered for discussion. All the samples were crimped in aluminum pans 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 (Cu anode target type producing Cu K α X-rays 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 the spatial resolution of 50 × 50 μ m per pixel at sample to detector distance of 265 mm. The measuring times of 30 s yielded sufficient measuring statistics. Scattering data that were read off from the imaging plate were first corrected for the absorption of the X-rays in the sample and 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. 4-Dodecyloxybenzaldehyde (**2c**)

In a 500 mL two necked flask, 12.5 g (90 mmol) of K₂CO₃ and 11.8 g (85 mmol) of 4-hydroxybenzaldehyde were taken and dissolved in 200 mL of DMF. The mixture was stirred and heated to 90 °C followed by the drop wise addition of 100 mL of DMF solution containing 22.4 g (90 mmol) of *n*-bromododecane. The temperature of the mixture was maintained at 90 °C for 5 h. Then the reaction mixture was poured into 1 L of distilled water; the product was extracted with 300 mL (3 × 100 mL) of diethyl ether. The organic layer was washed with 5% aqueous KOH solution followed by brine, dried over anhydrous sodium sulfate. The residue obtained after removal of the solvent was washed with hexane. The product was colorless liquid.

Yield: 73%. ¹H NMR ppm (CDCl₃): δ 9.80 (s, —CHO), 7.74 (d, *J* = 8.0, 2H), 6.92 (d, *J* = 8.0, 2H), 3.96 (t, *J* = 6.0, 2H), 1.74 (p, *J* = 5.5, 2H), 1.40 (p, *J* = 5.5, 2H), 1.27 (m, 16H), 0.82 (t, *J* = 5.5, 3H). ¹³C NMR ppm (CDCl₃): δ 190.72, 164.31, 131.99, 129.77, 114.76, 68.43, 31.98, 29.73, 29.68, 29.55, 29.41, 29.38, 29.12, 26.02, 22.75, 14.18. IR (KBr, cm⁻¹): 2924 and 2853 (—CH_{2str}), 2732 (—CHO), 1695 (C=O_{str} ester), 1601, 1577 and 1508 (C=C_{str} aromatic), 1467 (—CH_{ben}), 1159 (C—O—C_{str}). EI-MS *m/z*: 290.1 (M⁺).

2.3.2. 4-(4-Alkoxybenzoyloxy)benzaldehydes (**3a–c**)

Eighteen millimole of 4-ethoxybenzoic acid or 4-octyloxybenzoic acid or 4-dodecyloxy benzoic acid and 18 mmol (2.2 g) of 4-hydroxybenzaldehyde were taken and were dissolved in 60 mL of THF. To this stirred solution, dicyclohexylcarbodiimide (18 mmol) dissolved in 20 mL of THF was added followed by the addition of 4-dimethylaminopyridine (1.8 mmol) and stirring was continued at room temperature for overnight. Filtration of solid dicyclohexyl urea and subsequent evaporation of the solvent yielded a solid that was purified by recrystallization in isopropanol. The product was colorless crystalline solid.

2.3.3. 4-(4-Ethoxybenzoyloxy)benzaldehyde (**3a**)

Yield: 75%. m.p.: 120–122 °C. ¹H NMR (CDCl₃): δ 10.00 (s, —CHO), 8.14 (d, *J* = 8.5, 2H), 7.96 (d, *J* = 8.5, 2H), 7.39 (d, *J* = 8.0, 2H), 6.98 (d, *J* = 8.5, 2H), 4.13 (q, *J* = 6.0, 2H), 1.45 (t, *J* = 5.5, 3H). ¹³C NMR (CDCl₃): δ 191.15, 164.34, 163.75, 155.99, 133.96, 132.55, 131.35, 122.72, 120.93, 114.49, 63.98, 14.75. IR (KBr, cm⁻¹): 2937 and 2823 (—CH_{2str}), 2736 (—CHO), 1731 and 1690 (C=O_{str} ester), 1604 and 1506 (C=C_{str} aromatic), 1460 (—CH_{ben}), 1272 (C—O—C). EI-MS *m/z*: 270.1 (M⁺).

2.3.4. 4-(4-Octyloxybenzoyloxy)benzaldehyde (**3b**)

Yield: 75%. m.p.: 54–55 °C. ¹H NMR (CDCl₃): δ 9.99 (s, —CHO), 8.13 (d, *J* = 8.0, 2H), 7.94 (d, *J* = 8.0, 2H), 7.39 (d, *J* = 8.0, 2H), 6.97 (d, *J* = 8.0, 2H), 4.02 (t, *J* = 6.0, 2H), 1.81 (p, *J* = 5.5, 2H), 1.46 (p, *J* = 5.5, 2H), 1.32 (m, 8H), 0.88 (t, *J* = 6.0, 3H). ¹³C NMR (CDCl₃): δ 191.11, 164.32, 163.96, 155.99, 133.95, 132.52, 131.32, 122.71, 120.86, 114.51, 68.47, 31.89, 29.42, 29.33, 29.16, 26.07, 22.75, 14.22. IR (KBr, cm⁻¹): 2914 and 2846 (—CH_{2str}), 2736 (—CHO), 1736 and 1692 (C=O_{str} ester), 1602 and 1507 (C=C_{str} aromatic), 1465 (—CH_{ben}), 1272 (C—O—C_{str} of ester). EI-MS *m/z*: 354.3 (M⁺).

2.3.5. 4-(4-Dodecyloxybenzoyloxy)benzaldehyde (**3c**)

Yield: 75%. m.p.: 48–49 °C. ¹H NMR ppm (CDCl₃): δ 10.00 (s, —CHO), 8.13 (d, *J* = 7.5, 2H), 7.94 (d, *J* = 7.5, 2H), 7.39 (d, *J* = 7.0, 2H), 6.97 (d, *J* = 7.5, 2H), 4.02 (t, *J* = 6.0, 2H), 1.81 (p, *J* = 5.5, 2H), 1.46 (p, *J* = 5.5, 2H), 1.30 (m, 16H), 0.87 (t, *J* = 5.5, 3H). ¹³C NMR ppm (CDCl₃): δ 191.12, 164.34, 163.97, 156.00, 133.95, 132.52, 131.32, 122.71, 120.86, 114.51, 68.47, 32.02, 29.75, 29.74, 29.69, 29.66, 29.45, 29.16, 26.07, 22.79, 14.24. IR (KBr, cm⁻¹): 2916 and 2849 (—CH_{2str}), 2733 (—CHO), 1734 and 1694 (C=O_{str} ester),

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