

## STUDIES ON ATR SPECTRA OF PHENOXYPHENYLCHOLESTERYL CARBAMATES

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### Abstract

*Cholesteryl phenoxyphenyl carbamates, compounds with potential liquid crystals properties, were prepared by the reactions of cholesteryl chloroformate with diphenyl ether amines, in the presence of the pyridine to acid acceptor. These carbamates presented a selective reflection from solvents such as acetone, amyl alcohol, methyl-ethyl cetone. The selective reflection as well as the optical activity remarkably influences the optical appearance (textures) of cholesteric phases. The compounds were studied using FTIR-ATR spectroscopy. Urethanic and carbonyl group frequency from cholesteryl carbamates was obtained by the use of an attenuated total reflectance (ATR) attachment on FTIR. The data was ATR corrected. In addition, spectral data was obtained with a KBr transmission technique on FTIR. After advanced ATR correction the band shift to lower frequency in the C=O and NH stretch of carbamates are reduced. The Advanced ATR correction algorithm corrects for band intensity distortion, peak shifts, and non-polarization effects. Corrected spectra are highly comparable to their transmission equivalents.*

Keywords: cholesteryl carbamates, FTIR spectroscopy, attenuated total reflexion, liquid crystals

### 1. INTRODUCTION

Liquid crystals phases appear in materials composed of interacting molecules (thermotropics) or aggregates of molecules (lyotropics) that are anisotropic in shape. Generally, the thermotropic liquid crystals phases are observed in a given range of temperature.

Chirality in liquid crystals has been the subject of intense research in recent years, and is directly responsible for their important technological applications. Chiral liquid crystalline materials as well as chiral molecules forming liquid crystal phases are very special and unusual. [1]. The aim of the present papers is to display the some important vibrations of compounds with chiral liquid crystal properties. The presence of chiral molecules in a liquid crystal can have various consequences. The chirality may cause an intrinsic helical structure of the director field. Instead of the uniform alignment of the director field occurring in the achiral phases, the respective chiral phases exhibit a helical structure [2]; example of some important chiral phases are chiral nematic know as cholesteric mesogens.

The present paper presents ATR study for two cholesteryl carbamates with diphenyl ether moiety at C-3 sterolic. These compounds with

structure confirmed by RMN [3, 4] have mesogenic properties [5].

Attenuated total reflexion (ATR) is now the most common sampling technique in FTIR spectroscopy. ATR technique involves the collection of radiation reflected from the interface between sample and a prism, in which evanescent wave penetrated from the prism in sample is absorbed by substances [6 -8]

The profusion of ATR accessories on the market today attests to the utility of the technique. Each accessory is designed to achieve optimum performance with a particular sample type. Diamond ATR devices, such as the Thermo Scientific Smart Orbit accessory, are highly suitable for hard or corrosive samples, whereas a germanium accessory is preferred for highly absorbing materials. The development of these accessories has greatly simplified sampling for FTIR spectroscopy.

However, ATR does present some challenges. An infrared spectrum of a sample obtained using an ATR accessory is not identical to the spectrum obtained by transmission. The ATR technique introduces relative shifts in band intensity and absolute shifts in frequency. The relative intensity shift is well-known and is readily corrected. The shift in frequency, which can result in a displacement of the peak maximum by several wavenumbers, is at once more serious and yet less often accounted for.

As most commercially available spectral libraries and published peak tables contain and refer to transmission spectra, differences between ATR and transmission spectra can lead to poor spectral search results and ambiguous interpretation.

The transmission sampling technique dominated the first decades of infrared spectroscopy. The optical arrangement required for transmission sampling is very simple and introduces few artifacts into the spectra.

Consequently, most published peak tables are derived from transmission spectra. Furthermore, most commercial libraries contain transmission spectra. Spectrometer validation tests are usually performed using transmission samples because the band positions of standard materials are well known in the transmission sampling mode [9].

The optics involved in ATR is quite different from those used in the transmission experiment. As a result, the infrared spectrum of a sample obtained by ATR exhibits some significant differences when compared to its transmission counterpart. Some of these differences are desirable and have been used to considerable advantage. An example of an advantage of ATR is that it is sensitive to the surface of the sample. As a result, the technique has found utility in the characterization of coatings and the identification of surface contaminants. Less desirable characteristics of ATR are its distortion of the relative intensities of bands and the introduction of a shift to lower frequencies.

The shift of peak positions to lower frequencies is particularly problematic. When a spectrometer is validated by comparison of a peak position in the transmission spectrum of a standard material to its accepted value, peak shifts due to ATR characteristics may be difficult to rationalize. Searching an ATR spectrum against a transmission database is also compromised by peak shifts.

The distortion of relative peak intensities in an ATR spectrum is well known. In the transmission experiment, the pathlength is defined by the thickness of the sample and is therefore constant across the spectrum. However, in the ATR experiment, the depth to which the sample is penetrated by the infrared beam is a function of wavelength, as presented in equation (1):

$$d_p = \frac{\lambda}{2\pi \cdot n_1 \sqrt{\sin^2 \Phi - \left(\frac{n_2}{n_1}\right)^2}} \quad (1)$$

where  $d_p$ ,  $\lambda$ ,  $\Phi$ ,  $n_1$ , and  $n_2$  are the penetration depth, wavelength, incident angle, ATR crystal refractive index, and sample refractive index, respectively.

The relative intensity of bands in an ATR spectrum increases with wavelength. If  $n_2/n_1$  is constant or a smooth function over the frequency range of observations, the penetration depth increases linearly with wavelength. Most spectroscopic software packages include an ATR correction function that simply applies a linear ramp to the ATR spectrum in order to approximate the relative band intensities that would be found in a transmission experiment. However, because the refractive index of the sample,  $n_2$ , changes sharply around absorption bands, the wavelength dependence of  $d_p$  is further modified according to the term  $[\sin^2 \Phi - (n_2/n_1)]^{-1/2}$ .

The second characteristic feature is the shift of absorption bands to lower frequency. ATR intensity is given by equation (2), when the sample thickness is greater than the penetration depth.

$$A = \log_{10} e \frac{n_2}{n_1} \frac{E_0^2}{\cos \Phi} \frac{d_p}{2} \alpha \quad (2)$$

where  $E_0$  and  $\alpha$  are the electric fields of the evanescent wave at the boundary and the absorption coefficient per unit thickness of the sample, respectively.

As equation 2 indicates, the ATR spectrum is influenced by the refractive index of the sample. Also, according to Equation 1, penetration depth,  $d_p$ , depends on  $n_2$ . Thus, instead of  $\alpha$ ,  $n_2 \cdot d_p \cdot \alpha$  determines the absorption band positions. Because of the anomalous dispersion of the refractive index,  $n_2 \cdot d_p \cdot \alpha$  always introduces a band shift to lower frequency and this shift becomes particularly noticeable for strong bands. In other words, the presence of absorptions in the infrared spectrum represents a change in the refractive index of

the sample across the band and results in the shift to lower frequency.

In order to apply the advanced ATR correction, four inputs are required:

- The refractive index of the sample.
- The refractive index of the ATR crystal (or internal reflection element (IRE)).
- The angle of incidence.
- The number of bounces.

With these four inputs, the software automatically calculates the corrected ATR spectrum. The ATR spectrum itself is used to calculate the optical properties of the sample that lead to frequency shifts predicted by equation 2. Of the four parameters, three are determined by the accessory itself. The IRE refractive index is determined by the material of the crystal, and the angle and number of bounces by the design of the accessory. The index of refraction of the material depends, of course, upon the material. However, most organic materials have an index around 1.5; use of this value generally provides very good performance of the correction.

## 2. RESULTS AND DISCUSSION

In Figure 1 is shown the chemical structures of cholesteryl carbamates used.

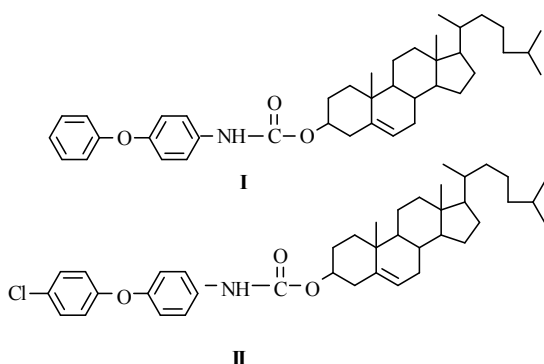


Figure 1. Structure of phenoxyphenylcholesteryl carbamates

Cholesterylcarbamates were prepared by direct reaction of cholesteryl chloroformate with diphenylthioether amines in dry toluene, in the presence of pyridine as acid acceptor. Pure crystals of desired cholesteryl carbamates were obtained after re-crystallization from amyl alcohol and a mixture of benzene and ethanol.

The synthesis and purity of carbamates **I** and **II** were checked by TLC and NMR spectra [1].

Table 1 shows the IR values obtained in KBr and by ATR technique for compounds **I** and **II**.

Table 1. IR values (cm<sup>-1</sup>) for cholesteryl carbamates

Comp.	$\nu_{C=O}$	$\nu_{C-(asim)}$	$\nu_{C-O(sim)}$	$\nu_{N-H}$
<b>I</b> <sub>KBr</sub>	1736,58	1211,08	1052,94	3407,67
<b>I</b> <sub>ATR</sub>	1733,69	1209,15	1051,01	3405,67
<b>I</b> <sub>ATRC</sub>	1736,58	1212,04	1053,91	3406,64
<b>II</b> <sub>KBr</sub>	1704,6	1218,79	1052,94	3405,67
<b>II</b> <sub>ATR</sub>	1702,84	1215,9	1051,01	3404,71
<b>II</b> <sub>ATRC</sub>	1703,8	1220,72	1052,94	3405,67

KBr-transmission, ATR- attenuated total reflection, ATRC – with advanced correction

The spectra of cholesterylcarbamates as run by transmission and ATR are presented in Figure 2 for compound **I** and Figure 3 for compound **II**, together with the corrected spectrum. Distorsions are eliminated by the advanced ATR corrections (Figure 4 and Figure 5).

In IR, the most important vibration of all compounds synthesized was carbonyl group vibration at 1702-1736 cm<sup>-1</sup> (strong) for C=O bond, 1209-1220 cm<sup>-1</sup> (very strong) for C-O bond and 3404-3407 cm<sup>-1</sup> (strong) for N-H bond.

The nucleus of the sterol is more difficult to interpretate by the IR spectrum. The vibrations at 2931-2970 cm<sup>-1</sup> ( $\nu_{asim}$ ) and 2866-2875 cm<sup>-1</sup> ( $\nu_{sim}$ ) characterize the methyl groups from steroid nucleus.

## 3. MATERIALS AND METHODS

The compounds with cholesteric structure and diphenylether at C-3 sterolic with confirmed liquid crystals properties were synthesized in Organic Chemistry laboratory of the Faculty of Science, University of Pitesti.

Cholesterylcarbamates are obtained by reaction of cholesteryl chloroformate with amines derivatives of diphenyl ether amines. The crystallization of carbamates from amyl alcohol and methyl-ethyl cetone leads to high purity compound.

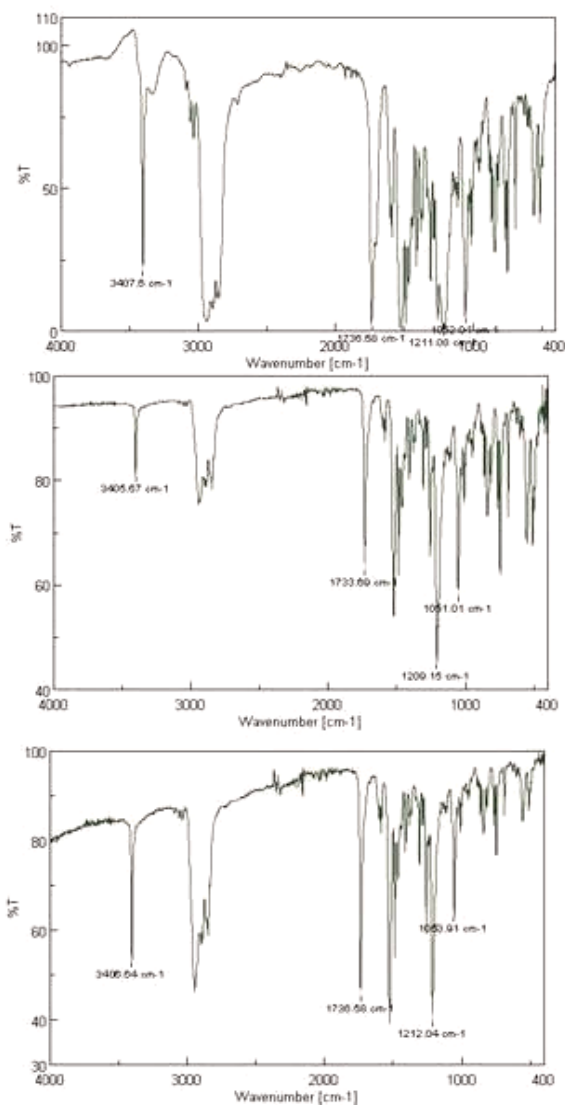


Figure 2. Cholesterylcarbamate I FT-IR spectra run by transmission (upper), by ATR (center), and by ATR correction (lower)

These carbamates presented a selective reflection from solvents such as acetone, amyl alcohol, methyl-ethyl cetone. The selective reflection as well as the optical activity remarkably influences the optical appearance (textures) of cholesteric phases. The purity of compounds was checked by TLC; 0.25 mm silica gel plates (Merk), eluent mixture of benzene and petroleum ether 9:1 and spectrally characterized (RMN techniques) [2].

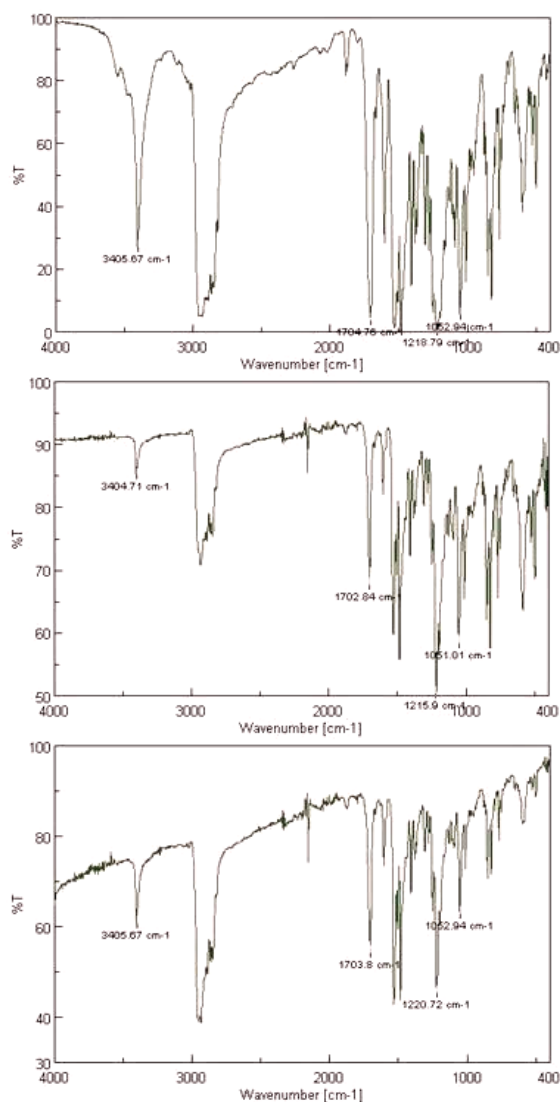


Figure 3. Cholesterylcarbamate II FT-IR spectra run by transmission (upper), by ATR (center), and by ATR correction (lower)

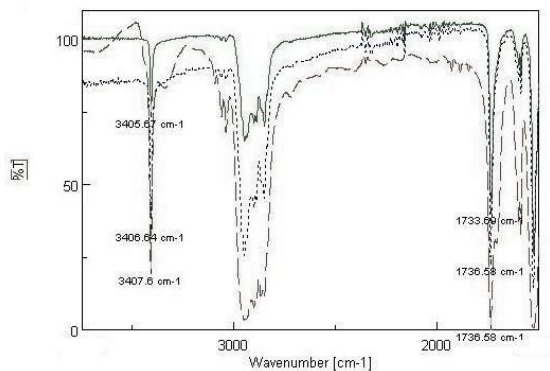
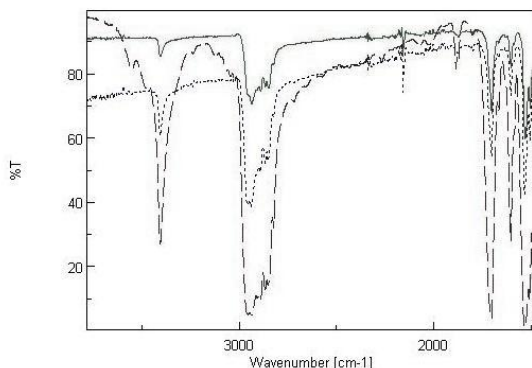


Figure 4. Cholesterylcarbamate I FT-IR spectra run by transmission (---), by ATR (—) and by ATR with advanced ATR correction (···)



**Figure 5. Cholesterylcarbamate II FT-IR spectra run by transmission (—), by ATR (---) and by ATR with advanced ATR correction (....)**

The cholesterylcarbamates used are presented in Figure 1. In our studies, we selected compounds with diphenyl ether moiety, a bulky polarizable substituent at C-3 of sterolic ring.

The transition path and thermodynamic functions were measured by differential scanning calorimetry (DSC) and Bötius thermomicroscopy (TM) [3].

IR spectra were recorded on a Jasco 6300 FT-IR spectrometer in the rangeregion 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.

#### 4. CONCLUSION

ATR spectroscopy provides a fast, easy, direct and flexible method to obtain IR spectra. ATR spectra are comparable to KBr spectra, in concordance with other studies [10].

#### 5. REFERENCES

- [1] Singh S., Liquid Crystals: Fundamentals, World Scientific Publishing Co. Pte. Ltd., 2002.
- [2] Kitzerow H. S, Bahr Ch. eds., Chirality in Liquid Crystals, Springer-Verlag, New York, 2001.
- [3] Baciu I., Drăghici C., Cîrlănușu-Topală C., Arsenescu N., Synthesis of Cholesterol Derivatives, Rev. Roum. Chim., 2000; 45(6): 525-529
- [4] Breitmaier E., Voelter W., <sup>13</sup>Carbon NMR Spectroscopy, sd Ed VCH, Weinheim, 1990, 272-293.
- [5] Meltzer V., Topală C., Pincu E., Thermodynamic Study of Cholesteryl and Stigmasteryl Esters, Revue Roumaine de Chimie, 2001; 46(12): 1281-1284.
- [6] Urban M. W., Koenig J. L., Shih L. B., Allaway J. L., Appl. Spectrosc., 1987; 41: 590.
- [7] Mirabella F. M., Internal Reflection Spectroscopy – Theory and Applications ed. F.M. Mirabella, Jr., Marcel Dekker, Inc New York, 1994.
- [8] Stuart H. B., Infrared Spectroscopy: Fundamentals and Applications, John Wiley & Sons, Ltd, 2004.
- [9] Bracewell R. N., The Fourier Transform and its Applications, McGraw-Hill, 3rd. Edition, 2000.
- [10] Takan T., Nagao S., Ogawa H., Analytical Sciences, 2001; 17: i1081.