ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 7, pp. 1606–1610. © Pleiades Publishing, Ltd., 2015.
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Synthesis of V-Shaped Liquid Crystal Benzoates

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Received February 26, 2015

Abstract—V-Shaped mesogens, benzene-1,2-diylbis[4-(4-alkoxybenzoyloxy)benzoates], were synthesized and their mesomorphic behavior was studied. For the homolog with terminal heptyloxy group, enantiotropic nematic and monotropic smectic *A* phases were observed; the subsequent homologs formed exclusively enantiotropic smectic *A* phase. It was found that the isomeric ester of benzene-1,2-dicarboxylic acid with heptyloxy groups at the phenol fragments did not possess mesomorphism.

Keywords: esters of 1,2-dihydroxybenzene and benzene-1,2-dicarboxylic acid, V-shaped mesogens

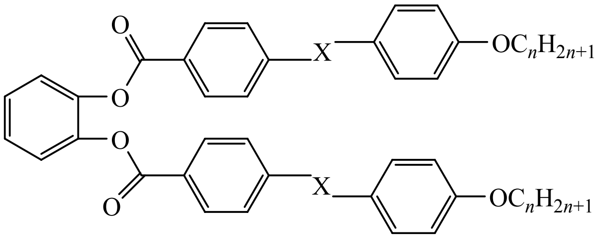
DOI: 10.1134/S1070363215070051

For the last 10 years the molecular design and synthesis of new classes of liquid crystal compounds in which anisotropic form of molecules varied from the classical calamitic or discotic shape are of interest. The bent-shaped molecules are classified by the following categories: banana-shaped [1, 2], club-shaped [3, 4], λ- [5, 6], W- [7, 8], and V(U)-shaped [9–11]. In the V (U)-shaped compounds the lateral fragments occupied the 1,2-positions of the central aromatic ring (Scheme 1).

Mesomorphic behavior of esters **I–IV** based on catechol and bearing azomethine (**I**, **II**) [12], azo- (**III**) [13] and azoxy group (**IV**) [14] as a linker at the side acidic fragment have been described. Benzene-1,2-diylbis[4-(4-alkoxybenzylidenamino)benzoates] **I**, **II** and their analogs bearing methyl group in the positions 3 and 4 of the benzene ring formed nematic, smectic *A* and *B* phases [12]. The synthesis of V-shaped compounds based on azobenzene **III**, which can form nematic, smectic *A*, and crystal *E* phases, has been described in [13]. 1,2-Benzene-1,2-diylbis[4-(4-ethoxyphenylazoxy)benzoate] **IV** is known to form nematic phase [14].

Analysis of the published data showed that the described compounds form mesophase in the high-temperature range and are prone to oxidation. Therefore for the investigation of the correlation structure–mesomorphic properties we synthesized benzene-1,2-diylbis[4-(4-alkoxybenzoyloxy)benzoates] **VIIa–VIIf** containing exclusively ester groups as the linkers (Scheme 2).

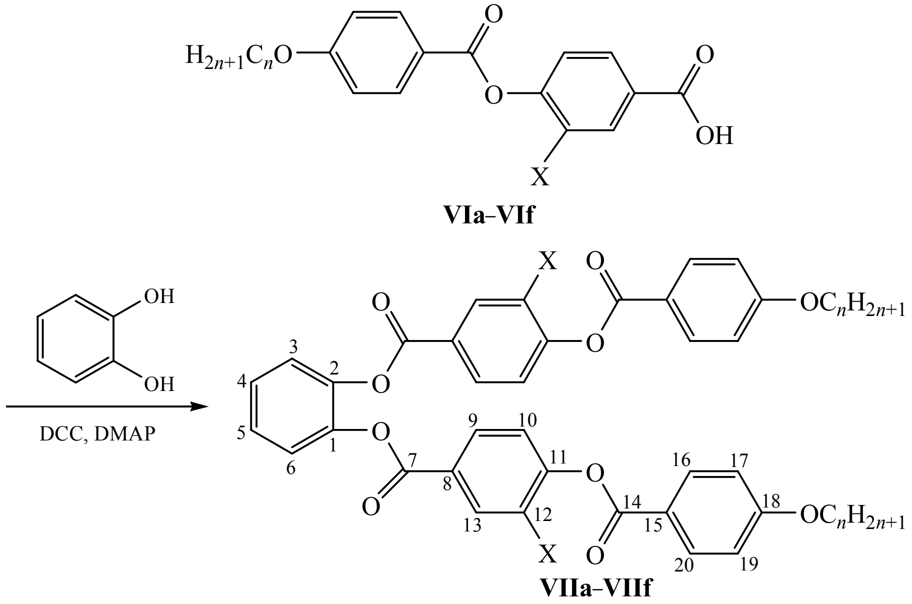
Scheme 1.



I–IV

X = –N=CH– (**I**), –CH=N– (**II**), –N=N– (**III**), –N=N(O)– (**IV**); n= 1–16 (**I, II**), 4–10 (**III**), 2 (**IV**).

Scheme 2.

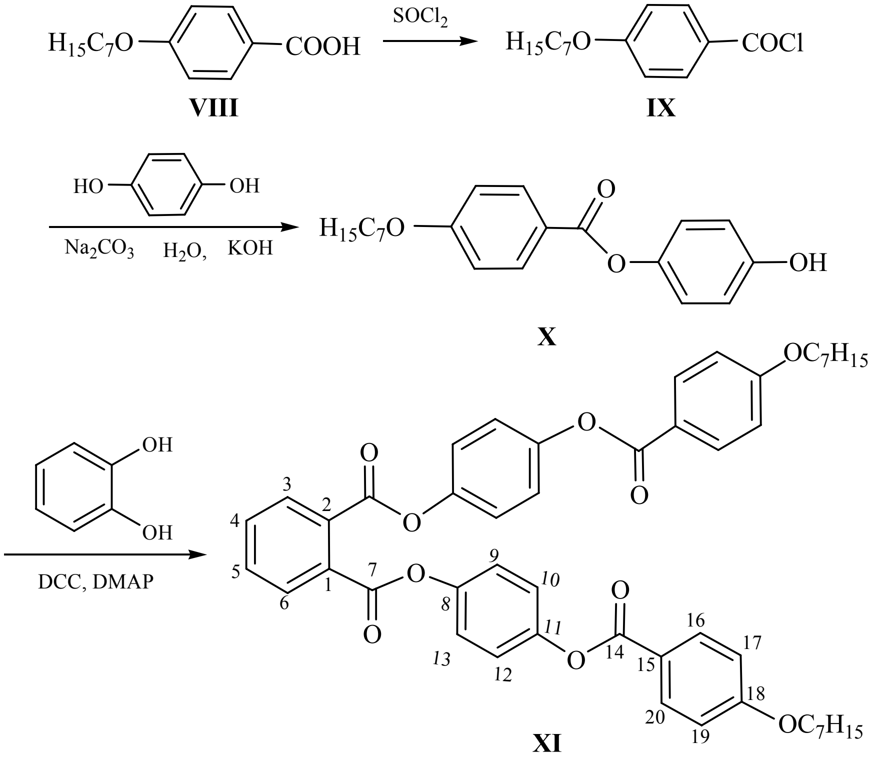


VIa–VIf

VIIa–VIIf

n = 7 (**a**), 8 (**b**), 9 (**c**), 10 (**d, f**), 12 (**e**); X = H (**a–e**), Cl (**f**).

Scheme 3.



VIII **IX** **X** **XI**

4-(4-Alkoxybenzoyloxy)benzoic acids **VIa–VIe** were prepared according to the known procedure [15] by acylation of 4-hydroxybenzaldehyde with the chlorides of the corresponding 4-alkoxybenzoic acids followed by oxidation of 4-(4-alkoxybenzoyloxy)-benzaldehydes with the Jones reagent. 4-(4-Decyloxybenzoyloxy)-3-chlorobenzoic acid **VIf** was prepared from 4-hydroxy-3-chlorobenzoic acid [16] by

Transition points (°C) of compounds **VIIa–VIIf** and **XI**[a]

Comp. no.	R	Cr	SmA	N	I
VIIa	OC_7H_{15}	• 151.1	• (150.4)	– 159.7	•
VIIb	OC_8H_{17}	• 154.1	•	– 157.2	•
VIIc	OC_9H_{19}	• 136.9	•	– 159.3	•
VIId	$OC_{10}H_{21}$	• 122.5	•	– 160.3	•
VIIe	$OC_{12}H_{25}$	• 121.8	•	– 165.9	•
VIIf	$OC_{10}H_{21}$	56.6	– •	79.1	•
XI	OC_7H_{15}	•	–	– 143.2	•

[a] (Cr) means crystal, (SmA) means smectic *A*, (N) means nematic, (I) means isotropic phase.

acylation with 4-decyloxybenzoic acid chloride. The reaction of acids **VIa–VIf** with 1,2-dihydroxybenzene in the presence of *N*,*N*'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) in anhydrous chloroform provided the target compounds **VIIa–VIIf**.

In addition, *o*-phthalic acid diester, bis[4-(4-heptyloxybenzoyloxy)phenyl]benzene-1,2-dicarboxylate **XI**, which is the isomer of benzene-1,2-diylbis[4-(4-heptyloxybenzoyloxy)benzoate] **VIIa**, was synthesized for the first time (Scheme 3).

The structure of compounds **VIIa–VIIf**, and **XI** was established based on the data of ^{1}H NMR spectroscopy. Mesomorphic properties of the synthesized compounds were investigated by polarization microscopy (see the table).

As seen from the table, diesters **VIIb–VIIe** formed enantiotropic smectic mesophase of *A* modification. An increase in the terminal group length the caused reduction of the transition point to liquid crystal state and a weakly pronounced increase in the transition point to isotropic liquid. Homolog **VIIa** formed enantiotropic nematic phase and monotropic SmA phase.

An introduction of a chlorine atom in the aromatic rings of the lateral acidic fragments caused virtually two-fold reduction of the temperature of the phase transitions for compound **VIIf** and the disappearance of the ordered smectic phase compared to the unsubstituted analog **VIIa**. Compound **XI** did not show mesomorphism probably due to the hampered rotation of the lateral fragments connected with the central aromatic ring by the carbonyl groups. Most probably, the conformation of molecule at which the angle between the lateral fragments 60°–70° cannot be attained that is a necessary condition for the formation of a mesophase by the V-shaped molecules. If the mobility of the lateral fragments increases due to the connection with the central aromatic ring through the oxygen of an ester group or the oxygen of ether with an aliphatic chain, such V-shaped structures can exhibit mesomorphism [9–11].

The data of small angle X-ray scattering for compounds **VIIa–VIIe** showed that the layer thickness in mesomorphic state was twice less than the molecule length; for example, for benzene-1, 2-diylbis[4-(4-octyloxybenzoyloxy)benzoate] **VIIb** the molecule length was 56.4 Å, and the layer thickness was 26.4 Å. The increased length of the terminal alkoxy groups in homologs **VIId** and **VIIe** caused an increase in the layer thickness in smectic *A* phase up to 29.1 and 31.9 Å, respectively.

EXPERIMENTAL

^{1}H NMR spectra for solutions in $CDCl_3$ were recorded on a Bruker AVANCE DRX 500 instrument operating at 500 MHz; internal reference TMS. The reaction progress and purity of the prepared compounds were monitored by the means of TLC on Sorbfil high effective aluminum UV plates in chloroform–methanol (10 : 1); the spots development was done with iodine vapor or under UV irradiation.

Transition points were investigated by polarization microscopy on a POLAM P-312 microscope. The X-ray phase analysis was done in the light reflected from free sample surface on a Bruker GAADS system. Dielectric response was measured with the use of an analyzer of complete resistance with the cell of 5 mm thickness and gold electrodes.

Compounds **V**, **VIa–VIf**, and **X** were prepared by the known methods [15–17].

4-(4-Decyloxybenzoyloxy)-3-chlorobenzoic acid (VIf). Yield 2.3 g (59%). ^{1}H NMR spectrum (DMSO-d_6), 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, ^3J 8.1 Hz), 7.60 d (1H, ArCl, *J* 8.0 Hz), 7.99–8.00 dd (1H, ArCl, ^3J 8.0 Hz, ^4J 0.8 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.

Benzene-1,2-diylbis[4-(4-alkoxybenzoyloxy)benzoates] (VIIa–VIIf) (*general procedure*). 4-(4-Alkoxybenzoyloxy)benzoic acid **VIa–VIf** (0.002 mol) and 4-dimethylaminopyridine (0.0002 mol) were added to a suspension of catechol (0.001 mol) in 30 mL of anhydrous chloroform. The mixture was stirred at room temperature for 10 min, then *N*,*N*'-dicyclohexylcarbodiimide (0.002 mol) was added. After 10 h, at room temperature, the formed solid was filtered off and washed with anhydrous chloroform (3 × 10 mL). The filtrate was evaporated. The residue was ground with cooled ethanol to form crystalline solid. The solid was filtered off, dried, recrystallized from a mixture of anhydrous benzene and ethanol (3 : 1), washed with anhydrous alcohol, and dried.

Benzene-1,2-diylbis[4-(4-heptyloxybenzoyloxy)-benzoate] (VIIa). Yield 0.6 g (90.9%), white amorphous powder. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (6H, CH_3, *J* 6.9 Hz), 1.25–1.45 m (12H, CH_2), 1.45–1.55 m (4H, $OCH_2CH_2C\underline{H}_2$), 1.80–1.90 m (4H, $OCH_2C\underline{H}_2$), 4.07 t (4H, OCH_2, *J* 6.6 Hz), 6.98 d (4H, $H^{17,19}$, *J* 8.6 Hz), 7.26–7.33 m (4H, $H^{10,12}$), 7.37–7.47 m (4H, $H^{3,4,5,6}$), 8.10–8.20 m (8H, $H^{9,13,16,20}$). Found, %: C 73.57; H 6.24. $C_{48}H_{50}O_{10}$. Calculated, %: C 73.28; H 6.36.

Benzene-1,2-diylbis[4-(4-octyloxybenzoyloxy)-benzoate] (VIIb). Yield 1.6 g (78.6%), white amorphous powder. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (6H, CH_3, *J* 6.1 Hz), 1.26–1.44 m (16H, CH_2), 1.45–1.56 m (4H, $OCH_2CH_2C\underline{H}_2$), 1.80–1.90 m (4H, $OCH_2C\underline{H}_2$), 4.07 t (4H, OCH_2, *J* 6.1 Hz), 6.98 d (4H, $H^{17,19}$, *J* 8.6 Hz), 7.25–7.33 m (4H, $H^{10,12}$), 7.37–7.47 m (4H, $H^{3,4,5,6}$), 8.21–8.07 m (8H, $H^{9,13,16,20}$). Found, %: C 73.79; H 6.71. $C_{50}H_{54}O_{10}$. Calculated, %: C 73.71; H 6.63.

Benzene-1,2-diylbis[4-(4-nonyloxybenzoyloxy)-benzoates] (VIIc). Yield 0.45 g (81.8%), white amorphous powder. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.93 t (6H, CH_3, *J* 6.6 Hz), 1.30–1.45 m (20H, CH_2), 1.45–1.55 m (4H, $OCH_2CH_2C\underline{H}_2$), 1.81–1.90 m (4H, $OCH_2C\underline{H}_2$), 4.07 t (4H, OCH_2, *J* 6.6 Hz), 6.98 d (4H, $H^{17,19}$, *J* 8.8 Hz), 7.26–7.33 m (4H, $H^{10,12}$), 7.37–7.47 m (4H, $H^{3,4,5,6}$), 8.12–8.17 m (8H, $H^{9,13,16,20}$). Found, %: C 69.79; H 7.8. $C_{52}H_{58}O_{10}$. Calculated, %: C 74.11; H 6.89.

Benzene-1,2-diylbis[4-(4-decyloxybenzoyloxy)-benzoate] (VIId). Yield 0.6 g (69%), white amorphous powder. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (6H, CH_3), 1.25–1.45 m (24H, CH_2), 1.45–1.55 m (4H, $OCH_2CH_2C\underline{H}_2$), 1.80–1.90 m (4H, $OCH_2C\underline{H}_2$), 4.07 t (4H, OCH_2, *J* 6.4 Hz) 6.98 d (4H, $H^{17,19}$, *J* 8.6 Hz), 7.26–7.33 m (4H, $H^{10,12}$), 7.37–7.47 m (4H, $H^{3,4,5,6}$), 8.10–8.20 m (8H, $H^{9,13,16,20}$). Found, %: C 74.59; H 7.03. $C_{54}H_{62}O_{10}$. Calculated, %: C 74.48; H 7.13.

Benzene-1,2-diylbis[4-(4-dodecyloxybenzoyloxy)-benzoate] (VIIe). Yield 0.5 g (43.1%), white amorphous powder. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (6H, CH_3, *J* 6.6 Hz), 1.23–1.44 m (32H, CH_2), 1.45–1.55 m (4H, $OCH_2CH_2C\underline{H}_2$), 1.81–1.90 m (4H, $OCH_2C\underline{H}_2$), 4.07 t (4H, OCH_2, *J* 6.6 Hz), 6.98 d (4H, $H^{17,19}$, *J* 8.8 Hz), 7.25–7.33 m (4H, $H^{10,12}$), 7.36–7.47 m (4H, $H^{3,4,5,6}$), 8.09–8.20 m (8H, $H^{9,13,16,20}$). Found, %: C 75.29; H 7.48. $C_{58}H_{70}O_{10}$. Calculated, %: C 75.16; H 7.56.

Benzene-1,2-diylbis[4-(4-decyloxybenzoyloxy)-benzoates] (VIIf). Yield 0.67 g (43.1%), white amorphous powder. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (6H, CH_3, *J* 6.8 Hz), 1.25–1.45 m (24H, CH_2), 1.45–1.55 m (4H, $OCH_2CH_2C\underline{H}_2$), 1.80–1.90 m (4H, $OCH_2C\underline{H}_2$), 4.07 t (4H, OCH_2, *J* 6.4 Hz) 6.98 d (4H, $H^{17,19}$, *J* 8.6 Hz), 7.26–7.33 m (4H, $H^{10,12}$), 7.37–7.47 m (4H, $H^{3,4,5,6}$), 8.10–8.20 m (8H, $H^{9,13,16,20}$). Found, %: C 68.89; H 6.33. $C_{54}H_{60}Cl_2O_{10}$. Calculated, %: C 69,01; H 6.39.

Bis[4-(4-heptyloxybenzoyloxy)phenyl]benzene-1,2-dicarboxylate (XI). A mixture of 4-hydroxy-phenyl-4-heptyloxybenzoate **X** (0.83 g, 2.5 mmol), *o*-phthalic acid (0.21 g, 1.25 mmol), 4-dimethylamino-pyridine (0.0305 g, 0.25 mmol), and 20 mL of anhyd-rous chloroform was stirred for 10 min followed by addition of *N*,*N*'-dicyclohexylcarbodiimide (0.515 g, 2.5 mmol). The reaction mixture was stirred for 20 h, at room temperature, the formed precipitate was filtered off and washed with anhydrous chloroform. The filtrate was evaporated; the residue was recrystallized from ethanol. Yield 0.8 g (81.6%), white amorphous powder, mp 142.3°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (6H, CH_3, *J* 6.6 Hz), 1.25–1.43 m (12H, CH_2), 1.43–1.53 m (4H, $OCH_2CH_2C\underline{H}_2$), 1.75–1.87 m (4H, $OCH_2C\underline{H}_2$), 4.04 t (4H, OCH_2, *J* 6.6 Hz), 6.98 m (4H, $H^{17,19}$), 7.22–7.33 m (8H, $H^{10,12,9,13}$), 7.37–7.47 m (4H, $H^{3,4,5,6}$), 7.70–7.75 m (2H, $H^{4,5}$), 7.98–8.04 m (2H, $H^{3,6}$) 8.10–8.20 m (4H, $H^{16,20}$). Found, %: C 73.14; H 6.58. $C_{48}H_{50}O_{10}$. Calculated, %: C 73.28; H 6.36.

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