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Crystal Structure as the Basis for the Lack of Enantiotropic Mesomorphism in 3-Hydroxy-4-Propionylphenyl-4'-*n*-Alkyloxybenzoates

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Abstract—Features of the molecular structure and crystal packing of the mesogenic compounds 3-hydroxy-4-propionylphenyl esters of 4-n-amyloxy (1), 4-n-hexyloxy (2), 4-n-heptyloxy (3), and 4-n-octyloxybenzoic acid (4) have been analyzed on the basis of X-ray diffraction (XRD) data. Comparison of the results of XRD and DSC studies of these compounds has shown that the crystalline modification studied for each of the compounds is not a precursor to the mesophase. The possibility of mesophase formation from the melt is discussed.

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Phenyl benzoates having an alkyl or alkyloxy chain as a substituent in the para-position on the benzene ring exhibit liquid crystal (LC) properties [1]. Being a nanostructured system, the mesophase is built from molecular assemblies in which the balance between van der Waals and directional weak interactions (secondary bonds) is maintained [2-6]. Organic compounds most frequently contain the following types of secondary bonds characterized by different energies: the ordinary hydrogen bonds, $\pi \dots \pi$ interaction, and weak hydrogen bonds C–H... π and X...H–C (X is a heteroatom). Since there are no direct experimental methods for studying the detailed structure of complex assemblies of the mesophase, we use an approach based on the assumption that the crystal structure of the compound is the precursor of the mesophase and, as such, can reflect the key structural features of the latter. If this assumption is true, an investigation of the crystal packing of liquid crystal compounds may shed light not only on the structure of the mesophase, but also on the mechanisms of phase transitions in the crystal-mesophase-isotrope system. Previously, we found that the number of phase transitions in the mesophase generally coincides with the number of types of secondary bonds in the crystal structure. This finding give grounds to suppose that as the temperature of the system increases, the successive degradation of different types of secondary bonds (i.e., the "support contacts" of the mesophase) resulting in a decrease in the level of its structuring causes phase transitions in the mesophase [7-18].

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In order to determine the relation of the crystal structure of compounds to their LC properties, we performed X-ray diffraction and thermographic investigation of compounds 1-4.



According to published data, the introduction of a side OH group in the 3-position of the phenol moiety of 4-propionylphenyl-4'-alkyloxybenzoates [19] reduces the isotropization temperature (T_i) and weakens the smectogenicity of these compounds.

EXPERIMENTAL

Synthesis of Compounds

3-Hydroxy-4-propionyl-4'-alkyloxybenzoates were prepared by reacting propionylresorcinol [20] with 4-alkylbenzoic acids in a methylene chloride solution in the presence of N, N'-dicyclohexylcarbodiimine [21] at room temperature. The resulting products were purified by column chromatography on silica gel followed by recrystallization from cyclohexane. The purity of the compounds was checked by thin layer chromatography.

Sample	CrI	CrII	SmA	N	Iso
1 <i>a</i> / <i>b</i>	• 76/1.2	• 88.6/36.7	•	• (77.5)/0.88	•
2 <i>a</i> / <i>b</i>	• 81.1/3.9	• 89.3/49.9	• (52.8)/0.48	• (84.6)/1.02	•
3 <i>a</i> / <i>b</i>	• 66.1/0.1	• 74.4/35.8	• (66.1)/0.94	• 83/0.53	•
4 <i>a</i> / <i>b</i>	• 56.3/37.15	• 66/2.6	• 77.1/1.18	• 87.7/1.05	•

 Table 1. Phase transition parameters as measured by DSC

a and b refer to the temperature (°C) and ΔH (kJ mol⁻¹), respectively.

Table 2. Unit cell parameters of 1–4 according to X-ray structure analysis (XSA) and X-ray phase analysis (XRD) data

Substance	Method -	Parameters					
		<i>a</i> , Å	b, Å	<i>c</i> , Å	β, °	<i>V</i> , Å ³	
1	XSA	12.5674(11)	9.0363(8)	16.6531(14)	93.309(2)	1888.0(3)	
	XRD	12.55(3)	9.02(2)	16.67(4)	93.2(2)	1884(1)	
2	XSA	12.7287(7)	9.2224(5)	16.7869(9)	92.618(1)	1968.5(2)	
	XRD	12.75(3)	9.23(2)	16.81(3)	92.6(1)	1976(1)	
3	XSA	18.069(2)	7.926(1)	14.745(2)	90	2111.8(5)	
	XRD	18.06(2)	7.92(1)	14.72(2)	90	2104(1)	
4	XSA	18.085(2)	7.956(1)	15.339(2)	90	2207.1(4)	
	XRD	18.07(2)	7.95(1)	15.33(2)	90	2203(1)	
		19.00(2)	12.45(1)	15.60(2)	92.7(1)	3684(1)	

Calorimetric Studies

The parameters of phase transitions were determined calorimetrically with a Mettler DSC 832e instrument at a scan rate of 5 K/min. Table 1 shows the results of measurements on polycrystalline samples in the heating mode and their subsequent cooling for detecting the monotropic phases.

X-ray Diffraction Phase Analysis

X-ray diffraction powder patterns of 1–4 were obtained using a Bruker D8 Advance diffractometer (CuK_{α} 1.5418 Å, Ni filter, LYNXEYE detector, reflection geometry). Measurements were made in the angular range of $2\theta = 5^{\circ}-40^{\circ}$. The diffraction patterns were processed (profile analysis, indexing, refining of the lattice parameters) using the software package STOE WinXPOW (Version 1.04, 07.01.1999). The theoretical X-ray diffraction patterns of 1–4 were calculated from the X-ray structure analysis data using the program Mercury (Version 3.1). The unit cell parameters of 1–4 are given in Table 2.

Investigation of Thermal Stability of Single Crystals

The thermal stability of 1-4 single crystals was studied by visual inspection with a microscope at temperatures of $23-85^{\circ}$ C. The heating of single crystals

1–3 to the melting point did not result in mechanical destruction. The crystals of 4 undergo cracking at temperatures above \sim 58°C.

X-ray Structure Analysis

Slow crystallization of compounds 1-4 from different mixtures of solvents resulted in only one crystalline modification. A single crystal of each of the compounds 1-4 suitable for X-ray structure analysis was placed on a CCD diffractometer (SMART APEX-II) under a flow of cooled nitrogen, and unit cell parameters and reflection intensities were measured using Mo- K_{α} radiation and a graphite monochromator. The primary processing of the experimental data was carried out using the program SAINT [22].

All the structures were solved by direct methods and refined by the F^2 least squares in the anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically, excluding the OH hydrogen atom localized in Fourier difference synthesis. All the hydrogen atoms were refined using a riding model.

The calculations were performed using the programs SHELXTL-Plus [23] and Olex-2 [24]. The main characteristics of X-ray diffraction experiments are shown in Tables 3 and 4.

Compound	1	2
Formula	C ₂₁ H ₂₄ O ₅	C ₂₂ H ₂₆ O ₅
Molecular weight	356.40	370.43
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	12.5674(11)	12.7287(7)
b/Å	9.0363(8)	9.2224(5)
c/Å	16.6531(14)	16.7869(9)
$\alpha, \beta, \gamma/^{\circ}$	90, 93.309(2), 90	90, 92.6180(10), 90
$V/Å^3$	1888.0(3)	1968.54(19)
Ζ	4	4
$\rho_{calc}/mg/m^3$	1.254	1.250
$\mu(MoK_{\alpha})/mm^{-1}$	0.089	0.088
Temperature/ K	296	296
Angle range $\theta/^{\circ}$	$2.57 \le \theta \le 29.00$	$2.43 \le \theta \le 28.00$
Intervals of h , k and l indices	$-17 \le h \le 17,$	$-16 \le h \le 16,$
	$-12 \le k \le 12,$	$-12 \le k \le 12,$
Deflections measured	$-21 \le l \le 21$	$-22 \le l \le 22$
Independent reflections	1/944 4076 P = 0.0364	$\frac{19777}{4746} P = 0.0260$
De Comment and it has	$4970, R_{int} = 0.0304$	$4740, R_{int} = 0.0200$
Refinement variables	235	248
Goodness of fit by F^2	0.992	1.038
<i>R</i> -factors by $I \ge 2\sigma(I)$	0.0542, 0.1457	0.0456, 0.1186
<i>R</i> -factors by all reflections	0.1205, 0.1675	0.0748, 0.1306
$\Delta \rho \ (min/max)/e \ \text{\AA}^{-3}$	-0.21/0.21	-0.21/0.17

 Table 3. Crystallographic data, solution and refinement parameters for 1 and 2

The structures have been deposited with CCDC under the numbers 1472457 (1), 14724578 (2), 1472459 (3), and 1472460 (4), where the corresponding CIF files can be freely obtained on request on the web site: www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

The calorimetric data (Table 1) show that the heating of polycrystalline samples of all the compounds results in a crystal–crystal phase transition in them.

The subsequent phase transitions in compounds 1 and 2 are monotropic. This means that the mesophase is not formed by melting these compounds. It appears only during cooling the isotropic melt. The transition to the nematic (N) phase for compound 3 is enantiotropic and that to the smectic (SmA) phase is monotropic. That is, only the nematic phase is formed during melting this compound and both the nematic and smectic phases emerge upon cooling the melt. For the middle members of the homologous series, the smectic phase is either absent (n = 5, compound 1) or the phase transition in it is monotropic in character (n = 6 or 7, compounds 2 and 3), i.e., occurs during cooling the N phase.

The crystal–crystal phase transition in polycrystalline **4** has a high enthalpy ($\Delta H = 37.15 \text{ kJ/mol}$), that is, this phase transition must be accompanied by a profound rearrangement of the crystal structure. The resulting high-temperature crystalline modification is the precursor of the SmA phase. The phase transition of this compound into the smectic phase and the subsequent transition to the nematic (N) phase are enantiotropic. During their heating, single crystals of **4** are destroyed at a temperature of ~58°, which is somewhat above the temperature of the crystal–crystal phase transition in the polycrystalline sample.

A comparison of the experimental and theoretical X-ray diffraction patterns of 1-3 shows that these are single-phase samples. The unit cell parameters obtained for substances 1-3 (Table 2) as a result of the X-ray structure analysis coincide within the error with those calculated from the powder diffraction data. Thus, the single crystals examined are exactly the

Compound	3	4	
Formula	C ₂₃ H ₂₈ O ₅	C ₂₄ H ₃₀ O ₅	
Molecular weight	384.45	398.48	
Crystal system	Rhombic	Rhombic	
Space group	$Pna2_1$	$Pna2_1$	
a/Å	18.069(2)	18.085(2)	
b/Å	7.9263(10)	7.9559(17)	
c/Å	14.7451(19)	15.3393(7)	
$\alpha, \beta, \alpha/^{\circ}$	90, 90, 90	90, 90, 90	
V/Å ³	2111.8(5)	2207.1(4)	
Ζ	4	4	
$\rho_{calc}/mg/m^3$	1.209	1.199	
$\mu(MoK_{\alpha})/mm^{-1}$	0.084	0.083	
Temperature/K	296	296	
Angle range $\theta/^{\circ}$	$2.25 \le \theta \le 28.0$	$2.25 \le \theta \le 27.6$	
Intervals of h , k and l indices	$-23 \le h \le 23$	$-23 \le h \le 23$	
	$-10 \le k \le 9$	$-10 \le k \le 10$	
	$-19 \le l \le 18$	$-19 \le l \le 19$	
Reflections measured	17441	21016	
Independent reflections	2645, $R_{\rm int} = 0.0889$	2654, $R_{\rm int} = 0.0361$	
Refinement variables	253	263	
Goodness of fit by F^2	0.899	1.009	
<i>R</i> -factors by $I > 2\sigma(I)$	0.0481, 0.0915	0.0385, 0.0912	
<i>R</i> -factors by all reflections	0.1558, 0.1143	0.0702, 0.1019	
$\Delta o (min/max)/e Å^{-3}$	-0.10/0.19	-0.14/0.12	

Table 4. Crystallographic data, solution and refinement parameters for 3 and 4

same substances as powdered 1-3 in their qualitative and quantitative compositions and structure.

The X-ray diffraction pattern of sample 4, in addition to lines corresponding to a single crystal, contains additional lines that have been indexed in the monoclinic system with the following parameters: a =19.00(2), b = 12.45(1), c = 15.60(2) Å, $\beta = 92.7(1)^{\circ}$, V = 3684(1) Å³. Phase transitions in powdered 4 dramatically differ from those in the powder of 3, whereas the single crystals of these compounds are isostructural. Therefore, it can be assumed that the difference between the thermograms of powdered 3 and 4 is due to the monoclinic form of compound 3, which we have failed to obtain via the slow crystallization of this compound.

Single crystals of 1-3 do not show outward signs of degradation until reaching the melting point. This means that the transition to a high-temperature crystalline modification occurs without the destruction of the single crystal, a fact that is consistent with their low enthalpy values. The molecular structure of 1-4 is shown in Fig. 1.

In the structure of 4, the C21...C22 segment of the aliphatic chain is disordered over two positions. There is no disorder of this kind in the structure of 3, but it is to be noted that the terminal atoms of the aliphatic chain have higher values of the temperature parameters than the other atoms of the molecules.

In all the four molecules, the OH group in the 3-position on the benzene ring C8...C13 forms an intramolecular hydrogen bond with the propionyl carbonyl group. The (O4)H4...O5 distances of 1.84, 1.69, 1.85, and 1.84 Å in 1, 2, 3, and 4, respectively, are common for the hydrogen bond that closes a sixmembered ring.

The molecules are nonplanar. The ester group lies in the plane of the benzene ring C2... C7, and the benzene ring C8...C13 is rotated around the O1–C8 bond out of this plane. The dihedral angle between the planes of the benzene rings is $67(1)^\circ$, $63(1)^\circ$, $59.5(4)^\circ$, or $60.9(3)^\circ$ in **1**, **2**, **3**, or **4**, respectively.

Previously, we showed that the crystal packing of thermotropic LC compounds have two specific features. First, they are composed of alternating loose



Fig. 1. Structure of molecules 1-4 (numbering from top down); ellipsoids of thermal standard deviations of the atoms are given at the confidence level of 50%.

and close areas. The loose areas include aliphatic moieties, and the close areas consist of conformationally rigid aromatic moieties. Second, in closely packed areas, is a system of secondary bonds, which are presumably responsible for the preservation of supramolecular assemblies in the mesophase; i.e., they are the "supporting contacts" of the mesophase [7-18].

In the crystal packing of 1 and 2 (Fig. 2), there are no loose aliphatic areas; that is, the first condition of mesophase formation is not fulfilled. On the basis of the calorimetric data obtained, it can be concluded that although the crystals of 1 and 2 grown from solutions at room temperature do not represent the hightemperature phase, they differ little from it, since the crystal–crystal phase transition has a low enthalpy and occurs without destruction of the single crystal. Therefore, it is clear that these compounds do not form a mesophase upon heating.

The crystal packing of isostructural compounds 3 and 4 also does not show the alternation of close aromatic and loose aliphatic areas. However, the disorder of the aliphatic chain segment in 4 and the high values of thermal parameters for the terminal atoms of the alkyl chain in 3 are indications that these moieties of the molecules occur in a quite loose crystalline environment. In addition, the end atoms of the alkyl chain form long intermolecular C...C contacts exceeding



Fig. 2. Fragment of the crystal packing of 1.

3.9 Å. It is likely that the transition to the high-temperature phase in the crystals of 3, which is not accompanied by the destruction of the single crystal with a relatively low enthalpy, is associated with the expansion of loose crystal areas, the presence of which is the first condition for the formation of the mesophase from the crystal. This explains the emergence of the nematic phase during the melting of the high-temperature modification of 3.

Regarding the examined crystalline modification of single crystals of **4**, it is not a precursor of the hightemperature modification that undergoes the phase transitions revealed (Table 1).

These structures belong pairwise to the monoclinic $(P2_1/c, \text{ structures 1 and 2})$ and orthorhombic $(Pna2_1, 3 \text{ and 4})$ crystal systems. Since compounds 1 and 2, are the closest homologues, as well as 3 and 4, the pairwise isostructural character is not surprising. At the same time, the buildup of differences in the molecular structure through the homologous series of 1-4 apparently leads to another, monoclinic crystalline modification in the last member of the series (4), whose structure of the rhombic modification of 3.

The second condition for the formation of the mesophase during the melting of crystals is the existence of secondary bonds responsible for melt structuring. Weak hydrogen bonds C–H...O, which link molecules in infinite chains developing around the helical axis 2_1 , were revealed in the crystals of **3** and **4**. Figure 3 shows one unit of the infinite chain in the structure of 3; a similar chain element was also found in the crystals of **4**, in which the O4...H6 distance is 2.58 Å. In intermolecular hydrogen bonding, the C4– H4 segment of the benzene ring acts as a proton donor. This segment is oriented onto the lone electron pair, located on the sp^2 orbital, of the oxygen atom O5. In addition, the hydrogen atoms of the C2...C7 benzene ring are pretty "acidic" because of the presence of two electron-withdrawing substituents, the ether and ester groups, on the ring. It is apparently these interactions



Fig. 3. Pair of molecules of 3 linked by the C-H...O hydrogen bond; the distance is given in Å.



Fig. 4. Centrosymmetric π - π dimer in the crystal packing of 1 (in two projections).



Fig. 5. Scheme. The graph showing two versions of the crystal packing of LC compounds; the rectangles represent the hard core of the molecule, and the zigzags depict aliphatic chains.

that are responsible for the appearance of the nematic phase during the melting of the high-temperature phase of crystals **3**.

In contrast to the crystals of **3** and **4**, there is π -stacking interaction yielding centrosymmetric dimers in the crystal packings of **1** and **2**. The structure of such a dimer in **1** is shown in Fig. 4; the dimer in **2** has a similar structure.

In the dimer, the conjugated segments of the C8...C13 benzene rings of the molecules and the closest substituents to them, the O atoms, are projected

onto one another. The interplanar distance (3.66 Å in 1 and 3.68 Å in 2) corresponds to weak directional π - π interaction.

The crystals of 1-4 were grown from the solutions at room temperature when the flexibility of aliphatic chains is less important for the self-organization of the molecules in the liquid phase prior to crystal nucleation and the subsequent crystal growth than in the case of crystallization from the melts. During the crystal growth from the melts, the flexibility of aliphatic chains is high, as well as the amplitude of their thermal vibrations. Therefore, they have a large effective size. During the crystallization from the melt, the optimization of two conflicting requirements, the close packing of the molecules and the presence of additional volume for mobility aliphatic chains, leads to the situation that the chains tend to stay in close proximity to each other. Indeed, in this case, an additional volume of the space required for the mobile aliphatic chain of one molecule (ΔV) is becoming common for the two adjacent molecules providing that their thermal fluctuations are synchronized. This reasoning can be extended further to a large number of molecules. For this reason, the crystal packing of LC compounds obtained by cooling the melt, must consist of alternating loose and dense areas, that is, be different from the one formed upon crystallization from solutions. The cooling of the melts is accompanied by the emergence of weak directional interactions between molecules to provide their frameworking, i.e., the appearance of the mesophase.

Analysis of XRD data for LC compounds [7-18] shows that there are two kinds of crystal packing of mesogenic crystals that undergo the crystal–meso-phase phase transition (scheme).

The molecules are packed in the head-to-tail mode in the upper graph and in the head-to-head mode in the lower graph. A greater distance of the aliphatic parts of the molecules from each other relative to the hard cores can be achieved in two ways, by arranging the aliphatic chains on the opposite sides of the rigid central core (top graph) and displacing the hard cores of adjacent molecules with respect to each other with a simultaneous bent of the aliphatic chains from the long axes of the rigid cores (bottom graph). Both kinds of arrangement of the aliphatic, rather than aromatic parts from each other; in both cases, the distances are $d_1 < d_2$. Both of these arrangements are met in crystal packings of LC compounds [7–18].

In the crystal structures of the test homologues, there can be two types of directional weak interactions, π -stacking and weak hydrogen bonding C– H...O. Therefore, the cooling of an isotropic melt can entail the successive appearance, first, of the nematic phase due to the formation of interactions of one type (in the case of compound 1) and, then, the smectic phase due to the formation of the second type of interaction, which is indeed the case observed in compounds 2, 3, and 4.

CONCLUSIONS

In the test crystals of compounds 1-4, the existing crystal packing is not of the type that precedes the formation of the mesophase. The presence of two types of weak directional interactions, the "supporting contacts", in the crystals opens the possibility for the formation of both the nematic or smectic phases upon cooling the isotropic melts of the compounds.

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