Synthesis and Liquid Crystalline Study of 2,4-bis(4′-n-heptyloxybenzoyloxy)-benzylidene-4″-n′-alkoxy aniline

Wali Mahmood Hamad

Chemistry Department- Faculty of Science and Health- Koya University
wali.hmd@koyauniversity.org

Received: 8 October 2017 **Accepted: 28 November 2017**

Abstract

The synthesis and study mesomorphic properties of a new series of 2,4-bis(4′-n-heptyloxybenzoyloxy)-benzylidene-4″-n′-alkoxy aniline (DC_7A_{1-10}) Have been reported. The structures of the prepared compounds were confirmed by FT-IR, ^{1}H-NMR and elemental analysis (CHN). The mesomorphic properties were studied by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) measurements. All compounds of the series exhibited nematic (N) phases but the smectic phases are appear in (DC_7A_3-A_{10}). The first two series (DC_7A_1, DC_7A_2) display only a nematic phases whereas the highest homologues (DC_7A_3-A_{10}) exhibit enanthiotropic dimorphism Nematic (N) and smectic (S) phases (the DC_7A_6 is only compound exhibit S_c and S_A phases). The liquid crystalline behavior has been analyzed in terms of structural property relationship. The mesomorphic properties and thermal stabilities of the present series (DC_7A_{1-10}) were compared with those structurally related homologous series.

Keywords: Mesomorphism, mesogen, enantiotropy, nematic, smectic.

DIYALA JOURNAL FOR PURE SCIENCES

Synthesis and Liquid Crystalline Study of 2,4-bis (4′-n-heptyloxybenzoyloxy) -benzylidene-4″-n′-alkoxy aniline

Wali Mahmood Hamad

تحضير و دراسة الصفات البلورات السائل لمشتقات(4,2- بس(4′-ن-هبتايلكسي بنزوايلوكسي) بنزايليدين-4″-ن′-الكوكسي انيلين

ولى محمود حمد

قسم الكيمياء - فاكلتى العلوم والصحة - جامعة كؤيه

الخلاصة

تم تحضير ودراسة الصفات البلورية السائلة لسلسلة جديدة 4,2- بس(4′-ن-هبتايلكسي بنزوايلوكسي) بنزايليدين-4″-ن′-الكوكسي انيلين (DC_7A_{1-10}) . شخصت المركبات المحضرة جميعا بواسطة اشعه تحت الحمراء(FT-IR)، الرنين النووى المغناطيسى (^{1}H-NMR) وكذلك تحليل العناصر (CHN). ودرست الصفات البلورية السائلة بواسطة المسح المسعرى التفاضلى (DSC) وكذلك المجهر ذات صور المستقطب (POM). جميع المركبات المحضرة الجديدة أظهرت الطور البلورى السائل النيماتى (N)، لكن الطور البلورى السائل السمكتي (S) فقد أظهرت مع المركبات (DC_7A_3-A_{10}) ان المركبين ذات تراكيب (DC_7A_1-DC_7A_2) أظهرت فقط الطور البلورى السائل النيماتي (N)، ولكن المركبات ذات عدد الكاربون عالي (DC_7A_3-DC_7A_{10}) أظهرت الصفات البلورى الانانشيوتروبي (السمكتي وكذلك النماتي). ولكن المركب الوحيد ضمن السلسلة المحضرة ذات تركيب (DC_7A_6) أظهرت مع الطور النيماتي الطور السمكتي (S_A & S_c). ولوحظ هناك علاقة قوية بين تراكيب الكيمياوية للمركبات وكذلك الاطوار البلورية السائلة. ودرس الاستقرار الحراري وجد بان ظهور الاطوار البلورية السائلة وقورنت مع مركبات محضرة ذات تراكيب مشابهة لهذة السلسلة.

الكلمات المفتاحية : البلورات السائله، ميزوجين، الطور السمكتى ، الطور النيماتى .

Introduction

Aromatic azomethine ester comprising of different polarity of substituent has been known to either promote or suppress the mesomorphic properties [1, 2]. The molecular breadth is usually derived from a lateral substitution. Lateral substitution plays an effective role in the mesomorphic properties at the compound [3]. Aziz H. J has been synthesized some new Schiff base diester compounds with the general structure [4] (Figure 1).

Synthesis and Liquid Crystalline Study of 2,4-bis (4′-n-heptyloxybenzoyloxy) -benzylidene-4″-n′-alkoxy aniline

Wali Mahmood Hamad

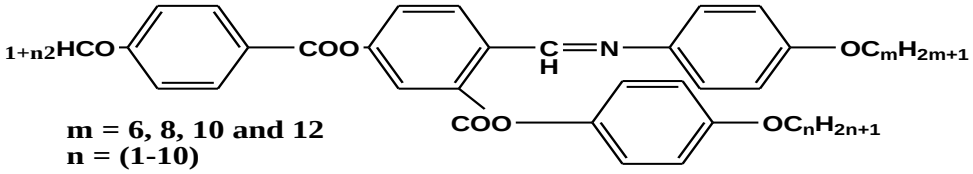


Figure 1

The mesomorphic behavior of this Schiff base compound show the (N), (Sc) and (SI) mesophases. In this work, we describe the synthesis and mesomorphic properties of homologous series (DC_7A_{1-10}) (Figure 1I).

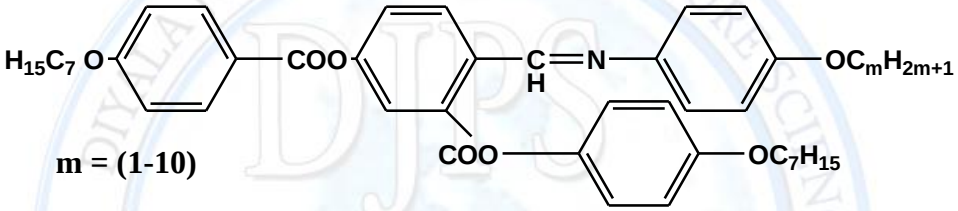


Figure 1I

Experimental

1- Materials

4-hydroxyaetanilide, 2,4-dihydroxybenzaldehyde, tetrahydrofuran(THF), triethylamine (Et_3N), benzene, absolute ethanol, thionyl chloride, potassium hydroxide, 4-hydroxy benzoic acid, hydrochloric acid, sodium carbonate and glacial acetic acid were purchased from Sigma-Aldrich. The chemicals were used as received.

2- Instrumentations

Elemental analysis (HN) was carried out using a Perkin-Elmer model 2400instrument. ^{1}H-NMR spectra obtained by (Bruker 500MHz) using (TMS) as the internal standard. Infrared spectra were recorded by FT-IR Shimadzu 8000 instrument, in wavenumber (4000 – 400 cm^{-1}), using KBr pellet. The optical behavior observations were made using Olympus BX40 microscope equipped with aLeitz Laborlux 12 puls hot stage and PR 600 controller. Photographs of texture were obtained using a camera model PM-10 AD made Olympus. The transition temperatures

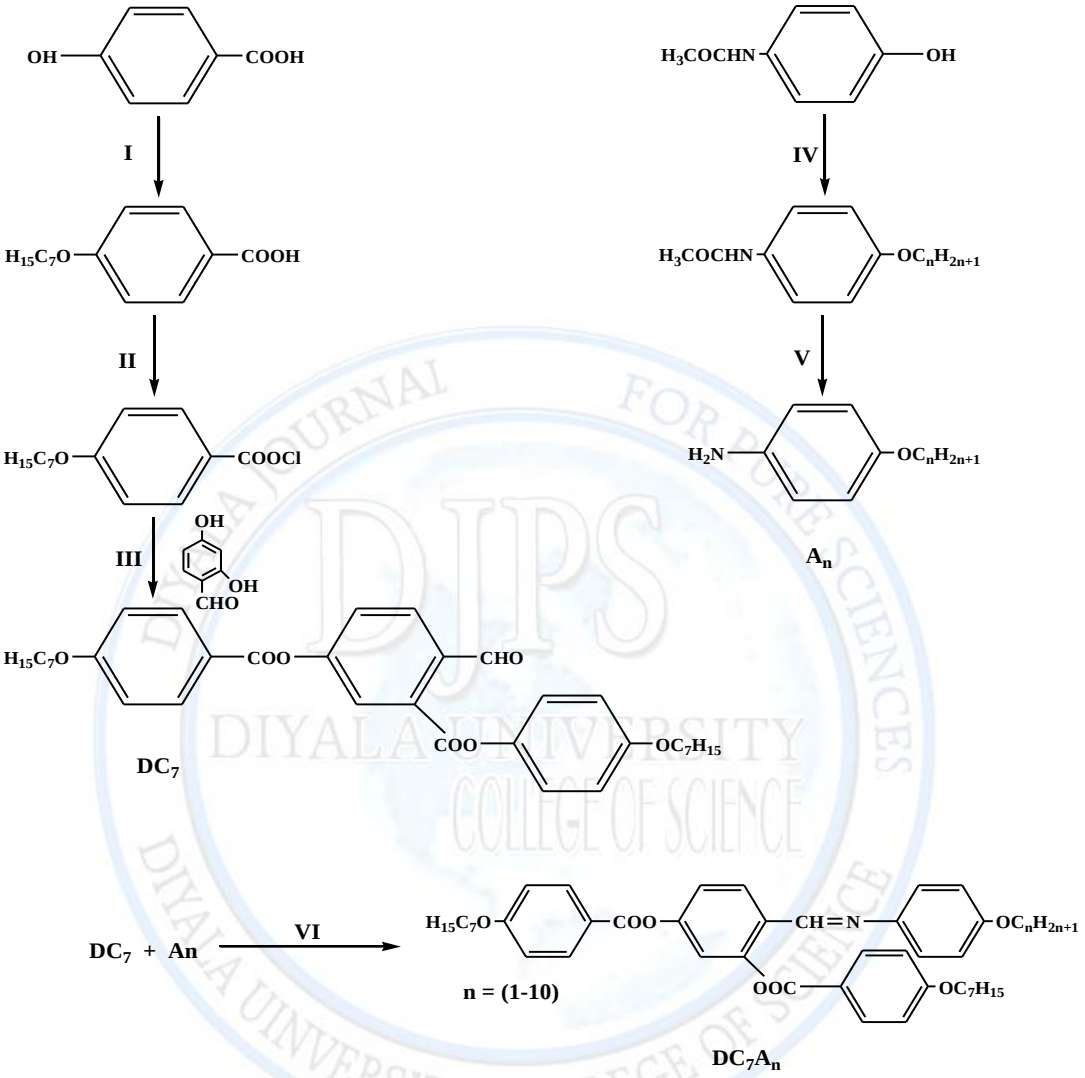
and enthalpies were investigated using differential scanning calorimetry DSC (TA instruments Q 1000 DSC), ramp rate: 10 ^{o}C/min under N_2 atmosphere.

3- Synthesis

4-n- heptyloxy benzoic acid, 4-n- heptyloxy benzoyl chloride, 4-n- alkoxy acetanilides and 4-n- alkoxy anilines derivatives were prepared according to the refs. [5, 6]. 2,4-bis(4^{-}-n-heptyloxybenzoyloxy)-benzaldehyde was synthesized by the method of Pugh and Schrock and Zhou et. al. [7, 8]. Synthesis of series 2,4-bis(4^{-}-n-heptyloxybenzoyloxy)-benzylidene-4$^{=}$-n-alkoxy aniline ($DC_7A_{1\text{-}10}$**).** The mixture of 2,4-bis(4^{-}-n-heptyloxybenzoyloxy)-benzaldehyde (0.5 mmol) and 4-n-alkoxy paceaniline (0.5 mmol) and a few drops of glacial acetic acid as catalyst in (10ml) of an absolute ethanal was refluxed for (6-7) hours. The yellow precipitate was formed during the cooling of mixture. Then it was filtered off, washed (2-3) times with cold ethanol. Finally, the obtained solid (DC_7A_n) was recrystallized from an absolute ethanol until the transition temperature remains constant. Yield (69-72%). The synthetic route used for the preparation of 2,4-bis(4^{-}-n-heptyloxybenzoyloxy)-benzylidene-4$^{=}$-n-alkoxy aniline (DC_7A_n) is shown in (scheme I).

Synthesis and Liquid Crystalline Study of 2,4-bis (4′-n-heptyloxybenzoyloxy) -benzylidene-4″-n′-alkoxy aniline

Wali Mahmood Hamad



(I) $C_7H_{15}Br$, KOH, Ethanol/H_2O, reflux, 25h., $SOCl_2$, C_6H_6, reflux, 1h. (II) THF, Et_3N, 5°C, 24h.

(III) C_nH_{2n}, Br, KOH, Ethanol, reflux, 24h. (IV) KOH, Ethanol, reflux, 4h. (V) Ethanol, glacial acetic acid, reflux, 7h.

Scheme I: synthetic route for compounds DC_7A_n

Results and Discussion

1- Characterization

FT-IR (KBr, cm^{-1}) 2960-2850 cm^{-1} (υ_{C-H} aliphatic); 1740-1725 cm^{-1} ($\upsilon_{C=O}$ ester); 1605-1625 cm^{-1} ($\upsilon_{C=N}$ azomethine); 1105-1250 cm^{-1} (υ_{C-O-C} aryl ether); 619-880 cm^{-1} (υ_{C-H} aromatic).

^{1}H-NMR (DMSO-d6), ppm; δ=8.61(s, 1H, -CH=N-); δ=6.87-8.13(dd, 15H, rings); δ=3.99-4.09(t, 6H, $-CH_2O$ -); δ=1.40-3.3(m, 15H, 6 $–CH_2$- and $–O-C-CH_3$) and δ=0.89-0.92(t, 6H, $-CH_3$-).

The elemental analysis:

Table 1: Elemental analysis of all compounds

No.	Compounds	Molecular weight	% Found (Calculated)		
			C	H	N
1	DC_7A_1	679.2	74.32(74.22)	7.01(7.21)	1.96(2.06)
2	DC_7A_2	693.3	74.38(74.74)	7.16(7.35)	1.82(2.02)
3	DC_7A_3	707.4	74.81(75.24)	7.30(7.49)	1.80(1.98)
4	DC_7A_4	721.0	75.32(75.72)	7.54(7.62)	1.79(1.94)
5	DC_7A_5	735.0	76.01(76.19)	7.78(7.75)	1.80(1.90)
6	DC_7A_6	749.0	76.23(76.63)	7.82(7.87)	1.74(1.86)
7	DC_7A_7	763.0	76.59(76.53)	8.01(7.99)	1.84(1.83)
8	DC_7A_8	777.0	76.80(76.96)	8.12(8.10)	1.72(1.80)
9	DC_7A_9	791.0	77.12(77.37)	8.18(8.21)	1.68(1.76)
10	DC_7A_{10}	805.0	77.82(78.01)	8.29(8.32)	1.62(1.73)

2- Mesomorphic properties:

The mesophases of the present series (DC_7A_{1-10}) were observed by polarized optical microscope (POM) during heating and cooling cycles. The thermal behaviors obtained by DSC are consistent with the data observed by (POM). The data obtained by DSC and POM analysis of the present series (DC_7A_{1-10}) are summarized in Table (2).

Table 2: Transition temperatures and total enthalpy changes of (DC_7A_n)

No.	Compounds	Transition temperatures ^oC (ΔH) (kJ/mol)
1	DC_7A_1	cr 257 N > 300 I (25.76)
2	DC_7A_2	cr 121 N 246 I (18.23)
3	DC_7A_3	cr 57 SmC 72 N 101 (13.89) I
4	DC_7A_4	cr 52 SmC 62 N 126 (15.76) I
5	DC_7A_5	cr 121 SmC 138 N 164 (12.20) I
6	DC_7A_6	cr 103 SmC 131 SmA 149 (15.40) N 182 I
7	DC_7A_7	cr 82 SmC 127 N 150 (14.80) I
8	DC_7A_8	cr 60 SmC 84 N 115 (22.89) I
9	DC_7A_9	cr 107 SmC 124 N 140 (19.52) I
10	DC_7A_{10}	cr 116 SmC 121 N 126 (9.53) I

cr=Crystal; N=Nematic; S_mA=Smectic A; S_mC=Smectic C; I=Isothipic transition.

All the members of series DC_7A_n exhibit enantiotropic mesophases. The DC_7A_1 and DC_7A_2 are homologues are purely enantiotropic mematogenic. With increasing length of Alkoxy chain of DC_7A_3 to DC_7A_{10} the enantiotropic smectic (C) phase was observed and accompanied the nematic phase. The nematic phase start from n=1 and persists up to the last number of the series. The persisting of nematic 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. The increasing of carbon chain (n>2) leads to the formation of smectic mesophase due to enhances lateral attraction as compared with terminal attractions, which facilitates lamellar packing that required for the formation of the smectic mesophase [9]. The appearance of S_mA phase for compound (DC_7A_6) was understandable and that could be that the three alkoxy terminal groups with 7, 7 and 6 carbon atoms give rise to more planner and polarizable geometrical structure of DC_5A_n [10]. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Figure 2). Showed the relation between carbon number (n) of alkoxy group and transition temp. of mesophases.

Synthesis and Liquid Crystalline Study of 2,4-bis (4′-n-heptyloxybenzoyloxy) -benzylidene-4″-n′-alkoxy aniline

Wali Mahmood Hamad

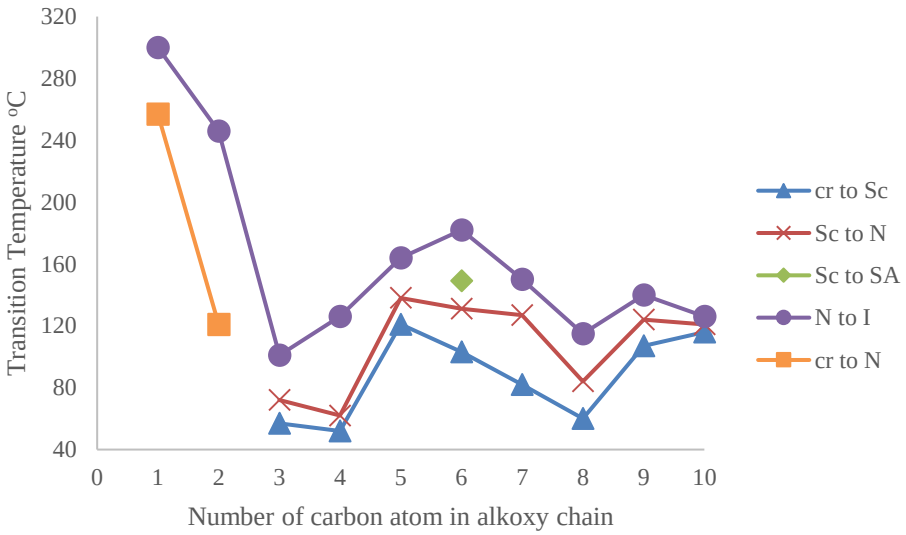


Figure 2: Dependence of transition temperature on the increasing number of carbon atom (n) in the terminal alkoxy chains for the $DC_7A_{1\text{-}10}$ series of compound

The mesophases exhibited by compounds of series $DC_7A_{1\text{-}10}$ were identify according to their optical textures, which were observed by POM, using the classification systems reported by Demus and Richter [11] and Dierking [12]. The optical photographs of DC_7A_3 are depicted in (Figure 3) as a representative illustration,

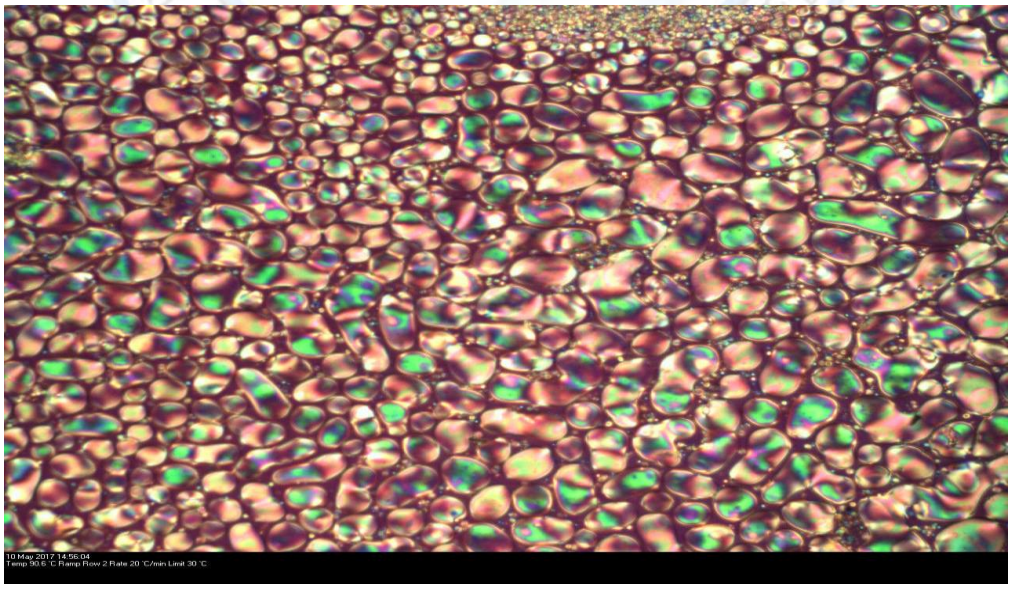


Figure 3: The Nematic droplet for the compound DC_7A_3

nematic droplet obtained in cooling. Upon cooling the isotropic liquid of each compound, nematic droplets appeared and Schlieren texture with characteristic two- and four- Brush singularities. When the compound further cooling (Figure 4) the thread like nematic was appeared.

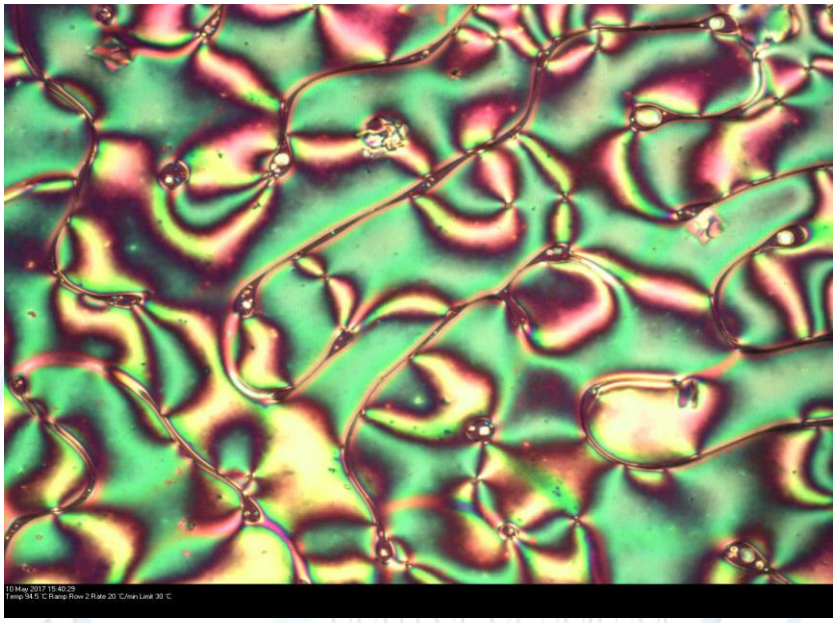


Figure 4: The Thread-like nematic of compound DC_7A_3

The typical S_mA for DC_7A_6 was appeared by cooling (Figure 5) as a broken focal conic S_mA.

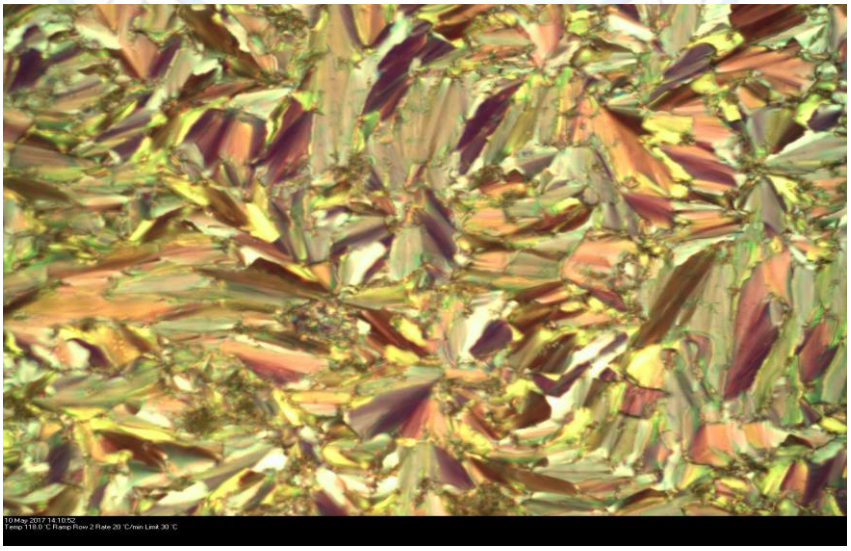


Figure 5: The Broken focal conic smectic A of compound DC_7A_6

When the compound DC_7A_8 cooling from isotropic phase the thread like S_mC appeared (Figure 6).

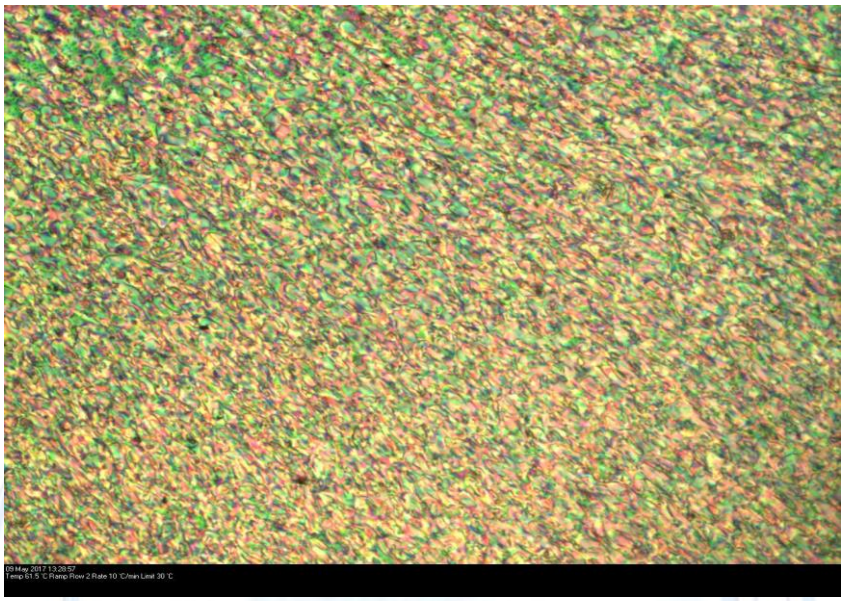
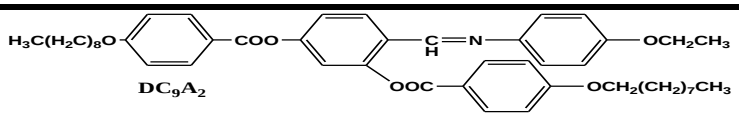
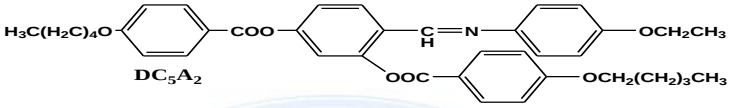


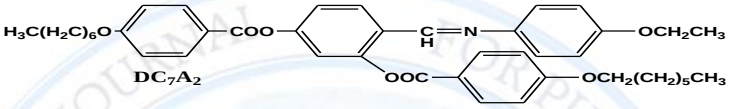
Figure 6: The Thread-like smectic C of compound DC_7A_8

It was found that there is close relationship between mesomorphism and molecular constitution of mesomorphic compounds [13, 1, 14]. This relationship could be correlated with the molecular constitution of these compounds by thermal stability, which is measure of mesomorphism. Table (3) shows the comparison of mesomorphic properties and thermal stability of the three series (present series, DC_7A_n and two presence series DC_9A_n [15] and $DC5A_n$ [10]) show a very similar mesomorphic behavior displaying nematic mesomorphic. The members in all series with short alkoxy chains (n=2) show a nematic mesophase.

Table 3: Comparison between transition temperatures, mesomorphism and average thermal stabilities for DC_9A_2, DC_5A_2 and DC_7A_2

1. 

2. 

3. 

No.	Compounds	Transition temperatures ^oC	ΔT
1	DC_9A_2	cr 127 N 167 I	40 ^oC
2	DC_5A_2	cr 109 N 216 I	107 ^oC
3	DC_7A_2	cr 121 N 246 I	125 ^oC

Conclusions

A new series of 2,4-bis (4-n-heptyloxybenzoyloxy)-benzylidene-4=-n-alkoxy aniline (DC_7A_n) have been prepared by changing the terminal alkoxy chain length (n=1-10). The chemical structures of the series were identified by IR, ^{1}H-NMR and elemental analysis. The results are in agreement with the considered molecular structure. The liquid crystal properties and optical textures of the compounds were studied by POM and DSC. The change in terminal alkoxy chain length has pronounced effect on the mesomorphic behavior. The first two homologues (DC_7A_1, DC_7A_2) exhibited only N phases but the others (DC_7A_3, DC_7A_{10}) display dimesomorphism N and S_mC phases. But with compound (DC_7A_6) the other S_mA phase was observed. The mesomorphic properties and thermal stabilities of the present series is compared with those of structurally related homologous series.

References

1. Ha, S.T., Koh, T. M., Lee, S. L., Yeap, G. Y., Lin, H. C. and Ong, S. T. "Synthesis of new Schiff-base ester liquid crystals with a benzothiazol core", *J. Matter. Chem., Liq. Cryst.*, Vol.37, P. 547-554, **2010**.
2. Murillas, D.L., Pinol, R., Ros, M. B., Serrano, J. L., Sierra, T., & Fuente, M. R., "Structure-activity studies of ferroelectric and anti-ferroelectric imine ligands and their palladium(II) complexes. An anti-ferroelectric metallomesognen", J. Materials Chem., Vol.14, P. 1117-1127, 2004.
3. Compillos E., Marcos M., Omenta A., & Muhsen M. A., "Synthesis and properties of copper (II) and oxovandium(IV) complexes derived from polar Schiff base", J. Mater. Chem., Vol.6(3), P. 349-355, 1996.
4. Aziz, H. J.," Synthesis and study of liquid-crystalline behaviors of novel Schiff base", Ph.D Thesis, University of Baghdad, (2000).
5. Dare, J. S., & Vora, R. A.," Mesomorphic behavious of the cholesteryl - I liquid crystals and ordered fluids", Plenum, New York, P. 477-487, 1970.
6. Keller, p., & Liebert, L., " Solid state physics " supplement 14, Academic press London, 1978.
7. Pugh, C., & Schrock, R. R., " Synthesis of side-chain liquid crystal polymers by living rings-opening metathesis polymerization. 3-influence of molecular weight, interconnecting unit, and substituent on the mesomorphic behavior of polymers with laterally attached mesogens ", Macromolecules, Vol.25(29), P. 6593-6604, 1992.
8. Zhou, Q. F., Li, H. M. & Feng, X. D., " Synthesis of a new class of side chain liquid crystal polymers with mesogens laterally attached via linkages to polymer backbones", Mol. Cryst. Liq. Cryst. Vol.155(1), P. 73-82, 1988.
9. Gray, G. W., " Molecular structure and properties of liquid crystals ", Academic press London, 1962.
10. Hamad, W. M., Hashim, J. A., & Ammar, H. Al-Dujaili., " Synthesis and mesomorphic properties of 2,4-bis(4--n-pentyloxybenzoyloxy)-benzylidene-4=-n-alkoxy aniline",

Molecular Crystals and Liquid Crystals, http://dx.doi.org/10.1080/15421406.2017.1357426, P. 1-9, 2017.

11. Demus, D., & Richter, L., " Textures of liquid crystals ", Verlag Chemie, New York, 1978.

12. Dieking, I., " Textures of liquid crystals ", Wiley-VCH, New York, 2003.

13. Weissflog, W., Wiegleben, A., Haddawi, S., & Demus, D., " Thermotropic liquid crystalline compounds with lateral long chain substituents part IX linking of lateral aliphatic chains to three-ring mesogens by different functional groups", Mol. Cryst. Liq. Cryst., Vol.281, P. 15-25, 1996.

14. Patel, P. K., & Shah, R. R., " Study of mesomorphism and laterally substituted nitro group ", Mol. Cryst. Liq. Cryst., Vol.634, P. 41-49, 2016.

15. Hamad, W. M., & Salih, Sh. K., " Synthesis and liquid crystal studies of 2,4-bis(4--n-nonyloxy)-benzylidene-4=-n-alkoxy aniline", ARO the scientific journal of Koya university, Vol.5(1), P. (24-29), 2017.