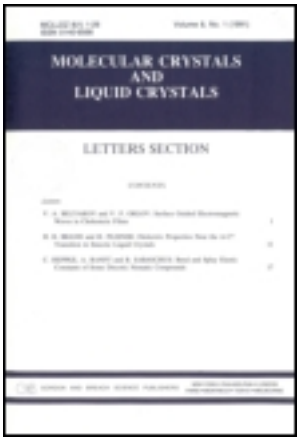

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X-Ray Diffraction Studies of 4-n-Decyl(oxy)phenyl-4′-n′-butyl(oxy)benzoate and 4-n-Decyl(oxy)phenyl-4′-n′-hexyl(oxy)benzoate

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X-Ray Diffraction Studies of 4-n-Decyl(oxy)phenyl-4'-n'-butyl(oxy)benzoate and 4-n-Decyl(oxy)phenyl-4'-n'-hexyl(oxy)benzoate

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*Liquid crystal aromatic esters of compositions $C_{10}H_{21}OC_6H_4C(O)OC_6H_4OC_4H_9$ (**1**) and $C_{10}H_{21}OC_6H_4C(O)OC_6H_4OC_6H_{13}$ (**2**) have been investigated by X-ray structural analysis. On temperature rise, these compounds undergo phase transitions crystal-smectic (S_A)-nematic-isotropic (**1**) and crystal-smectic (S_C)-smectic(S_A)-nematic-isotropic (**2**) at temperatures 64.5, 80.7, 89.1°C and 62.0, 77.0, 82.5, 88.5°C, respectively. Crystal packing of the compounds consists of alternating loosely packed aliphatic and closely packed aromatic regions. The number of types of weak directional interactions in aromatic regions in both crystal packings was found to be equal to a number of phase transitions in crystal-mesophase-isotropic systems.*

Keywords Aromatic esters; crystal packing; liquid crystals; weak interaction; X-ray structure

1. Introduction

According to statements of supramolecular chemistry, in liquid phase, structural unit self assembling takes place due to the weak directional interactions of different types [1]. These statements are also applicable to liquid crystals [2]. It is accepted that self assembly processes in liquid phase and crystal growth are based on interactions of the same nature – intermolecular weak directional interactions, such as hydrogen bonds, $\pi..\pi$ and C−H . . . π interactions, other weak interactions, and also van-der-Waals interactions. This means that the crystal packing and the mesophase formed from the crystal may be very close to one another in design, although the mesophase structure should be much less ordered and more loose. Crystal packing of mesogenic compounds is of great interest. An X-ray structure determination provides us not only with knowledge of the strict crystal packing but also somewhat indicates how it may alter in mesophase. Systems of weak directional interactions play a key role in particular crystal packing. These interactions partly retain in the mesophase; they are responsible for its structuring. Previously, we have investigated

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crystal packing for series of organic liquid crystals. Homologues of alkyloxybenzoic acids $C_nH_{2n+1}OC6H4COOH$ [3], alkylbenzoic acids $C_nH_{2n+1}C_6H_4COOH$ [4,5], toluidines [6–8], alkyloxycyanobiphenyls [9], alkylcyanobiphenyles [10], and several aromatic esters [11,12] are also among them. General peculiarity of all crystal packings is a separation of crystal on alternating loosely packed aliphatic regions and closely packed aromatic regions. The loose packing of aliphatic regions is, apparently, due to additional spatial requirements of these flexible groups during the crystal growth. On the contrary, aromatic regions are closely packed. Systems of weak directional interactions together with van-der-Waals interactions combine structure units in closely packed regions.

Aromatic esters of compositions $C_{10}H_{21}OC_6H_4C(O)OC_6H_4OC_4H_9$ (**1**) and $C_{10}H_{21}OC_6H_4C(O)OC_6H_4OC_6H_{13}$ (**2**) represent mesogenics. They are characterized by the phase transitions crystal-smectic(S_A)-nematic-isotropic (**1**) and crystal-smectic(S_C)-smectic(S_A)-nematic-isotropic (**2**) at temperatures 64.5, 80.7, 89.1°C and 62.0, 77.0, 82.5, 88.5°C, respectively [13].

2. Experimental

Single crystal of **1** and **2** of were grown from benzene-acetonitrile solution. Single crystals with sizes 0.44 × 0.28 × 0.18 mm (**1**) and 0.46 × 0.42 × 0.03 mm (**2**) were subjected to X-ray single crystal measurements at a Bruker CCD SMART diffractometer (SMART-6K for **1**, and SMART-APEX-II for **2**) using graphite monochromatized MoK_α radiation under a stream of cooled nitrogen. Data reduction was performed using SAINT program [14]. Both structures were solved by direct methods and refined on F^2 by full-matrix least-squares in anisotropic approximation for nonhydrogen atoms using SHELXTL-Plus software [15]. For both structures, positions of hydrogen atoms were calculated and refined using "riding" model. A summary of the crystallographic data and structure determination parameters is provided in Table 1.

3. Results and Discussion

3.1. Molecular Structure

Molecular structures of compounds **1** and **2** are shown in Figs. 1 and 2. Independent part of the crystal unit cell of **2** includes two molecules.

The molecules in both compounds are nonplanar, but composed of planar fragments. In **2**, these fragments are benzene ring C2 . . . C7 (C2A . . . C7A) with ester group—plane *a*; benzene ring C8 . . . C13 (C8A . . . C13A) – plane *b*; alkyloxy group O3 . . . C23

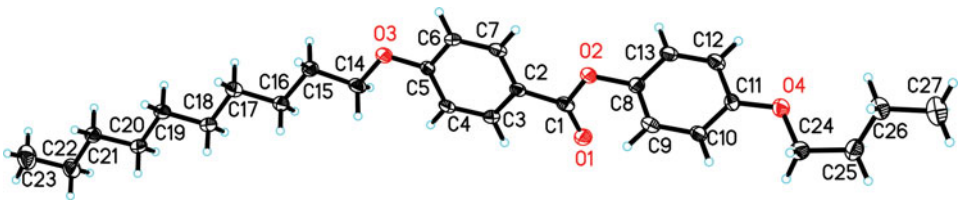

Figure 1. Molecular structure of compound **1**; ellipsoids of anisotropic temperature displacements are given at 50% probability level.

Table 1. Crystal data and structure refinement for compounds **1** and **2**

Compound	1 (10/4)	2 (10/6)
CCDC entry no.	932530	934165
Empirical formula	$C_{27}H_{38}O_4$	$C_{29}H_{42}O_4$
Formula weight	426.57	454.63
Temperature (K)	153(2)	123(2)
Space group	*C*2/*c*	*P* $\bar{1}$
a (Å)	38.146(5)	5.5816(5)
b (Å)	5.3593(6)	14.714(3)
c (Å)	24.062(3)	33.166(4)
α (°)	90	99.008(14)
β (°)	91.329(7)	90.802(9)
α (°)	90	91.760(12)
Volume (Å^3)	4917.8(11)	2688.4(7)
Z	8	4
D_{calc} (Mg m^{-3})	1.185	1.123
Absorption coeff. (mm^{-1})	0.077	0.073
F(000)	1904	992
Collected refl./uniq refl.	10,468/5472	27,662/12,984
Data/restraints/parameters	4394/ 0 /281	4502/0/595
GOF on F^2	0.921	0.945
R_1/wR_2 [$I > 2\sigma(I)$]	0.0652/0.1566	0.0981/0.1504
R_1/wR_2 (all data)	0.1604/0.2257	0.2518/0.2056
Largest peak/hole (e/A^3)	0.339 and –0.269	0.304 and –0.295

(O3A . . . C23A) – plane *c*; alkyloxy group O4 . . . C29 (O4A . . . C29A) – plane *d*. Dihedral angles *a*/*b*, *a*/*c*, and *b*/*d* are equal to 56.4 (57.8), 10.8 (15.1), and 10.9° (9.5°), respectively.

Similarly, the molecular structure of **1** contains planar fragments *a*, *b*, *c*, but rather short chain O4 . . . C27 is nonplanar. The O4-C24-C25-C26 torsion angle equals 62.6° which corresponds to "*gosh*", rather than "*anti*" conformation typical for long alkyl chains in mesogens. Torsion angle C10-C11-O4-C24 (2.5°, plane d) is close to zero, which is,

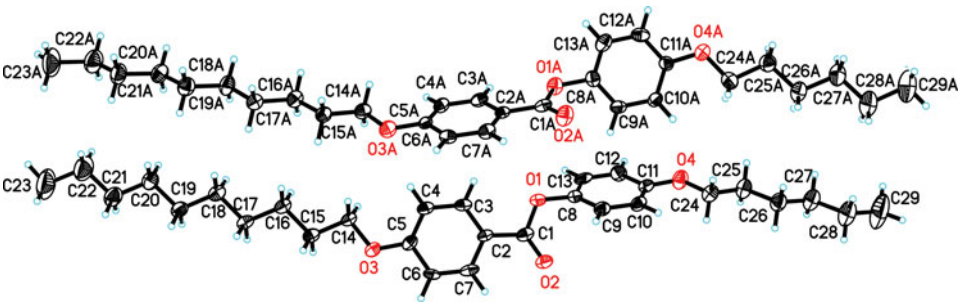

Figure 2. Molecular structure of compound **2**; ellipsoids of anisotropic temperature displacements are given at 50% probability level.

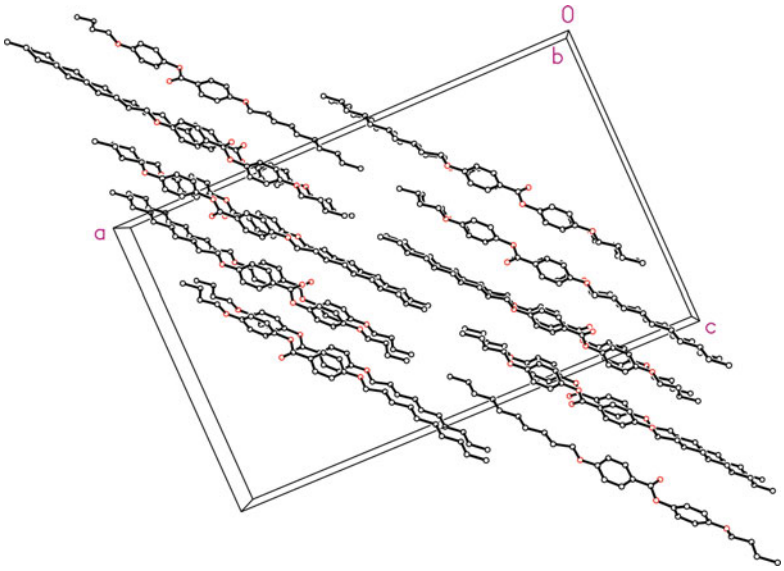

Figure 3. View of crystal packing of **1**.

apparently, due to a conjugation of O4 lone pair with the π-system of the corresponding benzene ring. Analogous torsion angle in molecule **2** also represents near planar geometry. In **1**, dihedral angles a/b, a/c, and b/d are equal to 64.6, 10.8, and 2.6°, respectively, and are close to the same angles in **2**. Dihedral angle between plane *b* and plane C25 C26 C27 is equal to 116.8°.

3.2. Crystal Packing

The shapes of molecules **1** and **2** are rather similar, so one may expect identical packing motifs for both compounds. The X-ray study shows that these crystal packings are different.

General views of crystal packing in **1** and **2** are shown at Figs. 3 and 4.

The main peculiarity of both crystal packings is an alternation of regions composed of aromatic and aliphatic fragments. This peculiarity is typical for other liquid crystals containing aromatic fragments [3–12]. "Aliphatic" regions are characterized by a very loose packing. Indeed, in crystals **1** and **2**, there are a few rather short contacts (~2.8 Å)

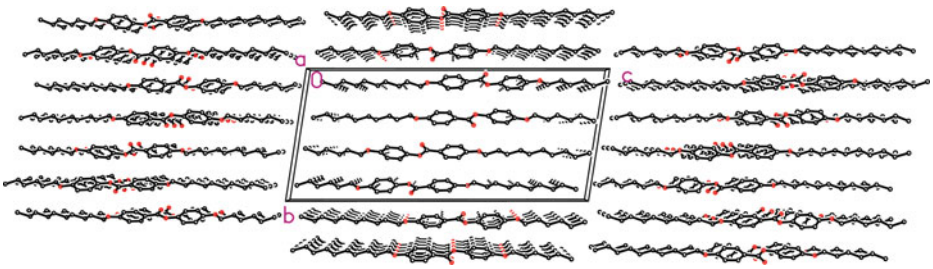

Figure 4. View of crystal packing of **2**.

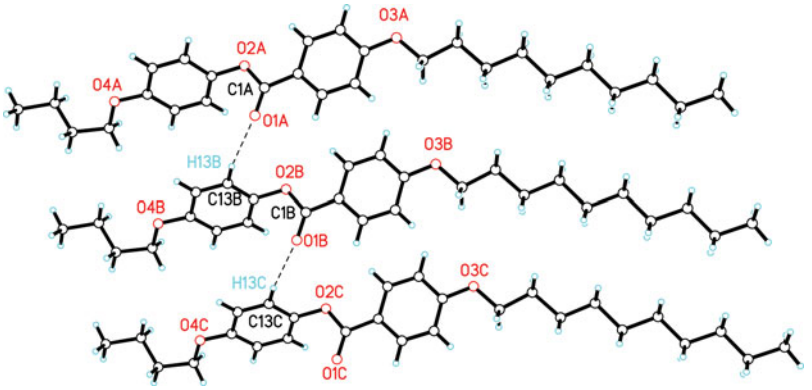

Figure 5. System of hydrogen bonds in **1**.

between hydrogen atoms of aliphatic groups. The other intermolecular distances of such type are longer than 3.0 Å. This may be explained by fluxionality of aliphatic fragments in preceding solution that required an additional volume for them in crystal.

By contrast, "aromatic regions" in crystals of **1** and **2** are characterized by a rather close packing due to intermolecular weak directional interactions. In crystals **1** and **2**, weak hydrogen bonds C−H . . . O occur (Figs. 5 and 6).

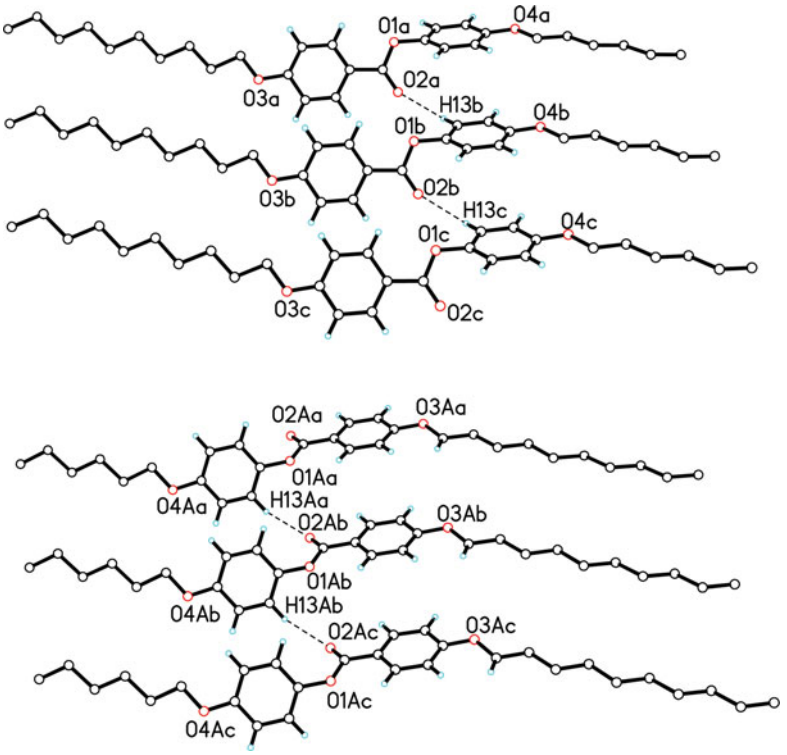

Figure 6. System of hydrogen bonds between crystallographically independent molecules in **2**.

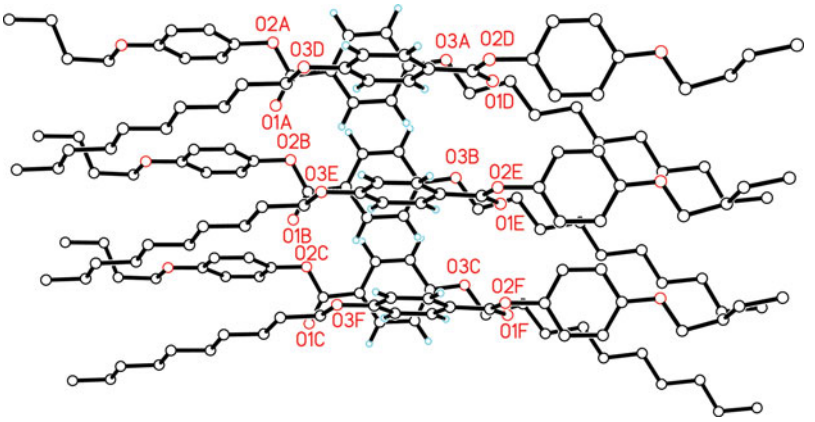

Figure 7. Fragment of crystal packing of **1** with C−H . . . π-system interactions.

Molecules in **1** and both independent molecules in **2** are combined in translation related infinite chains. These assemblies have "head-to-head" organization. Distance O . . . H and angles C=O . . . H13, O . . . H−C are equal to 2.45 Å and 142°, 161° in **1**, and 2.58 Å and 148°, 158° in **2**, respectively.

Other weak directional interactions in these structures are different. In crystal of **1**, the molecules form layers (Fig. 7), in which benzene rings C2 . . . C7 of adjacent molecules adopts T-shaped mutual organization characteristic of C−H . . . π-system interactions [16].

A pair of molecules that interact in this manner is shown at Fig. 8.

Atom H4 of benzene ring C2A . . . C7A is projected onto the π-system of adjacent ring C2B . . . C7B. The distances between of H4AA atom and atoms C2B, C3B, C4B 3.17, 2.92, 2.97 Å correspond to the weak interaction [16].

In crystals of **2**, this type of interactions is also observed between two independent molecules. Moreover, in this structure both benzene rings participate in this interaction according to the following scheme:

Closest distances in this couple are C3A . . . H3A (3.0 Å) and H9A . . . C8A (2.93 Å). These values correspond to usual values for this type interactions [17].

In addition, stacking interactions in the centrosymmetric pairs of both independent molecules is observed (Fig. 9).

Finally, one may conclude that crystal melting begins from the loose aliphatic regions of crystals. Under these conditions aromatic regions still hold their structure to give smectic

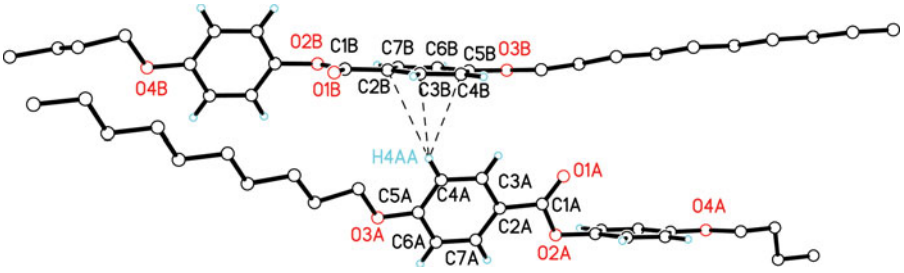

Figure 8. System of two molecules with C−H . . . π-system interactions.

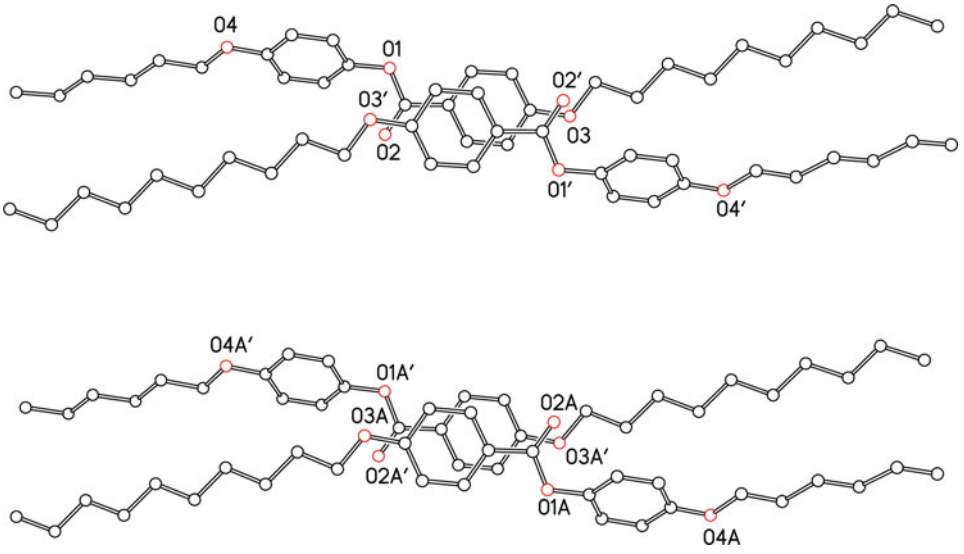

Figure 9. Mutual projecting in centrosymmetric pairs of molecules in **2**.

mesophase. With the further temperature rise the weakest of the interamolecular interactions destroy, and the system transits to the nematic phase in the case of **1**, whereas, in **2**, it converts into the second smectic phase. The further temperature rise results in transition to isotropic liquid.

Thus, crystal packing of **1** is characterized by a set of two weak directional interactions, and crystal packing of **2** – by a set of three weak interactions. Apparently, hydrogen bonds C−H . . . O are the strongest interactions among all weak directional interactions observed in the investigated crystals. The conclusion can be obtained from the fact that the last phase transitions in **1** and **2** occur at the same temperature.

The observed peculiarities of these crystal packings may explain their phase transitions in the mesogenic phase. In **1**, with the temperature increase, C–H . . . π interactions are destroyed first, and then hydrogen bonds C–H . . . O are subjected to destruction. In **2**, with the temperature increase, two interactions C–H . . . π or π–π are consequently destroyed at different temperatures, and finally, hydrogen bonds C–H . . . O are subjected to destruction. These schemes of weak interactions destruction correspond to the crystal-smectic(S_A)-nematic-isotropic (**1**) and crystal-smectic(S_C)-smectic(S_A)-nematic-isotropic (**2**) phase transitions, respectively.

4. Conclusions

Crystal packings of mesogenic esters $C_{10}H_{21}OC_6H_4C(O)OC_6H_4OC_4H_9$ (**1**) and $C_{10}H_{21}OC_6H_4C(O)OC_6H_4OC_6H_{13}$ (**2**) manifest different crystal packing motifs and different systems of weak directional interactions. The observed peculiarities of these crystal packings may explain peculiarities of their phase transitions in the mesogenic phase.

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