Synthesis and Study of Vitrescent Materials Based on the Alkoxybenzoic Acids Derivatives and Triethanolamine

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Received March 1, 2012

Abstract—Fifteen new branched triethanolamine esters of the benzoic acid derivatives were designed and the mesomorphism typical of discotic mesogens was forecast for them. In eight of the obtained compounds a manifestation of liquid crystal properties was predicted, for four derivatives equiprobable prognosis was given, and only three compounds were predicted not to form a mesophase. The obtained esters were characterized by elemental analysis, NMR and IR spectroscopy, gas chromatography-mass spectrometry. The main thermal characteristics that allow accounting for their phase behavior were determined.

DOI: 10.1134/S1070363213040075

Among the priorities of modern organic chemistry is the modeling and the creation of organic lightemitting diodes and semiconductors, including those based on discotic mesogens [1]. Organic light-emitting diodes (OLEDs) are semiconductor devices based on various organic compounds efficiently emitting light at passing an electric current through them. The H. Bock group was pioneering in the development of the OLEDs based on discotic mesogens [2]. They created two-layer sandwich red light emitting diodes with stable electroluminescence. The main application of the OLED technology is to create information displays, where the matching of energy levels to the minimal barriers of the injected charge carriers and the region of luminescence is important [1]. It is assumed that the production of such displays would be much cheaper than the current production of liquid crystal displays. It is also expected that the combination of the ordered liquid crystalline state of the oligomeric structure of branched macromolecules constructed on the basis of branching of dendrimers would lead to an ordered glassy state with a potential "hole" conductivity [3, 4].

The aim of this paper is designing new esters, the derivatives of alkoxybenzoic, benzoic, cyclohexylbenzoic and benzyloxybenzoic acids with triethanolamine (**Ia–Id**), the forecast of their possible mesomorphism, the synthesis and study of phase behavior, including the liquid crystalline state. It is assumed that such compounds should have unique thermal characteristics and the specific type of mesomorphism manifestation, useful later as a substrate in organic lightemitting diodes.



A forecast of possible manifestation of mesomorphism characteristic of discotic mesogens was performed by the method proposed in [5-8]. This method requires the calculation of the dimensionless molecular parameters: K, K_c , K_p , K_s , K_{ar} , M_m , M_r , which can be found from the molecular structure and models constructed by the HyperChem, Ver. Pro 6.0 software and optimized by the method of molecular mechanics (MM+). The calculation of these parameters for structures **Ia–Id** was carried out in automatic mode using a software module ChemCard [9] (Table 1, classification series I). The parameter K characterizes anisomety of the whole molecule, and the parameters K_c and K_p give the same for its separate parts (center and periphery). The parameter K_s reflects a degree of substitution of the central fragment with the peripheral substituents, K_{ar} takes into account the packing density of the peripheral substituents, and the parameter M_m accounts for the ratio of the masses of the central fragment and the peripheral substituents. Parameter $M_r = M_m \times K_s$ considers the number of substituents in the central core of the discogene molecule.

K 2.00-8.50; K_c 1.0-2.6; K_p 0.20-0.70; K_s 0.25-1.00; K_{ar} 0.080-0.450; M_m 0.30-0.80; M_r 0.15-0.80 (1) [8].

The results of calculation and the analysis of molecular parameters (Table 1) show that the esters that include the mesogenic fragments of alkoxybenzoic acids **Ia**, the homologs from first to eighth are predicted to be able to form columnar supramolecular packing in the mesophase. Four homolog, with n = 9 to 12, according to the forecast have an equal probability of transforming to the liquid-crystalline state, and to show no mesomorphism characteristic of discotic mesogens. The presence on the periphery of the more "rigid" fragments (unsubstituted benzene or cyclohexane ring) (Table 1, **Ib-Id**) are predicted to lead to the disappearance of liquid-crystalline properties. The

forecast was confirmed by the experimental data, which are discussed below.

The synthesis of branched esters **Ia–Id** was performed in several stages. Triethanolamine, a viscous liquid capable of vitrification, was chosen as the branching center. Alkoxybenzoic acids **II** were obtained along the Scheme 1 according to methods [10, 11] by the reaction of ethyl 4-hydroxybenzoate with alkyl bromides followed by the ester hydrolysis.

As the basis of the synthesis of alkoxybenzoic II, benzyloxybenzoic III, cyclohexsylbenzoic IV and benzoic V esters with triethanolamine VI was the

Comp. no.	E, kcal mol ⁻¹	K	K _p	K _{ar}	M _m	$P_{\rm Col+N}$
Ia , <i>n</i> = 1	39.54	4.42	0.57	0.116	0.72	+
Ia, $n = 2$	40.24	4.36	0.49	0.112	0.63	+
Ia , <i>n</i> = 3	42.85	5.04	0.42	0.106	0.57	+
Ia , $n = 4$	45.57	5.16	0.38	0.101	0.51	+
Ia , $n = 5$	48.25	5.56	0.33	0.096	0.47	+
Ia , $n = 6$	51.02	5.66	0.31	0.091	0.43	+
Ia , <i>n</i> = 7	53.72	6.04	0.28	0.083	0.40	+
Ia , <i>n</i> = 8	56.41	6.03	0.26	0.083	0.37	+
Ia , <i>n</i> = 9	59.11	6.38	0.24	0.079 ^b	0.35	±
Ia , <i>n</i> = 10	61.81	6.36	0.22	0.070^{b}	0.33	±
Ia , <i>n</i> = 11	64.51	6.66	0.21	0.073 ^b	0.31	±
Ia , <i>n</i> = 12	67.21	6.71	0.20	0.066 ^b	0.31	±
Ib	58.13	4.11	1.47 ^b	0.044 ^b	2.19 ^b	-
Ic	57.40	3.92	1.41 ^b	0.074 ^b	1.84 ^b	-
Id	32.68	3.57	0.79 ^b	0.143	1.00^{b}	_

Table 1. Molecular parameters and mesomorphism prediction of triethanolamine derivatives Ia–Id^a

^a $K_{\rm s} = 1.0$ for all compounds, $K_{\rm c} = 1.11$ for Ia, n = 1, $K_{\rm c} = 1.07$ for the other homolog; $P_{\rm Col + N}$ is forecast of mesomorphism characteristic of discotic mesogens. ^b Parameters that go beyond the classification series I.





method developed in [12], where the reaction was carried out under the action of dicyclohexylcarbodiimide on the carboxy and phenol groups of the initial reagents II-V and VI in the presence of dimethylaminopyridine as a catalyst, Scheme 2.

The structure of the synthesized compounds **Ia-Id** was confirmed by elemental analysis, NMR and IR spectroscopy, and GC-MS method. Table 2 lists the IR spectral parameters of the synthesized esters **Ia-Id**.

Compounds **Ia–Id** are fully substituted esters of triethanolamine and derivatives of benzoic acid. In the IR spectra they are characterized by three bands (Fig. 1, Table. 2) of the usual esters, due to the stretching vibrations of C=O (s), CO–O (s, as), and OCC (s, as) groups [13]. The peculiarity of the IR spectra of these compounds is that the band OCC (s, as) of compounds **Ia**, **Ib**, in contrast to that of the esters **Ic**, **Id**, is split in

two components due to the presence in these esters of an ether group.

Table 3 shows the values of the thermodynamic parameters of the synthesized compounds obtained by the method of differential scanning calorimetry (DSC) in a heating cycle. Esters of structure **Ia** have in their structure mesogenic fragments of alkoxybenzoic acids with the alkyl substituent from propyl to dodecyl. It was assumed that the range of the mesophase temperature of new derivatives will be substantially dependent on the length of the hydrocarbon radical. However, the study showed that the length of the hydrocarbon substituent weakly affected the and the vitrification of the mesophase (Table 3).

We succeeded to fix the phase transitions, which can be attributed to the enantiotropic mesophase followed by vitrification in the triethanolamine derivatives Ia, n = 3, 4, 6, 9, 12. The data in Table 1 show that the use of the longest alkyl group (dodecyl derivative) leads to the most significant result, namely, the sustainable mesophase in the glassy state.

At the first heating of the sample Ia, n = 12 the crystal-mesophase and mesophase-isotropic liquid transitions are observed (Fig. 1). In the cooling cycle a gradual vitrification of the sample occurs while maintaining the texture of the mesophase, which is confirmed by the data of polarization thermomicroscopy (Fig. 2). Thus, we found that all the synthesized derivatives of triethanolamine with structure Ia exhibited mesomorphism with the transition from the liquid crystalline to the vitreous state upon cooling, which agreed quite well with the results of the forecast presented in Table 1.

The derivatives of triethanolamine **1b-Id** did not exhibit the properties of liquid crystal, which is also in good agreement with the prediction (Table 1). Varying the substituent in the *para* position results only in the change in the melting temperature. The triethanolamine benzoate **Id** melted at the temperature of about 38°C. The introduction of cyclohexyl fragment increases the melting temperature of **Ic** to 123°C, while the introduction of the benzyloxy substituent (**Ib**) imparts amorphous structure to the material without a stable melting point, existing mostly in the glassy state.

EXPERIMENTAL

IR spectra were recorded on a Bruker Vertex 80 instrument in the range of 7500-350 cm⁻¹ from KBr tablets or films between two KRS-5 plates. ¹H and ¹³C NMR spectra were registered on Bruker AC-200 (200.13 MHz) and Bruker 500 instruments, solvent CDCl₃, internal reference TMS. Thin layer chromatography was performed on the chromatographic plates Silufol UV 254, Czech Republic. The spots were developed under UV irradiation, $\lambda = 254$ nm. Elemental analysis was performed using a FlashEA 1112 analyzer. Chromatograms and mass spectra were recorded on GC-MS Saturn 2000R instrument, carrier gas helium. Thermogravimetric analysis (TG) was performed on a NETZCH TG 209 F1 analyzer, in an argon flow of 20 ml min⁻¹ at a heating rate 10°C min⁻¹. Differential scanning calorimetry (DSC) was performed on a NETZCH DSC 204 F1 instrument, capsule material Al, the sample weight ≈ 20 mg, heating in N₂ atmosphere from -110 to 100°C, heating rate 10°C min⁻¹.

Tris[2-(4-propyloxybenzoyloxy)ethyl]amine (Ia, n = 3). A 4.25 g portion of propyloxybenzoic acid was dissolved in 75 ml of chloroform in a round-bottom 250 ml flask, and at permanent stirring 1.17 g of triethanolamine was added. The mixture was stirred for 10 min, then 3.47 g of 1,3-dicyclohexylcarbodiimide and a catalytic amount of dimethylaminopyridine was added. The mixture was stirred for 12 h. The reaction mixture was then filtered through a glass frit filter. The filtrate was washed with 5% acetic acid (2×25 ml), 5% sodium chloride solution (2×25 ml), distilled water (2×25 ml), and dried over sodium sulfate. The solvent was removed on a rotary evaporator, the residue was chromatographed on silica gel, eluent chloroform,

 Table 2. Absorption bands of ester groups in the IR spectra of esters Ia–Id

Compound	C=O	CO–O	0–C–C	
Ia , <i>n</i> = 3	1703.39	1233.47	1178.49-1172.59	
Ia , <i>n</i> = 4	1664.34	1232.91	1177.48-1173.33	
Ia , <i>n</i> = 6	1666.43	1233.03	1177.53–1171.33	
Ia , <i>n</i> = 9	1672.01	1231.01	1177.51-1171.61	
Ia , <i>n</i> = 12	1668.54	1232.97	1179.92–1171.47	
Ib	1786.88	1213.26	1186.54–1168.13	
Ic	1627.86	1230.71	1185.93	
Id	1781.31	1218.78	1168.39	



amine (Ia, n = 12): (1) heating and (2) cooling.

		1	1	1	1	1		1
Compound	mp, °C	$\Delta H_{\rm m}$, J g ⁻¹	$T_{\rm cr}$, °C	$\Delta H_{\rm cr}$, J g ⁻¹	T _g , ℃	$\Delta C_{\rm p}$, J g ⁻¹ K ⁻¹	$T_{\rm ph}$, °C	$\Delta H_{\rm ph},~{ m J~g}^{-1}$
Ia , $n = 3$	118.97	65.94	77.89	-57.9	17.86	0.79	88.93	-57.9
Ia , $n = 4$	123.84	81.16	79.79	-77.51	12.41	0.4	_	-
Ia , $n = 6$	127.23	75.49			-7.86	0.164	53.76	-59.9
							76.77	
Ia , $n = 9$	94.18	81.9	28.43	-20.45	-	_	-	-
Ia , <i>n</i> = 12	88.23	75.26	_	_	-	_	30.72	2.73
							57.40	0.74
Ib	—	_	_	_	-59.4	0.211	-	-
					7.29	0.203		
Ic	122.69	72.29	-	-	-2.13		53.87	-65.49
Id	38.18	4.02	10.06	4.021	-61.27	0.524	_	-
					23.47	0.077		
					23.47	0.052		

Table 3. The values of thermodynamic parameters of triethanolamine derivatives Ia–Id^a

^aData are given for the heating cycle.

followed by recrystallization from acetonitrile. The synthesized compound is a crystalline white substance, yield 85%, *M* 635.76. IR spectrum, v, cm⁻¹: 3147, 3032 s (C–H, Ar), 2971, 2889 s [(CH₂)_nCH₃], 2798 w, [(CH₂)_nCH₃], 1703.39 s, (C=O), 1233.47 s, (CO–O as), 1178.49–1172.59 s (O–C–C as), 1398 s (Ar, s). ¹H NMR spectrum (CDCl₃), δ , ppm: 1,04 m (9H, CH₃, *J*_{HH} 7.32 Hz,), 1.83 m (6H , PhOCH₂CH₂, *J*_{HH} 6.11 Hz), 3.52 m (6H, NCH₂, *J*_{HH} 7.34 Hz), 3.95 m (6H,



Fig. 2. Flower texture of tris[2-(4-dodecyloxybenzoyloxy) ethyl]amine (Ia, n = 12), 25°C, the cooling cycle, crossed nicols.

PhOCH₂CH₂, J_{HH} 6.1 Hz,), 4.14 m (6H, NCH₂CH₂, J_{HH} 12,2 Hz); 6.90 d (6H, H^{2, 6}–Ph, J_{HH} 8.5 Hz); 7,55 d (6H, H^{2,5}–Ph, J_{HH} 8.5 Hz). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 10.44 (CH₃); 22.44 (PhOCH₂); 57.48 (NCH₂); 63.51 (NCH₂CH₂); 69.70 (PhOCH₂); 114.29 (C^{2,6}-Ph); 129.10 (C^{3,5}-Ph); 166.2 (OCPh); 166.95 (PhCOO). Found, %: C 67.76, H 7.92, N 2.03. C₃₆H₄₅NO₉. Calculated, %: C 68.01, H 7.13, N 2.20.

Tris[2-(4-butyloxybenzoyloxy)ethyl]amine (Ia. n = 4) was obtained similarly. Yield: 81%, M =677.84. IR spectrum, v, cm⁻¹: 3147, 3032 s (C–H, Ar), 2971, 2889 s [(CH₂)_nCH₃], 2798 w, [(CH₂)_nCH₃], 1664.34 s (C=O), 1232.91 s, (CO-O as), 1177.48-1173.33 s (O-C-C as), 1398 s (Ar, s). ¹H NMR spectrum (CDCl₃) δ, ppm: 0.98 m (9H, CH₃, J_{HH} 7.324 Hz), 1.24 m (6H, CH₂CH₂, J_{HH} 12.5 Hz), 1.79 m (6H, PhOCH₂CH₂, J_{HH} 17.4 Hz), 3.49 m (6H, NCH₂, J_{HH} 14.3 Hz); 3.99 t (6H, PhOCH₂, $J_{\rm HH}$ = 6.7 Hz); 4.15 t (6H, NCH₂CH₂, J_{HH} 11.9 Hz), 6.86 d (6H, Ph-H, J_{HH} 8.24 Hz); 7.53 d (6H, Ph–H, $J_{\rm HH}$ = 8.5 Hz). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 13.71 (CH₃); 19.25 (CH₂); 30.68 (PhOCH₂); 49.99 (CH₂); 57.47 (NCH₂); 68.28 $(NCH_2CH_2);$ 114.38 $(C^{2,6}-Ph);$ 129.05 $(C^{3,5}-Ph);$ 154.85 (C-Ph); 161.6 (OCPh); 170.85 (PhCOO). Found, %: N 7.15, C 70.09; N 2.17. C₃₉H₅₁NO₉. Calculated, %: N 7.56, C 69.11; N 2.07.

Tris[2-(4-hexyloxybenzoyloxy)ethyl]amine (I, n = 6) was obtained similarly. Yield 78%. M = 761.49. IR spectrum, v, cm⁻¹: 3147, 3032 s (C–H, Ar), 2971, 2889 s [(CH₂)_nCH₃], 2798 w [(CH₂)_nCH₃], 1666.4 s

(C=O), 1233.03 s, (CO-O as), 1177.53-1171.33 s (O-C-C as), 1398 s (Ar, s). ¹H NMR spectrum (CDCl₃), δ, ppm: 0.92 t (9H, CH₃, J_{HH} 7.019 Hz), 1.25 m (6H, CH₂, J_{HH} 10.17 Hz), 1.59 m (6H, CH₂, J_{HH} 11.597 Hz), 1.80 (m, 6H, CH₂, J_{HH} 12.817 Hz) 2.05 m, (6H, OCH₂CH₂, J_{HH} 16.479 Hz); 3.99 t (6H, OCH₂, $J_{\rm HH} = 6.7$ Hz); 3.55 m (6H, NCH₂CH₂, $J_{\rm HH}$ 14.0 Hz); 4.21 m (6H, NCH₂, J_{HH} 11.9 Hz), 6.87 d (6H, Ph-H, $J_{\rm HH}$ 8.545 Hz); 7.52 d, (6H, Ph–H, $J_{\rm HH}$ 8.50 Hz). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 15.16 (CH₃); 30.23 (PhOCH₂); 31.83 (CH₂); 41.09 (CH₂); 41.13; 53.71 (CH₂); 61.11 (NCH₂); 66.05 (NCH₂CH₂); 114.38 (C^{2,6}-Ph); 128.02 (C^{3,5}-Ph); 131.01 (C–Ph); 134.47 (C– Ph); 161.9 (OCPh); 165.98 (PhCOO). Found, %: N 8.19, C 70.12; N 1.79. C₄₅H₆₃O₉N.Calculated, %: N 8.57, C 70.75; N 1.83.

Tris[2-(4-nonyloxybenzoyloxy)ethyl]amine (Ia. n = 9) was obtained similarly. Yield: 76%. M =888.24. IR spectrum, v, cm⁻¹: 3147, 3032 s (C–H, Ar), 2971, 2889 s $[(CH_2)_n CH_3]$, 2798 w, $[(CH_2)_n CH_3]$, 1672.01 s (C=O), 1231.01 s, (CO-O as), 1177.51-1171.61 s (O-C-C as), 1398 s (Ar, s). ¹H NMR spectrum (CDCl₃), δ, ppm: 0.89 t (9H, CH₃, J_{HH} 7.3 Hz), 1.28 m (12H, CH₂CH₃, J_{HH} 25.02 Hz), 1.54 m (12H, CH₂, J_{HH} 16.48 Hz); 1.78 m (12H, CH₂, J_{HH} 7.94 Hz); 2,04 m (6H, OCH₂CH₂, J_{HH} 12.21 Hz); 3.51 m (6H, NCH₂CH₂, J_{HH} 14.04 Hz); 3.98 t (6H, OCH₂, J_{HH} 6.1Hz), 4.14 m (6H, NCH₂, J_{HH} 11.59); 6.87 d (6H, Ph-H, J_{HH} 9.16 Hz,); 7.52 d (6H, Ph-H, J_{HH} 9.1 Hz). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 13.89 (CH₃); 22.59 (CH₂); 24.78 (CH₂); 29.19 (CH₂); 30.69 (PhOCH₂); 32.57 (CH₂); 49.37 (CH₂); 57.48 (NCH₂); 68.05 (NCH₂CH₂); 114.76 (C^{2,6}-Ph); 128.78 (C^{3,5}-Ph); 155.21(C-Ph); 161.43 (OCPh); 171.42 (PhCOO). Found, %: N 9.27, C 73.05; N 1.66. C₅₄H₈₁O₉N. Calculated, %: N 9.20, C 73.01; N 1.58.

Tris[2-(4-dodecyloxybenzoyloxy)ethyl]amine (Ia, n = 12) was obtained similarly. Yield 75% . M =1014.48. IR spectrum, v, cm⁻¹: 3147, 3032 s (C–H, Ar), 2971, 2889 s [(CH₂)_nCH₃], 2798 w, [(CH₂)_nCH₃], 1668.54 s (C=O), 1232.97 s, (CO–O as), 1179.92– 1171.47 s (O–C–C as), 1398 s (Ar, s). ¹H NMR spectrum (CDCl₃), δ, ppm: 0.88 t (9H, CH₃, J_{HH} 6.1 Hz,), 1.26 m (18H, CH₂, J_{HH} 25.02 Hz); 1.54 m,(18H, CH₂, J_{HH} 15.87 Hz); 1.78 m (18H, CH₂, J_{HH} 7.94 Hz); 2.03 m (6H, OCH₂CH₂, J_{HH} 12.21 Hz); 3.51 m (6H, NCH₂CH₂, J_{HH} 14,04 Hz); 3.98 t (6H, OCH₂, J_{HH} 6.71 Hz); 4.14 m (6H, NCH₂, J_{HH} 11.59 Hz); 6.87 d (6H, Ph–H, J_{HH} 9,16 Hz); 7.52 d (6H, Ph–H, J_{HH} 9.16 Hz). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 14.41 (CH₃); 22.71 (CH₂); 24.85 (CH₂); 29.38 (CH₂); 29.76 (CH₂); 30.98 (PhOCH₂); 32.98 (CH₂); 49.44 (CH₂); 57.54 (NCH₂); 68.22 (NCH₂CH₂); 114.22 ($C^{2,6}$ -Ph); 128.82 ($C^{3,5}$ -Ph); 155.04 (C–Ph); 161.43 (OCPh); 171.24 (PhCOO). Found, %: N 9.93, C 74.71; N 1.24. C₆₃H₉₉O₉N. Calculated, %: N 9.84, C 74.57; N 1.38.

Tris[2-(benzoyloxy)triethyl]amine (Id) was obtained similarly. Yield 77%. M = 461.52. IR spectrum, v, cm⁻¹: 3147, 3032 s (C–H, Ar), 2971, 2889 s [(CH₂)_nCH₃], 1786.88 s(C=O), 1213.26 s, (CO–O as), 1173.41 s (O–C–C as), 1398 s (Ar, s). ¹H NMR spectrum (CDCl₃), δ, ppm: 3.40 t (6H, NCH₂, J_{HH} 14,04 Hz); 7.03 m (6H, NCH₂CH₂, J_{HH} 11.56 Hz); 7.31 m (3H Ph⁴-H, J_{HH} 7.32 Hz); 7.46 m, (6H, Ph^{1,5}-H, J_{HH} 6.71 Hz,); 8.08 d (6H, Ph^{2,6}-H, J_{HH} 6.71 Hz). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 58.01 (NCH₂); 62.23 (NCH₂CH₂); 129.04 (C^{2,6}-Ph); 130.59 (C^{3,5}-Ph); 131.67 (C–Ph); 162.37 (OCPh); 171.59 (PhCOO). Found, %: N 5.85, C 70.12; N 3.02. C₂₇H₂₇O₆N. Calculated, %: N 5.90, C 70.27; N 3.03.

Tris[2-(4 benzyloxybenzoyloxy)ethyl]amine (Ib) was obtained similarly. Yield: 75% . M = 779.89. IR spectrum, v, cm⁻¹: 3147, 3032 s (C-H, Ar), 2971, 2889 s [(CH₂)_nCH₃], 2798 w [(CH₂)_nCH₃], 1627.86 s (C=O), 1230.71 s, (CO-O as), 1185.93 s (O-C-C as), 1398 s (Ar, s). ¹H NMR spectrum (CDCl₃), δ , ppm: 4.08 t (6H, NCH₂, J_{HH} 12,07 Hz); 4. 38 m (6H, NCH₂CH₂, J_{HH} 6.71 Hz), 5,14 s (6H, PhOCH₂Ph, J_{HH} 7.32 Hz); 7.00 d (6H, Ph-H, J_{HH} 8.55 Hz), 7.4 m (15H, Ph-H, $J_{\rm HH}$ 7.32 Hz,); 7.99 d (6H, Ph–H, $J_{\rm HH}$ = 9.155 Hz). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 41.70 (CH₂); 58.99 (NCH₂); 61.83 (NCH₂CH₂); 126.06 (C-Ph); 126.23 (C-Ph); 128.04 $(C^{2, 6}-Ph)$; 128.7 $(C^{2,6}-Ph)$; 129.11 (C^{3,5}-Ph); 129.13 (C^{3,5}-Ph); 176.46 (PhCOO). Found, %: N 5.79, C 73.89; N 1.78. C₄₂H₃₆O₉N. Calculated, %: N 5.82, C 73.92; N 1.79.

Tris[2-(4-cyclohexanebenzoyloxy)ethyl]amine (Ic) was obtained similarly. Yield 80%. M = 707.95. IR spectrum, v, cm⁻¹: 3147, 3032 s (C–H, Ar), 2971, 2889 s [(CH₂)_nCH₃], 2798 s [(CH₂)_nCH₃], 1781.31 s (C=O), 1218.78 s, (CO–O as), 1168.39 s (O–C–C as), 1398 s (Ar, s). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.42 m (12H, cyclo-CH₂, J_{HH} 10.38 Hz,); 1.76 m (6H, cyclo-CH₂, J_{HH} 12.82 Hz); 1.86 m (12H, cyclo-CH₂, J_{HH} 10.99 Hz); 2.50 t (6H, NCH₂, J_{HH} 11.59 Hz); 4.08 m (6H, NCH₂CH₂, J_{HH} 7.32 Hz); 7.34 d (6H, Ph–H, J_{HH} 7.94 Hz); 8.06 d (6H, Ph–H, J_{HH} 7.94 Hz). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 25.91 (cyclo-CH₂); 26.71 (cyclo-CH₂); 34.14 (cyclo-CH₂); 44.96 (CH); 81.98 (NCH₂); 83.38 (NCH₂CH₂); 114.78 (C–Ph); 127.21 $(C^{2,6}-Ph)$; 131.19 $(C^{3,5}-Ph)$; 155.27 (C-Ph); 162.09 (PhCOO). Found, %: N 8.15, C 76.41; N 2.04. $C_{45}H_{57}O_6N$. Calculated, %: N 8.12, C 76.35; N 1.98.

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