Dielectric , A.C. conductivity and electro optic properties of 4- pentyloxy benzaldehyde

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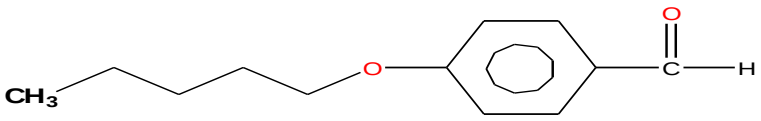
1. Abstract :

A low molecular weight liquid crystal based on Para hydroxy benzaldehyde was prepared. The molecular structure of the molecule was characterized with FTIR. Mesomorphic properties were characterized using differential scanning calorimetry (DSC)and polarizing optical microscopy(POM). The dielectric , A.C conductivity and electro optic response was studied at different temperatures and the dielectric anisotropy for the sample 4-pentyloxy benzaldehyde was found to be($\Delta\varepsilon$=-0.41),the conductivity anisotropy was found to be ($\Delta\sigma= 1.06x10^{-7}\Omega^{-1} .m^{-1}$), as well as the measured activation energy was found to be(E_{ac}= 0.844eV),and finally the threshold voltage for optical response of the nematic sample that is sandwiched in the liquid crystal cell was found to be (V_{th}= 2Volt).

2. Introduction :

With development of liquid crystal science and technology, more mesogens have been prepared and studied. Thermotropic liquid rystal is one type of mesogens currently extensively studied (Yuksel F. et .al , 2007).

Selection of mesogenic core, terminal groups and suitable length of flexible chain are among the essential criteria in designing new thermotropic liquid crystals (Gray G. , 1987). Low molecular mass compounds containing two unsaturated rings with one or multiple terminal substituents are capable of exhibiting mesomorphic properties (Colling P. et.al ,1998 **).** 1,4-Disubstituted phenyl ring often serves as an important core unit which ensures that molecules possess structural linearity and large molecular Polaris ability, thus consequently enables them to exhibit mesophase in low molar mass. Our efforts has been paid to prepare an a small molecule based on Para hydroxy benzaldehyde with a flexible chainof the form (C_nH_{2n+1} O) , and found it show liquid crystalline properties . However the structure of prepared molecule is shown in figure (1) :



4-(pentyloxy)benzaldehyde

Fig.(1) : molecular structure of 4-(pentyloxy)benzaldehyde

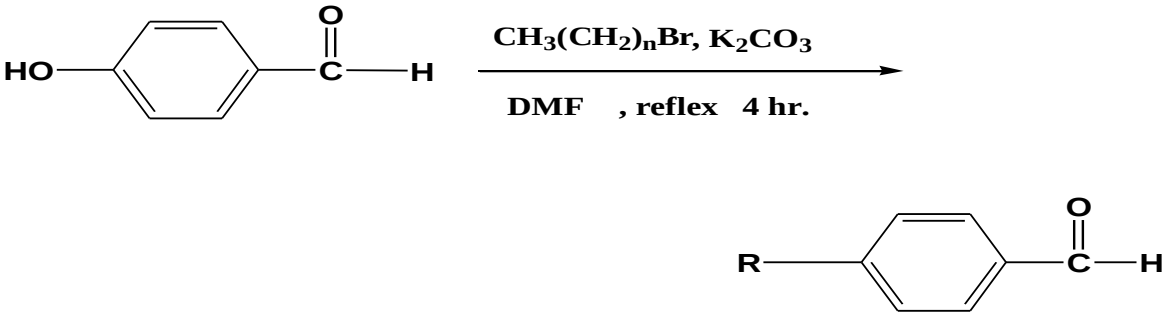
3. MATERIALS AND METHODS :

alkyl bromide ($C_nH_{2n+1}Br$,where n=4,5,6,7) , 4-hydroxy benzaldehyde and all solvent and reagents were purchased commercially and used without any further purification. IR spectra were recorded using SHMADZU System 8400 FT-IR Spectrometer . Phase transition temperatures were measured using Differential Scanning Calorimeter (type star˚sw-1000) at Iran polymer & petrochemical institute .

The temperature dependent studies of the liquid crystal was performed using Polarizing optical microscope equipped with a heating stage and a digital thermometer which was designed in our laboratory and Phase identification was made by comparing the observed textures with those reported in the literature**(**Dierking I. , 2003 **).**

3.1. Preparation and characterization :

4-(pentyloxy)benzaldehyde molecules and their derivatives were prepared via one step methods by alkylation of 4- Hydroxy benzaldehyde using a reported methods **(**Hasan A. et . al , 2011 **).** The preparation route of the molecules is illustrated in Fig .(2)



R = $C_n H_{2n+1}O$ n= 1,2,3,4,.....

Figure (2) : synthesis root for 4-pentyloxy benzaldehyde **and their derivatives**

4-Hydroxybenzaldehyde (1 m mol) and 1-Bromopentane ($CH_3(CH2)_4Br$) (1 m mol) were condensed with stirring at 120 $^{\circ}C$ temperature for four hours in appropriate amount of DMF(Dimethylformamide). The product was filtered out and then separated using Diethyl ether and distilled water, the Ether layer was dried via $MgSO_4$ and kept in Petri dish for two hours to evaporate the remaining solvent which give the final product as an oily substance that is characterized using IR spectroscopy as shown in the fig.(3) :

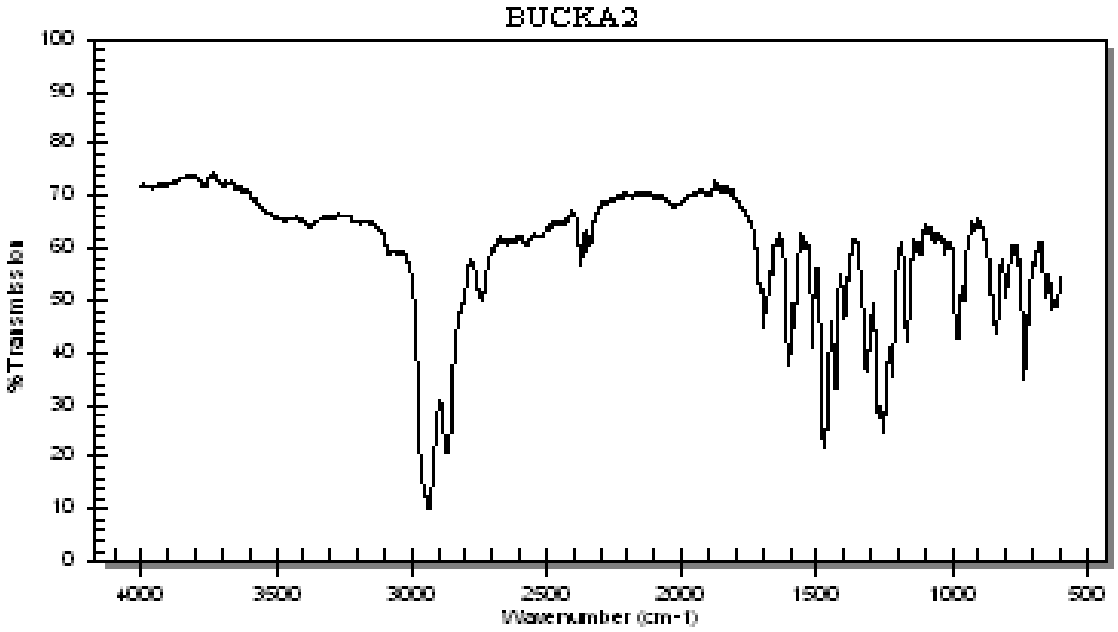


Fig. (3) : IR spectrum for 4-pentyloxy benzaldehyde

The stretching vibration of the functional groups for (4- pentyloxy benzaldehyde) was shown in table (1) .

Table (1): IR vibration frequency for functional groups in 4- pentyloxy benzaldehyde

Functional group	Vibration frequency (Cm^{-1})
C─H(methyl)	2870 , 2940
C─H(aldehyde)	2740
C=O(aldehyde)	1700
C=C(aromatic)	1600
C─C (aliphatic)	1300
C─O(ether)	1250

3.2. Mesomorphic properties :

One of the efficient methods to study the mesomorphic properties is the use of polarized optical microscope technique to show the phase transition of the studied organic materials as the temperature is raised from room temp. or by cooling from the isotropic liquid phase and in this research the optical textures of the prepared samples was done at cooling from isotropic liquid ,and the optical texture of the sample 4-pentyloxy benzaldehyde is shown in fig.(4) :

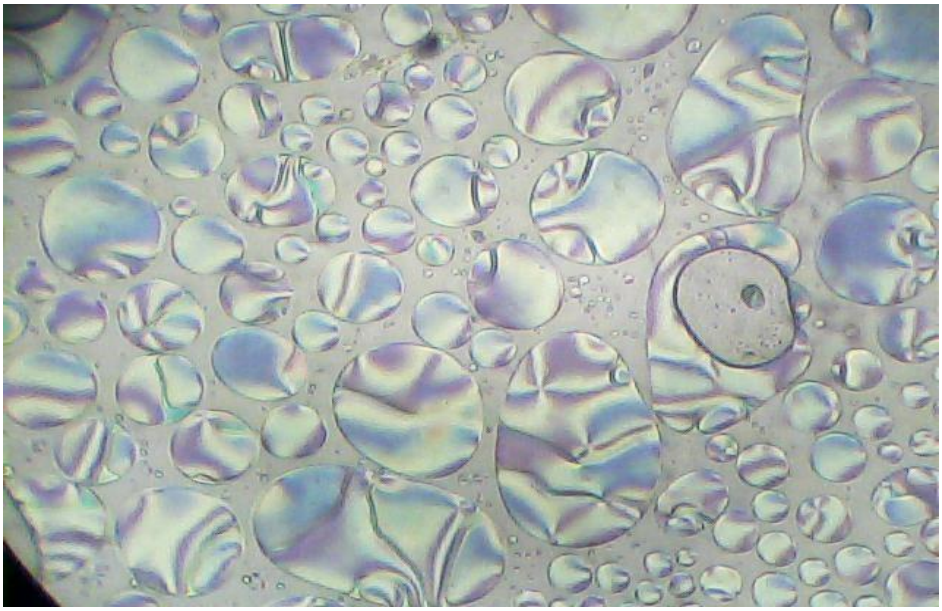


Fig.(4) : Optical texture for 4-pentyloxy benzaldehyde shows nematic droplet at phase transition (85 °C)by cooling from isotropic phase

Functional group	Vibration frequency (Cm^{-1})
C─H(methyl)	2870 , 2940
C─H(aldehyde)	2740
C=O(aldehyde)	1700
C=C(aromatic)	1600
C─C (aliphatic)	1300
C─O(ether)	1250

As well as the phase transition of the synthesized compounds was identified by a DSC thermogram for our sample at the Iran polymer &petrochemical institute and such thermogram show an efficient transition from crystal to nematic phase with a transition temperature range of about (25°C) as shown in the fig.(5) :

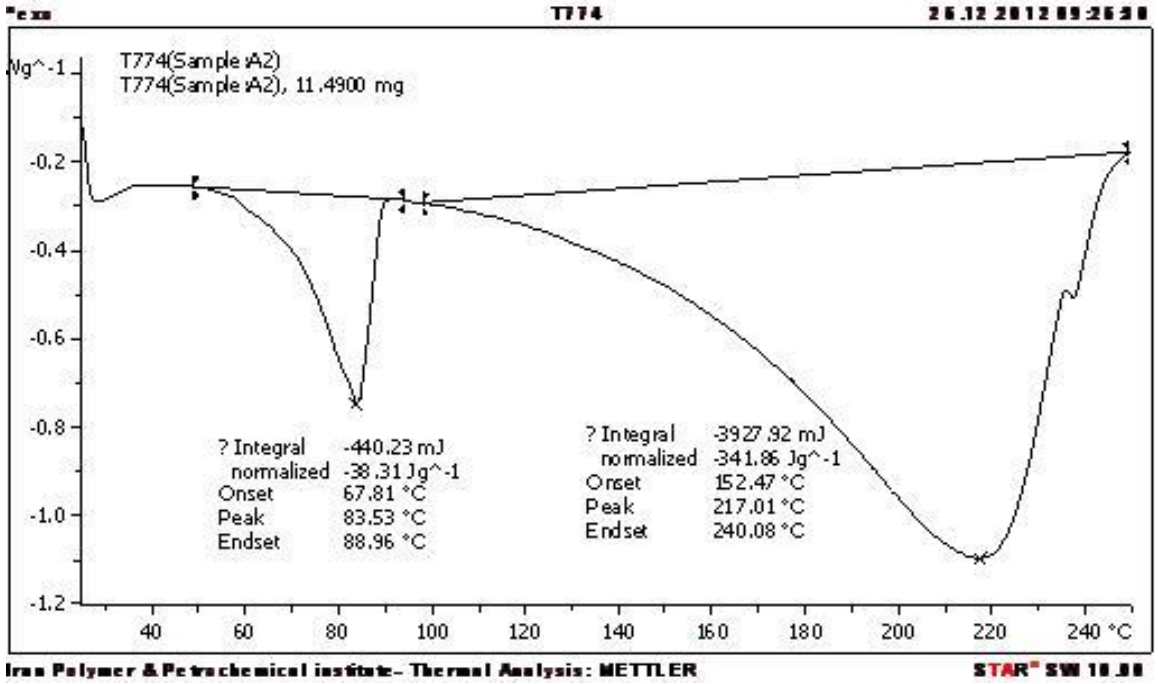


Fig.(5) : DSC thermogram for the liquid crystal compound A_2

4. Results and discussion :

4.1. Dielectric studies :

One of the most important physical property concerning the wide applications of liquid crystals is their dielectric behavior which determine their response to the electric fields . In this research we have been use (BK PRECISION Model 889B Bench LCR/ ESR Meter) to measure both the parallel and perpendicular dielectric constants at low frequency (100HZ) using an appropriate alignment methods **(**Kim H. et al , 2009 **)** ,and then measuring the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) as a function of temperature as shown in fig. (6) and (7) respectively:

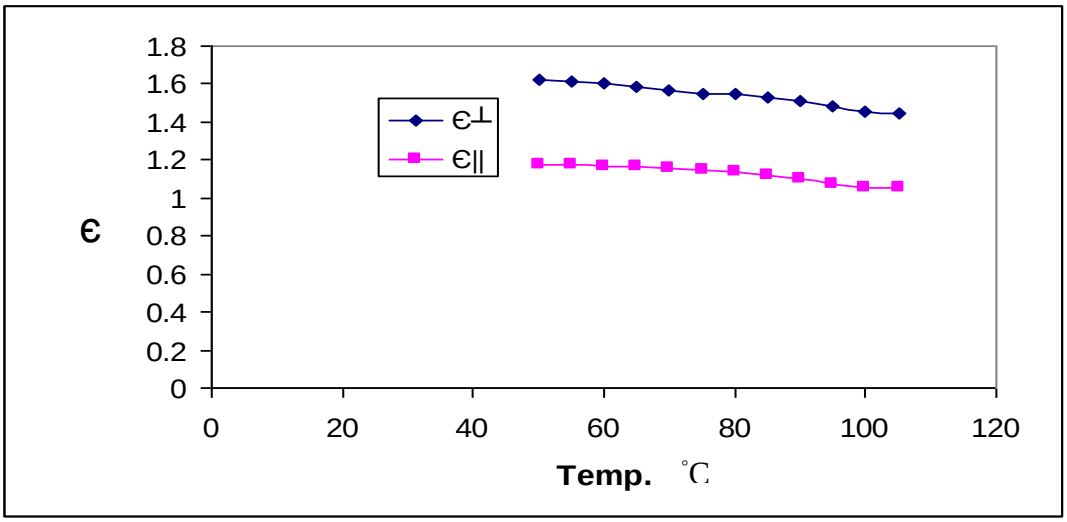


Fig.(6) : Variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for sample A_2 as a function of temperature at the nematic phase (85 ° C) by cooling from isotropic liquid .

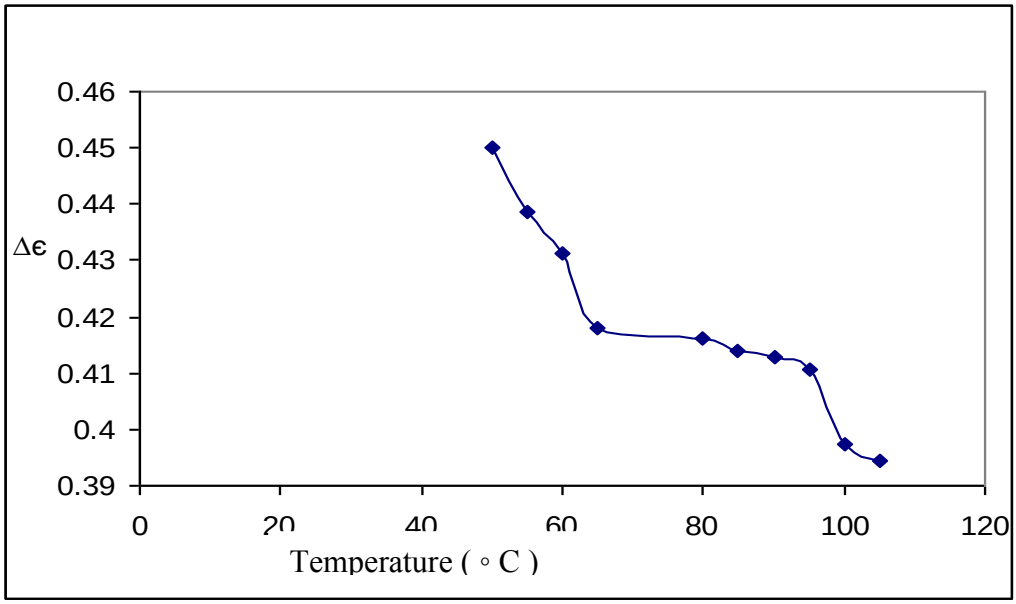


Fig.(7) : Variation of dielectric anisotropy(Δε)as a function of temperature at the nematic phase(85 ° C)by cooling from isotropic liquid .

The results show that our prepared samples are with negative dielectric anisotropy (Δε= $\varepsilon_{\parallel}$- $\varepsilon_{\perp}$ = -0.41)which can be attributed to the effects of transverse electric dipole moments with respect to the long molecular axis due to carbonyl group that is present in the compound 4-pentyloxy benzaldehyde (Wu S . T . et al, 1991),meanwhile the dielectric anisotropy was found to be decreases with increasing temperature which means that the high temperature will cause the dipole moments of previously aligned molecules to be more free

and responded rapidly with the applied field and consequently the difference between dielectric constants measured parallel and perpendicular decreases .

To show the effect of different frequencies on dielectric anisotropy the dielectric constant were measured at mid point of nematic phase and we found that the dielectric anisotropy at low frequencies 100Hz – 1kHz (static dielectric constant) remain almost the same as it is expected ,while changing frequency towards higher values 10 kHz – 100 kHz have a pronounced effect on the measured values of dielectric constant ,and we may attribute such behavior to the minimum time for such dipoles to be aligned with the varying electric field which is found to be in a good agreement with other researcher **(**Abd El Wahed M. et al , 2003 **)** as it is shown in fig.(8) .

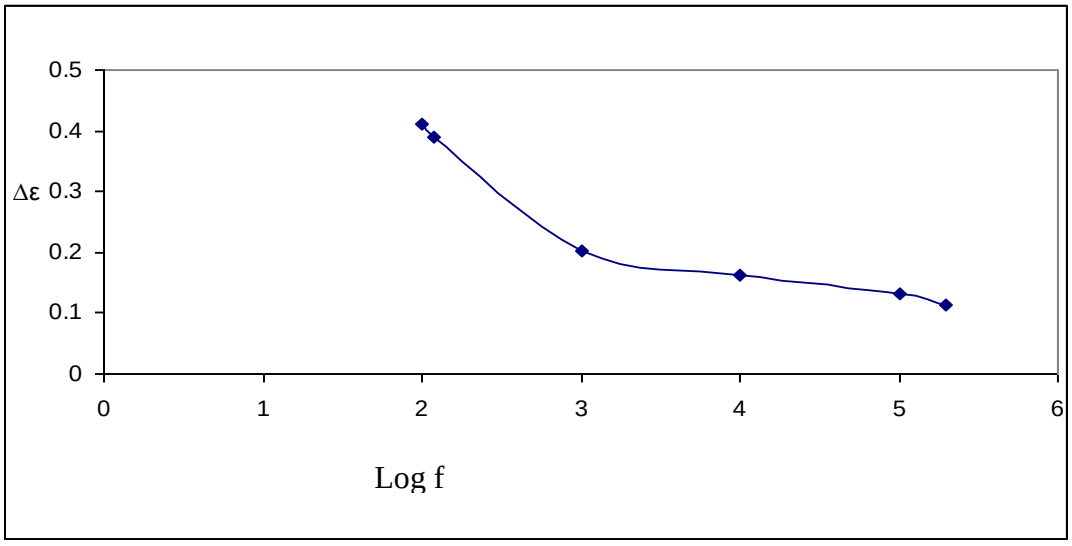


Fig.(8) : Variation of dielectric anisotropy as a function of frequency at the nematic phase (85° C)by cooling from isotropic liquid .

4. 2. A.C Conductivity measurements :

The A.C conductivity, dielectric constant, and dielectric loss can be related by the following equation **(**Bhat S. et al , 1995 **):**

$$\sigma_{ac} = 2\pi f \varepsilon_o \varepsilon_r \tan\delta$$

where ε_o is the permittivity of vacuum , ε_r is the dielectric constant of the sample, *f* is the frequency, and tan δ is the dielectric loss.

The measured value of conductivity anisotropy at nematic phase(85 ° **C)** was found to be about ($\Delta\sigma$= $1.06\text{x}10^{-7}\Omega^{-1}$ $.m^{-1}$) and the variation pattern of A.C conductivity at low

frequency (100 HZ) as well as conductivity anisotropy ($\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$)with temperature is shown in Figure (9) and (10) respectively :

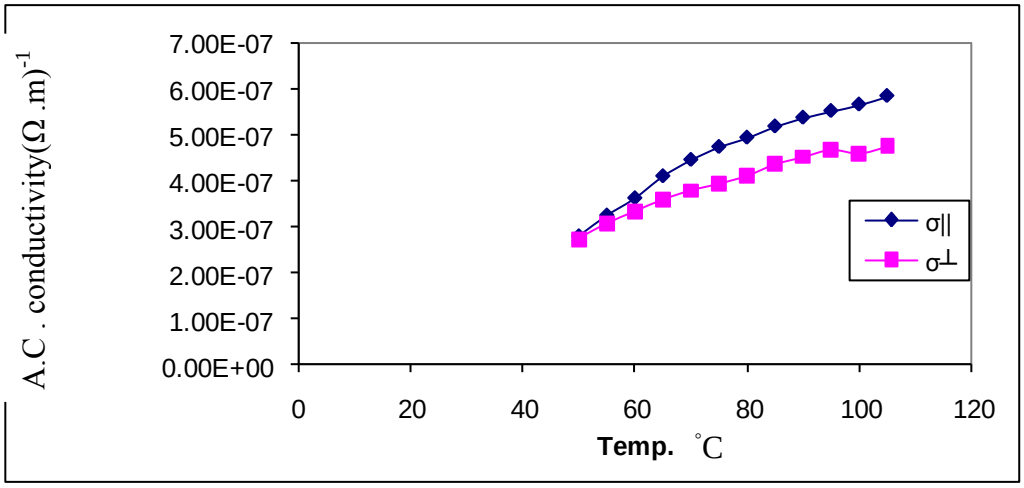


Fig.(9) : Variation of $\sigma_{\parallel}$ and $\sigma_{\perp}$ as a function of temperature at phase transition (85 ˚C)by cooling from isotropic liquid.

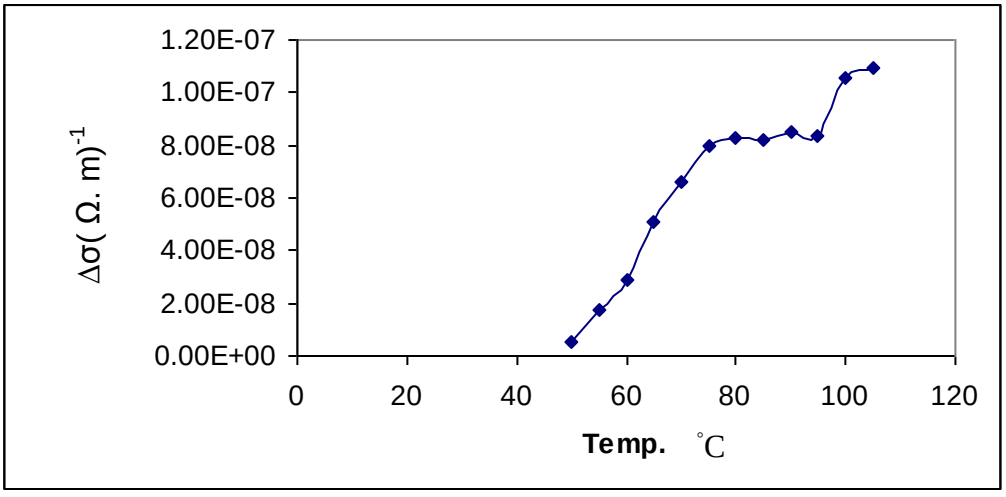


Figure (10) : Variation of conductivity anisotropy as a function of temperature.

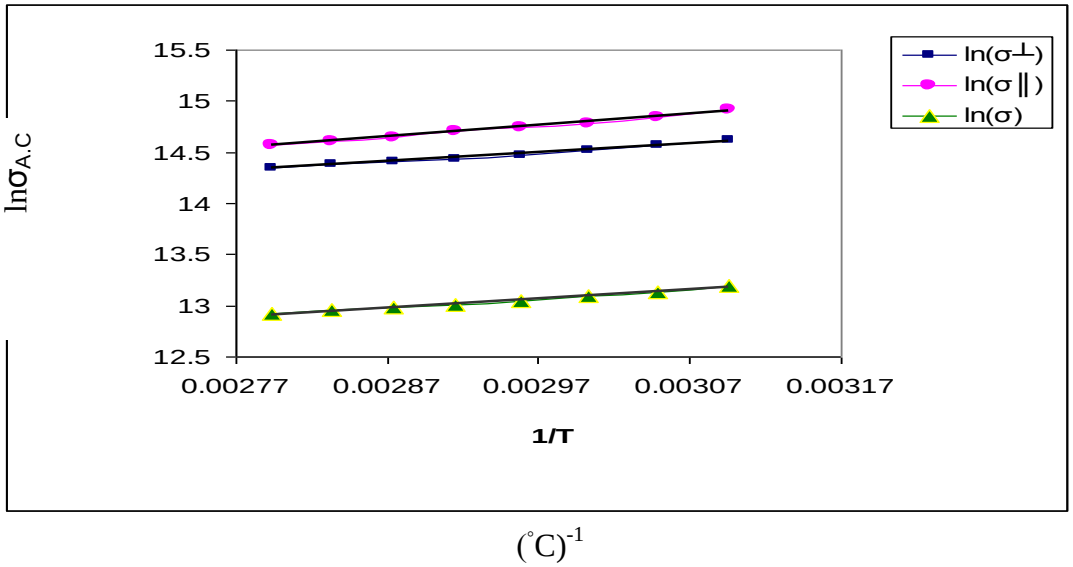
Results indicates that the A .C conductivity increases with temperature at low frequency (100 Hz). This is may be attributed to the increased mobility of ionic impurities with increasing temperature (Platon P. et al,2010).

As a result of conductivity variation with temperature the plot of ln σ versus l/T for both aligned and not aligned samples which is given in figure (11)is almost linear , from which the activation energy (E_{ac}) can be measured using

the following equation(Sridevi S. et al , 2010) :

$$\sigma = \sigma_{\circ} \exp\left[\frac{E_{ac}}{K_B T}\right]$$

Where σ_0 is a material-dependent parameter , K_B is the Boltzman constant , E_{ac} is the activation energy which is found to be about (E_{ac}= 0.844eV)



(°C)$^{-1}$

Figure(11):variation of $\ln \sigma_{A.C.}$ with 1/T in the parallel and perpendicular alignment as well as with out alignment at nematic phase

The variation of measured conductivity anisotropy at the nematic phase (Δσ) as a function of frequency was given in figure (12) .

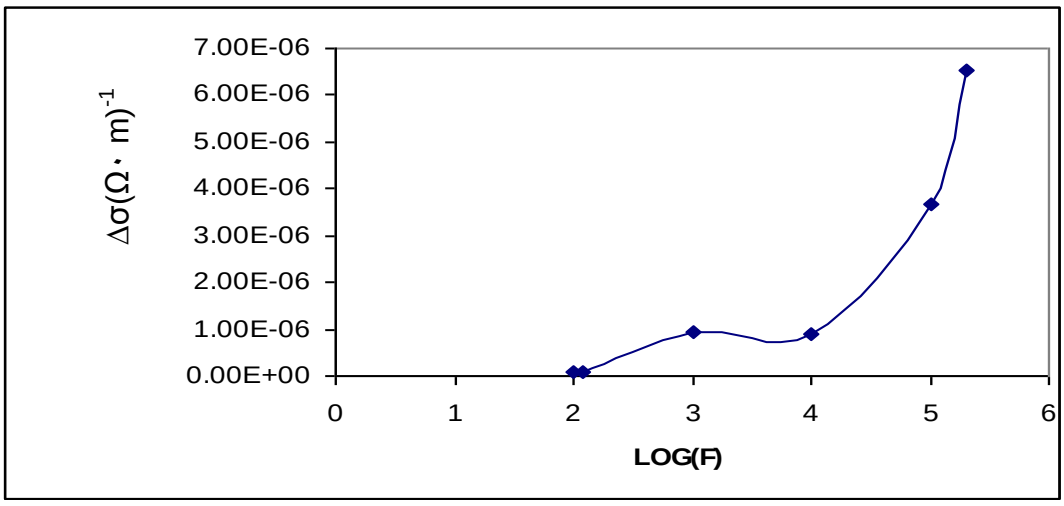


Figure (12) : variation of Δσ as a function of frequency at the phase transition temp.(85 °C)

From the figure(12), it is seen that the value of A.C conductivity anisotropy does not show much variation at lower frequencies; while above 100 KHz it shows a rapid increase with frequency. This is in accordance with the theory of dielectric materials, which predicts that the value of dielectric constant decrease with increasing frequency while the conductivity is increased, which is a normal dielectric behavior(Krishnakant G. Mishra et al,2011).

4.3. Electro optical response :

The common feature of dielectrically negative liquid crystals is that the presence of a dipole moment perpendicular to the long axis of the molecule, therefore the average molecular orientation (director orientation) without an electric field is perpendicular to the plain of the electrode . With this homeotropic orientation and crossed polarizers, the vertically aligned mode (Homeotropic) works in the so-called normally black mode. For incident light the liquid crystal in the off-state behaves like an isotropic medium (the light "sees" only the ordinary refractive index). As a consequence, very good black states can be achieved independent of the wavelength of the light and the operating temperature **(**Bruce D. et. al , 1996 **).**

From the application point of view we have studded the response of the liquid crystal cell encapsulated our prepared sample using a monochromatic light (Nd:YAG laser beam 523 nm) with perpendicular alignment and crossed polarizer as a function of applied A .c voltage which is the basis of most liquid crystal devices and the result is given in figure (13) .

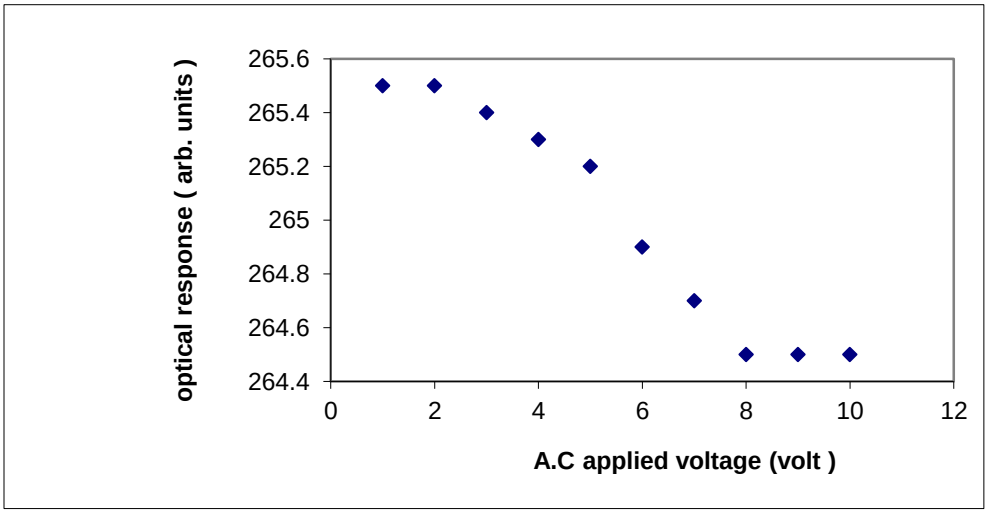


Figure (13) : Variation of optical response with A.c applied voltage at phase transition temp.

From figure (13) we calculate the threshold voltage for the optical response and found it of about (V_{th} = 2 volt) which is defined as the value at which optical transmission through the liquid crystal cell vary from 100% *to* 90% of it' s original value (Ruan L. Z, et al 2008). Such result revel that optical response in a liquid crystal sample with negative dielectric anisotropy aligned perpendicular to the electrode surface will decrease as the A.C. applied field increased and become at it' s minimum value which is called an off state in comparison with the on state that is mentioned at low applied fields which is found in good agreement with other researchers **(**Ha S. et . al , 2011 **).**

5. Conclusions :

From the results stated above we may conclude that mesomorphic properties can be achieved in an organic molecule with the required condition for liquid crystallinity such as , the rigid core , the polarity and flexible alkyl or alkoxy chain as it is the case in our prepared molecule .

We found that our sample show the nematic liquid crystalline phase at relatively low temperature (85 –110°C) with transition temperature range of about 25° C.

The dielectric effect studies for the prepared samples shows that our samples are with negative dielectric anisotropy of about ($\Delta\varepsilon$ = -0.41), as well as their conductivity anisotropy of about ($\Delta\sigma = 1.06\text{x}10^{-7}\ \Omega^{-1} . m^{-1}$) together with the activation energy of about (E_{ac} = 0.844 eV) .

The dipole moment due to carbonyl group (C═O)of the aldehyde is acting across the long molecular axis of the molecule and so we may conclude that this is the main reason that our sample show a negative dielectric anisotropy and consequently the electro optic behavior as mentioned above with a threshold voltage of about (V_{th} = 2 Volt).

Finely , and as a future work we found it easier for coupling our synthesized molecule with any aromatic amines via Schiff base group formation to get another liquid crystalline compounds with different polar groups and studying their physical properties as it is the case in our next research .

6. References :

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الخلاصة

تضمن البحثً تحضير مركب ذات وزن جزيئي صغير وبخطوه واحده وذلك بربط سلسلة الكوكسي بدل مجموعة الهيدروكسيل في مركب البارا هيدروكسي بنزلديهايد، وبعد التاكد من التركيب الكيمياوي عن طريق التشخيص باستخدام مطياف الاشعه تحت الحمراء تم استخدام المجهر ذو الضوء المستقطب وفحص المسح المسعري التفاضلي للتاكد من كونها تظهر طوارا بلوريا سائلا فتبين انها تظهر طوارا من النوع الخيطي على شكل قطرات ،كما تم دراسة بعض الخواص الفيزياويه لهذا المركب المحضر كثا بت العزل ، والتوصيليه ،وكذلك التاثير الكهربائي الضوئي بعد عمل التصفيف الموازي والعمودي للنموذج وتبين من خلال النتائج ان المركب 4- بنتيلوكسي بنزلديهايد يظهر تباينا في العزل الكهربائي مقداره ($\Delta\varepsilon$=- 0.41) ، بينما يظهر تباينا موجبا في التوصيليه الكهربائيه مقداره ($\Delta\sigma$=1.06x $10^{-7}\Omega^{-1}.m^{-1}$) وعند حساب طاقة التنشيط تبين انها في حدود (0.844eV) ، ومن خلال نتائج التا ثير الكهربائي الضوئي لهذا المركب ظهران فولتية العتبه هي في حدود (2 volt) .