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Synthesis of Liquid-Crystalline 4,4 '-Dodecyloxybenzoyloxybenzoyl-4-oxy-2-hydroxybenzaldehyde and Related Azomethine

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Abstract—4,4'-Dodecyloxybenzoyloxybenzoyl-4-hydroxy-2-hydroxybenzaldehyde and the related linear azomethine, the intermediates at the formation of iron(III)-containing complexes, were synthesized. These compounds were characterized by thin layer chromatography, elemental analysis, IR, NMR spectroscopy, mass spectrometry, and by the data of differential scanning calorimetry. The aldehyde and the azomethine show mesomorphic properties.

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The published methods of synthesis of alkyloxybenzoic acids esters [1–5] have both advantages and disadvantages. The classic way of esterification consists in the synthesis of acid halide through reaction of the acid with a halogenating reagent like $SOCl_2$, $POCl_3$, and PCl_5, followed by acylation of the phenol fragment and elongation of the molecule in the environment or in the presence of an organic base [1]. This method has several disadvantages, one of which is the occurrence of side reactions accompanied by the tarring of the products that significantly reduces the yield and increases the cost of purifying the synthesized compounds. Since the early 90-ies publications have appeared on the possible formation of the ester fragment by the interaction of the carboxy and phenol groups in the presence of dicyclohexylcarbodiimide in the medium of methylene chloride, chloroform or *N,N*-dimethylformamide (DMF) with catalytic amounts of dimethylaminopyridine [2]. The latter method allows obtaining materials of high purity in a high yield, and also gives an opportunity to use this method for setting and removing the protecting group for the controlled grow of the organic molecule in the size and length. A major shortcoming of this method is the use of expensive palladium on activated carbon and hydrogen for the debenzylation by hydrogenolysis.

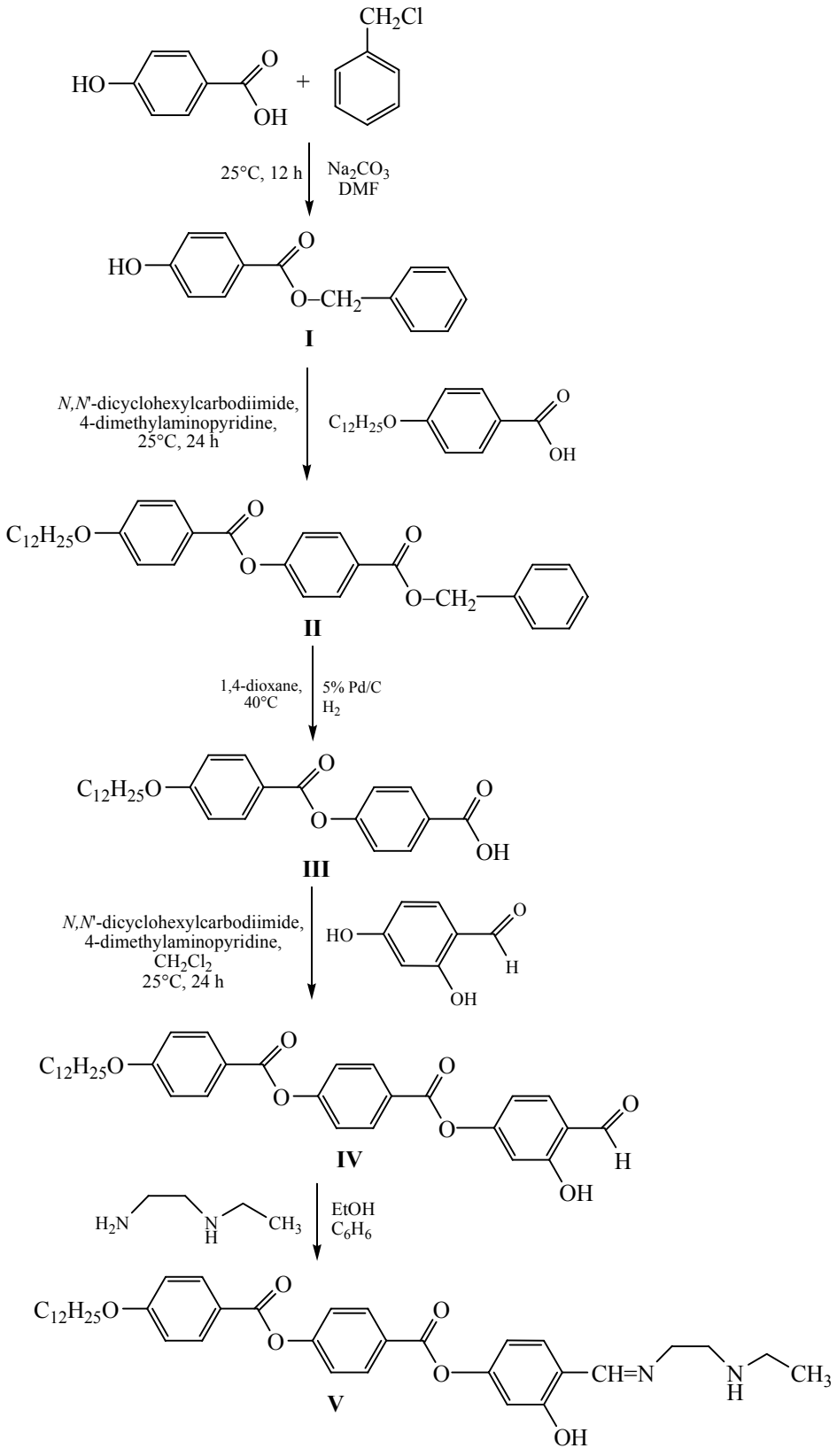
The widespread use of mesomorphic materials [6] gave an impetus to the study of compounds with an angular molecular structure exhibiting mesophases of various types [7, 8]. They are mostly the resorcinol derivatives, symmetrical relative to the central unit [2, 9]. A large number of bridging groups like azomethine, azo-, and ether moieties are used in the design and synthesis of these compounds with *p*-alkoxy-terminated chains.

We present here the results on the synthesis and study of mesomorphic behavior of asymmetric tridentante azomethine, 4,4'-dodecyloxybenzoyloxybenzoyl-4-salicylidene-*N*'-ethyl-*N*-ethylenediamine and its precursor, 4,4-dodecyloxybenzoyloxybenzoyl-4-hydroxy-2-hydroxybenzaldehyde.

Synthesis of 4,4'-dodecyloxybenzoyloxybenzoyl-4-hydroxy-2-hydroxybenzaldehyde **IV** was carried out through the reactions of intermediate products shown in Scheme 1. Benzyl 4-hydroxybenzoate (**I**) acting as a protection block in the esterification reaction was obtained in the first stage by alkylation of the carboxy group of *p*-hydroxybenzoic acid with benzyl bromide in a medium of water-free DMF [10]. Latter on, ester **I** was used for elongation of the chain of the *p*-dodecyloxybenzoic ester **II** [2] removing the protection by the cleavage of benzyl group in the form of toluene (debenzylation by hydrogenolysis).

From the obtained *p*-dodecyloxybenzoyloxybenzoic ester **III** aldehyde **IV** was synthesized. The formation of Schiff base **V** occurred as a result of

Scheme 1.


CH2Cl
HO
O
OH
+
25°C, 12 h
Na2CO3
DMF
HO
O
O–CH2
I
N,N'-dicyclohexylcarbodiimide,
4-dimethylaminopyridine,
25°C, 24 h
C12H25O
O
OH
C12H25O
O
O
O
O–CH2
II
1,4-dioxane,
40°C
5% Pd/C
H2
C12H25O
O
O
O
OH
III
N,N'-dicyclohexylcarbodiimide,
4-dimethylaminopyridine,
CH2Cl2
25°C, 24 h
HO
O
H
OH
C12H25O
O
O
O
O
H
OH
IV
H2N
N
H
CH3
EtOH
C6H6
C12H25O
O
O
O
O
CH=N
N
H
CH3
OH
V

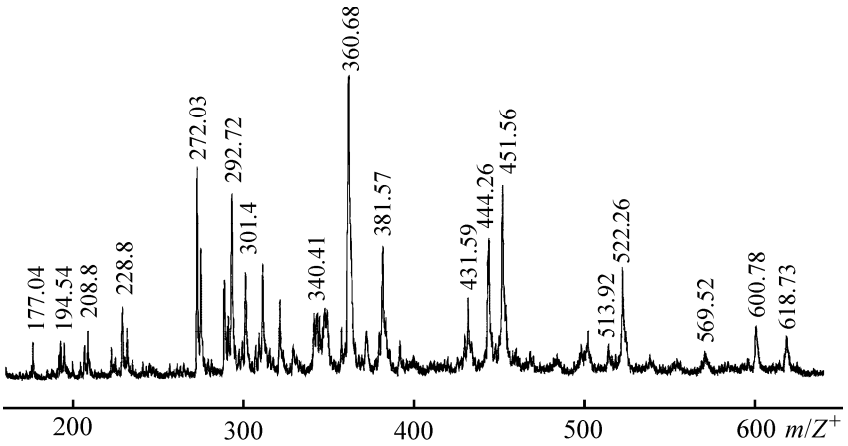


Fig. 1. Time-of-flight mass spectrum of the Schiff base.

reaction of the aldehyde group of compound **IV** with the amino group of *N*-ethylethylendiamine in a benzene–ethanol mixed solvent [11].

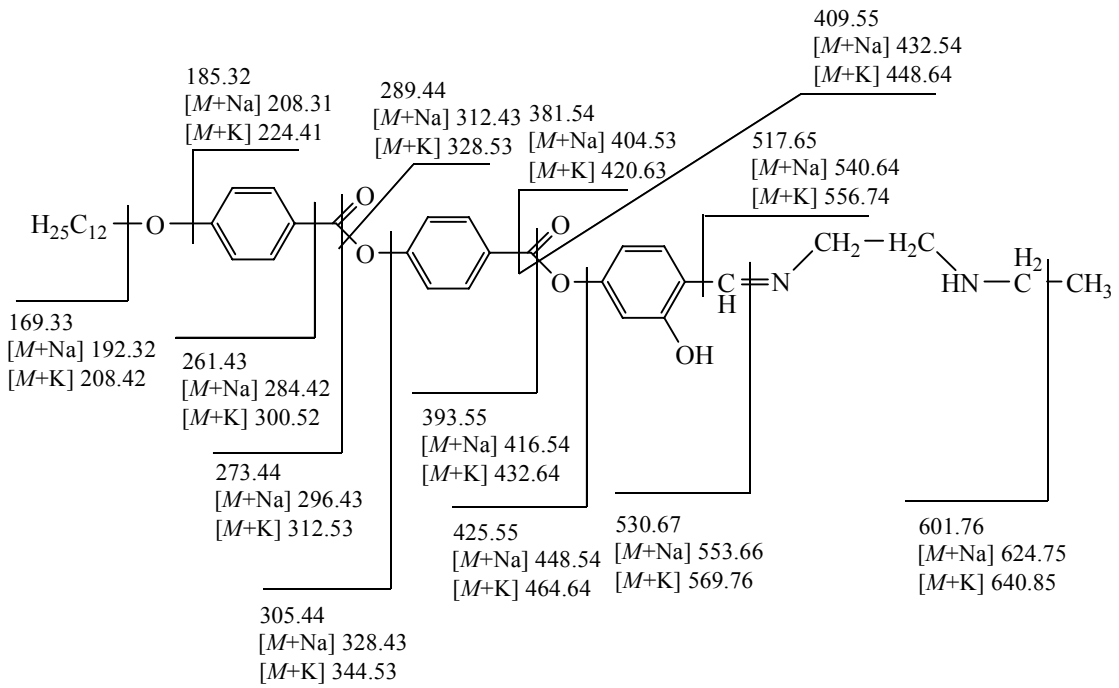
For a detailed study of the azomethine structure a mass-spectrometric investigation of a sample of 4,4'-dodecyloxybenzoyloxybenzoyl-4-salicylidene-*N*'-ethyl-*N*-ethylenediamine was performed. The mass spectra were recorded using the MALDI–TOF method. Figure 1 shows the time-of-flight mass spectrum of compound **V**.

Scheme 2 reflects the main directions of the characteristic fragmentation of compound **V** and the presence of its molecular ion, as well as the composition of the fragment ions. It should be noted that the fragmentation of molecule **V** occurs mainly at the bonds of the ester groups with a uniform defragmentation of the fragments.

Phase behavior. We confirmed the liquid-crystalline behavior of the substances in the study by thermal polarization microscopy and differential scanning calorimetry (see the table). The data of two methods are in good agreement.

As the initial liquid-crystalline compound was used *p*-dodecyloxybenzoic acid, from which was obtained *p*-dodecyloxybenzoyloxybenzoic acid **III**, which also

Scheme 2.



The phase transition temperatures according to the differential scanning calorimetry (DSC) in the heating cycle

Compound	T_{phase1}, °C	ΔH_1, J g^{-1}	T_{phase2}, °C	ΔH_2, J g^{-1}	T_{iso}, °C	ΔH_{iso}, J g^{-1}
$C_{26}H_{34}O_5$ (**III**)	125.14	54.04	212.72	9.01	220.5	15.86
$C_{33}H_{38}O_7$ (**IV**)	112.04	64.4	163.39	(4.47)[a]	172.76	(4.47)[a]
$C_{37}H_{48}N_2O_6$ (**V**)	88.67	8.38	110.12	0.69	219.57	117.54

[a] In parentheses the total area of two peaks is shown.

exhibits the mesomorphic properties (see the table) [2]. These results suggest that increasing the length of the molecule while maintaining its ability to form dimers by hydrogen bonds between the terminal carboxy or aldehyde groups should not lead to changes in the liquid-crystal properties. At the introduction of protective group to the carboxy group the substance loses mesomorphic phase transitions and only a low-temperature crystal–melt transition occurs. Indeed, in the cycle of first heating of aldehyde **IV** at 105°C a transition was registered of the crystal to the mesophase which existed in the temperature range 105–120°C (Fig. 2).

At 125°C an increase of mesomorphic spherulites in the mesophase occurs, presumably of A-smectics, which at 140°C transforms into the nematic phase. The transition to the isotropic phase was fixed at 155°C. A scheme of the phase behavior is as follows: Cr 105 M_1 120 SmA 140 N 155 I in the cycle of heating. In the cooling cycle the reverse is true: I 152 SmA 110 N 138 M_1 85 Cr. The latter observation allows to assert that compound **IV** is an enantiotropic liquid crystal.

For azomethine **V** two mesophases are typical in the heating cycle, at 88.67 and 110.12°C, and the transition to isotropic phase at 219.57°C with subsequent repetition upon cooling.

The compounds obtained were characterized by thin-layer chromatography, elemental analysis, IR, NMR spectroscopy, mass spectrometry, and by the data of differential scanning calorimetry. The final aldehyde and the azomethine obtained from it show liquid-crystalline phase behavior.

EXPERIMENTAL

All reagents and solvents were of chemically pure grade and were used without further purification. IR spectra of compounds were recorded on a Bruker Vertex 80V device in the regions of 7500–370 cm^{-1} and 670–190 cm^{-1} from pellets with KBr. The NMR spectral studies on the nuclei ^{1}H (500.17 MHz) and ^{13}C (125.76 MHz) were performed on a Bruker Avance-500 instrument. Elemental analyses of crystalline compounds were carried out on a FlashEA 1112 analyzer. Mass spectra were recorded using the MALDI–TOF method on a Bruker Daltonics Ultraflex mass-spectrometer in the positive ion mode using reflection option, the matrix was 2,5-dihydroxybenzoic acid. Thin layer chromatography was performed on the chromatographic plates PolyGRAM, Sil G/UV 254, eluent chloroform. Termopolarization microscopy was performed on a MIN-8 microscope with a heating plate of the original design.

Benzyl *p*-hydroxybenzoate (I). Samples of *p*-hydroxybenzoic acid (15 g, 0.109 mol) and anhydrous Na_2CO_3 (11.55 g, 0.109 mol) were dissolved in DMF (100 ml). At stirring benzyl chloride (12.54 ml, 0.109 mol) was added and the reaction mixture was stirred for 12 h at room temperature. The solution was

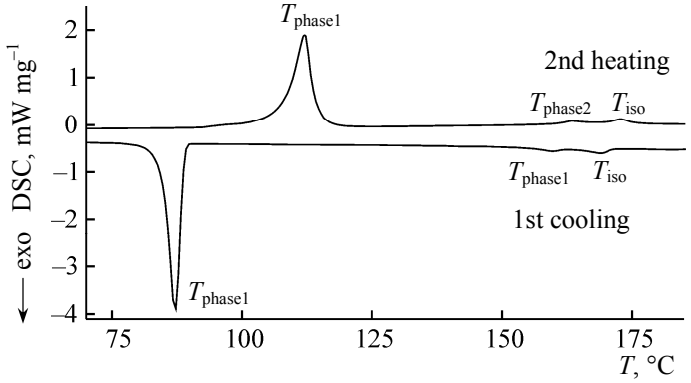


Fig. 2. DSC curves of 4,4'-dodecyloxybenzoyloxybenzoyl-4-hydroxy-2-hydroxybenzaldehyde in the heating and cooling cycles.

then mixed with 200 ml of distilled water, extracted with diethyl ether (5×25 ml), the combined organic extracts were washed with water (3×25 ml) and NaCl solution (20 ml). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in a vacuum. The residue was purified by recrystallization from a CH_2Cl_2–hexane (1:6) mixture. Yield 93.7% (23.04 g), mp 121°C. Found, %: C 73.06, H 5.71, O 21.23. $C_{14}H_{12}O_3$. Calculated, %: C 73.67, H 5.3, O 21.03. IR spectrum, ν, cm^{-1}: 3497.43 m (intramolecular hydrogen bond), 3388.42 s (OH), 3091.40, 3027.06 s (aromatic C–H), 2948.44 s (CH_2), 1685.05 s (C=O), 1605.45, 1585.28 s (aromatic C–H), 856.02 s (symmetric vibrations of 1,4-disubstituted aromatic ring), 731.10, 697.73 s (symmetric vibrations of monosubstituted aromatic ring). ^{1}H NMR spectrum (DMSO-d_6, TMS), δ, ppm: 5.28 s (2H, CH_2), 6.83 d (2H, H–Ph), 7.4 m (5H, H–Ph'), 7.82 d (2H, H–Ph). ^{13}C NMR spectrum (DMSO-d_6, TMS), δ_C, ppm: 66.60, 113.96, 121.27, 127.88, 132.41, 135.5, 165.30. Mass spectrum, *m/z*: (*M* 228.24), 228 [M^+].

Benzyl *p*-dodecyloxybenzoyloxybenzoate (II). A mixture of compound **I** (6.7 g, 0.029 mol), 4-dodecyloxybenzoic acid (9 g, 0.029 mol), catalytic amount of dimethylaminopyridine, and water-free CH_2Cl_2 (100 ml) was stirred for 10 min, 6.66 g (0.032 mol) of dicyclohexylcarbodiimide was added and the mixture was stirred for 24 h at room temperature. The precipitate was filtered off, the filtrate was washed successively with 5% of acetic acid (2×25 ml), 5% solution of NaOH (2×25 ml) and water (3×25 ml), dried over anhydrous Na_2SO_4. The solvent was distilled off on a rotary evaporator. The resulting yellowish solid residue was purified by chromatography on silica gel, eluent chloroform. The product was recrystallized from a chloroform–acetonitrile mixture. Yield 86% (13.1 g), mp 62–63°C. IR spectrum, ν, cm^{-1}: 2918 s (aromatic C–H), 2851 s [$(CH_2)_n$–CH_3], 1732 s (C=O), 1470 s (symmetrical vibrations of aromatic ring), 1292 s [Alk–C–O–C(Ph)]. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.86–0.90 t (3H, CH_3), 1.27–1.50 m (18H, $9CH_2$), 1.78–1.85 q (2H, $PhOCH_2C\underline{H}_2$) 4.02–4.06 m (2H, $PhOC\underline{H}_2$), 5.38 s (2H, OCH_2Ph), 6.96–6.98 d (2H, PhH), 7.28–7.30 d (2H, PhH), 7.35–7.46 m (5H, Ph–H), 8.12–8.16 m (4H, Ph–H). Found, %: C 76.65, H 7.94. $C_{33}H_{40}O_5$. Calculated, %: C 76.71, H 7.80.

***p*-Dodecyloxybenzoyloxybenzoic acid (III)**. A weighed sample of compound **II** (13.1 g, 0.025 mol) was dissolved in 1,4-dioxane (100 ml), a catalyst 5% Pd/C (2.7 g) was added, and the mixture was stirred at 40°C under hydrogen for 1 h. The reaction mixture was filtered and the solvent was distilled in a vacuum. The resulting product was recrystallized from a mixture of 1,4-dioxane–petroleum ether (bp 60–80°C). Yield 92% (9.9 g), mp 220.5°C. IR spectrum of **III**, ν, cm^{-1}: 3070, 2972 s (aromatic C–H), 2851 s [$(CH_2)_nCH_3$), 1732 s (C=O), 1688 s [C(O)O], 1261, 1470 s (symmetric vibrations of aromatic ring), 1292, 1161 s [Alk–P–OC(Ph)]. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.86–0.90 t (3H,CH_3), 1.26–1.51 m (18H, $9CH_2$), 1.79–1.86 q (2H, $PhOCH_2C\underline{H}_2$), 4.03–4.06 t (2H, $PhOCH_2$), 6.97–6.99 d (2H, PhH), 7.32–7.35 d (2H, PhH), 8.13–8.15 d (2H, PhH), 8.18–8.21 d (2H, Ph–H). Found, %: C 73.61, H 8.3. $C_{26}H_{34}O_5$. Calculated, %: C 73.21, H 8.03.

4,4-Dodecyloxybenzoyloxybenzoyl-4-hydroxy-2-hydroxybenzaldehyde (IV). Weighed samples of compounds **III** (6 g, 0.014 mol) and 2,4-dihydroxybenzaldehyde (1.94 g, 0.014 mol) were dissolved in 100 ml of CH_2Cl_2. Then a sample of dicyclohexylcarbodiimide (3.52 g, 0.017 mol) was added. The mixture was stirred until complete dissolution of the components, and then a catalytic amount of dimethylaminopyridine was added. The reaction mixture was stirred for 24 h. The precipitated urea was filtered off on a glass frit. The solvent was distilled off on a rotary evaporator. The resulting yellowish solid residue was purified by chromatography on silica gel, eluent chloroform. The product was recrystallized from acetonitrile. Yield 6.18 g (80.46%), mp 172.76°C. IR spectrum, ν, cm^{-1}: 3450 s (intramolecular hydrogen bond), 3099, 3053 s (aromatic C–H), 2956–2850 s [$(CH_2)_n$–CH_3], 2771–2625 w (CHO), 1731 s (C=O), 1415, 1393 s (Ph–CHO), 1285–1149 s [Alk–P–OC (Ph)], 829–795 s (symmetric vibrations of 1,4-disubstituted aromatic ring). ^{1}H NMR spectrum ($CDCl_3$, TMS) δ, ppm: 0.91 t (3H, CH_3), 1.28 m (18H, CH_2Alk), 1.85 t (2H, CH_2), 4.06 t (2H,OCH_2Alk), 6.95 m (4H, H–Ph), 7.01 d (2H, H–Ph), 7.62 d (2H, H–Ph), 8.15 d (2H, H–Ph), 8.26 d (2H, H–Ph), 9.9 s (1H, PhCOH), 11.29 s (1H, PhOH). ^{13}C NMR spectrum ($CDCl_3$, TMS), δ_C, ppm: 13.66, 14.65, 21.73, 22.72, 28.64, 69.4, 110.19, 113.37, 114.7, 115.08, 118.66, 120.81, 126.10, 131.31, 131.81, 132.62, 133.11, 134.38, 135.66, 155.74, 157.52, 163.19, 163.44, 164.24, 194.79, 196.21. Mass spectrum, *m/z*: (*M* 546.65), 545 [M^+]. Found, %: C 71.54, H 7.83, O 20.63. $C_{33}N_{38}O_7$. Calculated, %: C 72.51, H 7.01, O 20.48.

4,4'-Dodecyloxybenzoyloxybenzoyl-4-salicylidene-*N*'-ethyl-*N*-ethylenediamine (V). A sample of compound **IV** (0.45 g, 0.82 mmol) at permanent stirring was dissolved in a mixture of 30 ml of ethyl alcohol and 20 ml of benzene. An alcohol solution (10 ml) of *N*-ethylethylenediamine (0.07 g, 0.82 mmol) was added, and azeotrope (alcohol–benzene–water) was distilled off from the reaction mixture with the Dean–Stark trap. The reaction mixture was stirred for 2 h, and the solvent was distilled off in a vacuum of a water-jet pump. The product was recrystallized from an acetone–chloroform mixture. Yield 0.38 g (75%), mp 219°C. IR spectrum, ν, cm^{-1}: 3320 s (OH, NH), 3068 w (aromatic C–H), 2921–2848 s [$(CH_2)_n$–CH_3], 1729 s (C=O), 1639 s (CH=N bending), 1605 (Ar), 1250 s (in-plane bending vibrations of 1,2,4-substituted aromatic ring), 1166 s (C–O–C), 1100 w [Alk–C–OC(Ph)], 891–846 s (out-of-plane bending vibrations of 1,2,4-substituted aromatic ring). ^{1}H NMR spectrum [$(CD_3)_2CO$, TMS], δ, ppm: 0.88 s (3H, CH_3), 1.09 t (3H, CH_3), 1.29 m (8H, CH_2Alk), 1.49 s (2H, CH_2), 1.77 t (1H, NH), 2.70 t (2H, CH_2NH), 3.34 d (2H, =N–CH_2), 4.03 q (2H, OCH_2Alk), 4.15 d (2H, O$C\underline{H}_2CH_2$Alk), 6.87 m (2H, H–Ph), 6.95 m (2H, H–Ph), 7.11 d (2H, H–Ph), 7.32 d (2H, H–Ph), 7.79 d (1H, CH=N), 7.89 (m, 1H, H–Ph), 8.13 (d, 2H, H–Ph), 9.9 s (1H, Ph–COH). ^{13}C NMR spectrum [$(CD_3)_2CO$, TMS], δ_C, ppm: 14.90, 26.69, 39.80, 44.08, 49.38, 68.82, 115.68, 122.75, 129.97, 133.06. Mass spectrum, *m/z*: (*M* 616.79), 618.73 [M^+]. Found, %: C 72.57, H 7.94, N 4.43, O 15.06. $C_{37}H_{48}N_2O_6$. Calculated, %: C 72.05, H 7.84, N 4.54, O 15.56.

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