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IR, FIR, Ramna and Thermodynamic Investigations of p-n-Alkokybenzoic Acides in Their Solid, Mesomorphic and Isotropic Phases

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IR, FIR, Raman and Thermodynamic Investigations of *p-n*-Alkoxybenzoic Acids in Their Solid, Mesomorphic and Isotropic Phases

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Thermal properties and vibrational spectra (IR, FIR and Raman) of seven *p,n*-alkoxybenzoic acids beginning with butoxy and finishing with decyloxy homologue are investigated. The structure of different solid modifications formed upon heating and cooling is discussed.

INTRODUCTION

The investigation of the properties of the homologous series of *p-n*-alkoxybenzoic acids began long ago. Jones[1-3] first found that these acids, from *p,n*-propoxy to *p,n*-acetyloxybenzoic homologues inclusive, transform into liquid crystals with temperature. He suggested that the mesomorphism which occurs in these chemicals is due to the association of the molecules in dimers. Herbert[4] measured the transition temperatures for *p,n*-alkoxybenzoic acids from *n*-propyl to *n*-octadecyl homologue. The enthalpies of all the phase transitions (crystal to mesophase to isotropic liquid) for the same substances were also calculated.[4] Propyl through hexyl ethers showed only a nematic phase.

Solid-solid transitions were noted only upon heating for the propyl and hexyl materials in this sequence. For heptyl to tridecyl, both smectic and nematic phase were noted and solid-solid transitions were exhibited by the even carbon members of this group. Gray[5] also reported calorimetric measurements of this series. Ikeda[6] investigated the thermal properties of *p,n*-octadecyloxybenzoic acid and identified two metastable phases formed upon cooling of the smectic phase. The effect of the long paraffinic chain attached to the benzoic acid on the molecular motion in the mesophase is also discussed in his article. Derzhanski *et al.*[7] studied the NMR spectra of three nematic alkoxybenzoic acids, namely *p,n*-propoxy, *p,n*-butoxy and *p,n*-pentoxy benzoic acids in their solid state from room temperature to the melting point. Two regions are distinguished from the temperature dependence of the second moment—low temperature from 300°K to about 370°K and high temperature from 370°K to the melting point. The first one is characterized by a small activation energy. Higher temperatures affect the second moment of the NMR spectra in a stronger manner and also the activation energy is higher. These authors assume that in the higher temperature interval sizable translational motion of the molecules begins (partial translational melting).

A few IR investigations of the *p,n*-alkoxybenzoic acids are available in the literature. Azima *et al.*[8] recorded the IR spectra (4000–650 cm^{-1}) of *p,n*-heptyloxy and *p,n*-octyloxybenzoic acids in crystal, smectic C, nematic and isotropic phases. Attention was paid mostly to the spectra of these materials in dilute CCl_4 solution at different temperatures and concentrations. Bands due to OH and CO stretch vibration of the monomer and cyclic dimer were assigned. Later these authors[9] measured the IR spectra of *p,n*-hexyl, heptyl, octyl and nonyl homologues as a function of temperature. Kodzhaeva *et al.*[10] also studied the IR spectra (4000-650 cm^{-1}) of *p,n*-propyl, heptyl, nonyl and cetyloxybenzoic acids as a function of temperature and phase. However, they did not detect any bands due to free OH and CO and to open dimers and stated that the spectra of nematic and smectic phase are identical, while Azima[9] found the greatest change in the spectrum of the smectic at the smectic—nematic phase transition.

The FIR spectra of liquid crystals are, in general, rare. Bulkin first investigated the FIR spectra of crystal, nematic, isotropic and solution phases of PAA and MBBA.[11] He found that FIR absorption of the isotropic phase is virtually identical with that in the nematic phase. Venugopalan[12] investigated the FIR spectra (200–20 cm^{-1}) of PAA as a function of temperature. Recently, the same author[13] studied the FIR absorption of different solid modifications of *N-p*-cyanobenzylidene *p,n*-octyloxyaniline. FIR spectra of *p,n*-alkoxybenzoic acids, however, have not been reported up to now. This is unfortunate because low frequency vibrations yield precious information about intermolecular forces and structure of different phases.

Raman scattering studies of alkoxybenzoic acids are also very scarce. To

our knowledge only Koller[14] reported the Raman spectrum of *p,n*-butyloxybenzoic acid oriented by a magnetic field.

In spite of the research work already done on *p,n*-alkoxybenzoic acids their understanding is not complete—the structure of the different polymorphic modifications is not known, most of the bands especially those connected with hydrogen bond vibrations are not assigned, the changes in the spectral parameters through the phase transitions are not traced out and explained.

The purpose of the present paper is to investigate the IR, FIR and Raman spectra of some *p,n*-alkoxybenzoic acids from butoxy to decyloxy homologues in their crystal, mesomorphic and isotropic phases. Attention will be mostly paid to the determination of the structure of the solid modification formed during thermal cycles: an attempt to assign hydrogen bond vibrations in FIR spectra of these compounds will be also made.

EXPERIMENTAL PART

The middle IR spectra (4000–300 cm^{-1}) has been recorded with the Perkin-Elmer 621 spectrophotometer. For the FIR region between 500 and 40 cm^{-1} a Perkin-Elmer 180 instrument was used. The acids were purified by successive recrystallization. A variable temperature cell VLT-2 (RIIC) was used for the investigations of the IR spectra at different temperatures below and above room temperature. The desired temperature was reached and automatically maintained within 0.2°K. In order to record the FIR spectra the sample was placed between two wedge cut Si plates using a 50 μm Teflon spacer. The film thickness for the middle IR region was 12 μm.

Raman spectra between 10 and 2000 cm^{-1} were taken with a conventional Raman system consisting of CW Ar laser, Spex 1401 double monochromator, photon counting detection and either multichannel storage or strip chart recording. The 5145 Å Ar laser line was used for all measurements. The sample was placed in a good thermal contact with the cold finger of a variable temperature optical cryostat. The temperature was monitored with a Cu-constantan thermocouple, and was stable within 0.5°K.

A Dupont 990 and Perkin-Elmer DSC-1B differential scanning calorimeters were employed to detect the phase transitions. For quantitative measurements they were calibrated with water, mercury, indium and tin. The sample weight used for these experiments varied from 15 to 25 mg.

RESULTS AND DISCUSSION

A Differential scanning calorimetry

The DSC thermograms of *p,n*-octyloxybenzoic acid over the temperature range of 270°K to 450°K are shown in Figure 1. As the temperature increases (run 1) the thermogram of the sample involves four endothermic transitions.

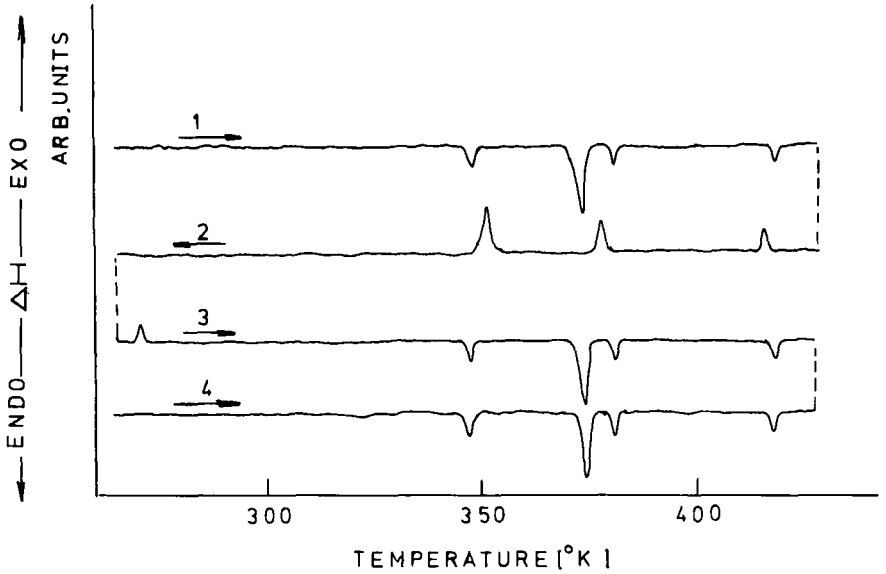


FIGURE 1 DSC thermograms of *p,n*-octyloxybenzoic acid; run 1—2,5°K/min (heating); run 2—about 5°K/min (cooling); run 3—2.5°K/min (heating); run 4—heating.

The first one at 348°K is a thermotropic phase transformation from the first solid modification into the other, the second one (at 374°K) is connected with melting of the sample and formation of the smectic C phase, the next one—at 381°K is related to the smectic-nematic transformation while the last one (419°K) is the nematic-isotropic liquid transition. During cooling (run 2) the transformations from liquid to the nematic and from nematic to smectic phases are obtained even with rapid cooling as fast as 50°K/min at almost the same temperatures as upon heating. However, the exotherm considered as the transition from the smectic to crystal phase appeared at about 340°K, which is about 30°K lower than the stable solid-smectic phase transition temperature, even with slow cooling at rates below 1°K/min. This difference is so large that it cannot be attributed to a simple thermal hysteresis. Run 3 is the heating thermogram of the sample which has been cooled from the isotropic phase (450°K) to 270°K with cooling rate of about 5°K/min. The peak at about 373°K which is connected with liberation of heat can be attributed to a metastable solid into a stable crystal conversion. Indeed, the heating thermogram of the sample annealed at 340°K is identical with run 1. Formation of anhydrides and decarboxylation were both cited as common reactions if alkoxybenzoic acids are held at higher temperatures for prolonged periods of time. The last run, however, is identical with the first one indicating that the sample integrity is not changed observably during one thermal cycle. This conclusion

TABLE I

Enthalpy of phase transitions (mean error about 5%)

Compound	ΔH [kcal/mol] Solid I-solid III†	Solid II-solid‡
p,n-hexyloxybenzoic acid	1.68	1.02
p,n-heptyloxybenzoic acid		1.58
p,n-octyloxybenzoic acid	4.28	1.76
p,n-nonyloxybenzoic acid		1.78
p,n-decyloxybenzoic acid	5.09	1.85

† Endothermic phase transition.
‡ Exothermic phase transition.

is confirmed by measurements of IR and Raman band frequencies and intensity. The DSC thermograms of the other acids are similar to that of the octyl homologue with some differences: 1) The *p,n*-butoxy and pentoxybenzoic acids do not form any metastable solid phases upon cooling but pass directly into stable crystalline phase. 2) All chemicals from heptyl through decyl homologues form also a smectic C phase before the nematic. 3) Only acids with an even number of carbon atoms in the paraffinic side chain show a high temperature solid phase upon heating, while for all investigated substances beginning with hexyl a metastable monotropic phase is obtained upon cooling from the melt.

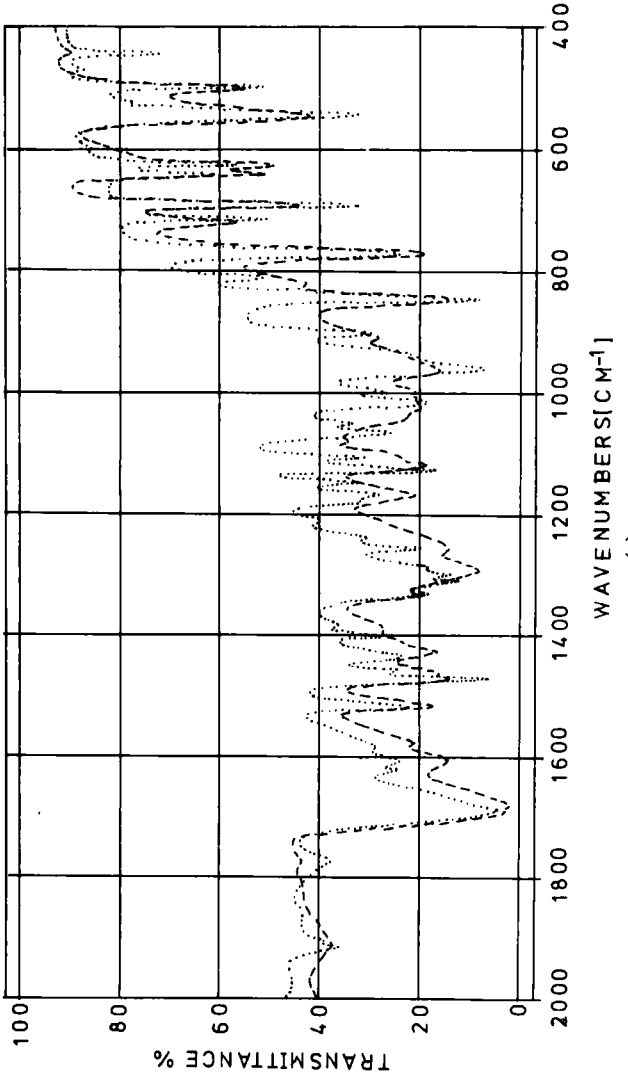
For convenience the first stable crystal form will be indicated hereafter as solid I, the second, higher temperature solid modification—as solid III and the metastable solid obtained upon cooling from the melt will be designated as solid II.

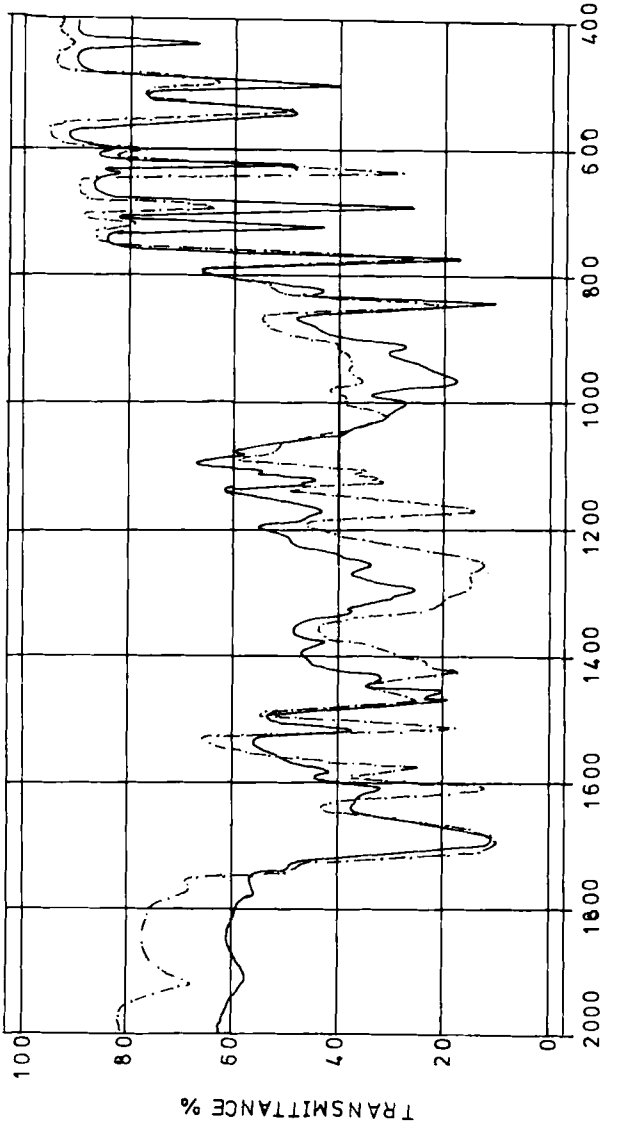
In Table I are collected the enthalpies of the phase transitions solid I—solid III and solid II—solid I observed in the compounds under investigation. The ΔH values for the transformations crystal to smectic C, to nematic, to isotropic phase are calculated by Herbert,[4] while the heat liberated at the transition from the metastable phase to the stable crystal modification is measured for the first time.

In order to discuss the mechanism of the phase transitions exhibited by *p,n*-alkoxybenzoic acid we have to know their structure. Vibrational spectroscopy could be of great use for this purpose providing us with both localized and general information on the molecular structure and intermolecular forces.

B IR and FIR absorption spectroscopy

Figures 2a and 2b compare the IR spectra (2000–400 cm^{-1}) of *p,n*-octyloxybenzoic acid in solid I, solid II, solid III and nematic phase. It is apparent that in solid I all IR modes including bending and stretching vibrations of paraffin





(b)

FIGURE 2 IR spectra (2000–400 cm^{-1}) of *p,n*-octyloxybenzoic acids; spectral slit width about 2 cm^{-1}; scanning speed—50 cm^{-1}/min; Perkin Elmer 621. (a) dotted line—solid I (293°K); dash line—solid III (363°K). (b) full line—solid II (303°K); alternate dash dotted line—nematic phase (393°K).

chains are narrow and sharp as it is typical of high purity crystals. Our spectroscopic data compared with X-ray diffraction measurements[15] indicate that this phase can be attributed to a β solid form. The same form is identified in normal higher alcohols.[16] Since the gradual lengthening of the alkyl chain in the homologous series appears to be a regular perturbation on the molecular structure we expect the IR absorption spectra to be similar to each other. Actually, the differences between two neighbors are quite apparent and concentrated in the region below 900 cm^{-1} where the bands are assignable to in plane and out-of-plane bending vibrations of the benzene ring and its substituents as well as to alkyl chain conformation. This fact indicates that the alkoxybenzoic acids adopt a variety of crystal structures, each individual structure being determined by the relative weights of the aromatic and aliphatic part of the molecules. However, more polarized IR and Raman measurements of single crystal alkoxybenzoic acids as well as X-ray diffraction studies are needed for a complete elucidation of the crystal structure of every acid.

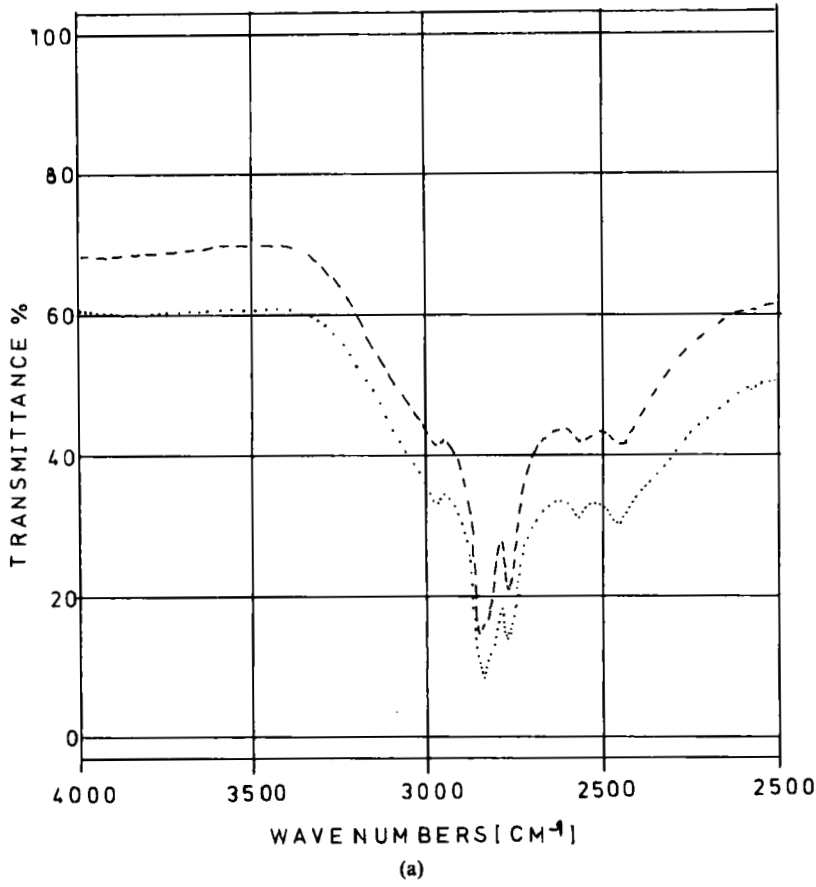
No significant modifications appear in the spectra even at higher temperatures (with small corrections for band broadening and intensity decrease); the spectra instead show dramatic changes after the phase transformation which is at about 350°K (348°K for hexyl and octyl, 359°K for decyl homologues). In this phase which exists up to melting point the bands assigned to the vibrations of the polymethylene chain (CH_2 bending around 1450 cm^{-1}, wagging and twisting modes between 1350 and 1200 cm^{-1}) broaden and decrease in intensity. The C—C stretch vibrations give weak bands in the IR spectra of *n*-paraffins. In the alkoxybenzoic acids the participation of the polar CO bond in the various skeletal vibrations causes a marked increase in the intensity of these bands. The C—C stretch modes in the region 1060–1020 cm^{-1} also broaden and their intensity decreases. The intensity of CH_2 rocking vibrations at 720 and 750 cm^{-1} also decreases strikingly. All these spectral changes can be explained with the presence of several rotational isomers in solid III phase. Having in mind our results supported also by X-ray diffraction measurements of similar species[16–18] this modification can be identified as a solid form, the detailed structure of which is still under investigation and will be subject of another communication. The same form, usually called "rotational" phase was observed in long chain paraffins,[17,18] normal higher alcohols,[16] alkyl bromides and alkyl acids.[19,20]

At α solid form—smectic C phase transition the molecules gain free translational motion in the smectic layers. Correspondingly we observe further changes in the spectrum. All CH_2 bending vibrations in the region 1300–1200 cm^{-1} merge into two broad bands. This implies that many rotational isomers exist in the mesophase while only one seems to be present in solid I. Two new bands appear in the liquid crystal spectrum—the first at 3550 cm^{-1} assigned to the OH stretching vibration of the monomer and another one at 1735 cm^{-1}

assigned to CO stretching mode of the free carbonyl. Both bands increase in intensity with temperature and in correspondence with phase transitions up to the isotropic liquid. In the spectra of the mesophase and in the liquid a broad shoulder appears at about 3300 cm^{-1}. The exact cause of this band is not entirely clear but all indications are that it is connected with the open dimers formed in the acids. This conclusion is supported by ultrasonic measurements[21] and by NMR studies.[22] Davies and Sutherlands[23] reached the same conclusion in interpreting their early IR spectra of benzoic acid. Moreover the carbonyl stretching band at 1675 cm^{-1} abruptly shifts 5 cm^{-1} approximately to higher frequencies at the phase transition smectic C—nematic for all investigated liquid crystal and then the shift continues slowly with increasing temperature. This result observed also by Azima *et al.*[8,9] can be explained with formation of open dimers as the temperature increases.

When comparing the spectra of the mesophase with those of solid II obtained by cooling from the melt it is apparent that these two spectra are similar, especially with regard to position and spectral shape of hydrogen bond vibrations at 1425 cm^{-1} and 965 cm^{-1}; such bands are assigned to in plane and out of plane deformations of dimerized OH group respectively. The broad shoulder around 3300 cm^{-1} assigned to open dimers and weak band at about 3550 cm^{-1} ascribed to free OH stretching are also present in solid II (Figure 3). These data indicate that the rapid cooling of the mesophase gives rise to a metastable solid phase with partially broken frozen hydrogen bonds. The investigations reported in[6] revealed that the number of hydrogen bonds in the metastable phase formed by cooling of *p,n*-octadecyloxybenzoic acid is almost equal to that in the smectic phase. This fact proves that the reformation of the hydrogen bonds is difficult to bring about through cooling from the mesophase. Left at room temperature the open dimers slowly regenerate and the stable crystal modification is restored. However, some of the bands assigned to bend vibrations of methyl mode at 1465 cm^{-1} appear again in solid II although broad and not well defined. Therefore a few relatively rigid rotational isomers still exist in this phase giving also their contribution to the formation of the metastable solid II form.

FIR spectroscopy can provide us with additional valuable information about the various hydrogen bond configurations. There are now a lot of papers on the studies of carboxylic acid, mostly formic, acetic, propanoic, butanoic and hexanoic acids.[24-29] Stanevich[30] recorded the FIR spectra of propanoic and butanoic acids in both liquid and solid phases and proposed an assignment for the observed frequencies. Later, he extended his investigations on phenol, nitrophenol, tricloracetic and benzoic acids. However, the FIR spectra of *p,n*-alkoxybenzoic acids have not been studied up to now. On the other hand, in order to compare the hydrogen bond configurations in different solid and mesomorphic phases the detailed assignment of their FIR spec-



(a)

tra is very important. Therefore we shall discuss this problem to some extent. Only six frequencies ($2A_g + 1B_u + 2A_u + 1B_g$) below 200 cm^{-1} belong to hydrogen bond vibrations. Three of them—ν_3 (B_u), ν_4 (A_u) and ν_5 (A_u) are IR active. In accordance with the previous investigations of carboxylic acids[24-30] we assigned the bands in the region 135–165 cm^{-1} to antisymmetric hydrogen bond stretching (ν_3) while the absorption band at 85–65 cm^{-1} should correspond to the twisting modes ν_4, while the last one—ν_5 (out of the plane bending vibration) should be below 40 cm^{-1}, i.e. beyond the range of our instrument. This interpretation is based on the following considerations:

1) The vibration ν_3, ν_4 and ν_5 are active in absorption and must appear in the spectra below 200 cm^{-1} while the condition $\nu_3 > \nu_4 > \nu_5$ must be fulfilled.[31]

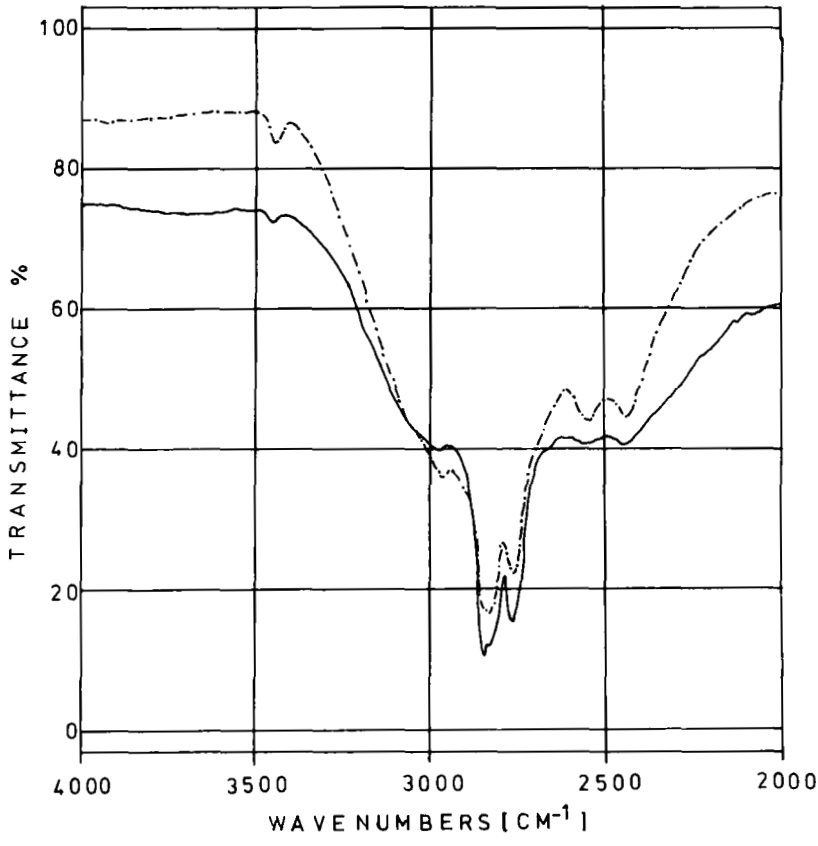
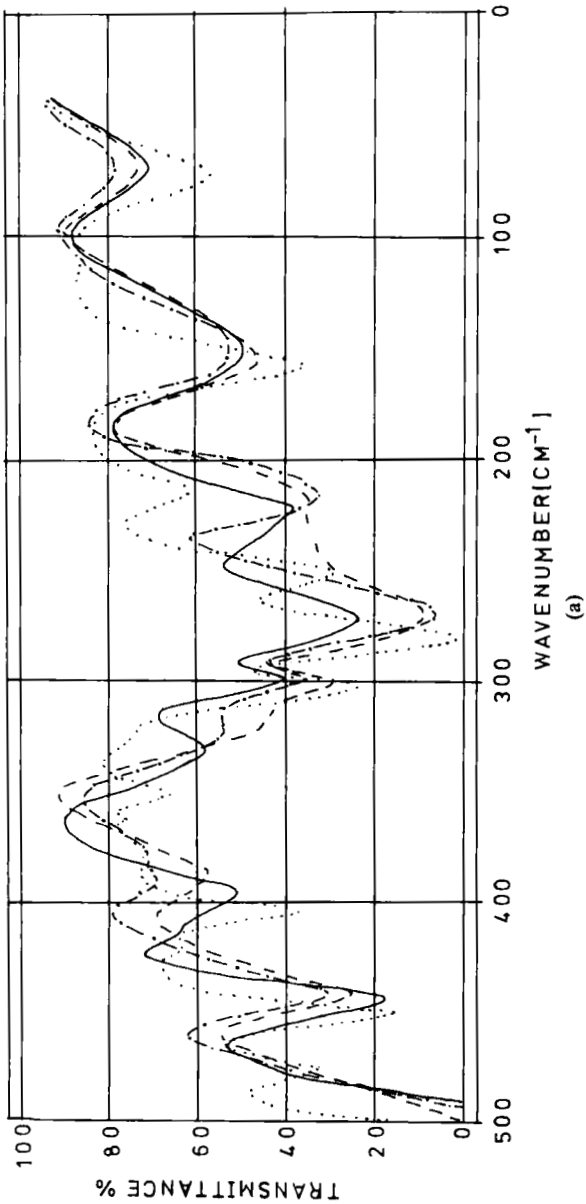


FIGURE 3 IR spectra (4000–2000 cm^{-1}) of *p,n*-hexyloxybenzoic acid; spectral slit about 1 cm^{-1}; scanning speed—50 cm^{-1}/min; Perkin-Elmer 180. (a) dotted line—solid I (293°K); dash line—solid III (368°K). (b) full line—solid II (308°K); alternate dash dotted line—nematic phase (598°K).

2) The frequency of hydrogen bond stretching vibration must correspond to the usual expression for the vibrations of the diatomic molecules:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{mf}{M}} \tag{1}$$

where f is the quasiforce constant of a single hydrogen bond, m is the number of the bonds ($m = 2$ in the case of the *p,n*-alkoxybenzoic acids) and M is the effective reduced mass. If f and the anharmonicity of the ν_3 vibration are the same for all investigated acids then the frequencies of the ν_3' and ν_3'' vibrations



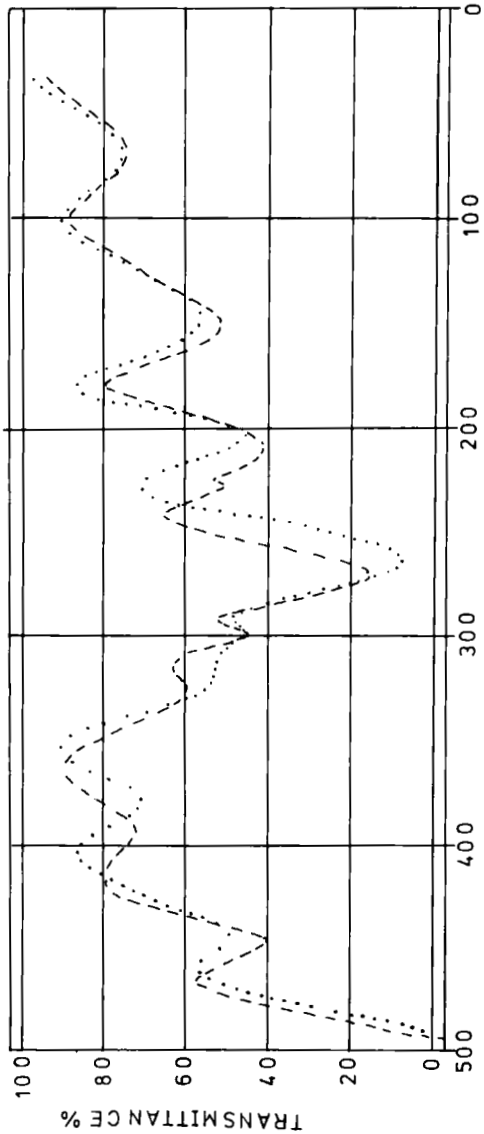


FIGURE 4 FIR spectra (500–40 cm^{-1}) of *p,n*-octyloxybenzoic acid; spectral slit width 6 cm^{-1}; average scanning speed 5 cm^{-1}/min, ordinate expansion 3 ×—Perkin Elmer 180. (a) dotted line—solid I (293°K); dash line—solid III (363°K); full line—solid II (303°K); alternate dash dotted line—smectic C (373°K). (b) dash line—nematic phase (393°K); dotted line—isotropic liquid (428°K).

of the dimers of the two different acids with reduced masses M' and M'' must to obey the relation

$$\left(\frac{\nu_3'}{\nu_3''}\right)^2 = \frac{M''}{M'} \tag{2}$$

Actually a weak but well expressed linear dependence connecting the ν_3 and the masses of the investigated acids is observed.

3) ν_4 and ν_5 bending vibrations of the acids affect the dimer ring and depend only slightly on the molecular residues.[30] Actually ν_4 and ν_5 modes lie close together for all investigated acids.

Figures 4a and 4b compare the FIR spectra of different solid modifications of *p,n*-octyloxybenzoic acid with those of smectic C, nematic and isotropic phases. At every phase transition the ν_3 band shifts to lower frequencies. The displacement is very weak as the sample passes from solid I to solid III (only about 1 cm^{-1}) but it is much bigger at the phase transition solid III—smectic and upon further heating up to isotropic liquid. This fact can be explained with the decrease in the hydrogen bond strength with temperature. ν_4, however, does not shift so significantly. Simultaneously with the displacement both hydrogen bond modes broaden markedly. This broadening arises from a number of factors: thermal energy, larger number of molecules in the excited states, interaction between molecules, mixture of different hydrogen bond configurations, etc. Most of the other changes occurring between 500 and 400 cm^{-1} and 300–200 cm^{-1} are connected with different ring bending and out of plane vibrations of the benzene ring and its substituents. It is obvious from the comparison between the spectra that those of solid II and smectic C phase are almost identical below 250 cm^{-1} especially in the region of the hydrogen bond vibrations. This result supports the previous conclusion made on the basis of middle IR spectroscopy that the formation of the metastable solid modification upon cooling of the mesophase is due mostly to the existence of broken (at least partially) and frozen hydrogen bonds.

C Raman spectroscopy

IR and Raman spectroscopy complement each other in giving structural information and both techniques should be used where reliable assignment of vibrational modes and precise determination of the composition of different phases are required. In our case FIR absorption is almost unique for the investigations of low frequency hydrogen bond modes while the lattice Raman scattering can give us precious information on the structure of different solid modifications and their changes through the phase transitions.

Figure 5 shows the changes in the low frequency Raman spectrum (10–400 cm^{-1}) of *p,n*-hexyloxybenzoic acid. Solid I is the most ordered phase; in fact

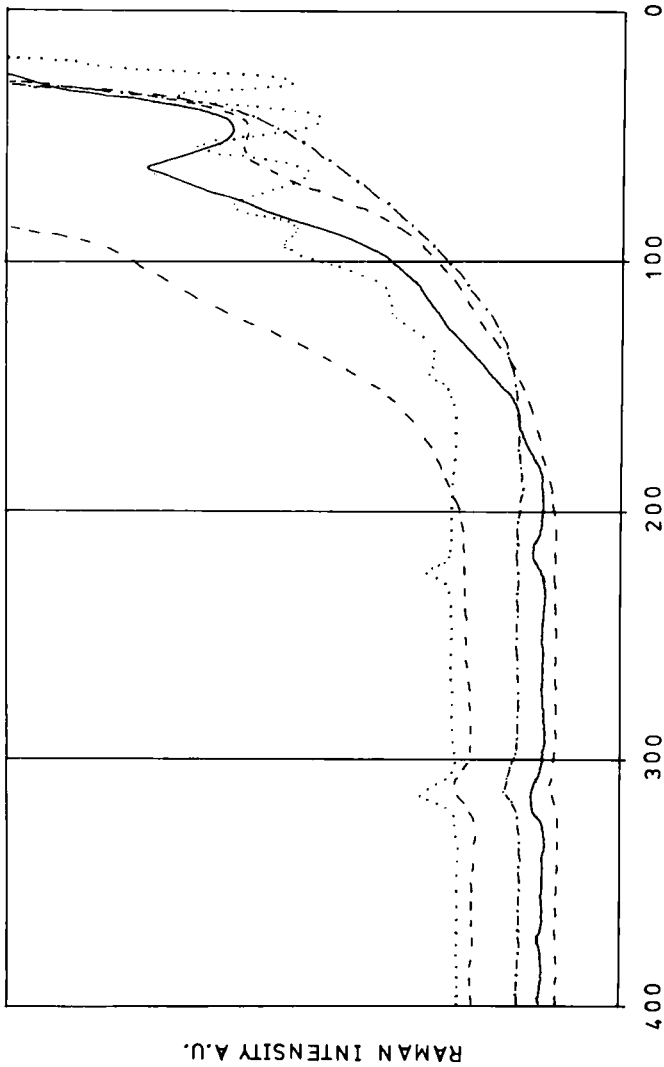


FIGURE 5 Low-frequency (10–400 cm^{-1}) Raman spectra of *p,n*-hexyloxybenzoic acid; spectral slit width—2.5 cm^{-1}, scanning speed—50 cm^{-1}/min; laser output—200 mW spectrometer Spex 1401; dotted line solid I (293°K), 3×10^4; dash line—solid III (363°K, 3×10^4 and 1×10^4 counts/sec), full line—solid II (303°K, 3×10^4 counts/sec), alternate dash dotted line—nematic phase (393°K, 1×10^4).

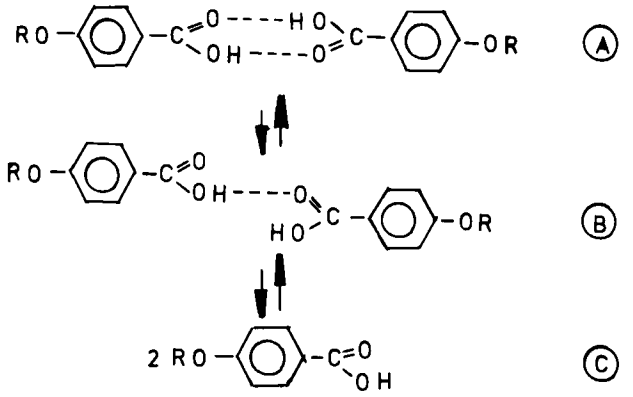


FIGURE 6 Hydrogen bond configuration in *p,n*-alkoxybenzoic acids.

low frequency peaks are narrow, sharp and scarcely splitted; Rayleigh wing, too, is less intense. The phase transition stable crystal phase—α form is connected with dramatic changes in the spectrum. The symmetric hydrogen bond vibration ν_1 (A_g) located between 90 and 100 cm^{-1} becomes so weak that it is not detectable.[32] The three bands connected with librations of the dimers around the main axes of intertia[32–34] are replaced with a broad shoulder. In the smectic phase the molecules gain a free translational motion within the smectic layer, while in the nematic phase they adopt an additional degree of free translation. As a result the low frequency bands (below 100 cm^{-1}) disappear completely and the Rayleigh wing becomes much more intense.

The Raman spectrum of solid II is characterized by a strong band centered at about 65 cm^{-1} which we can think of as composed mainly by librational bands broadened by the disordered interactions among the molecules.

CONCLUSION

All our experimental data allow us to formulate some conclusions about the structure of the different solid modifications. In the stable crystal phase (solid I) all molecules are associated in dimers (form *A*, Figure 6). The higher temperature modification (solid III) can be identified as α solid form in which the molecules may gain some rotational degrees of freedom around their long axes. Open dimers (*B* and monomers *C*) are partially contained in the smectic and nematic phase in addition to *A* form. The hydrogen bond configurations in the mesophase are frozen in the metastable solid obtained upon cooling of the liquid crystal phase (solid II). This conclusion confirms the previous NMR results of Deloche and Cabane.[22] They have found that two processes may contribute to $1/T_1$. The first one-cycle dimer $\rightleftharpoons$ open dimer is respon-

sible for the spin lattice relaxation of the deuterons at low frequencies, while the second one-open dimer $\rightleftharpoons$ 2 monomers is responsible for the high frequency limit. However we can not neglect entirely the role of the paraffinic chain in the formation of the metastable solids. At the phase transition solid I—solid III the alkyl chain acquires additional freedom and various rotational isomers appear. Their number increases in the liquid crystal state. When the acid is cooling from the mesomorphic phase the fully extended trans configuration of the alkyl chain is not entirely restored in solid II but still few rotational isomers persist in this phase. On the other hand it seems that the steric hindrance of the long paraffinic chain prevents the hydrogen bond from being formed rapidly in the temperature range where the thermally stable crystal exists. Obviously the crystallization process of the quenched species is controlled by the paraffinic chain attached to the aromatic ring. The modified hydrogen bond should be rearranged during the crystallization fast enough if the paraffinic chain is not so long. This retardation effect will increase with increasing the length of the chain. Indeed, the length of the butyl and pentyl alkoxy tails is inadequate to prevent the fast restoration of the hydrogen bond on cooling. Thus, these two acids do not form any metastable phases upon freezing. Obviously for more correct evaluation of the alkyl chain role for the formation of metastable phases quantitative measurements of the nucleation rates are needed.

However, the solid II, formed upon cooling of the mesophase of *p,n*-alkoxybenzoic acid is not a glassy liquid crystal but a metastable solid phase although not ordered. The confirmation for this classification we propose arises from three facts: (i) X-ray diffraction measurements of the two metastable phases formed by smectic *p,n*-octadecyloxybenzoic acid have been carried out[6] in order to examine whether such unstable solids are crystalline or amorphous. Both of these patterns were different from that of the stable modification but they exhibited sharp peaks typical of crystalline order although they were broader. (ii) In the low frequency Raman spectrum a well defined band in the region 50–70 cm^{-1} is observed which we think composed mainly by librational bands broadened by the disordered interactions among the molecules. For glassy liquid crystals, however, only a superposition of weak bands is detectable in this region.[35] In the high frequency Raman and IR region the spectrum of solid II formed by the investigated acids differs markedly from that of the mesophase while the strong similarity between the solid II phase formed by quenching of the mesophase of *p*-substituted Schiff bases[35] is outlined by similar frequencies, intensity and half-widths of all bands with some exceptions at lower frequency (below 200 cm^{-1}).

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