Temperature Effect on the FTIR Spectra of Tyrosine Derivatives

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The FTIR spectra of tyrosine and their derivatives: N-acetyl-L-tyrosine ethyl ether and 2-acethylamino-3-(4-cholesteryloxy-carbonyloxy)phenyl ethylpropionate were investigated in the temperature range 24-140°C. The changes in the IR spectra due to temperature variations were correlated with some structural characteristics.

Keywords: tyrosine, liquid crystals, attenuated total reflexion, cholesterylcarbonate

Interest in the temperature effects on the properties of crystalline amino acids was dictated by their utility as materials (ferroelectrics, piezoelectrics, and nonlinear optical materials) and bioimitation systems [1]. Amino acid crystals have structure-forming fragments similar to those in biopolymers, namely, “head-to-tail” chains that imitate peptide chains. The functional groups are activated in different temperature ranges and this is essential for the functioning of biopolymers [2]. The mobility of the molecular fragments of biopolymers plays an immense role in the functioning of the latter. All types of motion from bond vibrations to collective motions of large atomic groups are temperature-dependent [3]. Therefore, amino acid crystals are often used as additional model objects for dynamic studies of the individual molecular groups present in biopolymers [1]. This paper presents a study of the temperature effects on the IR spectra of tyrosine and of two derivatives. The compounds used are presented in figure 1.

L-tyrosine is one of the most abundant natural amino acid with low solubility in water. Esterification of carboxyl group and acylation of amino group leads to ethyl ester N-acetyl-L-tyrosine, specific enzymes necessary action in skeletal muscle, liver, intestine [4].

Experimental part
Material and methods
Tyrosine (I), N-acetyl-L-tyrosine ethyl ether (II) are Aldrich products.

Compound III, 2-acethylamino-3-(4-cholesteryloxy-carbonyloxy)phenyl ethylpropionate was synthesized from the reaction between cholesterylchloroformate and II. The crystallization of this cholesterylcarbonate from a mixture of benzene and acetone leads to high purity compound. This carbonate presented a selective reflexion from solvents such as acetone, amyl alcohol, methyl-ethyl cetone. The selective reflexion, as well as the optical activity (two asymmetric centers on the long axis of the molecule) remarkably influences the optical appearance (textures) of cholesteric phases. The purity of compound, III, was checked by TLC: 0.25 mm silica gel plates (Merk), eluent mixture of ethyl ether and petroleum ether 1:9 and spectrally characterized (NMR techniques) [5].

IR spectra were recorded on a Jasco 6300 FT-IR spectrometer in the region of 4000 – 400 cm⁻¹, detector TGS, apodization Cosine, software SpectraManager 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.

Results and discussions
Cholesteryl carbonates (III) is obtained by reaction of cholesteryl chloroformate with N-acetyl-L-tyrosine ethyl ether (II). Compound III liquid crystalline property: Cro115Ch145 [5]. Figures 2- 4 presents the FTIR spectra of tyrosine (I) and compounds II and III at different temperatures. For compound II melting points is at 78-81°C.

The study shows that there are considerable spectral changes at the crystal-isotrop phase transitions for compounds I and II, crystal-cholesteric and isotropic phase for cholesterylcarbonate, III. Most of the IR bands in the crystalline phase are sharp, including bending and stretching vibrations. With increases temperature many IR band shifts are broaden and change intensity as the molecules recover rotational and translational freedom.

When the temperature of the L-tyrosine samples changes in the range 20-140°C, the half-width of the absorption bands in the IR spectra increases, and the bands

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Fig.1. Tyrosine (I) and their derivatives (II, III, where Ch-the rest of cholesterol)
are shifted (the NH stretching at lower wavenumber from 3345.89 cm\(^{-1}\) at 24°C to 3333.36 cm\(^{-1}\) at 120°C). Some significant changes are obtained with increasing temperatures in IR spectra for compounds II and III (fig. 3 and fig. 4).

Table 1 shows the IR values obtained by ATR technique for compound II at different temperatures (80°C is melting point for II).

At melting point obvious changes occur in ATR spectra for compound II. The C=O stretching moving at higher wavenumber (1718.26 to 1728.87 cm\(^{-1}\)) and the NH stretching moving to lower wavenumber (1654.62 to 1649.8 cm\(^{-1}\)). When the temperature of the compound II changes in the range 40-120°C, the half-width of the absorption bands in the IR spectra increases (fig. 3, especially stretching vibrations C=O at 1223 cm\(^{-1}\)).

We also analyzed the effects of temperature on the half-width of spectral lines of studied spectra [6]. Characteristic for Doppler broadening is the increase of half-width directly proportional to square root of temperature and the independence of the pressure. Also, there is a splitting of the band stretching vibrations of NH at 60 and 80°C at 1654.62 cm\(^{-1}\) and 1648.84 cm\(^{-1}\) (fig. 5).

Table 2 shows the IR values obtained by ATR technique for compound III at different temperatures (115°C is melting point and 145°C is clearing point).

For methyl groups from steroid nucleus vibrations were at 2931.27-2902.34 cm\(^{-1}\) and 2864.74-2848.35 cm\(^{-1}\). There are weak changes for C=O stetching vibrations and obvious for NH stretching (table 2 and fig. 4) at transitions Cr \(\rightarrow\) Ch (moving at higher wavenumber and the half-width of the absorption bands spectra increases).

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. 6-8 for compound I, II and III). Those near 1600-1500 cm\(^{-1}\) are characteristic of...
Fig. 6. The ATR spectra of tyrosine at different temperatures (skeletal stretching vibrations of C-C bonds of the benzene rings, solid line at room temperatures, broken line at 80°C and dotted line at 120°C)

Fig. 7. The ATR spectra for II (skeletal stretching vibrations of C-C bonds of the benzene rings, solid line at room temperatures, broken line at 80°C and dotted line at 120°C)

Fig. 8. The ATR spectra for III (skeletal stretching vibrations of C-C bonds of the benzene rings, solid line at room temperatures, broken line at 120°C - cholesteric state and dotted line at 145°C - isotropic state)

aromatic ring itself and, together with CH stretching bands near 3000 cm⁻¹ they provide a good signature of the aromatic structure [7]. The actual positions of these bands are influenced to some extent by the nature and arrangement of the substituent groups around the ring. The frequency positions of two most prominent benzene ring stretching modes are 1610-1590 cm⁻¹ and 1525 – 1490 cm⁻¹ respectively. In mesomorphic molecule the higher wavenumber band is somewhat weaker than the other one. A weak ring band appears at 1600-1560 cm⁻¹, mainly as a shoulder to the stronger 1600 cm⁻¹ band. The fourth skeletal C-C ring frequency for investigated compounds is in the range 1470 – 1430 cm⁻¹ and is of moderate intensity. This band frequently overlaps with the strong CH₂ deformation modes and therefore its utility is reduced.

Conclusions
The vibrational spectrum of three compound derived from tyrosine 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 with increasing temperatures (at melting point) for compound I and II and crystal-liquid crystal transitions for compound III;
- with increasing temperature, vibrational bands broad. Broadening mechanisms are very complex, strongly determined by changes in internal symmetry occurred during the phase transitions;
- when the temperature of the compounds changes in the range 24 - 120°C, the half-width of the C=O, C-O, absorption bands in the IR spectra increases and for CH₂ from polenic chain decreases and the bands are shifted.

IR spectral changes occur at the melting temperature, clarification respectively.

References
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