Optical Properties and Phase Transition Measurements of Oriented Difluorophenylazophenyl Benzoate Liquid Crystal

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Abstract:

*Optical properties of the difluoro substituted 4-(2-(or 3-) fluoro phenylazo (-2'-(or 3'-) fluoro phenyl-4"-dodecyloxybenzoates thermotropic liquid crystal (**III**) were affected by the special new position and orientation of the two fluorine atoms. The compound **III** was dissolved in methylene chloride of different concentrations in order to determine its absorbance and transmittance in UV-visible region at room temperature. The maximum absorbance for the compound was in the blue region (447nm) and the molar absorption coefficient was found to be 0.93 (L. mMol^{-1}.cm^{-1}). The phase transition temperature was determined for the thermotropic LC compound **III** by using DSC, POM and modified spectrophotometer techniques as a new method. Nematic and smectic A phases during cooling process were observed. Refractive indices, birefringence, order parameter and thermal stability factor for compound III were measured. The molecular polarizability was determined also with different temperatures for the LC phases of compound **III**.*

Keywords: Optical parameters; Fluorine atoms; Refractive index; Birefringence; Order parameter, Modified spectrophotometer.

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1. Introduction

Liquid crystals (LCs) have properties between solid crystal and isotropic liquid. Many LC compounds exhibit one or more distinct mesophases depend on the basis of molecular order such as nematic (N) and layered Smectic (Sm) phases [1-3]. The use of LC in different applications depends on various parameters such as optical transmittance, absorption coefficient, order parameter, dielectric constant, birefringence, etc. The transmittance in thermotropic LCs, for a large interval of temperature, has been investigated in the nematic mesophase and isotropic liquid [4]. The refractive index and birefringence measurements were obtained by means of an Abbe refractometer and wedge method and Newton's

ring technique for the N and Sm A phases and the N-Sm A transition in LCs has been studied [5-8]. Also, in Yildiz *et al.* [9] measured the ordinary and extraordinary refractive indices of 10.O.4 by means of an Abbe refractometer. The optical birefringence based on a rotating-analyzer method are also measured [10,11]. Moreover, the temperature dependence of the ordinary (n_o) extraordinary (n_e) refractive indices, and birefringence, (Δn), for thermotropic LCs mesogens are studied [12-18]. The influence of lateral substituent of different kinds of mesogenic such as fluorine atoms on the optical parameters have been studied [19-21].

The aim of this work is interested in the critical effect of the special lateral location and orientation of two fluorine atoms on the phase transition and optical properties of the compound difluoro substituted 4-(2-(or 3-) fluoro phenylazo (-2'-(or 3'-) fluoro phenyl-4"-dodecyloxybenzoates thermotropic LC (**III**). the optical parameters such as ordinary and extraordinary refractive indices, birefringence, order parameter and polarizability were measured. It is worthwhile noting that this new position of fluorine atoms produced N and the Sm A phases for the LC compound **III** which can be investigated by using three different methods.

2. Prepared Material:

The liquid crystal compound difluorosubstituted-4-(2-(or 3-)fluoro phenylazo(-2'-(or 3'-)fluoro phenyl-4"-dodecyloxybenzoates was used as a new material, which was nominated as compound **(III)**. The compound was synthesized by Naoum M, et al. [22]. The chemical structure of compound **(III)** is shown in fig.1 and listed in table 1.

3. Results and Discussion

3.1 UV-Vis spectrophotometer

UV-Vis spectrophotometer (UV-1800 SHIMADZU, Japan) of ranging wavelength (200-800 nm) was used to measuring the transmission and absorption for the compound **III** dissolved in methylene chloride of different concentrations (0.1-0.5 *mMol/L*) at room temperature (300 K). It was found from fig.2a that the transmission intensity decreases as the concentration increases. Also, this compound is observed to have high transmittance and low scattering for a wavelength greater than 500 *nm*. As shown in fig.2b, the absorption maximum was centered about the maximum wavelength (λ_{max} = 447*nm*), which means that the compound **III** has a relatively strong absorption in the blue region due to n-π* transition of N=N chromophore. There is a slight blue shift in maximum absorbance wavelength from (452 to 444*nm*) by increasing the concentration from (0.1 to 0.5 *mMol/L*).

The relation between maximum absorbance (A) at (λ_{max}) and concentrations (*C*) of compound **III** is shown in fig.3, this relation is found to be directly proportional. The slope of this plotting gives the molar absorption or

extinction coefficient ε of the compound by Beer's Lambert law [23], $\varepsilon = \frac{A(\lambda_{max})}{Cd}$, where d is the thickness of the sample cell. The value of ε for the compound **III** is obtained as 0.93 (L. $mMol^{-1}.cm^{-1}$).

3.2 Phase Transition Measurements:

3.2.1 DSC transition temperature:

The phase transition temperature in Kelvin degrees (K) for the LC compound **III** was investigated by using differential scanning calorimetry (DSC) with a temperature scanning rate 2 °C/min during the measurements as shown in fig.4 and as listed in table 2. Figure 4 shows the DSC thermogram of compound **III** during heating and cooling processes. It was observed that, the LC compound **III** shows N phase during both heating and cooling processes but it shows Sm A phase during the cooling process only. As seen in fig. 4 and table 2, the compound **III** exhibits a broad temperature range for the N phase, (352.5- 374^{o}C) and (370- 337^{o}C) during heating and cooling processes respectively, which increases the stability of this compound in the N phase than in Sm phase (338-322 ^{o}C). The symbols Cr-N, N-I, N-S and S-Cr, in table 2 represent the transition from solid crystal to N, N to isotropic, N to Sm A and Sm A to solid crystal respectively.

3.2.2 POM transition temperature:

The polarizing optical microscope (POM) (Wild, Germany), with a homemade hot-stage, Brookfield temperature controller from England with a thermocouple is used for measuring the phase transition temperature and the texture appears by the LC mesogens. The morphological textures of compound **III** were presented in fig.5, which represent the N threaded texture, Sm A and crystalline phases at 350 K, 330 K and 313 K respectively. These photos are taken when the material placed between two crossed polarizers with magnification of 100X. The phase transition temperature detected by POM were in accordance with those obtained by DSC as in table 2.

3.2.3 Measuring phase transition by modified spectrophotometer:

The optical setup of modified spectrophotometer technique which can be used as a new method for determining the phase transition temperature by the transmission spectra during heating and cooling is shown in fig.6, where D is the diffraction grating, R is the rotating disc (Sample, blank, shutter), M is the mirror, B is the beam splitter, P1 and P2 are the polarizer and analyzer and S is the sample inside the electric oven. The sample of homogeneous alignment was sandwiched between two glass cover slides and separated by four spacers with thickness 40μm in uniform planar orientation with a director parallel to the cell walls. To prevent the leakage of the material by melting, the edges and end parts of the LC cell were sealed with a heat resistant adhesive. After that the sample cell was placed inside an electric oven with heating control system of rate 1^{o}C/min, and the whole system was then placed between two polarizers. The same two glass cover slides as a reference cell were put between two polarizers without placing a sample between them. The transmitted light intensity was measured as a

function of temperature at certain wavelength for compound **III** during the heating and cooling processes. It was found in fig.7 that the transmission intensity increases abruptly for the transition from solid to LC phase and then decreases abruptly for isotropic phase. The change of transmittance during LC phase occurs due to the rotation of the compound mesogens. Also, the transmission for N phase was higher than that for Sm A phase and the transmission intensity decreases slightly when the LC phase gets closer to isotropic phase which can be used as a detector for the phase's types. The phase transition temperatures resulted by this technique were in accordance with that obtained by DSC and POM methods.

3.3 Measuring of refractive indices:

Refractive index at different degree of temperature was measured by using Abbe refractometer technique with heating control unit of thermostat within ±0.1^{o}C around the prisms made by Bellingham, England. He-Ne laser of wavelength (543nm) was used as a source of light. For measuring the refractive indices n_o and n_e, the refractometer prisms were modulated to obtain the planar and homeotropic alignment required in the LC sample. The compound was exposed to a linearly polarized light and the data was taken during heating and cooling processes with an accuracy of ± 0.0005 as shown in fig.8. It was noticed that the values of n_o increase as the temperature increase while that of n_e decrease as the temperature increase,.

The effective geometry parameter α_{eg} is an important parameter for understanding the light spreading in LC and is connected with the director field orientation of the liquid crystals [24]. This parameter for LC is determined by: [25]

$$\alpha_{eg} = \frac{n_o}{n_e} \qquad (2)$$

The values of α_{eg} for compound **III** depend on temperature as shown in fig.9, where its magnitude increase with increasing temperature in the N and Sm A mesophases. The value of α_{eg} reached to unity at the isotropic phase transition which means that the orientational order in LC material vanished [26-28].

3.4 Birefringence measurements:

Birefringence Δn of the LC is one of the fundamental interests and is the key parameters which affect the operation of LC based electro-optic devices [29-31]. The values of ($\Delta n = n_e - n_o$) for compound **III** are determined from the measured values of n_o and n_e with different temperatures at wavelength (543nm) as shown in fig.10. It was observed that the values of Δn are decreased gradually with increasing temperature and there is a slight jump for Δn in the N–Sm A region of the phase transition [26-32]. The values of Δn for compound **III** in N phase between (0.10 - 0.17) are smaller than that in the Sm phase between (0.2 -0.25) as a function of the temperature which may be attributed to the higher molecular alignment in the Sm A phase [21, 26, 33].

Birefringence (Δn) can be measured also from the light intensity passing through the sample in LC phase by using the equation as follow [34-35]:

$$\frac{I_{\perp}(\lambda)}{I_{//}(\lambda)} = sin^2(\frac{\pi \Delta n\, t}{\lambda}) \qquad (3)$$

Where $I_{\perp}$ and $I_{//}$ are the transmission intensity of the light after passing through the sample placed between two crossed and parallel polarizers respectively in LC phase, t is the sample thickness in (μm), and λ is the wavelength of the light used. Since, the transmittance (T) of light measured by using the spectrophotometer is given by relation:

$$T = \frac{I(\lambda)}{I_o(\lambda)} \qquad (4)$$

Where $I_o\ (\lambda)$ and $I\ (\lambda)$ are the intensity of the incident and transmitted light respectively. The transmission of light produced while the sample was placed between two crossed and parallel polarizers $T_{\perp}$ and $T_{//}$ are:

$$T_{\perp}(\lambda) = \frac{I_{\perp}(\lambda)}{I_o(\lambda)}, \text{ and} \qquad T_{||}(\lambda) = \frac{I_{||}(\lambda)}{I_o(\lambda)} \qquad (5)$$

Therefore by using eqns. (3 & 5) Δn can be determined as follow:

$$\frac{I_{\perp}(\lambda)}{I_{//}(\lambda)} = \frac{T_{\perp}(\lambda)}{T_{//}(\lambda)} = sin^2(\frac{\pi \Delta n\, t}{\lambda}) \qquad (6)$$

$$\Delta n = \frac{\lambda}{\pi t} sin^{-1} \sqrt{\frac{T_{\perp}(\lambda)}{T_{//}(\lambda)}} \qquad (7)$$

The values of $T_{\perp}$ and $T_{//}$ at certain wavelength and temperature were measured for compound **III**. The thickness t of sample is equal to 40μm, which was measured by using traveling microscope. The values of Δn of **III** in N and Sm A phases at wavelength 543nm and at certain temperatures were listed in table 3. These results are closely equal to the values of Δn obtained from Abbe refractometer within error (± 0.005) at the same temperature degrees and wavelength as shown in fig.8.

3.5 Order parameter measurement:

The refractive indices data have been used to detect the orientational or microscopic order parameter **S** of the LC compound **III**. The order parameter **S** can be determined by using Vuks hypothesis as follow [36-37]:

$$\mathbf{S}\left(\frac{\Delta\alpha}{\alpha}\right) = \frac{(n_e^2 - n_o^2)}{\langle n^2 \rangle - 1} \qquad (8)$$

Where Δα is the polarizability anisotropy and α is the mean molecular polarizability. By using Haller's extrapolation method the order parameter **S** can be obtained by plotting [(ne2– no2)/(‹n2›-1)] as a function of ln [1-(T/Tc)] [31, 38-39], where T_C is the clearing temperature of the LC sample (the transition temperature from LC to isotropic phase). From the extrapolated interception of a straight line graph at T = 0 K, the value of scaling factor $\Delta\alpha/\alpha$ where **S** = 1 was determined. It was noticed that the scaling factor remain the same for all temperatures. Substituting the obtained values of $\Delta\alpha/\alpha$ (equal 0.4476, 0.6395 for N and Sm A phases respectively) in eqn. (8), the values of **S** can be evaluated for compound **III**. Figure 11 shows the values of **S** as a function of temperature in N

and Sm phases for compound **III**. It was observed that, the values of **S**, in Sm A phase, is higher than that in the N phase which reflecting the enhancement of the orientational order parameter in this phase. The relation of birefringence with the order parameter **S** for compound **III** is directly proportion as shown in fig.12. Also the relation between the effective geometry parameter α_{eg} with **S** for LC compound **III** is shown in fig.13. The parameter α_{eg} is linearly decreases with increasing birefringence and order parameter in Sm and nematic phases.

3.6 Molecular polarizabilities:

Molecular polarizability is an important parameter for liquid crystals. The ordinary (α_o) and extraordinary (α_e) polarizabilities representing the electric vector perpendicular and parallel to the optic axis of the LC are given by Vuks' method as [40-41]:

$$\alpha_e = \left(\frac{3}{4\pi N}\right)\left(\frac{n_e^2-1}{\langle n^2\rangle+2}\right) \qquad (9)$$

$$\alpha_o = \left(\frac{3}{4\pi N}\right)\left(\frac{n_o^2-1}{\langle n^2\rangle+2}\right) \qquad (10)$$

Where $N = N_A\,\rho/M$ is the number of molecules per cm^3, N_A is the Avogadro number, ρ is the density of the liquid crystal molecules and M is the molecular weight of the liquid crystal sample [22], and $\langle n^2\rangle$ is the mean square value of the refractive index which is given as follows:

$$\langle n^2\rangle = \frac{n_e^2+2n_o^2}{3} \qquad (11)$$

The values of α_e and α_o for N and Sm A phases of compound **III** at different temperatures are shown in fig.14. As seen in this figure, the values of α_e increase as the temperature decrease, while those of α_o increase as the temperature increase and the temperature dependence of α_e and α_o exhibit a same behavior as birefringence.

4. Conclusion:

*Optical parameters of the laterally difluoro substituted derivatives LC (**III**) are studied under the special position and orientation of the two fluorine atoms. The absorbance and transmittance for compound **III** when dissolved in methylene chloride of different concentrations were investigated at room temperature in UV- visible spectra. The maximum absorption band was observed in the blue region at (λ_{max} = 447 nm) and the molar absorption coefficient was found to be 0.93 (L. $mMol^{-1}.cm^{-1}$) for compound **III.** The phase transition temperature of the thermotropic liquid crystalline **III** was investigated during the heating and cooling processes by using DSC, POM and modified spectrophotometer techniques as a new method. Compound **III** has nematic smectic A phase during the cooling process. Thermal stability, refractive indices (n_o and n_e), birefringence, microscopic order parameter and molecular polarizabilities were measured for compound **III**. Birefringence was found to be*

inversely proportion with temperatures and directly proportion with order parameters.

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