Effects of temperature change on nematic liquid crystal

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We have investigated, at different temperatures, the ATR spectrum of 4-cyanophenyl-4'-hexylbenzoate (CP6B) in crystal, liquid crystal and isotropic phase. The changes in the IR spectra due to temperature variations (intensity, half width and wavenumber shift of spectral lines characteristic to some chemical bonds) were correlated with some structural characteristics. We have chosen to study CP6B because of the presence of the carbonyl group (C=O) in its molecular structure. This group is present in over 80 liquid crystals synthesized by us, in organic chemistry laboratory from University of Pitesti, whose spectral study we are performing in present.

1. Introduction

Liquid crystals find a rather wide application in modern industry. First of all, they are used for manufacturing the monitors of personal computers, TV sets, and other facilities to display information. That is why new liquid crystal substances are searched for and synthesized, and, respectively, the molecular mechanisms governing the macroscopic properties of mesogenes and their modifications are studied. Knowing the intramolecular processes and understanding their nature would allow the synthesis of liquid crystal substances with prespecified properties to be thoroughly dealt with. *p,p'*-Disubstituted biphenyls are interesting compounds: they have strong tendency to form low temperature liquid crystalline phase and are chemically and photochemically stable. Also, they have strong dielectric anisotropy and are very suitable for displays and other industrial applications.

A considerable number of liquid crystal substances have been synthesized during the last time. The most studied of them are substances with a benzylidene-aniline core. Benzylidene-anilines belong to a wide class of objects, which are capable to form the liquid crystal phase.

One of the most informative techniques to study both the intramolecular structure and the properties of a molecular environment is the vibrational spectroscopy. Vibrational spectroscopy can be useful, when determining molecular conformations in various phase states and order parameters, or to obtain some information on features of the intermolecular interaction and the dynamics [1-4].

In this paper we have performed FT-IR spectroscopy investigation in simple molecular nematic liquid crystals for characterization the molecular dynamics. Nematic liquid crystals are technologically important as a mesogenic unit for molecular engineering.

Liquid crystals above N-I transition, even though behaving as isotropic system at macroscopic level, may be structurally anisotropic at microscopic level for the persistence of short-lived, fluctuating nematic domains with temperature dependent sizes [5, 6].

In dipolar systems with large dipole-dipole interactions one of the dynamical processes for the vibrational dephasing, the resonance vibrational energy transfer, promotes a phenomenon known as the noncoincidence effect (NCE) [7,8]. This consists of a frequency separation between the anisotropic (I_{ani}) and the isotropic (I_{iso}) components of band associated with identical oscillators involved in the vibrational transfer process between adjacent identical molecules. It results rather remarkable in nanoscale-structured liquids, when it is brought about by a transition dipole coupling mechanism taking place in the presence of orientational order induced by dipole-dipole interactions [9-11].

The choice of cyanophenyl hexylbenzene (CP6B) in this study has been mainly dictate by the presence of the carbonyl group (C=O) in its molecular structure. This group is present in over 80 liquid crystals synthesized by us, in organic chemistry laboratory from University of Pitesti.

2. Experimental set-up and procedures, used substances

CP6B (4-cyanophenyl-4'-hexylbenzoate) was Aldrich products.

CP6B is a liquid crystal that exhibits, on heating, the phase sequence: K–N (46°) N–I (47.9°C).

It is stable in the presence of the ambient oxygen up to approximately 100 °C and above this temperature only under inert atmosphere.

IR spectra were recorded on a Jasco 6300 FT-IR spectrometer in the region of 4000 – 400 cm⁻¹, detector TGS, apodization Cosine, software Spectra Manager II. ATR spectra were obtained with an attenuated total reflection attachment Gladi ATR, apodization Cosine. The instrument had a spectral resolution of 4 cm⁻¹, which were used in all spectra determinations.

Gladi ATR with heated diamond crystal plate and temperature controller led to obtain spectra at different temperatures.

There are two main polar units in the CP6B molecule the ester (-COO-) and the cyano (-CN) group. Both groups contribute to the overall dipole moment. Its direction is no longer along to the long axis of the molecule like for the CB series there is a component of the dipole along the short axis of the molecule as well [12].

3. Results and discussion

The infrared spectrum of bulk CP6B shows strong and mostly non-overlapping bands, which can be assigned to both the rigid core and the flexible part of the molecule.

Internal vibrational assignment. In IR, the most important vibrations for compound were cyano group vibration around 2231 cm⁻¹ and carbonyl group vibration at 1731cm⁻¹ (strong) for C=O bond, 1217 cm⁻¹ (very strong) for C-O asym and 1068 cm⁻¹ for C-Osym (strong).

Table 1 shows the IR values obtained by ATR technique for CP6B at different temperatures.

Table 1. IR values (cm⁻¹) for CP6B at different temperatures.

t(°C)	ν_{CN}	$\nu_{C=O}$	$\nu_{C-O\ asym}$	$\nu_{C-O\ sym}$
25	2231,24	1731,76	1217,83	1068,37
30	2231,24	1731,76	1217,83	1068,37
40	2231,24	1731,76	1217,83	1068,37
45	**2230,27**	**1731,76**	**1211,08**	**1059,69**
47	**2229,31**	**1734,66**	**1207,22**	**1055,84**
48	**2229,31**	**1736,58**	**1205,29**	**1053,91**
50	2229,31	1736,58	1205,29	1053,91
53	2229,31	1736,58	1205,29	1052,94
60	2229,31	1736,58	1205,29	1052,94
65	2229,31	1736,58	1205,29	1052,94
75	2229,31	1736,58	1205,29	1052,94

The transitions from solid - to liquid- crystalline and to isotropic phase were accompanied by specific intensity changes strongly correlated with the orientation of these molecules. FT-IR study has been focused mainly on band assignments and analysis of the intensity changes taking place at selected wavenumbers, as we was also presented [13].

Except for the CH stretching vibrations in the 2800 - 3100 cm⁻¹ region, most modes are concentrated below 1700 cm⁻¹ in IR spectra.

The characteristics skeletal stretching vibrations of C-C bonds of the benzene rings cause the appearance of four bands between 1600 - 1400 cm⁻¹ (Fig. 1). Those near 1600-1500 cm⁻¹ are characteristic of aromatic ring itself and, together with CH stretching bands near 3000 cm⁻¹ they provide a good signature of the aromatic structure [14]. The actual positions of these bands are influenced to some extent by the nature and arrangement of the substituent groups around the ring. Figure 1 presents ATR spectra of CP6B at different temperatures, in crystal (25°C), liquid crystal (45°C) and in isotropic phase (50°C).
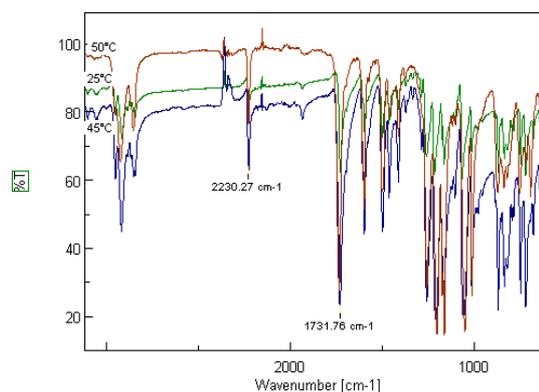
Fig. 1. ATR spectra of CP6B at different temperatures.

Strong bands appear in the region 1000-600 cm⁻¹ due to out-of-plane deformations of hydrogen atoms in the rings. Their frequency is determined almost totally by the positions rather than the nature of the substituents. Thus they provide a very sensitive method to detect the type of substitution.

The strong out-of- plane bending mode of the aromatic CH group yields a band at 860-800 cm⁻¹ which is characteristic of 4-substituted systems. The other CH out-of-plane deformation modes appear at 780-720 cm⁻¹.

Spectral changes at phase transitions

The study shows that there are considerable spectral changes at the crystal-nematic phase transitions for both molecules studied. This is not surprising, since in this strongly first order transition both ΔH and ΔS are large , implying that most of the changes in the motional freedom and intermolecular forces occur here, rather than at the nematic-isotropic point.

Most of the IR bands in the crystalline phase are sharp, including bending and stretching vibrations of the buthyl chain. In the nematic phase many IR band shifts are broaden and change intensity as the molecules recover rotational and translational freedom.

When the temperature of CP6B changes in the range 45 - 48 °C the absorption bands of   in the IR spectra decreases and the bands are shifted (Fig. 3 and 4).

An accessible explanation of these observation, based on the theory of interaction dipoles – electromagnetic field [15] can be expressed as follows: the resonance frequency

of an oscillator having mass m (oscillating dipole represented by the chemical bond) is given by the relation:

$$\omega_0 = \left(\frac{k}{m}\right)^{1/2} \qquad (1)$$

where the elastic constant $k = k_f + k_i$ is composed by k_f – natural elastic constant of free oscillator and k_i – elastic constant determined by the molecular field generated by the influence of the other molecules in crystal, depending on the symmetry degree and on anisotropy degree of dipoles orientation in the internal structure of the considered state. Differences in these properties between solid, liquid crystal and isotropic liquid justify the frequency shift of transmission band during the heating of studied substance.

As for modification of the amplitude of absorption peaks during the heating, the following considerations can be made:

Absorption cross section of electromagnetic radiation by an oscillating dipole is of the form:

$$\sigma_{osc}(\omega) = const \cdot \frac{\omega^4}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2 \lambda_t^2} \qquad (2)$$

It has maximum value for resonant frequency ($\omega = \omega_0$), $\sigma_{osc}^{max}(\omega_0) = const \cdot \frac{\omega_0^2}{\lambda_t^2}$, where λ_t represents a dissipative term, also depending on the internal symmetry of the considered state of substance. Resonance amplitude of dipolar vibration is even greater as dissipative term is lower.

Experimental results show that dissipative processes are the least intense in liquid crystal state, so the intensity of absorption band is highest in this state. Also, dissipative processes are less intense in solid state than in isotropic liquid one is suggested.

Bands are most intense in the liquid crystal state. It shows a shift of the $\nu_{C=O}$ to higher wavelength (Fig. 2) and the ν_{CN}, (Fig. 3), $\nu_{C-Oasym}$ and ν_{C-Osym} bands to lower wavenumbers (Fig. 7).
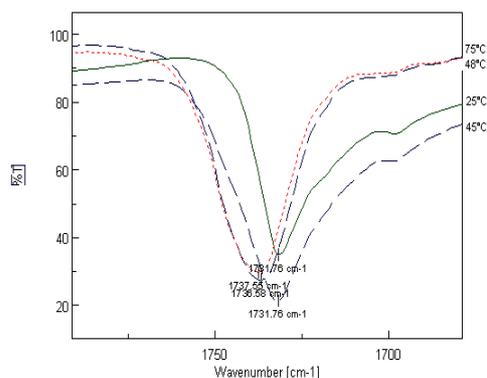
Fig. 2. Transmission band at 25°C, 45°, 48° and 80°C for ν(CO).
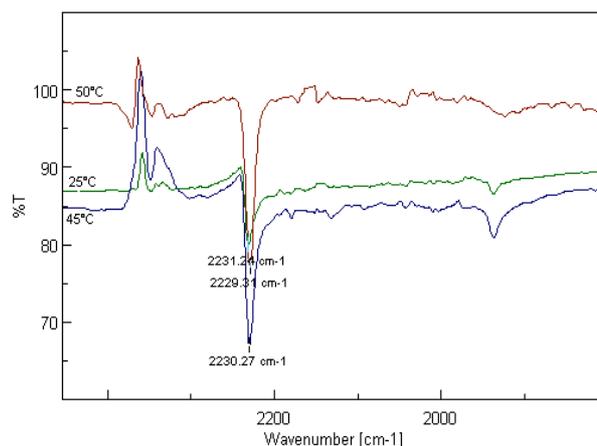
Fig. 3. Transmission band at 25°C, 45° and 50°C for ν(C≡N).

The isotropic and anisotropic spectral distributions of the CO vibrational mode are reported in Fig. 2 in the isotropic phases at 48°C and 75°C (broken line). These oscillators are good candidates for investigating the occurrence of two dynamical processes: the vibrational and orientational relaxations from -CN, and the resonant vibrational energy transfer from CO. Both oscillators are spectrally rather well separated from other intramolecular oscillators. In addition the position of the CN group, approximately aligned along the long molecular axis, and its strong polarizability anisotropy makes the corresponding stretching mode, in principle, a good probe for the tumbling motion of the whole orientational dynamics.

For semi-unsaturated C-C bonds of benzene ring the four bands between 1600-1464 cm^{-1} in crystal, liquid crystal and isotropic liquid are presented in Table 2 and Fig. 4.

Table 2. IR values (cm^{-1}) for C-C bond of benzene ring at different temperatures.

t(°C)	band 1 (s) cm^{-1}	band 2 (s) cm^{-1}	band 3 (w) cm^{-1}	band 4 (m) cm^{-1}
25	1599,66	1501,31	1581,34	1465,63
45	1600,63	1500,35	1581,34	1465,63
50	1600,63	1504,2	1575,56	1464,67

The frequency positions of the two most prominent benzene ring stretching modes are 1599,66 cm^{-1} and 1501,31 cm^{-1} in crystal state. With increasing temperature, the bands are moves and in isotropic state the second band is at 1504,2 cm^{-1} (Fig. 4). The third ring band appears weak at 1582,34 cm^{-1}, moved to lower wavenumber in isotropic state (1575,56 cm^{-1}). Intensity of this band in isotropic state is considerably enhanced. The fourth skeletal C-C ring frequencity is at 1465,63 cm^{-1} both in crystal and liquid crystal state and has moderate intensity.
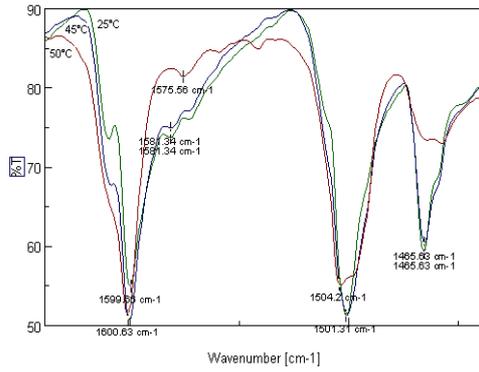
Fig. 4. Transmission band at at 25°C, 45° and 50°C for C-C bonds of benzene ring.

Vibrational bands broadening

We also analyzed the effects of temperature on the half-width of spectral lines of studied spectra.

Due to thermal motion of the emitting dipoles, which intensifies with increasing temperature, Doppler broadening leads to a Gaussian shape of the spectral line profile expressed by the relation:

$$i(\nu) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(\nu - \nu_0)^2}{2\sigma^2} \right] \tag{3}$$

where $i(\nu)$ represents the intensity of the line as a function of frequency ν, ν_0 is the corresponding to the maximum intensity value of frequency, σ is the standard deviation of Gauss distribution, also representing the width of the spectral line, having the expression:

$$\sigma = \frac{\nu_0}{c}\sqrt{\frac{RT}{\mu}} \tag{4}$$

where c is light speed, R is the universal gas constant, μ is molar mass of source and T absolute temperature.

The half-width of spectral lines is often used in spectroscopy, being given by:

$$\Delta\nu_D = \frac{\nu_0}{c}\sqrt{\frac{2\sqrt{2}\cdot RT}{\mu}} \tag{5}$$

or, expressed in wavenumbers or wavelengths the half-width of Doppler profile of spectral lines becomes:

$$\Delta\tilde{\nu}_D = \frac{\tilde{\nu}_0}{c^2}\sqrt{\frac{2\sqrt{2}\cdot RT}{\mu}} \tag{6}$$

respectively:

$$\Delta\lambda_D = \frac{2\lambda_0}{c}\sqrt{\frac{2\sqrt{2}\cdot RT}{\mu}} \tag{7}$$

where $\tilde{\nu}_0$ and λ_0 are the corresponding to the maximum intensity value of wavenumber respectively of wavelength.

Characteristic for Doppler broadening is the increase of half-width directly proportional to square root of temperature and the independence of the pressure.

Other processes, the most important being collision between emitting dipoles due to pressure growth or to other causes or to the action of electric internal fields into the radiation source, strongly dependant of the internal symmetry, leads to broadening mechanisms (pressure, collisional, Stark broadenings) characterized by Lorentz shape of spectral line , expressed by the relation:

$$i(\nu) = i_0 \frac{(\Delta\nu_L/2)}{(\nu_0 - \nu)^2 + (\Delta\nu_L/2)^2} \tag{8}$$

where $\Delta\nu_L$ is the half-width (Lorentz half-width) of the spectral line and ν_0, corresponding to i_0, the maximum intensity value of frequency.

Important features of Lorentz broadening are direct proportionality to total pressure, and inverse proportionality to the square-root of temperature of Lorentz half-width. Doppler broadening, on the other hand, is independent of pressure and increases with the square-root of temperature [16].

Each of the presented mechanisms can act in isolation or in combination with others. Assuming each effect is independent, the observed line profile is a convolution of the line profiles of each mechanism. However, the different line broadening mechanisms are not always independent; so, for example, the collisional or Stark effects and the motional Doppler shifts can act in a coherent manner, resulting under some conditions even a narrowing of spectral line [17].

Analyzing the studied spectra, we can notice the followings:

Some lines, characteristic to CH aromatic out of plane deformations present a continuous increase of half-width of spectral lines as temperature raises (Fig. 5). So, in the case of these bonds, Doppler broadening prevails towards other types of broadening.
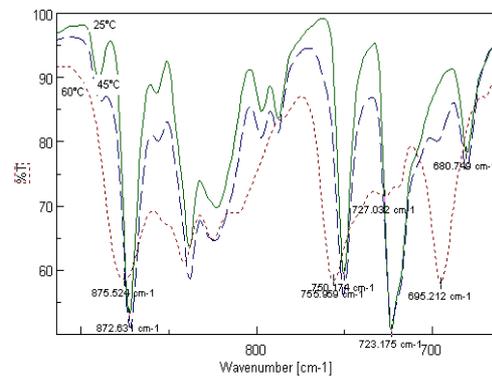
Fig. 5. Transmission band for CH out of plane deformation at different temperatures.

In the case of other lines (Fig. 6), characteristic to CH vibrations of ring in plane, the width of spectral lines decrease as temperature raises, cases in which the mechanisms leading to Lorentz shape of spectral lines prevails.
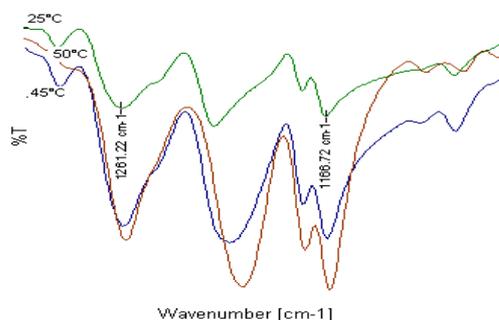
Fig. 6. Transmission band at at 25°C, 45° and 50°C for δ_{CH}

For more spectral lines, characteristic of C=O, C-H, C-O$_{asym}$ and C-O$_{sym}$ bonds (Fig. 2, 5 and 6) we noticed that at temperature growth, the half-width of spectral lines increase at solid – liquid crystal transition (when Doppler broadening prevails) and decrease at liquid crystal – isotropic liquid transition (when Lorentz mechanisms related to changes in the internal substance symmetry) exceed the broadening due to Doppler effect.

With increasing temperature is observed vibrational bands are broadening and shift to lower wavenumbers (Fig. 7) or to higher wave numbers (Fig. 2, 5).
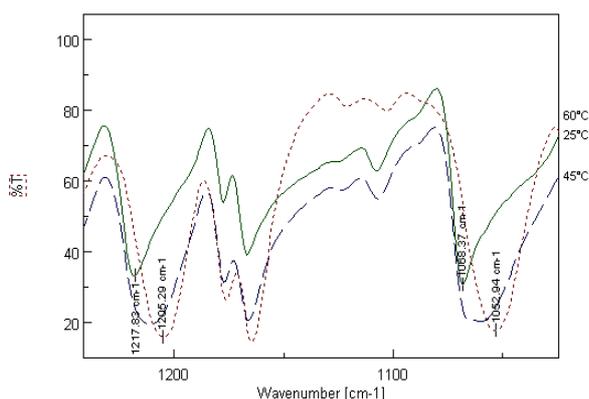
Fig. 7. Transmission band for C-O asym and C-O sym (the bands are widening), green at 25°C, blue at 45°C and red at 60°C.

The C-O$_{sym}$ and C-O$_{sym}$ bands are widening with increasing temperature, especially at crystal-liquid crystal transitions. Also, C=O stretching vibration become broader, shifts to higher wavenumber (from 1731,76 cm^{-1} at 25°C to 1734,76°C at 45°C) and becomes most intense (Fig. 2).
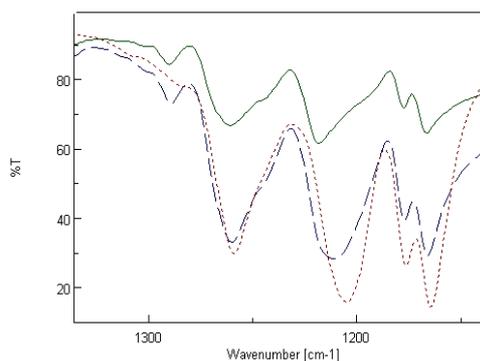
Fig. 8. ATR spectra of polienic chain (green at 25°C, blue at 45°C and red at 60°C).

For polienic chain, at 1300-1150 cm^{-1}, with increasing temperature, bands are narrowing for liquid crystal 1 - isotropic liquid transition and they shift to lower wave numbers (Fig. 8).

Broadening decrease is typical for modes of the polymethilene chain, such as CH$_2$ bending at 1450 cm^{-1}, wagging and twisting modes between 1350 and 1190 cm^{-1}. The C-C stretching modes at 1060-1020 cm^{-1}, the CH$_2$ and CH$_3$ rocking vibrations etc., also become broader in the mesomorphic state.

5. Conclusions

The vibrational spectrum of CP6B liquid crystal has been analyzed and interpreted. The main experimental conclusions are:

Temperature-induced changes in the skeletal and functional group vibrations in the IR spectra, especially at liquid crystal - crystal transitions;

With increasing temperature, vibrational bands broad. Broadening mechanisms are very complex, strongly determined by changes in internal symmetry occurred during the phase transitions. The analyzed spectra reveal the fact that in liquid crystal phase, the symmetry properties of the internal structure as well as the internal electric field features are significantly different from those specific of crystalline and isotropic liquid phases.

When temperature of CP6B changes in the range 25° - 75°C, the half-width of the C=O, C-O, C≡N absorption bands in the IR spectra increases and for CH$_2$ from polienic chain decreases and the bands are shifted.

The largest shift is experienced by the absorption bands belonging to the vibrations of the groups directly involved in molecule polarizability. During the cooling process, the mixtures present a wide interval of temperature in which phases coexist.

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