Journal of Molecular Structure 1040 (2013) 112–116

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Temperature dynamics of dimer formation in behenic acid: FT-IR spectroscopic study

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HIGHLIGHTS

- Behenic acid dimers were investigated in a wide temperature range 10–365 K.
- Two dimer conformations, *cis* and *trans*, coexist in a crystal phase at all temperatures.
- The *trans* configuration prevails at low temperatures and amounts to 96% at $T = 10$ K.
- At heating *trans* dimers transform gradually into the *cis* form.
- The hydrogen bonding energy for both types of behenic acid dimers is ~8 kcal/mol.

ARTICLE INFO

Article history:
Received 12 January 2013
Received in revised form 24 February 2013
Accepted 26 February 2013
Available online 5 March 2013

Keywords:
Behenic acid
Dimers
Cis-, *trans*-conformations
FT-IR spectroscopy

ABSTRACT

The structural evolution of behenic acid molecule dimers has been investigated in a wide temperature range 10–365 K by FT-IR spectroscopy. In a crystal phase the two dimer conformations, *cis* and *trans* forms, coexist in the whole temperature region up to the melting point. The *trans* configuration prevails at low temperatures and amounts to 96% at $T = 10$ K. At heating these associates transform gradually into the *cis* form. The dynamic equilibrium of 75% *cis* and 25% *trans* dimer configurations is established at $T = 250$ K and retains up to the melting, where dimers start to dissociate to monomers. The calculated hydrogen bonding energy for both types of behenic acid dimers is ~8 kcal/mol in average, being 0.3–0.8 kcal/mol (depending on temperature) higher for the *trans* form. At heating the energy of both dimer configurations drops gradually, i.e. the hydrogen bonding in a crystal weakens slowly with temperature. The results can be generalized and applied for other homologues of carboxylic fatty acids.

1. Introduction

Fatty (carboxylic) acids and their derivatives form an important class of biological systems, building all complex lipids such as phospholipids, being abundantly present in biological organs, and providing the hydrophobic part of biomembranes by the acyl chains [1–3]. Furthermore, these compounds have been widely used in many industrial products, in particular, foods, cosmetics, detergents and lubricants.

One of the important characteristics of long-chain molecules is their conformational flexibility and mobility, which determine the overall physicochemical properties of these substances, peculiarities in their molecular aggregations, mechanisms of solid-state or solid-melt phase transitions, etc. The hydrocarbon moieties can reveal various configurations and lateral packing, which results in a diversity of molecule alignments and condensed phases [4–7]. The understanding of molecular structure dynamics and conformation polymorphism has been a matter of active research and has been investigated for some representatives of fatty acids [8–12].

Carboxyl groups are known as those which are responsible for molecular packing of fatty acids [7,12,13]. They act as proton donors (O—H bonds) and as proton acceptors (C=O bonds), and hence can form hydrogen bonds between each other as cyclic dimers or as open arrays. The exceptional stability of carboxylic acid dimers makes them one of the most suitable classes for studying the hydrogen bonded complexes [14].

In this work, the structural evolution of behenic acid molecule dimers has been studied in a wide temperature range by Fourier transform infrared (FT-IR) spectroscopy. Some results obtained can be generalized and applied for other representatives of carboxylic fatty acid homologous series.

2. Experimental

Behenic or docosanoic (C22) fatty acid, $CH_3(CH_2)_{20}COOH$, was purchased from Sigma–Aldrich, Inc. (Germany) at a stated 99%

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0022-2860/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molstruc.2013.02.034

purity and was used without further purification. It consists of cream-white powder with a melting point of ~80 °C and boiling point of 306 °C.

FT-IR spectra were acquired using an IFS-88 Bruker spectrometer in the spectral range 400–4000 cm^{-1} (spectral slit width 1 cm^{-1}, 32 scans). The sample was preliminary melted between two KBr plates and then slowly cooled to room temperature. Then it was placed in a special (Bruker) cell, equipped with a thermostating system; the accuracy of temperature maintenance was ±1°. The sample thickness was determined by spaces and equal to 15 μm. The IR-spectra were recorded in the temperature range 10–365 K at heating regime. The sample was thermostated at least for 10 min at each temperature before the measurement. After the sample was cooled down to the room temperature, its spectrum was completely restored.

IR-spectral contour analysis and determination of band component parameters were carried out by the Jandel Peakfit software package. Band fitting was done by a Gauss function with the minimum number of spectral components used for the fitting process, and was undertaken until reproducible results were obtained with squared correlations greater than 0.995.

3. Results and discussion

All carboxylic acids usually crystallize as head-to-head centrosymmetric dimers with the center of inversion within the eight-membered ring formed by two carboxyl groups [13,15]. The molecules in each dimer are linked through two C═O···H—O hydrogen bonds and in a crystal are packed in bilayers with terminal methyl groups at both external faces. In the IR-spectra of these compounds, formation and dynamics of hydrogen bonds mainly affect the frequency values and spectral contours of hydroxyl group deformation and stretching vibrations, and also have an influence on the different vibrations of dimer ring atoms.

Contrary to stretching vibrations Q(OH), deformation ones ρ(OH) are more sensitive to the intermolecular interactions and conformation transitions, which makes them more informative in the studies of crystals with H-bonds. Fig. 1 presents the IR-spectra of C22 at various temperatures in the region of OH out-of-plane bending modes, which are seen as intense spectral bands, overlapping by very weak band series of Q(C—C) in-plane stretching vibrations of carbon framework (916, 920 cm^{-1}) and ψ(CH_2) out-of-plane rocking vibrations of methylene chain (988 cm^{-1}). Low intensity of the latest bands evidences about the absence of significant mixing between these vibrations and ρ(OH). In addition,

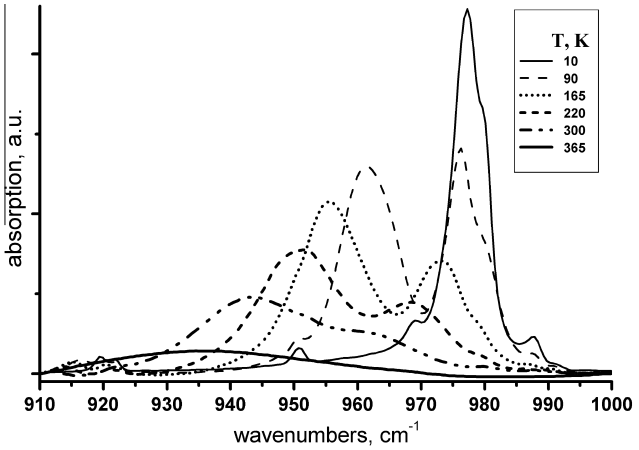

Fig. 1. IR-spectral region of ρ(OH) bending vibrations for behenic acid molecules in the temperature range 10–365 K (spectra at intermediate temperatures were removed for better performance).

theoretical calculations [16] showed that as a whole the effects of the methylene chain on vibration frequencies of the dimer ring are small.

The ρ(OH) spectral region of behenic acid contains two well-pronounced IR-bands, which are characterized by different temperature behaviors. Detail dependencies on temperature of their spectral parameters (peak position, intensity, and half-width) are given in Fig. 2. At low temperature, T = 10 K, a high-frequency band (I) at 977 cm^{-1} possesses maximum intensity, while a low-frequency one (II) at 968 cm^{-1} is practically unseen in the spectrum. At heating, the band I shifts towards low frequencies by 26 cm^{-1} in the C22 crystal state (Fig. 2a) and drops exponentially in intensity (Fig. 2b). Contrary to this, at temperature increase the spectral band II grows initially, reaching its maximum intensity at T = 90 K, and then quenches gradually. Its peak position also shifts slowly to the low-frequency side, but larger (by 32 cm^{-1}), than the band I. Under heating, both bands become significantly wider, up to 20 cm^{-1} in the half-width in a crystal phase of C22 (Fig. 2c), and finally, decrease much in intensity (practically to zero near the C22 melting point). In a liquid phase, only very weak "diffused" on broad frequency region absorption with a center at 937 cm^{-1} is observed in a range of ρ(OH) vibrations (Fig. 1), which evidences about the minimum quantity of dimers present in behenic acid melt. The confirmation of C22 dimer dissociation to monomers under melting can be also an appearance of the IR-band at 630 cm^{-1}, being seen quite intensively in the spectrum even at T = 360 K. Results of IR-spectroscopic studies, carried out for the different long-chain alkyl- and alkoxybenzoic acids in CCl_4 solutions and as a gas phase [16–18], showed that this spectral region contains ρ(OH) deformation vibrations of fatty acid monomers. This allowed to assign the 630 cm^{-1} band, observed in high-temperature IR-spectra of behenic acid to the vibrations of C22 monomers and to conclude about their primary presence in the melt of this substance. It should be also noted that the band I possesses a complex contour with an additional spectral component at 980 cm^{-1}. This component loses significantly its intensity under temperature increase and disappears practically at C22 melting. But contrary to the described above bands I and II, it retains its frequency position during the whole process of heating.

The spectral position of ρ(OH) deformation vibrations gives a possibility to evaluate energy values of hydrogen bonding for the two types of behenic acid dimers. To determine the enthalpy, ΔH, of hydrogen bonding in crystals, one can use experimentally established correlation between a spectral shift of the ρ(OH) band and ΔH, namely, Iogansen's frequency rule [19]:

$$-\Delta H = 1.6 \times 10^{-5}(\rho_d^2 - \rho_m^2),$$

where ρ_d and ρ_m – frequencies of ρ(OH) vibrations of dimer and monomer molecules, correspondingly. Taking into account that ρ_m = 630 cm^{-1} for behenic acid, the calculated hydrogen bonding energy in the dimers of type I is 8.9 kcal/mol, and in the case of type II it is 8.6 kcal/mol for one H-bond at T = 10 K. When the C22 crystal is heated up to the melting temperature, energy for the both types of dimers drops gradually; this value decreases to 8.3 kcal/mol in the case of type I associates and to 7.5 kcal/mol for the type II ones. It should be noticed that the determined here energy values for behenic acid are comparable in magnitude with hydrogen bonding energy, obtained for the dimers of other substances from the series of long-chain acids [16–18].

The existence of two distinct configurations of the dimers has been studied in the crystals of some fatty acids [4,20–22]. It has been suggested that the *trans* configuration is present together with the *cis* configuration – in other words, the hydrogen atoms fluctuate randomly between two equilibrium positions for *cis* and *trans* configurations (Fig. 3). Although some randomness in the