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Thermal Properties of *p-n*-Octadecyloxybenzoic Acid (Part II)†

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Thermal properties of metastable and liquid crystalline properties of *p-n*-octadecyloxybenzoic acid were investigated by differential scanning calorimetry. The glass transition found in the metastable crystal obtained by cooling the smectic phase suggested the existence of a disordered phase. Heat capacities of thermally stable and metastable crystals of the deuterated acid also support this conclusion.

From measurements of infrared absorption spectra of the original and the deuterated acids with increasing temperature, the differences in molecular conformation among phases is discussed. It is concluded that the molecules of the carboxylic acids are associated in pairs by hydrogen bonds in the thermally stable crystal, while the hydrogen bonds are partially destroyed in the metastable crystal and in the smectic phase.

INTRODUCTION

The authors previously found[1] that *p-n*-octadecyloxybenzoic acid had two metastable crystalline states and that the crystals were in alterable states at an arbitrary temperature below the transition temperature from metastable to stable crystal. This phenomenon may indicate that the molecular conformation in such metastable crystalline states is readily altered. Haida *et al.*[2] and Suga *et al.*[3] found a glass transition of the supercooled metastable crystal of cyclohexene and suggested the general and wide occurrence of

† This paper follows Part-I presented in *Mol. Cryst. Liquid Cryst.*, **33**, 201 (1976).

"frozen-in" phenomena of the disordered phase. If the metastable crystals of *p-n*-octadecyloxybenzoic acid formed by cooling from the smectic phase have disorder like that of cyclohexene, it may be expected that the glass transition of the supercooled metastable crystal is encountered at elevated temperature. One of the purposes of this paper is to study whether the metastable crystal of *p-n*-octadecyloxybenzoic acid has a disordered phase in which certain degrees of freedom of the molecule may be liberated.

As well-known,[1,4] this liquid crystal consists of rectilinear molecules of the carboxylic acid which are associated in pairs by hydrogen-bonds connecting their acid groups. In their thermally stable crystalline state such dimer molecules are placed in order. According to measurements of the nuclear quadrupolar spin-lattice relaxation rate $1/T_1$ of deuterons on the hydrogen bonds of the liquid crystal *p-n*-hexyloxybenzoic acid, Deloche *et al.*[5] reported that rupture of the hydrogen bonds consequently took place through a coupling of the motions with association-dissociation processes of hydrogen bonds. In other words, the mesomorphic state is an equilibrium state to which the association-dissociation processes of the hydrogen bonds are related. In this study the dimer molecules of *p-n*-octadecyloxybenzoic acid was deuterated and the effect of the hydrogen bonds on the thermal properties were evaluated.

Infrared absorption spectrum of each phase of *p-n*-octadecyloxybenzoic acid was measured in order to investigate the molecular structure. Particularly, the changes of the hydrogen bond configuration among the phases were pursued by deuteration.

EXPERIMENTAL

Preparation

The deuterated acid of *p-n*-octadecyloxybenzoic acid was prepared by the same method reported previously.[6] The compound was confirmed by use of infrared spectroscopy and was identified simultaneously for the extent of deuterization. The crystal had a deuterium content of about 92%. Samples of *p-n*-octadecyloxybenzoic acid and the deuterated acid used for thermal experiments were recrystallized from hot toluene solution and dried under high vacuum at room temperature for 24 hours.

Apparatus

Observation of the glass transition phenomenon of *p-n*-octadecyloxybenzoic acid was carried out by using a Perkin–Elmer DSC Model-II calorimeter. Also, the apparatus equipped with a calculator system gave heat capacities

of the deuterated acid. Their values were evaluated from the heat capacity of a single sheet of amorphous alumina as the standard. The error in the heat capacity was found to be 4% based on repeated measurements. A sensitivity of 5 mcal sec^{-1} and a heating rate of 10 K min^{-1} were adopted in all experiments of heat capacity.

Measurements of infrared absorption spectra were carried out by using HITACHI 345 Infrared Spectrometer equipped with heating apparatus. Potassium bromide pellets of the sample were prepared by mixing 2 mg of the sample with 200 mg of KBr. Care was taken to eliminate water. The temperature control during the measurements was $\pm 2°C$.

RESULTS AND DISCUSSIONS

Thermal analysis

The existence of the metastable, glassy crystal phase in liquid crystals has not been reported, though the glassy liquid crystal phases of many mesomorphic phases have been discovered.[4] However, it was expected that the glassy state existed in the case of *p-n*-octadecyloxybenzoic acid because two metastable crystals appeared in thermal analysis. Using the sample formed by cooling at a rate of 10 K min^{-1} in the smectic phase to 300 K, we tried to thermodynamically prove the existence of a glassy state. A Perkin–Elmer DSC Model-II calorimeter which has high sensitivity enabled us to observe a very small jump of the heat content at a glass transition temperature. Figure 1 shows a series of thermograms exhibiting the glass transition phenomenon of the sample formed by the thermal treatment described above and quenched from 300 K to 160 K by using liquid nitrogen with careful attention to water condensation. The first thermogram presented by the subscript of $t = 0$ hr in the Figure was the curve obtained by heating the sample at the rate of 10 K min^{-1} from 160°K. At 193 K° an endothermic jump on the curve was observed. In order to confirm that this jump is attributed to glass transition, the sample was annealed for a long time at 191°K and enthalpy relaxation was analyzed. The samples annealed for 10 and 24 hours are shown in Figure 1 as the second and third thermograms, respectively. Height of the jump increased with increasing annealing time. Consequently, it was decided that the jump at 193 K° corresponds to glass transition. This glass transition temperature depended on the cooling rate of the smectic phase. For instance, the glass transition of a sample formed by immersion in liquid nitrogen from the smectic phase occurred at 198 K°. This result demonstrates that the glassy crystal state of the metastable crystal exists and suggests that molecular conformation in the smectic state is confined to the metastable crystal state.

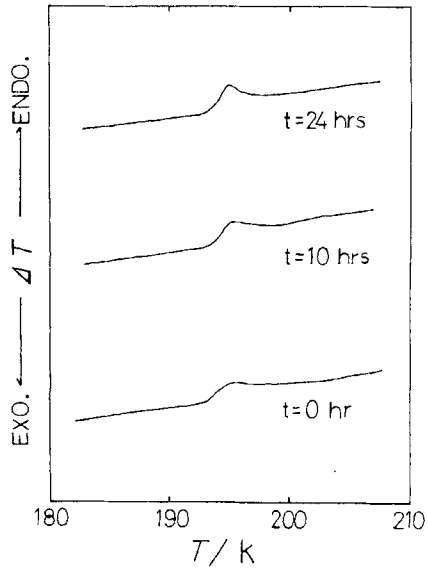

FIGURE 1 DSC thermograms for analysis of enthalpy relaxation effect in the vicinity of the glass transition of *p-n*-octadecyloxybenzoic acid.

It has been suggested[7] that the mesomorphism of *p-n*-octadecyloxybenzoic acid solid is due to the association of the acid into dimers. Heat capacities of the deuterated acid in the solid state were established by various thermal treatments. Three solids were formed by recrystallization as follows: (1) cooling at the rate of 5 K° min^{-1} from 380 K° (smectic phase) to 358 K°; (2) cooling at the rate of 40 K° min^{-1} from 390 K° (smectic phase) to 300 K°; and, (3) cooling over the range of 300 K° to 420 K°. The solids were abbreviated as crystal-I, crystal-II and crystal-III, respectively. The results are shown in Figure 2 and Table I.

Thermodynamic relations among crystal-I, crystal-II and crystal-III are similar to those of *p-n*-octadecyloxybenzoic acid.[1] Comparing the phase transition temperatures from each crystalline state to smectic phase and from smectic phase to isotropic liquid of *p-n*-octadecyloxybenzoic acid, those of the deuterated acid were somewhat lower than the regular acid. This fact hints that a change of the strength of the intermolecular interaction through hydrogen bonds is involved in the crystal–smectic phase transition.

Transition enthalpies and entropies of the deuterated acid were calculated from the transition peak areas of the thermograms and listed in Table II along with those of *p-n*-octadecyloxybenzoic acid. It should be noted that the values are for the deuterated acid with a deuterium content of about

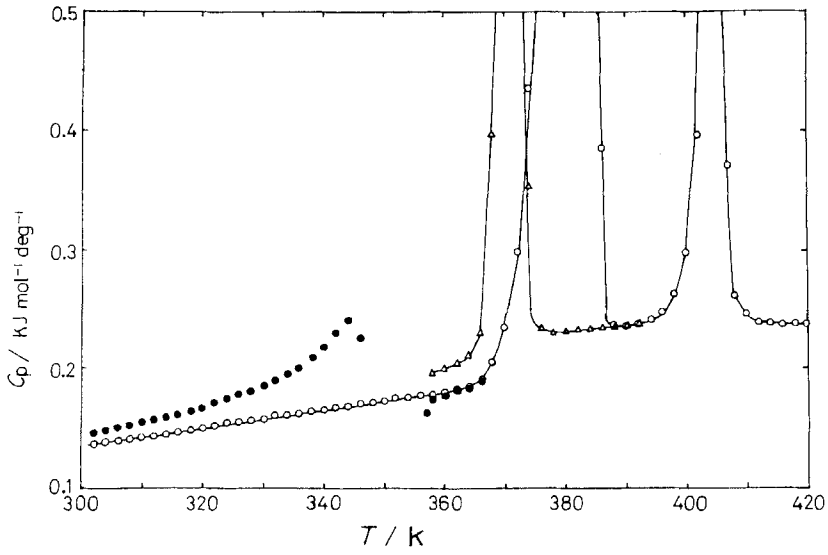

FIGURE 2 Curves of heat capacities of the deuterated acid solids formed by various thermal treatment; (○) recrystallized sample (crystal-I), (△) the sample formed by cooling at the rate of 5 K min^{-1} from 380 K to 356 K (crystal-II) and (●) the sample formed by cooling at the rate of 40 K min^{-1} from 395 K to 300 K (crystal-III).

92%. The discrepancy in transition enthalpies and entropies of both compounds may be ignored if we take into account the error of calculation.

In our previous paper[1] we suggested that the long paraffinic chain conformation in the metastable crystal state of *p-n*-octadecyloxybenzoic acid might retain the same form in the smectic phase. According to the thermal analysis of the deuterated acid described above, it seems that the strength of intermolecular interaction through hydrogen bonds in the stable crystal state changes at the crystal–smectic phase transition temperature, since substitution of deuteron for proton in the carboxyl group shifted the crystal–smectic phase transition temperature toward a lower value. The above results support the idea that the transition temperature from the crystal to smectic phase is determined primarily by the strength of the intermolecular interaction through hydrogen bonds.

Infrared spectroscopy

In the thermally stable crystal states of alkoxy benzoic acid the molecules tend to arrange regularly, associating in pairs ("dimers") with hydrogen bonds connecting their respective acid groups as discussed in the previous

TABLE I

The values of heat capacities of the deuterized acid of *p*-*n*-octadecyloxy benzoic acid

Temperature K	C_p (crystal-I) KJ K^{-1} mol^{-1}	C_p (crystal-II) KJ K^{-1} mol^{-1}	C_p (crystal-III) KJ K^{-1} mol^{-1}
302	0.137	—	0.146
304	0.138	—	0.148
306	0.140	—	0.150
308	0.141	—	0.152
310	0.143	—	0.155
312	0.144	—	0.157
314	0.146	—	0.159
316	0.148	—	0.162
318	0.149	—	0.165
320	0.150	—	0.167
322	0.152	—	0.172
324	0.155	—	0.176
326	0.156	—	0.179
328	0.157	—	0.182
330	0.158	—	0.186
332	0.161	—	0.191
334	0.162	—	0.196
336	0.163	—	0.201
338	0.164	—	0.209
340	0.167	—	0.218
342	0.169	—	0.230
344	0.171	—	0.241
346	0.172	—	—
348	0.173	—	—
350	0.174	—	—
352	0.176	—	—
354	0.176	—	—
356	0.177	—	—
358	0.178	0.196	0.174
360	0.180	0.202	0.177
362	0.182	0.205	0.180
364	0.185	0.212	0.183
366	0.191	0.231	0.187
368	0.205	0.398	0.197
370	0.235	—	—
372	0.298	—	—
374	0.435	0.355	—
376	0.785	0.234	—
378	1.978	0.230	—
380	1.795	0.232	—
382	1.518	0.233	—
384	1.046	0.234	—
386	0.385	0.234	—
388	0.237	0.235	—
390	0.235	0.236	—
392	0.238	0.238	—
394	0.241	—	—

TABLE I (*continued*)

The values of heat capacities of the deuterized acid of *p-n*-octadecyloxy benzoic acid

Temperature K	C_p (crystal-I) KJ K^{-1} mol^{-1}	C_p (crystal-II) KJ K^{-1} mol^{-1}	C_p (crystal-III) KJ K^{-1} mol^{-1}
396	0.248	—	—
398	0.263	—	—
400	0.276	—	—
402	0.396	—	—
404	0.719	—	—
406	1.029	—	—
408	0.261	—	—
410	0.246	—	—
412	0.239	—	—
414	0.238	—	—
416	0.237	—	—
418	0.237	—	—
420	0.237	—	—

section. The concrete evidence was drawn in Figure 3, which shows infrared spectra of *p-n*-octadecyloxybenzoic acid (A), the deuterized acid (B) and *p-n*-octadecyloxybenzoic acid methyl ester (C) in the stable crystal states. The problem of water contamination was excluded from all spectra as shown in Figure 3 where the stretching vibration spectrum (ν_{O-H}) due to free water was not found in the vicinity of 3500 cm^{-1}. The stretching vibration spectra (ν_{O-H}) in the range of 2550 to 2650 cm^{-1} are attributed to hydrogen bonds of the acid groups. When the acid was deuterated (B), the stretching vibration spectra (ν_{O-D}) were lowered toward the range of 2030 to 2200

TABLE II

Phase transition temperatures, enthalpies and entropies of the deuterized acid in comparison with those of *p-n*-octadecyloxybenzoic acid.

Phase Transition	Transition Temperature K		Transition Enthalpies KJ mol^{-1}		Transition Entropies KJ mol^{-1} K^{-1}	
	H^a	D^b	H	D	H	D
Cryst.-I-Smectic	379.5	374.2	67.3	65.7	0.177	0.176
Cryst.-II-Smectic	371.0	365.7	38.9	36.5	0.105	0.101
Cryst.-III-Smectic	342.5	340.2	—	—	—	—
Smectic-Iso. Liq.	408.5	402.5	13.3	14.4	0.032	0.035

[a] *p-n*-octadecyloxybenzoic acid.
[b] the deuterized acid.

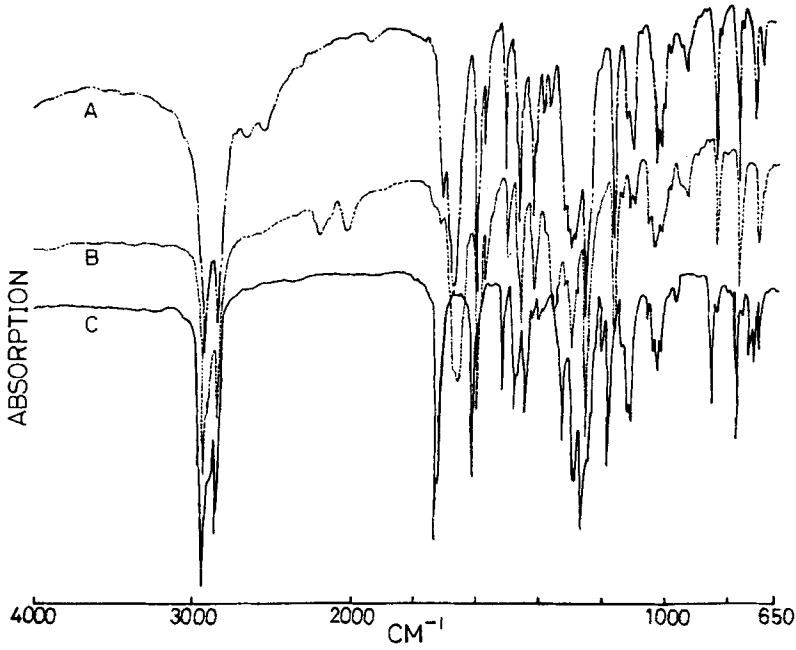

FIGURE 3 Infrared spectra of *p-n*-octadecyloxybenzoic acid (A), the deuterated acid (B) and *p-n*-octadecyloxybenzoic acid methyl ester (C) at 295 K°.

cm^{-1}.[8] As shown in C, substitution of the acid for the acid methyl ester naturally eliminated the ν_{O-H} spectrum.

Assignments of the infrared spectra are listed in Table III. The marked descrepancy between A and B in Figure 3 may be interpreted as whether there is an overlap of C—H stretching vibration spectrum (ν_{C-H}) and $\nu_{O-H}(\nu_{O-D})$, The intensity and shape symbols in Table III have the usual meanings as follows: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder and sp = sharp. The following abbreviations have been used for representing simply many kinds of vibration frequencies: ν(C—H) (C—H stretching of CH, CH_2 and CH_3); γ(C—H) (out-of-plane C—H deformation in benzene ring); ϕ(C—C) (out-of-plane ring deformation); ν(C=C) (C=C stretching in benzene); ν(C=O) (C=O stretching); ν(C—O) (C—O—C stretching in ether group); ν(C—C) (C—C stretching in alkyl group).

We have mentioned that *p-n*-octadecyloxybenzoic acid and the deuterated acid produce metastable crystals on thermal treatments. It is very important to know what kinds of molecular structure and arrangement the metastable crystals adopt. Previously, Deloche *et al.*[5] measured the nuclear spin-lattice

TABLE III

Infrared spectrum of *p-n*-octadecyloxybenzoic acid at 21°C

(Crystal-I) cm^{-1}	Assignment	cm^{-1}	Assignment
3050 sh	ν(C—H)	965 w	
2955 sh	ν(C—H)	955 w	
2920 vs	ν(C—H) CH_2	945 m, br	COOH(O—H) def.
2850 vs	ν(C—H) CH_2	910 w	
2660[a] m	ν(O—H) association	845 s, sp	
2550[a] m	ν(O—H) association	770 s, sp	
1685 v, sp	ν(C=O)	730 s, sp	
1605 vs	ν(C=C) anti-sym.	720 sh	
1580 s	ν(C=C) sym.	695 s, sp	γ(C—H)
1510 s	ν(C—C)	645 vs	ϕ(C—C)
1475 s, sp	ν(C—C)	550 s	
1440 s, sp	ν(C—C)	505 m	
1425 s, sp	COOH vibrations		
1355 sh	CH_2 deformation		
1330 s	CH_2 deformation		
1320 sh	CH_2 deformation		
1315 s	CH_2 deformation		
1300 sh	CH_2 deformation		
1285 sh	CH_2 deformation		
1255 vs	ν(C—O)		
1240 sh	CH_2 deformation		
1230 sh	CH_2 deformation		
1215 w	CH_2 deformation		
1170 s, sp	CH_2 def. (rocking)		
1145 m			
1125 m	ν(C—C)		
1105 m			
1065 m	ν(C—C)		
1048 w			
1035 w			
1020 m			

[a] A mean value is given for these two bands: 2660 ± 20 cm^{-1} and 2550 ± 20 cm^{-1}.

relaxation rates of $1/T_1$ by using *p-n*-hexyloxybenzoic acid. According to the temperature and frequency dependences of T_1 in the mesomorphic state, they proposed that the molecules associating through hydrogen bonds are partially dissociated in the mesomorphic state. Assuming that such an association-dissociation equilibrium of other homologous acid molecules is attained in the mesomorphic states, a rapid cooling of the mesomorphic states may give rise to metastable solids where disorder due to breaking hydrogen bonds is put under restraint. If the assumption is valid in the original and deuterated *p-n*-octadecyloxybenzoic acids, the intensity of the ν_{O-H} or ν_{O-D} infrared spectrum obtained in the thermally stable crystals will

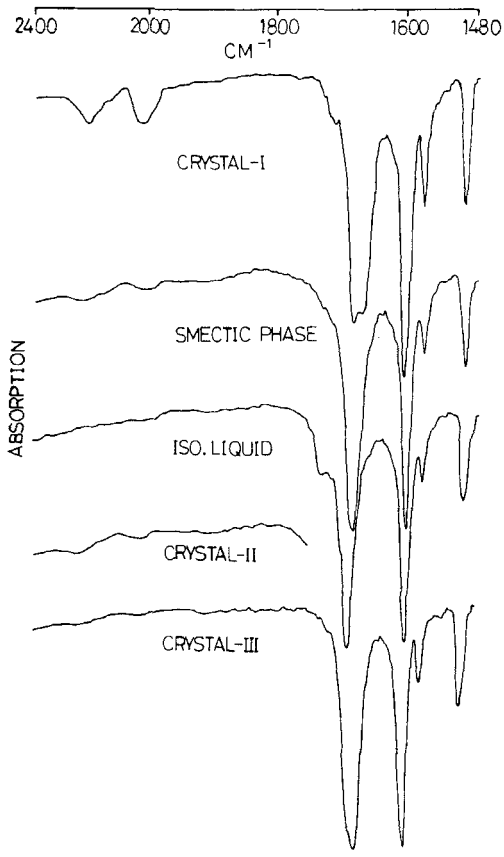

FIGURE 4 Infrared spectra in each phase of the deuterated acid.

decline in those of the smectic phases and metastable crystals. Figure 4 gives infrared spectra of the deuterated acid in the range of 1480 to 2400 cm^{-1} measured isothermally at various temperatures.

As shown in the spectra, the intensity distinctly decreased in the smectic phase and the metastable crystals. Here, the thermally stable crystal, the metastable crystals and isotropic liquid were abbreviated as crystal-I, crystal-II (formed by the cooling rate of 5 K° min^{-1} from 380 K° (smectic phase) to 358 K°), crystal-III (formed by the cooling rate of 40 K° min^{-1} from 390 K° (smectic phase) to 300 K°) and isotropic liquid, respectively. In Table IV the comparison of the intensity (I) of ν_{O-D} in each phase with that (I_0) of crystal-I was listed by reducing them to the absorption spectral intensities of both 1600 cm^{-1} and 1550 cm^{-1} as the internal criteria, using the base-line optical density method.[9] In order to get accurate values of

TABLE IV

Comparison the spectral intensity of ν(O—D) in crystal-I phase of the deuterized acid with those in different phases.

Phase	Temperature (K)	I(phase)/I(crystal-I)
Crystal-I	295	1.00
Crystal-II	295	0.27
Crystal-III	295	0.20
Smectic phase	380	0.26
Isotropic Liquid	413	0.13

their intensities, the ν_{O-D} bonds were expanded in by 5 times in the range from 2400 to 1800 cm^{-1} to distinguish the absorption peak from background. Clear spectra enabled us to calculate the base-line optical density[9] for all samples.

The number of hydrogen bonds in the smectic phase at 380 K° was about one-fourth of that in crystal-I. The value further decreased in the isotropic liquid phase. The phenomenon shows that the dimer structure of the molecules gradually diminishes with increasing temperature. It is revealed from this table that the number of hydrogen bonds in the metastable crystals are almost equal to those in the smectic phase. This fact proves that the reproduction of the hydrogen bonds is difficult to bring about through cooling from the smectic phase. Exactly, a slight difference between crystal-II and crystal-III seems to reflect the number of hydrogen bonds in the smectic phase at 380 K° or 390 K°. The partially broken hydrogen bonds in the smectic phase may be frozen in the metastable crystal states without regeneration. Enthalpies[4] of the crystal-I-smectic phase and the crystal-II-smectic phase transitions given in Table II are 65.7 KJ mol^{-1} and 36.5 KJ mol^{-1}, respectively. Assuming that the hydrogen bond energy[10] of benzoic acid is about 40.2 KJ mol^{-1} and the number of hydrogen bonds in the smectic phase is 25% of that in crystal-I where all of the molecules associate with hydrogen bonds in pairs, (Table IV), then the transition enthalpy expended in the conformational change of the long paraffinic chain at the crystal-I-smectic phase transition temperature will be 35.4 KJ mol^{-1}. This value nearly corresponds to the crystal-II smectic phase transition enthalpy of 36.5 KJ mol^{-1}. Therefore, this identification seems to give the evidence that the number of hydrogen bonds in crystal-II (a metastable crystal state) is equal to that in the smectic phase.

From previous experimental results, the following modification with respect to the molecular structure of *p-n*-octadecyloxybenzoic acid in each phase is suggested as shown in Figure 5. In the crystal-I phase, the molecules take A-form. B-form and C-form may be partially contained in the smectic

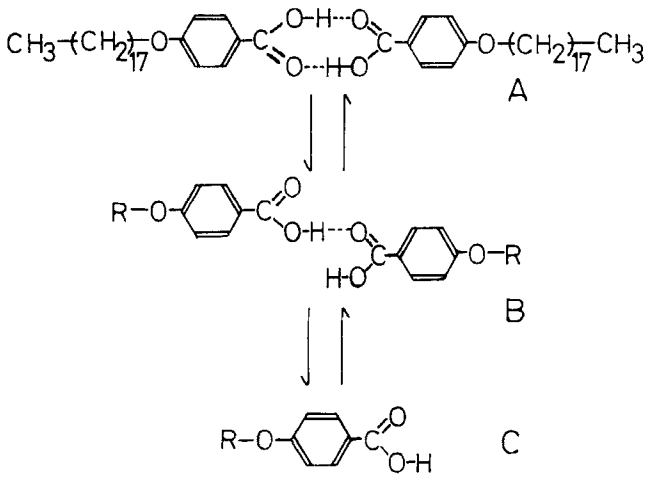

FIGURE 5 Modification of hydrogen bond configurations of *p-n*-octadecyloxybenzoic acid molecules.

phase in addition to A-form. Deloche *et al.*[5] proposed that equilibrium reactions of the type of A-form (cyclic dimer) $\rightleftharpoons$ B-form (open dimer), the type of A-form $\rightleftharpoons$ C-form (2 monomers) and the type of B-form $\rightleftharpoons$ C-form appear in the mesomorphic phase on the basis of measurements of temperature and the frequency dependences of spin-lattice relaxation time T_1. Our results of thermal analysis and infrared absorption spectra of *p-n*-octadecyloxybenzoic acid and the deuterated acid also suggest that such equilibrium reactions are brought about by the collective orientational motions of the paraffinic chains with regard to the hydrogen bond configurations in the smectic phase. The hydrogen bond configurations in the smectic phase may be frozen in the metastable crystal states. On the other hand, it seems that a stereo-hinderance for the long paraffinic chain prevents the hydrogen bonds from being reproduced in the temperature range where the thermally stable crystal exists. Consequently, the glassy crystal state of the metastable crystals may involve the disorder of the hydrogen bond configurations in the molecular arrangement. The fact[11] that the homologous acids from *p-n*-heptyloxybenzoic acid to higher homologues have individually such a metastable crystal solid relates to the disorder of hydrogen bond configuration and the long paraffinic chain conformation.

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