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Impact of fluorine orientation on the optical properties of difluorophenylazophenyl benzoates liquid crystal

Ayman A. Zaki[a,b,*], H.A. Ahmed[c,d], Mohamed Hagar[c,e]

[a] College of Sciences, Physics Department, Yanbu, Taibah University, Saudi Arabia
[b] Faculty of Sciences, Physics Department, Banha University, Banha, Egypt
[c] College of Sciences, Chemistry Department, Yanbu, Taibah University, Saudi Arabia
[d] Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt
[e] Faculty of Science, Chemistry Department, Alexandria University, Alexandria, Egypt

HIGHLIGHTS

- The position and direction of fluorine atoms caused a great effect on LC phase.
- UV–Vis spectrophotometer modulated can be used as a detector of LC phase transitions.
- Birefringence and order parameter can be determined by modulated spectrophotometer.
- Optical properties varied and measured with different temperatures.

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ABSTRACT

The orientation effect of two laterally fluorine atoms on the optical properties of difluoro substituted-4-(2′-(or 3′-) fluorophenylazo)-2-(or3-) fluoro phenyl-4″-dodecyloxybenzoates thermotropic liquid crystals (**I** & **II**) were investigated. The compounds **(I, II)** were dissolved in methylene chloride in order to detect its absorption and transmission in UV–visible region at room temperature. The maximum absorption for the compounds was in the blue visible region (440–445 nm). The phase transition temperature by using DSC, POM and spectrophotometer techniques was investigated at variable temperatures for the compounds used. Nematic phase was observed for compound I during heating and cooling processes when the two fluorine atoms directed towards the molecular core while the smectic phase appears when the two atoms directed outward the molecular core. Refractive indices, birefringence, order parameters and thermal stability factors for compounds **I** and **II** were measured. Birefringence values of compounds **I** & **II,** reached 0.32 and 0.22 for nematic and smectic phase respectively.

1. Introduction

Liquid crystals (LCs) are anisotropic fluid materials of long orientational order, which share the properties of both ordinary liquids and crystalline solids. Although many of LC materials are very similar, each compound has its own specific molecular structure that identifies its specific phase morphology which possesses definite values of melting points and transition temperatures [1]. The transmittance in thermotropic liquid crystals, for a large interval of temperature, has been investigated at the regions of direct and reverse phase transitions between the nematic mesophase and isotropic liquid [2]. Temperature dependence of the ordinary (n_o) extraordinary (n_e) refractive indices, and birefringence, (Δn), of nematogenic mesogens have been investigated [3]. Refractive index and Birefringence values were measured for thermotropic LCs in the mesophase and isotropic liquid at different wavelengths in the visible region [4,5]. Birefringence of thermotropic liquid crystal mixtures was measured at different wavelengths in the visible region using speckle interferometry technique [6]. The ordinary and extraordinary indices of refraction or birefringence of a homogeneously oriented nematic liquid crystal were observed under polarized optical light [7]. Optical and thermal properties of hydrogen-bonded LC mixtures of 4-hexylbenzoic acid and 4-hexyl-4′-biphenylcarbonitrile mesogens were investigated, wide nematic ranges were observed depending on the mixture ratio of the two components [8]. The temperature dependence of the refractive indices n_e, n_o and the optical activity for uniaxial LCs was measured [9]. Optical parameters have been obtained for two fluorinated isothiocyanato nematic LC compounds. Refractive indices and birefringence of some compounds

* Corresponding author. Faculty of Sciences, Physics Department, Banha University, Banha, Egypt.
E-mail address: ayman_a73@hotmail.com (A.A. Zaki).

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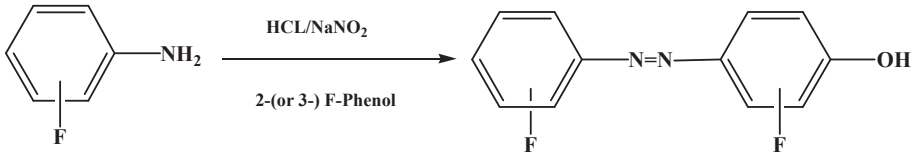
were determined [10]. The magnitude and temperature dependence of the refractive indices of TiO_2 NPs doped into NLCs are reported [11]. Variation of the phase transition temperatures and existence of different number of mesophases, for liquid crystals compounds p-ethoxybenzylidine p-heptylaniline (EBHA) and p-butoxybenzylidine p-heptylaniline (BBHA) have been studied by using POM and DSC. Refractive indices as a function of temperature of these compounds were also measured [12]. The mesogenic properties and physical chemical properties (viscosity, birefringence, refractive indices, dielectric anisotropy and elastic constants) of compounds being cyano, fluoro, isothiocyanato derivatives of biphenyl etc., were compared [13].

In the present work the optical parameters of two thermotropic LCs (**I, II**) (the difluoro substituted 4-(2-(or 3-) fluoro phenylazo (− 2'-(or 3'-) fluoro phenyl-4″-dodecyloxybenzoates) locally prepared with different lateral locations of fluorine atoms are measured. The position and the orientation of the two lateral fluoro-substituents were found to have an effect on the mesomorphic properties of the compounds. The phase transition temperatures and the phase identification were evaluated by differential scanning calorimetry (DSC), the polarizing optical microscope (POM) and modified spectrophotometer techniques. The molar absorption coefficient, ordinary and extraordinary refractive indices, birefringence, the thermal stability and the order parameters were measured for LC compounds used.

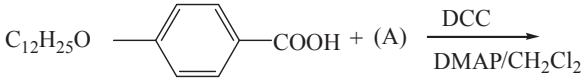
2. Materials and methods

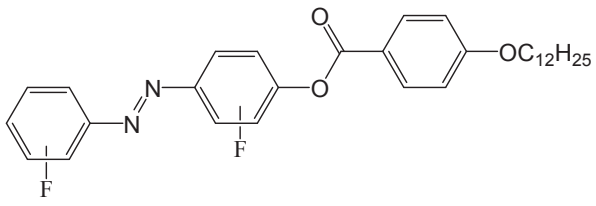
2.1. Preparation of compounds

Structure of compounds **I** and **II** liquid crystal materials were prepared as follows:



(A)





I & II

Molar equivalents of the 4-(2(or 3-) fluoro phenylazo)-2-(or 3-) fluoro phenol **(A)** and 4-n-dodecyloxy benzoic acid (0.05 mol each) were dissolved in 25 mL dry methylene chloride. To the resulting solution, two-molar equivalents of dicyclohexylcarbodiimide (DCC, 0.1 mol) and few crystals of 4-(dimethylamino)pyridine (DMAP), as catalyst, were added and the solution was stirred for 72 h at room temperature. The solid was filtered off and the solution was evaporated. The solid product was recrystallized twice from acetic acid and twice from ethanol to give pure products agree with the literature method [14].

Table 1
The elemental analyses for compounds **I& II.**

Comp. No.	Analyses Calculated (Found)			
	%C	% H	% N	%F
I	71.24(71.27)	6.94(6.90)	5.36(5.31)	7.27(7.22)
II	71.24(71.19)	6.94(6.91)	5.36(5.35)	7.27(7.21)

Table 2
Characteristic Infrared absorption bands (in cm-1) for compounds **I& II.**

Comp.	$\nu_{CH3Asym.}$	$\nu_{CH3\ Sym.}$	$\nu_{C=O}$	$\nu_{C=N}$	ν_{C-O}	ν_{C-O}	ν_{C-F}
I	2922	2857	1741	1607	1487	1248	1048
II	2923	2854	1735	1604	1482	1241	1065

For confirmation of molecular structures; infrared, ^{1}H NMR, and elemental analyses for the compounds were investigated. Representative elemental analyses, infrared and ^{1}H NMR spectra are given in Tables 1–3, respectively.

Nearly identical infrared spectra were observed for the investigated compounds (**I, II**) and their spectra are collected in Table 2. As shown in Table 2, the C=O stretching absorption ($\upsilon_{C=O}$) appears at a narrow range, 1732-1741 cm^{-1}, as a result of the electron-withdrawing effect of the lateral F-atom irrespective of their locations.

^{1}H-NMR-spectra showed the expected integrated aliphatic to aromatic proton ratios in all compounds investigated, compound **I** taken as a representative example (Table 3).

2.2. Characterization techniques

Infrared spectra were recorded using Perkin-Elmer B25 spectrophotometer (Perkin-Elmer, Inc., Shelton, CT USA). ^{1}H NMR spectra were performed using a Varian EM 350L 300 MHz spectrometer (Oxford, UK) using tetramethyl silane as internal standard and $CDCl_3$ as solvent; the chemical shift values recorded as δ (ppm units). Elemental analyses for final products were carried out on Thermo Scientific Flash 2000 CHS/O Elemental Analyzer, Milan, Italy.

Calorimetric measurements were carried out using a TA Instruments