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Solid-Phase Polymorphism of *p*-*n*-Hexyloxy- and *p*-*n*-Heptyloxybenzoic Acids

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Abstract—The solubility of *p*-*n*-hexyloxy- and *p*-*n*-heptyloxybenzoic acids in nonaqueous solvents of different polarities was determined over the temperature range from –20 to 60°C. Acid polymorphs were obtained by crystallization from solutions and melts and by the thermal shock method. The temperatures and enthalpies of phase transitions and X-ray characteristics of the new polymorphs were determined.

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INTRODUCTION

Solid-phase polymorphism is characteristic of liquid crystals, or mesogens. The number of conformations close in stability is fairly large for such systems, and the existence of their three or four polymorphs that crystallize in low-symmetry molecular lattices is therefore not infrequent [1].

The objects of our study were *p*-*n*-hexyl- (**I**) and *p*-*n*-heptyl- (**II**) oxybenzoic acids, which form both nematic and smectic (**II**) mesophases. Information about solid-phase polymorphs of these acids is contradictory. According to [2], **I** experiences four phase transitions (at 58, 71, 87, and 99°C) before the transition to the nematic phase. The authors were able to isolate crystals of two forms. Crystallization from tetrahydrofuran gave the monoclinic form (a = 14.689(3) Å, b = 4.957(2) Å, c = 21.888 Å, β = 128.68°, space group $P2_1/c$, Z = 4 [2]), and crystallization from glacial acetic acid, the triclinic form (a = 33(1) Å, b = 14.5(05) Å, c = 8.0(5) Å, α = 93°, β = 90°, γ = 90°, space group $P1$ [3]). The authors of [4] reported the existence of only two polymorphs of **I** with the transition point 66°C. In [5], the structure of the triclinic polymorph with the unit cell parameters a = 7.8854(4) Å, b = 14.3021(7) Å, c = 33.0513(16) Å, α = 88.738(1)°, β = 85.701(1)°, γ = 78.331(1)°, space group $P1$, Z = 12 was studied. In both forms, crystal packing elements were dimers linked by H-bonds, which closed carboxyl groups [2, 5]. The existence of three polymorphs of **I** was reported in [6, 7].

According to the literature, there exist several forms of **II** [7–13]. The structure data on the triclinic form of **II** with the unit cell parameters a = 4.739(5) Å, b = 8.034(7) Å, c = 17.948(18) Å, α = 93.78°, β = 82.32°, γ = 102.19°, space group ${}^{-}P1$, Z = 2 were obtained in [14]. Database [8] contains a diffractogram of **II**, however, without metric data on the unit cell. In [9–13], both the phase transition temperatures and the numbers of polymorphs observed are different. The authors of [9, 10] reported the absence of phase transitions of **II** up to its transition into the smectic phase. According to [11, 12, 14], **II** forms two polymorphs. In [13], three phase transitions of **II** were observed at 80, 84, and 92°C before **II** melted into the smectic phase at 96°C.

The purpose of this work was to study the crystallization of **I** and **II** and refine data on their solid-phase polymorphism.

EXPERIMENTAL

The initial substances were *p*-*n*-alkyloxybenzoic acids of ch. d. a. (pure for analysis) grade. To select conditions for the purification of the acids and growth of their crystals, we studied their solubility polytherms over the temperature range from –25 to 60°C (Table 1). The acids were purified by recrystallization from ethanol and ethyl acetate, because the polytherms of **I** and **II** in these solvents had fairly high temperature coefficients and the solvents were easy to remove from precipitates.

To obtain various polymorphs, the substances were crystallized by several methods, by isothermal vaporization from solvents of different polarities (experiments of series A), by slowly cooling from melts (series B); and by thermal shock from melts (series C).

Samples **I** and **II** were studied by polythermal polarization microscopy (PPM), differential thermal analysis (DTA) [15], differential scanning calorimetry (DSC), and X-ray powder diffraction (XPD). The samples were examined by polythermal polarization microscopy on a MIN-8 microscope under heating

Table 1. Solubility of *p*-*n*-hexyl- and *p*-*n*-heptyloxybenzoic acids in various solvents (mol %)

Solvent	–20°C	–10°C	0°C	20°C	40°C	60°C
I						
Ethyl acetate	0.350	0.488	0.626	2.117	4.930	7.872
Ethanol	0.011	0.188	0.367	1.068	3.725	5.062
n-Hexane	0.009	0.014	0.320	0.165	0.310	0.380
Toluene	0.146	0.235	0.324	1.350	6.788	9.723
II						
Ethyl acetate	0.044	0.182	0.321	0.610	3.043	4.286
Ethanol	0.032	0.067	0.166	0.489	2.729	3.875
n-Hexane	0.014	0.016	0.017	0.057	0.253	0.351
Toluene	0.042	0.052	0.093	0.617	2.216	2.983

(0.2 K/min) close to phase transition temperatures. Differential scanning calorimetry measurements were taken using a TG-2400 (Setaram) instrument for thermogravimetric and differential thermal analysis (sample weight was 40 mg and heating rate was 5 K/min).

The X-ray powder patterns were obtained on a DRON-4-13 automated diffractometer using CuK_α radiation. Data processing and phase analysis were performed with the help of the RAPID package (Nevskii). The theoretical X-ray pattern of **I** was calculated from the structural data using the POWTOOL program (Efremov).

Samples **I** of series A were isolated as splices of transparent needles during isothermal vaporization (Fig. 1a). Mass crystallization resulted in the formation of fibrous crystals ~5 μm thick (Fig. 1b). In series B experiments, dense agglomerates of small-sized crystals were obtained.

The X-ray powder patterns of all crystals **I** obtained by crystallization at temperatures from –25 to 70°C (series A) were identical to the X-ray powder pattern of the monoclinic form of **I** calculated by us from the structural data [2] (Table 2). The refined unit cell parameters, a = 14.75(2) Å, b = 4.969(6) Å, c = 21.90(3) Å, and β = 128.9(9)°, were close to those reported in [2]. Crystals obtained in series B experiments were a high-temperature polymorph. No corresponding X-ray data were published (Fig. 2).

Thermal analysis of the monoclinic polymorph (series A) showed that the crystals underwent the transition to the high-temperature form at 69 ± 1.0°C, melted into the nematic phase at 105.9 ± 0.5°C (enthalpy 8.41 ± 0.06 kJ/mol) and into the isotropic phase at 153.1 ± 0.3°C (enthalpy 1.70 ± 0.05 kJ/mol). These temperatures are close to those reported in [4, 16]. Samples of series B did not undergo polymorphic transitions and melted into the nematic phase at 105.5 ± 0.4°C (enthalpy 7.34 ± 0.05 kJ/mol). The temperature of clearing of **I** was 152.0 ± 0.4°C (enthalpy 1.54 ± 0.05 kJ/mol). These data were reproduced when the samples were repeatedly studied after storage at ~22°C for a month, which was evidence that the phase obtained was stable. Our differential scanning calorimetry study of *p*-*n*-hexyloxybenzoic acid crystallized from toluene at 10°C gave the enthalpy of polymorphic transition at ≈70°C that coincided with that reported in [6].

Samples **II** of series A were either long prismatic crystals (solvents ethanol and hexane, Fig. 1a) or aggregates of thin tabular crystals (solvent ethyl acetate,

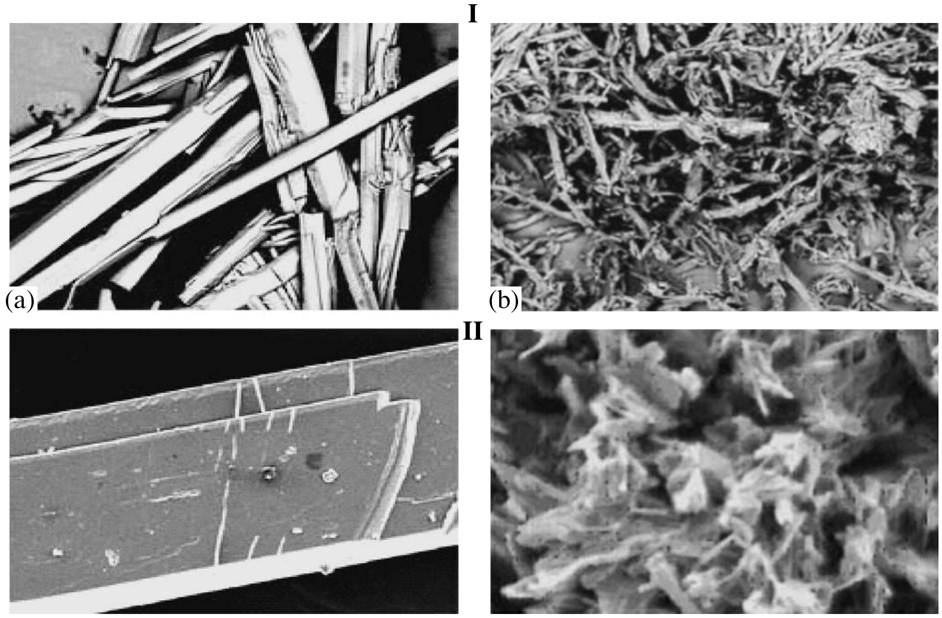

Fig. 1. Crystals of *p*-*n*-hexyloxybenzoic (**I**) and *p*-*n*-heptyloxybenzoic (**II**) acids. See text for the notation.

Table 2. Powder pattern indexing for a sample of series A and comparison with the data on the monoclinic polymorph of $C_{13}H_{18}O_3$

h	*k*	*l*	I/I_0	*d*, Å	$2\theta_{expt}$, deg	$2\theta_{calcd}$, deg	I/I_0	*d*, Å
			Experimental			Calculated from the data [2]		
1	0	−2	69	10.9	8.10	8.15	100	10.8
2	0	−2	30	7.37	11.991	12.010	44	7.33
1	0	−4	4	5.221	16.967	17.053	4	5.21
3	0	−4	100	4.652	19.063	19.091	90	4.628
1	1	0	15	4.566	19.425	19.450	28	4.532
2	1	−2	9	4.120	21.550	21.559	13	4.114
1	1	−3	10	4.099	21.663	21.735	14	4.083
0	1	3	10	3.756	23.668	23.768	18	3.741
1	1	2	33	3.672	24.213	24.304	56	3.656
1	1	−4	17	3.612	24.628	24.784	20	3.593
2	1	1	4	3.399	26.198	26.282	9	3.384
4	0	−6	9	3.309	26.917	26.916	6	3.198
0	1	4	14	3.251	27.414	27.551	25	3.236
1	1	−5	13	3.144	28.367	28.489	21	3.131
2	1	−6	11	2.916	30.642	30.679	11	2.913
4	0	0	3	2.869	31.148	31.130	4	2.866
4	1	−6	3	2.755	32.473	32.478	5	2.744

Fig. 1b) depending on crystallization conditions. Differential thermal and polythermal polarization microscopy analyses of *p*-*n*-heptyloxybenzoic acid of various series showed that the substance underwent a phase transition at 92.5 ± 0.2°C. The smectic phase was formed at 95.0 ± 0.2°C, and the transition to the nematic phase occurred at 100.0 ± 0.1°C. The isotropic phase appeared at 146.2 ± 0.2°C. The phase transition was fixed irrespective of the thermal prehistory of the sample.

The X-ray patterns of all samples of **II** contained similarly arranged reflections but were characterized by different reflection intensity distributions (Fig. 3). Most of the reflections were indexed using triclinic lattice parameters. The refined parameters, $a = 4.738(8)$ Å, $b = 8.040(10)$ Å, $c = 17.947(14)$ Å, $\alpha = 93.8(6)°$, $\beta = 82.2(5)°$, and $\gamma = 102.1(7)°$, were close to those reported in [14]. Substantial differences in the intensity of reflections cannot be explained solely by different crystal morphologies and textures. Also, the X-ray patterns contained additional reflections that could not be indexed in triclinic lattice parameters (these are marked by crosses in Fig. 3). The X-ray patterns of our samples were also different from that given for **II** in [8]. This led us to suggest the existence of one more polymorph of **II** not described in the literature.

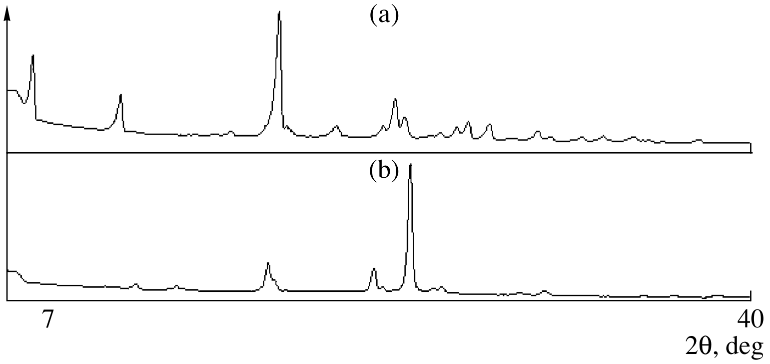

Fig. 2. X-ray powder patterns of *p*-*n*-hexyloxybenzoic acid samples of series (a) A and (b) B.

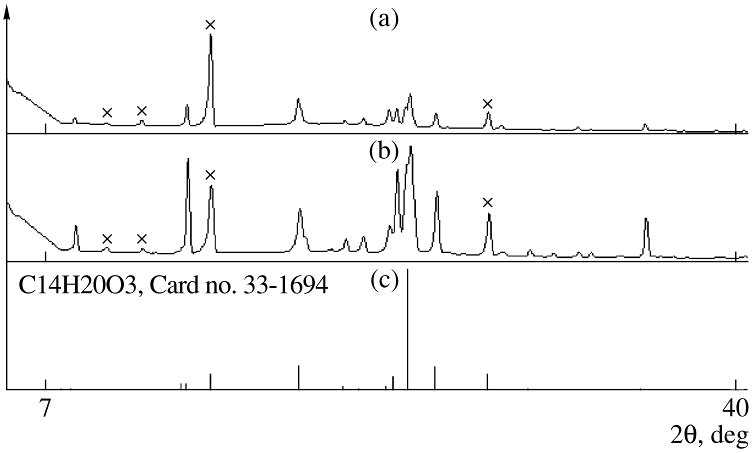

Fig. 3. X-ray powder patterns of *p*-*n*-heptyloxybenzoic acid samples of series (a) A and (b) B and (c) theoretical X-ray pattern calculated from the data presented in [8].

RESULTS AND DISCUSSION

An analysis of the literature data and data obtained in this work shows that *p*-*n*-hexyloxybenzoic acid has three stable polymorphs, namely, low-temperature triclinic, monoclinic, and a high-temperature polymorph whose structure was not studied. Their individual character was substantiated by the X-ray data. The triclinic form can be obtained from glacial acetic acid [2], it is stable below 0°C. The X-ray study of its single crystal and the determination of its X-ray parameters were performed in [5] at –153°C. The thermal characteristics of the monoclinic polymorph obtained in this work by statistically processing the experimental data were close to those reported in [7]. The high-temperature form of **I** with a 105.5 ± 0.4°C temperature of melting into the mesophase was obtained by crystallization from melts; the phase was stable under normal conditions. Both the data reported in [2, 15, 16] and the results obtained in our study of the thermal behavior of this acid are evidence of the existence of one more polymorph stable above 75°C. In certain instances, studies of samples of series A by differential scanning calorimetry gave different enthalpies of the polymorphic transition, and the difference exceeded measurement errors. This can be explained by the presence of a metastable phase.

As far as *p*-*n*-heptyloxybenzoic acid is concerned, the conditions for the preparation of its polymorphs should be studied more thoroughly, because our samples of **II** were mixtures of polymorphs, one of which was not described in the literature. The polymorphic transition in crystals **II** of various series was observed at 92.5 ± 0.2°C.

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