

Synthesis and Mesomorphic Properties of Esters Derived from Alkanediols

S. I. Maksimenko, N. S. Novikova, R. V. Kondrat'eva, V. E. Kuz'min,
L. N. Ognichenko, and M. Yu. Yarkova

Bogatskii Physicochemical Institute, National Academy of Sciences of Ukraine,
Lyustdorfskaya doroga 86, Odessa, 65080 Ukraine
e-mail: physchem@paco.net; nadyanovikova@rambler.ru

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Abstract—New alkane- α,ω -diyl esters, propane-1,3-diyl and butane-1,4-diyl bis[4-(4-alkoxybenzoyloxy)-3-bromobenzoates], were synthesized and were found to form nematic mesophase. The effects of the lateral substituent and the length of the central and terminal hydrocarbon chains on the mesomorphic properties of butane-1,4-diyl bis[4-(4-alkoxybenzoyloxy)-3-bromobenzoates] were studied. Structural factors responsible for mesogenic properties of these compounds were determined by conformation analysis.

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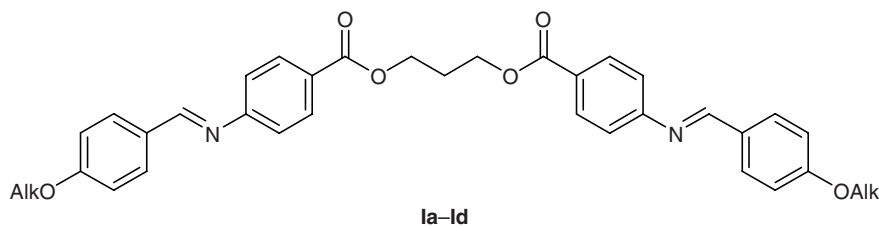
Liquid crystalline compounds with a bent structure (so-called banana-shaped) find increasing applications as components for LCD materials; therefore, studies on the relations between the structure and liquid crystalline properties constitute an important problem. Most compounds of this type contain five aromatic rings and are either benzylideneimino derivatives or esters derived from resorcinol, naphthalene-2,7-diol, or biphenyl-3,4'-diol and benzene-1,3-dicarboxylic acid [1–3]. In some cases, the central fragment was an alkane chain rather than aromatic ring [1, 4]. Examples of such structures are compounds **Ia–Id** which are called *twin mesogens* or *dimeric liquid crystals* [4].

The lateral fragments of alkanediol esters **I** include a C=N group; therefore, there is a necessity of separating mixtures of *syn* and *anti* isomers, and their phase transition temperatures are fairly high. Aromatic carboxylic acid esters are free from the above disadvantages; therefore, in the present work we synthesized

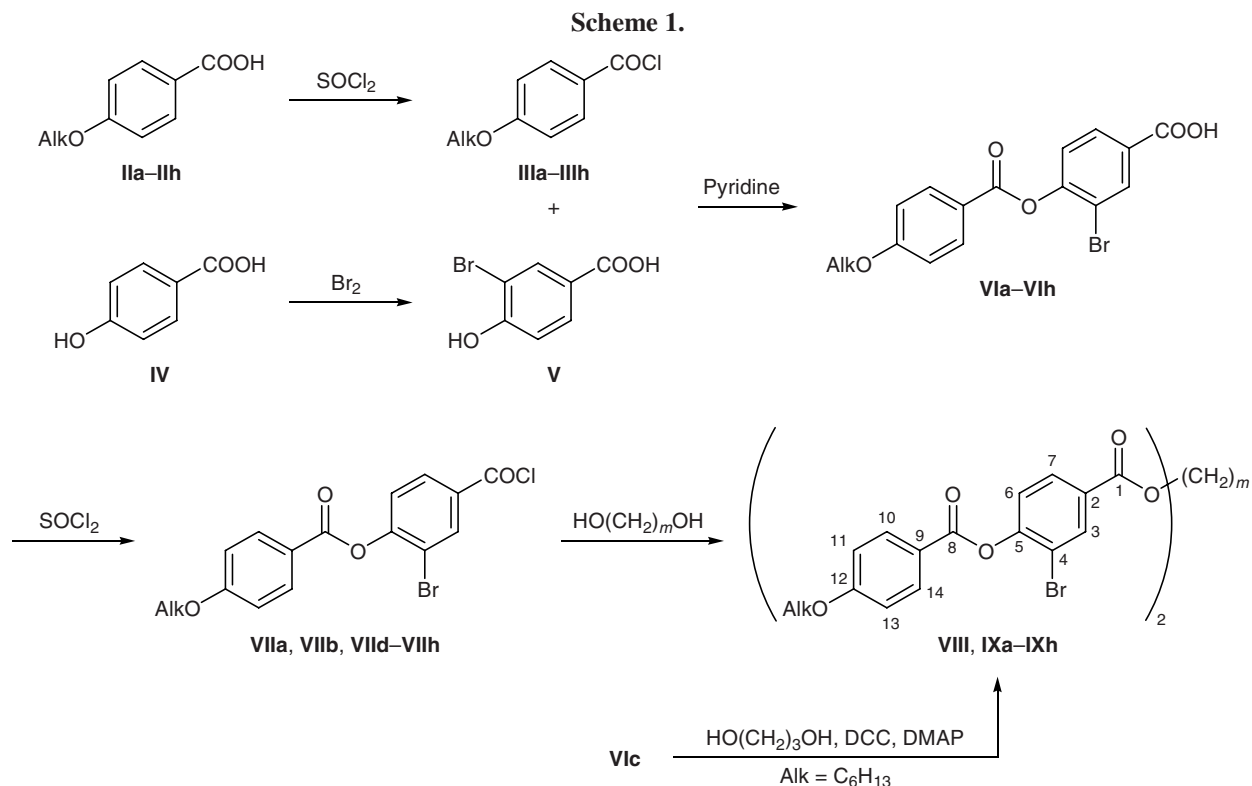
compounds having exclusively ester groups as bridging fragments. Taking into account empirical data for liquid crystals [5], we anticipated to obtain molecular structures favoring reduced mesophase temperature via introduction of a lateral substituent into the aromatic ring linked to the central aliphatic fragment.

Alkane- α,ω -diyl bis[4-(4-alkoxybenzoyloxy)-3-bromobenzoates] **VIII** and **IX** were synthesized as shown in Scheme 1. 3-Bromo-4-hydroxybenzoic acid (**V**) prepared according to the known procedure [6] was acylated with 4-alkoxybenzoyl chlorides in anhydrous pyridine. As intermediate compounds we isolated 4-(4-alkoxybenzoyloxy)-3-bromobenzoic acids **VIa–VIh** [7] some of which (compounds **VIa–VIc** and **VIh**) were not reported previously. The purity of acids **VIa–VIh** was checked by thin-layer chromatography, and their structure was proved by the ^1H NMR data.

All (alkoxybenzoyloxy)benzoic acids **VIa–VIh** are mesogenic: they give rise to nematic mesophase, and



Alk = $\text{C}_n\text{H}_{2n+1}$; $n = 4, 7-9$.



higher homolog **VIh** additionally has smectic phase. The phase transition temperatures and types of mesophases of compounds **VIa–VIh**, determined by polarizing microscopy, are given in Table 1. Comparison of the mesomorphic properties of 4-(4-alkoxybenzoyloxy)-3-bromobenzoic acids **VIa–VIh** and their unsubstituted analogs [8] shows that the presence of a bulky bromine atom reduces the phase transition temperature to isotropic liquid.

Propane-1,3-diyl and butane-1,4-diyl bis[4-(4-alkoxybenzoyloxy)-3-bromobenzoates] **VIII** and **IX** were synthesized by two methods: (1) direct reaction of acids **VI** with the corresponding alkanediols in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) in anhydrous methylene chloride and (2) transformation of acids **VI** into acid chlorides **VII** and subsequent acylation of propane-1,3-diol and butane-1,4-diol in anhydrous benzene. The first procedure includes only one step, but the yields of the final products are poor, and their purification is more difficult. Therefore, most syntheses were carried out according to the second two-step procedure.

Compounds **VIII** and **IX** were purified by column chromatography, their purity was checked by TLC, and

the structure was confirmed by ¹H NMR spectroscopy. Table 2 contains phase transition temperatures of bisesters **VIII** and **IXa–IXh**, determined by polarizing microscopy. The data in Table 2 show that propane-1,3-diyl bis[3-bromo-4-(4-nonyloxybenzoyloxy)benzoate] (**VIII**) is not mesogenic and that extension of the central hydrocarbon chain by one methylene group gives rise to mesophase in the series of butane-1,4-diyl bis[4-(4-alkoxybenzoyloxy)-3-bromobenzoates] **IXa–IXh**. Compounds **IX** exhibit monotropic nematic phase (the type of mesomorphism was determined according to textures observed under polarized light).

Comparison of mesomorphic properties of bisesters **VIII** and **IX** and previously reported propane-1,3-diyl [4-(4-alkoxybenzylideneimino)benzoates] **Ia–Id** [4] having similar terminal substituents shows that replacement of azomethine bridging group by ester linker and introduction of an additional lateral substituent (bromine atom) reduces the phase transition temperature and changes the type of mesophase or even eliminates mesogenic properties (compound **VIII**). In order to interpret these data from the viewpoint of molecular conformations, the structures of some compounds were simulated using SPARTAN 04 program implementing molecular-mechanics conformational

Table 1. Phase transition temperatures of 3-bromo-4-[4-alkoxybenzoyloxy]benzoic acids **VIa–VIh**

Compound no.	Phase transition temperature, ^a °C						
	Cr	<i>T</i> ₁	Sm	<i>T</i> ₂	N	<i>T</i> ₃	I
VIa	•	142	–	–	–	199.3	•
	•	(72)	–	–	•	197.1) ^b	•
VIb	•	126	–	–	–	196.4	•
	•	(85.2)	–	–	•	194.6)	•
VIc	•	140	–	–	–	192.3	•
	•	(79)	–	–	•	181.7)	•
VI d	•	121	–	–	–	186	•
	•	(99)	–	–	•	186)	•
VIe	•	111	–	–	–	173	•
	•	(93)	–	–	•	173)	•
VI f	•	144	–	–	–	183	•
	•	(117)	–	–	•	183)	•
VI g	•	117	–	–	–	187	•
	•	(104)	–	–	•	186)	•
VI h	•	113.3	–	–	•	161.4	•
	•	(97.4)	•	110.6	•	160.8)	•

^a Cr stands for crystalline phase, Sm for smectic phase, N for nematic phase, and I for isotropic liquid.

^b In parentheses are given the data for monotropic mesophase which is formed upon cooling the isotropic liquid.

search. Figures 1–3 show the most thermodynamically stable conformations of molecules **Id**, **VIII**, and **IXf** having nonyloxy groups as terminal substituents; the strain energies are also given.

As follows from the results of calculations (Fig. 1), the benzene rings adjacent to the central alkane fragment in molecule **Id** are almost coplanar to each other. The benzene rings bearing terminal substituents also

lie in parallel planes, thus forcing the terminal substituents to adopt an extended shape. Such structure is characterized by the minimal strain energy, and it displays the most ordered smectic mesophase (Table 2). Mutual repulsion of the large bromine atoms in molecule **VIII** (Fig. 2) distorts coplanar arrangement of the aromatic rings adjacent to the central aliphatic fragment, and replacement of the azomethine group by

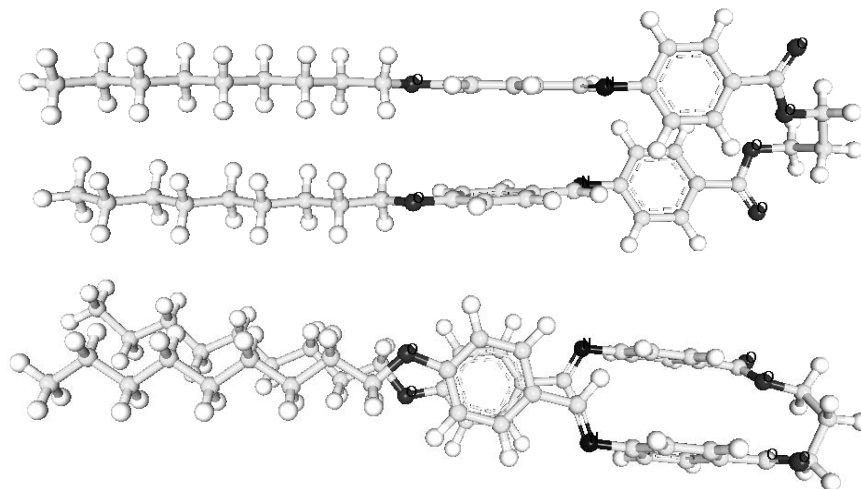


Fig. 1. Calculated structure of propane-1,3-diyl bis[4-(4-nonyloxybenzylideneimino)benzoate] (**Id**); different projections are shown; *E* = 87 kcal/mol.

Table 2. Phase transition temperatures of alkane- α,ω -diyl bis[4-(4-alkoxybenzoyloxy)-3-bromobenzoates **VIII** and **IXa–IXh** and propane-1,3-diyl bis[4-(4-alkoxybenzylideneimino)benzoates] **Ia–Id**

Compound no.	Phase transition temperatures, ^a °C						
	Cr	T_1	Sm	T_2	N	T_3	I
VIII	•	72	–	–	–	–	•
IXa	•	122	–	–	–	–	•
	•	(57	–	–	•	82.7)	•
IXb	•	100	–	–	–	–	•
	•	(68.8	–	–	•	81.7)	•
IXc	•	108	–	–	–	–	•
	•	(66.0	–	–	M_x^b	85)	•
IXd	•	102	–	–	–	–	•
	•	(64.8	–	–	•	72.5)	•
IXe	•	93	–	–	–	–	•
	•	(74.4	–	–	•	89.5)	•
IXf	•	90.1	–	–	–	–	•
	•	(67	–	–	•	71.9)	•
IXg	•	68.9	–	–	–	–	•
	•	(30	–	–	•	58.7)	•
IXh	•	77	–	–	–	–	•
	•	(43.7	–	–	•	60.7)	•
Ia	•	142	•	143	–	–	•
Ib	•	122	–	–	–	–	•
	•	^c	(•	108) ^d	–	–	•
Ic	•	119	–	–	–	–	•
	•	^c	(•	104)	–	–	•
Id	•	121	–	–	–	–	•
	•	^c	(•	98)	–	–	•

^a For notations, see note ^a to Table 1.

^b Unidentified mesophase.

^c Crystallization temperatures were not given in [4].

^d In parentheses are given the data for monotropic mesophase which is formed upon cooling the isotropic liquid.

ester leads to flexure of the terminal fragments, so that the molecule loses its rod-like shape and hence mesogenic properties. Extension of the central hydrocarbon bridge (Fig. 3) restores coplanar arrangement of the adjacent aromatic rings, but orientation of the terminal substituents implies that such molecular structure could give rise to less ordered (than smectic) nematic phase.

EXPERIMENTAL

The ¹H NMR spectra were measured from 5–10% solutions on a Varian VXR-300 spectrometer (300 MHz) relative to tetramethylsilane as internal

reference. The phase transition temperatures were determined by polarizing microscopy using a POLAM P-312 microscope. The purity of the products was checked by TLC on Silufol UV-254 plates (detection under UV light). Aluminum oxide L (5–40 μ m) was used for column chromatography (eluent benzene–acetone, 10:1).

4-Alkoxybenzoyl chlorides IIIa–IIIh were synthesized according to the procedure described in [9]. Compound **IIIa**: yield 83%, bp 130°C (2 mm), $n_D^{20} = 1.5487$; **IIIb**: yield 95%, bp 140°C (2 mm), $n_D^{20} = 1.5422$; **IIIc**: yield 91%, bp 190°C (3 mm), $n_D^{20} = 1.5370$; **IIId**: yield 77.6%, bp 208°C (4 mm), $n_D^{20} = 1.5310$; **IIIe**: yield 77.3%, bp 200°C (3 mm), $n_D^{20} =$

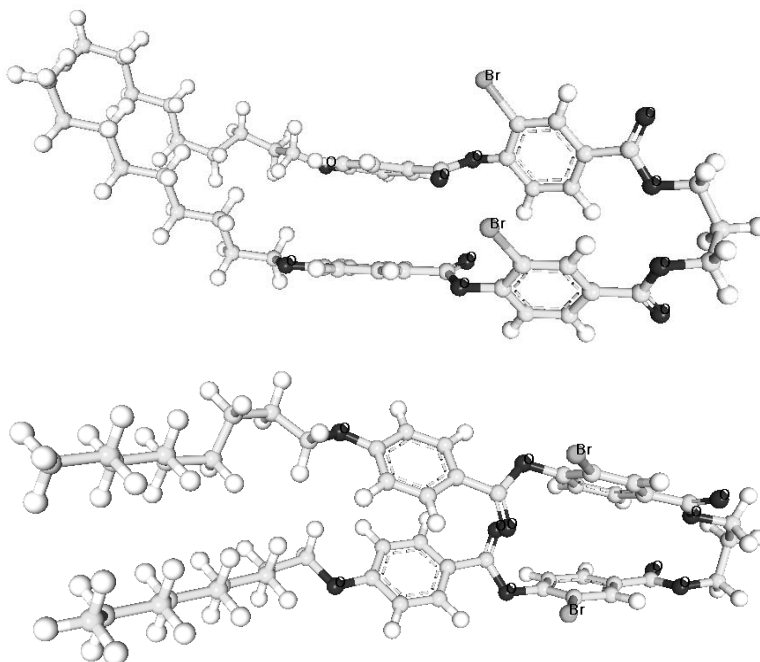


Fig. 2. Calculated structure of propane-1,3-diyl bis[3-bromo-4-(4-nonyloxybenzoyloxy)benzoate] (**VIII**); different projections are shown; $E = 134$ kcal/mol.

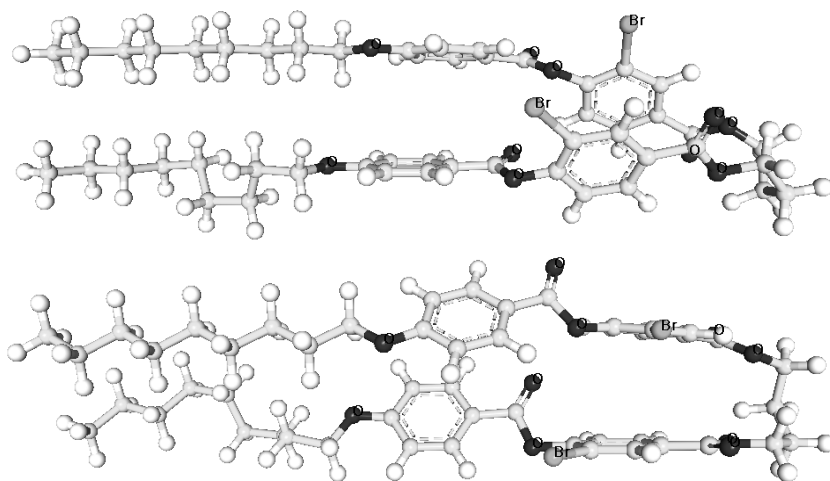


Fig. 3. Calculated structure of butane-1,4-diyl bis[3-bromo-4-(4-nonyloxybenzoyloxy)benzoate] (**IXd**); different projections are shown; $E = 136$ kkal/mol.

1.5281; **III**f: yield 78.3%, bp 220°C (3 mm), $n_D^{20} = 1.5246$; **III**g: yield 87.9%, bp 200°C (3 mm), $n_D^{20} = 1.5234$; **III**h: yield 95%, mp 50°C.

3-Bromo-4-hydroxybenzoic acid (V) was prepared as described in [6]. Yield 65%, mp 178°C; published data [6]: mp 177.5°C. ^1H NMR spectrum (CDCl_3), δ , ppm: 7.09 d (1H, 5-H), 7.98–8.01 d.d (1H, 6-H), 8.26 d (1H, 2-H).

4-(4-Alkoxybenzoyloxy)-3-bromobenzoic acids VIa–VIh (general procedure). Benzoyl chloride **III**a–**III**h, 24 mmol, was added dropwise to a suspension of

24 mmol of acid **V** in 30 ml of anhydrous pyridine, and the mixture was stirred for 21 h at 20°C. It was then poured into ice-cold water and acidified with hydrochloric acid to pH 2, the colorless crystalline solid was filtered off, washed with water until neutral washings (pH 7), dried, and dispersed in ~300 ml of cold alcohol, and the precipitate was filtered off and recrystallized from benzene.

3-Bromo-4-(4-butoxybenzoyloxy)benzoic acid (VIa). Yield 88%. ^1H NMR spectrum (CDCl_3), δ , ppm: 0.89 t (3H, CH_3), 1.41–1.55 m (2H, CH_2CH_2), 1.76–

1.89 m (2H, OCH₂CH₂), 4.06 t (2H, CH₂O), 6.99 d (2H, C₆H₄), 7.43 d (1H, C₆H₃), 8.11–8.13 d.d (1H, C₆H₃), 8.20 d (2H, C₆H₄), 8.42 d (1H, C₆H₃). Found, %: C 54.82; H 4.43; Br 20.18. C₁₈H₁₇BrO₅. Calculated, %: C 54.98; H 4.36; Br 20.32.

3-Bromo-4-(4-pentyloxybenzoyloxy)benzoic acid (VIb). Yield 71%. ¹H NMR spectrum (CDCl₃), δ, ppm: 0.89 t (3H, CH₃), 1.15–1.41 m (2H, CH₂), 1.41–1.55 m (2H, CH₂CH₂CH₂), 1.76–1.89 m (2H, OCH₂CH₂), 4.06 t (2H, OCH₂), 6.99 d (2H, C₆H₄), 7.43 d (1H, C₆H₃), 8.11–8.13 d.d (1H, C₆H₃), 8.20 d (2H, C₆H₄), 8.42 d (1H, C₆H₃). Found, %: C 56.09; H 4.86; Br 19.45. C₁₉H₁₉BrO₅. Calculated, %: C 56.03; H 4.70; Br 19.62.

3-Bromo-4-(4-hexyloxybenzoyloxy)benzoic acid (VIc). Yield 67%. ¹H NMR spectrum (CDCl₃), δ, ppm: 0.88 t (3H, CH₃), 1.15–1.40 m (4H, CH₂), 1.41–1.56 m [2H, CH₂(CH₂)₂O], 1.76–1.89 m (2H, CH₂CH₂O), 4.06 t (2H, CH₂O), 7.00 d (2H, C₆H₄), 7.43 d (1H, C₆H₃), 8.12–8.14 d.d (1H, C₆H₃), 8.20 d (2H, C₆H₄), 8.42 d (1H, C₆H₃). Found, %: C 56.77; H 4.89; Br 18.81. C₂₀H₂₁BrO₅. Calculated, %: C 57.02; H 5.02; Br 18.97.

3-Bromo-4-(4-heptyloxybenzoyloxy)benzoic acid (VIId) [7]. Yield 57%. ¹H NMR spectrum (CDCl₃), δ, ppm: 0.88 t (3H, CH₃), 1.15–1.40 m (6H, CH₂), 1.41–1.56 m (2H, OCH₂CH₂CH₂), 1.77–1.89 m (2H, OCH₂CH₂), 4.06 t (2H, OCH₂), 7.00 d (2H, C₆H₄), 7.43 d (1H, C₆H₃), 8.12–8.14 d.d (1H, C₆H₃), 8.20 d (2H, C₆H₄), 8.42 d (1H, C₆H₃).

3-Bromo-4-(4-octyloxybenzoyloxy)benzoic acid (VIe) [7]. Yield 77%. ¹H NMR spectrum (CDCl₃), δ, ppm: 0.89 t (3H, CH₃), 1.16–1.40 m (8H, CH₂), 1.41–1.56 m (2H, OCH₂CH₂CH₂), 1.75–1.89 m (2H, OCH₂CH₂), 4.06 t (2H, OCH₂), 7.00 d (2H, C₆H₄), 7.43 d (1H, C₆H₃), 8.11–8.13 d.d (1H, C₆H₃), 8.20 d (2H, C₆H₄), 8.42 d (1H, C₆H₃).

3-Bromo-4-(4-nonyloxybenzoyloxy)benzoic acid (VIIf) [7]. Yield 64%. ¹H NMR spectrum (CDCl₃), δ, ppm: 0.89 t (3H, CH₃), 1.19–1.41 m (10H, CH₂), 1.41–1.55 m (2H, OCH₂CH₂CH₂), 1.77–1.89 m (2H, OCH₂CH₂), 4.06 t (2H, OCH₂), 6.99 d (2H, C₆H₄), 7.43 d (1H, C₆H₃), 8.12–8.14 d.d (1H, C₆H₃), 8.20 d (2H, C₆H₄), 8.42 d (1H, C₆H₃).

3-Bromo-4-(4-decyloxybenzoyloxy)benzoic acid (VIg) [7]. Yield 46%. ¹H NMR spectrum (CDCl₃), δ, ppm: 0.89 t (3H, CH₃), 1.15–1.41 m (12H, CH₂), 1.41–1.55 m (2H, OCH₂CH₂CH₂), 1.76–1.89 m (2H, OCH₂CH₂), 4.06 t (2H, OCH₂), 6.99 d (2H, C₆H₄),

7.43 d (1H, C₆H₃), 8.11–8.13 d.d (1H, C₆H₃), 8.20 d (2H, C₆H₄), 8.42 d (1H, C₆H₃).

3-Bromo-4-(4-hexadecyloxybenzoyloxy)benzoic acid (VIh). Yield 73%. ¹H NMR spectrum (CDCl₃), δ, ppm: 0.88 t (3H, CH₃), 1.18–1.41 m (24H, CH₂), 1.42–1.56 m (2H, OCH₂CH₂CH₂), 1.74–1.92 m (2H, OCH₂CH₂), 4.06 t (2H, CH₂O), 7.00 d (2H, C₆H₄), 7.42 d (1H, C₆H₃), 8.11–8.13 d.d (1H, C₆H₃), 8.19 d (2H, C₆H₄), 8.42 d (1H, C₆H₃). Found, %: C 64.27; H 7.20; Br 14.27. C₃₀H₄₁BrO₅. Calculated, %: C 64.17; H 7.36; Br 14.23.

4-(4-Alkoxybenzoyloxy)-3-bromobenzoyl chlorides VIIa–VIIh (general procedure). Thionyl chloride, 14.8 mmol, was added over a period of 30 min under stirring and cooling to a solution of 4.2 mmol of acid VIa–VIh in 20 ml of anhydrous benzene. The mixture was then heated for 9 h under reflux on a water bath, the solvent and excess thionyl chloride were distilled off under reduced pressure, 15 ml of anhydrous benzene was added to the residue, and the solvent was distilled off under reduced pressure. The products were used in further syntheses without additional purification.

Propane-1,3-diyl [3-bromo-4-(4-nonyloxybenzoyloxy)benzoate] (VIII). Triethylamine, 1 ml, was added to a solution of 2.08 g (4.2 mmol) of benzoyl chloride VIIf in 15 ml of anhydrous benzene, 0.189 g (2.1 mmol) of propane-1,3-diol was added on cooling, and the mixture was stirred for 15 h at 25°C, the progress of the reaction being monitored by TLC. The mixture was poured onto crushed ice and extracted with chloroform (2 × 20 ml), and the extract was dried over anhydrous magnesium sulfate, filtered from the drying agent, and evaporated under reduced pressure. The residue, a dark yellow oily substance, was washed with ethanol (3 × 30 ml). Yield 1.2 g (19%), off-white powder. ¹H NMR spectrum (CDCl₃), δ, ppm: 0.89 t (6H, CH₃, *J* = 6.53 Hz), 1.29–1.61 m (24H, CH₂), 1.78–1.87 m (4H, OCH₂CH₂), 2.22–2.35 m (2H, OCH₂CH₂CH₂O), 4.05 t (4H, OCH₂, *J* = 6.53 Hz), 4.43 s (4H, OCH₂CH₂CH₂O), 6.98 d (4H, 11-H, 13-H, *J* = 9.02 Hz), 7.37 d (2H, 6-H, *J* = 8.09 Hz), 8.04–8.07 d.d (2H, 7-H, *J*₁ = 8.4, *J*₂ = 1.87 Hz), 8.17 d (4H, 10-H, 14-H, *J* = 9.02 Hz), 8.34 d (2H, 3-H, *J* = 1.86 Hz). Found, %: C 60.68; H 5.91; Br 16.38. C₄₉H₅₈Br₂O₁₀. Calculated, %: C 60.87; H 6.05; Br 16.53.

Compounds IXa, IXb, and IXd–IXh were synthesized in a similar way.

Butane-1,4-diyl bis[3-bromo-4-(4-butoxybenzoyloxy)benzoate] (IXa) was obtained from 2 g (9.4 mmol) of compound **VIIa** and 0.423 g (4.7 mmol) of butane-1,4-diol. Yield 1.5 g (38%). ^1H NMR spectrum (CDCl_3), δ , ppm: 0.89 t (6H, CH_3 , $J = 6.53$ Hz), 1.28–1.53 m (4H, CH_2), 1.78–1.87 m (4H, OCH_2CH_2), 1.96 br.s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 4.05 t (4H, OCH_2 , $J = 6.53$ Hz), 4.43 s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 6.98 d (4H, 11-H, 13-H, $J = 9.02$ Hz), 7.37 d (2H, 6-H, $J = 8.09$ Hz), 8.04–8.07 d.d (2H, 7-H, $J_1 = 8.4$, $J_2 = 1.87$ Hz), 8.17 d (4H, 10-H, 14-H, $J = 9.02$ Hz), 8.33 d (2H, 3-H, $J = 1.86$ Hz). Found, %: C 57.35; H 4.60; Br 19.08. $\text{C}_{40}\text{H}_{40}\text{Br}_2\text{O}_{10}$. Calculated, %: C 57.16; H 4.80; Br 19.01.

Butane-1,4-diyl bis[3-bromo-4-(4-pentyloxybenzoyloxy)benzoate] (IXb) was obtained from 3.15 g (7.4 mmol) of compound **VIIb** and 0.33 g (3.7 mmol) of butane-1,4-diol. Yield 0.683 g (21%). ^1H NMR spectrum (CDCl_3), δ , ppm: 0.89 t (6H, CH_3 , $J = 6.53$ Hz), 1.29–1.61 m (8H, CH_2), 1.78–1.87 m (4H, OCH_2CH_2), 1.96 br.s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 4.05 t (4H, OCH_2 , $J = 6.53$ Hz), 4.43 s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 6.98 d (4H, 11-H, 13-H, $J = 9.02$ Hz), 7.37 d (2H, 6-H, $J = 8.09$ Hz), 8.04–8.07 d.d (2H, 7-H, $J_1 = 8.4$, $J_2 = 1.87$ Hz), 8.17 d (4H, 10-H, 14-H, $J = 9.02$ Hz), 8.34 d (2H, 3-H, $J = 1.86$ Hz). Found, %: C 57.87; H 5.26; Br 18.33. $\text{C}_{42}\text{H}_{44}\text{Br}_2\text{O}_{10}$. Calculated, %: C 58.08; H 5.11; Br 18.40.

Butane-1,4-diyl bis[3-bromo-4-(4-heptyloxybenzoyloxy)benzoate] (IXd) was obtained from 2.09 g (4.6 mmol) of compound **VIIc** and 0.207 g (2.3 mmol) of butane-1,4-diol. Yield 0.297 g (14%). ^1H NMR spectrum (CDCl_3), δ , ppm: 0.90 t (6H, CH_3 , $J = 6.53$ Hz), 1.23–1.54 m (16H, CH_2), 1.75–1.90 m (4H, OCH_2CH_2), 1.96 br.s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 4.05 t (4H, OCH_2 , $J = 6.53$ Hz), 4.43 s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 6.98 d (4H, 11-H, 13-H, $J = 9.02$ Hz), 7.37 d (2H, 6-H, $J = 8.09$ Hz), 8.04–8.07 d.d (2H, 7-H, $J_1 = 8.4$, $J_2 = 1.87$ Hz), 8.17 d (4H, 10-H, 14-H, $J = 9.02$ Hz), 8.33 d (2H, 3-H, $J = 1.86$ Hz). Found, %: C 59.91; H 5.55; Br 17.50. $\text{C}_{46}\text{H}_{52}\text{Br}_2\text{O}_{10}$. Calculated, %: C 59.75; H 5.67; Br 17.28.

Butane-1,4-diyl bis[3-bromo-4-(4-octyloxybenzoyloxy)benzoate] (IXe) was obtained from 2.1 g (4.5 mmol) of compound **VIIe** and 0.203 g (2.25 mmol) of butane-1,4-diol. Yield 0.218 g (10%). ^1H NMR spectrum (CDCl_3), δ , ppm: 0.90 t (6H, CH_3 , $J = 6.23$ Hz), 1.30–1.50 m (20H, CH_2), 1.78–1.87 m (4H, OCH_2CH_2), 1.96 br.s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 4.05 t (4H, OCH_2 , $J = 6.54$ Hz), 4.43 s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 6.98 d (4H, 11-H, 13-H, $J = 8.72$ Hz),

7.37 d (2H, 6-H, $J = 8.41$ Hz), 8.04–8.07 d.d (2H, 7-H, $J_1 = 8.4$, $J_2 = 1.86$ Hz), 8.17 d (4H, 10-H, 14-H, $J = 8.72$ Hz), 8.33 d (2H, 3-H, $J = 1.87$ Hz). Found, %: C 60.32; H 6.02; Br 16.77. $\text{C}_{48}\text{H}_{56}\text{Br}_2\text{O}_{10}$. Calculated, %: C 60.51; H 5.92; Br 16.77.

Butane-1,4-diyl bis[3-bromo-4-(4-nonyloxybenzoyloxy)benzoate] (IXf) was obtained from 3.65 g (7.6 mmol) of compound **VIIe** and 0.34 g (3.8 mmol) of butane-1,4-diol. Yield 0.4 g (11%). ^1H NMR spectrum (CDCl_3), δ , ppm: 0.89 t (6H, CH_3 , $J = 6.53$ Hz), 1.29–1.61 m (24H, CH_2), 1.78–1.87 m (4H, OCH_2CH_2), 1.96 br.s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 4.05 t (4H, OCH_2 , $J = 6.53$ Hz), 4.43 s (4H), 6.98 d (4H, 11-H, 13-H, $J = 8.71$ Hz), 7.37 d (2H, 6-H, $J = 8.09$ Hz), 8.04–8.07 d.d (2H, 7-H, $J_1 = 8.4$, $J_2 = 1.56$ Hz), 8.17 d (4H, 10-H, 14-H, $J = 8.71$ Hz), 8.34 d (2H, 3-H, $J = 1.24$ Hz). Found, %: C 61.09; H 6.34; Br 16.36. $\text{C}_{50}\text{H}_{60}\text{Br}_2\text{O}_{10}$. Calculated, %: C 61.23; H 6.17; Br 16.29.

Butane-1,4-diyl bis[3-bromo-4-(4-decyloxybenzoyloxy)benzoate] (IXg) was obtained from 3.12 g (6.5 mmol) of compound **VIIg** and 0.25 g (3.3 mmol) of butane-1,4-diol. Yield 0.3 g (14%). ^1H NMR spectrum (CDCl_3), δ , ppm: 0.89 t (6H, CH_3 , $J = 6.53$ Hz), 1.28–1.53 m (28H, CH_2), 1.78–1.87 m (4H, OCH_2CH_2), 1.96 br.s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 4.05 t (4H, OCH_2 , $J = 6.53$ Hz), 4.43 s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 6.98 d (4H, 11-H, 13-H, $J = 8.71$ Hz), 7.37 d (2H, 6-H, $J = 8.09$ Hz), 8.04–8.07 d.d (2H, 7-H, $J_1 = 8.4$, $J_2 = 1.56$ Hz), 8.17 d (4H, 10-H, 14-H, $J = 8.71$ Hz), 8.33 d (2H, 3-H, $J = 1.24$ Hz). Found, %: C 61.87; H 6.34; Br 16.94. $\text{C}_{52}\text{H}_{64}\text{Br}_2\text{O}_{10}$. Calculated, %: C 61.91; H 6.39; Br 15.84.

Butane-1,4-diyl bis[3-bromo-4-(4-hexadecyloxybenzoyloxy)benzoate] (IXh) was obtained from 2.09 g (3.6 mmol) of compound **VIIh** and 0.162 g (1.8 mmol) of butane-1,4-diol. Yield 0.213 g (10%). ^1H NMR spectrum (CDCl_3), δ , ppm: 0.89 t (6H, CH_3 , $J = 6.53$ Hz), 1.28–1.64 m (4H, CH_2), 1.78–1.87 m (4H, OCH_2CH_2), 1.96 br.s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 4.05 t (4H, OCH_2 , $J = 6.53$ Hz), 4.43 s [4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 6.98 d (4H, 11-H, 13-H, $J = 8.71$ Hz), 7.37 d (2H, 6-H, $J = 8.09$ Hz), 8.04–8.07 d.d (2H, 7-H, $J_1 = 8.4$, $J_2 = 1.56$ Hz), 8.17 d (4H, 10-H, 14-H, $J = 8.71$ Hz), 8.34 d (2H, 3-H, $J = 1.24$ Hz). Found, %: C 65.20; H 7.44; Br 13.49. $\text{C}_{64}\text{H}_{88}\text{Br}_2\text{O}_{10}$. Calculated, %: C 65.30; H 7.54; Br 13.58.

Butane-1,4-diyl bis[3-bromo-4-(4-hexyloxybenzoyloxy)benzoate] (IXc). A mixture of 2 g (4.8 mmol) of 3-bromo-4-(4-hexyloxybenzoyloxy)benzoic acid (**VIc**), 0.096 g (0.48 mmol) of 4-dimethylamino-

pyridine, and 0.216 g (2.4 mmol) of butane-1,4-diol in 20 ml of anhydrous methylene chloride was stirred for 10 min, 0.988 g (4.8 mmol) of *N,N'*-dicyclohexylcarbodiimide was added, and the mixture was stirred for 16 h at room temperature. When the reaction was complete (TLC), the precipitate was filtered off, and the filtrate was diluted with 30 ml of methylene chloride, washed in succession with a 5% solution of acetic acid (2 × 50 ml), 5% aqueous sodium hydroxide (2 × 25 ml), and water (3 × 25 ml) to pH 7, and dried over anhydrous magnesium sulfate. The solvent was distilled off under reduced pressure, and the residue was recrystallized from hexane–diethyl ether (1:3) and additionally purified by column chromatography. Yield 0.097 g (5%). ¹H NMR spectrum (CDCl₃), δ, ppm: 0.89 t (6H, CH₃, *J* = 6.53 Hz), 1.29–1.61 m (12H, CH₂), 1.78–1.87 m (4H, OCH₂CH₂), 1.96 br.s [4H, OCH₂(CH₂)₂CH₂O], 4.05 t (4H, OCH₂, *J* = 6.53 Hz), 4.43 s [4H, OCH₂(CH₂)₂CH₂O], 6.98 d (4H, 11-H, 13-H, *J* = 8.71 Hz), 7.37 d (2H, 6-H, *J* = 8.09 Hz), 8.04–8.07 d.d (2H, 7-H, *J*₁ = 8.4, *J*₂ = 1.56 Hz), 8.17 d (4H, 10-H, 14-H, *J* = 8.71 Hz), 8.34 d (2H, 3-H, *J* = 1.24 Hz). Found, %: C 58.93; H 5.20; Br 17.80. C₄₄H₄₈Br₂O₁₀. Calculated, %: C 58.94; H 5.40; Br 17.82.

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