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## MESOGENIC NAPHTHYL WITH AZOMETHINE CENTRAL LINKAGES

## RESEARCH ARTICLE

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### ABSTRACT

New mesogenic homologous series of liquid crystalline namely, 2''-Naphthyl- [4-(4'-n-alkoxy benzylideneamino) benzoates (I) having naphthalene moiety with diverse central linkages have been synthesized and characterized by an elemental analysis and standard spectroscopic methods. In series (I), all the twelve synthesized compounds reveal mesomorphism. Methoxy to n-tetra decyloxy derivatives revealed enantiotropic nematic mesophase. The SmA mesophase commences from n-pentyloxy derivative as a enantiotropic and persist up to the last homologue synthesized. All the twelve compounds exhibit mesomorphism.

KEYWORDS: Naphthalene moiety, mesomorphism and azomethine.

### INTRODUCTION

Polymers containing mesogenic side groups attached laterally in the main chain are known as side chain liquid crystalline polymers (SCLCPs) because of their liquid crystalline bulk properties[1]. SCLCPs reveal distinctive properties such as high heat resistance, flame retardant, comparatively low cost and etc., which depend on the diverse parameters, such as, the nature and length of the spacer, the type of mesogen[2–4] and the nature of the polymer backbone. Altering the length of alkyl chain has often been used as an easy and systematic way by which to understand trends in phase transition temperatures[5]. However, many other structural factors can also be manipulated in order to adjust the melting and clearing temperatures as well as the mesophase temperature ranges like, introduction of terminal[6] or lateral[7] fluorine-containing units, the introduction of double bonds into the terminal chains[8] and the introduction of a cyano group[9]; each of these approaches has been shown to exert a great impact on transition temperatures as well as on mesogenic properties. Symmetry lowering has also played a significant position in controlling the transition temperatures and temperature ranges of liquid crystals[10].

A vast number of mesogenic naphthalene derivatives are reported in the literature [11–16], as naphthalene derivatives exhibit wealthy mesomorphism if properly designed. The intention of synthesis is to keep on the investigate for new mesogenic compounds containing a naphthalene moiety and to study the effect of naphthalene moiety and diverse central linkages on mesomorphism.

### EXPERIMENTAL

IR spectra were resolved by Shimadzu IR-408 spectrophotometer. <sup>1</sup>H NMR spectra were gained with a Perkin-Elmer R-32 spectrometer. The phase assignments and transition temperatures were resolved by thermal polarizing optical microscopy using a polarizing microscope (Leitz Laborlux 12 POL) equipped with a heating stage.

**Synthesis of 2''-Naphthyl-[4-(4'-n-alkoxybenzylideneamino) benzoates(I) [Series I]:** Twelve Schiff's bases of series I were synthesized by condensing equimolar quantities of 4-n-alkoxybenzaldehydes[17] and 4-aminobenzoic acid in boiling ethanol[18]. 0.1 Mole of 4-(4'-n-alkoxybenzylideneamino)benzoic acids [B], 0.1 mole of 2-naphthol, 0.1 mole of DCC[19] and 0.1 mole of DMAP were dissolved in dry THF and stirred at room temperature for overnight. The crude product was repeatedly crystallized from the ethanol. UV Spectrum (MDC) nm: 325, IR spectrum (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3066, 2929, 1724 (-COO-), 1627, 1591 (-CH=N-), 1510, 1411, 1260, 1165, 889, 813, 744.  $^1\text{H}$  NMR(400 MHz):  $\delta$  0.90 (t, 3H, -CH<sub>3</sub>), 1.2-1.57 (m, 26H, 13 x -CH<sub>2</sub>-), 1.85 (quant., 2H, Ar-O-C-CH<sub>2</sub>-), 4.02 (t, 2H, O-CH<sub>2</sub>-), 6.80 (d, 2H, Ar-H at C-3' and C-5'), 7.36 (d, 2H of naphthalene ring system at C-3'' and C-4''), 7.47-7.51(m, 4H of naphthalene ring system at C-5'', C-6'', C-7'' and C-8''), 7.70 (s, 1H of naphthalene ring system at C-1''), 7.80-7.90 (m, 4H, Ar-H at C-2, C-6, C-2' and C-6'), 8.27 (d, 2H, Ar-H at C-3 and C-5), 8.39 (s, 1H -CH=N-).

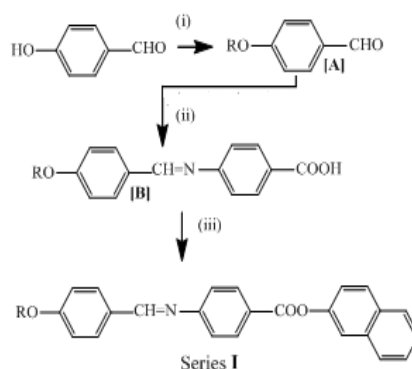


Fig. 1 Scheme 1: Synthetic route to series I compounds

Where, R = -C<sub>n</sub>H<sub>2n+1</sub>, n = 1 to 8, 10, 12, 14 and 16. (i) R-Br, Anh.K<sub>2</sub>CO<sub>3</sub>/Dry acetone (ii) 4-Amino benzoic acid/hot ethanol, acetic acid (iii) 2-Naphthol, DCC, DMAP, Dry THF (iv) NaNO<sub>2</sub>, HCl, 0-5°C (v) 0-10°C, Phenol/NaOH (vi) R-Br, Ethanol/KOH.

## RESULTS AND DISCUSSION

As initial study, the mesophases revealed by compounds of series I was concluded by the optical microscopic studies. On cooling, isotropic liquids of series I compounds ( $n=1-14$ ) formed small droplets that coalesced to the classical schlieren texture of the nematic phase (Plate 1) and *n*-pentyloxy to *n*-tetradecyloxy derivatives on further cooling exhibited focal conic texture characteristic of smectic A mesophase (Plate 2). On cooling, isotropic liquids of *n*-hexadecyloxy derivatives exhibited focal only conic texture characteristic of smectic A mesophase.

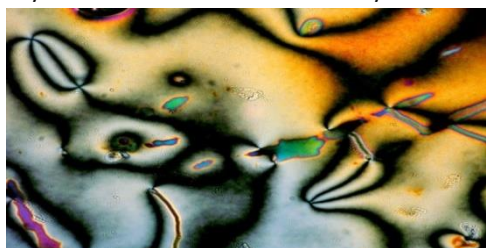


Plate 1: Microphotograph of schlieren texture of nematic mesophase (Series I;  $n=14$ ) at 190 °C

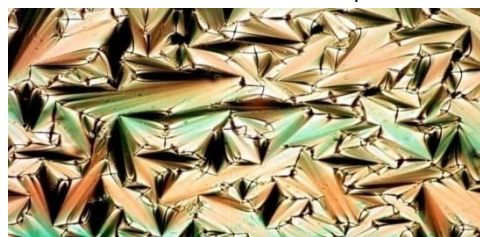


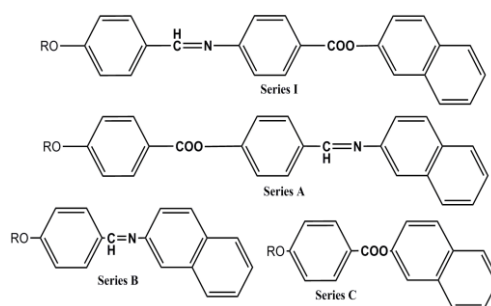
Plate 2: Microphotograph of focal conic texture of SmA mesophase (Series I;  $n=14$ ) at 125 °C

Fig. 2 Microphotograph of schlieren texture of phase.

All the twelve compounds synthesized exhibit mesomorphism. Methoxy to *n*-tetradecyloxy derivatives exhibited enantiotropic nematic mesophase. The SmA mesophase commences from *n*-pentyloxy derivative as an enantiotropic and persist up to the last homologue synthesized. The transition temperatures are recorded, which exhibited rising tendency in SmA-N transition temperatures, N-I transition temperatures decrease with the increase in the length of terminal alkoxy chain and exhibit usual odd-even effect. The crystal melting transition temperatures decrease with the increase in the length of terminal alkoxy chain with the exception of compounds 3, 4 and 12 in series.

The analysis of mesophase length, phase transition and comparative molecular structure of *n*-dodecyloxy derivative of Series I and A to C, shows that the smectic mesophase length of series I is higher by 54°C, whereas the smectic thermal stability is higher by 118°C, whereas the nematic mesophase length thermal stability of series I is higher by 39°C and 157°C, respectively than series C. Both the compounds differ in the number of benzene ring and central linkage. Series I is longer and more polarizable as compared to the series C due to the presence of additional azomethine central linkage and benzene moiety, which is responsible for the greater mesophase length and higher thermal stabilities of series I. The smectic and nematic thermal stability of series I are higher by 23°C and 30°C respectively, compared to series A. It seems that due to presence of flexible ester group near the naphthalene moiety the molecules are packed in such a way that its thermal stability becomes little higher compared to series A.

The smectic mesophase length and thermal stabilities of series I is higher by 58°C and 104°C respectively, as well as nematic mesophase length and thermal stability is also higher by 45°C and 149°C respectively as compared to series C. The molecule of series I and C are differ in the number of phenyl ring and central linkage. The molecule of series I is more longer and polarizable due to the additional phenyl ring and central linkage, which is responsible for the greater mesophase length and higher thermal stability for series I. The series I exhibit mesomorphic properties with good mesophase length and higher thermal stabilities.



Where R = -C<sub>12</sub>H<sub>25</sub>

Fig. 3 Structures of various series.

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