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# Synthesis and mesomorphic properties of 2,4-bis(4'-n-pentyloxybenzoyloxy)- benzylidine-4"n-alkoxyaniline

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#### ABSTRACT

The synthesis and mesomorphic properties of a new series of 2,4-bis(4'npentyloxybenzoyloxy)- benzylidine-4" -n-alkoxyaniline (DC5An) are reported. The molecular structure of compounds was confirmed by FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, mass spectroscopy and elemental analysis. The mesomorphic properties were studied by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) measurements. All compounds of the series exhibit nematic (N) and smectic C (SmC) phases. The first four homologues (DC5A1-DC5A4) display a N mesophase, whereas the highest homologues (DC5A5-DC5A10) exhibit an enantiotropic dimorphism N and SmC phases. The mesomorphic properties of the present series are compared and discussed with other structurally related series. **KEYWORDS** 

Enantiotropy; lateral substituent; mesomorphism; mesogen; nematic; smectic

### Introduction

For low molecular weight mesomorphic compounds, a major point receiving great attention is the detailed analysis of the relationship between chemical composition, structure, and mesomorphic properties [1–3]. Mesomorphic materials have become good candidates for a potentially wide range of applications, such as in the optical, electrical, and biological medical fields [4–14].

Aromatic azomethine ester comprising of different polarity of substituents has been known to either promote or suppress the mesomorphic properties [15, 16]. The aromatic esters are known for their thermal stability, easy synthesis, and relative resistance to hydrolysis [17].

In this work, we describe the synthesis and mesomorphic properties of homologous series containing three rings in the main core linked through ester and azomethine central linkages and substituted by a lateral aromatic branch on the central benzene ring, and investigated the influence of the lateral alkoxy group on mesomorphism.

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## Experimental

## Materials

4-Hydroxyacetanilide, 2,4-dihydroxybenzaldehyde, tetrahydrofuran (THF), triethylamine (Et<sub>3</sub>N), benzene, absolute ethanol, thionyl chloride, potassium hydroxide, 4-hydroxybenzoic acid, hydrochloric acid, sodium carbonate, and glacial acetic acid were of reagent grade obtained from Sigma-Aldrich Chemicals and used as received.

#### Instrumentations

Elemental analyses (C, H, N) were carried out using a Perkin-Elmer model 2400 instrument. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained with Avance III Bruker 500 MHz instrument using tetramethylsilane as the internal standard. Infrared spectra were recorded on a Shimadzu 8000 FTIR spectrophotometer in the wave number range 4000–400 cm<sup>-1</sup> using KBr discs or films. Mass spectra were recorded on IEOL JMS-7 high resolution instrument.

The optical behavior observations were made using Olympus BX40 microscope equipped with a Leitz Laborlux 12 Pols hot stage and PR600 controller. The textures shown by the compounds were observed using polarized light with crossed polarizer (POM) with the sample in a thin film sandwiched between a glass slide and cover slip. Photographs of texture were obtained using a camera Olympus PM-10AD model. The transition temperatures and enthalpies were investigated using differential scanning calorimetry DSC (TA instruments Q1000 DSC), ramp rate: 10°C per min under nitrogen atmosphere. Temperature and heat flow calibrated with standard indium of purity <99.99%.

#### Synthesis

4-n-pentyloxybenzoic acid, 4-n-pentyloxybenzoyl chloride, 4-n-alkyoxyacetanilides, and 4-n-alkoxyanilines were prepared using conventional methodologies [18, 19]. 2,4-Bis(4'-n-heptyloxybenzoyloxy) benzaldehyde (DC5) was synthesized by the method of Pugh and Schrock and Zhou et al. [20, 21].

# Synthesis of series 2,4-bis(4'-n-heptyloxybenzoyloxy)-benzylidine-4"-n-alkyloxyaniline (DC5An)

2,4-Bis(4'-n-pentyloxybenzoyloxy) benzaldehyde (0.31 g, 0.5 mmol) and 4-n-alkyloxyanilines (0.5 mmol) and a few drops of glacial acetic acid as catalyst in (10 mL) of an absolute ethanol were refluxed for 6–7 hr. The yellow precipitate formed during the cooling of mixture was filtered off, washed two or three times with cold ethanol. Finally, the solid that was obtained (DC5An) was recrystallized from an absolute ethanol until the transition temperature remained constant. Yield (69%–72%).

#### FTIR Spectra for AC5A2

FTIR (KBr, cm<sup>-1</sup>): 2960–2850 ( $\nu_{C-H}$ , aliphatic); 1740–1725 ( $\nu_{C=O}$ , ester); 1605–1625 ( $\nu_{C=N}$ , azomethine); 1105–1250 ( $\nu_{C-O-C}$ , aryl-ether); 619–889 ( $\nu_{C-H}$ , aromatic).

#### <sup>1</sup>H-NMR spectra for AC5A2

<sup>1</sup>H-NMR (DMSO-d6), ppm:  $\delta$  = 8.61 (s, 1H, -CH=N-); 6.87–8.13 (dd, 15H, aromatic rings); 3.99–4.09 (t, 6H, -CH<sub>2</sub>O-); 1.40–3.35 (m, 15H, 6 -CH<sub>2</sub>- and -O-C-CH<sub>3</sub>) and 0.89–0.92 (t, 6H, -CH<sub>3</sub>).

### <sup>13</sup>C–NMR spectra for AC5A2

<sup>13</sup>C–NMR (DMSO-d6), ppm: δ = 163.91–164.55 (–COO–); 162.08 (–C=N–); 158.3, 154.45, 152.79, 144.21, 133.78, 132.64, 126.75, 123.11, 188.16, 115.33, 110.57 for aromatic carbons; 68.5, 63.61 (–CH<sub>2</sub>O–); 40.62, 40.01, 39.57, 35.55, 28.6, 28.07, 22.34 for methylene carbons; 15.11, 14.36 [–CH<sub>3</sub>].

#### **Results and discussion**

#### **Characterizations**

The synthetic route used for the preparation of 2,4-bis(4'-n-pentnyloxybenzoyloxy) benzylidine-4"-n-alkyloxyaniline (DC5An) is shown in Scheme 1. All compounds were characterized by elemental analysis, FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C–NMR spectroscopy. The percentage yields and analytical data of each compound in the series are listed in Table 1. The percentages of C, H, and N from the elemental analysis were in good agreement with the calculated values for compounds DC5An.

The FTIR spectrum of compounds of series CD5An showed bands at 2960–2850 ( $\nu_{C-H}$ , aliphatic); 1740–1725 ( $\nu_{C=O}$ , ester); 1605–1625 ( $\nu_{C=N}$ , azomethine); 1105–1250 ( $\nu_{C-O-C}$ , aryl-ether); 619–889 ( $\nu_{C-H}$ , aromatic).

The <sup>1</sup>H-NMR spectrum of series CD5An showed the following characteristic absorptions:  $\delta = 8.61-8.72$  singlet for -CH=N- group; 6.55-8.33 doublet of doublet for aromatic rings; 3.99-4.09 triplet for -CH<sub>2</sub>O- in heptyloxy terminal groups; 3.35-3.53 triplet or quartet for -CH<sub>2</sub>O- group of alkoxy terminal group attached to the aniline ring; 1.76-1.80 triplet for -CH<sub>3</sub> of alkoxy terminal groups attached to the aniline ring; 1.31-1.52 multiplet for -CH<sub>2</sub>- units in alkoxy chain; 0.89-0.92 triplet for methyl group of pentyloxy terminal chain.

The <sup>13</sup>C–NMR spectrum of compounds of series CD5An showed the following signals: <sup>13</sup>C–NMR (DMSO-d6), ppm:  $\delta$  = 163.91–164.55 (–COO–); 162.08 (–C=N–); 158.3– 110.57 for aromatic carbons; 68.5–63.61 (–CH<sub>2</sub>O–); 40.62– 22.34 for methylene carbons; 15.11– 14.36 [–CH<sub>3</sub>]. The data of FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C–NMR spectrum along with elemental analyses data confirmed the structural formula of the synthesized compounds.

#### Mesomorphic properties

The phase transition temperatures and corresponding enthalpy changes of series DC5An were determined using a DSC. The mesophases of all the compounds were observed under a polarizing optical microscopy (POM) during heating and cooling cycles. The thermal behavior obtained by DSC is consistent with the data observed by POM, where it was possible to identify the mesomorphic character of the mesophases. The data obtained from the DSC and POM analyses are summarized in Table 2. On heating, the first endothermic peak accompanied with high enthalpy indicates a transition from solid crystalline state to a liquid crystalline mesophase. The second and third endothermic transitions at higher temperature



**Scheme 1.** Synthetic route for compounds DC5An, reagents, and conditions: (i)  $C_9H_{19}Br$ , KOH, Ethanol/ $H_2O$ , Reflux, 24 hr; (ii) SOCl<sub>2</sub>,  $C_6H_6$ , Reflux, 1 hr; (iii) THF, Et<sub>3</sub>N, 5°C, 24 hr; (iv)  $C_nH_{2n+1}Br$ , KOH, Ethanol, Reflux, 24 hr; (v) KOH, Ethanol, Reflux, 4 hr; and (vi) Ethanol, Glacial acetic acid, Reflux, 7 hr.

presented lower associated enthalpy, which indicates transitions between distinct mesophases and to the isotropic state.

All the members of series DC5An exhibit enantiotropic mesophases. The CD5A1 to CD5A4 homologues are purely enantiotropic nematogenic. With a further increase in the length of the alkoxy chain from DC5A5 to DC5A10 the enantiotropic smectic C (SmC) phase was observed, which accompanied the nematic (N) phase. The N phase starts from n = 1 and persists up to the last member of the series. The persisting of N phase indicates that the net effect imparted due to the end-to-end cohesive forces in this series is similar as all the other molecular forces are the same.

			Analysis % found (calcd.)		
Compound	Molecular formula	Molecular weight (g mol $^{-1}$ )	C	Н	N
(DC5A1)	C <sub>38</sub> H <sub>41</sub> O <sub>7</sub> N	623	73.36(73.19)	6.57(6.58)	1.98(2.25)
(DC5A2)	$C_{30}H_{43}O_{7}N$	637	74.18(73.47)	6.86(6.75)	2.06(2.20)
(DC5A3)	$C_{40}H_{45}O_{7}N$	651	74.63(73.73)	6.85(6.91)	1.95(2.15)
(DC5A4)	$C_{A1}^{40}H_{A7}O_{7}N$	665	74.59(73.98)	6.84(7.07)	1.97(2.11)
(DC5A5)	$C_{42}H_{40}O_{7}N$	679	75.25(74.23)	6.78(7.22)	1.56(2.06)
(DC5A6)	$C_{42}^{42}H_{51}^{49}O_{7}N$	693	74.85(74.46)	7.09(7.36)	1.47(2.02)
(DC5A7)	C <sup>4</sup> <sub>4</sub> H <sup>5</sup> <sub>5</sub> O <sub>7</sub> N	707	74.89(74.68)	7.27(7.50)	2.26(1.98)
(DC5A8)	$C_{45}^{44}H_{55}^{55}O_7^{\prime}N$	721	75.26(74.90)	7.82(7.63)	1.98(1.94)
(DC5A9)	C <sub>46</sub> H <sub>57</sub> O <sub>7</sub> N	735	74.93(75.10)	8.77(7.76)	1.86(1.90)
(DC5A10)	C <sub>47</sub> H <sub>59</sub> O <sub>7</sub> N	749	74.29(75.49)	7.74(7.99)	1.98(1.87)

#### Table 1. Elemental analysis data for the series DC5An.

The increasing of carbon chain (n > 4) in the studied series aids the formation of smectic mesophase due to enhanced lateral attraction as compared with terminal attractions, which facilitates lamellar packing required for the formation of the smectic mesophase [22]. In contrast, the short terminal alkoxy group in the first four compounds enables the significant forces of attraction which serve to stabilize parallel orientation by end-to-end molecular attractions required for the formation of N mesophase only. The appearance of smectic A (SmA) phase for compound DC5A9 was understandable, but could be due to the fact that the three alkoxy terminal groups with 5, 5, and 9 carbon atoms give rise to more planar and polarizable geometrical structure.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Fig. 1) shows a steady fall in N $\rightarrow$ I transition temperatures and exhibits a marked odd–even effect up to the n-octyloxy derivative and then falls as series is ascended. The SmC $\rightarrow$ N transitions curve rises up to the DC5A8 derivative and then falls smoothly for the last higher members. The Cr $\rightarrow$ SmC transition curve rises, passes through maxima at n-octyloxy derivative, and descends in a usual expected manner.

The mesophases exhibited by compounds of series DC5An were identified according to their optical textures, which were observed by POM, using the classification systems reported by Demus, and Richter [23] and Dierking [24].

All of the compounds in the series DC5An display N mesophase. The optical photomicrographs of DC5A4 are depicted in Fig. 2 as a representative illustration. Upon cooling the isotropic liquid of each compound, N droplets appeared and coalesced to form the typical schlieren texture with characteristic two- and four-brush singularities.

Compound	Transition temperatures (°C)( $\Delta$ H, kJ mol <sup>-1</sup> )
DC5A1	Cr 101 (9.43) N 131 (2.87) I
DC5A2	Cr 109 (12.54) N 216 (3.04) I
DC5A3	Cr 82 (9.33) N 111 (4.30) I
DC5A4	Cr 102 (13.99) N 118 (0.76) I
DC5A5	Cr 76 (9.92) SmC 114 (0.74) N 205 (0.44) I
DC5A6	Cr 87 (14.68) SmC 107 (0.66) N 156 (0.51) I
DC5A6	Cr 114 (12 51) SmC 124 (0.95) N 138 (0.71) I
DC5A8	Cr 123 (21.95) SmC 208 (1.37) N 165 (0.65) I
DC5A9	Cr 104 (16.28) SmC 124 (1.23) SmA 137 (1.15) N 178 (0.34) I
DC5A10	Cr 75 (6.48) SmC 84 (0.31) N 109 (0.68)

Cr = Crystal; N = Nematic; SmA = smectic A; SmC=smectic C; I = Isotropic Transition



Figure 1. Dependence of transition temperatures on the increasing number of carbon atoms (*n*) in the terminal alkoxy chains for the CD5An series compounds.

The homologues with longest alkoxy chain (n = 5-10) exhibit an enantiotropic dimorphism N and SmC except for the homologue with n = 9 additional SmA phase is observed. As indicated above, upon further cooling of the N phase, the emergence of the SmC phase was observed in its schlieren texture (Figs. 3 and 4). Figure 5 displays the SmA mesophase texture which was identified by the appearance of a broken focal-conic texture.

It was found that there is a close relationship between mesomorphism and molecular constitution of mesomorphic compounds [25–31]. This relationship could be correlated with the molecular constitution of these compounds by the thermal stability, which is a measure of mesomorphism (the mean value of the transition temperature from the mesomorphic state to the isotropic liquid state).

Table 3 shows the comparison of transition temperatures, mesomorphic properties, and the thermal stability, of the present series (DC5An) and the structurally related compounds I [14], II [13], and DC9A2 [32] reported in literature. Compounds DC9A2 and DC5A2 show a very similar mesomorphic behavior (in terms of transition temperatures and mesophase type), displaying N mesomorphism. The members in both series with short alkoxy chain (n = 2) show a N mesophase; a lateral interaction to give rise to a layered smectic order is not favored because of the difference of the volume occupied by the flexible melted chains (one



**Figure 2.** Mesophase optical texture of the N phase obtained on cooling. A schlieren texture and the typical N droplets (200× magnification) for the compound DC5A4 at 118°C.



**Figure 3.** Mesophase optical texture of the transition stripes at N (thread-like texture) to SmC (schlieren texture) phase transition during the cooling ( $200 \times$  magnification) for the compound DC5A8 at 119°C.



**Figure 4.** Mesophase optical textures exhibited by (DC5A5) on heating from crystal phase, the typical thread-like (schlieren) texture of (SmC) phase at  $103^{\circ}C$  ( $200 \times$  magnification).

side is fixed in C9 and C5, respectively), and only a short range positional order is achieved. As the length of both alkoxy chains becomes longer, the smectic order is favored.

The Schiff's bases (series DC5An and DC9An) and the azo compounds (series I and II) have the same central rigid core and the same alkoxy chain. The difference between these



**Figure 5.** Mesophase optical texture of the SmA phase obtained on cooling. A typical focal-conic fan texture ( $200 \times$  magnification) for the compound DC5A9 at 124°C.





series is in the azomethine and azo linkage group. The results show that the azomethine compounds have a higher thermal stability than azo compounds. It seems likely that, in comparison, the increased mesogenic character of Schiff base compounds is due to the azomethine group which is coplanar with the aromatic rigid core; these compounds therefore have a higher conjugated character and a major polarizability, both of which favor mesophase formation and, in particular, smectic phases.

## Conclusions

A new series of 2,4-bis(4'-n-pentyloxybenzoyloxy)benzylidine-4"-n-alkoxyaniline (DC5An) has been prepared by varying terminal lateral alkoxy chain length (n = 1-10). The chemical structures of these compounds were examined by elemental analysis, FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and mass spectroscopy. The results are in agreement with the considered molecular structure. The mesomorphic properties and optical textures of the resultant compounds were characterized by DSC and POM. The change in terminal alkoxy chain length has

pronounced effect on the mesomorphic behavior. The first four homologues, i.e., (DC5A1– DC5A4) exhibited N mesophase and that DC5A5–DC5A10 displayed dimesomorphism N and SmC phases. The mesomorphic properties and thermal stabilities of the present series are compared with those of structurally related homologous series.

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