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V. P. Privalko [a], G. A. Puchkovskaya [b], E. N. Shermatov [b] & A. A. Yakubov [b]

[a] Institute of Macromolecular Chemistry, Academy of Sciences of the Ukrainian SSR, 252160, Kiev, USSR

[b] Institute of Physics, Academy of Sciences of the Ukrainian SSR, 252028, Kiev, USSR

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Polymorphic Transitions in Alkylbenzoic Acids

V. P. PRIVALKO

Institute of Macromolecular Chemistry, Academy of Sciences of the Ukrainian SSR, 252160, Kiev, USSR

and

G. A. PUCHKOVSKAYA, E. N. SHERMATOV and A. A. YAKUBOV

Institute of Physics, Academy of Sciences of the Ukrainian SSR, 252028, Kiev, USSR

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This paper describes detailed studies of the phase transitions and other physical properties of the series of 4-*n*-alkylbenzoic acids ($CH_3(CH_2)_nC_6H_4COOH$) with alkyl groups ranging from propyl to heptyl.

INTRODUCTION

Measurements of the melting and isotropization points for a series of 4-*n*-alkylbenzoic acids (hereafter referred to as ABA) of general formula $CH_3(CH_2)_nC_6H_4COOH$, with $n = 3 - 9$, were reported as early as 1940,[1] although detailed thermal data for these acids were not obtained. We also are not aware of papers concerned with X-ray analysis and *IR* vibration spectroscopy of ABA. Since these substances exhibit liquid-crystalline behavior and find wide practical application, it seemed worthwhile to carry out detailed studies of their phase transitions and physical properties in a broad temperature range.

EXPERIMENTAL

We studied ABA materials with $n = 2$–6 by differential calorimetry and *IR* spectroscopy with the aim of establishing a relationship between molecular structure and polymorphic transitions.

Thermal analysis

The specific heat in the temperature range 130–450 K was measured with the aid of a differential calorimeter on a diathermal shell at a heating rate about 2 K/min. We studied original (org) powdery samples after preliminary compacting in a calorimeter cell, and quenched (qnc) samples obtained by an instant quench in liquid nitrogen of the melt heated to 430–450 K. Transition temperatures were measured to within 1 K; heats (ΔH) and entropies (ΔS) of separate transitions, and the integral entropies of all phase transitions ($\sum \Delta S$) were determined with a relative error about 3% (see Table I).

IR spectroscopy

Absorption IR spectra were obtained with the aid of a spectrophotometer, model UR-20 (slit programs 2 and 4) in the wavenumber range from 4000 to 400 cm^{-1} and in the temperature interval from 100 to 450 K. Oriented films of ABA were prepared between carefully polished, plates of KBr and NaCl, one-dimensionally rubbed with chamois leather, by slow cooling of the melt and by the thermal gradient method. Sample thickness varied within the range 20 to 40 microns; its quality was monitored with the aid of a polarizing microscope, model MIN-8. Temperature-dependent measurements were made according to a procedure already described.[3]

RESULTS AND DISCUSSION

Thermal analysis

Heating thermograms of the samples (fig. 1) exhibit several endothermic effects, that with maximum intensity giving a peak at a temperature T_m corresponding to melting of a solid crystalline (SC) phase. In the temperature interval above T_m for butyl-ABA and higher members, one observes a transition to the nematic liquid crystalline (LC) phase accompanied by an enthalpy change of 1.6 ± 0.4 kJ/mol; the

TABLE I

Thermodynamic parameters of transitions in ABA[a]

		Transitions in solid crystalline phase									Melting			Isotropization			
n	Sample	T_3	ΔH_3	ΔS_3	T_2	ΔH_2	ΔS_2	T_1	ΔH_1	ΔS_1	T_m	ΔH_m	ΔS_m	T	ΔH	ΔS	$\sum \Delta S$
2	org	—	—	—	—	—	—	301	3.4	10.9	422	23.3	55.0	—	—	—	66.0
	qnc	—	—	—	—	—	—	294	2.0	6.8	415	19.9	48.0	—	—	—	54.8
3	org	257	-1.7	− 6.6	279	0.7	2.5	313	7.8	24.9	377	13.3	35.0	387	1.3	3.2	59.0
	qnc	241	0.3	0.1	280	0.6	2.3	310	6.2	20.0	374	13.4	35.8	385	1.7	4.3	62.5
4	org	—	—	—	—	—	—	252	2.6	10.4	362	9.9	27.3	395	1.5	3.7	41.4
	qnc	—	—	—	—	—	—	239	2.9	12.0	358	10.2	28.0	393	0.9	2.4	42.4
5	org	—	—	—	—	—	—	—	—	—	371	17.4	47.0	380	2.4	6.4	53.4
	qnc	—	—	—	—	—	—	—	—	—	367	16.3	44.4	378	2.0	5.2	49.6
6	org	238	0.5	2.3	273	0.4	1.6	321	6.3	19.6	376	13.6	36.2	391	1.3	3.3	63.0
	qnc	268	5.9	22.0	293	0.4	1.5	315	1.0	3.1	374	14.8	39.7	390	1.6	4.0	70.3

[a] temperatures in K; ΔH in kJ/mol; ΔS in J/mol · K; org—original; qnc—quenched

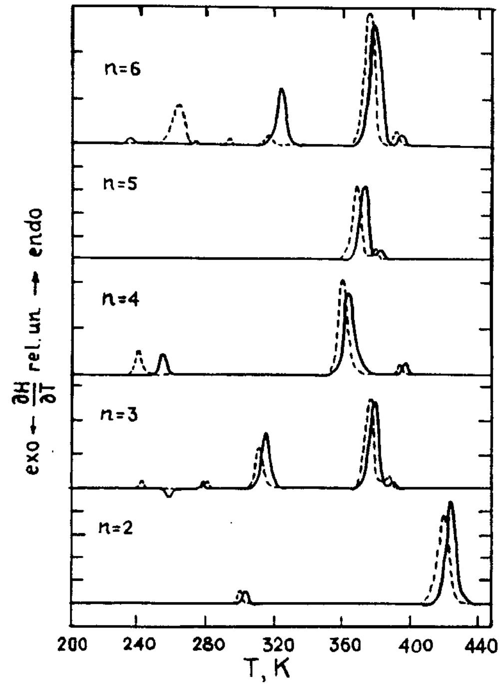

FIGURE 1 Heating thermograms of original (full lines) and quenched (broken lines) samples of ABA.

temperature interval of existence of the mesophase broader for ABA materials with even values of *n*.

The existence of either one or several peaks on the thermograms below T_m suggests the presence of a set of crystalline, polymorphic modifications in our ABA's. However, judging by the relatively low absolute values of the corresponding ΔH and ΔS data, the thermodynamic stability of these structures is rather similar. Obviously, the presence of flexible aliphatic chains with "intrinsic" conformational degrees of freedom predetermines the possibility of formation of a set of nearly equi-energetic crystalline forms in our ABA's.

As might have been expected, temperatures and heats of transition depend on the thermal prehistory of the sample. For example, in some cases an instant quench of the melt resulted in formation of crystalline modifications with transition temperatures and heats different from those for the original samples (cf. fig. 1).

The dependence of the integral entropy of the transitions ($\sum \Delta S$) on the length of the alkyl chain shows a complex pattern (fig. 2). As is

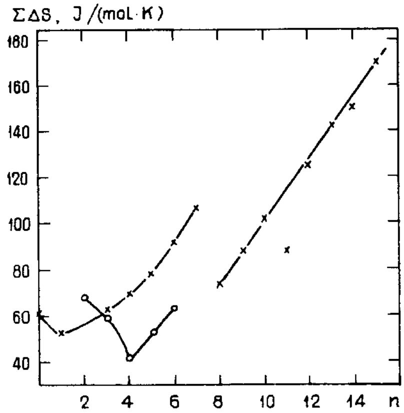

FIGURE 2 Dependence of the integral entropy of transitions on alkyl chain length for cholesteric esters (-×-)[2] and alkylbenzoic acids (-O-).

the case with other LC substances, this pattern is determined by the relative sizes of the alkyl "tail" and the stiff "nucleus" of the molecule. The slopes of dependences of $\Sigma\Delta S$ on n are approximately the same for cholesteric esters, 4-n-alkoxybenzoic acids and ABA, which is suggestive of rather similar values of the entropy increment per methylenic group (13.5 ± 0.5,[2] 10 ± 1[4] and 11 ± 1 J/mol · K, respectively). In other words, interactions between atoms of alkyl chains have a dominating influence on the molecular packing in various series commencing with a certain value of n (e.g., 8 for cholesteric esters and 4 for ABA).

Spectroscopic data

IR absorption spectra for the different phases of heptyl-ABA are shown in fig. 3. Assignment of the main IR bands observed at 100 K (Table II) was made on the basis of published data on benzoic acids,[5,6] n-alkanoic acids[7] and n-paraffins.[8]

It follows from comparative analyses of spectra for different phases that the degree of molecular ordering in the LC phase is not much higher than that in an isotropic liquid (IL) since the respective spectra have much in common. During phase transitions, the most significant changes are observed for those absorption bands which refer to vibrations of bonds and valence angles common to benzene rings, carboxyl groups and alkyl chains. This observation is suggestive of the possibility of a variation of an angle between these molecular fragments on internal rotation around single C-C bonds.

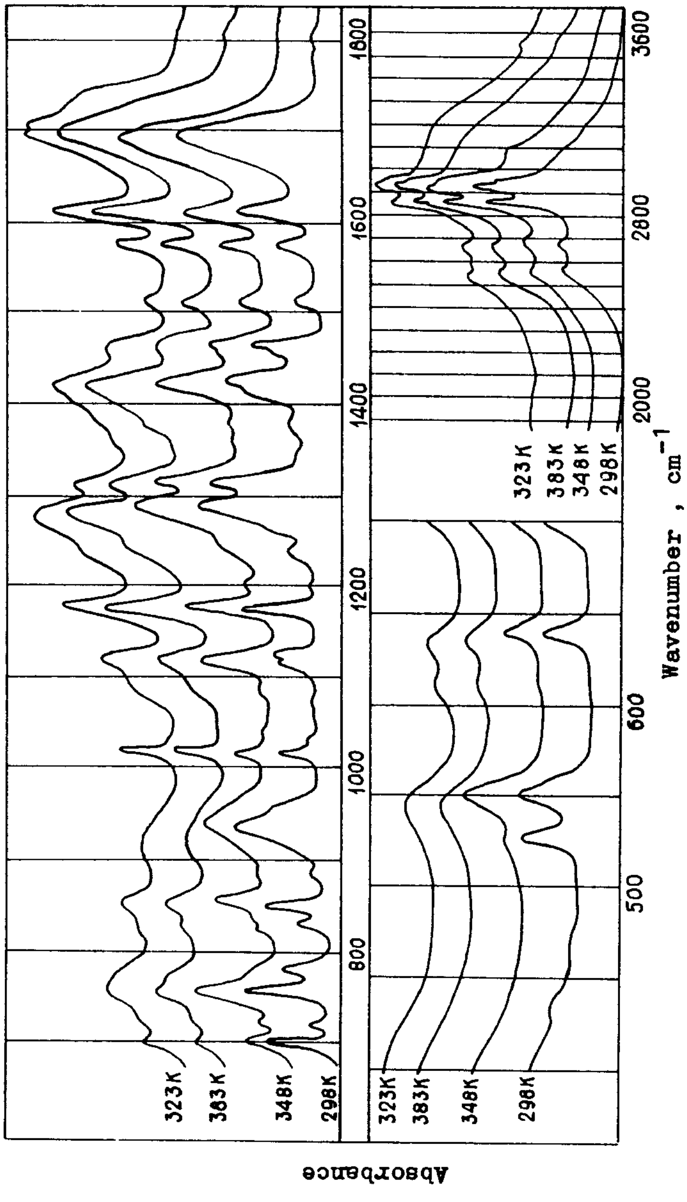

FIGURE 3 IR absorption spectra of heptyl-ABA in the solid, nematic, and isotropic phases.

TABLE II

Interpretation of IR spectra of 4-*n*-alkylbenzoic acids at 100 K[a]

Frequency, cm^{-1}		Assignment	Frequency, cm^{-1}		Assignment
435 ± 5	w	γ(C-C-C)	1290 ± 5	vs	ν(C-O)
465	w	γ(C-C-C)	1375	w	$\delta_s CH_3$
525	m	γ(C-C-C)	1410	s	$\varphi^s(C\alpha H_2)$
550	m	γ(OCC)	1420	s	δ(COH)
640	m	γ(OCO)	1450	m	$\delta_{as} CH_3$
700	m	γ(C = CH)	1460	s	φCH_2
725	m	ρCH_2	1510	w	ν(C = C)
760	s	γ(C = CH)	1575	m	ν(C = C)
780	m	δ(C = CH)	1610	s	ν(C = C)
835	m	δ(C = CH)	1690	vs	ν_{as}(C = O)
860	m	γ(C = CH)	2570	m	Fermi resonance
890	m	ρCH_3	2600	m	Fermi resonance
940	s	γ(OH)	2680	m	Fermi resonance
1020	m	δ(C = CH)	2900	s	ν(OH)
1030	w	δ(C = CH)	2855	vs	$\nu_s CH_2$
1060	w	δ(C = CH)	2880	vs	$\nu_s CH_3$
1080	w	δ(C = CH)	2925	vs	$\nu_{as} CH_2$
1125	m	ν_{as}(C-C)	2960	vs	$\nu_{as} CH_3$
1180–1350		$\omega CH_2 + \gamma CH_2$	3080	s	νCH

[a] w—weak; m—medium; s—strong; vs—very strong (band intensities); ν and δ(φ, ρ, γ, ω)—corresponding stretching and bending (scissoring, rocking, twisting and wagging) vibrations.

Bands at about 2900, 1692 and 940 cm^{-1} observed in the IR spectra of all phases may be explained by association of ABA molecules into cyclic dimers (CD) by means of hydrogen bonds. We estimated the energy of H-bonds in different phases by the Iogansen method.[9] Vibration frequencies of γOH monomer were determined from IR spectra of ABA in the gaseous state at 540–550 K, and in CCl_4 solution. For all ABA's studied, these frequencies were approximately the same, 612 cm^{-1}. The H-bond energy in the SC phase at 100 K is about 36 ± 1 kJ/mol (34 ± 1 kJ/mol at 300 K), and this decreases at the phase transitions, SC → LC → IL.

Concomitant to the phase transition, SC → LC, we observed the appearance and a gradual rise in intensity with increasing temperature of bands at 3300 (νOH), 1703 (νC = O), 3555 (νOH), 1740 (νC = O), 1090 (νC-O) and 612 (γOH) cm^{-1}, of which the first pair was attributed to an opened dimer (OD), and the remainder to monomer. Moreover, the band at 940 cm^{-1} starts to diminish and shift to the low-frequency side. All these changes indicate that appearance of OD and monomers proceeds simultaneously with dissociation of CD. According to our estimates, the energy of the H-bonds in OD is nearly 4.5 kJ/mol lower than that in CD.

CD, OD and monomers also coexist in the liquid phase, while in the gaseous phase above 550 K the molecules of these ABA are likely to exist primarily in monomeric form.

When the molten acid is rapidly cooled, one observes the formation of a metastable solid modification (qnc samples in Table I). IR spectra of this modification suggest the presence of CD as well as OD and monomers; hence, in quenched samples the dimerization of ABA molecules is by no means complete. As evidenced by the gradual intensity fall of a band at 3550 cm^{-1}, a stable crystalline modification is slowly restored during a substantially long period of time (of the order of several days).

Analysis of the IR spectra shows, further, that quenched samples of all studied ABA undergo low-temperature phase transitions in the temperature interval from 300 to 100 K. It follows, therefore, that it is the low-temperature phase which is the most ordered, since all bands are narrow and sharp. Moreover, we observed Davydov splitting of CH_2 rocking vibrations at 720 cm^{-1} in heptyl-ABA at 100 K, concomitant to the increase of H-bond energy by approximately 2 kJ/mol as compared to this value at room temperature. We recall that such splitting is characteristic of the densely packed, fully extended methylene chains in a crystal, in the unit cell of which there are at least two translationally non-equivalent units.

CONCLUSIONS

The polymorphic transitions and molecular structures of a series of 4-*n*-alkylbenzoic acids ($CH_3(CH_2)_nC_6H_4COOH$, with $n = 2–6$) have been studied by differential calorimetry and IR absorption spectroscopy in the temperature interval 100–450 K; temperatures, enthalpies, and entropies of phase transitions have been determined. The diversity of observed polymorphic structures is shown to reflect the possibility of formation of various conformers due to the presence of flexible, mobile alkyl chains in the molecules. The acids studied have been proved to exist in the form of cyclic and opened dimers formed by means of hydrogen bonds; energies of the latter bonds have been estimated for the different phases. Davydov splitting of rocking vibrations of the methylenic chain in crystalline heptylbenzoic acid ($n = 6$) at 100 K suggests that the packing pattern and intermolecular interactions in this phase are determined primarily by densely packed, fully extended alkyl chains.

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