Studies on ATR spectra of mesogenic cholesteryl carbamates

C. TOPALĂ[*], S. ANGHEL
University of Piteşti, Faculty of Science, Târgu din Vale No.1, Piteşti – 110040, Romania

Mesogenic cholesteryl carbamates, liquid crystals synthesized in Organic Chemistry laboratory of the Faculty of Science, University of Pitesti, 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.

1. Introduction

In the last few years many homologous series of carbamates with cholesterol skeleton, at 3β-position in A ring, have been prepared [1-4]. The mesogenic properties of steroids derivatives depend on both the structure of sterol and the nature of the substituents in 3β-position. Phase transition (mesomorphic and polymorpic) in these homologous series have been thorough examined.

A lot of interest in liquid crystals came from their technological potential. One of the main properties of liquid crystals is their thermal stability; its knowledge is important because the upper limit of their applications may be governed by it. It had been proved that mesomorphic properties of cholesteryl derivatives depends both on the nature of sterol and on the nature of substituents at C-3.

The present paper presents ATR study for two cholesteryl carbamates with heterocyclic moiety at C-3 sterolic. These compounds with structure confirmed by RMN [4] have mesogenic properties [5, 6].

Attenuated total reflexion (ATR) is now the most common sampling technique in FT/IR 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 [5, 7]

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 FT-IR 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 [8].

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):

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

where dp , λ, Φ, 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 dp is further modified according to the term $[\sin^2\Phi - (n2/n1)]^{-1/2}$.

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.

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

where E_0 and α 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, dp, depends on n_2. Thus, instead of α, $n_2 \cdot d$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 excellent performance of the correction.

The objectives of this study were: 1) to characterize two new cholesteryl derivatives with liquid crystals properties by ATR technique; 2) to compare the ATR spectra of cholesteryl derivatives with FTIR transmission spectra using KBr pellets (KBr spectra); 3) to evaluate the differences in spectra bands of CO and NH on cholesteryl derivatives with uretanic group at C-3 sterolic.

2. Experimental set-up and procedures; substances used

Cholesteryl carbamates are obtained by reaction of cholesteryl chloroformate with amines derivatives of heterocycle compounds: 2-fluorenamine (compound I) and 2-amino-phenoxathiine (compound II). The crystallization of carbamates from amyl alcohol and methyl-ethyl cetone leads to high purity compound. 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].

The cholesterylcarbamates used are presented in Fig. 1. In our studies, we selected compounds with heterocyclic 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 Böetius thermomicroscopy (TM) [6].

IR spectra were recorded on a Jasco 6300 FT-IR spectrometer in the region of 4000 – 400 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 cm^{-1}, which were used in all spectra determinations.

3. Results and discussion

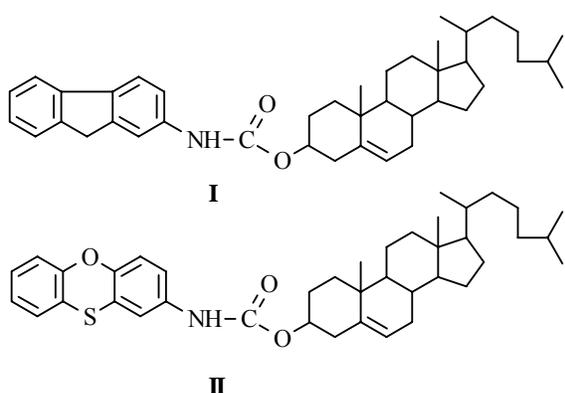In Fig. 1 is shown the chemical structure of the cholesteryl carbamates used.

Fig. 1.Structure of cholesterylcarbamates.

Cholesterylcarbamates were prepared by direct reaction of cholesteryl chloroformate with heterocyclic 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 [4].

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

Table I. IR values (cm^{-1}) for cholesterylcarbamates.

Comp.	$\nu_{C=O}$	$\nu_{C-(asim)}$	$\nu_{C-O(sim)}$	ν_{N-H}
I_{KBr}	1728,87	1215,9	1053,91	3403,75
I_{ATR}	1725,01	1213,97	1051,98	3400,85
I_{ATRc}	1726,94	1216,86	1053,91	3401,82
II_{KBr}	1730,8	1210,11	1054,87	3403,74
II_{ATR}	1726,94	1204,33	1056,8	3399,89
II_{ATRc}	1727,91	1208,18	1057,76	3400,85

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

In IR, the most important vibration of all compounds synthesized was carbonyl group vibration at 1720-1722 cm-1 (strong) for C=O bond, 1220, 1212, 1250 cm-1 (very strong) for C-O bond and 3350, 3400-3425 cm-1 (strong) for N-H bond.

The nucleus of the sterol is more difficult to interpret by the IR spectrum. The vibrations at 2931-2970 cm-1 (ν_{asim}) and 2866-2875 cm-1 (ν_{sim}) characterize the methyl groups from steroid nucleus.

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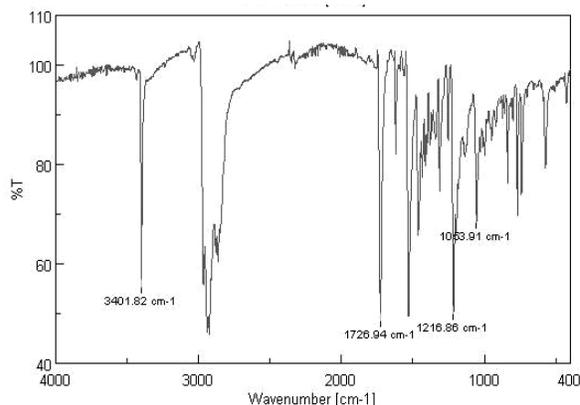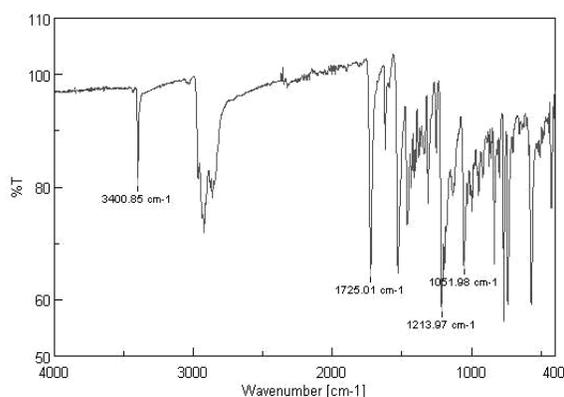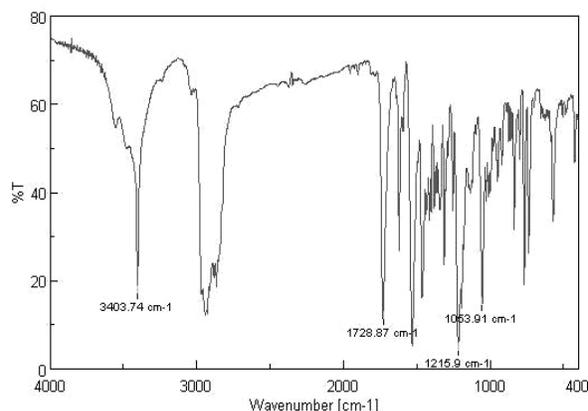

*Fig. 2. Cholesterylcarbamate **I** FT-IR spectra run by transmission (upper), by ATR (center), and by ATR correction (lower).*
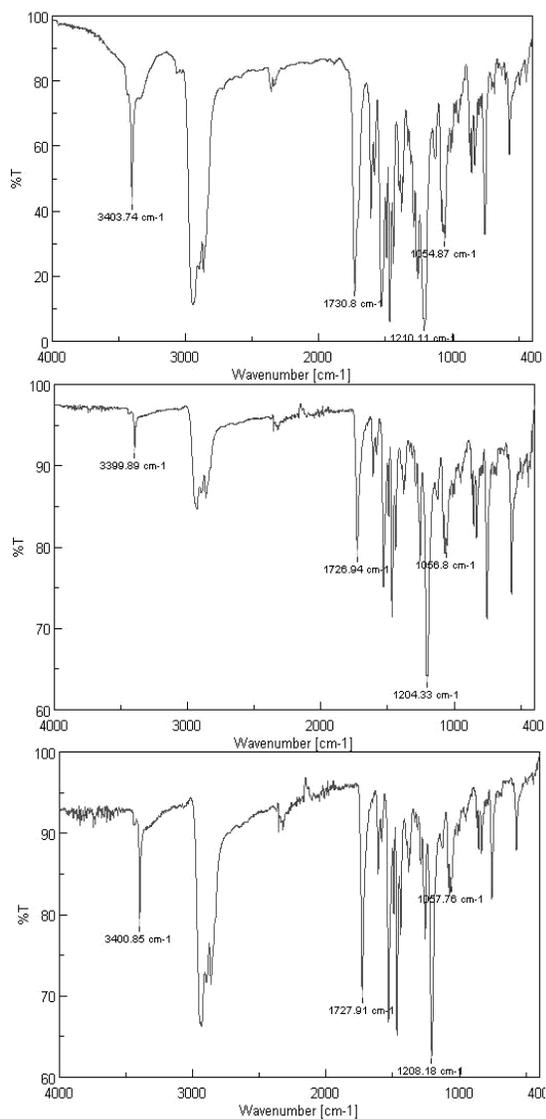
*Fig. 3. Cholesterylcarbamate **II** FT-IR spectra run by transmission (upper), by ATR (center), and by ATR correction (lower).*
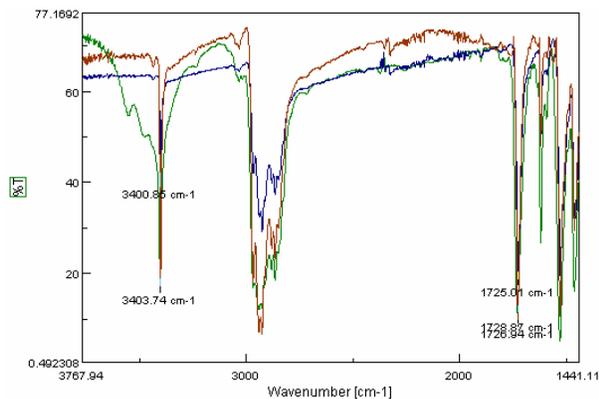

*Fig. 4. Cholesterylcarbamate **I** FT-IR spectra run by transmission (green), by ATR (blue) and by ATR with advanced ATR correction (red).*
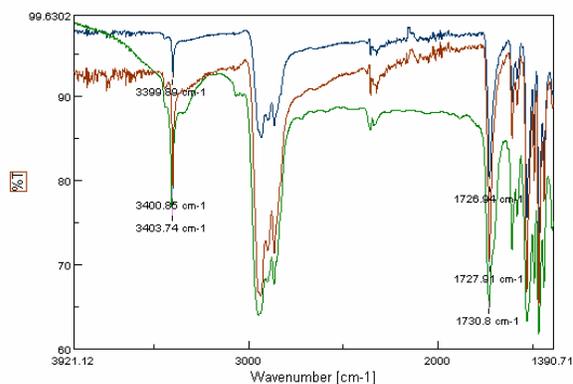

*Fig. 5. Cholesterylcarbamate **II** FT-IR spectra run by transmission (green), by ATR (blue) and by ATR with advanced ATR correction (red).*

4. Conclusions

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 [9].

The ATR technique is highly popular and yet introduces some distortions into spectra. Such distortions create problems when comparing spectra obtained by ATR and transmission. The Advanced ATR correction algorithm corrects for band intensity distortion, peak shifts, and non-polarization effects. The corrected spectra are highly comparable to their transmission equivalents.

These compounds with confirmed liquid crystals properties were synthesized in Organic Chemistry laboratory of the Faculty of Science, University of Pitesti.

References

[1] C. Topală, V. Meltzer, C. Drăghici, Revue Roumaine de Chimie **50**(2), 125 (2005).
[2] C. Topală, I. Baciu, V. Meltzer, G. Ioniţă, C. Drăghici, Revista de Chimie (Bucureşti) **54**(5), 402, (2003).
[3] C. Topală, V. Meltzer, E. Pincu, C. Drăghici, Revue Roumaine de Chimie, **47**(6), 539 (2002).
[4] I. Baciu, C. Cîrlănaru - Topală, G. Ioniţă, C. Drăghici, Revue Roumaine de Chimie **46**(6), 633 (2001).
[5] M. W. Urban, J. L. Koenig, L. B. Shih, J. L. Allaway, Appl. Spectrosc., **41**, 590 (1987).
[6] V. Meltzer, C. Topală, I. Baciu, E. Pincu, Revue Roumaine de Chimie **47**(8-9), 839 (2002).
[7] F. M. Mirabella, Internal Reflection Spectroscopy – Theory and Applications ed. F. M. Mirabella, Jr., Marcel Dekker, Inc New York, 1994.
[8] R. N. Bracewell, The Fourier Transform and its Applications, McGraw-Hill, 3rd. Edition, 2000.
[9] T. Takana, S. Nagao, H. Ogawa, Analytical Sciences, **17**, i1081 (2001).

*Corresponding author: carmen.topala@upit.ro
carmen.topala@gmail.com