Molecular Crystals and Liquid Crystals

Dispersion of Pentadentate Schiff Bases and Their Transition Metal Complexes in Liquid Crystals

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Absorption spectra of two pentadentate Schiff base type systems in ordinary organic solvents and liquid crystal (LC) media have been measured as a function of temperature, between 25 and 60°C. The interactions between solute and LC molecules were investigated on the basis of their spectral properties in both isotropic and nematic phases of the LC. The results revealed strong interactions between the ligand and LC molecules, which are probably due to the specific or non specific intermolecular forces. Moreover, the influence of the presence of the solutes on the phase transition temperature of 4-cyano-4'-n-pentyl-biphenyl (5CB) and 4-cyano-4'-n-heptyl-biphenyl (7CB) has been studied and a correlation between the chemical structure of the solutes and their spectroscopic behaviour has also been discussed.

Keywords: intermolecular interaction; liquid crystal; phase transition; schiff bases

1. INTRODUCTION

Intermolecular interactions in nematic liquid crystals (LCs) have been subject of a large number of reports in the past, and continue to attract much attention of research groups because of their important applications in various fields of technology [1–3]. A wide variety of molecules

like dichroic dyes were used as "guest" molecules and dissolved in different nematic LCs which act as "host" [4–6]. These types of systems were first described by Zanoni and Heilmeier [7], and are currently employed in LC display devices, using the so-called guest-host interactions. This phenomenon is based on the intermolecular forces between the solute and the nematic molecules.

Only few studies are available in the literature where Schiff bases were employed as solutes in nematic solutions [8,9]. Nevertheless, among the currently used organic reagents, Schiff bases possess important features, because of their easy preparation procedures, and their high chemical and photochemical stability. This class of molecules is known for colouring isotropic solvents, and absorb light intensively in the UV-visible region of the spectrum [10,11]. These advantages make them suitable as advanced materials for a large number of photonic applications, and can be considered as dye models to produce coloured LCD devices of the guest-host type.

In the present work, we report on the spectroscopic properties of two pentadentate Schiff bases: 1, 3-Bis (salicylideneamino)-2-propanol (L1), and 1, 3-Bis (2-hydroxy-1-naphthylideneamino)-2-propanol (L2), and copper (II) complex derived from L2, in isotropic and anisotropic media. The chemical structures of L1 and L2 are displayed in Figure 1.

These compounds are of particular interest because of their structures containing a large π-electron system. The principal aim of this work is to correlate the structure of these compounds with their spectroscopic behaviour in various environments, especially in nematic LCs. Therefore, the interactions of both solute-solvent and the phase transition behaviour of LC can be detected from their absorption spectra in the UV-visible region. The results are discussed on the basis of intensity and shape of different bands, and the shift and the optical density of the maximum of the absorption band (λmax). Our interest is also focussed on the effect of these compounds on the phase transition temperature T_{NI} of two LCs, 4-cyano-4′-n-pentyl-biphenyl (5CB) and 4-cyano-4′-n-heptyl-biphenyl (7CB).
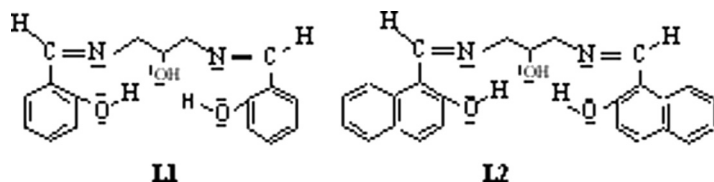

FIGURE 1 Chemical structures of the pentadentate Schiff bases.

To the best of our knowledge, the use of pentadentate Schiff bases and their copper (II) complexes for modifying some properties of nematic solvents has not been reported before. Furthermore, this fundamental approach is very important for further studies involving investigation of the order parameter and improvement of the viewing angle of LCs.

2. EXPERIMENTAL PART

2.1. Materials

Two cyanobiphenyl type LCs, 5CB and 7CB (Synthon Chemicals, Wolfen, Germany) were used as nematic solvents. Ethanol (from Merck, p.a. grade) and acetonitrile (from Sigma-Aldrich, purity 99.93+%) were used as isotropic solvents. The Schiff bases and the L2-Copper (II) complex were prepared and purified according to the general method described in the literature [12–14], and were used as solutes. The concentrations of isotropic and anisotropic solutions were 10^{-4} M and 0.1–0.3 weight%, respectively. All samples were analyzed by the following methods.

2.2. Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectra of 1 mm thickness KBr pellets were recorded in the transmission mode with a Perkin Elmer 2000 model. The number of accumulated scans was 16 with a spectral resolution of $4\,cm^{-1}$. The concentration of the samples was chosen at 1.5 weight-%. In general, the same experiment was repeated five times to check the reproducibility of the results.

2.3. Nuclear Magnetic Resonance

The ^{1}H-NMR spectra of the ligands were taken on a FT-NMR (300 MHz) Bruker instrument. Deuterated Chloroform (with 0.03% Tetramethylsilan) and deuterated Dimethylsulfoxide (with 0.06% Tetramethylsilan) were used as NMR solvents. They were obtained from Eurisotop (Gif sur Yvette, France) and used as received.

2.4. Ultraviolet/Visible Spectroscopy

The absorption spectra of all solutions were obtained from a Varian Cary 50 UV-visible single-beam spectrophotometer, equipped with a single cell Peltier accessory for precise temperature control ($\pm 0.1^{\circ}$C).

The measurements were made as a function of temperature in Hellma quartz cells (100-QS) of 1 and 10 mm thickness, for nematic and isotropic solutions, respectively. A linear increasing temperature ramp was applied from 25 to 60°C with steps of 1°C using appropriate hold times to obtain a thermodynamic stable state. This temperature interval was reduced to 0.5°C around the phase transition temperature. No temperature effect in the case of isotropic solvents was observed on the spectra. The data obtained from acetonitrile and ethanol solutions at room temperature can thus be used to compare with data from isotropic LC solutions at 45°C.

3. RESULTS AND DISCUSSION

3.1. Sample Analysis

Infrared spectra of both ligands L1 and L2, show strong sharp bands at 1630 and 1637 cm^{-1}, respectively, which are characteristic for C=N stretching vibrations. The broad absorption band at 3200–3500 cm^{-1} corresponds to the hydrogen bonded hydroxyl stretching vibration. Upon complexation, the azomethine group (C=N) stretching band undergoes a negative shift of 15 cm^{-1}; which may be attributed to the coordination of the nitrogen atom of the imine group to the metal center (Cu^{2+}). The ^{1}H-NMR data of L1 and L2 are represented by multiplets, situated at 3.7−4 and 4.6 ppm, and are characteristic of 4 C=N-CH$_2$ protons and one HO-CH proton, respectively. All aromatic protons are represented by a broad massif at 6.9–8 ppm. The two protons attached to the imine groups **H-**C=N are characterized by a singlet situated at 8.5 ppm.

3.2. Solvent Effect on the Absorption Spectra of the Ligand in the UV-Visible Region

The UV-visible spectra of all substrates in ethanol and acetonitrile as isotropic solvents, and in 5CB and 7CB as LCs, were obtained at 45°C. At this temperature, all solutions are in the isotropic phase. Figure 2 illustrates the spectroscopic behaviour of L2 in various environments. The absorption spectra of the Schiff base in LC with large dipole moment (about 4.6 D), obtained in the wavelength range from $\lambda = 230$ nm to 500 nm, are red shifted compared to those in ordinary organic solvents. This effect can be explained by relatively strong ligand-LC interactions. Indeed, the structures of both LC and L2 present a strong π-electron system due to the presence of two and four aromatic rings, respectively. Such structures favour largely extra π-π
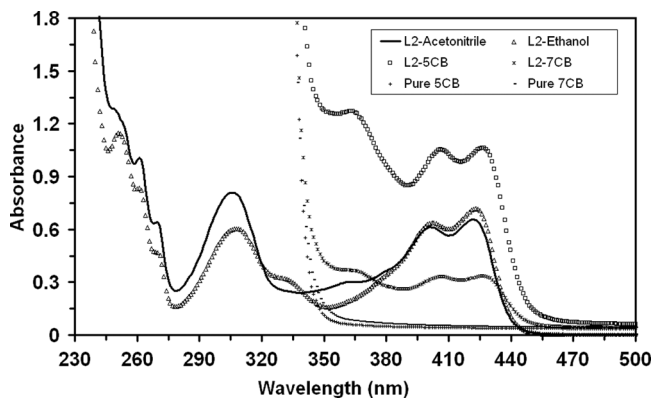
FIGURE 2 Spectrophotometric behaviour of L2 in ordinary organic solvents and LCs, in the isotropic phase (T = 45°C).

interactions (π-stacking) between the aromatic rings of the solute and the LC. In addition, the spectra of L2 in ethanol as polar and protic solvent and in acetonitrile as polar and aprotic solvent are similar in shape and position of the maxima of the bands. Such results suggest that hydrogen bonding is not the dominated intermolecular force in these solvents, even if ethanol can establish H-bonding with the Schiff base molecules. Furthermore, it was reported in the literature that the nematic "hosts" like 5CB and 7CB, possessing large dielectric constants, may act as ionic media, thus stabilizing the "guest" species in the excited state [15]. This effect can largely contribute to the red shift observed in the LC environment.

Two types of hydroxyl groups can be distinguished in the structure of the ligand: Aromatic hydroxyls (Ar-OH) which are attached to the naphtyl rings, and an alcohol group which is attached to the aliphatic chain. The Ar-OH has an acid character because of the high resonance (delocalized π-electron system), and can easily establish intramolecular hydrogen bonding with the azomethine groups. The formation of keto-enol equilibrium is thus expressed in all media by the dual band in the range from 395 to 435 nm. These absorption bands represent maxima at 402 and 422 nm in organic solvents, which undergo a red shift to 406 and 427 nm in LC media, respectively. The keto form dominates in ethanol ($A_{ketone}/A_{enol} = 1.124$), compared to acetonitrile ($A_{ketone}/A_{enol} = 1.072$). This effect can be explained by the stabilization of the keto form in the protic solvent by H-bonding. In both LCs, the two forms represent the same percentage ($A_{ketone}/A_{enol} = 1$), so that a stable equilibrium between enol and keto forms was obtained in this

media. The bands observed in the spectra of organic solvents, in the range from 240 to 320 nm, which are assigned to the low energy $\pi \rightarrow \pi^*$ transition of the aromatic rings, are absent in those of the LCs. The band situated at 330 nm in ethanol, which is assigned to the $n \rightarrow \pi^*$ transition (excitation of electrons of the azomethine group), is red shifted to 362 nm in both acetonitrile and LC media, due to the presence of a cyano group, involving a high dipolar moment.

3.3. Solvent Effect on the Absorption Spectra of L2Cu Complex in UV-Visible Region

UV-visible spectra of the L2-Cu complex in similar environments are shown in Figure 3. The maxima of the wavelength in acetonitrile and ethanol, situated at 619 nm, undergo hypsochromic shift to 613 nm in LC media. Such phenomenon indicates probably formation of H-aggregates of solute molecules resulting from π-stacking of aromatic units of the solute.

3.4. UV-Visible Spectra of L2 and L2-Cu in the Nematic and Isotropic Phases of 7CB

The UV-visible spectra of solutions of the ligand L2 and its copper (II) complex in 7CB are shown in Figure 4. The data were obtained in the nematic phase (N) of the LC at 25°C as well as in the isotropic phase (I) of 7CB at 45°C. In general, the absorbance is enhanced if the LC is in
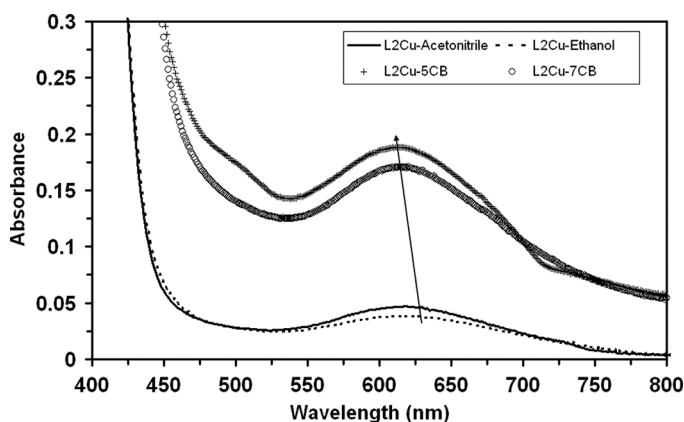

FIGURE 3 Spectrophotometric behaviour of L2-Cu complex in ordinary organic solvents and LCs, in the isotropic phase (T = 45°C).
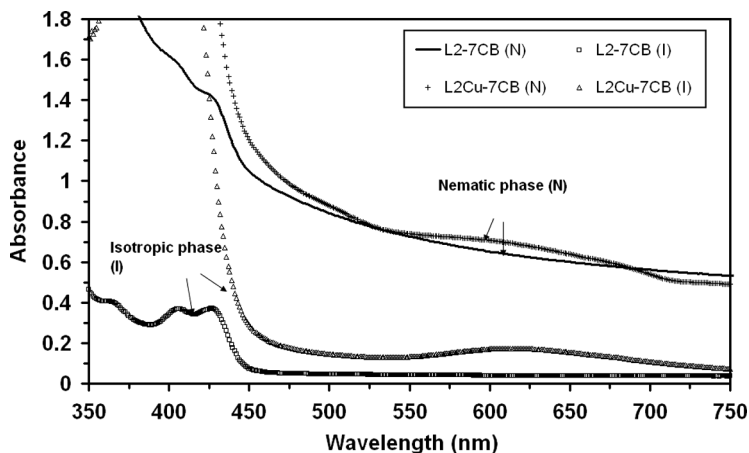
FIGURE 4 UV-visible spectra of L2 and L2-Cu in nematic (N) (T = 27°C) and isotropic (I) (T = 45°C) phases of 7CB.

its nematic phase, due to the reduced transmittance of the cloudy nematic blend compared to the highly transparent isotropic state.

The spectrum of the L2-Cu complex shows a broad band with low intensity and a maximum at 613 nm, which is responsible for the green colour of the LC-solution. The other bands of the complex are shifted to the lower wavelength range beyond the scale of this Figure. The ligand L2 does not show any detectable absorption at $\lambda > 450$ nm.

3.5. Phase Transition Measurements of LCs

The phase transition behaviour of LCs in the presence of solutes has been largely reported in the literature since these systems can be used in LC displays [16,17]. The phase behaviour of 5CB/L1, 7CB/L1, 5CB/L2, 7CB/L2, 5CB/L2-Cu, and 7CB/L2-Cu systems was measured by UV-visible spectroscopy as function of temperature in the range from 25°C to 60°C. The results were compared with data obtained from pure 5CB and 7CB.

The optical densities of the samples are phase dependent, and Figure 5 displays the results of all systems. Both ligands L1 and L2 reduce the N-I-transition temperature of 7CB by 0.5 and 1°C, respectively. For 5CB systems, L1 and L2 provoke a decrease of T_{NI} by 1°C and 0.5°C, respectively. This behaviour of the phase transition of 5CB and 7CB may be explained by the difference in ligand-LC interactions. The N-I phase transition temperature of 7CB is not influenced by the presence of L2-Cu complex but the transmittance is reduced
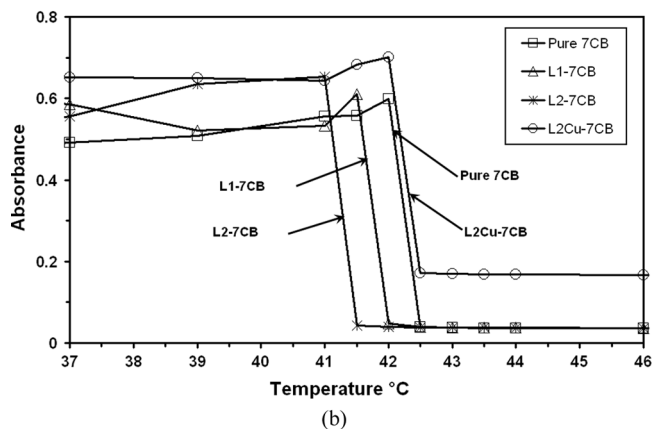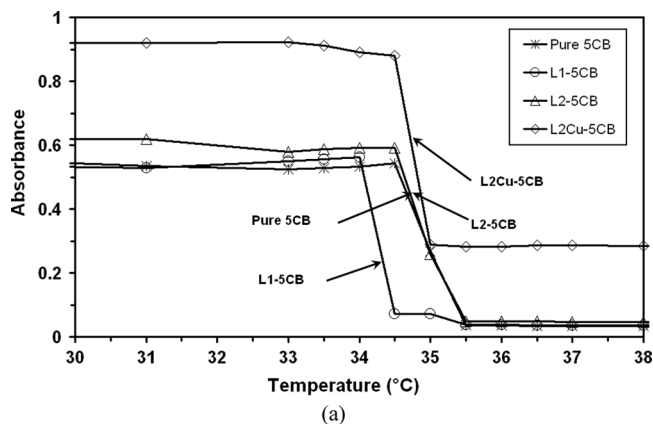
(a)

(b)

FIGURE 5 Nematic-isotropic phase transition behaviour of (a) 7CB-solute systems and (b) 5CB-solute systems regarding from their absorbance-temperature dependence.

in all cases. Almost constant absorbance values are obtained for $T < T_{NI}$ and $T > T_{NI}$.

CONCLUSION

The spectroscopic behaviour of pentadentate Schiff base type systems was examined in isotropic and anisotropic environments. The experimental results indicated that relatively strong ligand-LC interactions occurred which can be explained by π-π interactions of the aromatic rings of the LCs and the solute. Furthermore, the ligands reduce the nematic-isotropic transition temperature of LCs without changing

its transmittance. An inverse effect was observed for the L2-Cu complex.

In order to obtain more information about the effect of solute-LC interactions on the transmittance and the phase transition behaviour of LCs, the order parameters of the LC systems will be studied by polarized absorption spectroscopy using an external electrical field.

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