ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 8, pp. 1559–1564. © Pleiades Publishing, Ltd., 2008.
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Dipole Architecture of Molecules and Mesomorphic Behavior of Liquid Crystals with Rigid *T*-Shaped Mesogenic Fragment

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Received January 31, 2008

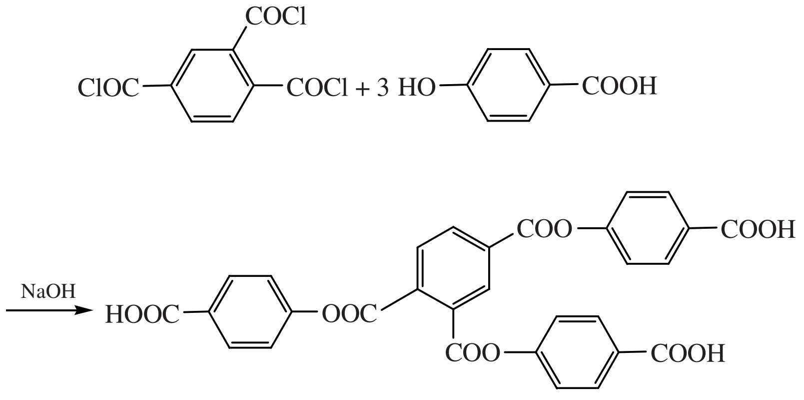
Abstract—A number of liquid crystalline polyesters having a rigid *T*-shaped mesogenic fragment and differing in dipole architecture were synthesized and examined by polarizing optical microscopy, differential scanning calorimetry, and IR and ^{1}H NMR spectroscopy. The thermal stability of the mesophase in the given series of compounds was shown to increase with extension of arms in the *T*-shaped mesogenic fragment, as well as on replacement of the terminal ester groups (COOAlk) therein by ether moieties (OAlk). Such replacement also enhances smectogenic properties.

DOI: 10.1134/S107036320808015X

Development of synthetic methods initiates a discovery of new liquid crystalline compounds whose molecular structure is untypical of common liquid crystals. The liquid crystalline order is controlled by fine balance between the molecular and dipole architecture of molecules. I previously synthesized a series of compounds having a rigid *T*-shaped mesogenic fragment [1]. The goal of the present work was to synthesize aromatic oligoesters with *T*-shaped mesogenic fragment and to study their phase behavior and its dependence on the molecular and dipole architecture. The results of calculations in terms of the extended Flory–Huggins lattice theory showed that appearance of liquid crystalline order in *T*-shaped mesogenic systems was possible only when each arm of the mesogenic fragment itself was capable of acting as mesogen in common (calamitic) liquid crystals [2]. Therefore, one step of the study was to elucidate the effect of the size of the arm in the mesogenic fragment on the mesomorphic behavior of such compounds.

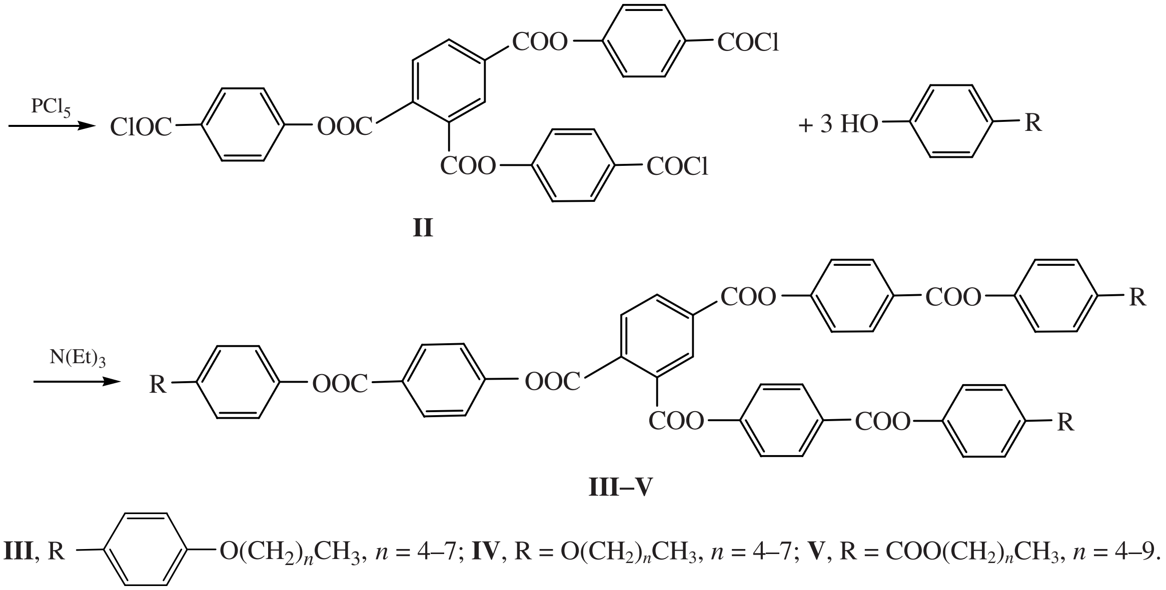
An appropriate method for building up complex monomeric structures having a potential mesogenic fragment was described in [3]. This approach makes it possible to simplify synthetic routines related to variation of molecular structure in the series of compounds under study. Following this approach, trimellitic (benzene-1,2,4-tricarboxylic) acid was

Scheme 1.



I

Scheme 1. (Contd.)



II

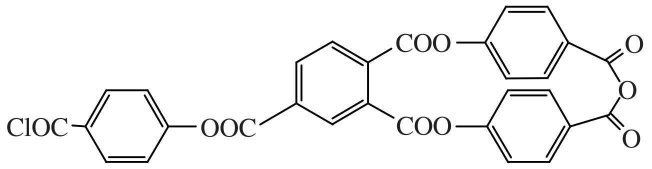
III–V

III, R = 4-C$_6$H$_4$O(CH$_2$)$_n$CH$_3$, n = 4–7; **IV**, R = O(CH$_2$)$_n$CH$_3$, n = 4–7; **V**, R = COO(CH$_2$)$_n$CH$_3$, n = 4–9.

selected as a base fragment. Esterification of the corresponding acid chloride with *p*-hydroxybenzoic acid gave compound **I** which was treated with phosphorus pentachloride to obtain the desired monomer **II**. The latter was brought into reactions with various phenols, and a series of liquid crystalline compounds **III**–**V** with different molecular and dipole architectures was thus synthesized (see Scheme 1).

The above procedure for the synthesis of compounds **III**–**V** is specific due to the use of phosphorus pentachloride instead of more convenient thionyl chloride. The reason is that treatment of **II** (as well as of trimellitic acid [4]) with thionyl chloride gives anhydride **VI** rather than the desired tricarbonyl trichloride (Scheme 2).

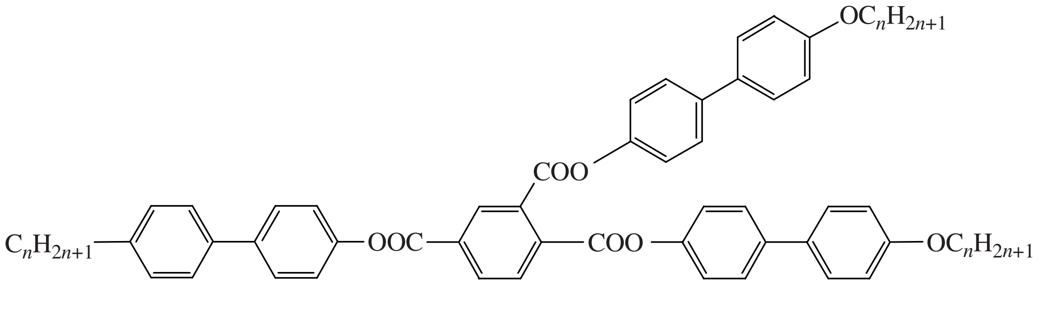
Scheme 2.



VI

The properties of compounds **III**–**V** as liquid crystals were examined by polarizing optical microscopy and differential scanning calorimetry (see table). Liquid crystalline 1,2,4-tris(4'-alkoxybiphenyl-4-yloxycarbonyl)benzenes of the general formula **VII** were studied previously [1] (Scheme(3).

Scheme 3.



VII, n = 5–8.

The arm of the mesogenic fragment in molecules **III** is longer than that in **VII** by a benzoate moiety. The melting points of compounds **III** increase by 35–40°C as compared to **VII**, and the temperature range of their liquid crystalline phase sharply extends, so that no transition to the isotropic state is observed up to decomposition temperature of **III**, i.e., above 300°C. Thus the extension of the arm in the mesogenic fragment by a benzoate moiety increases the thermal stability of the mesophase by more than 150°C. Analogous enhancement of the thermal stability of mesophase with rise in the number of *para*-linked benzene rings in the mesogenic fragment is typical of calamitic liquid crystals [5]. All compounds **III** show smectic mesomorphism, as follows from the confocal textures of the liquid crystalline phase observed using polarizing optical microscope. This means that extension of arms in *T*-shaped mesogenic fragment either leads to loss of nematic mesomorphism or the transition temperature to the nematic phase falls beyond the thermal stability range of compounds **III**.

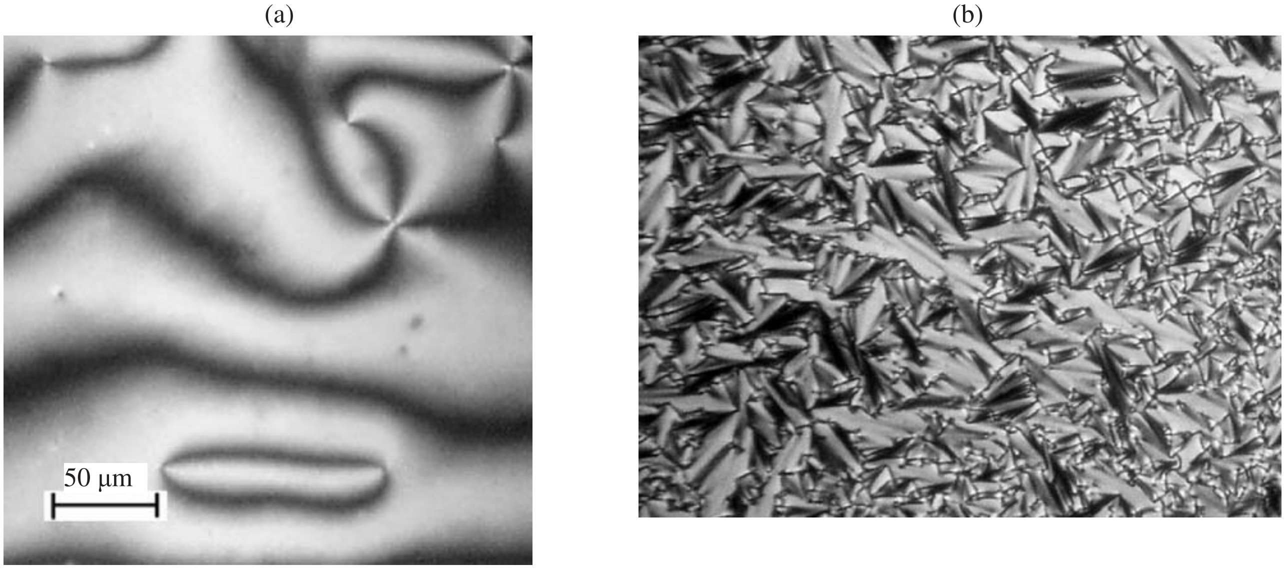
In the next step of the study, the effect of dipole architecture of *T*-shaped mesogenic fragments on their mesomorphic behavior was examined. For this purpose, the structure of compounds **VII** was modified via introduction of an ester group between the benzene rings in the arms (compounds **IV**). In going from **VII** to **IV**, the length of the arm changes relatively slightly, but the latter contain a group possessing a dipole moment directed at an angle of ~55° with respect to the principal molecular axis of the arm. The result is that the melting points of **IV** are lower by 15–20°C than those of analogous compounds **VII** (see table), and the temperature of transition into the isotropic phase increases by about 50°C. In other words, introduction of additional dipolar components into the *T*-shaped mesogenic fragment (as well as increase of its polarizability) enhances the thermal stability of the mesophase, and reduction of the melting point (due to lower molecular symmetry) leads to considerable extension of the temperature range of liquid crystalline state. Increased polarizability and dipole moment of the mesogenic fragment in **IV** strongly destabilize nematic mesophase of these compounds as compared to structures **VII**. As follows from the data of polarizing microscopy and differential scanning calorimetry, nematic phase is observed only in a temperature range of about 1°C before transition to isotropic phase for *n*-pentyl and *n*-hexyl derivatives **IV**. These compounds displayed schlieren textures with singularities of ±1/2 and ±1, which is typical of nematics [6] (see figure, a), while confocal textures typical of smectics [6] were observed in the other ranges of liquid crystalline state (see figure, b). Thus increase in the polarizability and dipole constituent of the arms in the *T*-shaped mesogenic fragment enhances the smectogenity and thermal stability of the mesophase.

Properties of compounds **III–V**

Comp. no.	*n*	mp, °C	ΔH_m, J g^{-1}	T_i,[a] °C	ΔH_i,[a] J g^{-1}
III	4	173.9	5.0	–	–
	5	175.2	6.7	–	–
	6	174.1	5.6	–	–
	7	172.0	5.8	–	–
IV	4	127.0	27.5	190.7[b]	2.6
	5	125.0	28.6	188.0[c]	2.8
	6	121.3	26.4	187.0	2.1
	7	118.0	26.2	188.9	3.0
V	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

[a] T_i and ΔH_i stand, respectively for the temperature and enthalpy of transition into isotropic state. [b] Smectic–nematic phase transition temperature 189.6°C. [c] Smectic–nematic phase transition temperature 186.8°C.

The phase behavior and thermal stability of calamitic liquid crystals are largely determined by the nature of the terminal groups [5]. With a view to reveal analogous relations in the series of *T*-shaped mesogens, the terminal alkoxy groups in **IV** were replaced by ester moieties (compounds **V**). It turned out that such replacement leads to lowering of both melting points and temperatures of transition into isotropic state (see table). All compounds **V** showed only smectic mesophase. An analogous pattern is observed for calamitic liquid crystals: terminal ester



Textures of compound **IV** ($n = 5$) at (a) 190 and (b) 180°C.

groups give rise to pronounced smectogenity as compared to alkoxy groups and reduce themal stability of the mesophase. It is interesting that the isotropization temperature of compounds **V** increases with extension of the alkyl substituent, reaching the maximum value at $n = 7$. Here, unlike compounds **III** and **IV**, a strong odd–even effect of *n* on the phase transition temperature is observed. Some compounds **V** ($n = 6, 9$) form liquid crystalline state even at room temperature.

Thus the results of the present study showed that the phase behavior of *T*-shaped liquid crystals generally follows the relations known for calamitic systems: extension of the arms in the *T*-shaped mesogenic fragment leads to enhanced smectogenity and increases the thermal stability of the mesophase. The smectogenity also increases with rise in the polarizability and dipole constituent of the arms. Increase in the number of ester groups in the mesogenic fragment (and hence increase in the lateral constituent of the dipole moment) makes the mesophase less thermally stable.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker MSL 400 spectrometer at 400 MHz. The IR spectra were measured on a Bruker Vertex instrument. The phase transition temperatures were determined on a melting point apparatus coupled with a Boëtius polarizing microscope, as well as by differential scanning calorimetry on a Shimadzu 60 microcalorimeter at a heating rate of 2–5 deg min^{-1}.

4-*n*-Alkoxyphenols and 4'-*n*-alkoxybiphenyl-4-ols were synthesized by the Williamson reaction from the corresponding alkyl bromides and hydroquinone or biphenyl-4,4'-diol in the presence of potassium carbonate [7]. *n*-Alkyl 4-hydroxybenzoates were obtained by esterification of 4-hydroxybenzoic acid with the corresponding alcohols in benzene in the presence of sulfuric acid with simultaneous removal of the liberated water as azeotrope. Benzene-1,2,4-tricarbonyl trichloride was prepared according to the procedure described in [4].

1,2,4-Tris(4-carboxyphenyloxycarbonyl)benzene (I). A solution of 5 g of benzene-1,2,4-tricarbonyl trichloride in 30 ml of anhydrous carbon tetrachloride was added dropwise over a period of 15 min under vigorous stirring to a solution of 12 g of 4-hydroxybenzoic acid in 150 ml of 0.1 N aqueous sodium hydroxide. The mixture was stirred for 3 h and adjusted to pH 8 by adding 0.1 N hydrochloric acid. The precipitate was filtered off, washed with water, 0.1 N hydrochloric acid, and water again, and dried under reduced pressure. Yield 7.5 g (66%), white powder which did not melt up to decomposition point (300°C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1,2,4-C_6H_3: 8.79 s (1H), 8.56 d (1H, $J = 7.85$), 8.31 d (1H, $J = 7.85$); OC_6H_4COOH: 7.41–7.45 m (4H, *m*-H), 7.50 d (2H, *m*-H), 8.02–8.07 m (6H, *o*-H), 10.29 s (OH). IR spectrum (KBr), ν, cm^{-1}: 3400–3100, 2869, 2860, 1740 (C=O), 1608, 1496, 1455, 1398, 1286, 1049, 1001, 937, 806, 742. Found, %: C 63.45; H 3.50. $C_{30}H_{18}O_{12}$. Calculated, %: C 63.16; H 3.18.

1,2,4-Tris(4-chloroformylphenyloxycarbonyl)benzene (II). A mixture of 5 g of compound **I** and 10 g of phosphorus pentachloride was heated for 5 h at 140°C. Phosphoryl chloride was distilled off, and the residue was recrystallized from chloroform. Yield 4.85 g (88%), yellow crystals, mp 126°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 1,2,4-C_6H_3: 8.86 s (1H), 8.56 d (1H, J = 8.14), 8.15 d (1H, J = 8.14); OC_6H_4COOH: 8.28–8.35 m (4H, *o*-H, J = 8.7), 8.11–8.17 (2H, *o*-H, J = 8.7), 7.43 d (4H, *m*-H, J = 8.8), 7.46 d (2H, *m*-H, J = 8.8). IR spectrum (KBr), ν, cm^{-1}: 2869, 2860, 2782, 1750 (C=O), 1608, 1496, 1455, 1398, 1286, 1251, 1226, 1201, 1049, 1001, 937, 806, 742. Found, %: C 57.40; H 2.70; Cl 17.23. $C_{30}H_{15}O_9Cl_3$. Calculated, %: C 57.58; H 2.42; Cl 17.00.

1,2,4-Tris[4-(4′-*n*-pentyloxybiphenyl-4-yloxycarbonyl)phenyloxycarbonyl]benzene (III, *n* = 4). A solution of 210 mg of trichloride **II**, 50 mg of 4'-pentyloxybiphenyl-4-ol, and 0.2 ml of triethylamine in 10 ml of anhydrous dichloroethane was stirred for 5 h at room temperature using a magnetic stirrer. The solution was poured into 50 ml of ethanol, and the precipitate was filtered off, dried, and reprecipitated once again from chloroform into ethanol. Yield 350 mg (90%), white crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 1,2,4-C_6H_3: 8.88 s (1H), 8.56 d (1H, J = 8.08), 8.31 d (1H, J = 8.08); OC_6H_4CO: 8.28–8.36 m (4H, *o*-H), 8.11–8.17 d (2H, *o*-H), 7.38 d (6H, *m*-H, J 8.08); $AlkOC_6H_4C_6H_4$: 6.86–7.01 m (12H, *o*-H), 7.30–7.35 m (6H, *m*-H), 7.40–7.65m (6H, *m*-H), 4.0 t (6H, OCH_2), 1.79–1.80 m (6H), 1.60–1.67 m (6H), 1.39–1.47 m (6H), 0.95 t (9H). IR spectrum (KBr), ν, cm^{-1}: 3039, 2927, 2854, 1740 (C=O), 1604, 1498, 1441, 1269, 1251, 1197, 1160, 1072, 1001, 917, 802, 756. Found, %: C 75.40; H 5.70. $C_{81}H_{72}O_{15}$. Calculated, %: C 75.68; H 5.65.

The other compounds of series **III** were synthesized in a similar way; yield 85–90%.

1,2,4-Tris[4-(4-*n*-pentyloxyphenyloxycarbonyl)phenyloxycarbonyl]benzene (IV, *n* = 4) was synthesized as described above for compound **III** (*n* = 4). Yield 87%, white crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 1,2,4-C_6H_3: 8.89 d (1H, J = 1.64), 8.58 d.d (1H, J = 8.08, 1.64), 8.16 d.d (1H, J = 8.08, 1.64); OC_6H_4CO: 8.28 d (4H, *o*-H, J = 8.08), 8.33 d (2H, *o*-H, J = 8.08), 6.98 d (4H, *m*-H, J = 8.08), 6.93 d (2H, *m*-H, J = 8.08); $AlkOC_6H_4O$: 7.11 d (6H, *o*-H, J = 8.08), 7.44 d (6H, *m*-H, J = 8.08), 3.98 t (6H, OCH_2), 1.79–1.80 m (6H), 1.60–1.67 m (6H), 1.39–1.47 m (6H), 0.95 t (9H). IR spectrum (KBr), ν, cm^{-1}: 3039, 2927, 2854, 1740 (C=O), 1604, 1498, 1441, 1269, 1251, 1197, 1160, 1072, 1001, 917, 802, 756. Found, %: C 71.87; H 5.90. $C_{63}H_{60}O_{15}$. Calculated, %: C 71.58; H 5.72.

The other compounds of series **IV** were synthesized in a similar way; yield 85–90%.

1,2,4-Tris[4-(4-*n*-pentyloxycarbonylphenyloxycarbonyl)phenyloxycarbonyl]benzene (V, *n* = 4) was synthesized as described above for compound **III** (*n* = 4). Yield 88%, white crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 1,2,4-C_6H_3: 8.90 d (1H, J = 1.64), 8.50 d.d (1H, J = 8.08, 1.64), 8.17 d.d (1H, J = 8.08, 1.64); OC_6H_4CO: 8.30 d (4H, *o*-H, J = 8.08), 8.35 d (2H, *o*-H, J = 8.08), 7.45 d (4H, *m*-H, J = 8.08), 7.47 d (2H, *m*-H, J = 8.08); $AlkOC_6H_4CO$: 7.32 d (6H, *o*-H, J = 8.08), 8.13 d (6H, *m*-H, J = 8.08), 4.33 t (6H, OCH_2), 1.73–1.80 m (6H), 1.60–1.67 m (6H), 1.39–1.47 m (6H), 0.95 t (9H). IR spectrum (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. Found, %: C 69.80; H 5.10. $C_{66}H_{60}O_{18}$. Calculated, %: C 69.46; H 5.30.

The other compounds of series **V** were synthesized in a similar way; yield 85–90%.

4-Chloroformylphenyl 3,5,8,10-tetraoxo-2,6,9-trioxa-1,7(1,4),4(1,2)-tribenzenacyclodecaphane-4^4-carboxylate (VI). A mixture of 5 g of compound **I** and 50 ml of thionyl chloride was heated for 5 h under reflux. Excess thionyl chloride was distilled off, and the residue was recrystallized from chloroform. Yield 4.60 g (83%), yellow crystals, mp 147°C. ^{1}H NMR spectrum (DMF-d_7), δ, ppm (J, Hz): 1,2,4-C_6H_3: 8.91 s (1H); 8.65 d (1H, J = 7.85); 8.41 d (1H, J = 7.85); $ClCOC_6H_4O$: 8.04 d (2H, *o*-H, J = 8.08), 6.97 d (2H, *m*-H, J = 8.08); $C_6H_4COOCOC_6H_4$: 8.15 d (4H, *o*-H, J = 8.08), 7.56 d (4H, *m*-H, J = 8.08). ^{13}C NMR spectrum (DMF-d_7), δ_C, ppm: 167.74 (COCl); 167.10, 167.04 (CO, anhydride); 165.31, 164.69, 164.40 (C=O); 154.73, 154.52, 154.47; 134.47, 133.09, 132.77, 132.34, 132.03, 131.69, 131.62, 131.53, 131.43, 129.89, 129.73, 129.03, 122.65, 122,57, 122.43, 122.33, 116.24, 115.66. IR spectrum (KBr), ν, cm^{-1}: 2869, 2860, 1760 (C=O), 1603, 1504, 1455, 1398, 1286, 1049, 1001, 937, 744. Found, %: C 63.40;

N2.70; Cl 6.23. $C_{30}H_{15}O_{10}Cl$. Calculated, %: C 63.12; H 2.65; Cl 6.21.

ACKNOWLEDGMENTS

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 06-08-00195a).

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