

## TEMPERATURE EFFECTS ON THE FTIR SPECTRA OF NEMATIC LIQUID CRYSTALS

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### Abstract

We have investigated the FT-IR of the  $\nu(\text{CN})$  and  $\nu(\text{C}=\text{O})$  groups of the nematic liquid crystal CP6B (4-cyanophenyl-4'-hexylbenzoate) at different temperatures (solid, liquid crystalline and isotropic phase). When the temperature of CP6B changes in the range 45 - 80 °C the absorption bands of in the IR spectra decreases and the bands are shifted. Even at the highest temperature reached in this study 80°C above the nematic-isotropic transition, the liquid has not yet achieved the structure of the simple liquid. The vibrational and orientational relaxations occur in very different time scales. 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.

Keywords: liquid crystal, ATR, cyano and carbonyl group, resonance frequency

### 1. INTRODUCTION

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 [1,2].

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) [3,4]. 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 [5-7].

The choice of cyanophenyl hexylbenzene (CP6B) in this study has been mainly dictated by

the presence of the carbonyl group (C=O) in its molecular structure. This group is presented in over 70 liquid crystals synthesized by us, in organic chemistry laboratory from University of Pitești.

### 2. MATERIALS AND METHODS

4-cyanophenyl-4'-hexylbenzoate is a Merck product.

IR spectra were recorded on a Jasco 6300 FT-IR spectrometer in the range region of 4000 – 400  $\text{cm}^{-1}$ , equipped with DTGS detector, apodization Cosine. All spectra were baseline corrected using SpectraManager II software.

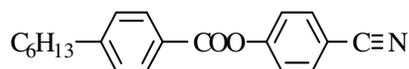
ATR spectra were obtained with an attenuated total reflection attachment Gladi ATR, apodization Cosine.

The instrument had a spectral resolution of 4  $\text{cm}^{-1}$ , which were used in all spectra determinations. Four hundred and twenty five scans were accumulated each time.

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

### 3. RESULTS AND DISCUSSION

CP6B (4-cyanophenyl-4'-hexylbenzoate):



is a liquid crystal that exhibits, on heating, the phase sequence: K-N (46°C), N-I (47,9°C). It is stable in the presence of the ambient oxygen up to approximately 200°C and above this temperature only under inert atmosphere.

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 [8].

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.

In IR, the most important vibrations for compound were cyano group vibration around 2231 cm<sup>-1</sup> and carbonyl group vibration at 1731 cm<sup>-1</sup> (strong) for C=O bond, 1217 cm<sup>-1</sup> (very strong) for C-O<sub>asim</sub> and 1068 cm<sup>-1</sup> for C-O<sub>sym</sub> (strong).

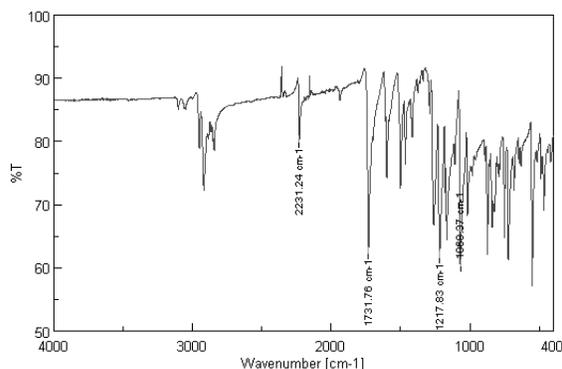
Table 1 shows the IR values obtained by ATR technique for CP6B at different temperatures.

**Table 1. IR values (cm<sup>-1</sup>) for CP6B at different temperatures**

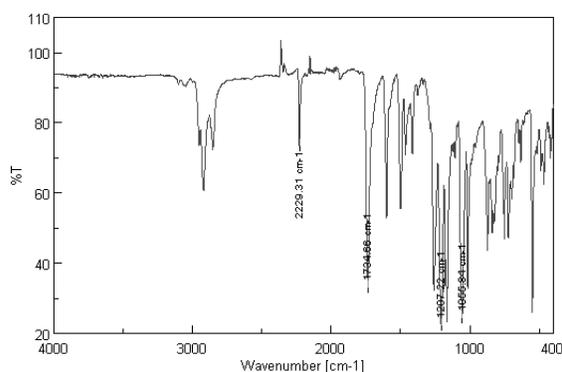
t(°C)	V <sub>CN</sub>	V <sub>C=O</sub>	V <sub>C-O<sub>asim</sub></sub>	V <sub>C-O<sub>sym</sub></sub>
25	2231,24	1731,76	1217,83	1068,37
30	2231,24	1731,76	1217,83	1068,37
40	2231,24	1731,76	1217,83	1068,37
<b>45</b>	<b>2230,27</b>	<b>1731,76</b>	<b>1211,08</b>	<b>1059,69</b>
<b>47</b>	<b>2229,31</b>	<b>1734,66</b>	<b>1207,22</b>	<b>1055,84</b>
<b>48</b>	<b>2229,31</b>	<b>1736,58</b>	<b>1205,29</b>	<b>1053,91</b>
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 spectra of CP6B by ATR are presented in Figure 1 at 27°C and Figure 2 at 47°C (liquid crystal phase). Distorsions are eliminated by the advanced ATR corrections.

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 a selected wavenumbers.



**Figure 1. ATR FT-IR spectra of CP6B at 25°C**



**Figure 2. ATR FT-IR spectra of CP6B at 47°C**

**Change in the IR spectra in the range 45 - 48°C.** 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 (figure 3 and 4).

An accessible explanation of these observation, based on the theory of interaction dipoles – electromagnetic field [9] 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:

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

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:

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

It has maximum value for resonant frequency

$$(\omega = \omega_0), \sigma_{osc}^{max}(\omega_0) = const \cdot \frac{\omega_0^2}{\lambda_t^2}, \text{ where } \lambda_t$$

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.

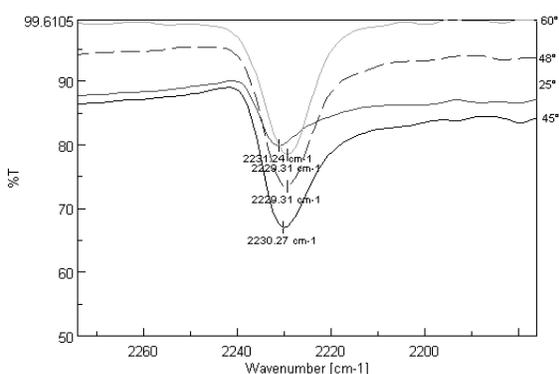


Figure 3. Transmission band at 25°C, 45°, 48° and 80°C for ν(CN)

Bands are most intense in the liquid crystal state. It shows a shift of the ν<sub>CN</sub> (figure 3), ν<sub>C-O</sub> and ν<sub>C-O<sub>asym</sub></sub> and ν<sub>C-O<sub>sym</sub></sub> bands to lower wavenumbers

and a shift to higher wavelengths for ν<sub>C=O</sub> (figure 4).

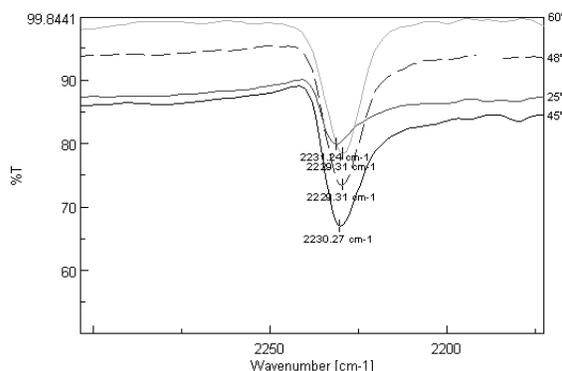


Figure 4. Transmission band at 25°C, 45°, 48° and 80°C for ν(CO).

The isotropic and anisotropic spectral distributions of the CN vibrational mode are reported in Fig. 3 in the isotropic phases at 48°C and 80°C. The analog spectral distributions for the vibrational mode CO are shown in Fig. 4. 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

#### 4. CONCLUSION

Temperature-induced changes in the skeletal and functional group vibrations in the IR spectra.

When the temperature of the CP6B changes in the range 45° - 48°C, in liquid crystalline state the intensity bands in the IR spectra increases and the bands are little shifted. The largest shift is experienced by the absorption bands belonging to the vibrations of the groups directly involved in molecule polarizability.

**5. REFERENCES**

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