Synthesis and Liquid Crystalline Studies of 2,4-bis(4'-n-nonyloxybenzoyloxy)benzylidene-4''-n-alkoxyaniline

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Abstract–**In this paper, a series of new Schiff-bases: 2,4-bis (4'-n-nonyloxy -benzoyloxy)benzylidene-4''-n-alkyloxyaniline (DC_9A_n) were synthesized. The characterization of compounds was achieved through using (ultra violet, infrared, [1]H-nuclear magnetic resonance) measurements. This series comprises 10 members differ by the length of n-alkoxy chain (i.e., OC_nH_{2n+1}, n=1-10). Their liquid crystalline properties were studied using differential scanning calorimetry and polarizing optical microscopy. The lower series such as n=1-3 are purely nematogenic liquid crystals, but the other means (n=4-7) have nematic and smectic phases (S_mC and S_mA). The higher members (n=8-10) are purely smectogenic liquid crystals.**

Index Terms—**Liquid Crystals, Schiff-bases, Nematic, Smectic.**

I. Introduction

The geometric shape of the molecules, thereby influencing the type of mesophase, the transition temperatures, and the dielectric constant and other properties of the mesogens (Ha, et al., 2010). Aromatic azomethine ester comprising different polarity of substituents has been known to either promote or suppress the mesomorphic properties (Lee, et al., 2010). The aromatic esters are known for their thermal stability, easy synthesis, and relative resistance to hydrolysis (Sandhya, 2014). The molecular breadth is usually derived from a lateral substitution. Lateral substitution plays an effective role in the mesomorphic properties of the compound. However, some Schiff-base–ester liquid crystal compounds have been studied, in different structures and mesophases. Baumeister, et al. (1990) synthesized a compound 4-ethoxy-2′-(4-ethoxy-phenyliminomethyl)-4'-(4-methoxybenzoyloxy) azobenzene with the observation of the nematic (N) phase. Same feature was observed in the study done by Diele, et al., 1991, where the N and S_mA phases were been observed. Berdague, et al.

(1993) reported new laterally aromatic branched liquid crystal (LC) materials with the N and S_mC phases. In another study done by Haddawi, et al. (1994) about the lateral aryl substituents, the synthesized compound shows the N and S_mA phases. Aziz (2000) synthesize some new Schiff-base–diester compounds, during this study, the mesomorphic behavior of the Schiff-base compounds shows the N, S_mC, and S_mI mesophases (Fig. 1) with m=6, 8, 10, 12. The aims of this work are synthesize a homologous series of Schiff-base–diester compounds (DC_9A_n) were m=9 and n=1-10, and study their liquid crystalline behavior (Fig. 1).

II. Measurements and Materials

A. Measurements

Melting points of the compounds were measured using digital (BUCHI B-540) melting apparatus with zooming function. Ultraviolet–visible (UV-Vis) spectra of the compounds were measured over the wavelength range 200-800 nm using chloroform as a solvent, using Agilent Cary 100 UV-Vis instrument. Infrared spectra of the compounds were recovered over the frequency range 400-4000/cm by FTIR-SHIMADZU instruments. The samples were prepared in KBr pellet form. [1]H-nuclear magnetic resonance (NMR)-Bruker (400 MHZ) Ultrashield was used for analyzing the ^{1}H-NMR spectra of compounds. The samples were dissolved in deuterated chloroform ($CDCl_3$) at room temperature (298 K). Tetramethylsilane was used as internal standard. The final products were tested for ^{1}H-NMR at the range of the chemical shift (δ=0.0-17.0) ppm. Differential scanning calorimetry (DSC) measurements of transition temperatures of the various liquid crystal phases and calculation of the enthalpy change were carried out using DSC-60 SHIMADZU. The various liquid crystalline
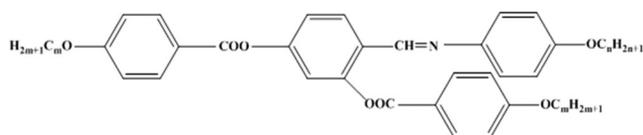
Fig. 1. The general structure of studied compound 2,4-bis(4'-n-alkyloxybenzoyloxy)benzylidene-4''-n-alkyloxyaniline

textures of the compounds throughout the investigations of all compounds were taken by the high-resolution digital camera equipped with the Leica DM750P polarized optical microscope coupled with Linkam heating-cooling stage.

B. Materials

4-hydroxyacetanilide, tetrahydrofuran (THF), triethylamine (Et$_3$N), anhydrous magnesium sulfate, benzene, absolute ethanol (Aldrich), n-alkyl bromide, thionyl chloride (Fluka), potassium hydroxide (KOH), 4-hydroxybenzoic acid, hydrochloric acid (HCl), sodium carbonate, and glacial acetic acid (Scharlau) were used as received.

C. Synthesis

4-n-nonyloxybenzoic Acid (C$_9$)

4-hydroxybenzoic acid (50 mmol, 6.900 g), n-nonyl bromide (55 mmol), and potassium hydroxide (KOH 110 mmol, 6.160 g) were dissolved in ethanol/water 160/16 mL in a round-bottom flask fitted with a reflux condenser and refluxed the mixture on hot plate with magnetic stirrer for 24 h. A 60 ml (20%) of KOH was added to the reaction mixture, and reflux was continued for 5 h. The solution was cooled to room temperature and the reaction mixture was acidified by adding ice cooled (2M, HCl), and the formed white precipitate was filtered and washed with water until the filtrate became neutral. The crude product was dried in vacuum oven, and then, recrystallized in ethanol (absolute) until constant transition temperature is obtained (Cativiela, et al., 1995) which was 144°C and agrees with the values by Dave and Vora, (1970) and Keller and Liebert (1978) and it almost similar to reported value (Isotropic point=144°C). (Yield: 85%).

4-n-nonyloxy Benzoylchloride

Thionyl chloride SOCl$_2$ (150 mmol) and 4-n-nonyloxybenzoic acid (100 mmol) were dissolved in dry benzene (75 mL), and the resulting solution was refluxed until the evolution of HCl and SO$_2$ ceases, after refluxing for 3 h the reaction is ended. The excess of thionylchloride was removed on rotary evaporator to give the product. The yield was 98% in most cases. The acid chloride is very sensitive to moisture and it has been used immediately after synthesis without any purification for the synthesis of 2,4-bis(4'-n-nonyloxybenzoyloxy) benzaldehyde in the next step (Dave and Vora, 1970; Keller and Liebert, 1978).

Synthesis of 2,4-bis(4'-n-nonyloxybenzoyloxy) Benzaldehyde (DC$_9$)

A solution of 2,4-dihydroxybenzaldehyde (3 g, 22 mmol) in 20 mL THF was added dropwise to a mixture of 4-n-nonyloxybenzoyl chloride (14.1 g, 50 mmol) in 500 mL THF and 7.4 mL of triethy1amine (Et$_3$N) with vigorous stirring at 10°C in an ice bath. After the addition, the reaction was allowed to reach room temperature and stirred for 38 h. The precipitate product and the triethylamine-HC1 salt were then poured into 500 mL cold water. The resulting precipitate was filtered and washed with water, and 500 mL, 5% Na$_2$CO$_3$ solution and then water until the filtrate became neutral, and the product was dried (Pugh and Schrock, 1992; Zhou, et al.,

1988), Finally, recrystallized by ethanol (absolute) to yield 79% of product with melting point (47-49°C).

4-n-alkyloxyacetanilides (AA$_n$)

4-hydroxyacetanilide (100 mmol) was dissolved in 75 mL of hot ethanol with stirring and then cooled. After cooling, a solution of 5 mL, 125 mmol KOH is added slowly, followed by dropwise addition of 110 mmol n-alkyl bromide in 25 mL of in ethanol. The mixture was refluxed for one hour, then, the mixture was cooled to room temperature, and then, 25 mL of water was added with cooling. The resulting white precipitate was filtered off, washed twice or three times with water until the filtrate became neutral, dried in a desiccator, and recrystallized with ethanol/water (75/25 mL) (Keller and Liebert, 1978). Yield (69-88%).

4-n-alkyloxyanilines (A$_n$)

4-n-alkyloxyacetanilide (50 mmol) in 50 mL of ethanol was refluxed, and then, during the reflux (12.5 mL, 20 N), KOH was added dropwise, and then, reflux was continued for 5 h. Ethanol was removed using rotary evaporator, and the residue (A$_n$) was extracted twice with 50 mL of benzene using centrifuge technique. The combined organic layers were washed with water for neutralization and then dried using anhydrous magnesium sulfate. The solvent (benzene) was removed using rotary evaporator to give the products (A1-A10) (Yield: 78-85%) (Keller and Liebert, 1978).

Synthesis of Schiff-bases

0.2 mmol of DC$_9$, 0.2 mmol of A$_n$, and few drops of glacial acetic acid as catalyst in 10 mL of ethanol (absolute) were refluxed for 6-7 h. The yellow precipitate formed during the cooling of mixture, it was filtered off, washed 2 or 3 times with cold ethanol. Finally, recrystallized in ethanol (absolute) until the transition temperature remains constant. Yield (69-72%).

III. Spectroscopic Identification

A. UV Spectra Measurements of Schiff-bases

The UV-Vis spectra of the compounds (DC$_9$A$_n$) were studied in chloroform as a solvent. The Schiff-bases shows similar UV spectra. These compounds characterized by the appearance of three bands between 200 and 500 nm (Silverstein, et al., 1974). The first band appears with λmax. of 260-263 nm, attributed to transitions of excited electrons from π-π* in aromatic rings. The second band is shoulder, appears at 343-348 nm, attributed to transitions of excited electrons from π-π* in aniline ring. The third band appears at 350-356 nm, attributed to transitions of excited electrons from n-π* (Aziz, 2000).

B. Fourier Transform Infrared Spectra Measurements

C$_9$: 2400-3300 cm^{-1} (O-H) stretching (str.), 1678/cm (C=O$_{str.}$), 1604/cm (C=C$_{str.}$), 2856-2954/cm and 3050-3080/cm (-C-H$_{str.}$) and (=C-H$_{str.}$), respectively, 1261/cm (C-O-C$_{str.}$).

DC$_9$: 1722/cm (C=O$_{str.}$) (Ester), 1686/cm (C=O$_{str.}$) (Aldehyde). 1608/cm (C=C$_{str.}$), 2854/cm and 2916/cm symmetric and asymmetric (-C-H$_{str.}$), respectively, 3070/cm (=C-H$_{str.}$) and 1260/cm (C-O-C$_{str.}$).

AA_n: 3286-3330/cm (N-H$_{str.}$), 1658-1660/cm (C=O$_{str.}$), 1596-1610/cm (C=C$_{str.}$), 2848-2953/cm and 3065-3075/cm (C-H$_{str.}$) and (=C-H$_{str.}$), respectively. 1532-1554/cm (N-H$_{bending\ (bend.)}$).

A_n: 3312-3420/cm (N-H$_{str.}$), 1516-1518/cm (N-H$_{bend.}$), 2850-2955/cm (C-H$_{str.}$), 3050-3070/cm (=C-H$_{str.}$), 1250/cm (C-O-C$_{str.}$)

DC_9A_n: 1625-1633/cm (C=N$_{str.}$), 1732-1741/cm (C=O$_{str.}$) (Ester). 1605-1608/cm (C=N$_{str.}$), 1570-1580/cm (C=C$_{str.}$). 2850-2954/cm and 3055-3093/cm (C-H$_{str.}$) and (=C-H$_{str.}$), respectively. 1245-1249/cm (C-O-C$_{str.}$).

C. ^{1}H-NMR Measurements

DC_9: s, 1H, at 10.2 ppm. aldehyde group. m, 11H, at 6.96-8.19 ppm. benzene rings. t, 4H, at 4.05-4.09 ppm. –OCH$_2$ groups. m, 4H, at (1.81-1.87) ppm. two –CH$_2$ groups neighbor with –OCH$_2$ groups. m, 24H, at 1.31-1.49 ppm. –CH$_2$ groups in the terminal groups. t, 6H at 0.9 ppm. –CH$_3$ groups at the end of terminal groups. DC_9A_1: s, 1H, at 8.7 ppm. imine proton (a). d, 4H, at 8.1-8.19 ppm. benzoate benzene rings (b). d, 2H, at 7.82-7.85 ppm. aniline benzene ring (f) closer to nitrogen atom. s, 1H, at 7.68 ppm. benzylidene ring lying between two ester groups (g). d, 1H, at 7.53-7.58 ppm. benzylidene ring closer to ester group (d). d,1H at 7.38-7.43 ppm. benzylidene ring closer to imine group (e). m, 6H, at 6.5-7.1 ppm. benzene ring closer to –OCH$_2$ groups (c). m, 4H, at 3.8 ppm. –OCH$_2$ groups (j). s, 3H, at 4 ppm. -OCH$_3$ protons (N'). m, 4H, at 1.8-1.86 ppm. two –CH$_2$ groups which are neighbor with –OCH$_2$ groups (K). m, 24H, at 1.31-1.5 ppm. other –CH$_2$ groups in the two other terminal groups (l). t, 6H, at 0.89-0.92 ppm, two other –CH$_3$ groups in the two other terminal groups (m) (Figs. 2 and 3).

IV. Results and Discussion

A. DSC and Polarizing Optical Microscopy (POM) Studies

DC_9 shows no liquid crystalline mesophases, which was proved by DSC and POM analysis. The DSC of this compound has only one transition corresponding to the transition from crystal (Cr) phase to isotropic (I) phase which takes place at 53.45°C with high change of enthalpy ΔH of transition 132.38 J/mol and high change of entropy ΔS of transition 0.405 J/mol/K The phase transition temperatures and corresponding enthalpy changes ΔH of all Schiff-base compounds determined using DSC and POM are summarized in Tables I and II. Phase transition temperatures and enthalpy changes were measured at heating rates (20 C/min). DSC heating curves of the compounds DC_9A_1 and DC_9A_6 as representative examples are shown in Figs. 4 and 5. All compounds exhibited liquid-crystalline properties. DSC studies revealed that the differences in liquid-crystalline properties of all compounds along with increasing length of aliphatic chain are clearly observed.

B. Phase Transition Temperatures Against Number of Carbon

The S_mA phase range T_{SmA-I} increased linearly for n=8-10, and increases drastically to 42°C, for n=10 during heating. We assume that competing effects of vibrational motions and attractive forces in the alkyloxy chains occur in the S_mA

TABLE I
PHASE TRANSITION TEMPERATURES/°C TAKEN BY POM SCHIEF-BASES
ENTHALPY CHANGES WITH MESOPHASE THERMAL STABILITY RANGES (ΔT_M)

Compound	Enthalpy change (ΔH) in (J/mol)				
	Transitions				
	Cr-Cr	Cr-N, Cr-S$_m$C	Total (ΔH) for Cr-mesophase	S_mC-S_mA	S$_m$C-N, S$_m$A-N
DC_9A_1	41.74	79.1	120.84		
DC_9A_2	22.81	47.07	69.88		
DC_9A_3	49.14	12.71	72.2		
	10.35				
DC_9A_4		61.38	61.38		Not recorded on DSC curve
DC_9A_5		68.7	68.7		2.68
DC_9A_6	10.5	28.94	39.44		15.28
DC_9A_7		17.22	17.22	8.86	1.87
DC_9A_8		55.89	55.89	3.28	
DC_9A_9	20.4	2.27	22.67	4.69	
DC_9A_{10}		17.17	17.17	3.36	

DSC: Differential scanning calorimetry, POM: Polarizing optical microscopy
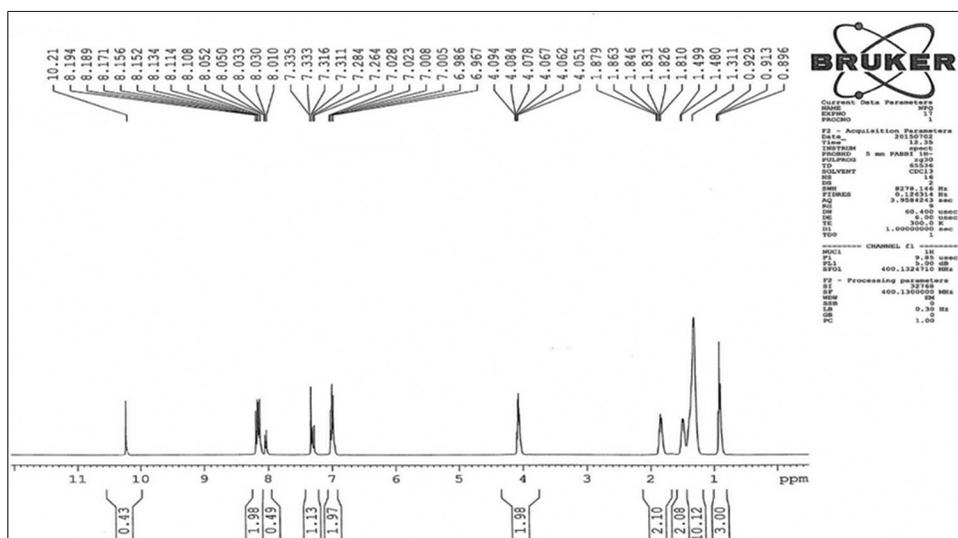
Fig. 2. Full ^{1}H-nuclear magnetic resonance spectrum of 2,4-bis(4'-n-nonyloxybenzoyloxy) benzaldehyde (DC$_9$)

TABLE II
Enthalpy Changes of Transitions for Schief-bases

Compound	Cr-Cr	S_mC		S_mA		N		I		ΔT_m
	DSC	DSC	POM	DSC	POM	DSC	POM	DSC	POM	POM
DC_9A_1	96.69					150.49	112		155	43
DC_9A_2	109.15					153.88	127		167	40
DC_9A_3	67.83					134.37	112		143	31
	110.01									
DC_9A_4		66.72	55				77		93	38
DC_9A_5		63.51	48			88.10	78		104	56
DC_9A_6	61.10	100.19	92			135.98	115		150	59
	66.69									
DC_9A_7		101.18	90	130.20	120	152.85	152		166	76
DC_9A_8		85.20	73	111.54	105				122	49
DC_9A_9	87.69	96.60	85	116.17	112				137	52
DC_9A_{10}		87.00	77	130.36	105				147	70

DSC: Differential scanning calorimetry, POM: Polarizing optical microscopy
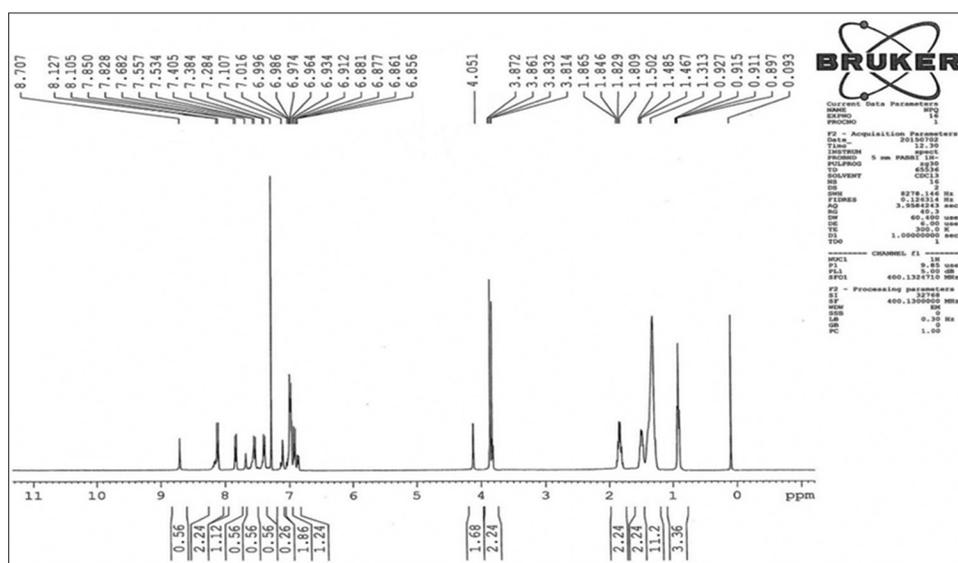
Fig. 3. Full ^{1}H-nuclear magnetic resonance spectrum of DC_9A_1
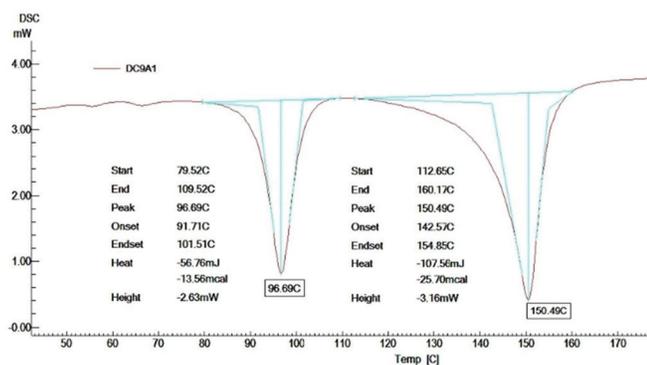
Fig. 4. Heating differential scanning calorimetry curve of DC_9A_1
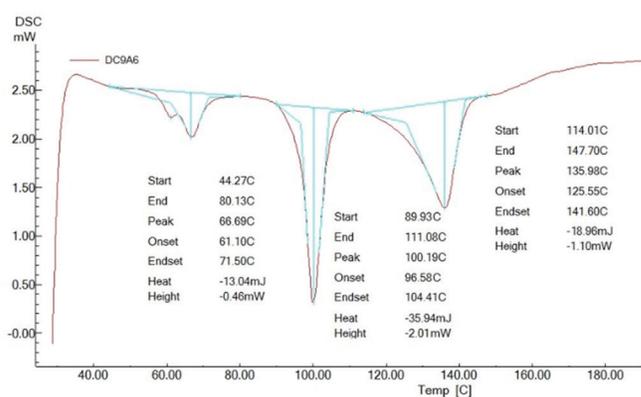
Fig. 5. Heating differential scanning calorimetry curve of DC_9A_6

phase. When chain length reaches 10 (decyl), the alkyloxy chain attractive forces substantially outweigh the chain vibrational motions, resulting in the formation of a long-range of S_mA phase. Conversely, short alkyloxy chain lengths (n=8) tend to disrupt lamellar packing. For S_mC-S_mA transition, the curve is very regular for the last four compounds where n=7-10 which show an odd-even effect phenomena, in which the compounds with odd number of carbon atoms has higher ($T_{SmC-SmA}$) than the compounds with even number of carbon atoms. For Cr-S_mC transition, the curve is very regular for n=4-7 with odd-even effect phenomena, in which the compounds which show an odd number of carbon atoms has lower (T_{Cr-SmC}) than the compounds with even number of

carbon atoms. There is only one transition from S_mA-N for the member (n=7) (Fig. 6).

C. Mesophase Thermal Stability Ranges (ΔTm)

From Table II, it was noted that the widest nematic thermal stability range ΔT_N=43°C which exhibited by the first member (n=1) in the series. The widest smectic thermal stability range ΔT_{Sm}=70°C in the last member (n=10) in the series.

D. Enthalpy and Entropy of Transitions

The total enthalpy or entropy change of crystal (Cr) to liquid crystal phase (N or S_mC) transition is very regular for the first six compounds where n=1-6 in the series which shows an odd-even effect phenomena, in which the compounds with odd number of carbon atoms have higher ΔH and ΔS value than the compounds with even number of carbon atoms. The enthalpy or entropy change of S_mC-S_mA transition is very regular for the past four compounds where n=6-10 in the series which shows an odd-even effect phenomena, in which the compounds with odd number

of carbon atoms have higher ΔH and ΔS value than the compounds with even number of carbon atoms. The enthalpy or entropy change of S_mC-N and S_mA-N transition is very regular for the members (n=5-7) in the series which shows an odd-even effect phenomena, in which the compounds with odd number of carbon atoms (n=5 and 7) have lower ΔH and ΔS value than the compound with even number of carbon atoms. The value of Enthalpy or entropy change for S_mA-N transition when n=7 is lower than the value of enthalpy or entropy change for S_mC-N transition when n=5 and 6.

E. Liquid Crystal Textures

Nematic Phase Textures

The (N) phase generally exhibits a thread-like texture; this is confirmed by the schlieren texture of the NLC (Fig. 7) and the droplet texture (Fig. 8). The schlieren texture shows dark brushes, which correspond to the extinction orientation of the NLC. Accordingly, the director (n)^ lies either parallel or perpendicular to the polarizer axes. The points, where two or four brushes meet, correspond to the director singularities and are called disclinations in the structure.
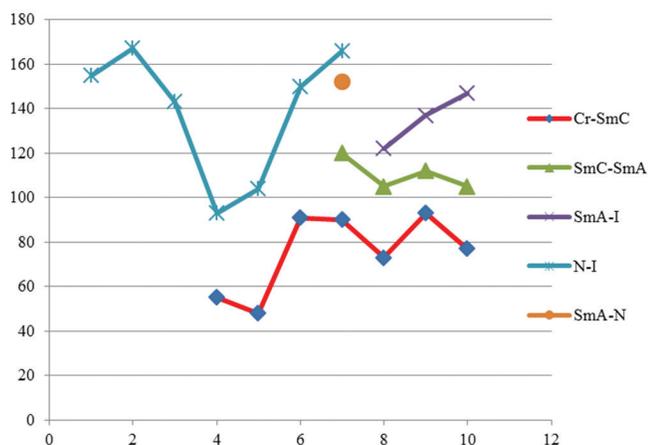
Fig. 6. The dependence of the transition temperatures taken by polarizing optical microscopy on the number of carbon atoms (n) in the terminal alkyloxy chains for DC$_9$A$_n$

Fig. 8. The optical texture exhibited by DC$_9$A$_1$ on cooling from isotropic liquid, Nematic droplets near isotropic transition point at 150°C

Fig. 7. The optical texture exhibited by DC$_9$A$_1$ on heating from crystal phase (Cr$_2$), the Schlieren texture of the (N) phase at 140°C
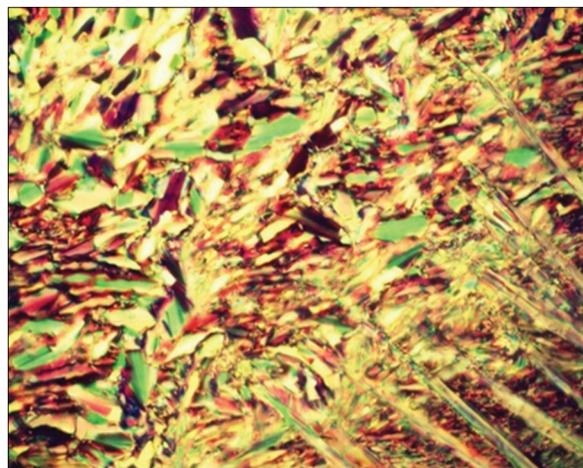
Fig. 9. The optical textures exhibited by DC$_9$A$_6$ on heating from crystal phase, the typical broken focal-conic fan texture of the S_mC phase at 105°C
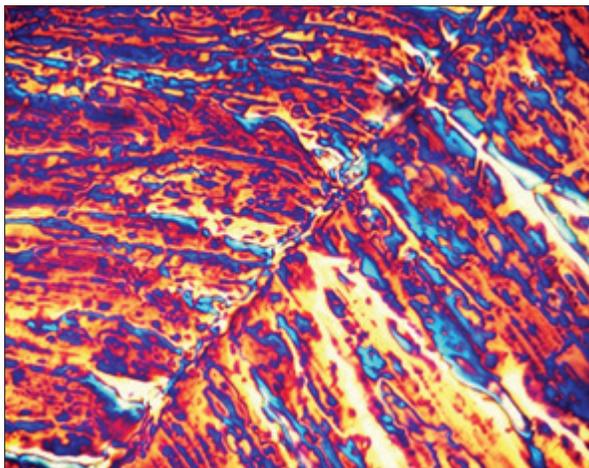
Fig. 10. The optical textures exhibited by DC_9A_7 on heating from crystal phase, the typical thread-like (schlieren) texture of the S_mC phase at 103°C
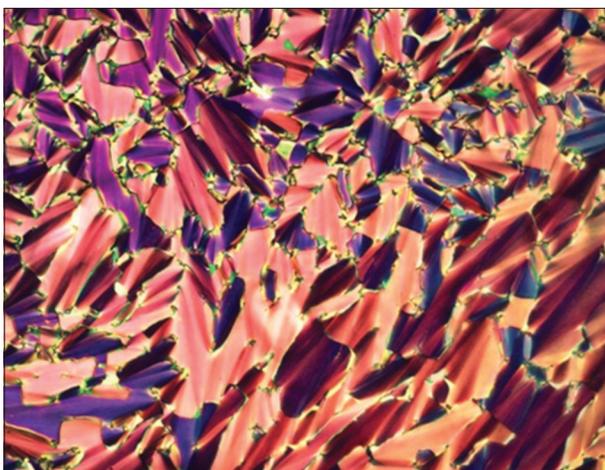
Fig. 11. The optical textures exhibited by DC_9A_7 on heating from S_mC phase, the typical focal-conic fan texture of the S_mA phase at 131.1°C

Smectic Phase Textures

S_mC phase exhibits the broken focal-conic fan shaped (Fig. 9) and schlieren texture (Fig. 10). S_mA phase exhibits the focal-conic fan shaped (Fig. 11) and batonnet textures.

V. Conclusion

Synthesis of a series of new Schiff-base–ester compounds and study their liquid crystalline behavior. From the obtained result, it can be concluded that, when more than one mesophase is possible, the smectic state increases in thermal stability, at the expense of the nematic, as chain length increases. It is often seen that, while the lower homologs are purely nematogenic (LCs) as in DC_9A_1, DC_9A_2 and DC_9A_3, the higher are purely smectogenic (LCs) (disappearance of the nematic phase) as in DC_9A_8, DC_9A_9 and DC_9A_{10}, and the intermediate homologs exhibit both mesophases (nematic and smectic phases) as in DC_9A_4, DC_9A_5, DC_9A_6 and DC_9A_7. Furthermore, it can be concluded that 2,4-bis(4'-n-nonyloxybenzoyloxy) benzaldehyde (DC_9) is not liquid crystalline compound.

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