Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Lev Babkov, Galina Puchkovskaya & Ekatherina Vedyaeva (2001): Conformational Mobility and Phase Transitions in Alkyloxybenzoate of Cholesterol, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 364:1, 795-799

To link to this article: http://dx.doi.org/10.1080/10587250108025050

Mol. Cryst. and Liq. Cryst., 2001, Vol. 364, pp. 795-799
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Conformational Mobility and Phase Transitions in Alkyloxybenzoate of Cholesterol

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The structural particularities of polymorphic modifications and cholesterol liquid crystal phase have been investigated by theoretical and experimental IR spectroscopy methods. The spectra were recorded in the interval of temperatures 293–523 K within the range of 600–3600 cm^{-1}. The frequencies of normal modes and intensities in the IR spectra have been calculated for the alkyloxybenzoate of cholesterol conformers, which may be realized under certain temperatures. Comparison of results of theoretical modelling and recorded spectra confirmed suggestion about conformational mobility basically defined with changing of steroid kennel orientation comparatively stayed part of molecule in the different phase state.

Keywords: mesophase; polymorphism; structure; IR spectra; conformational mobility

INTRODUCTION

Butiloxybenzoate of cholesterol (C_4AOBC) has attracted our attention, because it has a polymorphism feature. These compounds are interest for biophysics and solid physics [1]. In this work structural changes of C_4AOBC on the phase transition and temperature increasing are investigated by the methods of IR spectroscopy.

Molecule of butiloxybenzoic of cholesterol consists of alkyl radical (I), which between oxygen connect with benzoic ring (II) and cholesterol (III). Structure of C_4AOBC is shown in fig 1.

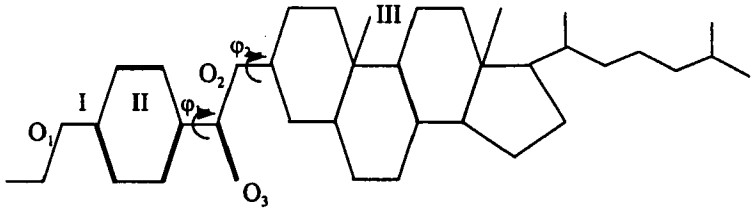

FIGURE 1. Structure of butiloxybenzoate of cholesterol

The aim of the present study is to prove that polymorphism of this compounds has a conformational character and to investigate influence of transition solid crystal (SC) - liquid crystal (LC) - isotropic liquid (I) on the molecular conformational of molecule.

EXPERIMENTAL AND METHODS

Following transition for the C_4AOBC was installed by the calorimeter methods [2, 3]:

$$SC1 \xrightarrow{396\text{-}399K} SC2 \xrightarrow{407\ K} LC \xrightarrow{518\text{-}520K} I$$

For the clarification of structural particularities of polymorphic modifications and cholesterol liquid crystal phase, IR absorbing spectra was measured. These spectra were recorded in the 600-3600 cm^{-1} spectral region and 293-523 K temperatures range for various SC modifications, LC, I. The modelling of infrared spectra was based on the theory of vibrations of polyatomic molecules by using of fragment method [4-5]. Decaline, metylcyclohexane, pentane, oxybenzol were taken as fragments.

RESULTS AND DISCUSSION

The experimental spectra are interpreted on the basic of their comparison with the results of calculations. Observing the differences of spectra measured under different temperatures are explained by polymorphic conversions, which may have, supposedly, conformational character. To prove this position, theoretical spectra modelling of different C_4AOBC conformers, that may be realized under certain temperatures, was carried out. Calculations of spectra were conduct in the framework of the vibration theory of multiatomic molecule by using of fragment method [6]. These calculations were realized for the fragments of C_4AOBC conformer, in which steroid kernel have different orientation comparatively stayed part of molecule. Angles φ_1 and φ_2 were changed. During calculations it was found out that orientation of plane, containing benzoic ring and carbon skeleton of alkyl radical with the atom of oxygen comparatively stayed part of molecule C_4AOBC did not affect on the calculated IR spectra. It is correspond to literature materials about native compounds ($\varphi_1=0^0$).

According to result of roentgen analysis respectively dihedral angle $\varphi_2=157^0$ in reasonable conditions forms. This angle varies by changing of temperature and phase transition. Calculation was conducted for the different angles φ_2, lying within the range of $80\text{-}160^0$. There are chosen bands in the recorded and calculated spectra, which changed by the temperature increasing. These changes can be explained by conformational mobility of the C_4AOBC molecule.

Frequencies of vibrations β(CCH) of all fragments of molecule are more sensitive to the conformational changes. The bands of the vibrations, which are most sensitive to the changes of φ_2 lie in the spectral regions 1200-1400 cm^{-1}.

The fragments of IR spectra of C_4AOBC are shown in Fig. 2. The measured spectra (Fig. 2a, c) at room temperature (curve 1), 391 K (curve 2) and 408 K (curve 3) are coincided with the calculated spectra (Fig. 2b, d) for the conformers with $\varphi_2=100^0$ (curve 1), $\varphi_2=130^0$ (curve 2), $\varphi_2=150^0$ (curve 3).

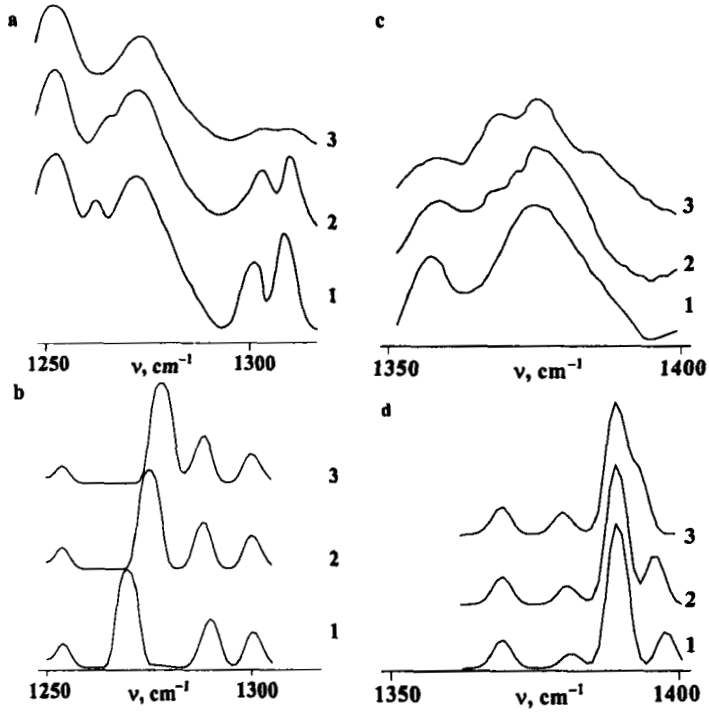

FIGURE 2. IR absorption spectra of C_4AOBC at 293 (1, SC1) 391 (2, SC2), 408 K (3, NLC) **(a, c)**; theoretical spectra of conformers (1–φ_2=100°, 2–φ_2=130°, 3–φ_2=150°) **(b, d)**

In the region 1250-1300 cm^{-1} 3 peaks may observe in the spectrum of C_4AOBC at the room temperature. The number of bands decreases with increasing of the temperature. Spectra become more structural. Calculations give 3 modes in this region, which correspond to vibrations β(CCH) in benzyl (ν_{64}, ν_{65}) and in cyclohexane (ν_{66}). The change of φ_2 affects the theoretical spectra. The band ν_{65} shifts to the low-frequency side of the spectrum. The band ν_{66} shifts to the high-frequency side of the spectrum. We may conclude that the homogeneous of conformational composition are breaking in solid

crystal phase but in the liquid phase present molecule of C_4AOBC with equal φ_2.

In the region 1350-1400 cm^{-1} it can be observed 2 bands at the room temperature in the experimental spectra of C_4AOBC. The contour of these bands transform with the temperature increase: appear new peaks, redistribute intensity. Calculations show that spectrum in these region consists of 6 modes.

Table 1. Vibrational frequencies of different conformers of C_4AOBC

Frequency (intensity), cm^{-1}			Assignment
φ_2=150°	φ_2=130°	φ_2=100°	
ν_{76}=1371 (0.1)	ν_{76}=1370 (0.01)	ν_{76}=1370 (0.01)	β_{III}(CCH)
ν_{77}=1371 (0.8)	ν_{77}=1371 (0.8)	ν_{77}=1371 (0.8)	β_I(CCH), α_I(HCH)
ν_{78}=1383 (0.4)	ν_{78}=1382 (0.6)	ν_{78}=1381 (0.7)	β_{III}(CCH)
ν_{79}=1384 (0.1)	ν_{79}=1384 (0.1)	ν_{79}=1384 (0.1)	β_{III}(CCH), β_I(CCH), q_I(CH)
ν_{80}=1391 (6.7)	ν_{80}=1391 (6.3)	ν_{80}=1391 (5.7)	β_I(CCH)
ν_{81}=1399 (1.0)	ν_{81}=1397 (1.7)	ν_{81}=1394 (2.2)	β_{III}(CCH)

The band ν_{66} shifts to the high-frequency side of the spectrum with the change φ_2. The temperature changes of spectra correspond to the changes of molecule C_4AOBC conformational.
Comparison of results of theoretical modelling and recorded spectra confirmed suggestion about conformational mobility in this type of molecule. Analyze of results of this comparison let us to conclude that transitions to liquid crystal are accompanied with transformations of φ_2. In the nematic liquid crystal conformers with $\varphi_2=100\pm10^0$ are prevail.

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