ISSN 1070-3632, Russian Journal of General Chemistry, 2016, Vol. 86, No. 6, pp. 1339–1344. © Pleiades Publishing, Ltd., 2016.
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N- and O-Acylated Phthalocyanines with Gallic Acid Moieties

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Received November 16, 2015

Abstract—Phthalocyanines containing gallic acid moieties were synthesized and investigated by the method of electron absorption spectroscopy. It was shown that in organic solvents the prepared phthalocyanines exist predominantly in associated form.

Keywords: acylation, phthalocyanines, electronic absorption spectra, association

DOI: 10.1134/S1070363216060190

Metal complexes of phthalocyanines (MPc) possess valuable practical properties allowing their use in various fields of science and engineering [1, 2]. Of specific interest are phthalocyanine-containing ester and amide groups possessing enhanced solubility in organic solvents. Earlier it was shown that copper complexes of this type could be used as lipid-soluble dyes [3, 4] and exhibited liquid crystalline properties [5]. Liquid crystalline materials, which are capable of hardening to solid without crystallization and with retention of the mesophase texture, are promising as materials for electrooptical devices, like electroluminescence cells, photogalvanic elements, organic photoconductors [6]. The use of such compounds improves the performance characteristics of the cell material due to to the replacement of the two-component system “glass forming material–dye” by an individual compound. It is known that phthalocyanine derivatives having the ability to glass formation combine the transparency of the glass layer with the ability to absorb light in strictly fixed region of spectrum [6].

In the present report, we report the data on the synthesis and investigation of physicochemical properties of N- and O-acylated phthalocyanines containing the substituted residues of gallic acid.

The presence of electronwithdrawing substituents (CN, COOH) in the molecules of substrates results in a decrease in their reactivity in the electrophilic substitution reaction, so the most suitable reagents for acylation are substituted benzoyl chlorides [7].

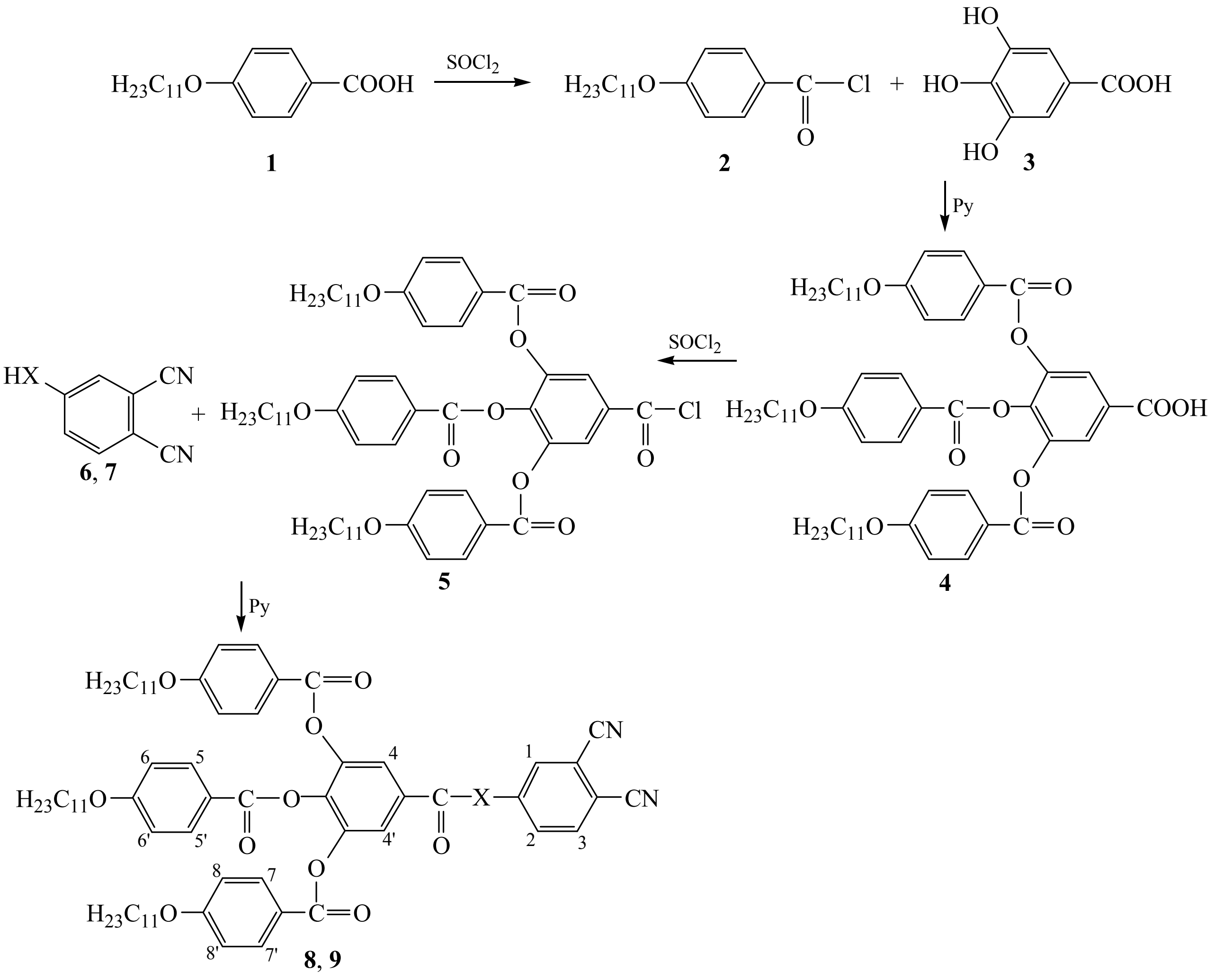
Acylation with acyl chlorides can be performed in aqueous sodium alkali (the Schotten-Baumann method) or in the presence of an organic base, pyridine (the Einhorn reaction). We have used the latter method since in this case pyridine plays the role of both the solvent and the catalyst of the reaction forming reactive species of the N-benzoylpyridinium type or causing a partial ionization of the hydroxy compound in the case of O-acylation. Besides, this allows to exclude the hydrolysis of esters or amides, thus increasing the yield of the target products. By the aforementioned scheme, the acyloxy- (**8**) and acylaminophthalonitriles (**9**) were obtained (Scheme 1).

Phthalonitriles **8, 9** are waxy compounds, insoluble in water but soluble in organic solvents (acetone, chloroform, benzene). The structure of the products was determined by the elemental analysis, MALDI TOF mass spectrometry, IR and ^{1}H NMR spectroscopy.

In the IR spectra of phthalonitriles **8, 9** the band of stretching vibrations of the nitrile group (2237–2240 cm^{-1}) is retained and appears the absorption band of the ester or amide C=O group (1688–1742 cm^{-1}), C–H (2850–2920 cm^{-1}), and C-O-C bands (1250–1257 cm^{-1}). In the spectrum of compound **9** the absorption bands were observed at 3339 and 1614 cm^{-1} (stretching and bending vibrations of the secondary amino group) and at 1387 cm^{-1} (C–N vibrations) [8].

In the second stage the synthesis of metal complexes was performed using the “nitrile” method,

Scheme 1.



X = O (**6**, **8**), NH (**7**, **9**).

by the reaction of the obtained precursors with metal salts at 170–175°C (**10, 11a, 11b**) (Scheme 2).

The physicochemical properties of the obtained phthalocyanines are determined by the nature of the functional substituents. Thus, tetra-4-hydroxyphthalocyanines are soluble in aqueous alkali and, moderately, in DMF, while their analogs with bulky substituents having the fragments of gallic acid are insoluble in these media but soluble in organic solvents (chloroform, benzene). The N-acylated phthalocyanines retain the solubility in DMF, like tetra-4-aminophthalocyanines, and they are also soluble in such organic solvents as chloroform and benzene.

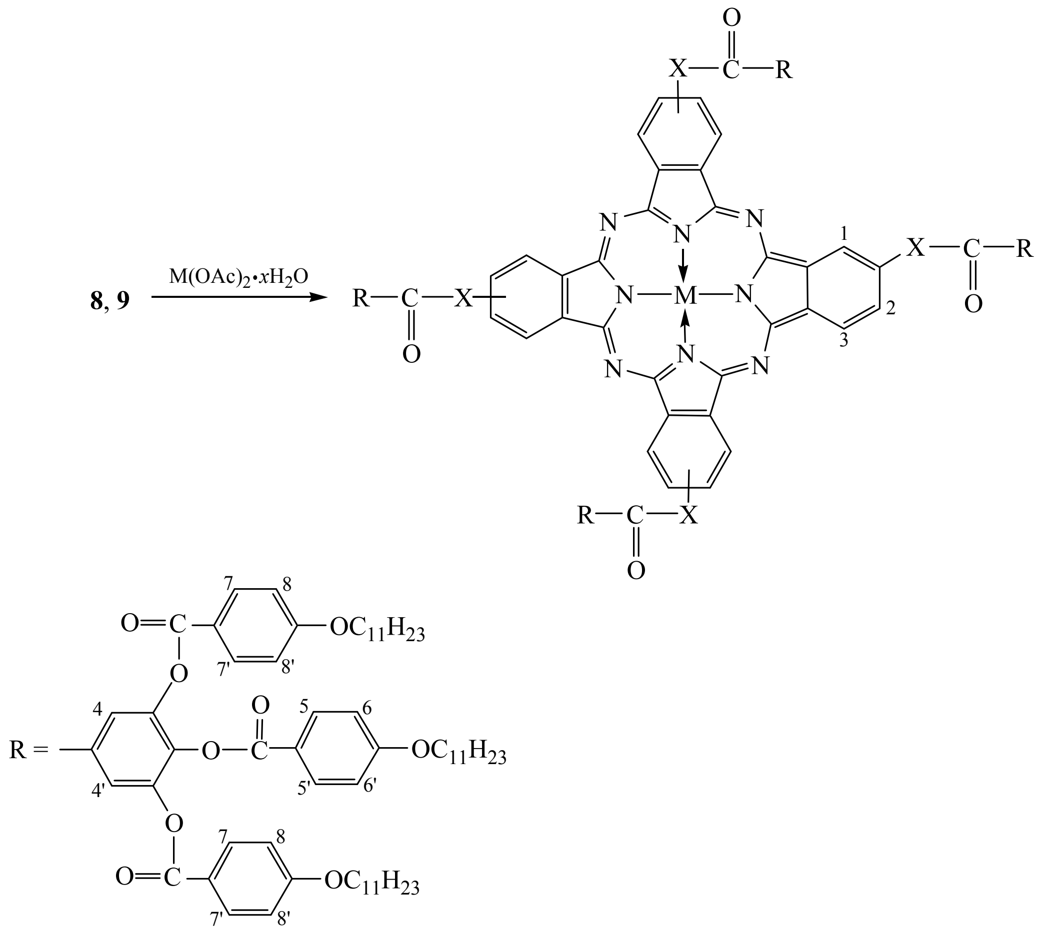
The obtained compounds are dark-green powders. The structure and composition of the synthesized phthalocyanines was proved by the methods of MALDI TOF mass spectrometry, elemental analysis, IR and ^{1}H NMR and electronic spectroscopy.

The IR spectra of compounds **10** and **11** have absorption bands typical of phthalocyanines [9], and retain the absorption bands of the acyl residues present in the spectra of the corresponding phthalonitriles.

The ^{1}H NMR spectra of all obtained complexes are similar and contain the signals of aliphatic protons in strong field and aromatic protons in weak field. The signal of the secondary amino group was not observed, apparently, because of the presence of four substituted fragments of gallic acid, shielding the bridging groups.

An effect of the nature of the bridging group on the character and position of absorption bands in the electron absorption spectra was observed (see the table).

Scheme 2.



X = O (**10**), NH (**11**); M = Cu (x = 2) (**a**), Ni (x = 4) (**b**).

The electron absorption spectra of N-acylated phthalocyanines **11a** and **11b** in chloroform are characterized by the presence of an intense broadened absorption band in the range 620–629 nm (see figure and table). In going to the O-acylated complexes **10a** and **10b**, two bands were detected in the longwave region of the electronic spectrum (see table), their ratio of intensities being dependent on concentration of the examined phthalocyanines.

Electron absorption spectra of the synthesized complexes **10, 11**

Comp. no.	λ_{max}, nm (D_{rel})[a]		
	chloroform	DMF[b]	conc. H_2SO_4
10a	619 (0.70), 673 (1.00)	–	838
10b	633 (0.52), 665 (1.00)	–	722 (0.31), 808 (1.00)
11a	629	623 (0.35), 691 (1.00)	642 (0.42), 764 (1.00)
11b	625	635 (0.65), 687 (1.00)	690 (0.31), 770 (1.00)

[a] Absorption bands intensities are given relative to the most intense one. [b] Insoluble.

In going from chloroform as a solvent to DMF, the character of the spectra of **11a** and **11b** is somewhat changed. Irrespective of the nature of the complex-forming metal, two absorption bands are observed in the ranges 620–622 and 687–691 nm (see figure and table). On dilution of the solvent, the intensity of the longwave band decreases to a lesser extent than that of the shortwave band.

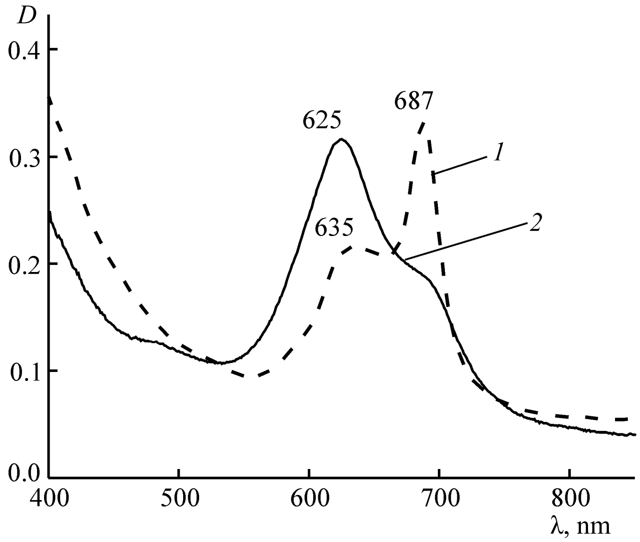
It is known [10–12] that the association of the phthalocyanine molecules may occur either by hydrogen bond formation of peripheral substituents or due to π–π interactions. In solution both types of associates may exist.

Different character of the spectra is apparently connected with different propensity of phthalocyanines to association depending on the polarity of the solvent. Small dielectric constant of nonpolar and low polar solvents results in weakening of the effect of shielding of intermolecular Pc–Pc interaction by the solvent and, as a result, favors the formation of associates and increases their stability, as compared to polar solvents (DMF) [10]. Therefore, the amount of associates formed by π–π interactions in DMF substantially decreases and, as a consequence, the intensity of the short-wave band is lowered.

Going from organic solvents to conc. sulfuric acid all synthesized phthalocyanines demonstrate a significant red shift of absorption bands caused by the processes of protonation of the nitrogen *meso*-atoms [13]. It is shown that in H_2SO_4 the absorption bands of the N-acylated complexes suffer a blue shift with respect to the corresponding O-derivatives (see the table). The latter effect is explained by the fact that the protonation first occurs on the nitrogen atoms of aminogroups. Probably, this lowers the basicity of the nitrogen *meso*-atoms and, as a result, decreases the degree of their protonation.

Depending on the nature of the complex-forming metal, in going from nickel to copper, the red shift of the absorption bands is observed in all solvents (see the table).

Therefore, using the reaction of acylation of 4-hydroxy(amino)phthalonitriles with 4-[(3,4,5-tris{undecyloxybenzoyloxy)benzoyl chloride, phthalonitriles were synthesized. On their basis, the corresponding metal complexes were obtained and their electron absorption spectra were investigated. The propensity of the phthalocyanines molecules to association in solution was found to increase when replacing the ester group in the substituent by the amide group, as well as at going from DMF as a solvent to chloroform.



Electron absorption spectra of complex **11b**: (*1*) in chloroform and (*2*) in DMF.

EXPERIMENTAL

Electron absorption spectra in DMF, chloroform, and conc. sulfuric acid (325–900 nm) were recorded on a HITACHI U-2001 spectrophotometer at room temperature. IR spectra were recorded from KBr pellets (400–4000 cm^{-1}) on an Avatar 360 FT-IR ESP spectrometer. MALDI-TOF mass spectra were obtained on a Shimadzu Biotech Axima Confidence mass spectrometer in positive and negative ion modes. 2-(4-Hydroxybenzoazo)benzoic acid was used as a matrix. ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer from 5% solutions in $CDCl_3$ with TMS as an internal reference. Elemental analysis was performed on an elemental analyzer CHNS-O FlashEA, 1112 series.

Investigation of physicochemical characteristics of the studied compounds was performed in the Center for Joint Usage of Ivanovo State University of Chemistry and Technology.

Synthesis of 4-[(3,4,5-tris{undecyloxybenzoyloxy}benzoyl)oxy]- and 4-[(3,4,5-tris{undecyloxybenzoyloxy}benzoyl)amino]phthalonitriles. Mixture of 1.00 g (3.6 mmol) of 4-undecyloxybenzoic acid and 0.5 mL (7 mmol) of thionyl chloride was stirred at 50°C for 2 h until evolution of gas bubbles (SO_2 and HCl) ceased, then the excess of thionyl chloride was distilled off. To the obtained acid chloride, 0.18 g (1.06 mmol) of gallic acid and 3.0 mL of pyridine were added. The reaction mixture was kept for 10 h at 80°C, then poured into water, the formed precipitate was filtered off and dried. 4-[(3,4,5-Tris{undecyloxybenzoyloxy)benzoic acid was extracted with acetone, the solvent removed, the target product dried. Yield 0.97 g (90 %). IR spectrum, ν, cm^{-1}: 1747 br (C=O), 2918, 2850 (CH), 1700 (COOH). Found, %: C 73.2; H 9.0. $C_{61}H_{84}O_{11}$. Calculated, %: C 73.8; H 8.5.

To 1.0 g (1 mmol) of 4-[(3,4,5-tris{undecyloxybenzoyloxy)benzoic acid 0.28 mL (4 mmol) of thionyl chloride was added and the reaction mixture was heated to 50°C with stirring, kept for 2 h until evolution of gas bubbles (SO_2 and HCl) ceased, the excess of thionyl chloride was distilled off. To the obtained 4-[(3,4,5-tris{undecyloxybenzoyloxy)benzoyl chloride 0.17 g (1.2 mmol) of 4-hydroxyphthalonitrile or 0.17 g (1.2 mmol) of 4-aminophthalonitrile and 2.5 mL of pyridine was added. The reaction mixture was kept at 85°C for 17 h, then poured into water. The formed viscous mass was filtered and dried. The target products were isolated by extraction with chloroform. After removal of the solvent, the nitriles were washed with the mixture methanol–acetone (4 : 1).

4-[(3,4,5-Tris{undecyloxybenzoyloxy}benzoyl)oxy]-phthalonitrile (8). Yield 0.78 g (70 %). mp 59°C. IR spectrum, ν, cm^{-1}: 2237 (C≡N), 1743, 1688 br (C=O), 2920, 2850 (CH). ^1H NMR spectrum, δ, ppm: 8.02 d (6H, $H^{5,5',7,7'}$, J = 6.4 Hz), 7.67 d (2H, $H^{4,4'}$, J = 8.9 Hz), 7.49 s (1H, H^1), 7.37 d (2H, $H^{2,3}$, J = 8.5 Hz) 7.08 d (6H, $H^{6,6',8,8'}$, J = 8.2 Hz), 3.75 t (6H, OCH_2, J = 6.9 Hz), 1.66–1.70 m (6H, $OCCH_2$), 1.26-1.29 m (48H, other CH_2 in $C_{11}H_{23}$), 0.84–0.90 m (9H, CH_3). Mass spectrum, *m/z*: 1118.19 $[M]^-$, calculated *M* 1118.46. Found, %: C 73.8; H 8.0; N 2.3. $C_{69}O_{11}N_2H_{86}$. Calculated, %: C 74.0; H 7.7; N 2.5.

4-[(3,4,5-Tris{undecyloxybenzoyloxy}benzoyl)-amino]phthalonitrile (9). Yield 0.77 g (69 %). mp 75°C. IR spectrum, ν, cm^{-1}: 2240 (C≡N), 1742 br (C=O), 1671, 3339 (NH), 2920. 2850 (CH), 1256 (C–O–C). ^1H NMR spectrum, δ, ppm: 9.36 s (1H, NH), 8.24 d (6H, $H^{5,5',7,7'}$, J = 8.2 Hz), 8.06 d (2H, $H^{4,4'}$, J = 8.6 Hz), 7.85 d (2H, $H^{2,3}$, J = 8.3 Hz), 7.49 s (1H, H^1), 6.97 d (6H, $H^{6,6',8,8'}$, J = 8.0 Hz), 4.04 t (6H, OCH_2, J = 7.3 Hz), 1.82–1.86 m (6H, $OCCH_2$), 1.25-1.31 m (48H, other CH_2 in $C_{11}H_{23}$), 0.84–0.90 m (9H, CH_3). Mass spectrum, *m/z*: 1141.46 $[M\text{+Na}]^+$, calculated *M* 1119.45. Found, %: C 73.9; H 8.1; N 3.6. $C_{69}O_{10}N_3H_{87}$. Calculated, %: C 74.1; H 7.8; N 3.8.

Synthesis of tetra-4-(4’-benzoyl-substituted)hydroxy(amino)phthalocyanines. The mixture of 1 mol of substituted phthalonitrile **8** or **9** and 0.3 mmol of copper or nickel acetate salt was thoroughly ground and kept in quartz ampule at 170–175°C for 2 h. The melt was thoroughly ground, the target product was extracted with chloroform and purified by column chromatography on alumina of the II activity level (eluent chloroform–methanol, 4 : 1).

Copper tetra-4-(4-[(3,4,5-tris{undecyloxybenzoyl-oxy}benzoyl)oxy])phthalocyanine (10a). Yield 0.86 g (19.0 %). IR spectrum, ν, cm^{-1}: 1743, 1688 br (C=O), 2920, 2850 (CH). Found, %: C 73.2; H 8.0; N 2.3. $C_{276}H_{344}CuN_8O_{44}$. Calculated, %: C 73.00; H 7.64; N 2.47.

Nickel tetra-4-(4-[(3,4,5-tris{undecyloxybenzoyl-oxy}benzoyl)oxy])phthalocyanine (10b). Yield 0.90 g (19.2 %). IR spectrum, ν, cm^{-1}: 1743, 1688 br (C=O), 2920, 2850 (CH). ^1H NMR spectrum, δ, ppm: 8.16 d (24H, $H^{5,5',7,7'}$, J = 8.0 Hz), 7.95 d (8H, $H^{4,4'}$, J = 8.4 Hz), 7.49 s (4H, H^1), 7.38 d (8H, $H^{2,3}$, J = 8.2 Hz), 7.08 d (24H, $H^{6,6',8,8'}$, J = 8.6 Hz), 5.32 t (24H, OCH_2, J = 7.3 Hz), 1.58–1.62 m (24H, $OCCH_2$), 1.26–1.30 m (192H, other CH_2 in $C_{11}H_{23}$), 0.84-0.91 m (36H, CH_3). Mass spectrum, *m/z*: 4539.66 $[M + 3H]^+$, calculated *M* 4536.48. Found, %: C 73.21; H 8.00; N 2.40. $C_{276}H_{344}N_8O_{44}Ni$. Calculated, %: C 73.07; H 7.64; N 2.47.

Copper tetra-4-(4-[(3,4,5-tris{undecyloxybenzoyl-oxy}benzoyl)amino])phthalocyanine (11a). Yield 1.13 g (25.2 %). IR spectrum, ν, cm^{-1}: 2240 (C≡N), 1742 br (C=O), 1671, 3339 (NH), 2920. 2850 (CH), 1256 (C–O–C). Found, %: C 73.40; H 8.01; N 3.52. $C_{276}H_{348}N_{12}CuO_{40}$. Calculated, %: C 73.06; H 7.73; N 3.70.

Nickel tetra-4-(4-[(3,4,5-tris{undecyloxybenzoyl-oxy}benzoyl)amino])phthalocyanine (11b). Yield 0.99 g (22.0 %). IR spectrum, ν, cm^{-1}: 2240 (C≡N), 1742 br (C=O), 1671, 3339 (NH), 2920, 2850 (CH), 1256 (C–O–C). ^1H NMR spectrum, δ, ppm: 8.04 d (24H, $H^{5,5'7,7'}$, J = 8.2 Hz), 7.86 m (4H, NH), 7.79 d (8H, $H^{4,4'}$, J = 8.5 Hz), 7.49 s (4H, H^1), 7.38 d (8H, $H^{2,3}$, J = 7.2 Hz), 6.95 d (24H, $H^{6,6',8,8'}$, J = 9.0 Hz), 4.02 t (24H, OCH_2, J = 7.0 Hz), 1.56-1.62 m (24H, $OCCH_2$), 1.26–1.32 m (192H, other CH_2 in $C_{11}H_{23}$), 0.84–0.90 m (36H, CH_3). Mass spectrum, *m/z*: 4554.68 $[M + \text{Na}]^+$, calculated *M* 4532.55. Found, %: C 73.10; H 8.01; N 3.54. $C_{276}H_{348}N_{12}NiO_{40}$. Calculated, %: C 73.14; H 7.74; N 3.71.

ACKNOWLEDGMENTS

This work was performed within the framework of the State contract of the Ministry of Education and Science of Russian Federation “Synthesis and investigation of physicochemical properties of 4-[(3,4,5-tris{undecyloxybenziyloxy}benzoyl)oxy-4-[(3,4,5-tris{undecyloxybenzoyloxy}benzoyl)amino] phthalonitriles” and with the support from the Russian Scientific Foundation (project 14-23-00204).

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