



Effect of azo and ester linkages on rod shaped Schiff base liquid crystals and their photophysical investigations



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ABSTRACT

Two new series of rod shaped Schiff base containing liquid crystal compounds with azo and ester linkages have been synthesized and characterized respectively. The rod like molecules containing cinnamate linkages with four different alkyl spacers ($n = 6, 8, 10$ and 12) and influence of linking group have been elucidated. Considerable changes in mesomorphic properties were noticed starting from Nematic to Smectic-C on changing of azo and ester linkages along with different terminal alkyl chain lengths. The mesomorphic properties of both series are compared. Photosensitive azobenzene group undergoes photoisomerization under UV light and monitored by UV–Visible spectroscopy.

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1. Introduction

Azobenzene based liquid crystalline material have been frequently discussed for their sensitivity of chromophoric group towards light and found to exhibit interesting optical properties, enable us to study the materials in holography, optical storage device, optical switching and establish widespread applications in display technology [1–5]. By virtue of their fluidity and translational periodicity, liquid crystal molecules are more easily induced into a new arrangement when triggered by an electric field [6,7], temperature [8–10], and light [11–16]. Photo-induced phenomenon is one of the research domain which include incident light brings about molecular ordering and disordering of liquid crystalline system [17]. The designing of liquid crystalline compounds containing double bond as an additional functional group in their molecular structure brings special features. The double bond present in cinnamic acid has already been of research interest in the domain of liquid crystals [18]. Thus upon bringing a double bond in the skeletal frame work enables the compound to have mesomorphic properties [19], photoisomerization and photo-crosslinking in the liquid crystalline state [20].

The rigid skeleton of rod like azobenzene structure and ester

linkage aligns themselves as suitable candidates for exhibiting liquid crystal properties [21–24]. Nevertheless, the inimitable characteristics of azobenzene molecules provide prospect of molecular motion in response to heat or light and thus offer many chances in photonic applications. The azo moiety is usually incorporated into cinnamate ester backbone to form liquid crystal depending upon the terminal substituents of azobenzenes [25]. Azobenzene molecules are known to exhibit reversible photoisomerization transformations upon irradiation with UV–visible light [26]. Azo linkage based low and high molecular weight liquid crystalline materials have received attention ascribed to their unique photo-switchable properties induced by light [27–30]. This reveals that azo-cinnamate ester with Schiff base linkage in the skeleton of compound have advantages over substances with other linkages such as ester and silyl group. Several studies reported on ester with Schiff base containing benzene and naphthalene core on liquid crystals. Dave and Prajapati [31] have synthesized rod like liquid crystal materials for number of Schiff base homologous series containing naphthalene moiety. Recently, Prajapati et al. have also reported a few mesogenic homologous series of Schiff base esters [32] and azo-esters [33] based rod like mesomorphic nature of naphthalene group.

In the present work, an attempt has been made to study the mesophase stabilities of azomethine-azo and azomethine-ester as part of the frame work which hitherto unreported in the literature. This led us to prepare such compounds that would help further in

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understanding the effect of central linkage and spacer length on mesomorphism. Herein, the Schiff base containing two series of molecules consist of linking group azo and ester respectively connected to terminal alkyl chains with even number of carbon atoms (6, 8, 10 and 12). Furthermore, this observation assumes significance from the fact that introduction of azo linkage in the first series involve in a new dimension to this field, namely photochromism. These cinnamate ester based azobenzene groups undergo photochemical process in tetrahydrofuran also discussed. The two series have rod shaped cinnamate molecules bearing one side alkyl chain length with azomethine-azo and ester-azomethine linkages respectively with different chain length. Being geometrically closely related to known rod shaped molecules, upon introduction of cinnamate group, containing azo and ester linkages, these systems provided improved liquid crystalline property.

The mesomorphic behaviour was controlled mainly by length of alkyl chain and olefinic character containing cinnamate group. The amine containing azo and ester linking group connected to central core of cinnamate linkage to form Schiff base and changes mesomorphic textures with unique sequence of Nematic and Smectic phases have been noticed. Structural parameters of different calamitic phases were analysed and compared. The synthesis of rod shaped liquid crystal compounds is depicted in Scheme 1.

2. Experimental

2.1. Techniques and materials

All the chemicals and solvents were obtained from commercial sources. The crude samples were purified by column chromatography using silica gel (400 mesh). Thin layer chromatography was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60 and F254). The infrared spectra of compounds were recorded using KBr disk in Perkin Elmer FT-IR spectrometer. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were performed on a Bruker spectrometer using TMS as an internal standard. Compositions of the compounds were determined by Heraeus CHN elemental analyzer. The enthalpies of transitions were determined

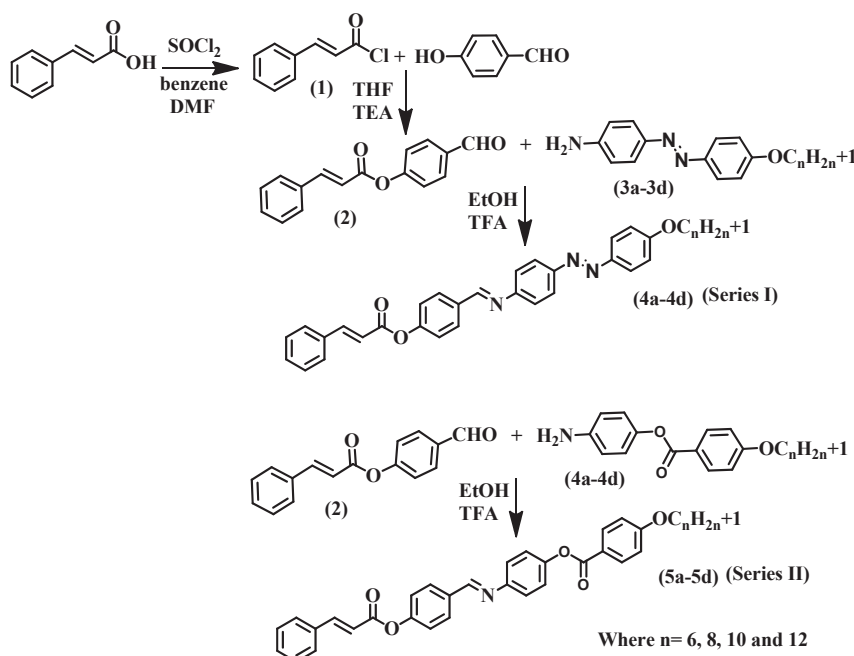
from thermogram recorded on a differential scanning calorimeter on heating/cooling run at a rate of $5\text{ }^\circ\text{C min}^{-1}$. The transition temperatures for the compounds were determined using a Linkem HFS91 hot stage and controlled processor in conjunction with Linkem HFS91 polarizing optical microscope with a TP-93 temperature programmer connected to 1000D camera. Samples were placed in between two thin glass cover slips and melted with heating and cooling at the rate of $2\text{ }^\circ\text{C min}^{-1}$. UV absorption spectra were recorded on a UV-1650PC UV-Vis absorption spectrophotometer (Shimadzu). The chloroform solution was prepared with concentration of $1 \times 10^{-5}\text{ M}$.

2.2. Synthesis of 4-formylphenyl cinnamate (2)

The cinnamoyl acid chloride (1) (5 gm, 3.37 mmol) was added drop wise to the reaction mixture containing 4-hydroxybenzaldehyde (4.12 gm, 3.37 mmol) and triethylamine (3.35 mmol) dissolved in dry THF and stirred for 24 h. After completion of reaction, triethylamine hydrochloride was precipitated out and removed by filtration. The crude product was subjected to column chromatography (hexane:ethylacetate (95:5%)) to obtain colorless compound 2. Yield: 77%. M.p: $120\text{ }^\circ\text{C}$. Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_3$: C, 76.18; H, 4.79. Found (%): C 75.72, H 4.21. FT-IR (KBr pellet, cm^{-1}): 2856–2921 cm^{-1} (C–H str. aliphatic), 1727 cm^{-1} (C=O str. of ester), 1608 cm^{-1} (C=C str. vinyl group of cinnamate), 1494 cm^{-1} (C=C str. of aromatic), 1255–1023 cm^{-1} (C–O–C str. of alkoxy), 1102 cm^{-1} (C–O str. of ester). ^1H NMR (400 MHz, CDCl_3) δ 9.90 (s, 1H, CHO), 7.86 (d, 2H, $J = 8.6\text{ Hz}$, aromatic-H), 7.84 (d, 2H, $J = 8.6\text{ Hz}$, aromatic-H), 7.83 (d, 2H, $J = 8.3\text{ Hz}$, aromatic-H), 7.79 (d, 2H, $J = 8.5\text{ Hz}$, aromatic-H), 7.31–7.28 (d, 1H, $J = 8.1\text{ Hz}$, aromatic-H), 7.51 (d, $J = 14.2\text{ Hz}$, 1H, olefinic-H), 6.56–6.52 (d, $J = 14.4\text{ Hz}$, 1H, olefinic-H). ^{13}C NMR (100 MHz, CDCl_3) δ 115.54, 121.38, 127.39, 128.03, 130.19, 132.88, 146.51, 154.54, 163.59, 189.92.

2.3. Synthesis of 4-((E)-4-(cinnamoyloxy)benzylidene)amino phenyl 4-(hexyloxy) benzoate (4a)

4-Aminophenyl 4-(hexyloxy)benzoate (3)(0.1 gm, 0.39 mmol)



Scheme 1. Synthesis of rod shaped liquid crystal compounds.

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