Hydrogen Bonded Thermotropic Liquid Crystalline Properties of some New Schiff Basses

S.H.Ridha, A.J.Al-Najem
Chemistry Department, College of Education for Girls, Kufa University, Kufa/Iraq. sajida2274@yahoo.come

I.Latif
Chemistry Department, College of Education , Ibn-Al-Haitham, Baghdad University, Baghdad/Iraq
dr_issam2003@yahoo.com

Abstract

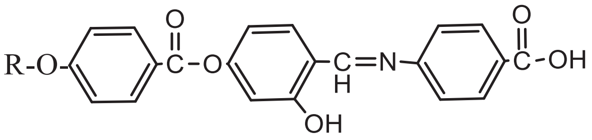
A new homologous series of Schiff bases ester,2-hydroxybenzylidineanilines:N-[4-(4'-n-(alkoxybenzoyloxy)-2-hydroxybenzylidine]-4''-carboxyanilines (HAHC) were (n=1-10) synthesized and characterized by spectroscopic techniques (IR and ^{1}HNMR) and microelemental analysis. Mesomorphic behavior and phase transitions were studied using polarized hot stage optical microscopy (POM) and differential scanning calorimetry (DSC). It has been found that the compounds with(C_1-C_3) of the series exhibit enantiotropic nematic phase only while those compounds with (C_4-C_7) show smectic C in addition to nematic phase. While compounds with (C_8-C_{10}) show smectic C phase only.

Key words: Schiff Basses Liquid crystals , Thermotropic liquid crystals, Nematic phase , Synthesis of Liquid Crystalline compounds , Smectic C phase , Hydrogen bonded liquid crystals phases

1. Introduction

Organic compounds with rode- or disc like structure exhibit thermotropic liquid crystal (LC). Mesophase molecular structure is fundamental for synthesis of new mesogens with desirable properties and application [1]. Comprehensive studies on the Schiff base core system have been conducted since the discovery of N-(4-methoxybenzylidine) -4-butylaniline (MBBA) which exhibited a nematic phase at room temperature [2]. Aromatic azomethine ester comprising of different polarity of substitutes has been known to either promote or suppress the mesomorphic properties [3-6]. The hydroxyl group leads to a strong chelation ring by means of intrahydrogene bond [7-9]. The mesomorphism is due to increase in molecular planarity by appearance of local permanent dipole moment and at the same time of anisotropy of the electronic poarizability. Many physical properties of alkoxy and alkenoxy benzoic acid structures have been investigated [10], including their properties in binary systems [11], intermolecular hydrogen bonding formation [12–14], IR, Raman and thermodynamic investigations [15], the temperature dependence of their Raman spectra [16], dielectric anisotropy [18] and their self-assembly [19].

N-[4-(4,-n-alkoxybenzoyloxy)-2-hydroxybenzyline]-4,,-pentoxy [20] or heptoxy anilines[21] were synthesized and their mesogenic behavior was studied. The compounds N-[4-(4, -n-decoxybenzoyloxy) -2-hydroxybenzylidine] -4, -alkoxyanilines and their complexes were synthesized and their mesogenic properties were studied [22]. In this work new Schiff bases have been synthesized and characterized by IR and HNMR spectra and CHN analysis the compounds N-[4-n-(alkyloxybenzoyloxy) -2-hydroxybenzoyloxy-2-hydroxybenzylidine] -4' -carboxyanilines compound (1). It was found that compounds with (C_1-C_{10}) show thermotropic liquid crystalline behavior when examined by hot stage polarizing microscope and DSC analysis.



(Compound 1)

$$R = C_nH_{2n+1} \qquad n = 1\text{-}10$$

2. Experimental

2.1. Materials

All unsynthesized compounds were commercial products of analar grade and were used without further purification.

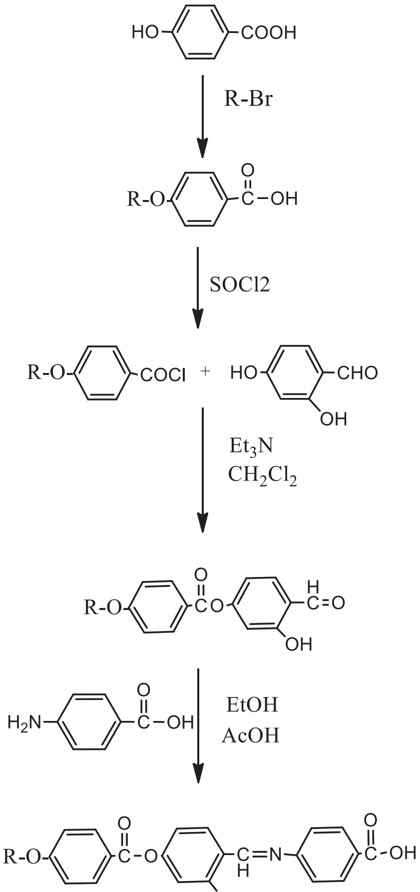
2.2. Instrumentation

Analytical data were performed on Micro analytical unit Euro Vector S.P.A.E.A 300-CHN Elemental Analyzer, FT-IR data were recorded on Shimadzu FT-IR 8400S Fourier transform infrared spectrophotometer (KBr disc), ^{1}HNMR spectra were recorded in DMSO-d_6 on NMR-Bruker hiospin SA, F-67166 Ultra Shield 400MHZ.Switzerland, France. The phase transition temperatures for the investigated compounds were determined using a differential scanning calorimetry Shimadzu TA-60WS, the optical microscopy studies were carried out with a polarizing microscope equipped with a Mettler hot stage.

2.3. *Synthesis of Schiff Bases*

The aldehydes with (C_1-C_{10}) were prepared following the route shown in scheme 1 using methods previously reported [10]. The imines were synthesized by mixing an equimolar amount of compound I with p-aminobenzoic acid, both dissolved in absolute ethanol with three drops of acetic acid used as catalyst. The reaction mixture was refluxed for three hours with stirring before it filtered. The yellowish crystalline of imines thus obtained were recrystallized from ethanol. These compounds were characterized by elemental analysis and spectroscopic techniques.

Scheme 1



$R = C_n H_{2n+1}$ n = 1-10

Scheme 1: The synthetic route of (HAHC)

3. Results and Discussion

3.1. *Characterization of the synthesized compounds*

The aldehydes I exhibited intense IR absorption near 1720 cm^{-1} (ν C=O), near 1600 cm^{-1} (ν C=C), and near 1250 cm^{-1} (ν C-O-C). Medium absorptions were recorded near 3050 cm^{-1} (ν C=C-H) and near 2930 cm^{-1} (ν C-C-H).

The ^1H NMR data for the aldehyde I (C_8) δ ppm ($CDCl_3$): 0.95 (t, 3H, CH_3), 1.2-2 [m, 12H $(CH_2)_6$], 4.0 (t, 2H, OCH_2), 6.8-8.3 (7H, ring protons), 9.9 (s, 1H, CHO) and 11.3 (s, 1H, OH).

The Schiff bases II (C_1-C_{10}) exhibited intense IR absorption near 1730 cm^{-1} (ν C=O) of ester group, near 1680 cm^{-1} (ν C=O) of carboxylic group, near 1600 cm^{-1} (ν C=N) and 1250 cm^{-1} (ν C-O-C). Medium were also recorded near 3060 cm^{-1} (C=C-H) and near 2930 cm^{-1} (ν C-C-H).

The ^1H NMR data for the Schiff base (C_5) δ ppm(DMSO): 0.9(t,3H,CH_3),1.3(m,4H,CH_2CH_2), 1.4(m,2H,-CH_2-), 4.08(t, 2H, OCH_2), 6.8-8.1(11 H, ring protons), 9.02(s,1H,CH=N), 12.8(s,1H,OH), 13.1(s,1H,COOH).
The ^1H NMR data for the Schiff base (C_9) δ ppm(DMSO): 0.87(t,3H,CH_3),1.2[m,10H,$(CH_2)_5$], 1.4(m,2H,-CH_2-), 1.7(m,2H,-CH_2-), 4.09(t, 2H, OCH_2), 6.9-8.09(11 H, ring protons), 9.03(s,1H,CH=N), 12.9(s,1H,OH), 13.05(s,1H,COOH).
The Schiff base compounds (C_6-C_9) had satisfactory elemental analyses and are consistent with those expected (Table 1).

3.2. Mesomorphic behavior

The thermotropic properties of the HAHC were characterized with a Schimatzu DSC instrument.The rate of heating was 10°C min^{-1} , the weight of the sample was 10 mg, and indium and zinc were used for calibration. The peak maximum was taken as the phase transition temperature. The DSC thermograms of the HAHC compounds (C_1-C_{10}) (Figure 2) exhibited in (C_1-C_3) and in (C_8-C_{10}) two endothermic peaks. But the compounds in(C_4-C_7) show three endothermic peaks on the heating run, leading to the conclusion that these compounds are enantiotropic. The investigation with POM were show the members (C_1-C_3) nematic phase only, the members (C_4-C_7) show smectic C and nematic phase, while the members (C_8-C_{10}) show smectic C phase only. In table 2 and 3 respectively are summarized the phase transition temperatures and associated enthalpy and entropy changes of all title compounds. It should be mentioned that all the phase transition temperatures evaluated on the basis texture changes are in good accord with those measured by DSC(figure 2).
The liquid crystalline samples were put between untreated glass plates, the molecules oriented with their director parallel to the substrates. The textures of these samples were observed under a polarizing microscope (POM) and show Schlieren textures [24-26] and the identification of the phases were made by comparing the observed textures with reported in the literature [27,28]. Observation under POM upon the compound with(C_1-C_7), during melting process exhibit a typical shlieren threaded or texture of a nematic phase figure 3. The smectic C exhibited by the compounds (C_4-C_{10}) is shown in (figure 4).
Figure 5 shows a plot of the transition temperatures against the number of carbon atom n of the terminal alkoxy chain for (n=C_1-C_{10}). The plot shows the typical monogamous behavior. The nematic-isotropic transition temperature curve is a filling and with some indication of odd-even effect. The smectic C phase range was increased as the terminal chain length increases n>7. The effect of a flexible substituent in depressing the mesophase stability is greater in more ordered phases such as smectic than nematic [28]. The linker groups used in our present work are CH=N (an azomethine group) and ester linker group (COO). The azomethine group generally will have a higher transition temperature when compared to the ester linker group. In the later the oxygen atom of the central carbonyl group will be bumped into the non-bonded sides of the adjacent hydrogen in the aromatic ring thereby causing considerable strain on the molecules [29]. This will cause some twist around the C-O bond and force the benzene ring with ester linkage out of the plane in the molecules. The other terminal group COOH makes the association of the acid in double molecules. Such physical association (dimer formation) of the acid makes molecules longer with high transition temperatures.

4. References

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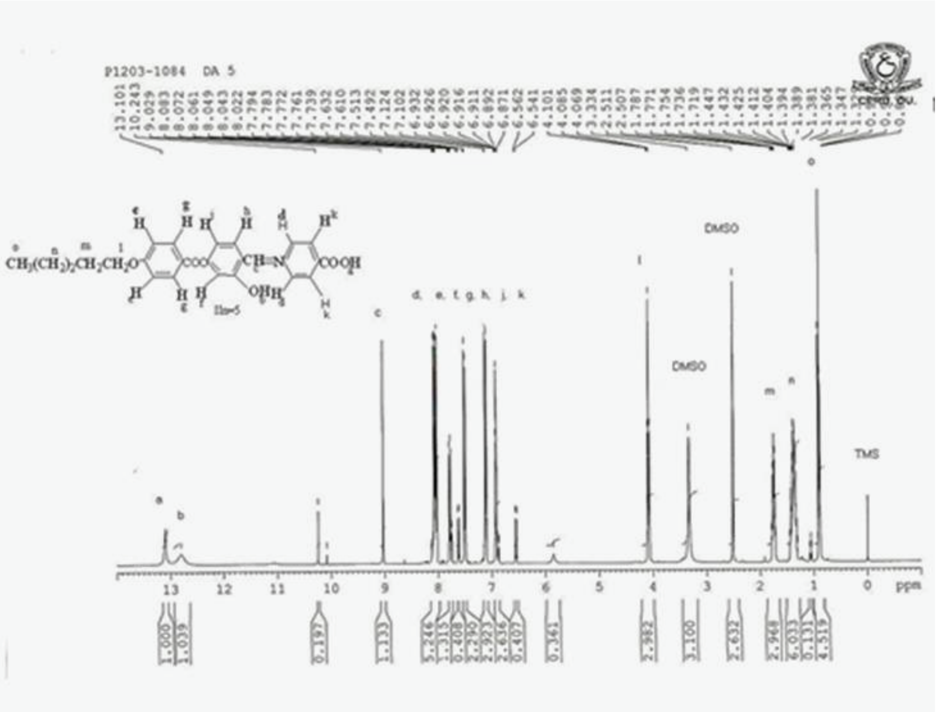


Figure1. 1H NMR data for the N-[4-n-pentyloxybenzoyloxy) -2-hydroxybenzoyloxy) -2-hydroxybenzylidine) -4, -carboxyanilines

Table 1 . Elemental analytical data (calculated values in parentheses).

Compound	Molecular Formula	C (%)	H (%)	N (%)
n=6	$C_{27}H_{27}NO6$	70.364(70.281)	6.098(5.856)	3.096(3.036)
n=7	$C_{28}H_{29}NO6$	69.930(70.736)	6.127(6.105)	3.229(2.947)
n=8	$C_{29}H_{31}NO6$	72.755(71.165)	6.817(6.339)	3.463(2.862)
n=9	$C_{30}H_{33}NO6$	72.336(71.570)	7.066(6.560)	3.113(2.783)

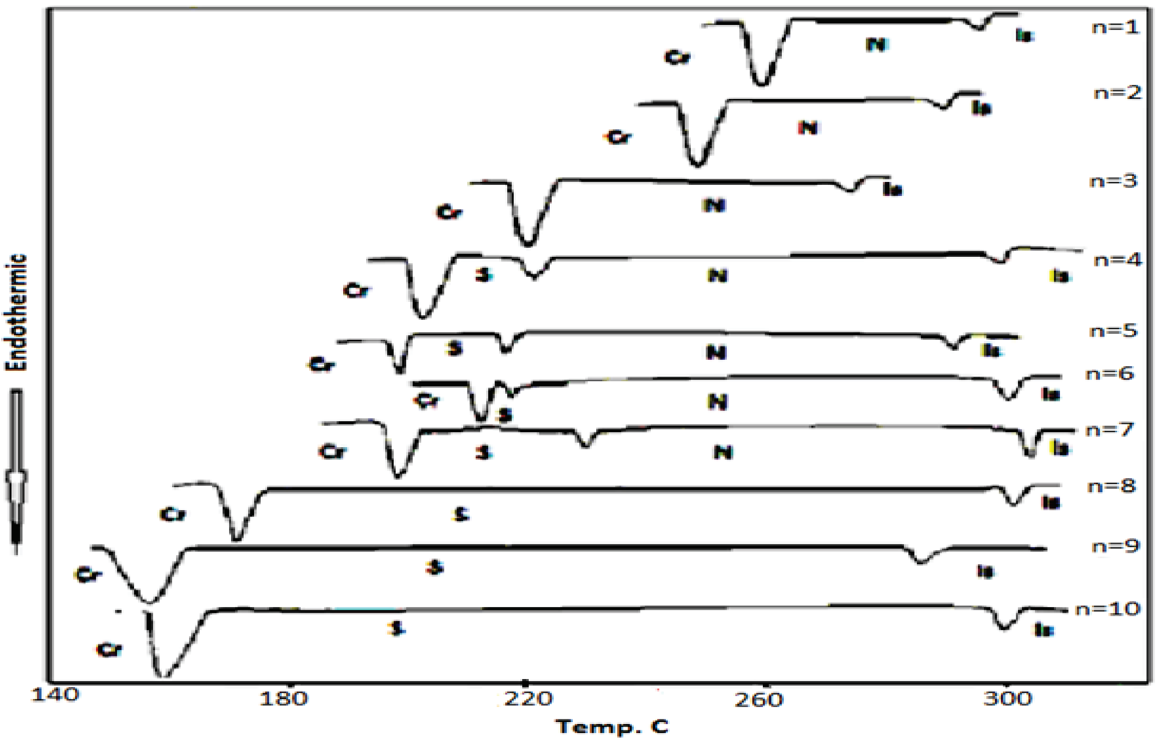


Figure.2 DSC thermograms of series (n=1-10) during heating cycle

Table 2 Phase transition temperatures C^{0} for the series II (n=1-10) DSC data in parentheses

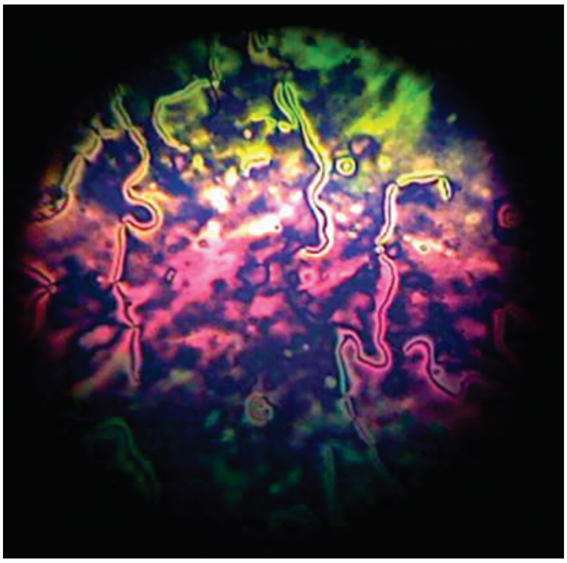
n	*Cr------Sc*	*Sc-----N*	*Cr-----N*	*N/Sc------Is*	*s*	*T_N*
1			*264 (260)*	*303 (296)*	*---------*	*36*
2			*254 (248)*	*295 (291)*	*----------*	*43*
3			*227 (221)*	*280 (274)*	*----------*	*53*
4	*206 (201)*	*218 (213)*		*304 (299)*	*12*	*86*
5	*201 (196)*	*220 (215)*		*295 (292)*	*19*	*77*
6	*217 (212)*	*222 (218)*		*308 (303)*	*5*	*85*
7	*202 (196)*	*236 (230)*		*312 (306)*	*34*	*76*
8	*176 (171)*			*309 (303)*	*173*	*--------*
9	*161 (157)*			*292 (287)*	*131*	*--------*
10	*164 (159)*			*307 (302)*	*143*	*--------*

Cr:Crystal; Sc: Smectic C; N: Nematic; Is:Isotropic

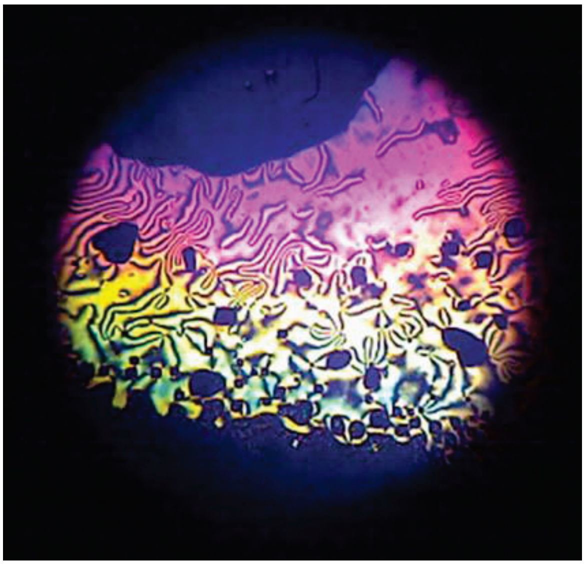
Table 3.Associated Enthalpy and Entropy in (parentheses) Changes of the series (n=1-10)

n	*Cr------Sc*	*Sc-----N*	*Cr-----N*	*N/Sc------I*
1			*37.8 (70.89)*	*3.0 (5.27)*
2			*38.1 (73.11)*	*2.1 (3.72)*
3			*39.5 (79.87)*	*3.6 (6.58)*
4	*41.2 (86.9)*	*3.18 (6.54)*		*2.06 (3.60)*
5	*10.7 (22.81)*	*4.14 (8.48)*		*2.29 (4.05)*
6	*19.7 (40.6)*	*4.01 (8.16)*		*2.38 (5.86)*
7	*27.8 (59.25)*	*4.63 (9.20)*		*2.34 (4.04)*
8	*29.9 (67.32)*			*15.1 (26.21)*
9	*45.5 (105.87)*			*17.9 (31.95)*
10	*76.1 (176.09)*			*22.5 (39.12)*

$Jmol^{-1}K^{-1}$ HKJmol^{-1}, S



Nematic phase n=5 at 252° C
n =5



transition of nematic to isotrop at 294°C

Figure 3: nematic phase images of compound n=5

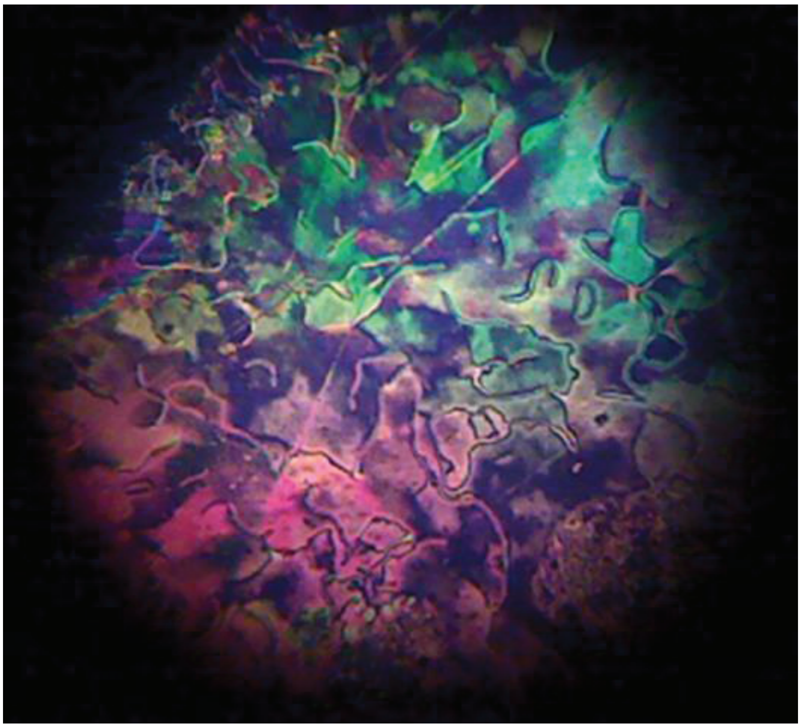


Figure 4: Schlieren texture of a Smectic C phase of compound n=10 at 268°C

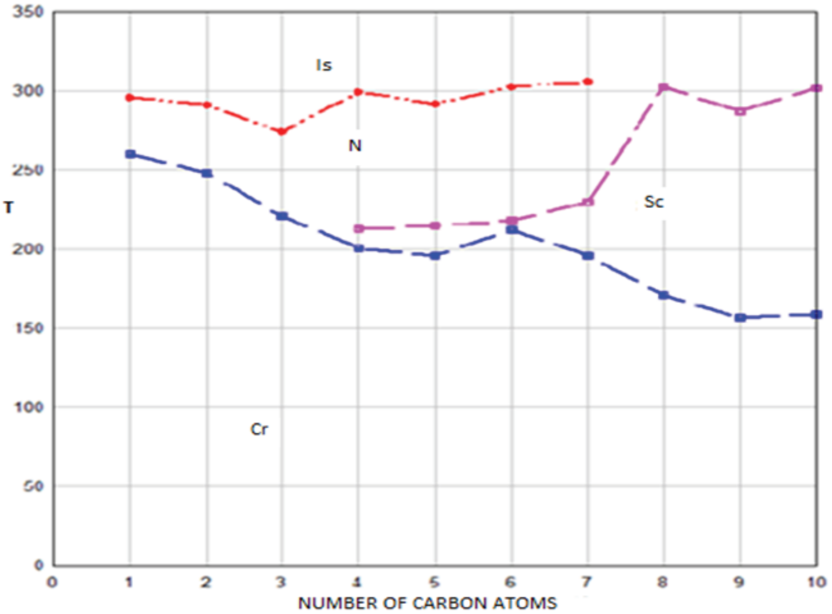


Figure 5: Plot of phase transition temperatures against number of carbon atoms (n) in alkoxy chain.