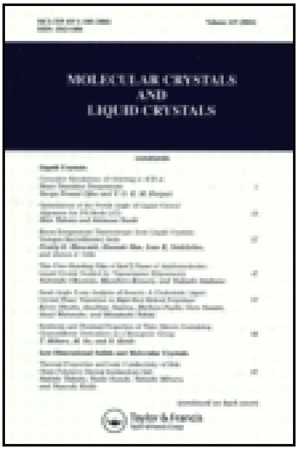

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Conformational Polymorphism of Fluorinated Derivatives of Alcylcyclohexanecarboxylic Acids

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The results of investigations of polymorphism and mesomorphic states of fluorinated derivatives of alkylcyclohexanecaroxylic acids nFACHCA (where n is the number of carbon atoms in the fluoroalkil radicals) and new results for n=4, 7 have been discussed. The methods of vibrational spectroscopy (experimental, theoretical modeling) have been used. The samples have been investigated in the 290–500 K temperature range. The spectra have been recoded in the range of 33–4000 cm^{-1}. The frequencies of normal modes and intensities of bonds of IR spectra have been calculated for conformers of H-complexes with various orientations of fluoroalkyl radical and carboxylic group relative to the rest part of the molecular complex. The polymorphism of the nFACHCA is conformational. The influence of H-bonds on dynamic of H-complex, polymorphic crystalline modification and mesophase formation were determined. The transitions solid crystal- liquid crystal-isotropic liquid and solution are accompanied by H-bonds system reconstruction: the dimmers, associates, chain associates and monomers have been appeared.

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

INTRODUCTION

Work is a part of wide area research of polymorphism and pattern of mesomorphic phases of long-chain aliphatic compounds.

The search of new liquid crystals (LCs) possessing the desired operational characteristics attracted our attention to this compounds.

The structure, polymorphism and mesomorphic properties of homologous series of carboxylic acids (RCOOH) and derivatives of biphenyl (fomyl-, alkoxy-, amino-, hydroxy-, nitro-) have been investigated in Refs. [1-3]. The molecules of all the studied carboxylic acids are linked from cyclic dimmers in the solid crystal (SC), liquid crystal (LC) and isotropic liquid (I) states and in CCL4 solution (S). Here R is $C_{nF2n+1}C_6H_4$- (nFABA, n=0,1,3-7,9), $C_{nF2n+1}C_6H_{10}$- (nACHCA, n=4-6) and $C_{nF2n+1}C_6H_{10}$- (nFACHCA, n=3-5). The polymorphism of homologues, its type and peculiarities, the influence of the length of flexible AR or rigid FAR on the molecular packing in crystal, and the influence of AR fluorination and H-bond on the mesomorphic states have been investigated in [1-3].

The aim of our study was to investigate the structural aspects of polymorphism and of mesomorphic states and the dynamics of H-complexes in different states. For this purpose we use the methods of infrared spectroscopy.

4FACHCA and 7 FACHCA (See Figure 1) were studied. These acids will derivate nematic LC in an interval 378-450K and 390-404K correspondingly. The polymorphism is generic for all molecules of carboxylic acids, including investigated one. By H-bond they can derivate dimmers and different associates in all phases (See Figure 2).

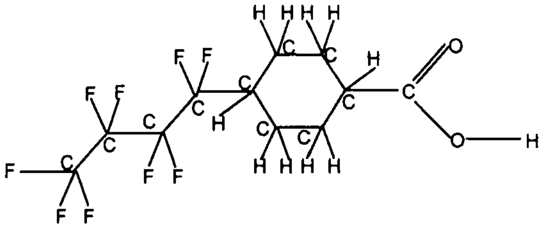

FIGURE 1. Structure of 4FACHCA.

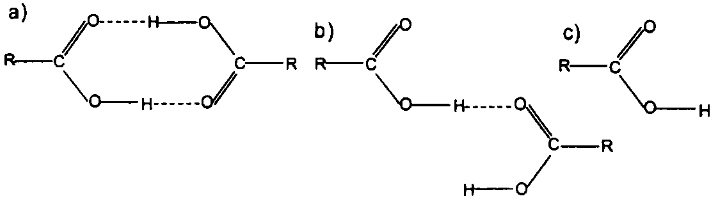

FIGURE 2. Structure of dimmer (a), associate (b), and monomer (c).

EXPERIMENTAL

Polymorphic transitions to the SC, LC and I were investigated visually by using of the Reinhert polarizing microscope equipped with a Koffler heating table. Temperatures, enthalpies and entropies of phase transitions were determined of the differential scanning calorimeter in 100-500 K temperature range [2]. The IR spectra were recorded in the 33-4000 cm^{-1} spectral regions and 100-500 K temperature range for various SC modifications, LC, IL and gas phase and solutions in CCL_4 [1-3].

RESULTS AND DISCUSSIONS

Analysis of experimental spectra of investigated compounds shows, which at the variation of temperature or phase state of substance, pattern and position of some bands in spectrum change, new bands are appeared.

This fact can be explained by the hypothesis about conformation mobility of investigated compounds. One of its demonstrations is the rotation of carboxylic group. Owing to these rotations the disordering of carbonyl groups in practically any phase is possible. The XRDA data for TFBCHCA indicate such capability [4]. Temperature and the phase transitions change energy of H-bond. It is necessary to take into account this change at simulation of IR spectra. It has an effect on a force field of a core of H-complex or its part (dimmer ring). One more reason of complicating of spectra can be existence of several kinds of H-complexes in matter simultaneously.

Listed gears result in increase of width and complicating of pattern of bands in a spectrum.

The calculation of frequencies, shapes and intensities of normal vibrations of H-complexes was conducted. The modeling of infrared spectra was based on the theory of vibrations of polyatomic molecules [5] and the complex of programs described in [6]. Benzene, cyclohexane, dimeric ring $-(COOH)_2-$, n-paraffins and their fluorinated derivatives were taken as fragments. Detailed data on calculations of IR absorption spectra of carboxylic acids are given in Ref. [1-3]. Cyclohexane, carbonyl group with-bond, group CCF_3 and group CCH_3 are taken as fragments.

Calculations of the models with different orientation angles of carbonyl group: φ=90,60,30 degrees (for 7FACHCA) and φ=90,40,0 degrees (for 4FACHCA), with a different force field of a dimeric ring (Table 1) and with different combinations of these two parameters are conducted. The final version of a ratio of an angle φ and force field is following: 90↔1, 60↔2, 30↔3 (for 7FACHCA) and 90↔1, 40↔2, 0↔3 (for 4FACHCA). The results of calculations confirmed our hypotheses. That well agrees with experimental data, which confirms their regularity and indicates successful selection of parameters.

Table 1. Force constants of dimeric ring of 4FACHCA and 7FACHCA (U, cm^{-2}x 10^{-6})

	Conformer 1		Conformer 2		Conformer 3	
	4FACHCA	7FACHCA	4FACHCA	7FACHCA	4FACHCA	7FACHCA
U(O-H)	9,0	9	9,8	9,25	10,3	9,5
U(C=O)	16,8	16	17,25	16,5	17,7	17
U(C-O)	9,87	9,87	10,4	10,17	11,0	10,47
U(COH)	1,6	1,6	1,5	1,55	1,4	1,5
U(ρ_{OH})	0,2	0,2	0,185	0,19	0,17	0,18

In the present paper, we will give analysis of several most interesting areas.

In the range 900 – 1000 cm^{-1} (Fig. 3a) two peaks corresponding to ρ(OH) and ρ(CC) vibrations of dimmer of 7 FACHCA are observed. With increase of temperature they displace in long-wave area and most probable became conformers with a smaller angle φ and smaller energy of H-bond (Fig. 3b).

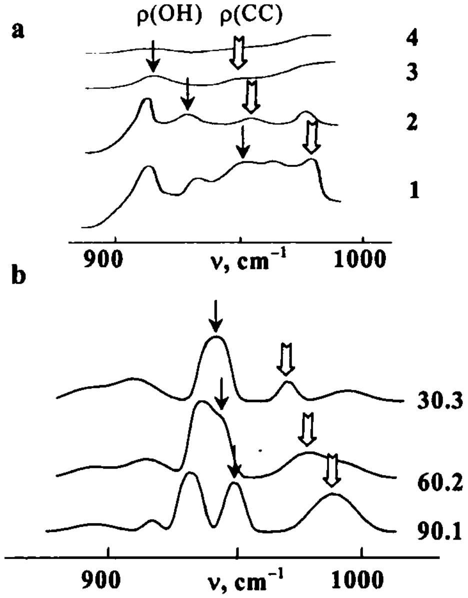

FIGURE 3. IR absorption spectra of 7FACHCA at 293 (1, SC) 363 (2, SC), 443 (3, LC), 463 K (4, I) **(a)**; theoretical spectra of conformers with difference force filde of dimeric ring (1–$\varphi=90^0$, 2–$\varphi=60^0$, 3–$\varphi=30^0$) **(b)**

In the area 1700 cm^{-1} (Fig. 4a) the vibration Q(C=O) is observed. The band has the composite shape: it is possible to choose some pikes in it. The intensity of one varies at heating. The number of spikes grows with increase of temperature. It is possible to explain such changes in a spectrum by simultaneous presence in matter different conformers of dimmer, different associates and even monomers (Fig. 4b).

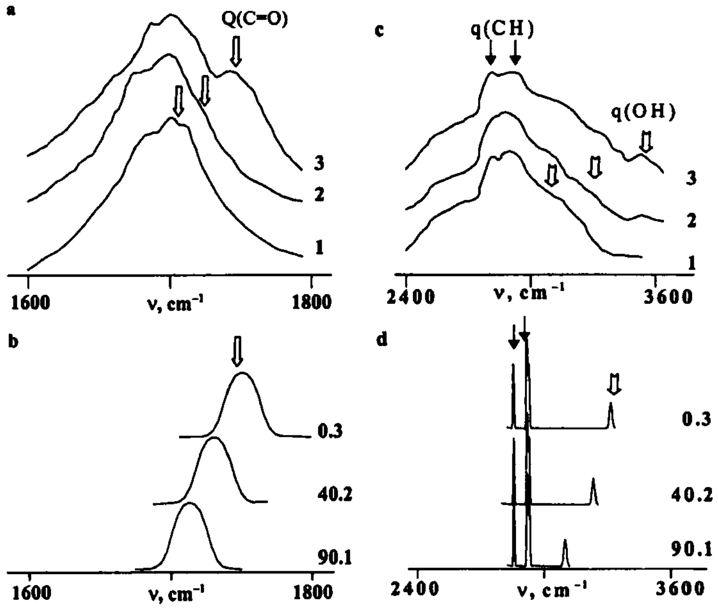

FIGURE 4. IR absorption spectra of 4FACHCA at 298 (1, SC) 398 (2, NLC), 413 K (3, I) **(a,c)**; theoretical spectra of conformers with difference force filde of dimeric ring (1–$\varphi=90^0$, 2–$\varphi=40^0$, 3–$\varphi=0^0$) **(b,d)**

One more area is 3000 cm^{-1} (Fig. 4c). Here the broad band corresponding to vibrations q (CH) and q (OH). Its center of gravity displaces by temperature rise in short-wave area, and band becomes wider. It is possible to explain this by a disordering of carbonyl group: simultaneously exist different conformers with different percentage. By increase of temperature most probable became conformers with a smaller angle φ and smaller energy of H-bond (Fig. 4d).

In the result of the work the hypothesis about conformation properties of polymorphism: influencing of the rotation and disordering of carbonyl groups in molecules of carboxylic acids, and the variations of H-bond energy on IR absorption spectrums of molecules was affirmed.

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