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Banana-Shaped Liquid Crystals Based on 2,7-Dihydroxynaphthalene Derivatives

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Abstract—New mono- and dichloro-substituted derivatives of 2,7-dihydroxynaphthalene were synthesized, and their mesomorphic properties were investigated. Bis-2,7-[4-(4-*n*-alkoxybenzoyloxy)-3-chlorobenzoyloxy]-naphthalenes with the terminal nonyloxy or decyloxy group were found to form nematic and B_1 mesophases; the homolog with dodecyloxy group formed B_2 modification exclusively. Bis-2,7-[4-(4-*n*-alkoxybenzoyloxy)-3,5-dichlorobenzoyloxy]naphthalenes occurred to be non-mesomorphic and vitrified from isotropic liquid.

Keywords: 2,7-dihydroxynaphthalene derivatives, mesomorphic properties, banana-shaped liquid crystals

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Banana-shaped compounds are known to form seven modifications of biaxial smectic mesophase [1]. The eighth modification has been described in [2]. Compounds which can form mesophase B_2 with ferroelectric properties and possess twisting ability have practical importance for increasing the response speed of the liquid-crystal displays. Therefore the study of the relation between the structure of the banana-shaped compounds and their ability to form mesophase B_2 is an urgent problem.

It is known that introduction of the fluorine atom into the structure of banana-shaped compounds usually leads to the appearance of phase B_2. The synthesis and mesomorphic properties of unsubstituted and fluorine-substituted 2,7-dihydroxynaphthalene diesters have been reported in [3]. The majority of the compounds form mesophases B_1 and B_2. For the fluoro-substituted diesters the reduction of the phase-transition temperatures was observed; their lower homologs form only a nematic phase.

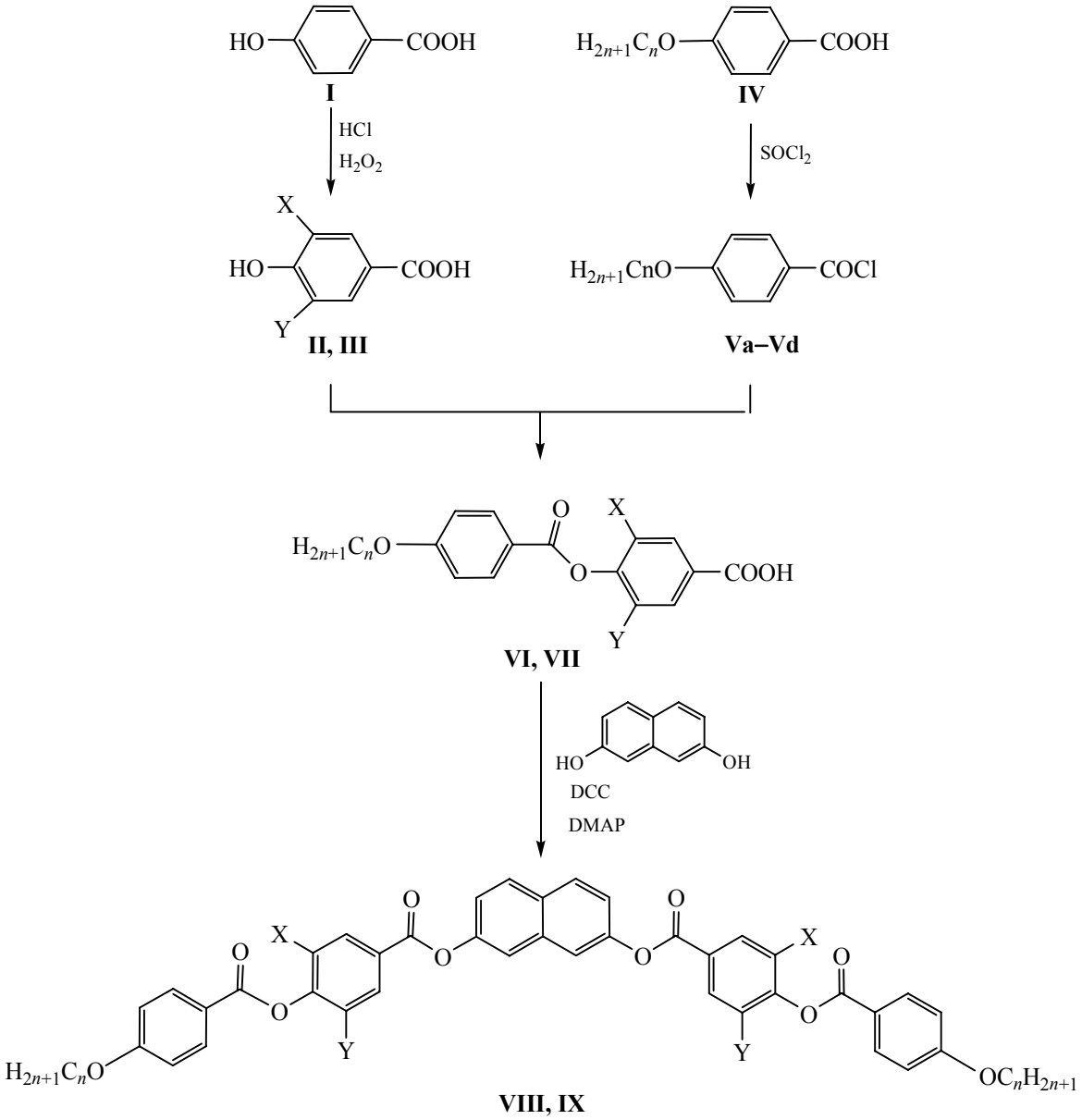
The same researchers [4] investigated mesomorphic properties of 2,7-dihydroxynaphthalene diesters containing a fluoro-substituted aromatic moiety. In both cases the B_2 phase appeared if the terminal alkoxy group contained no less than 10–11 carbon atoms. The mesomorphism of 4-chloro-1,3-dihydroxybenzene diester containing a terminal nonyloxy group and forming nematic mesophase has been reported in [5]. The increase in the terminal group length up to 14 carbon atoms caused appearance of unidentified smectic phase together with the nematic one [6]. The presence of a double bond in the terminal decyloxy group reduced the temperature range of the nematic phase existence [7].

1-Chloro-2,7-dihydroxynaphthalene diesters are known to form mesophase B_2 if the terminal alkoxy group contained 12 carbon atoms [8].

In the present work the method of synthesis of banana-shaped 2,7-dihydroxynaphthalene esters containing chloro-substituted aromatic rings was developed; moreover, the impact of the substituents structure on mesogenic property of the molecules was investigated.

The target 2,7-dihydroxynaphthalene derivatives **VIIIa**–**VIIIc** and **IXa**–**IXd** were prepared by esterification of 4-(4-*n*-alkoxybenzoyloxy)-3-chloro- and 4-(4-*n*-alkoxybenzoyloxy)-3,5-dichlorobenzoic acids **VIa**–**VIc** and **VIIa**–**VIId** using carbodiimide procedure. 3-Chloro- and 3,5-dichlorobenzoic acids **II** and **III** were prepared by the known method [9]. 4-Alkoxybenzoic acid chlorides **Va**–**Vd** were obtained

Scheme 1.



X = H, Y = Cl (**II**); X = Y = Cl (**III**); *n* = 9 (**Va**), 10 (**Vb**), 12 (**Vc**), 16 (**Vd**); X = H, Y = Cl, *n* = 9 (**VIa, VIIIa**) 10 (**VIb, VIIIb**), 12 (**VIc, VIIIc**); X = Y = Cl, *n* = 9 (**VIIa, IXa**), 10 (**VIIb, IXb**), 12 (**VIIc, IXc**), 16 (**VIId, IXd**).

by treating the corresponding acids with thionyl chloride [10] (Scheme 1).

The structures of new chlorine-containing acids **VIa**–**VIc** and **VIIa**–**VIId**, and the target products **VIIIa**–**VIIIc** and **IXa**–**IXd** were established by ^{1}H NMR spectroscopy.

Transition points and mesomorphism type of 4-(4-*n*-alkoxybenzoyloxy)benzoic acids **VIa**–**VIc** and **VIIa**–**VIId** were determined by polarization microscopy method (Table 1); for comparison, characteristics of unsubstituted 4-(4-*n*-alkoxybenzoyl-oxy) benzoic acids **VII'a**–**VII'd** are also provided [8].

The presented data indicate the reduction of the transition point to isotropic liquid as follows: **VII'a**–**VII'd** > **VIa**–**VIc** > **VIIa**–**VIId**.

The introduction of the chlorine atom into the molecule led to the absence of polymorphism in both mono- and dichloro-substituted acids whereas their

Table 1. Transition points of 4-(4-*n*-alkoxybenzoyloxy)-3-chlorobenzoic acids **VIa**–**VIc**, 4-(4-*n*-alkoxybenzoyloxy)-3,5-dichlorobenzoic acids **VIIa**–**VIId**, and their unsubstituted analogs **VII'a**–**VII'd**[a]

Comp. no.	*n*	X	Y	Transition point, °C							
				Cr		Sm		N			I
VIa	9	Cl	H	•	95.4	−		•	177		•
VIb	10	Cl	H	•	108.2	−		•	173		•
VIc	12	Cl	H	•	95.4	−		•	157.2		•
VIIa	9	Cl	Cl	•	148	−		−			•
VIIb	10	Cl	Cl	•	120	−		(•	112)		•
VIIc	12	Cl	Cl	•	117	−		(•	110)		•
VIId	16	Cl	Cl	•	92.3	−		(•	85.6)		•
VII'a	9	H	H	•	125	•	140	•	205		•
VII'b	10	H	H	•	133	•	204	•	218		•
VII'c	12	H	H	•	120	•	182	•	213		•
VII'd	16	H	H	•	115	•	>200	•	[b]		•

[a] Here and further: Cr is solid crystal, N is nematic phase, Sm is smectic phase, I is isotropic liquid, (•) is monotropic mesophase, *n* is the number of the carbon atoms in the terminal alkoxygroup. [b] Measurement of the transition point to isotropic liquid did not succeed.

unsubstituted analogs **VII'a**–**VII'd** formed nematic and smectic phases. Comparison of mesomorphism of mono- and dichloro-substituted acids showed that 4-(4-*n*-alkoxybenzoyloxy)-3-chlorobenzoic acids **VIa**–**VIc** exhibited the enantiotropic nematic mesophase while for their dichloro-analogs **VIIa**–**VIId** the monotropic nematic phase was observed. Compounds **VIIa** containing nine carbon atoms in the terminal chain did not possess mesogenic capability that was apparently caused by distortion of the geometric anisotropy of the molecule (insufficient length of the terminal fragment).

Mesomorphic characteristics of bis-2,7-[4-(4-*n*-alkoxybenzoyloxy)-3-chlorobenzoyloxy]naphthalenes **VIIIa**–**VIIIc** and bis-2,7-[4-(4-*n*-alkoxybenzoyloxy)-3,5-dichlorobenzoyloxy]naphthalenes **IXa**–**IXd** are given in Table 2; for comparison, characteristics of their unsubstituted analogs **IX'a**–**IX'd** are also provided [3].

The data presented in the Table 3 demonstrate that all banana-shaped compounds containing one chlorine atom at the aromatic ring are mesomorphic. Monochloro-substituted 2,7-dihydroxynaphthalene diester with terminal nonyloxy group **VIIIa** formed enantiotropic nematic and biaxial smectic modification B_1. The mesophase type and packing of the molecules were determined from the data of small angle X-ray scattering (see the figure). According to the data of X-ray phase analysis, the molecules in the blocks are oriented by their long axes along the length of the crystallographic cell.

The next homolog **VIIIb** displayed insignificant reduction of the transition points values, and the phase B_1 became monotropic. Further elongation of the terminal chain led to the appearance of the modification of banana-shaped mesophase B_2 in bis-2,7-[4-(4-*n*-dodecyloxybenzoyloxy)-3-chlorobenzoyloxy]naphthalene **VIIIc**. The data of small angle X-ray scattering of the sample of the compound oriented in magnetic field confirmed this modification formation. It was found that compound **VIIIc** formed mesophase with the layer thickness of 34.7 Å, and the molecules in the layer were tilted with respect to the plane of the layer by an angle of approximately 45° that corresponded to the bilayer banana-shaped smectic phase.

Introduction of the second chlorine atom into the aromatic ring of the side fragments led to the loss of mesogenic capability in compounds **IXa**–**IXd** (Table 2). At the same time melting points of bis-2,7-[4-(4-*n*-alkoxybenzoyloxy)-3,5-dichlorobenzoyloxy]naphthalenes **IXa**–**IXd** are significantly reduced compared to bis-2,7-[4-(4-*n*-alkoxybenzoyloxy)-3-chlorobenzoyloxy]-naphthalenes **VIIIa**–**VIIIc**, and the dichlorinated

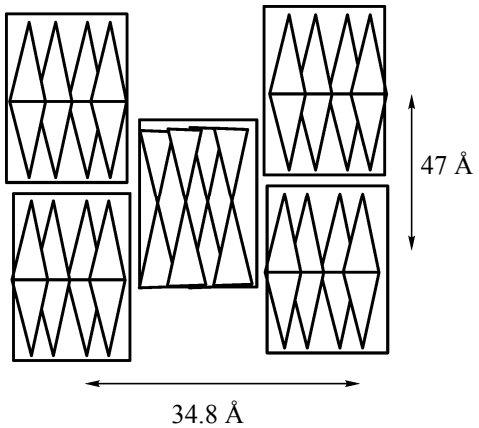
Table 2. Transition points of chlorine-containing (**VIIIa**–**VIIIc**, **IXa**–**IXd**) and unsubstituted 2,7-dihydroxynaphthalene esters (**IX'a**–**IX'd**)[a]

Comp. no.	*n*	X	Y	Transition point, °C								
				Cr		B_1		B_2	N			I
VIIIa	9	Cl	H	•	111.2	•	116.3	–	•	116.6	•	
VIIIb	10	Cl	H	•	104.8	•	(104.9)	–	•	112.9	•	
VIIIc	12	Cl	H	•	76.2	–		•	–	80.4	•	
IXa	9	Cl	Cl	•	(32.7)	–		–	–	68	•	
IXb	10	Cl	Cl	•	(21)	–		–	–	68	•	
IXc	12	Cl	Cl	•	(36.2)	–		–	–	75	•	
IXd	16	Cl	Cl	•	(40.2)	–		–	–	78.4	•	
IX'a	9	H	H	•	143	•		–	–	175	•	
IX'b	10	H	H	•	131	•		–	–	168	•	
IX'c	12	H	H	•	122	–		–	•	170	•	
IX'd	16	H	H	•	122	–		•	–	173	•	

[a] See Table 1.

analogs **IXa**–**IXd** are capable of supercooling and vitrification at room temperature.

In summary, bis-2,7-[4-(4-*n*-alkoxybenzoyloxy)-3-chlorobenzoyloxy]naphthalenes **VIIIa** and **VIIIb** are characterized by the appearance of an additional nematic phase compared to the unsubstituted analogs **IX'a** and **IX'b** which formed only mesophase B_1. For the formation of phase B_2 both the monochloro-substituted and unsubstituted 2,7-dihydroxynaphthalene diesters should contain no less than 12 carbon atoms in the terminal alkoxy group. In the case of bis-2,7-[4-(4-*n*-dodecyloxybenzoyloxy)-3-chlorobenzoyloxy]naphthalene **VIIIc** phase B_2 formation was observed under ordinary conditions and there was no necessity to place the sample in an electric field.



Packing of the molecules of compound **VIIIa** in mesophase B_1.

EXPERIMENTAL

^{1}H NMR spectra of the solutions in $CDCl_3$, DMSO-d_6, and CD_3OD were recorded on a Varian VXR-300 (300 MHz) and Bruker AVANCE DRX 500 (500 MHz) spectrometers, internal reference TMS. The reaction progress was monitored by TLC using Sorbifol AF-V-UV plates, eluting with acetone–hexane mixture (2 : 5) and developing with iodine vapor or UV light.

Transition points were determined by polarization microscopy method on a POLAM P-312 microscope. The X-ray phase analysis was done on a Bruker GAADS system. Dielectric response was measured with the use of analyzer of terminating impedance with the cell of 5 mm thickness and gold electrodes.

3-Chloro-4-hydroxybenzoic acid (II). 2 mL of 33% hydrogen peroxide was added to a suspension of 3.5 g (0.025 mol) of 4-hydroxybenzoic acid **I** in 10 mL of hydrochloric acid. The reaction proceeded almost instantly with self-heating of the reaction mixture up to 70°C. After cooling to room temperature, 70 mL of distilled water was added. The precipitate was filtered off, washed with water to pH 7, and recrystallized

from hot water. Yield 2.9 g (67.44%), white crystals, mp 174°C. ^{1}H NMR spectrum, δ, ppm: 7.05 d (1H, H^5, ^3J 7.53 Hz), 7.67–7.93 m (2H, $H^{2,6}$), 11.07 br.s (1H, OH), 12.79 br.s (1H, COOH).

3,5-Dichloro-4-hydroxybenzoic acid (III). 10 mL of 33% hydrogen peroxide was added to a suspension of 3.5 g (0.025 mol) of 4-hydroxybenzoic acid **I** in 10 mL of hydrochloric acid and 20 mL of water. The formed white precipitate was filtered off, washed with hot water, and recrystallized from ethanol. Yield 3.19 g (63.5%), white crystals, mp 265°C. ^{1}H NMR spectrum, δ, ppm: 7.84 s (2H, $H^{2,6}$). Found, %: C 40.64; H 1.87; Cl 34.34. $C_7H_4Cl_2O_2$. Calculated, %: C 40.58; H 1.93; Cl 34.30.

4-(4-*n*-Alkoxybenzoyloxy)-3-chlorobenzoic acids (VIa–VId) (general procedure). To a suspension of 6 mL of 3-chloro-4-hydroxybenzoic acid **II** in 25 mL of anhydrous pyridine was added dropwise 6 mmol of the corresponding 4-*n*-alkoxybenzoic acid chloride **V**. The reaction mixture was stirred at room temperature for 30 h then poured into ice water and acidified to pH 3. The formed white precipitate was filtered off, washed with water to pH 7, and then suspended in ethanol (100 mL) at room temperature followed by repeated filtration and drying.

4-(4-*n*-Nonyloxybenzoyloxy)-3-chlorobenzoic acid (VIa). Yield 1.5 g (62.1%), white amorphous powder. ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm: 0.89 t (3H, CH_3, *J* 6.9 Hz), 1.22–1.55 m (10H, CH_2), 1.77–1.91 m (2H, CH_2), 1.66–1.81 m (2H, CH_2), 4.10 t (2H, OCH_2 *J* 5.7 Hz), 7.15 d (2H, ArOAlk, *J* 8.1 Hz), 7.6 d (1H, ArCl, *J* 8.1 Hz), 8.00–7.98 d.d (1H, ArCl, *J* 8.1, 0.8 Hz), 8.09–8.12 m (3H, ArOAlk, ArCl). Found, %: C 65.99; H 6.38; Cl 8.42. $C_{23}H_{27}ClO_5$. Calculated, %: C 65.95; H 6.45; Cl 8.48.

4-(4-*n*-Decyloxybenzoyloxy)-3-chlorobenzoic acid (VIb). Yield 2.3 g (59%), white amorphous powder. ^{1}H NMR spectrum (DMSO-d_6, 500 MHz), δ, ppm: 0.86 t (3H, CH_3, *J* 5.7 Hz), 1.15–1.52 m (16H, CH_2), 1.68–1.85 m (2H, CH_2), 4.10 t (2H, OCH_2, *J* 5.7 Hz), 7.14 d (2H, ArOAlk, *J* 8.1 Hz), 7.60 d (1H, ArCl, *J* 8.0 Hz), 7.99–8.00 d.d (1H, ArCl, *J* 8.04, 0.78 Hz), 8.05–8.2 m (3H, ArOAlk, ArCl), 13.42 br.s (1H, COOH). Found, %: C 66.67; H 6.79; Cl 8.29. $C_{24}H_{29}ClO_5$. Calculated, %: C 66.59; H 6.71; Cl 8.21.

4-(4-*n*-Dodecyloxybenzoyloxy)-3-chlorobenzoic acid (VIc). Yield 1.9 g (59%), white amorphous powder. ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm: 0.86 t (3H, CH_3, *J* 6.9 Hz), 1.15–1.51 m (16 H, CH_2), 1.64–1.86 m (2H, CH_2), 4.09 t (2H, OCH_2, *J* 6.2 Hz), 7.15 d (2H, ArOAlk, *J* 8.7 Hz), 7.59 d (1H, ArCl, *J* 8.4 Hz), 7.98–8.00 d.d (1H, ArCl, *J* 8.4, 1.3 Hz), 8.06–8.26 m (3H, ArOAlk, ArCl). Found, %: C 67.81; H 7.12; Cl 7.78%. $C_{26}H_{33}ClO_5$. Calculated, %: C 67.75; H 7.17; Cl 7.71.

4-(4-*n*-Hexadecyloxybenzoyloxy)-3-chlorobenzoic acid (VId). Yield 1.73 g (48%), white amorphous powder. ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm: 0.85 t (3H, CH_3, *J* 6.9 Hz), 1.15–1.49 m (CH_2, 26H), 1.65–1.82 m (2H, CH_2), 4.09 t (2H, OCH_2, *J* 6.9 Hz), 7.14 d (2H, ArOAlk, *J* 8.7 Hz), 7.59 d (1H, ArCl, *J* 8.7 Hz), 7.98–8.00 d.d (1H, ArCl, *J* 8.4, 1.6 Hz), 8.07–8.20 m (3H, ArOAlk, ArCl). Found, %: C 69.79; H 7.8; Cl 6.95%. $C_{30}H_{41}ClO_5$. Calculated, %: C 69.70; H 7.94; Cl 6.87.

4-(4-*n*-Alkoxybenzoyloxy)-3,5-dichlorobenzoic acids (VIIa–VIId) *(general procedure)*. To a suspension of 4 mmol of 3,5-dichloro-4-hydroxybenzoic acid **III** in 25 mL of anhydrous pyridine was added dropwise 4 mmol of the corresponding 4-*n*-alkoxybenzoic acid chloride **V**. The reaction mixture was stirred at room temperature for 30 h, and then poured into ice. Four hours later the precipitate formed was filtered off, washed with cold ethanol (50 mL), and dried. The prepared compounds were white powders.

4-(4-*n*-Nonyloxybenzoyloxy)-3,5-dichlorobenzoic acid (VIIa). Yield 0.9 g (51.5%). ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm: 0.86 t (3H, CH_3, *J* 6.5 Hz), 1.16–1.52 m (CH_2, 12H), 1.68–1.85 m (2H, CH_2), 4.11 t (2H, OCH_2, *J* 6.5 Hz), 7.17 d (2H, ArOAlk, *J* 7.8 Hz), 8.05–8.26 m (4H, $ArCl_2$, ArOAlk). Found, %: C 60.85; H 5.79; Cl 15.76. $C_{23}H_{26}Cl_2O_5$. Calculated, %: C 60.93; H 5.74; Cl 15.67.

4-(4-*n*-Decyloxybenzoyloxy)-3,5-dichlorobenzoic acid (VIIb). Yield 5.56 g (79.5%). ^{1}H NMR spectrum (CD_3OD, 300 MHz), δ, ppm: 0.90 t (3H, CH_3, *J* 6.4 Hz), 1.26–1.52 m (CH_2, 14H), 1.70–1.95 m (2H, CH_2), 4.11 t (2H, OCH_2, *J* 6.4 Hz), 7.10 d (2H, ArOAlk, *J* 8.7 Hz), 8.08–8.19 m (4H, $ArCl_2$, ArOAlk). Found, %: C 61.77; H 5.92; Cl 15.29. $C_{24}H_{28}Cl_2O_5$. Calculated, %: C 61.67; H 6.00; Cl 15.20.

4-(4-*n*-Dodecyloxybenzoyloxy)-3,5-dichlorobenzoic acid (VIIc). Yield 6.0 g (71.3%). ^{1}H NMR spectrum (CD_3OD, 300 MHz), δ, ppm: 0.88 t (3H, CH_3, *J* 6.9 Hz), 1.52–1.18 m (CH_2, 18H), 1.75–1.90 m (2H, CH_2), 4.10 t (2H, OCH_2, *J* 6.9 Hz), 7.09 d (2H,

ArOAlk, *J* 8.7 Hz), 8.06–8.23 m (4H, $ArCl_2$, ArOAlk). Found, %: C 63.11; H 6.38; Cl 14.41. $C_{26}H_{32}Cl_2O_5$. Calculated, %: C 63.03; H 6.47; Cl 14.34.

4-(4-*n*-Hexadecyloxybenzoyloxy)-3,5-dichlorobenzoic acid (VIId). Yield 1.6 g (42.0%). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.88 t (3H, CH_3, *J* 6.9 Hz), 1.16–1.52 m (26H, CH_2), 1.76–1.90 m (2H, CH_2), 4.10 t (2H, OCH_2, *J* 6.9 Hz), 7.09 d (2H, ArOAlk, *J* 8.7 Hz), 8.04–8.26 m (4H, $ArCl_2$, ArOAlk). Found, %: C 65.45; H 7.35; Cl 12.80. $C_{30}H_{40}Cl_2O_5$. Calculated, %: C 65.34; H 7.26; Cl 12.89.

2,7-Bis[4-(4-*n*-alkoxybenzoyloxy)-3-chlorobenzoyloxy]naphthalenes (VIIIa–VIIIc) (*general preocedure)*. A suspension of 1.5 mmol of the corresponding 4-(4-*n*-alkoxybenzoyloxy)-3-chlorobenzoic acid **VIa**–**VIc**, 0.75 mmol of 2,7-dihydroxynaphthalene, and 0.15 mmol of 4-(dimethylamino)pyridine in 20 mL of anhydrous chloroform was stirred for 10 min at room temperature. Then 1.5 mmol of *N*,*N*'-dicyclohexylcarbodiimide was added. The reaction mixture was stirred for 20 h at room temperature. The precipitate formed was filtered off and washed with chloroform (3 × 20 mL). The organic layers were combined, washed, and evaporated. The residue was triturated with ethanol, and the crystalline solid obtained was recrystallized from a mixture benzene–ethanol. The prepared compounds were white powders.

2,7-Bis[4-(4-*n*-nonyloxybenzoyloxy)-3-chlorobenzoyloxy]naphthalene (VIIIa). Yield 0.4 g (55.6%). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.89 t (6H, CH_3, *J* 6.9 Hz), 1.23–1.59 m (24H, CH_2), 1.77–1.89 m (4H, $\underline{CH_2}CH_2O$), 4.06 t (4H, OCH_2, *J* 6.5 Hz), 7.00 d (4H, ArOAlk, *J* 9.0 Hz), 7.37–7.4 d.d (2H, naphthalene, *J* 9.0, 2.2 Hz), 7.49 d (2H, ArCl, *J* 8.7 Hz), 7.71 s (2H, naphthalene), 7.95 d (2H, naphthalene, *J* 8.7 Hz), 8.14–8.30 m (4H, ArOAlk, ArCl), 8.40 s (2H, ArCl). Found, %: C 69.99; H 6.13; Cl 7.48. $C_{56}H_{58}Cl_2O_{10}$. Calculated, %: C 69.93; H 6.04; Cl 7.39.

2,7-Bis[4-(4-*n*-decyloxybenzoyloxy)-3-chlorobenzoyloxy]naphthalene (VIIIb). Yield 0.68 g (68.2%). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.91 t (6H, CH_3, *J* 6.4 Hz), 1.19–1.55 m (28H, CH_2), 1.78–1.89 m (4H, $\underline{CH_2}CH_2O$), 4.07 t (4H, OCH_2, *J* 6.4 Hz), 7.01 d (4H, ArOAlk, *J* 8.7 Hz), 7.38–7.40 d.d (2H, naphthalene, *J* 7.9, 2.2 Hz), 7.49 d (2H, ArCl, *J* 8.7 Hz), 7.71 s (2H, naphthalene), 7.96 d (2H, naphthalene, *J* 8.7 Hz), 8.13–8.29 m (6H, ArOAlk, ArCl), 8.39 s (2H, ArCl). Found, %: C 70.48; H 6.33; Cl 7.26%. $C_{58}H_{62}Cl_2O_{10}$. Calculated, %: C 70.37; H 6.27; Cl 7.18.

2,7-Bis[4-(4-*n*-dodecyloxybenzoyloxy)-3-chlorobenzoyloxy]naphthalene (VIIIc). Yield 0.6 g (57.4%). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.89 t (6H, CH_3, *J* 6.9 Hz), 1.15–1.70 m (36H, CH_2), 1.70–1.95 m (4H, $\underline{CH_2}CH_2O$), 4.06 t (4H, OCH_2, *J* 6.5 Hz), 7.00 d (4H, ArOAlk, *J* 8.7 Hz), 7.36–7.39 d.d (2H, naphthalene, *J* 8.9, 2.2 Hz), 7.48 d (2H, ArCl, *J* 8.7 Hz), 7.70 s (2H, naphthalene), 7.97 d (2H, naphthalene, *J* 8.7 Hz), 8.15–8.32 m (6H, ArOAlk, ArCl), 8.39 s (2H, ArCl). Found, %: C 71.29; H 6.63; Cl 6.89. $C_{62}H_{70}Cl_2O_{10}$. Calculated, %: C 71.20; H 6.70; Cl 6.80.

2,7-Bis[4-(4-*n*-alkoxybenzoyloxy)-3,5-dichlorobenzoyloxy]naphthalenes **IXa**–**IXd** were prepared similarly.

2,7-Bis[4-(4-*n*-nonyloxybenzoyloxy)-3,5-dichlorobenzoyloxy]naphthalene (IXa). Yield 0.2 g (38.8%). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.89 t (6H, CH_3 *J* 6.5 Hz), 1.20–1.66 m (24H, CH_2), 1.75–1.90 m (4H, $\underline{CH_2}CH_2O$), 4.07 t (4H, OCH_2, *J* 6.5 Hz), 7.02 d (4H, ArOAlk, *J* 8.7 Hz), 7.36–7.39 d.d (2H, naphthalene, *J* 8.7, 2.2 Hz), 7.71 s (2H, naphthalene), 7.97 d (2H, naphthalene, *J* 8.7 Hz), 8.15–8.36 m (6H, ArOAlk, $ArCl_2$). Found, %: C 65.32; H 5.36; Cl 13.86. $C_{56}H_{56}Cl_4O_{10}$. Calculated, %: C 65.24; H 5.44; Cl 13.79.

2,7-Bis[4-(4-*n*-decyloxybenzoyloxy)-3,5-dichlorobenzoyloxy]naphthalene (IXb). Yield 3.2 g (61.0%). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.89 t (6H, CH_3, *J* 6.6 Hz), 1.20–1.70 m (28H, CH_2), 1.75–1.90 m (4H, $\underline{CH_2}CH_2O$), 4.07 t (4H, OCH_2, *J* 6.5 Hz), 7.02 d (4H, ArOAlk, *J* 8.7 Hz), 7.36–7.39 d.d (2H, naphthalene, *J* 8.7, 2.2 Hz), 7.71 s (2H, naphthalene), 7.97 d (2H, naphthalene, *J* 9.0 Hz), 8.15–8.35 m (6H, ArOAlk, $ArCl_2$). Found, %: C 65.70; H 5.77; Cl 13.49. $C_{58}H_{60}Cl_4O_{10}$. Calculated, %: C 65.78; H 5.67; Cl 13.42.

2,7-Bis[4-(4-*n*-dodecyloxybenzoyloxy)-3,5-dichlorobenzoyloxy]naphthalene (IXc). Yield 0.36 g (42.0%). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.89 t (6H, CH_3, *J* 6.5 Hz), 1.20–1.65 m (36H, CH_2), 1.70–2.00 m (4H, $\underline{CH_2}CH_2O$), 4.06 t (4H, OCH_2, *J* 6.5 Hz), 7.02 d (4H, ArOAlk, *J* 8.4 Hz), 7.37–7.39 d.d (2H, naphthalene, *J* 8.4, 1.2 Hz), 7.71 s (2H, naphthalene), 7.97 d (2H, naphthalene, *J* 8.7 Hz), 8.15–8.38 m (6H, ArOAlk, $ArCl_2$). Found, %: C 66.70; H 6.18; Cl 12.68. $C_{62}H_{68}Cl_4O_{10}$. Calculated, %: C 66.79; H 6.10; Cl 12.75.

2,7-Bis[4-(4-*n*-hexadecyloxybenzoyloxy)-3,5-dichlorobenzoyloxy]naphthalene (IXd). Yield 1.8 g

(48.0%). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.91 t (6H, CH_3, *J* 6.9 Hz), 1.18–1.65 m (52H, CH_2), 1.78–1.93 m (4H, $\underline{CH_2}CH_2O$), 4.09 t (4H, OCH_2, *J* 6.5 Hz), 7.04 d (4H, ArOAlk, *J* 8.3 Hz), 7.39–7.41 d.d (2H, naphthalene, *J* 8.3, 1.2 Hz), 7.73 s (2H, naphthalene), 7.99 d (2H, naphthalene, *J* 8.8 Hz), 8.15–8.38 m (6H, ArOAlk, $ArCl_2$). Found, %: C 68.60; H 6.78; Cl 11.68. $C_{70}H_{84}Cl_4O_{10}$. Calculated, %: C 68.52; H 6.85; Cl 11.58.

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