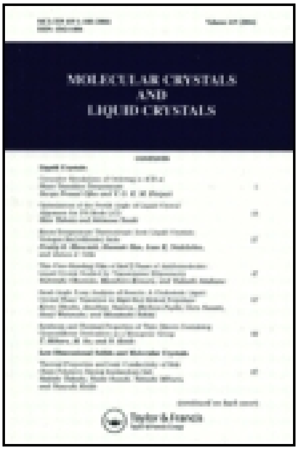

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Synthesis of Y-Shaped Liquid Crystals and the Influence of Their Structure on the Phase Behavior

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Synthesis of Y-Shaped Liquid Crystals and the Influence of Their Structure on the Phase Behavior

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A series of the Y-shaped liquid crystalline (LC) materials based on central 1,2,4-benzenetricarboxylic core was synthesized with variation of the arm length (two or three para-linked phenyl rings) in the Y-shaped mesogen and their dipole architecture (ether or ester terminal and linked groups). Our results indicate that main relationships between molecular structure and mesomorphic behavior well known for the calamitic LC are valid for the Y-shaped compounds too. Smectic mesophases might be obtained by lengthening the mesogen with an additional aromatic core in the arm or with an alkyl chain at the tail. The substitution of the alkoxy terminal groups on to alkanoyl also leads to the enhanced smectic behavior of the Y-shaped molecules.

Keywords: mesomorphic behavior; synthesis; Y-shaped compounds

1. INTRODUCTION

Although liquid crystalline (LC) materials have been known for over a century, an amazing richness and complexity of new behavior has been continually discovered, fueling innovation and the development of novel applications. In many instances, new and non-conventional LC systems have molecular architectures that do not fall into the traditional categories of rod-like or disc-like but are characterized by systems of intermediate shape, which in turn contain several elements capable of being independently manipulated. This has led to the discovery of new types of mesophases with fascinating structures, which have been summarized in several papers [1,2]. From these studies it is clear that architecture and functionalization are essential

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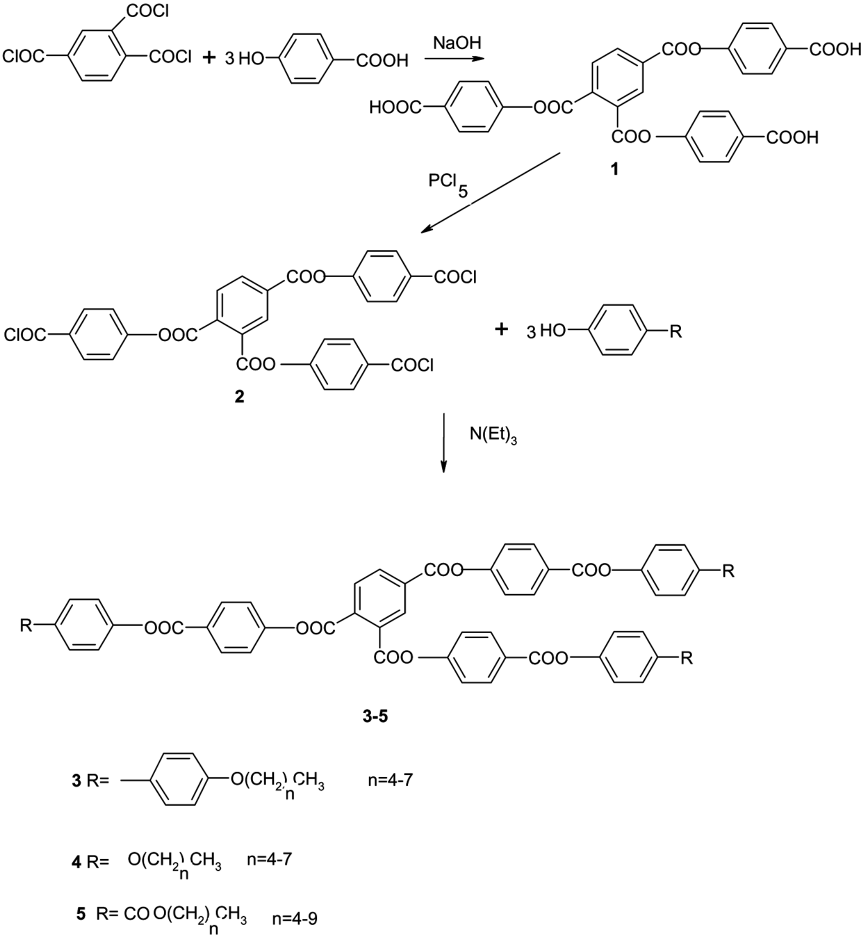
aspects in the molecular engineering of liquid crystals for controlling the physical properties that ultimately define the self-organizing process that leads to mesophase formation; molecular shape, dipole architecture, space filling effects, deformation ability, chirality, minimal interfacial curvature, microphase segregation, and self-assembly are all aspects that contribute to and determine the mesophase structure.

In this context, our article is concerned with Y-shaped LC compounds. Their basic building blocks are linear rod-like groups connected via suitable bridging in such a way that they span a two-dimensional space. Wendorff *et al.* [3,4] published the first article concerning such mesogenic molecules. Molecular modeling and synthesis indicated that such molecules should have a tendency to display a nematic phase at least for short tails (methyl through butyl). The aim of the present article was investigating the influence of length of terminal alkyl tail, length of arms, and type of bridging groups in the arms of the Y-shaped mesogens on mesomorphic behavior of two-dimensional LC compounds.

The number of synthesized LC compounds with the rigid Y-shaped mesogens is still very limited. The polyesters with the azomethine based Y-shaped mesogens were synthesized [5,6] but, as mentioned by the authors themselves, due to the conformational flexibility of the azomethine group this type of polymer cannot be strictly considered as Y-shaped segmented LC polymers. The numerous T-shaped LC compounds synthesized by Tshierske *et al.* [7] are different because in all cases one arm of these mesogens is flexible. Similarly the most other synthesized Y-shaped LC compounds contained the flexible spacers between the rigid blocks [2,8].

2. RESULTS AND DISCUSSION

The synthesis of such range of materials with functional groups in specific positions in order to produce the required physical properties needed careful consideration. 1,2,4-benzenetricarboxylic acid was selected as central core for building of Y-shaped mesogen. It allows us to compare our results with results of Wendorff *et al.* [3,4]. To exclude laborious synthesis of intermediate 4-alkoxyphenyl- and 4-alkylcarboxy-4-hydroxybenzoates, we prepared 1,2,4-(4-carboxyphenyloxycarbonyl)benzene acid **1** using interphase condensation of the acid chloride of 1,2,4-benzenetricarboxylic acid with p-4-hydroxybenzoic acid (Scheme 1). It was converted in one step to chloride **2**, which was used for synthesis of Y-shaped compounds **3–5** by condensation with available para-alkoxy or -alkylcarboxyphenols. This method



SCHEME 1 A synthetic pathway to the Y-shaped compounds **3–5**.

was chosen for the preparation of compounds **3–5** because the scale of reaction may be large and a good yield was essential. The properties of compounds **3–5** are given in the table. Compounds **3** have high melting points (about 170°C). The clearing temperatures are unachievable because the compounds degrade in the temperature range of interest (about 300°C).

By optical microscopy, each homologue **3** from $n = 4$ to $n = 7$ showed a single smectic A phase. The texture of the phase was either focal-conic or homeotropic. The comparison with results of Wendorff *et al.* (compounds **4** $n = 0$–3 [3,4]) shows that extension of the length of the arm Y-shaped mesogen from two to three para-connected benzene rings leads to a dramatic increase of clearing temperatures. Surprisingly, the type of mesophase was changed from nematic to smectic A. Lattice calculations performed by Wendorff *et al.* [3,4] for these molecules using an extended version of the Flory lattice treatment of rod-like molecules predicted that they should be able to form only nematic phases. This was supported by synthesis of compounds **4** n = 0–3 [3,4].

However, the extension of the arm in the Y-shaped mesogen from two to three para-connected benzene rings leads to smectic phases in compounds **3**. This result stimulated us to synthesize compounds **4** with longer terminal alkoxy substituents. These homologues of **4** have melting points close to value of the butoxy derivative (132C) synthesized by Wendorff *et al.* [3] (Table 1). The increase of length of alkoxy substituents had very little effect on the clearing point. However, mesomorphic behavior was changed dramatically. Microscopy

TABLE 1 Phase Transition Temperatures, Transitions Enthalpies of Compounds **3–6**

Compound	n	$T_m{}^a$/°C	$\Delta_1 H_m{}^b$/J g^{-1}	$T_{SN}{}^c$/°C	$T_i{}^d$/°C	Δ $H_i{}^e$/J g^{-1}
3	4	173.9	5.0	—	—	—
	5	175.2	6.7	—	—	—
	6	174.1	5.6	—	—	—
	7	172.0	5.8	—	—	—
4	4	127.0	27.5	189.6	190.7[6]	2.6
	5	125.0	28.6	186.8	188.0[B]	2.8
	6	121.3	26.4	—	187.0	2.1
	7	118.0	26.2	—	188.9	3.0
5	3	91.2	29.4	—	124.0	1.8
	4	86.3	28.1	—	138.0	1.7
	5	74.2	20.1	—	144.0	1.2
	6	17.0	15.6	—	72.5	1.0
	7	68.0	18.3	—	152.0	2.6
	8	13.0	5.2	—	—	—
	9	16.0	4.3	—	92.0	0.5
6	4	142.0	25.6	—	146.7	1.7
	5	140.0	24.6	161.5	164.0	2.1
	6	135.5	26.3	152.0	158.5	2.4
	7	144.5	22.8	—	148.0	1.9

[a] Melting point.

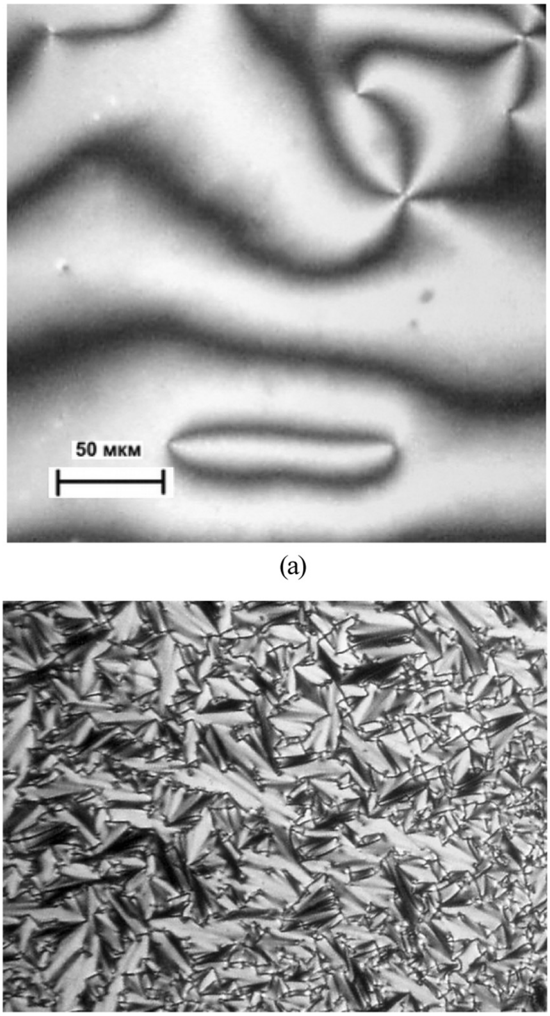
[b] Enthalpy at T_m.

[c] Smectic A–nematic transition temperature.

[d] Clearing temperature.

[e] Enthalpy at T_i.

investigations revealed that these compounds have a tendency to display smectic A phases, as is apparent from the focal-conic texture (Fig. 1b). For the compounds **4** n = 4 and 5, a nematic state appeared upon cooling from isotropic state with a typical schlieren textures (Fig. 1a) in a very narrow temperature interval (about 1°C). Therefore, with extension of the alkoxy chain length the smectic behavior of

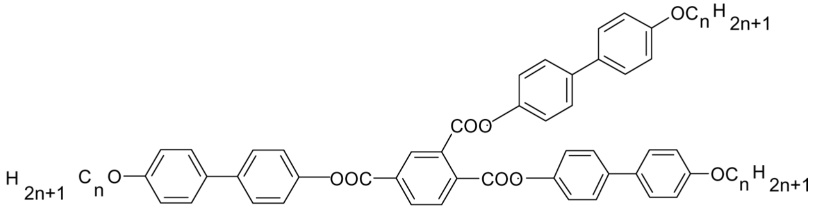


(a)

(b)

FIGURE 1 Optical textures of compound **5** (n = 5) obtained on cooling from the isotropic liquid at 190°C (a); (b) at 180°C.

Y-shaped molecules increases as is typical for usual calamitic LC compounds [1]. To verify this assumption a set of compounds **5** was synthesized. For calamitic LC compounds it is well known that substitution of a terminal ether group in mesogenic fragments for an ester leads to enhanced smectic behavior [1]. Indeed, this is so in our case because all compounds **5** display only a smectic A phase according to their textures (focal-conic). The replacement of the terminal ether group with an alkanoyl moiety decreases the melting point, thereby the compounds **5** n = 6 and 9 display LC state at room temperature. To extend our comparison with calamitic LC compounds, we synthesized compounds **6** which did not contain an ester group into the arm in the Y-shaped mesogen that should leads to enhanced nematic behavior in compare with compounds **4**.



6, n=4-7

The higher melting point values when compared to the **4** analogues are due to increased polarizability of biphenyl fragment. Also compounds **6** are more compact and may pack efficiently. This is responsible for the high melting point. However, the result of this structural change is a significant decrease in a clearing point. For the compounds **6** with n = 4, 5, 6, upon cooling, a nematic phase appeared with a schlieren texture: this schlieren texture changed on further cooling for compounds **6** with n = 5 and 6 to focal-conic which were identified as S_A phase. On cooling, the compounds with n = 7 only exhibited S_A phase. Hence, compounds **6** have a tendency to enhanced namatic behavior in compare to compounds **4**. It allows us to come to conclusion that main relationships between molecular structure and mesomorphic behavior well known for the calamitic LC are valid for the Y-shaped compounds too. Our investigation supports the prediction of Wendorff *et al.* [3,4] that for appearance of LC behavior at the Y-shaped molecules each arm of the Y-shaped mesogen should be quasi mesogen in calamitic LC compounds. Indeed, the results of Takenaka *et al.* [9] as well as our investigation [10] were shown that if the Y-shaped molecules of 1,2,4-trisubstituted benzenes have at least in one arm of the Y-shaped mesogen only one substituted phenyl rings these compounds may displayed only monotropic mesophase (nematic or smectic A in dependence from alkyl tail). Calamitic analogues of compounds **5** n = 4–9 (bisalkyl 4,4′-(terephtaloyldioxy) dibenzoates) displayed at similar alkyl tails only smectic A mesophase with increased isotropization temperatures on 20–50°C [11,12].

3. CONCLUSION

A series of the Y-shaped LC materials was synthesized with variation of the arm length in the Y-shaped mesogen and their dipole architecture. Our results indicate that main relationships between molecular structure and mesomorphic behavior well known for the calamitic LC are valid for the Y-shaped compounds too. Smectic mesophases might be obtained by lengthening the mesogen with an additional aromatic core in the arm or with an alkyl chain at the tail. The substitution of the alkoxy terminal groups on to alkanoyl leads also to enhanced smectic behavior of the Y-shaped molecules.

4. EXPERIMENTAL

4.1. Characterization of Materials

The chemical structures for the target materials were identified by ^{1}H NMR spectroscopy using a Bruker MSL 400 spectrometer and IR spectroscopy using a Bruker Vertex instrument. The purity of the final compounds was assessed by thin layer chromatography, and further confirmed by elemental analysis. The analytical data showed that the percentage errors for the carbon, hydrogen, and chlorine contents for the target materials were less than 1% as compared with the calculated results. The transition temperatures and enthalpies for all materials were determined by differential scanning calorimetry using a Shimadzu 60 calorimeter at a rate of 5°C min^{-1}. Mesophases were identified by microscopic textures using a Boetius optical microscope with hot stage (Germany).

4.2. Preparation of Materials

4-n-Alkoxyphenols and 4-n-alkoxy-4′-hydroxybiphenyls was synthesized as described by Williamson reaction from bromoalkanes and hydroquinone or 4,4′-biphenol in the presence of anhydrous potassium carbonate [13]. 4-Alkylesters of p-hydroxybenzoic acid were obtained by azeotrope esterification with benzene as solvent and sulfuric acid as catalyst. Chloride of 1,2,4-benzenetricarboxylic acid was obtained by method [14].

4.2.1. *1,2,4-Tris(4-carboxyphenyloxycarbonyl)benzene* (1)

A solution of 5 g (20 mmol) chloride of 1,2,4-benzenetricarboxylic acid in 30 ml carbon tetrachloride was ultrasonically dispersed with solution of 12 g of p-oxybenzoic acid in 150 ml of 1 N solution of NaOH for 5 min. After that the pH of solution was reduced to 8 by addition of 0.1 N hydrochloric acid. The residue was filtered off, and washed well with water, 0.1 N hydrochloric acid, again water, and dried in vacuo. Yield 7.5 g (66%) as white unfusible (before 300°C) powder. ^{1}H NMR (DMSO-d6), δ, (J, Hz): fragment of 1,2,4-benzene: 8.79 s (1 H); 8.56 d, (1 H, J 7.85); 8. 31 d, (1 H, J 7.85); fragment of oxybenzoate 7.41–7.45 m (4 H, *meta*); 7.50 d (2 H, *meta*); 8.02–8.07 m (6 H, *ortho*); 10.29 s(OH). IR (KBr, ν, cm^{-1}): 3400–3100, 2869, 2860, 1740(C=O), 1608, 1496, 1455, 1398, 1286, 1049, 1001, 937, 806, 742. Elemental analysis: found, %: C 63.45; H 3.50; calc for $C_{30}H_{18}O_{12}$, %: C 63.16; H 3.18.

4.2.2. *Chloride of 1,2,4-Tris(4-carboxyphenyloxycarbonyl) benzene* (2)

Five gram (8 mmol) of **1** was heated with 10 g (50 mmol) of PCl_5 for 5 h at 140°C;. The phosphorus oxychloride was removed in vacuo, and residue was recrystallized from chloroform to yield pale yellow crystals. Yield 4.85 g (88%); m.p. 126 C. ^{1}H NMR ($CDCl_3$), δ, (J, Hz): fragment of 1,2,4-benzene 8.86 s (1 H); 8.56 d, (1 H, J 8.14); 8.15 d, (1 H, J 8.14); fragment of oxybenzoate 8.28–8.35 m (4 H, *ortho*, J 8.7); 8.11–8.17 m (2 H, *ortho*, J 8.7); 7.43 d (4 H, *meta*, J 8.8); 7.46 d (2 H, *meta*, J 8.8). IR (KBr, ν, cm^{-1}): 2869, 2860, 2782, 1750 (C=O), 1608, 1496, 1455, 1398, 1286, 1251, 1226, 1201, 1049, 1001, 937, 806, 742. Elemental analysis: found, %: C 57.40; H 2.70; Cl 17.23; calc for $C_{30}H_{15}O_9Cl_3$, %: C 57.58; H 2.42; Cl 17.00.

4.2.3. *1,2,4-Tris(4′-n-amyloxybiphenyl-4-oxycarbonylphenyl-oxycarbonyl)benzene* (3, *n* = *4*)

A solution of 210 mg (0.3 mmol) of acid chloride **2**, 50 mg (1.5 mmol) 4-hydroxy-4′-amyloxybiphenyl, and 0.2 ml of triethylamine in 10 ml of anhydrous dichloroethane was stirred for 5 h at room temperature. The resulting solution was poured in 50 ml of ethanol, the residue was filtered off, dried, and twice recrystallized from a chloroform-ethanol mixture to yield white crystals. Yield 350 mg (90%). ^{1}H NMR ($CDCl_3$), δ, (J,Hz): fragment of 1,2,4-benzene 8.88 s (1 H); 8.56 d, (1 H, J 8.08); 8.31 d, (1 H, J 8.08); fragment of oxybenzoate 8.28–8.36 m (4 H, *ortho*); 8.11–8.17 m (2 H, *ortho*); 7.38 d (6 H, *meta*, J 8.08); fragment of biphenyl 6.86–7.01 m (12 H, *ortho*); 7.30–7.35 m (6 H, *ortho*); 7.40–7.65 m (6 H, *meta*); 4.0 t (6 H, OCH_2); 1.79–1.80 m (6 H); 1.60–1.67 m (6 H); 1.39–1.47 m (6 H); 0.95 t (9 H). IR (KBr, ν, cm^{-1}): 3039, 2927, 2854, 1740 (C=O), 1604, 1498, 1441, 1269, 1251, 1197, 1160, 1072, 1001, 917, 802, 756. Elemental analysis: found, %: C 75.40; H 5.70; calc for $C_{81}H_{72}O_{15}$, %: C 75.68; H 5.65.

Other compounds **3** were synthesized in a similar way with yields of 85–90%.

4.2.4. *1,2,4-Tris(4′-n-amyloxyphenyl-4-oxycarbonylphenyloxycarbonyl)benzene* (4, *n* = *4*)

It was synthesized in a similar way with compounds **3** with yield of 87%.

^{1}H NMR ($CDCl_3$), δ, (J, Hz): fragment of 1,2,4-benzene 8.89 d (1 H, J 1.64); 8.58 dd, (1 H, J 8.08, J 1.64); 8.16 dd, (1 H, J 8.08, J 1.64); fragment of oxybenzoate 8.28 d (4 H, *ortho*, J 8.08); 8.33 d (2 H, *ortho*, J 8.08); 6.98 d (4 H, *meta*, J 8.08); 6.93 d (2 H, *meta*, J 8.08); fragment of phenol 7.11 d (6 H, *ortho*, J 8.08); 7.44 d (6 H, *meta*, J 8.08); 3.98 t (6 H, OCH_2); 1.79–1.80 m (6 H); 1.60–1.67 m (6 H); 1.39–1.47 m (6 H); 0.95 t (9 H). IR (KBr, ν, cm^{-1}): 3039, 2927, 2854, 1740 (C=O), 1604, 1498, 1441, 1269, 1251, 1197, 1160, 1072,1001, 917, 802, 756. Elemental analysis: found, %: C 71.87; H 5.90 calc for $C_{63}H_{60}O_{15}$, %: C 71.58; H 5.72.

Other compounds **4** were synthesized in a similar way with yields of 85–90%.

4.2.5. *1,2,4-Tris(4′-n-amyloxcarbonylyphenyl-4-oxycarbonylphenyloxycarbonyl)benzene* (5, *n* = *4*)

It was synthesized in a similar way with compounds **3** with yield of 88%. ^{1}NMR ($CDCl_3$), δ, (J, Hz): fragment of 1,2,4-benzene 8.90 d (1 H, J 1.64); 8.50 dd, (1 H, J 8.08, J 1.64); 8.17 dd, (1 H, J 8.08, J 1.64); fragment of oxybenzoate 8.30 d (4 H, *ortho*, J 8.08); 8.35 d (2 H, ortho, J 8.08) 7.45 d (4 H, *meta*, J 8.08); 7.47 d (2 H, *meta*, J 8.08); terminal fragment of oxybenzoate 7.32 d (6 H, ortho, J 8.08); 8.13 d (6 H, *meta*, J 8.08); 4.33 t (6 H, OCH_2); 1.73–1.80 m (6 H); 1.60–1.67 m (6 H); 1.39–1.47 m (6 H); 0.95 t (9 H). IR (KBr, ν, cm^{-1}): 3076, 2960, 2933, 2873, 1742, 1717(C=O), 1602, 1506, 1466, 1414, 1385, 1260, 1227, 1197, 1160, 1072, 1001, 917, 802, 756. Elemental analysis: found, %: C 69.80; H 5.10; calc for $C_{66}H_{60}O_{18}$, %: C 69.46; H 5.30.

Other compounds **5** were synthesized in a similar way with yields of 85–90%.

4.2.6. *1,2,4-Tris(4′-n-amyloxybiphenylloxycarbonyl)benzene* (**6**, *n* = *4*)

It was synthesized in a similar way with compounds **3** with use instead of acid chloride **2** of chloride of 1,2,4-benzenetricarboxylic acid with yield of 88%. ^{1}H NMR ($CDCl_3$), δ, (J, Hz): fragment of 1,2,4-benzene 8.88 s (1 H); 8.54 d, (1 H, J 8.08); 8.13 d, (1 H, J 8.08); fragment of biphenyl 6.95–7.01 m (6 H, *ortho*); 7.30–7.32 m (6 M, *meta*); 7.47–7.65 m (12 H); 4.0 t (6 H, OCH_2); 1.79–1.80 m (6 H); 1.60–1.67 m (6 H); 1.39–1.47 m (6 H); 0.95 t (9 H). IR (KBr, ν, cm^{-1}): 3040, 2960, 2933, 2869, 2860, 2782, 1743 (C=O), 1608, 1496, 1455, 1398, 1286, 1251, 1226, 1201, 1166, 1100, 1049, 1001, 937, 806, 742. Elemental analysis: found, %: C 77.45; H 6.50; calc for $C_{60}H_{60}O_9$,%: C 77.90; H 6.54.

Other compounds **6** were synthesized in a similar way with yields of 85–90%.

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