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Paper
Статья

Synthesis of Cu(II) and Ni(II) Phthalocyanines Bearing Nitro and 4–(1–Methyl–1–phenylethyl)phenoxy Groups

Serafima A. Znoyko,[a@] Anastasia I. Mikhailova,[a] Olga B. Akopova,[b]
Natalia V. Bumbina,[b] Nadezhda V. Usol'tseva,[b] Vladimir E. Maizlish,[a]
and Gennady P. Shaposhnikov[a]

Dedicated to Oleg A. Golubchikov on the occasion of his 70th anniversary

[a]*Research Institute of Macroheterocycles, Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russia*
[b]*Research Institute of Nanomaterials, Ivanovo State University, 153025 Ivanovo, Russia*
[@]*Corresponding author E-mail: znoykosa@yandex.ru*

Bifunctional substituted copper and nickel phthalocyanines were synthesized. These compounds were modified by introduction of sulfonic and sulfonamide groups into aryloxy fragments. Spectral and mesomorphic properties of synthesized compounds were studied.

Keywords: Bifunctional substituted phthalocyanines, synthesis, mesomorphism.

Синтез комплексов фталоцианинов с медью(II) и никелем(II), содержащих нитро– и 4–(1–метил–1–фенилэтил)фенокси–группы

С. А. Знойко,[a@] А. И. Михайлова,[a] О. Б. Акопова,[b] Н. В. Бумбина,[b]
Н. В. Усольцева,[b] В. Е. Майзлиш,[a] Г. П. Шапошников[a]

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[a]*НИИ химии макрогетероциклических соединений, Ивановский государственный химико-технологический университет, 153000 Иваново, Россия*
[b]*НИИ наноматериалов, Ивановский государственный университет, 153025 Иваново, Россия*
[@]*E-mail: znoykosa@yandex.ru*

Осуществлен синтез фталоцианинов меди и никеля с 4-(1-метил-1-фенилэтил)фенокси- и нитрогруппами. Путем введения алкилсульфамоильных групп в имеющиеся оксиарильные фрагменты проведена его дальнейшая модификация. Исследованы физико-химические, в частности, мезоморфные, свойства синтезированных соединений. Обнаружено, что замена бензотриазольных фрагментов 2,9,16,23-тетра(1-бензотриазолил)-3,10,17,24-тетра[4-(1-метил-1-фенилэтил)фенокси]фталоцианина меди на нитрогруппы приводит к неспособности данного производного фталоцианина формировать мезофазу как при нагревании, так и в различных растворителях. Введение на периферию 2,9,16,23-тетра[4-(1-метил-1-фенилэтил)фенокси]-3,10,17,24-тетранитрофталоцианина меди диэтил- или октадецилсульфамоильных заместителей придает указанным соединениям мезоморфные свойства.

Ключевые слова: Бифункционально-замещенные фталоцианины, синтез, мезоморфизм.

Introduction

The investigation of the liquid crystalline (meso-morphic) state of low-molecular organic compounds has more than a half of century history.[1-2] However, the study of the influence of the structure peculiarities on the thermotropic mesomorphism of disc-like compounds began only in the 80s of the previous century. This study is primarily associated with Prof. S. Chandrasekhar, who was the first to show the possibility of conceptually new supramolecular mesogens of this type packing into columnar ensembles.[3]

The first proof of liquid crystallinity of porphyrin derivatives was obtained in the 1990s and it immediately drew attention to these mesogens in the aspect of studying the influence of the features of their structure on mesomorphic properties and the type of supramolecular organization.[1,4-6]

The steadily increasing interest to the mesomorphism of phthalocyanine derivatives is determined by the unique properties of these compounds: one-dimensional conductivity along the column axis,[7] high thermal and chemical stability,[8] the ability to vitrify,[9,10] photoactivity,[11-13] absorption in the visible and near-IR regions of the spectrum,[14] sensing,[15] and photoconduction[16] which suggest a great potential for their use as nanomaterials.

At the first stages of studying phthalocyanine derivatives, the main attention was paid to the analysis of the effect of aliphatic (and related to them in structure) substituents on homo-substitution in the peripheral and non-peripheral positions of the phthalocyanine macroheterocycle.[1,4,17,18]

It was later shown that the presence of aliphatic substituents was not absolutely necessary for the formation of columnar mesophases.[19] The so-called flying-seeds-like compounds (FSLM) synthesized by Ohta et al.,[20-24] unlike classical discotic mesogens, did not contain extended aliphatic substituents in the molecule. Nevertheless, the mesophase was formed due to the filling of free volumes at the periphery of the columns with mobile aromatic substituents.[25] All these compounds had only electron-donating fragments (from 4 to 8). A typical example of the FSLM compound is the 2,9,16,23-tetra[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanine copper(II) complex.[20] On heating this compound exhibits two different types of mesophases, which exist in an extremely wide temperature range of 480 °C (from the melting point to the decomposition).

As it was shown previously,[26-28] the mix-substituted phthalocyanines without aliphatic substituents but having both donor oxyaryl and acceptor benzotriazolyl functional groups exhibit mesomorphic properties as well as a tendency to vitrify (Figure 1). While the presence of only 1-benzotriazole groups on periphery of homosubstituted phthalocyanines is not accompanied by the appearance of liquid crystalline phases.[28]

Moreover, the introduction of the electron-withdrawing 1-benzotriazole fragment into the mesogenic 2,9,16,23-tetra[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanine copper(II) complex (1e, Figure 1), studied earlier by Ohta,[20] leads to substantial increase of the melting point (Cr→Mes phase transition temperature of 1e is 131 °C) and narrowing of the mesophase existence temperature range to 43 °C. Further modification of the electron-donor substituent by introducing in it a sulfo group causes an increase the Cr→Mes phase transition temperature to 183 °C. In contrast, the introduction of the octadecylsulfamoyl group leads to a decrease of temperature of the indicated phase transition to 108 °C and to an expansion of the mesophase existence temperature range to 89 °C.[26]

Therefore, our studies showed a significant change of mesomorphic behavior, crystalline phase thermostability and the manifestation of glass state due to variation of the oxyaryl group structure acting as electron donor substituent. At the same time, the influence of the electron-withdrawing group (EWG) nature on the mesomorphic behavior of the studied phthalocyanines has not been investigated.
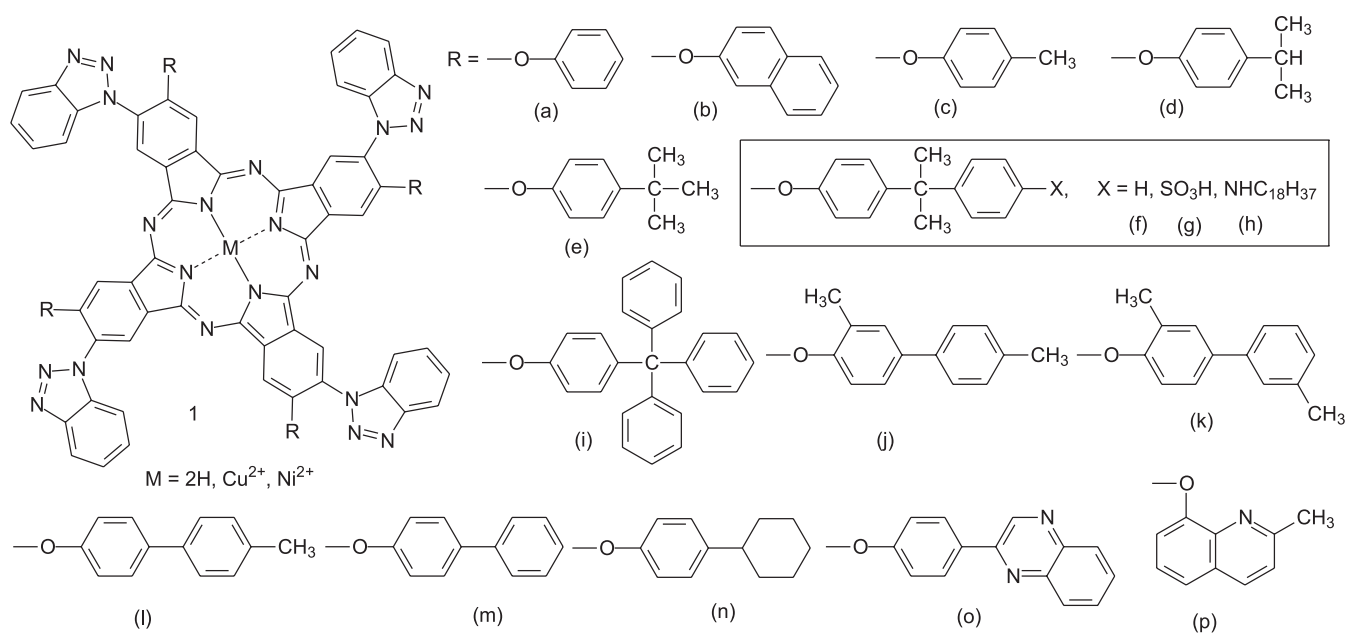

Figure 1. Structural formula of mix-substituted phthalocyanines and their metal complexes (**1a-p**) with four peripheral benzotriazolyl and oxyaryl fragments;[26-28] 4-(1-methyl-1-phenylethyl)phenoxy substituent is framed.

All the above mentioned motivated us to analyze the effect of the chemical nature of the electron-withdrawing group on mesomorphic behavior of 4-(1-methyl-1-phenylethyl)phenoxy substituted phthalocyanines (on the example of replacing the benzotriazolyl acceptor group with a nitro group). In this case, modification of phthalocyanines by the variation of EWG structure will allow to establish its effect on the ability to form a mesomorphic state. In addition, the results obtained should contribute to further deepening of the notion of a correlation between the structure of bifunctional-substituted phthalocyanines and the manifestation of LC properties. The latter will contribute to the development of the condensed phase theory in general.

Experimental

Spectral studies and elemental analysis were carried out on the equipment of the Center for Collective Use (Ivanovo, ISUCT). UV-Vis spectra of solutions of the synthesized phthalocyanines in DMF, chloroform and sulfuric acid were recorded by HITACHI U-2001 spectrophotometer at room temperature within the spectral range 325–900 nm. IR spectra of phthalocyanines **2-5** were recorded by Avatar 360 FT-IR ESP spectrophotometer at room temperature in the 400-4000 cm^{-1} region in thin films (chloroform) or KBr pellets. NMR ^{1}H spectra of [D$_6$]DMSO and CDCl$_3$ test solutions of **2-5** with internal standard tetramethylsilane (TMS) were recorded by «Bruker DRX-500». Elemental analysis of the synthesized compounds was performed on Thermo FlashEA-1112 (CHNS-O).

Mass spectra (MALDI-TOF) were obtained using a MALDI-TOF mass spectrometry (Axima Confidence, Shimadzu Biotech) in positive ions mode. 2-(4-Hydroxybenzoazo)benzoic acid was used as the matrix. The samples were prepared by dissolving the investigated compound in chloroform (**2**, **4**, **5**) or ethanol (**3**) (C=10^{-5}–10^{-4} mol/l) and mixing at the ratio 1:1 (v/v) with the matrix solution (30 mg/ml) in tetrahydrofuran.

Thermooxidative degradation investigation of synthesized phthalocyanines was carried out using a thermogravimetric-DSC synchronous thermal analyzer (STA 449 F3 Jupiter by NETZSCH, Germany) under oxygen-argon atmosphere, heating rate 5 °C/min, in platinum crucible. Before carrying out the elemental and thermogravimetric analysis, the samples of the investigated compounds were heat treated at 110 °C for 2 hours.

Phase state of phthalocyanine derivatives **2-5** was studied using the polarization microscopy method (a microscope MIN-8 with a heating table and a camera "Zorkiy" as equipment, heating rate 2 deg/min)

The method for modeling and prognosing mesomorphism in discotic compounds using molecular parameters (MP) of single molecules,[26-31] was used. The parameters were calculated in the original CMP ChemCard program,[31] which involves the molecules geometry construction and optimization, using the HyperChem software package. The benefits of this method include ease of use, short operating time and sufficiently high degree of prognosis reliability (70–90 %). According to the conditions of this method, a significant deviation of at least one of the calculated MP values from the boundary values of the classification series {1}[26-31] indicates the inability of the compound to the mesophase formation, typical for discotic mesogens (DM). In case of a slight deviation of the calculated MP values a latent mesophase can appear.

4-Bromo-5-nitrophthalonitrile was synthesized according to the well-known method.[32]

4-[4-(1-Methyl-1-phenylethyl)phenoxy]-5-nitrophthalonitrile was synthesized according to known procedure.[33]

Copper(II) (2a) and nickel(II) (2b) complexes of 2,9,16,23-tetra[4-(1-methyl-1-phenylethyl)phenoxy]-3,10,17,24-

tetranitrophthalocyaines. General method 1. Thoroughly triturated mixture of 0.38 g (1 mmol) of 4-[4-(1-methyl-1-phenylethyl)phenoxy]-5-nitrophthalonitrile, 0.05 g (0.8 mmol) of urea, and 0.34 g (0.2 mmol) of (CH$_3$COO)$_2$Cu·2H$_2$O or 0.97 g (0.2 mmol) of (CH$_3$COO)$_2$Ni·4H$_2$O was heated at 155–170 °C for 1.5 h, after which it was dissolved in chloroform and chromatographed on aluminum oxide (eluent – chloroform).

Copper(II) complex of 2,9,16,23-tetra[4-(1-methyl-1-phenylethyl)phenoxy]-3,10,17,24-tetranitrophthalocyaine (2a). (0.35 g, 0.09 mmol, 87 % on 4-bromo-5-nitrophthalonitrile **1**). Found, %: C 69.00, H 4.56, N 10.20. C$_{92}$H$_{68}$CuN$_{12}$O$_{12}$. Requires, %: C 69.19, H 4.29, N 10.52. *m/z* (MALDI-TOF) 1597.42 [M]$^+$. IR (KBr) ν$_{max}$ cm^{-1}: 2964, 2923, 2850 (CH$_3$), 1538 (NO$_2$, unsym.), 1346 (NO$_2$, sym.), 1245 (Ar-O-Ar). ^{1}H NMR (CDCl$_3$) δ$_H$ ppm: 8.33 (s, H1, 4H), 7.83 (m, H2, 4H), 7.17 (m, H5,6,7, 24H), 7.05 (m, H3,4, 16H), 1.75 (s, -CH$_3$, 24H).

Nickel(II) complex of 2,9,16,23-tetra[4-(1-methyl-1-phenylethyl)phenoxy]-3,10,17,24-tetranitrophthalocyaine (2b). (0.32 g, 0.08 mmol, 84 % on 4-bromo-5-nitrophthalonitrile **1**). Found, %: C 69.16, H 4.42, N 10.18. C$_{92}$H$_{68}$NiN$_{12}$O$_{12}$. Requires, %: C 69.40, H 4.30, N 10.56. *m/z* (MALDI-TOF) 1608.42 [M+H$_2$O]$^+$. IR (KBr) ν$_{max}$ cm^{-1}: 2964, 2929, 2866 (CH$_3$), 1542 (NO$_2$, unsym.), 1346 (NO$_2$, sym.), 1251 (Ar-O-Ar). ^{1}H NMR (CDCl$_3$) δ$_H$ ppm: 8.29 (s, H1, 4H), 7.83 (m, H2, 4H), 7.22 (m, H5,6,7, 24H), 7.08 (m, H3,4, 16H), 1.65 (s, -CH$_3$, 24H).

Copper(II) and nickel(II) complexes of 2,9,16,23-tetra{4-[1-methyl-1-(4-sulfophenyl)ethyl]phenoxy}-3,10,17,24-tetranitrophthalocyanine (3a,b). General method 2. The interaction between compounds **2a** (160 mg, 0.1 mmol) or **2b** (158 mg, 0.1 mmol) in 2 ml (18 mmol) of mixture of chlorosulfonic acid and 2 ml (18 mmol) of mixture of thionyl chloride at room temperature for 2 h was carried out. At the end of the stirring, the reaction mixture was poured into ice treated with sodium chloride. The precipitate was collected on a Schott filter, then dried in a desiccator above sulfuric acid for 72 h. The obtained sulfochloride was extracted with acetone. The solvent was distilled off and then boiled with water until complete dissolution. Then the solvent was distilled off. Final purification of **3a,b** was carried out using column chromatography: eluent – DMF, sorbent – silica M 60. The products obtained are dark green solid materials soluble in DMF, water, ammonia, aqueous-alkaline solutions.

Copper(II) complex of 2,9,16,23-tetra{4-[1-methyl-1-(4-sulfophenyl)ethyl]phenoxy}-3,10,17,24-tetranitrophthalocyanine (3a). (76 % on **2a**). Found, %: C 52.98, N 8.08, H 4.30, S 6.14. C$_{92}$H$_{68}$CuN$_{12}$O$_{24}$S$_4$·8H$_2$O. Requires, %: C 53.60, N 8.15, H 4.11, S 6.22. *m/z* (MALDI-TOF) 1916.76 [M]$^+$. IR (KBr) ν$_{max}$ cm^{-1}: 2989, 2923, 2856 (CH$_3$), 1532 (NO$_2$, unsym.), 1385 (NO$_2$, sym.), 1130 (S=O), 1043 (C-S). ^{1}H NMR ([D6]DMSO) δ$_H$ ppm: 8.98 (s, SO$_3$H, 12H), 8.35 (s, H1, 4H), 7.83 (m, H2, 4H), 7.74 (m, H5,6, 16H), 7.05 (m, H3,4, 16H), 1.72 (s, CH3, 24H).

Nickel(II) complex of 2,9,16,23-tetra{4-[1-methyl-1-(4-sulfophenyl)ethyl]phenoxy}-3,10,17,24-tetranitrophthalocyanine (3b). (0.13 g, 70 % on **2b**). Found, %: C 53.32, N 8.29, H 4.45, S 6.12. C$_{92}$H$_{68}$NiN$_{12}$O$_{24}$S$_4$·8H$_2$O. Requires, %: C 53.73, N 8.17, H 4.12, S 6.24. IR (KBr) ν$_{max}$ cm^{-1}: 2922, 2852 (CH$_3$), 1505 (NO$_2$, unsym.), 1360 (NO$_2$, sym.), 1170 (S=O), 1021 (C-S).

Synthesis of metallocomplexes of 2,9,16,23-tetra{4-[1-methyl-1-(4-alkylsulfamoylphenyl)ethyl]phenoxy}-3,10,17,24-tetranitrophthalocyanines (4, 5). General method 3. The interaction between compounds **2a,b** (0.1 mmol) in 2 ml mixture (18 mmol) of chlorosulfonic acid and 2 ml (18 mmol) mixture of thionyl chloride at room temperature for 2 h was carried out. At the end of the stirring, the reaction mixture was poured into ice treated with sodium chloride. The precipitate was collected on a Schott filter, then dried in a desiccator above sulfuric acid for 72 h. The obtained sulfochloride was extracted with acetone. 8-Fold molar excess (0.06 g, 0.4 ml, ρ=0.7056 g/cm^3) of diethylamine (**4a,b**) or 0.22 g of octadecylamine (**5a,b**) was added to the obtained solution

in acetone and boiled at 60 °C for 1–1.5 h. The process was controlled by the completeness of the reaction mass sample dissolving in chloroform. At the end of the reaction the acetone was distilled off. The products (**4, 5**) were extracted from the reaction mixture with chloroform. Final purification was carried out using column chromatography: eluent – chloroform, sorbent – silica M 60. The products obtained are dark green solid materials partially soluble in DMF, highly soluble in benzene, acetone, chloroform.

Copper(II) complex of 2,9,16,23-tetra[4-{1-methyl-1-(4-diethylsulfamoylphenyl)ethyl}phenoxy]-3,10,17,23-tetrakisnitrophthalocyanine (4a) was synthesized according to general method 3 from 160 mg of **2a**. (171 mg, 0.08 mmol, 80 % on **2a**). Found, %: C 60.15, N 10.16, H 5.02, S 5.82. $C_{108}H_{104}CuN_{16}O_{20}S_4$. Requires, %: C 60.68, N 10.48, H 4.90, S 6.00. *m/z* (MALDI-TOF) 2332.82 [M+H]+. IR (KBr) ν_{max} cm−1: 2923, 2850 (-CH2, -CH3), 1538 (NO2, unsym.), 1347 (NO2, sym.), 1111 (S=O, sym.), 1035 (C-S). 1H NMR (CDCl3) δ_H ppm: 8.57 (s, H1, 4H), 7.80 (s, H2, 4H), 7.49 (m, H5, 8H), 7.34 (m, H6, 8H), 7.07 (s, H3, 8H), 7.07 (s, H4, 8H), 3.28 (m, CH2, 16H), 1.47 (s, CH3, 24H), 1.16 (s, CH3 of N(C2H5)2, 24H).

Nickel(II) complex of 2,9,16,23-tetrakis[4-{1-methyl-1-(4-diethylsulfamoylphenyl)ethyl}phenoxy]-3,10,17,23-tetranitrophthalocyanine (4b) was synthesized according to general method 3 from 159 mg of **2b**. (170 mg, 0.08 mmol, 80 % on **2b**). Found, %: C 60.40, N 10.30, H 5.00, S 5.90. $C_{108}H_{104}CuN_{16}O_{20}S_4$. Requires, %: C 60.68, N 10.48, H 4.90, S 6.00. *m/z* (MALDI-TOF) 2326.66 [M+H]+. IR (KBr) ν_{max} cm−1: 2907, 2823 (CH2, CH3), 1535 (NO2, unsym.), 1332 (NO2, sym.), 1163 (S=O, sym.), 1115 (C-S). 1H NMR (CDCl3) δ_H ppm: 8.28 (s, H1, 4H), 7.86 (s, H2, 4H), 7.46 (m, H5, 8H), 7.31 (m, H6, 8H), 7.14 (s, H3, 8H), 7.04 (s, H4, 8H), 3.16 (m, CH2, 16H), 1.45 (s, CH3, 24H), 1.15 (s, CH3 of N(C2H5)2, 24H).

Copper(II) complex of 2,9,16,23-tetrakis[4-{1-methyl-1-(4-octadecylsulfamoylphenyl)ethyl}phenoxy]-3,10,17,24-tetranitrophthalocyanine (5a) was synthesized by general method from 160 mg of **2a**. (210 mg, 0.07 mmol, 72 % on **2a**). Found, %: C 66.98, N 7.35, H 5.13, S 4.23. $C_{164}H_{216}CuN_{16}O_{20}S_4$. Requires, %: C 67.38, N 7.67, H 4.90, S 4.39. IR (KBr) ν_{max} cm−1: 3015 (-NH), 2919, 2851 (CH2, CH3), 1631 (NHsec, def.), 1374 (NO2, sym.), 1311 (NHsec, val.), 1246 (Ar-O-Ar), 1129 (S=O, sym.), 1038 (C-S). 1H NMR (CDCl3) δ_H ppm: 8.31 (s, H1, 4H), 7.84 (s, H2, 4H), 7.07 (s, H3, 8H), 7.49 (m, H5, 8H), 7.29 (m, H6, 8H), 7.07 (s, H4, 8H), 5.38 (s, N-H, 4H), 4.11 (s, C(1)H2, 8H), 3.25 (s, C(2)H2, 8H), 1.79 (s, CH3, 24H), 1.75 (C(3)H2, 8H), 1.27 (C(4-16)H2, 96H), 0.89 (s, CH3 of C18H37, 12H).

Nickel(II) complex of 2,9,16,23-tetrakis[4-{1-methyl-1-(4-octadecylsulfamoylphenyl)ethyl}phenoxy]-3,10,17,24-tetranitrophthalocyanine (5b) was synthesized by general method from 159 mg of **2b**. (200 mg, 0.06 mmol, 64 % on **2b**). Found, %: C 67.20, N 7.42, H 5.03, S 4.33. $C_{164}H_{216}NiN_{16}O_{20}S_4$. Requires, %: C 67.38, N 7.67, H 4.90, S 4.39. IR (KBr) ν_{max} cm−1: 3055 (NH), 2954, 2918, 2850 (CH2, CH3), 1637 (NHsec, def.), 1548 (NO2, unsym.), 1336 (NO2, sym.), 1310 (NHsec, val), 1251 (Ar-O-Ar), 1143 (S=O,

sym.), 1118 (C-S). 1H NMR (CDCl3) δ_H ppm: 8.27 (s, H1, 4H), 7.87 (s, H2, 4H), 7.10 (s, H3, 8H), 7.51 (m, H5, 8H), 7.29 (m, H6, 8H), 7.07 (s, H4, 8H), 5.16 (s, NH, 4H), 4.08 (s, C(1)H2, 8H), 3.25 (s, C(2)H2, 8H), 1.79 (s, CH3, 24H), 1.75 (C(3)H2, 8H), 1.27 (C(4-16)H2, 96H), 0.89 (s, CH3 of C18H37, 12H).

Results and Discussion

This work consists of several stages. At the first stage, the ability of phthalocyanines **2-5** to form mesophases, typical for discotic mesogens (DM), was predicted. At the second stage, the synthesis of the initial phthalonitrile with nitro- and 4-(1-methyl-1-phenylethyl)phenoxy groups was carried out, on the basis of which the corresponding copper and nickel phthalocyanine derivatives of different structures were obtained (**2-5**). At the third stage, the spectral and mesomorphic properties and thermodegradation processes upon the application of heat of synthesized bifunctional-substituted phthalocyanines were investigated. The predicted results were brought into correlation with the experimentally obtained data.

Prognosis of mesomorphism of phthalocyanines 2-5

The mesomorphism prognosis of a new series of phthalocyanine derivatives (**2a,b-5a,b**) was carried out according to above-mentioned methods.[26,27,29-31] The construction and optimization of molecular models (**2a,b-5a,b**) was carried out using the method of molecular mechanics (MM+). Then the geometric characteristics required for calculating of the molecular parameters (MP) were extracted from the obtained models and introduced into CMP Chem-Card.[31] Samples of optimized models are given in Figure 2. For the compounds of specified structure the prediction of the ability to form columnar and nematic mesomorphism was carried out by analyzing and comparing the calculated MP values with the classification series (I) (Table 1):

$$K=2-8.5; K_c=1-2.6; K_p=0.2-0.7; K_s=0.25-1.00;$$
$$M_m=0.2-0.8; M_r=0.15-0.80; K_{ar}=0.08-0.30 \text{ (I)}$$

Deviation of at least one of the calculated MP values from the limiting values of the reference number shows the inability of the designed compound to exhibit mesomorphism typical for DM.

Table 1. Calculated MP and data of prognosis for substituted phthalocyanines **2-5**.

Compound	E_{opt}, kcal/mol	M_m	M_r	K_p	K	K_c	K_{ar}	P_{Col+N}
2a	91.78	1.04'	0.34	0.72*	3.21	1.31	0.19	−
2b	90.05	1.04'	0.34	0.61	2.38	1.00	0.21	−
3a	203.93	0.74	0.30	0.61	3.46	1.00	0.19	+
3b	206.36	0.74	0.30	1.88'	3.28	1.00	0.18	−
4a	239.34	0.62	0.20	0.50	3.19	1.31	0.17	+
4b	247.67	0.61	0.20	0.43	1.77'	1.00	0.19	−
5a	169.62	0.44	0.15	0.20	2.23	1.31	0.07*	+/−
5b	168.95	0.44	0.15	0.20	3.07	1.01	0.07*	+/−

Note: E_{opt} – optimization energy, K_s = 0.50 for all compounds, *P* – prognosis of mesomorphism typical for DM.
MP* value closed to the boundary of classified number (1). MP' value deviated significantly from number (1).

According to Table 1, the compounds **2a**, **2b**, **3b** can't exhibit mesomorhism. The prognosis is positive for the compound **3a**, and equally probable for **4a** and **4b**.

The prognosis is probable for the alkylsulfamoyl derivatives **4a,b-5a,b** and positive for the complexes **3a**, **4a**.

The data in Table 1 (the last two columns) show that in general there is a correspondence between the results of the prediction and the experiment on the mesomorphism study of this compound series. Thus, the reliability of the prediction is 75 %.

Synthesis

On the basis of the previously described method,[33] 4-[4-(1-methyl-1-phenylethyl)phenoxy]-5-nitrophthalonitrile was synthesized by nucleophilic aromatic substitution of the bromine atom for the 4-(1-methyl-1-phenylethyl) phenol residue in 4-bromo-5-nitrophthalonitrile (Scheme 1). The reaction was carried out in aqueous DMF in the presence of potassium carbonate at room temperature for 0.5 hour. At the end of the reaction, the formed precipitate was filtered off, washed with 2-propanol, then with water and winded at 70–80 °C.

Then the corresponding bifunctional-substituted phthalocyanines of copper and nickel (**2a,b**) were synthesized by heating the phthalonitrile (**1**) and copper acetate dihydrate or nickel acetate tetrahydrate to 180–190 °C for 2 hours in the presence of urea. Then the corresponding sulfochloride (Scheme 1) was synthesized at room temperature by the reaction of phthalocyanines **2a,b** and a mixture of thionyl chloride and chlorosulfonic acid (Scheme), which were then either converted to the corresponding sulfonic acids by hydrolysis or to sulfonamides by interaction with the corresponding amines.

Purification of the synthesized copper and nickel phthalocyanines (**2a,b**) and alkylsulfamoyl derivatives (**3-4**) on their basis was carried out by liquid column chromatography.
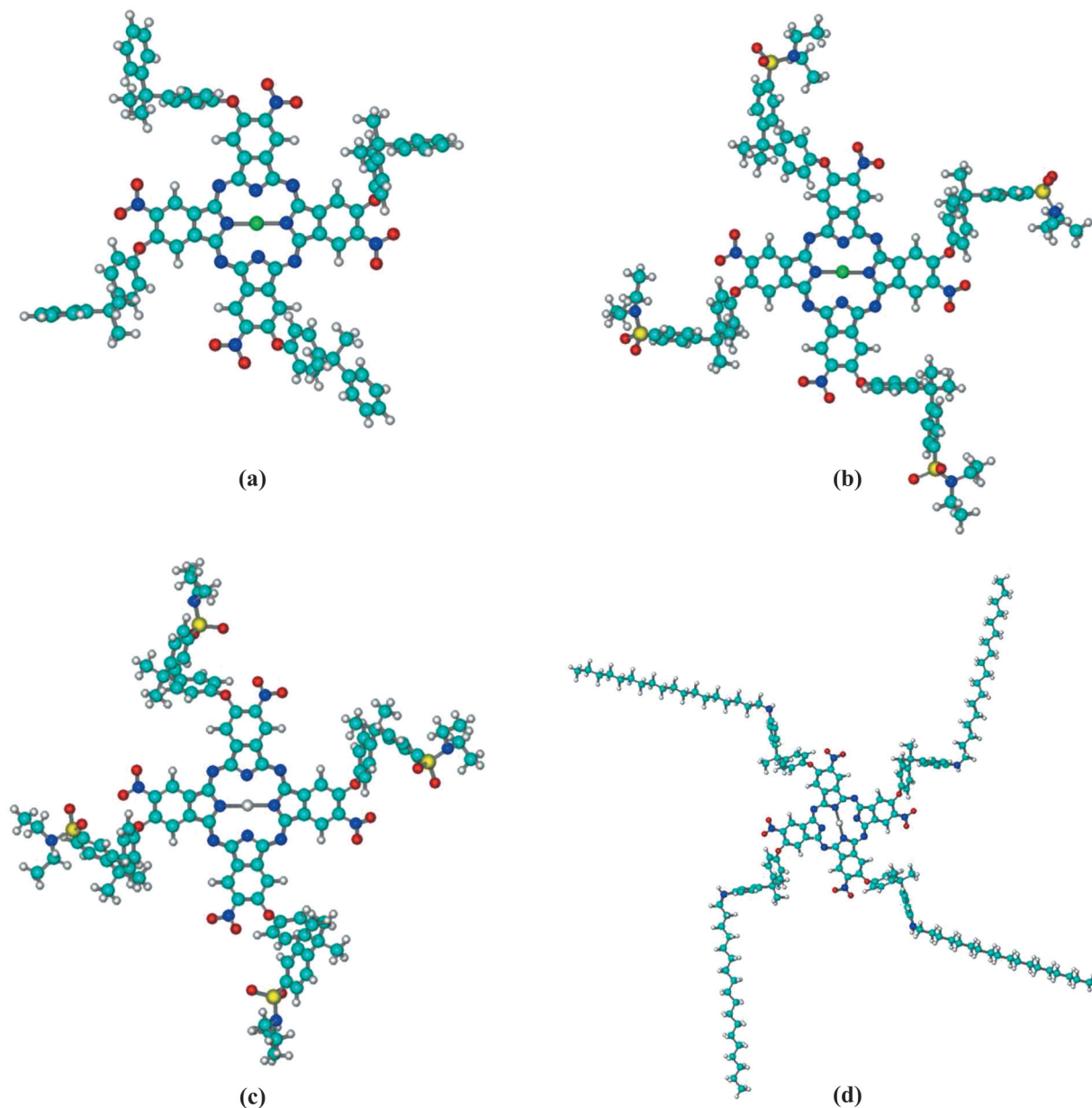

(a)

(b)

(c)

(d)

Figure 2. Samples of optimized models of molecule of compounds **2a** (a), **4a** (b), **4b** (c) and **5a** (d).

In the IR spectra of compounds **2a,b-5a,b** symmetric (1340–1360 cm⁻¹) and asymmetric (1530–1560 cm⁻¹) stretch of nitro groups were observed. The stretching bands of the C–S (1035–1118 cm⁻¹) bonds, symmetric (1129–1163 cm⁻¹) and asymmetric (1329–1360 cm⁻¹) S=O stretching vibration were recorded in the spectra of compounds **3-5**.[34] In the IR spectra of alkylsulfamoyl derivatives (**3-4**), the stretching bands (1310–1311 cm⁻¹) and bending bands (1630–1640 cm⁻¹) vibrations of secondary amino groups were observed, as well as a band in 3015–3150 cm⁻¹ region indicating the presence of N-H bond.

In the ¹H NMR spectra of compounds **2a,b**, the proton signals of the phenoxy substituent (7.05–7.07 ppm) and benzene rings of the phthalocyanine molecule (8.27–8.33 and 7.83–7.88 ppm) were recorded. Their position was not affected by the introduction of sulfo- or alkylsulfamoyl groups. 1-Methyl-1-phenylethyl fragment proton signals were observed at 7.17–7.14 ppm as a multiplet.

As for the compounds with sulfo- and alkylsulfamoyl substituents in the oxyaryl moieties, the proton signal at position 6 was shifted to the weaker field region (7.74 ppm
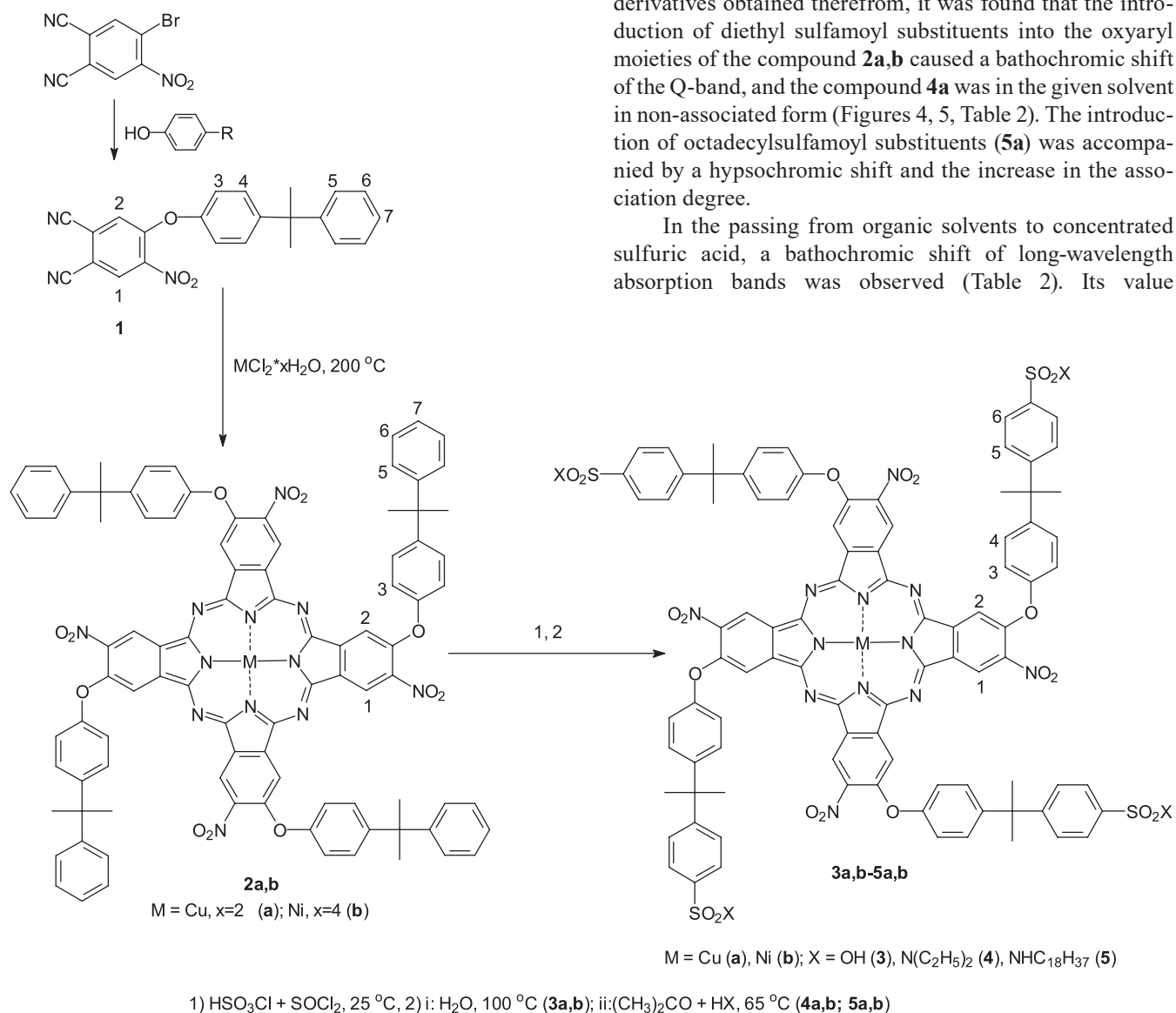
for compounds **3a,b**, and 7.29–7.34 ppm for compounds **4a,b-5a,b**). This fact confirmed the modification of the compounds **3a,b-4a,b** by the *para* positions of 4-(1-methyl-1-phenylethyl) phenoxy substituent phenyl rings, since the proton signal (pos. 2, Scheme 2) located in the *ortho* position to the aryloxy fragment (7.80–7.84 ppm in spectra of **3**, **4**) was observed almost in the same region as in the spectrum of the initial compounds **2a,b** (7.83 ppm).

Further, UV-Vis spectra of the synthesized phthalocyanines were studied (Table 2).

In DMF and chloroform, 2,9,16,23-tetrakis[4-(1-methyl-1-phenylethyl)phenoxy]-3,10,17,24-tetrakis-nitrophthalocyanines (**2a,b**) were in the associated form (Figure 3), in contrast to benzotriazolyl-substituted analogues.[35] In addition, the substitution of 1-benzotriazole fragments for nitro groups was accompanied by a bathochromic shift of long-wavelength absorption bands.
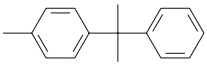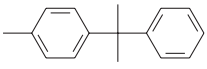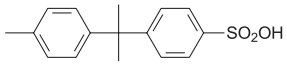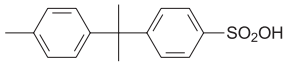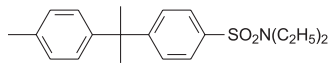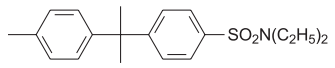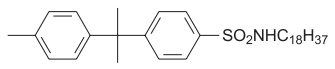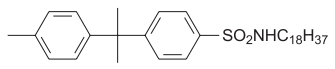
The passing from copper(II) complexes to nickel(II) complexes was accompanied by a hypsochromic shift of long-wavelength absorption bands in organic solvents (Table 2). Comparing the UV-Vis spectra of phthalocyanines (**2a,b**) in chloroform with the spectrum of the alkylsulfamoyl derivatives obtained therefrom, it was found that the introduction of diethyl sulfamoyl substituents into the oxyaryl moieties of the compound **2a,b** caused a bathochromic shift of the Q-band, and the compound **4a** was in the given solvent in non-associated form (Figures 4, 5, Table 2). The introduction of octadecylsulfamoyl substituents (**5a**) was accompanied by a hypsochromic shift and the increase in the association degree.

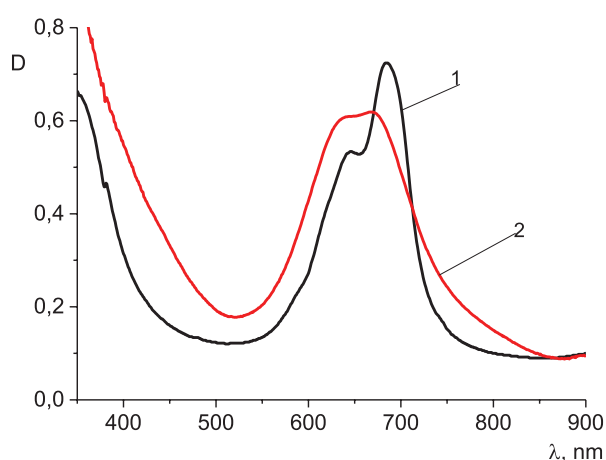In the passing from organic solvents to concentrated sulfuric acid, a bathochromic shift of long-wavelength absorption bands was observed (Table 2). Its value

2a,b
M = Cu, x=2 (**a**); Ni, x=4 (**b**)

3a,b-5a,b

M = Cu (**a**), Ni (**b**); X = OH (**3**), N(C₂H₅)₂ (**4**), NHC₁₈H₃₇ (**5**)

1) HSO₃Cl + SOCl₂, 25 °C, 2) i: H₂O, 100 °C (**3a,b**); ii:(CH₃)₂CO + HX, 65 °C (**4a,b; 5a,b**)

Scheme 1.

Table 2. UV-Vis spectra of compounds **2-4**.

№	R	M	UV-Vis spectra, λ_{max}, nm		
			DMF	CHCl$_3$	H$_2$SO$_4$
2a		Cu	685	696	804
2b		Ni	667	683	813
3a	SO$_2$OH	Cu	651, 690	–	788, 794
3b		Ni	649	–	796
4a	SO$_2$N(C$_2$H$_5$)$_2$	Cu	693	698	782
4b		Ni	683	688	791
5a	SO$_2$NHC$_{18}$H$_{37}$	Cu	692	693	790
5b		Ni	689	677	792

Figure 3. UV-Vis spectra in DMF (*C*=1.05·10^{-5} mol/l):
1 – (**2a**); 2 – (**2b**).
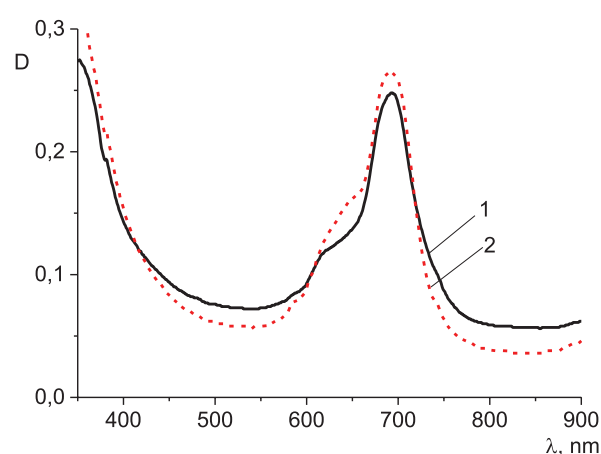
Figure 4. UV-Vis spectra in DMF (*C*=0.65·10^{-5} mol/l):
1 – (**4a**); 2 – (**5a**).

in the series of corresponding metal complexes decreases depending on the nature of the substituent introduced to 4-(1-methyl-1-phenylethyl)phenoxy group:

R = O—⟨benzene⟩—C—⟨benzene⟩—X
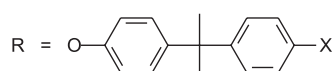
M = Cu, X = -H (**2a**) > -OH (**3a**) > -SO$_2$NHC$_{18}$H$_{37}$ (**5a**) > -SO$_2$N(C$_2$H$_5$)$_2$ (**4a**)
    108 nm   104 nm   97 nm   84 nm

M = Ni, X = -H (**2b**), -OH (**3b**) > -SO$_2$NHC$_{18}$H$_{37}$ (**5b**) > -SO$_2$N(C$_2$H$_5$)$_2$ (**4b**)
    120 nm   115 nm   103 nm

It should be noted that the values of the bathochromic displacement for the corresponding nickel complexes are larger in comparison with copper complexes.

Study of mesomorphic properties of compounds 2-5

Synthesized phthalocyanines **2-5** were studied using polarization microscopy method. It was found that compounds **2a,b**, **3a,b** were not mesomorphic, what was coincided with the prognosis data (Table 1), except compound **3a**, for which the prognosis was positive. The sulfo derivative **3a** was powdery at room temperature. Its sample passed into isotropic liquid at 158 °C. On cooling, typical
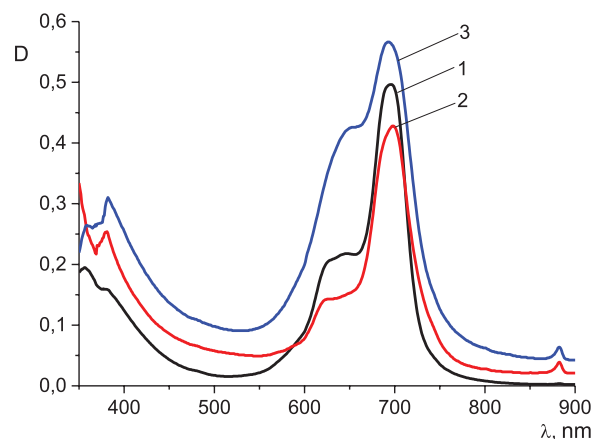
Figure 5. UV-Vis spectra in CHCl$_3$ (*C*=0.85·10^{-5} mol/l):
1 – (**2a**); 2 – (**4a**); 3 – (**5a**).

crystals grew (Figure 6) starting from needle-like at 155 °C to dendritic at 110 °C.

The diethyl sulfamoyl derivative **4a** in heating cycle immediately melted into isotropic liquid at 115 °C (Table 3). On cooling to 98 °C, mesophase appeared with
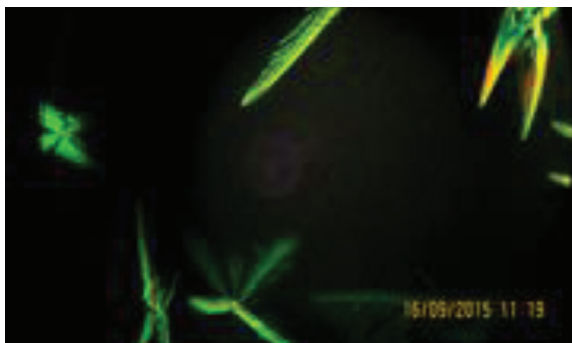
Figure 6. The growth of individual crystals of **3a** from isotropic phase, cooling cycle, 110 °C, polarizers crossed.

DM-characteristic flower-like domains (Figure 7), *i.e.* exhibited a monotrophic mesomorphism.

Figure 7. Flower-like domains **4a** growth from an isotropic phase, cooling cycle, 75 °C, polarizers crossed.

Compound (**5a**) exhibited enantiotropic mesomorphism. In heating cycle, at 65 °C the substance sample transformed into a mesophase with a small-domain structure in spherulite form. On further heating, the spherulites grew to flower-like formations, along the edges of which a wavy dark rim appeared (Figure 8). At 182 °C the mesophase entered an isotropic state. On cooling, the appearance of mesophase was observed with a slight delay (170 °C).
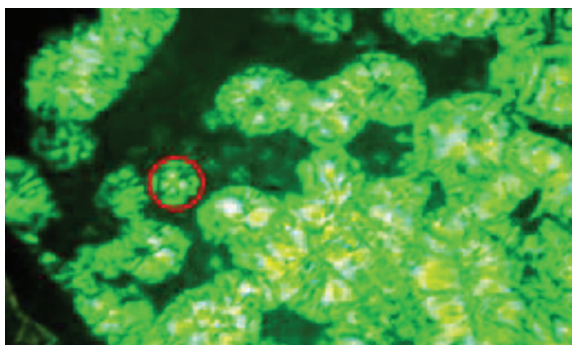

Figure 8. Texture with flower-like domains and a dark rim around the edges of the domains. Heating cycle, 126 °C, polarizers crossed.

There were spindle-shaped domains, like a columnar-lamellar mesophase. On further cooling, they became larger, merged and obtained the broken fan-shaped texture. Orientation by shear deformation led to the appearance of a layered texture in the form of domains oriented in one direction, which on further cooling spontaneously grew while the thickness of the sample decreased (Figure 9). Further cooling to 80 °C led to glass transition of the sample while maintaining the mesophase texture.

It was found that the substitution of 2,9,16,23-tetra(1-benzotriazolyl)-3,10,17,23-tetra{4-[1-methyl-1-(4-octadecylsulfamoylphenyl)-ethyl]phenoxy}benzotriazole fragments of copper phthalocyanine[26,36] (**5c**) for nitro groups caused an expansion of the mesophase existence temperature range (**5a**) in comparison with **5c** and a decrease in the phase transition temperature of Cr→Mes (Table 3).

The study of the phthalocyanine **2b-5b** derivatives mesomorphism with a nickel atom at the coordination site in comparison with corresponding derivatives **2a-5a** containing a copper atom in the coordination site showed a number of differences in the mesophase formation (Table 3).

Thus, the phthalocyanine derivatives **2a-5a** exhibited less thermal stability than **2b-5b**. Compound **2a** did not form mesophases and melted at 160 °C. Compound **2b** melted at 168 °C without passing to the mesophase and was vitrified on cooling. Compound **4b**, unlike derivative **4a**, did not even form a monotrophic mesophase; on heating, it immediately melted and passed into an isotropic liquid at 120 °C, behaved like an amorphous substance, did not crystallize on cooling.

Finally, **5b**, which was in the crystalline state at room temperature, when heated to 110 °C revealed a mesophase that at 167 °C passed into isotropic liquid (Table 3, Figures 10–12). On cooling, the mesophase appeared with a slight delay (supercooling) at 145 °C in the form of large spherulites or spindle-shaped domains, subsequently it was vitrified at 82 °C while maintaining the texture of the mesophase (Figure 12). It was found that, in comparison with the corresponding copper complex (**5a**), an increase in the temperature of the Cr→Mes phase transition was observed in the nickel complex (**5b**). The observed textures were very similar to the textures of the compound (**5a**). Thus, the introduction of Ni atom instead of Cu into the coordination site of the indicated phthalocyanines significantly affected the mesophase existence interval, which narrowed almost twofold due to a decrease in the thermal stability of the mesophase.

In case of the mesogenic copper complex (**5c**), the substitution of the benzotriazole group for the nitro group (**5a**) broadened the temperature range of mesophase existence. Perhaps, in that case the introduction of a less voluminous acceptor substituent (NO_2 group) made it possible to improve π-π stacking interaction and make stacking of the columns in the mesophase in a wider temperature range. This was cooperated by long hydrocarbon radicals along the molecule periphery.

For copper complexes **1f** and **1h**, the substitution of the benzotriazole group for the nitro group, on the contrary, led to a deterioration of the mesophase formation conditions for the compounds **2a**, **3a**. In this case, the tri-

Table 3. LC properties of **2-5**.

№	M	Compound	Mesomorphism
2a	Cu	[structure: phthalocyanine fragment with O–C6H4–C(CH3)2–C6H5 and NO2 substituent]	*Heating:* Cr · 160 °C Iso *Cooling:* Iso · 150 G
2b	Ni		*Heating:* Cr ·168 °C Iso *Cooling:* Iso · 161 G
1f	Cu	[structure with O–C6H4–C(CH3)2–C6H5 and benzotriazole substituent] [26]	*Heating:* Cr · 131 °C Mes · 174 °C Iso *Cooling:* Iso · 112 °C Mes · 75 °C G
	Ni		*Heating:* Cr · 151 °C Mes · 184 °C Iso *Cooling:* Iso · 175 °C Mes · 114 °C G
3a	Cu	[structure with O–C6H4–C(CH3)2–C6H4–SO2OH and NO2 substituent]	*Heating:* Cr · 158 °C Iso *Cooling:* Iso · 155 °C Cr
3b	Ni		*Heating:* Cr · 165 °C Iso *Cooling:* Iso · 157 G
1h	Cu	[structure with O–C6H4–C(CH3)2–C6H4–SO2OH [26] and benzotriazole substituent]	*Heating:* Cr · 183 °C Mes · 227 °C Iso *Cooling:* Iso · 209 °C Mes · 164 °C Cr
4a	Cu	[structure with O–C6H4–C(CH3)2–C6H4–SO2N(C2H5)2 and NO2 substituent]	*Heating:* Cr · 115 °C Iso *Cooling:* Iso · 98 °C Mes · 45 °C G
4b	Ni		*Heating:* Cr · 120 °C · Iso *Cooling:* Iso · 112 Amorphous powder
5a	Cu	[structure with O–C6H4–C(CH3)2–C6H4–SO2NHC18H37 and NO2 substituent]	*Heating:* Cr · 65 °C Mes 182 °C·Iso *Cooling:* Iso · 170 °C Mes · 80 °C G
5b	Ni		*Heating:* Cr · 110 °C Mes 167 °C· I *Cooling:* Iso · 145 °C Mes · 82 °C G
1g	Cu	[structure with O–C6H4–C(CH3)2–C6H4–SO2NHC18H37 [26] and benzotriazole substituent]	*Heating:* Cr · 108 °C Mes 197 °C Iso *Cooling:* Iso · 170 °C Mes · 70 °C G

azole group played a positive role in mesophase formation, increasing the hydrophobicity of the periphery and decreasing the interaction in the center.

Along with the investigation of the mesomorphic properties of phthalocyanines **2-5**, a study on their thermooxidative degradation was undertaken, which was important for establishing the thermal and oxidative stability of **2-5** (Table 4). The introduction of sulfo groups into 4-(1-methyl-1-phenylethyl)phenoxy substituents caused a decrease in the temperature of the maximum exoeffect. In addition, the appearance of the endopic at 210–230 °C was observed on the DSC curves of sulfo derivatives (**3a,b**). It was found that these compounds, being heated at this temperature, practically lost their solubility in water. Apparently, processes involving sulfo groups occured in this temperature range.

It was found that the process of thermooxidative degradation of **3a** began at 229 °C.

Comparison of the nickel **3b** phthalocyanine sulfo derivative with previously obtained[35] benzotriazolyl-substituted nickel phthalocyanine showed that the substitution of benzotriazole fragments for nitro groups caused a decrease in the thermal stability of nitro substituted compound **3b** (Table 4).

The passing from the sulfo derivative **3b** to the corresponding diethylsulfamoyl derivative **4b** was accompanied by temperature increase in both the onset of mass loss and the maximum exoeffect. Mesogenic compound **4a** retained its structure to 278 °C, whereas the range of its mesophase existence was in the range of 98–45 °C (Table 3). In addition, it was noted that the copper complex **4a** was a bit more stable than the corresponding nickel complex **4b**.

The substitution of diethylsulfamoyl **4a** fragments for more extended octadecylsulfamoyl caused increase in the thermal stability of the corresponding phthalocyanine derivative **5a** due to additional shielding of nitro groups and the metal atom in the coordination cavity of the phthalocyanine molecule. An oxidizer-oxygen molecule interacted in these groups, which resulted in thermal destruction of the compounds (Table 4).
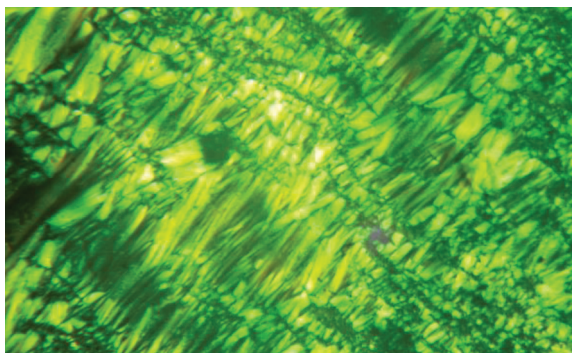
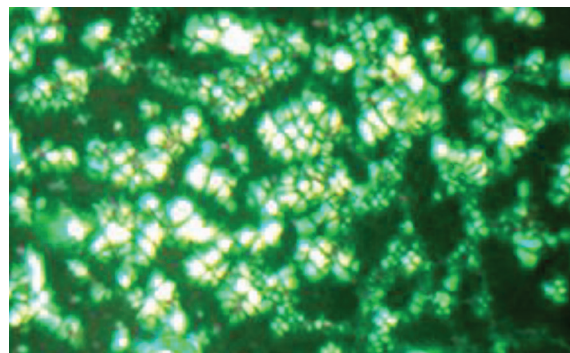**Figure 9.** Layers of **5a** domains oriented by shear deformation. Cooling cycle, 90 °C, polarizers crossed.

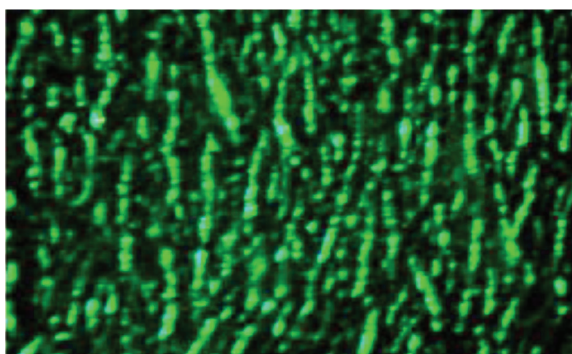**Figure 11.** Texture **5b** in the 2nd heating cycle. Polarizers crossed, 128 °C.

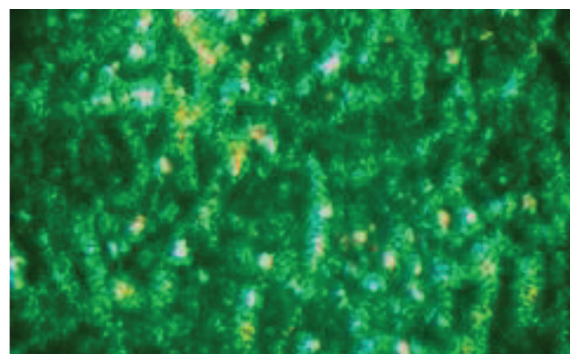**Figure 10.** Spindle-shaped domains **5b** oriented by shear deformation. Polarizers crossed, 1st heating cycle, 135 °C.

Figure 12. Texture of vitrified mesophase **5b**. Polarizers crossed, 82 °C.

Table 4. Thermogravimetrical study of compounds **2-5**.

№	M	Compound	T_{exo}, °C		ΔT, °C
			I	II	
2b	Ni		478	619	525–665
3a	Cu		229	459	380–535
3b	Ni		204	441	380–540
1g	Ni		265	486	418–498
4b	Ni		266	567	480–660
4a	Cu		284	599	408–660
5a	Cu		363	497	438–580

Note: I – 1 exopic, II – 2 exopic

Conclusions

The synthesis of copper and nickel phthalocyanines with 4-(1-methyl-1-phenylethyl)phenoxy and nitro groups was carried out. By introducing alkylsulfamoyl groups into the available oxyaryl moieties, further modification was carried out. Physicochemical, particularly mesomorphic, properties of the synthesized compounds were studied, their comparative analysis was carried out.

It was found that the substitution of benzotriazole fragments of copper 2,9,16,23-tetra(1-benzotriazolyl)-3,10,17,24-tetra[4-(1-methyl-1-phenylethyl)phenoxy]-phthalocyanine for nitro groups led to the inability of this phthalocyanine derivative to form a mesophase. Introduction of 2,9,16,23-tetra[4-(1-methyl-1-phenylethyl)phenoxy]-3,10,17,24-tetranitrophthalocyanine copper diethyl or octadecyl sulfamoyl substituents gave these compounds mesomorphic properties, but led to decreasing the stability to thermal destruction. It was also established that for the mesogenic copper complex **5c**, the substitution of the benzotriazole group for the nitro group (**5a**) broadened the temperature range of mesophase existence.

It was shown that the introduction of Ni atom instead of Cu into the coordination site of the phthalocyanines significantly affected the mesophase existence interval, which narrowed almost twofold due to a decrease in the thermal stability of the mesophase.

The repeatability of the prognosis with the experimental data was 75 %.

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