Effect of Different Polar Groups on the Mesomorphic and Physical Properties of Synthesized Schiff Base Liquid Crystalline Compounds

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ABSTRACT

Five compounds of calamitic Schiff base with liquid crystalline behavior were synthesized and characterized. The terminal of compounds were substituted with different types of polar groups are - OCH_3, -$COCH_3$, - Br, and -$COOC_2H_5$, -CF_3. The chemical structures of all compounds were characterized by FTIR spectroscopy while the phase transitions and optical textures of the samples were observed by polarized optical microscope. Furthermore, the transition temperatures of the compounds and their liquid crystalline temperature range were determined by using differential scanning coulometer. All compounds showed a higher tendency to exhibit an antiotropic nematic mesophases with different transition temperature range. Moreover, the dielectric and electrical conductivity were investigated. Using different polar groups in the synthesized liquid crystalline compounds is accompanied by significant changes in mesophase thermal stabilities as well as physical properties and all samples are with positive dielectric anisotropy.

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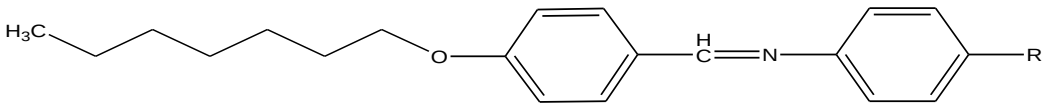
1. Introduction

Organic materials that show liquid crystalline properties have been studied by many researchers because of their wide applications in different fields of our life. Therefore, the physical properties such as dielectric, electrical conductivity and optical anisotropy, response to external fields have been studded [1-3]. Materials for practical use have been synthesized by many researcher in the field of liquid crystals to provide the specific physical properties necessary for various applications , so this research introduces a preparation of compounds with different polar groups to ensure that physical properties may affected by the polar groups which may be necessary to prepare new materials and provide those properties such as dielectric and conductivity anisotropy ($\Delta\varepsilon$, $\Delta\sigma$) which is the basis for most fabricated devices as well as their importance in the field of molecular physics [4-7]. The difference between measured dielectric constant for mesomorphic materials that is aligned parallel and perpendicular to the electrodes of the cell is called dielectric anisotropy ($\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$) , and the sign of dielectric anisotropy and its value depend on the anisotropy of their molecular dipoles and the distribution of dipole moments of a polar group with respect to the long axis of the molecule, i.e. director $\hat{n}$ [8-10]. In the present work, five Schiff base liquid crystalline compounds are synthesized and characterized.

2. Experimental

2.1 Synthesis of Samples

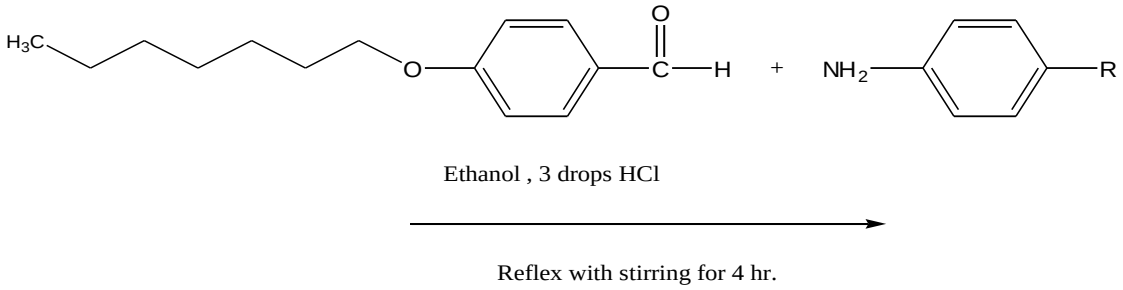
All solvents and primary aromatic amines and aldehydes were purchased commercially and used without any further purification. Equivalent molar quantities of 4-heptyloxy benzaldehyde which was previously synthesized by other work [11] and primary aromatic amines were condensed upon stirring at room temperature for four hours in appropriate amount of Ethanol. Precipitate formed and separated by evaporation of solvent and washed several times with methanol to give appropriate yield of the target compound. The general structure of our prepared liquid crystalline samples is shown in Fig.1.

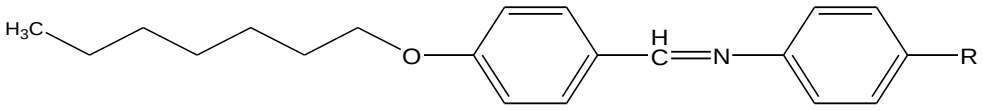


(R=-OCH_3, -$COCH_3$, -Br , -$COOC_2H_5$, -CF_3)

Figure 1: General structure of synthesized Schiff base liquid crystalline compounds

The synthesis route of the title compounds is shown in Fig.2.





(R=-OCH_3, -$COCH_3$, -Br , -$COOC_2H_5$, -CF_3)

Figure2: Synthesized route of Schiff base liquid crystalline compounds

3. Results and discussions

3.1 1FTIR characterization

The structure of synthesized Schiff base compounds was characterized using FTIR spectroscopy technique. Figure 3 shows the FTIR spectrum for the prepared Schiff base sample with the polar

group (OCH_3). The vibration frequency for functional groups in the synthesized Schiff base compound is summarized in Table 1.

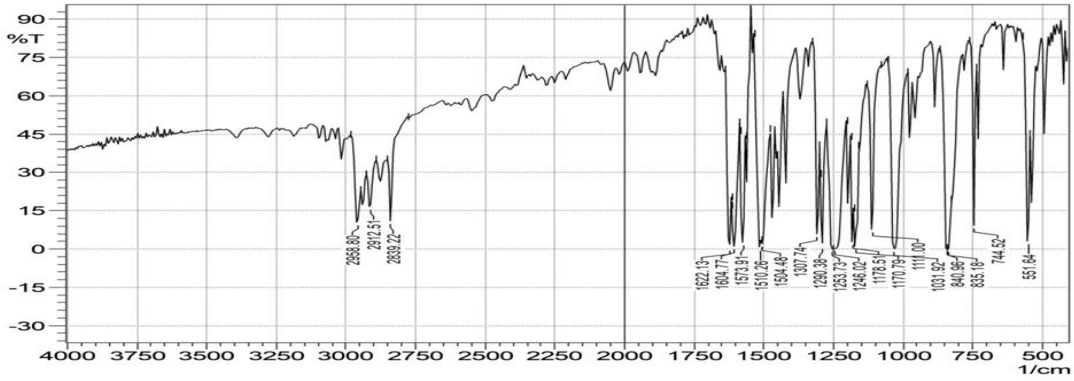


Figure3: FTIR spectrum for the Schiff base sample with the polar group (OCH_3)

Table1: FTIR vibration frequency of functional groups of Schiff base compound with polar group (- OCH_3)

Functional groups	Vibration frequency (cm^{-1})
C─C(aliphatic)	2958.8
C─O(ether)	1307.74
C=C(aromatic)	1573.7
C─H(aromatic)	3050
C=N(imines)	1622.13
C─O─C(ether)	1031

3.2 Optical texture

The synthesized Schiff base compounds show a thermo tropic liquid crystalline type, and their transition from solid to liquid crystalline state was carefully monitored during both heating and cooling scans by using Polarized optical microscope. Figures 4a & 4b show the optical textures for two of synthesized Schiff base compounds **as** the representative illustration.

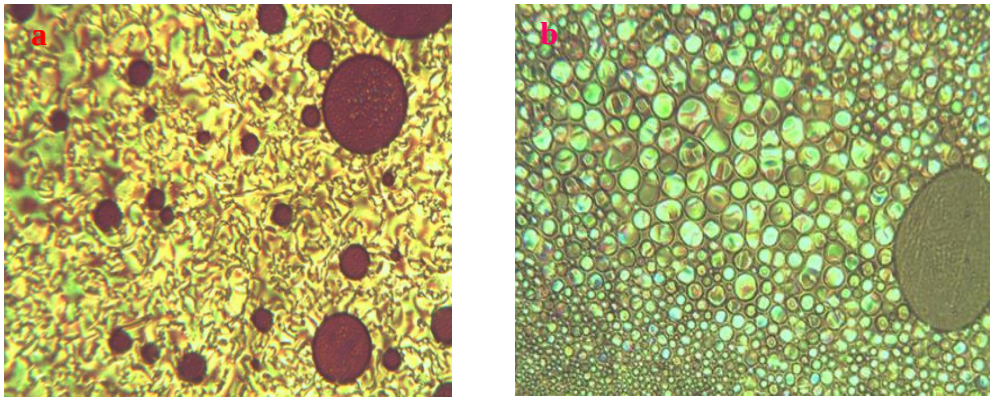


Figure4: (a) Nematic Schlieren view of Schiff base compound with (a) (-OCH_3) polar group upon cooling from isotropic liquid, (b) (- CF_3) polar group upon cooling from isotropic liquid

3.3 Thermal analysis

The transition to liquid crystalline state as given from observation of polarized optical microscope was verified by the differential scanning calometer as given in Fig.5. The Fig. shows transition from solid to liquid crystals for one of the prepared compounds while phase transition temperature ranges are summarized in Table 2.

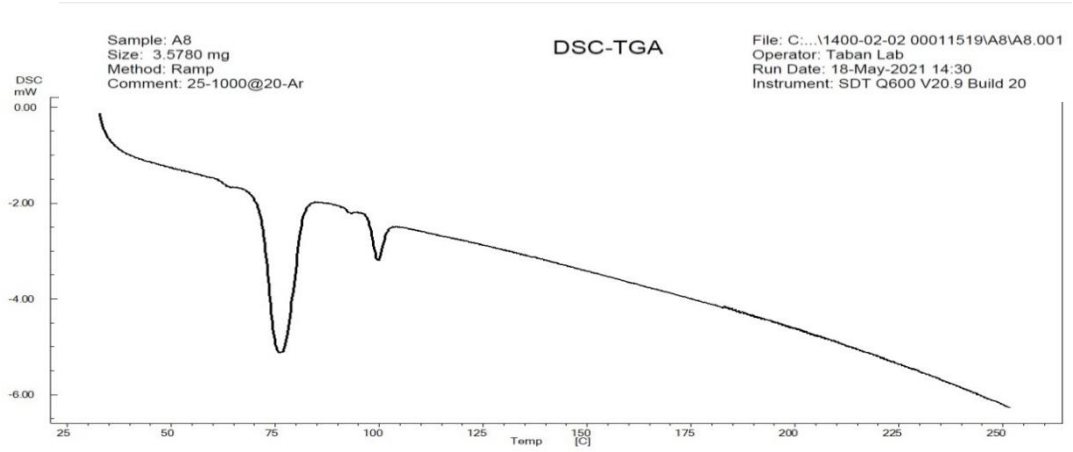


Figure5: DSC thermogram for Schiff base sample with polar group

Table2: Transition temperatures for the different compounds

Sample	Polar group	Temperature (°C)		Temperature range ΔT ˚C
		Nematic	Isotropic	
Ab_1	Br	62.5	94.5	32
Ab_2	$COCH_3$	76	112.5	36.5
Ab_3	$-CF_3$	73	105	32
Ab_4	$-COOC_2H_5$	68	90	22
Ab_5	$-OCH_3$	76.5	100	23.5

3.4 Dielectric constant

The dielectric properties of the compounds samples given in figure(1) was measured using (LCR/ESR meter) type(PROGRAMABLE AUTOMATIC RLC METER(FLUKE - PM6306) , and the temperature of the sample under study was measured by using digital thermometer with a thermocouple in contact with the ITO glass of the cell encapsulated our sample. The dielectric constant variation with temperature at frequency of5 kHZ was given in Fig.6.

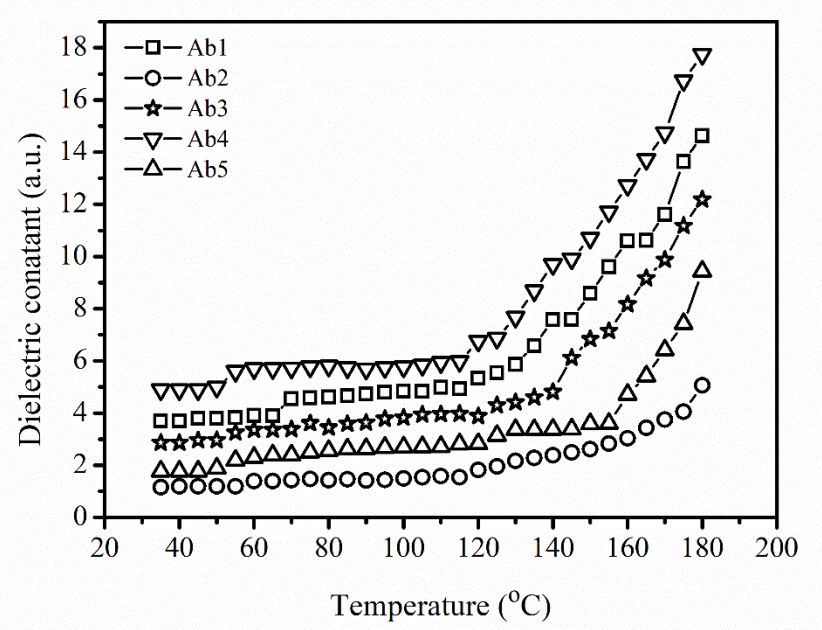


Figure6: Behavior of dielectric constant for Schiff base liquid crystalline compounds at different temperatures *including the nematic phase

Such results revel the pronounced difference in dielectric constant as temperature is raised, which may attributed to the different polarity exhibited by the synthesized Schiff base liquid crystalline compounds which is in a good agreement with other researcher [12,13]. The dielectric constant is measured with the samples aligned parallel and perpendicular to the long molecular axis at frequency of 5 kHZ as a function of temperature and consequently their dielectric anisotropy (Δε) using the equation below [14]:

$\Lambda\varepsilon=\varepsilon_{||}-\varepsilon_{\perp}$ …… 1

The dielectric anisotropy was measured for all aligned samples parallel and perpendicular as a function of temperature ,figure (8) show the variation of dielectric constant with temperature for one of a schiff base liquid crystalline compounds with alignment parallel and perpendicular to the ITO electrode

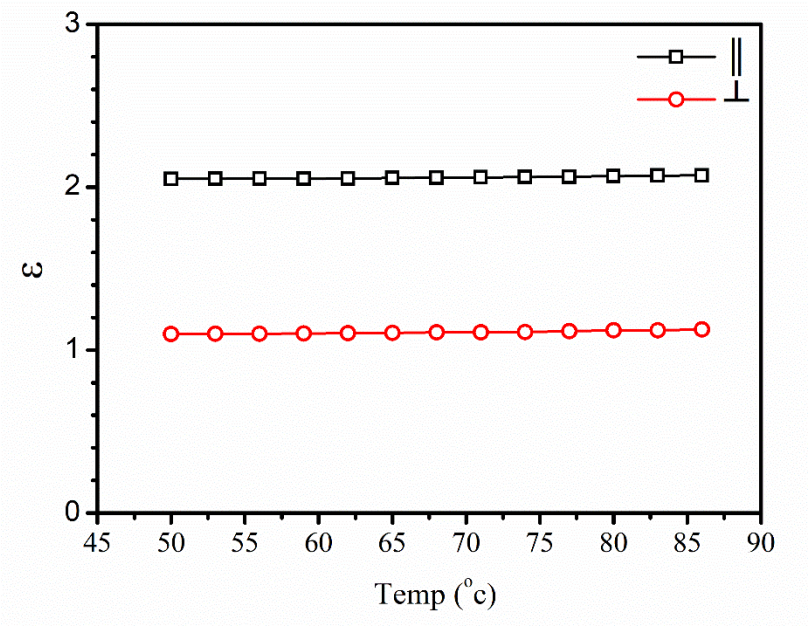


Figure7: Dielectric constant as a function of temperature for aligned Schiff base compound with polar group of -Br

The values of dielectric anisotropy at the nematic phase for the schiff base compounds are summarized in Table 3.

Table3: The dielectric anisotropy for the prepared compounds with different polar groups at different frequencies

Sample	Polar group	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
Ab_1	-Br	2.05961	1.1098	0.94981
Ab_2	$-COCH_3$	1.55935	1.16881	0.39054
Ab_3	$-CF_3$	4.44585	1.26796	3.17789
Ab_4	$-COOC_2H_5$	5.39438	1.07513	4.31925
Ab_5	$-OCH_3$	1.4874	1.17996	0.30744

The positive dielectric anisotropy of the prepared samples indicate that the dipole moments of our synthesized liquid crystalline compounds was predomenently acting along their molecular axis and so the dielectric constant for homogeneous alignment was found to be greater than that for homeotropic alignment [15].

3.5 Conductivity measurements

The conductivity of synthesized Schiff base liquid crystalline samples was measured from dissipation factor and capacitance at the frequency of 5 kHz by using the same RCL bridge used for dielectric measurements making use of the following equation[16]:

$$\sigma(w)_{ac}=\frac{d}{AR_p} \quad \ldots.2$$

$$R_p=\frac{1}{DwC_p} \quad \ldots. \quad 3$$

Where A is the area of electrode, d is the thickness of the cell, D is the dissipation factor, R_p is the equivalent parallel resistance of the circuit, $C_p$is the parallel capacitance of the cell and w=2πf.

Using homogeneous and homeotropic alignments for Schiff base liquid crystalline compounds the conductivity anisotropy was measured at the nematic temperature range. Figure 8 shows the variation of conductivity with temperature for one sample with polar group (-Br).

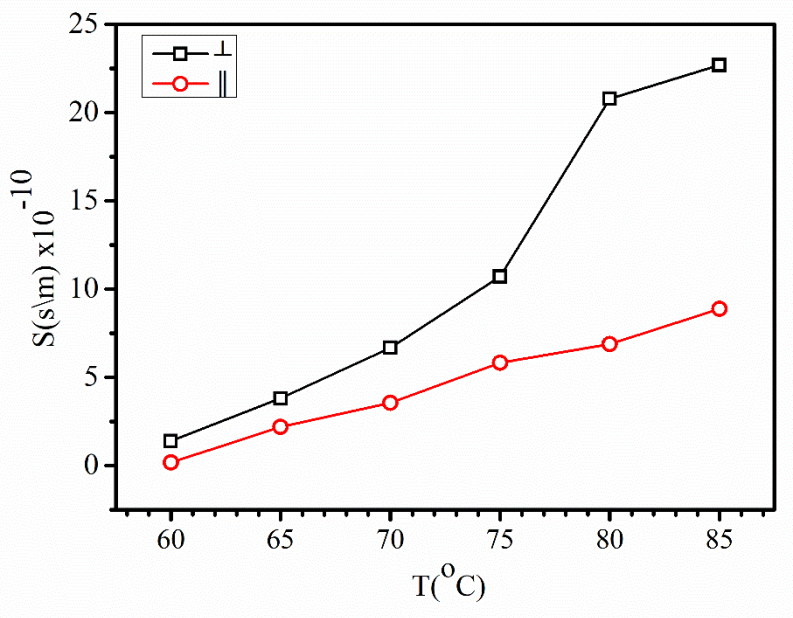


Figure8: Conductivity as a function of temperature for homogeneous and homoeotropic alignments for the sample with polar group of -Br

The result mentioned clearly a significant increase in conductivity as the temperature increased and this is attributed to the increased mobility of ionic impurities charge which is apparently different for different molecular structures as it is the case in our prepared samples and we found it in a good agreement with the other researcher [17, 18]. The measured conductivity for aligned samples ($\sigma_{\parallel}$) and ($\sigma_{\perp}$) , as well as conductivity anisotropy ($\Delta\sigma$) for the prepared compounds with different polar groups at the nematic phase was given in Table4.

Table 4: Average values of $\sigma_{\parallel}$, $\sigma_{\perp}$ and $\Delta\sigma$ for different compounds at the nematic phase

Sample no.	Polar group	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\Delta\sigma$
Ab_1	-Br	$4.76053X10^{-10}$	$7.50699\ X10^{-10}$	$-2.74645\ X10^{-10}$
Ab_2	$-COCH_3$	$3.71304\ X10^{-10}$	$6.704177\ X10^{-10}$	$-2.99113\ X10^{-10}$
Ab_3	$-CF_3$	$9.09918\ X10^{-9}$	$17.88148\ X10^{-9}$	$-8.7823\ X10^{-9}$
Ab_4	$-COOC_2H_5$	$.08938\ X10^{-9}$	$5.06214\ X10^{-9}$	$-2.9727\ X10^{-9}$
Ab_5	$-OCH_3$	$3.19418\ X10^{-10}$	$6.09571\ X10^{-10}$	$-2.90153\ X10^{-10}$

4. Conclusions

The prepared compounds with different polar groups show a significant nematic phase with different transition temperature ranges (ΔT =22 - 36.5 °C) . the measured physical properties have much dependence on molecular structures with a pronounced effect on the measured physical properties for strong dipole moment in Sc_7-$COOC_2H_5$with($\Delta\varepsilon$= 4.319,$\Delta\sigma$ =- 2.972 $x10^{-9}SCm^{-1}$) ,while a small effect have been detected for a weak polar group in Sc_7- $COCH_3$ ($\Delta\varepsilon$= 0.390 , $\Delta\sigma$ = -2.991 $x10^{-10}S\ Cm^{-1}$).

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تأثير المجموعات القطبية المختلفة على الاطوار الوسطيه و الخواص الفيزيائية لبعض المركبات البلورية السائلة المحضره من نوع قاعدة شيف

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المستخلص

تم تحضير وتشخيص خمسة مركبات من نوع قاعدة شيف ذات الطور البلوري السائل, حيث تم استبدال طرف هذه المركبات بأنواع مختلفة من المجموعات القطبية ($-OCH_3$ ، $-COCH_3$ ، $-Br$ ، $-COOC_2H_5$ ، $-CF_3$) , لقد تم تشخيص التراكيب الكيميائية لجميع المركبات بواسطة التحليل الطيفي(FTIR) ، بينما لوحظت انتقالات الطور والتراكيب النسيجيه للعينات بواسطة المجهر ذو الضوء المستقطب ، وتم تحديد درجات حرارة الانتقال للمركبات ومدى درجة الحرارة للاطوار البلورية السائلة باستخدام جهاز المسح المسعري التفاضلي. أظهرت جميع المركبات ميلًا أعلى لإظهار أطوار وسطيه من النوع النيماتي مع مديات درجات حرارة مختلفة. تم قياس التوصيليه الكهربائية وثابت العازل وعلاقتهما مع درجة الحراره عند التصفيف الموازي والعمودي . إن استخدام مجموعات قطبية مختلفة في المركبات البلورية السائلة لوحظ بانه مصحوبًا بتغيرات في الاستقرار الحراري للاطوار البلوريه السائله بالإضافة إلى الخصائص الفيزيائية وجميع العينات اظهرت تباينا في العزل الكهربائي من النوع الموجب.