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**SYNTHESIS AND PROPERTIES OF SULFO AND ALKYL SULFAMOYL SUBSTITUTED
PHTHALOCYANINES AND THEIR COPPER (II) COMPLEXES BEARING
1-BENZOTRIAZOLYL AND 4-CYCLOHEXYLPHENOXY GROUPS**

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New sulfo and alkylsulfamoyl substituted 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis(4-cyclohexylphenoxy)phthalocyanines and their Cu(II) complexes were synthesized. Their physicochemical properties such as electronic absorption, solubility in organic solvents, thermostability and mesomorphism were investigated. It was established that introduction of sulfo group into cyclohexylphenoxy fragment of the studied phthalocyanines causes bathochromic shift of long wave bands in both DMF and concentrated sulfuric acid solutions. In contrast, introduction of octadecylsulfamoyl substituents does not influence the position of Q band in DMF, but shifts this band hypsochromically. The performed synthesis revealed that introduction of bulky fragments into ortho-position with respect to the oxygen atom of aryloxy group excludes manifestation of liquid crystalline properties. While substitution by the same substituent in para-position leads to formation of mesophase. This fact can be connected with the sterical hindrance of liquid crystalline molecular packing. Thus, it was established that the presence of donor and acceptor fragments in mix-substituted phthalocyanines is important but not determining factor for their mesophase formation. The forecast data on the absence of mesomorphism of new phthalocyanine derivatives with sulfo and alkylsulfamoyl groups are in a good agreement with the experimental data, which is the evidence of the applicability of the method used to identify mesogen / non-mesogen structures for this class of compounds.

Key words: *phthalocyanines, synthesis, mesomorphism, solubility, thermostability, mesomorphism prognosis.*

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**СИНТЕЗ И СВОЙСТВА СУЛЬФОКИСЛОТ И АЛКИЛСУЛЬФАМОИЛ-ЗАМЕЩЕННЫХ
ФТАЛОЦИАНИНОВ И ИХ КОМПЛЕКСОВ С МЕДЬЮ, СОДЕРЖАЩИХ
1-БЕНЗОТРИАЗОЛЬНЫЕ И 4-ЦИКЛОГЕКСИЛФЕНОКСИ ГРУППЫ**

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Взаимодействием 2,9,16,23-тетра(1-бензотриазолил)-3,10,17,24-тетра(4-циклогексилфенокси) фталоцианина и его комплекса с медью со смесью тионилхлорида и хлорсульфоновой кислоты получены соответствующие сульфохлориды. Гидролизом сульфохлоридов синтезированы новые сульфокислоты

бензотриазолилзамещенных фталоцианинов. Реакцией сульфохлорида 2,9,16,23-тетра(1-бензотриазолил)-3,10,17,24-тетра(4-циклогексилфеноксифталоцианина меди с октадециламином в ацетоне получено соответствующее октадецил октадецилсульфамойлпроизводное. Изучены спектральные свойства целевых соединений, их термическая устойчивость, растворимость в органических растворителях и мезоморфизм. Установлено, что при введении сульфогрупп в циклогексилфеноксифрагмент исследуемых фталоцианинов в спектрах поглощения наблюдается bathochromный сдвиг длинноволновых полос как в ДМФА, так и в концентрированной серной кислоте. Введение октадецилсульфамойльных заместителей не оказывает влияние на положение Q полосы в ДМФА, но приводит к гипсохромному сдвигу этой полосы в концентрированной серной кислоте. Показано, что введение объемных сульфо- и алкилсульфамойл фрагментов в орто-положение по отношению к атому кислорода арилокси группы производных фталоцианина, исключает проявление мезоморфных свойств, в то время как аналогичное замещение в пара-положении приводит к формированию мезофазы. Данный факт объяснен стерическими влияниями на возможность межмолекулярного взаимодействия данных соединений, оптимального для формирования мезофаз. Проведенные исследования впервые позволили установить, что наличие донорных и акцепторных групп в смешанно-замещенных фталоцианинах является важным, но не решающим фактором в проявлении ими мезоморфных свойств. Полученные по прогнозу данные об отсутствии мезофаз у новых производных фталоцианина с сульфо- и алкилсульфамойл группами находятся в хорошем согласии с экспериментом, что свидетельствует о применимости использованного метода к выявлению мезоген /немезогенных структур у подобного класса соединений.

Ключевые слова: фталоцианины, синтез, мезоморфизм, растворимость, термогравиметрия, прогноз мезоморфизма.

Introduction

Study of the relationship between structure and properties of phthalocyanine derivatives and their mesomorphism is the fundamental task of physical chemistry of condensed matter.

At present time, experimental data on mesomorphism of bifunctionally substituted phthalocyanines are limited. The expansion of the number of such compounds will help to come closer to solve the problem of the dependence of liquid crystal properties on the structure of organic compound [1].

In this work, we continue investigations concerning synthesis of sulfo- and alkylsulfamoyl derivatives of aryloxy-substituted phthalocyanines [2–3]. We have previously shown that the presence of donor and acceptor substituents imparts the ability for non-mesogenic compounds to show thermotropic mesomorphism [4–7]. While the introduction of sulfo or alkylsulfamoyl fragments into *para*-position with

respect to the oxygen atom of aryloxy group of mix-substituted phthalocyanines does not affect the ability of these compounds to exhibit mesomorphism. Such substitution shifts the mesophase existence region to higher temperatures [3]. We have studied compounds with 1-methyl-1-phenylethyl substituents in phenoxy groups, these are the fragments in which sulfo and sulfonamide moieties are located [3]. In contrast to the previously investigated compounds, the new target phthalocyanines **1–2**, due to presence of cyclohexyl group in *para*-position of phenoxy groups, contain sulfo and alkylsulfamoyl groups in *ortho*-positions with respect to oxygen atom of phenoxy fragment (Fig. 1). Such change should significantly influence physicochemical and mesomorphic properties.

The aim of this work is the synthesis and investigation of physicochemical properties of sulfonic acids **1** and alkylsulfamoyl derivatives **2** of the mix-substituted phthalocyanines containing 1-benzotriazolyl and 4-cyclohexylphenoxy fragments.

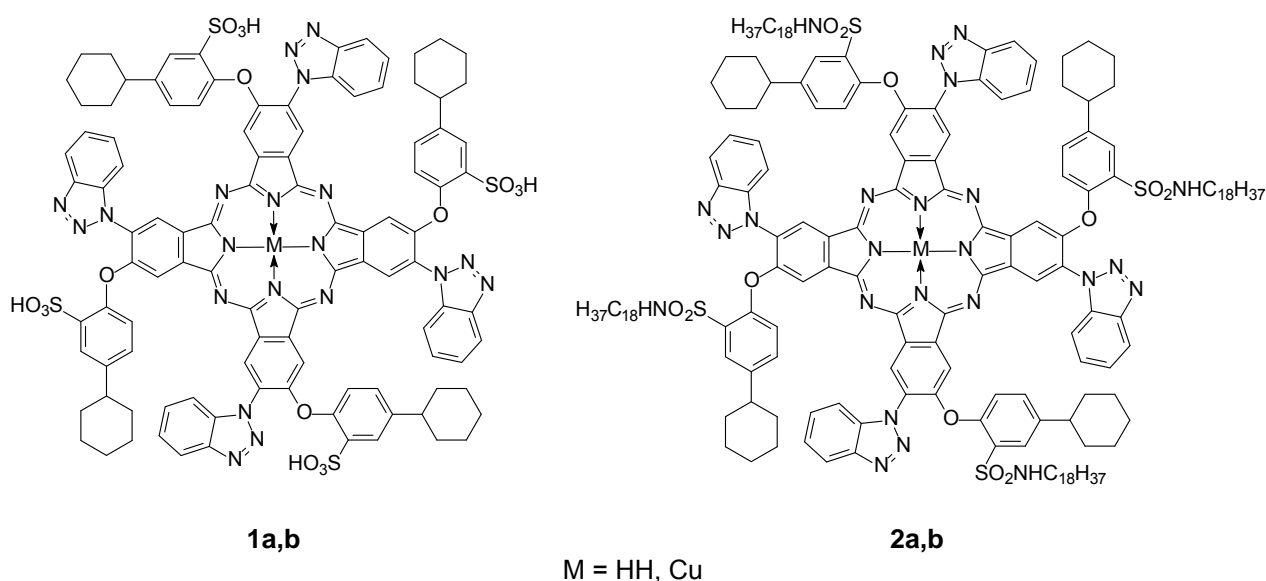


Fig. 1. Structural formulas of the studied compounds

Experimental

UV-Vis spectra of solutions of the synthesized phthalocyanines in DMF and chloroform were obtained on HITACHI U-2001 spectrophotometer at a room temperature on the spectral range of 325–900 nm. IR spectra were recorded on Avatar 360 FT-IR ESP spectrophotometer at a room temperature. ^1H NMR spectra of **1a**, **2b** in DMSO- d_6 and CDCl_3 with TMS as internal standard were carried out on «Bruker DRX-500». Elemental analysis was performed on Flash EATM 1112 instrument. Spectral studies and elemental analysis were carried out on the equipment of the Centre for Collective Use (Ivanovo, ISUCT).

Study of solubility of 2,9,16,23-tetrakis-(1-benzotriazolyl)-3,9,17,24-tetrakis(4-cyclohexylphenoxy)phthalocyanines and its copper complexes as well as their sulfonic acids was carried out according to the known procedure [8] at 298 K by isothermal saturation with spectrophotometric control of concentration. The systematic error in the solubility's value due to an error in the determination of the molar extinction coefficient was 5 %. The absorption bands with maxima at 684 (**4a**), 685 (**4b**), 683 (**1a**), 685 (**1b**) in DMF and 688 (**4a**), 692 (**4b**) in chloroform were selected as analytical bands.

Mesomorphism of sulfo- (**1a**, **b**) and octadecylsulfamoyl- (**2b**) phthalocyanine derivatives

was studied by optical polarizing microscopy (polarizing microscope «Leitz Laborlux 12 Pol» equipped with «Mettler FP 82» heating stage, heating/cooling rate 10 °C/min). Lyotropic mesomorphism of binary systems of the studied compounds with organic solvents (DMF, DMSO, toluene, CHCl_3) and aqueous solutions was tested by contact preparation technique on the equipment of the Nanomaterials Research Institute (Ivanovo State University).

Prediction of columnar mesomorphism for compounds **1–2** was performed using the original program *CMP ChemCard* [9]. The program gives the possibility to calculate the molecular parameters (*MP*) of individual molecule and to predict whether the compound can be potential discotic mesogen. Among the advantages of this method is the simplicity of use, low cost of machine time and sufficiently high degree of reliability of the prediction (70–90 %). Prior the prediction, geometry optimization of molecular structures was performed by *HyperChem* software package (method MM^+).

*Synthesis of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-cyclohexylphenoxy] phthalocyanine and its copper complex (**4a,b**)* was performed according to the known procedure [10].

Synthesis of sulfonic acids of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-cyclohexylphenoxy] phthalocyanine and its copper complex (1a,b)

0.1 mmol of compounds **4a,b** reacted with a mixture of 2 ml (18 mmol) of chlorosulfonic acid and 2 ml (18 mmol) of thionyl chloride at room temperature and stirred during 1 hour (in the case of metal-free phthalocyanine) or 2 hours (in the case of the corresponding copper complex). After stirring, the reaction mixture was poured onto ice and treated with sodium chloride. The precipitate was collected on a sinter and dried in a desiccator over sulfuric acid for 3 days. The resultant sulfonic chloride was extracted with acetone, the solvent was evaporated under reduced pressure. The crude product was boiled in water until it was completely dissolved. The resultant sulfonic acid was extracted with DMF, the solution was filtered through a paper filter and the solvent was evaporated. The obtained products were dark green solids, soluble in water, ammonia and aqueous alkaline solutions.

The final purification was performed by column chromatography on silica gel (M 60) using DMF as the eluent. The desired products were dried in the air at 80–90 °C.

2,9,16,23-Tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis(2-sulfo-4-cyclohexylphenoxy)phthalocyanine (1a) was synthesized according to the main procedure from 174 mg of compound **4a**. (Yield 191 mg, 92 %). Found, %: C 62.45, H 4.33, N 14.01, S 6.41; $C_{112}H_{78}N_{20}O_{16}S_4$. Requires: C 61.94, H 4.70, N 14.29, S 6.54; ν_{max} (KBr)/ cm^{-1} : 3418 (–OH), 2925, 2850 (CH_2 , CH_3), 1358 (Ar–O–Ar), 1330 (S=O *asymm*), 1091 (C–S), 1047 (N=N), 1024 (H_2Pc), 747 (C–N). δ_H ($[D_6]DMSO$, numeration of protons is presented in Scheme 3): 9.22 (*s*, 4H, SO_3H); 8.70 (*t*, 4H, H1); 8.38 (*s*, 4H, H2); 8.29 (*s*, 4H, H3); 8.20–8.10 (*m*, 4H, H6); 7.83–7.90 (*m*, 4H, H4); 7.62 (*s*, 4H, H8); 7.48–7.53 (*m*, 4H, H5); 7.28 (*t*, 4H, H9); 2.18 (*m*, 4H, H10); 1.66; 1.54–1.51 (*m*, 10H, H11,12).

2,9,16,23-Tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis(2-sulfo-4-cyclohexylphenoxy)phthalocyanine copper complex (1b) was obtained according to the main procedure from 188 mg of compound **4b**. (Yield 178 mg, 80 %). Found, %: C 59.98, N 13.26, H 4.30, S 6.00; $C_{104}H_{184}CuN_{20}O_{16}S_4$. Requires: C 60.59, N 13.59, H 4.11, S 6.22; ν_{max} (KBr)/ cm^{-1} : 3386 (OH), 2924, 2849, 2781 (CH_2 , CH_3), 1395, 1349 (S=O *asymm*), 1206 (Ar–O–Ar), 1175 (S=O *symm*), 1088 (C–S), 1058 (N=N), 745 C–N.

Synthesis of 2,9,16,23-tetrakis(1-benzotriazolyl) 3, 10, 17,24-tetrakis-(2-octadecylsulfamoyl-4-cyclohexylphenoxy)phthalocyanine copper complex (2b)

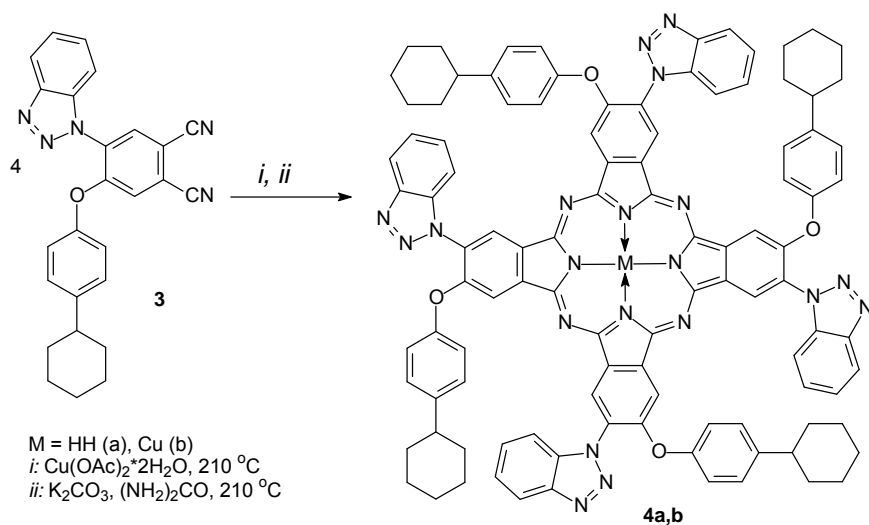
Compound **4b** (172 mg, 0.1 mmol) reacted with a mixture of chlorosulfonic acid 2 ml (18 mmol) and thionyl chloride 2 ml (18 mmol) at room temperature for 2 hours. After stirring, the reaction mixture was poured onto ice and treated with sodium chloride. The precipitate was collected on a sinter and dried in a desiccator over sulfuric acid for 3 days. The target sulfochloride was extracted with acetone. An 8-fold molar excess of octadecylamine (0.22 g, 0.8 mmol) was added to the obtained acetone solution and the mixture was heated at 60 °C for 1–1.5 hours. The process was controlled by the completeness of the dissolution of the reaction mixture in chloroform. After the reaction was finished, the acetone was distilled off. The desired product was extracted from the reaction mixture with chloroform. Final purification was performed by column chromatography on silica gel (M 60) using chloroform as eluent. The resulting product was dark green solid, partially soluble in DMF, highly soluble in benzene, acetone and chloroform. (Yield 233 mg, 77 %). Found, %: C 68.35, N 10.55, H 8.38, S 4.07; $C_{176}H_{232}CuN_{24}O_{12}S_4$. Requires: C 68.91, N 10.96, H 7.62, S 4.18. ν_{max} (KBr)/ cm^{-1} : 2920, 2851 (– CH_2 , – CH_3), 1617 (– NH_{sec} , def.), 1533 (NH_{sec} , val), 1388 (S=O *asymm*), 1242 (Ar–O–Ar), 1088 (C–S), 1050 (N=N), 746 (C–N); δ_H ($CDCl_3$, numeration of protons is presented in Scheme 3): 8.71 (*t*, 4H, H1); 8.23 (*t*, 4H, H3); 8.12 (*m*, 4H, H2); 8.03–8.05 (*m*, 4H, H6); 7.87–7.77 (*m*, 4H, H4); 7.49 (*t*, 4H, H5); 7.26 (H8); 6.90 (*m*, 4H, H7); 5.40 (*s*, 4H, NH); 3.15 (*m*, 4H, H9); 2.98–2.91 (H10); 1.36 (H11,12); 1.89, 1.79, 1.44 (– CH_2 in $NHC_{18}H_{37}$); 0.91 (*s*, 12H, – CH_3).

Results and discussions

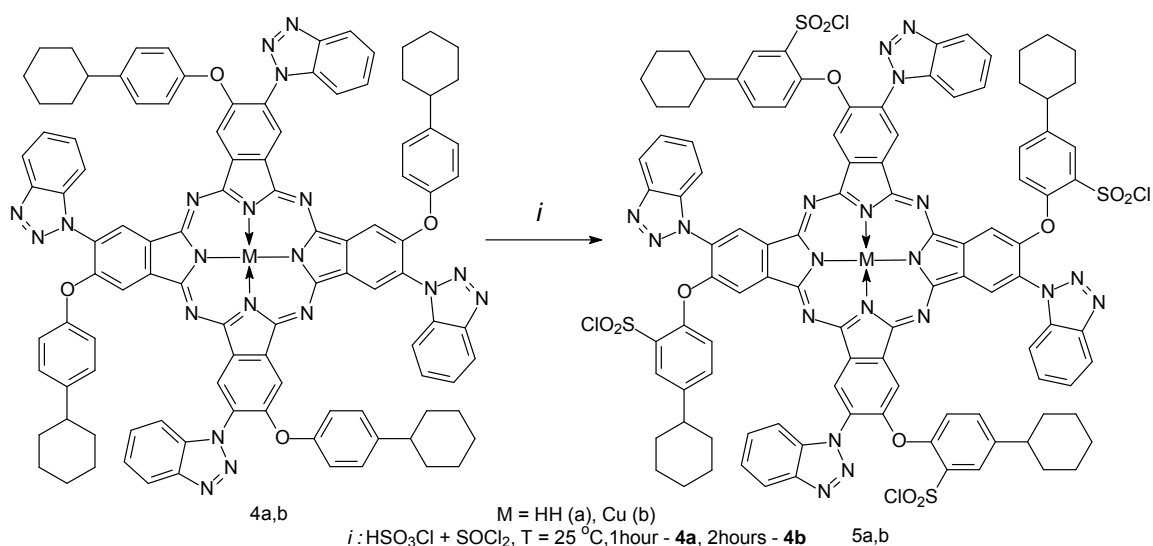
Synthesis

Synthesis of the target compounds was carried out starting from the corresponding bifunctionally substituted phthalocyanines **4a,b**. These were obtained according to the known procedure [10] using "nitrile" method, consisting in heating the phthalonitrile **3** with copper acetate or anhydrous potassium carbonate (Scheme 1).

Then phthalocyanine derivatives **4a,b** were separated from the reaction mixture and treated with a mixture of thionyl chloride and chlorosulfonic acid according to the method described in [2–3] (Scheme 2).



Scheme 1



Scheme 2

The interaction time was determined by the nature of the coordination center: in the case of copper complex it was 2 hours, for metal-free phthalocyanine – 1 hour. The resulting sulfonyl chlorides **5a,b** were isolated by pouring reaction mixture onto ice. The formed precipitate was filtered off and dried thoroughly.

For the synthesis of the corresponding sulfonic acids **1a,b** the sulfonyl chlorides were extracted with acetone. The obtained solution was filtered and the

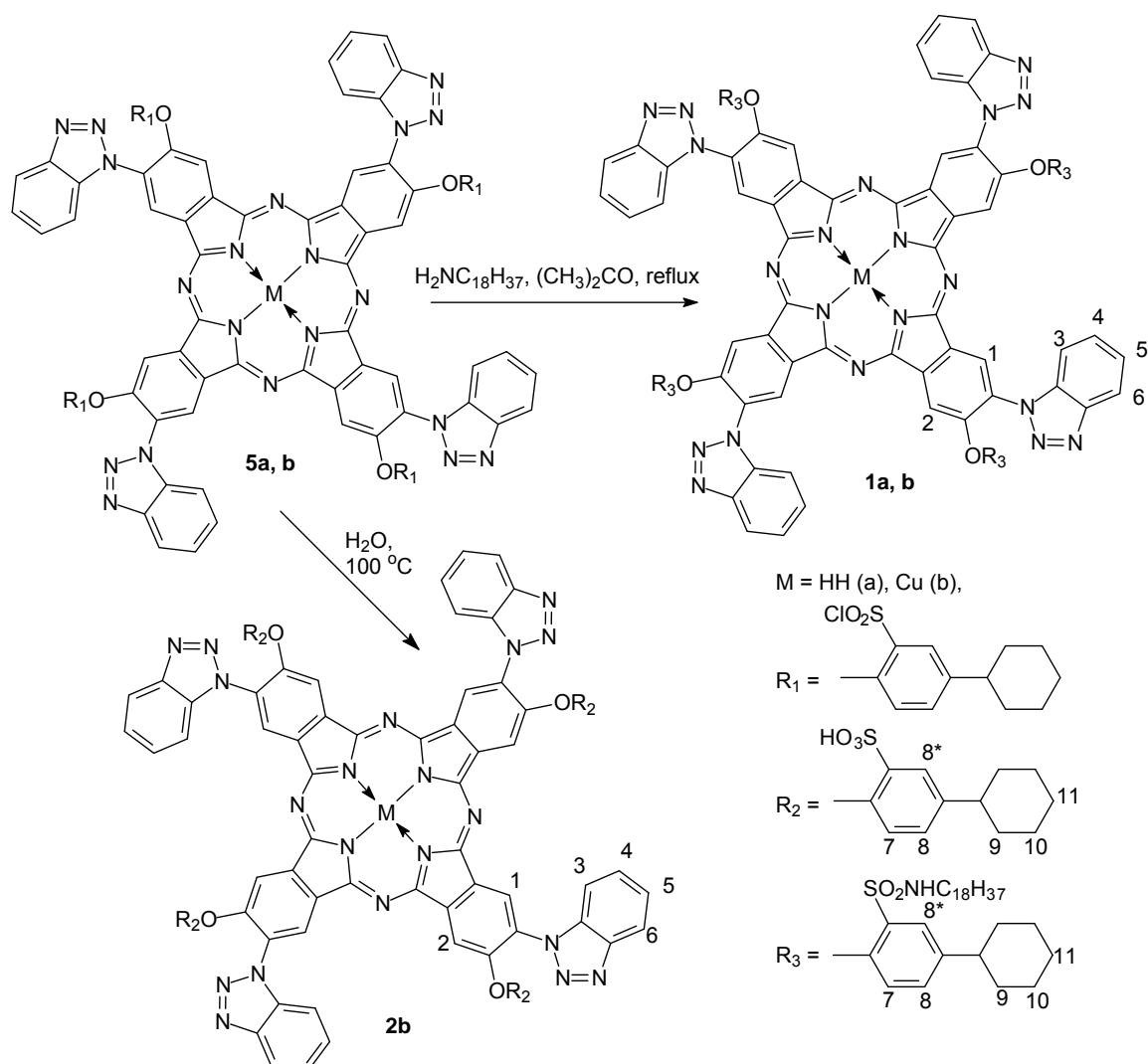
acetone was distilled off. After that, the crude product was refluxed in water until its complete dissolution, and then the water was removed (Scheme 3).

For the synthesis of the octadecylsulfamoyl derivatives an 8-fold molar excess of octadecylamine was added into the acetone extract. The resulting solution was refluxed until the test showed complete dissolution of the reaction mixture in chloroform (Scheme 3). The attempt to obtain metal-free alkyl-

sulfamoyl phthalocyanine **4a** by this method failed.

Identification of the synthesized compounds was performed by elemental analysis, ^1H NMR-, IR- and electron spectroscopy. In the ^1H NMR spectrum of the sulfonic acid **1a** the appearance of four protons of sulfo groups at 9.07 ppm as well as a new signal at 8.38 ppm, which was absent in the spectrum of the original phthalocyanine **4a**, were detected in the weak field region. The signal at 8.04 ppm, which was observed in the spectrum of the "parent"

phthalocyanine **4a** [10] and corresponded to the proton in the 2-position, was absent. This fact confirms the introduction of sulfo group into aryl fragment exactly in the *ortho*-position to the oxygen bridge. A similar change in the ^1H NMR spectrum was observed in the case of the previously studied 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis(1,6-disulfo-2-naphthoxy)phthalocyanine [2], which also contains sulfo group in the *ortho*-position to the oxygen bridge in the phenyloxy fragment.



Scheme 3

In the ^1H NMR spectrum of alkylsulfamoyl derivative **2b** the intense signals of methylene groups belonging to octadecyl substituents were observed in strong field region at 3.2–1.2 ppm. The signal of the protons of methyl groups of alkyl chains were detected at 0.92 ppm. In the strong field region (at 2.90–3.15 ppm) there were signals of methylene groups of cyclohexyl substituents, which were previously found in the spectra of the starting compounds [10]. The signal of protons of the secondary amino groups of the octadecylsulfamoyl substituents was detected in lower field (at 5.40 ppm).

Introduction of sulfo groups into the molecule of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis(4-cyclohexylphenoxy)phthalocyanine **1a** or its copper complex **1b** causes the appearance in the IR spectrum of symmetric (at 1175 cm^{-1}) and asymmetric (at $1330\text{--}1349\text{ cm}^{-1}$) vibrations characteristic of S=O bonds and stretching vibrations of C–S bonds (at $1088\text{--}1091\text{ cm}^{-1}$). In the IR spectrum of compound **1a** the band specific to metal-free phthalocyanine (usually

observed at 1005 cm^{-1}) was shifted to the region of higher frequency (1024 cm^{-1}). Introduction of alkylsulfamoyl fragments was accompanied in the IR spectrum by the appearance of stretching bands (1533 cm^{-1}) and deformation oscillations (1617 cm^{-1}) of the secondary amino groups.

Since sulfo groups of sulfonic acids **1a,b** were introduced into sterically closed position of phenyloxy substituent and shielded from interaction with water molecules by hydrophobic cyclohexyl fragments, both compounds were insoluble in the water, but soluble in aqueous-alkaline solutions and DMF. Octadecylsulfamoyl derivative **2b** is highly soluble in acetone and chloroform, but low soluble in DMF.

Electronic absorption spectra

By analyzing spectra of sulfonic acids **1a,b** in 5 % aqueous ammonium hydroxide solution, it was found that the presence of copper atom in the coordination center of phthalocyanine molecule reduces its tendency to association (Fig. 1).

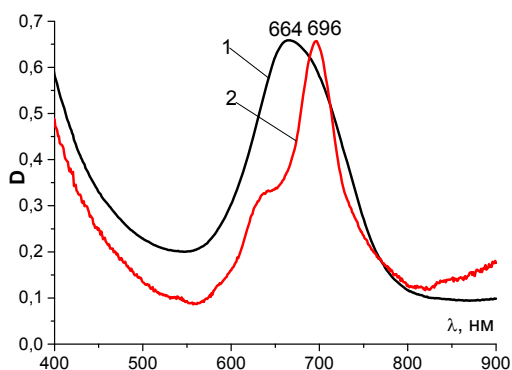


Fig. 2. Electronic absorption spectra in aqueous NH_4OH (5 %) ($C = 0.6 \cdot 10^{-5}\text{ mol/l}$): 1 – **1a**, 2 – **1b**

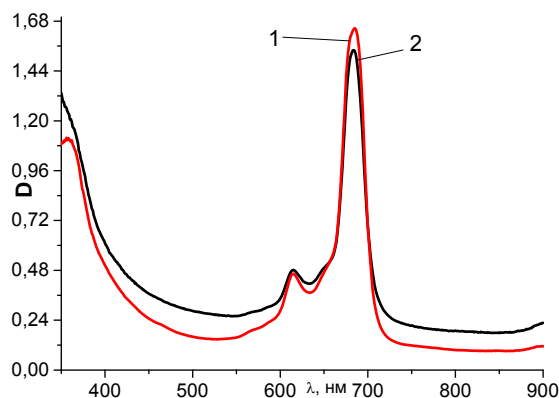


Fig. 3. Electronic absorption spectra in DMF ($C = 0.85 \cdot 10^{-5}\text{ mol/l}$): 1 – **1a**, 2 – **1b**

Table 1. UV-Vis spectroscopy data for compounds **1a,b**, **2b** and **4a,b** in different solvents

№	R	M	UV-Vis spectra, λ_{max} , nm			
			NH_4OH (5%)	DMF	CHCl_3	H_2SO_4
1a		HH	664	694	–	803
1b		Cu	642, 697	692	–	769, 791
2b		Cu	–	684	684	767, 790
4a		HH	–	684	689	795, 836
4b		Cu	–	685	675, 710	802

Considering the character of electronic absorption spectra in DMF, one can conclude that the sulfonic acids **1a,b** were unassociated (Fig. 3). In the spectrum of alkylsulfamoyl copper phthalocyanine **2b** in chloroform, a broadening of absorption bands located in the visible region, and disobedience to the Lambert-Bouguer-Beer law were observed, which indicate the association processes (Fig. 4). According to the nature of its absorption spectrum, compound **2b** in DMF solution was in unassociated form (Fig. 4), but due to poor solubility of this phthalocyanine in DMF it was not possible to determine its extinction coefficient.

The change of organic solvent for the concentrated sulfuric acid, as expected, causes a bathochromic shift of the absorption bands in the electronic absorption spectra, but this shift is smaller in comparison with “parent” compounds **4a,b** (Table 1 [10]). As in the case of **4a,b**, the spectral curves are diffuse.

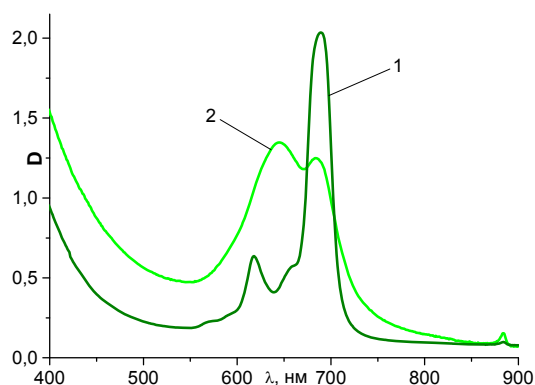


Fig. 4. Electronic absorption spectra for compound **2b** in organic solvents ($C = 1.0 \cdot 10^{-5}$ mol/l): 1 – DMF, 2 – CHCl_3

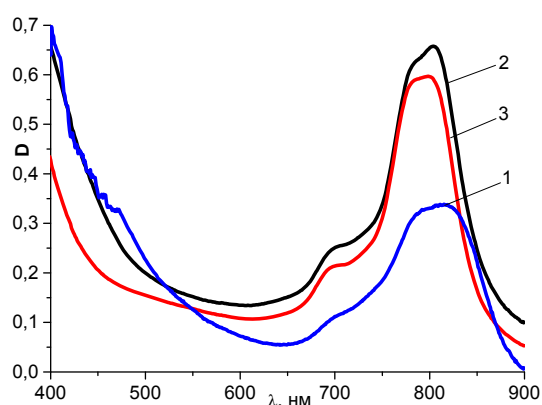


Fig. 5. Electronic absorption spectra in H_2SO_4 : 1 – **4a**, 2 – **1a**, 3 – **1b**

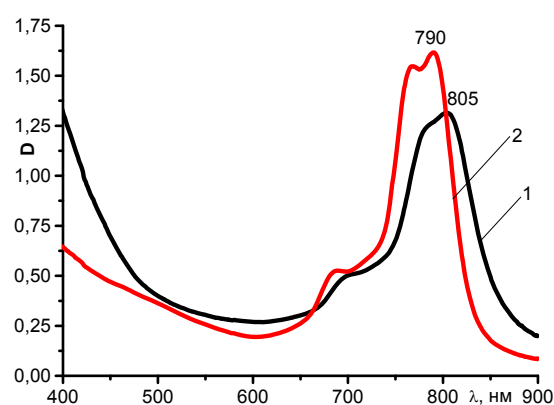


Fig. 6. Electronic absorption spectra in H_2SO_4 : 1 – **4b**, 2 – **2b**

Comparing the “parent” compound **4a** with its sulfonic acid **1a** a hypsochromic shift of Q-band at 33 nm was detected. Introduction of copper atom into the molecule **1a** causes a hypsochromic shift of Q-band for further 12 nm (Fig. 5). The transition from copper phthalocyanine **4b** to its octadecylsulfamoyl derivative **2b** is also accompanied by a hypsochromic shift of Q-band at 14 nm (Fig. 6).

Solubility study

Solubility of macroheterocyclic compounds has its own specificity, which is generally determined by two factors: the strength of the crystal lattice of these compounds and solvation by solvent molecules. The

complexity and diversity of phthalocyanine structures define the specific behavior of these compounds in chemical reactions and physicochemical processes that take place in solutions [11].

It is known that the unsubstituted phthalocyanine and its complexes at normal conditions are insoluble in either water or in organic solvents [12]. The modification of the phthalocyanine molecule by introduction of functional substituents of different nature can impart solubility in organic solvents by introducing the centers of specific solvation and loosening the molecular lattice. Changing the structure of the molecule and its effective volume should be accompanied by a change in the crystal lattice

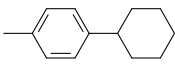
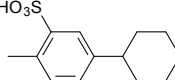
strength due to intermolecular interactions in crystal and, as a consequence, different inclinations of compound to undergo transition into solution. The solubility study of bifunctionally substituted phthalocyanines in various solvents is of interest. Therefore, the solubility of compounds **1a,b** and **4a,b** in DMF and chloroform has been investigated.

The presence of bulky substituents affects the strength of the crystal lattice due to its loosening, thereby makes compounds soluble in organic solvents. Solubility of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis(4-cyclohexylphenoxy)phthalocyanine **4a** and its copper complex **4b** as well as their sulfonic acids **1a,b** in DMF at 298 K is 10^{-2} mol/l (Table. 2).

The experimental data on solubility of compounds **4a,b** in DMF and chloroform at 298 K show that solubility in chloroform is lower than in DMF. This fact can indirectly indicate a decrease in the strength of the molecular lattice, as well as an

increased affinity of large organic molecules to DMF. This difference is due to the nature and the solvating ability of the used solvents. Thus, chloroform is weakly polar, proton-donor non-coordinating solvent, it is practically not associated with proton acceptors and gives a strong hydrogen bond. $AN = 23.1$, $\epsilon = 4.80$. On the other hand, DMF is dipolar solvent with a strong electron-donating function ($DN = 26$). Considering the nature in solubility changes of compounds **4a** and **4b** in chloroform, we may conclude that despite the presence of specific solvation centers, they are sterically shielded from chloroform molecules. Therefore the solubility of compounds **4a,b** is slightly different from solubility of similar structure copper phthalocyanine containing unsubstituted phenoxy groups [13]. Reduction of solubility in DMF in the case of sulfonic acids **1a,b** in comparison with their “parent” compounds **4a** and **4b** was also detected.

Table 2. Solubility of compounds **1a,b** and **4a,b** in organic solvents

Compound	M	R	S ± 0.05 (CHCl ₃)			S ± 0.05 (DMF)		
			λ_{max} , nm, (lgε)	mol/l	g/l	λ_{max} , nm, (lgε)	mol/l	g/l
4a	HH		688 (4.92)	2.1	3.59	684, (4.82)	10.52	17.98
4b	Cu		692 (4.92)	3.1	4.81	685, (4.87)	10.29	17.85
1a	HH		insoluble			694 (4.78)	7.71	15.90
1b	Cu					692 (4.87)	7.72	16.05

S – solubility

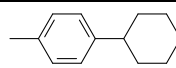
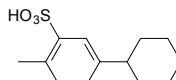
Thermogravimetry

The thermal oxidative degradation process of metal-free phthalocyanines **1a** and **4a** was studied. The results are given in Table 3.

The thermal decomposition process of compounds **1a** and **4a** consists of two stages. The first one occurs in the temperature range 280–360 °C. According to the weight loss value observed on TG curves (27.91 % for **4a** and 23.35 % for **1a**), the decomposition occurs with the participation of benzotriazolyl substituents, as it was found previously for other phthalocyanines combining on the periphery benzotriazolyl and oxyaryl groups [14]. For example for compounds **4a** and **1a**, heated up to 290 °C, in the IR spectra there was no band corresponding to the stretching vibrations of N=N bond of benzotriazolyl

fragment (1040–1050 cm^{-1}). At the same time, it was found that compound **4a** retains solubility in chloroform and compound **1a** – in aqueous alkaline solutions. That is, the mass loss at this stage can be caused by the removal of benzotriazole, but not aryloxy fragments.

Table 3. Data of thermogravimetric study

Compound	R	ΔT , °	T_{exo} , °C
4a		462–604	563
1a		423–543	531

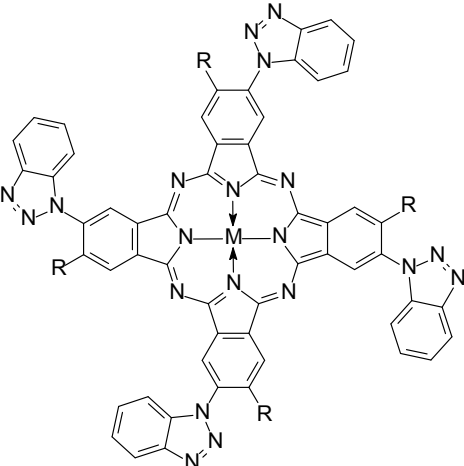
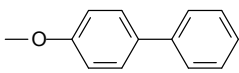
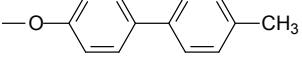
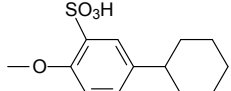
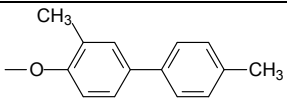
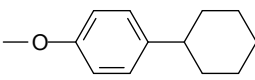
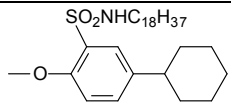
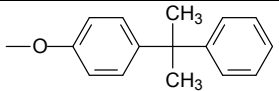
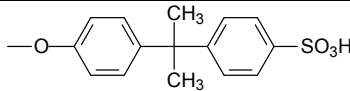
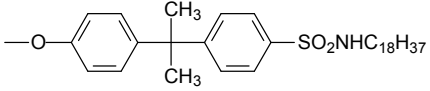
ΔT – temperature range corresponding to the maximum weight loss of the sample, T_{exo} – maximum temperature of *exo*-effect

Table 3 shows that introduction of sulfo groups into the molecule of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis(4-cyclohexylphenoxy) phthalocyanine causes a decrease in the thermal stability of the corresponding sulfo-derivative on 33 °C.

Mesomorphic properties

Phthalocyanine derivatives **1b** and **2b** were investigated by polarizing microscopy to study possibility to show mesomorphic properties. Previously, it was found that compounds **4a,b** form a thermotropic mesophase [15].

Table 4. Influence of donor fragment structure on mesogeneity of mix-substituted phthalocyanines

		M = HH, Cu
Mesogenic derivatives, R		Non-mesogenic derivatives, R
	 [15]	
	 [15]	
		
 [3]		

Introduction of sulfo or alkylsulfamoyl groups into donor fragments of the previously studied mix-substituted phthalocyanines with benzotriazolyl substituents (Table 4) did not lead to the disappearance of mesomorphic properties. Moreover, in comparison with non-mesogenic homosubstituted phthalocyanine with eight benzotriazolyl substituents such substitution induced liquid crystallinity. However, we have found that the behavior of the compounds presented in this work is fundamentally different. Thus, sulfo-substituted copper phthalocyanine **1b** melts at 200–220 °C and displays no mesomorphic properties. Compound **2b** with

octadecylsulfamoyl fragments melts at much lower temperature – 80–85 °C, while it also does not show mesomorphism. Therefore, both compounds showed no inclination to the mesophase formation.

Prognosis of mesomorphism

To explain the difference in mesomorphic behavior, molecular modeling of phthalocyanine derivatives **1–2** was performed with the help of *HyperChem* software using the method of molecular mechanics (MM+). On the basis of the modeling the molecular parameters (MP) were calculated and analyzed. MPs are the dimensionless parameters

extracted from the structure of single molecules by comparing the calculated values with the classification series {1} [3, 15–19]:

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

Parameter K characterizes anisometry of a molecule as a whole. Parameters K_c and K_p characterize the central part and the periphery of molecule, respectively. Parameter K_s indicates the substitution degree of the central part by the

peripheral substituents. Parameter M_m takes into account the ratio of the central part mass and the periphery mass of the molecule. Parameter M_r takes into account the surrounding degree of the central part of the molecule by the peripheral substituents. Parameter K_{ar} is proposed to take into account the packing density of the peripheral substituents [15–19].

Examples of the optimized models are presented in Figure 7.

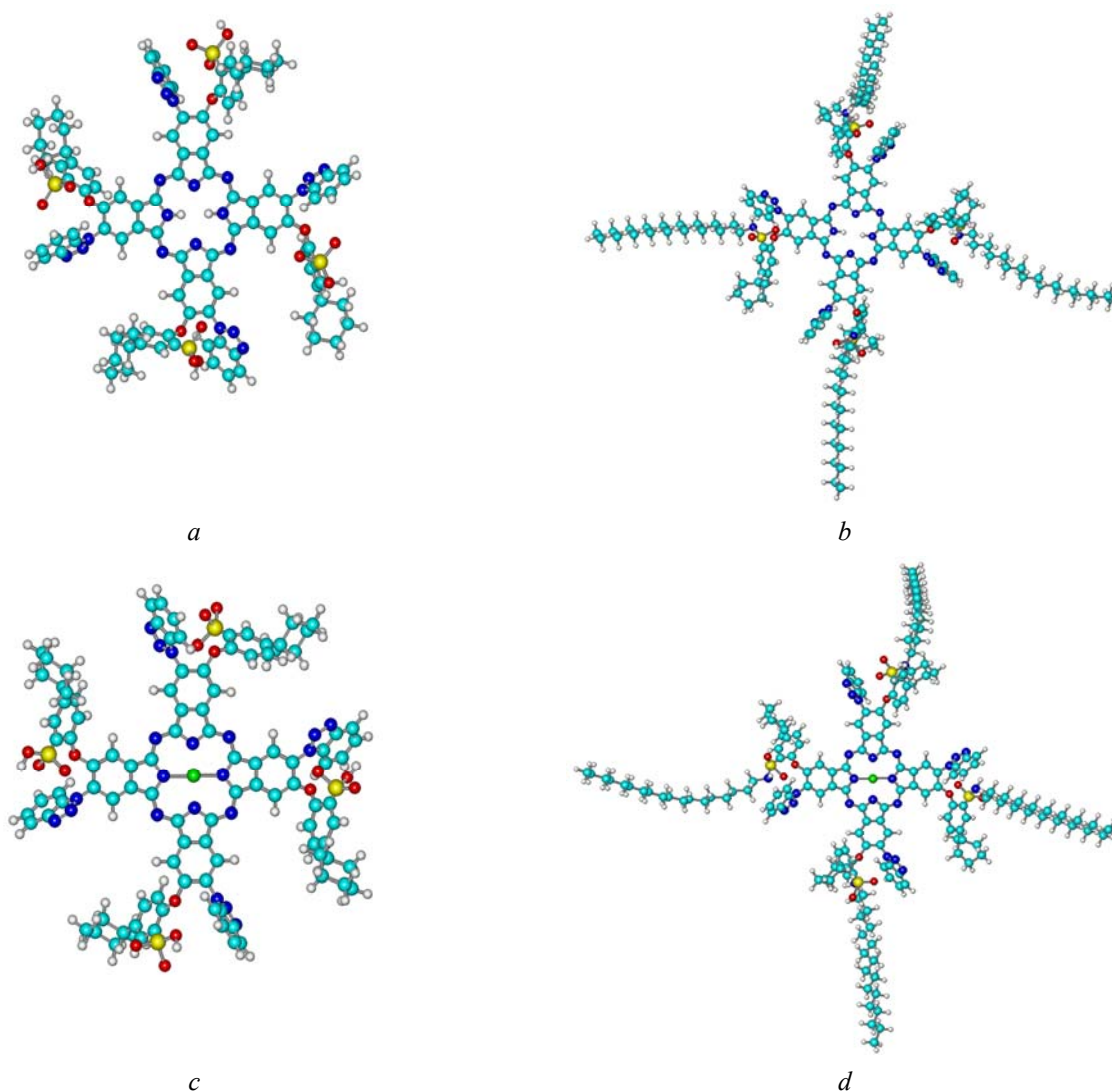


Fig. 7. Samples of optimized models of molecule of compounds **1a** (a), **2a** (b), **1b** (c) and **2b** (d)

Table 5. Calculated molecular parameters (*MP*) and the prognosis data for phthalocyanines **1a,b** and **2a,b**

Compound	E_{opt} kCal/mol	Molecular parameter (<i>MP</i>)						<i>P</i>	<i>E</i>
		M_m	M_r	K_p	K	K_c	K_{ar}		
1a	246.79	0.40	0.20	0.69	1.73 [∘]	1.17	0.27	–	–
1b	283.16	0.44	0.22	0.69	1.73 [∘]	1.17	0.27	–	–
2a	361.60	0.23	0.12 [*]	0.24	1.45 [∘]	1.16	0.12	–	–
2b	386.17	0.26	0.13 [*]	0.24	1.37 [∘]	1.16	0.13	–	–

E_{opt} – optimization energy, $K_s = 0.50$ for all compounds, *P* – prognosis of mesomorphism typical for *DM*; *E* – result of experiment.
^{*} – *MP* values closed to the boundary of the classification series {1}. [∘] – *MP* values deviated significantly from the classification series {1}. Description of *MPs* – see in the text

The data on mesomorphism prognosis characteristic for *DM* showed that liquid crystalline properties for the synthesized compounds should not be expected (Table 5). In general, the negative prognosis is given for one of *MPs*, namely the *K* parameter, which characterizes the flatness of the molecule, i.e. the ratio of the maximum length of the molecule to its thickness. Since the molecules, according to the simulation data, are quite flat, they are located close to each other, thus creating the conditions for effective interaction between their π -systems. At the same time, in order to achieve a “crystal – mesophase” phase transition the system requires more energy, i.e. transition temperature to liquid crystal state is higher than the melting point of the compound. The enhancement of intermolecular interactions at introduction of sulfo groups can explain the decrease in solubility of compounds **1a,b** in DMF, in comparison with the “parent” compounds **4a,b**.

For octadecylsulfamoyl derivatives **2a,b** the molecular parameter *K* as well as the molecular parameter M_r (M_r takes into account the number of substituents on the periphery) locate beyond the boundaries of the classification series {1}. The value of M_r is less than its lower boundary value in the classification series {1} (Table 5). This indicates the presence of free volume excess in the intermolecular space around molecules that impairs the microsegregation (i.e. it prevents molecules to self-organise and form supramolecular ensembles, which are mesophase structural units).

Conclusions

New sulfo and alkylsulfamoyl derivatives of phthalocyanine combining at the periphery 1-benzo-

triazolyl and cyclohexylphenoxy groups were synthesized. Elemental analysis proved that the studied phthalocyanines contain 4 sulfo or alkylsulfamoyl fragments. ¹H NMR spectroscopy revealed that the substitution by sulfo groups occurs in the *ortho*-position to the oxygen bridge of the phenoxy-substituent. The effect of introduction of sulfo- and octadecylsulfamoyl groups into aryloxy substituents on the location of long-wave absorption bands of the synthesized compounds in concentrated sulfuric acid was found. The effect is expressed in hypsochromic shift of absorption bands in comparison with the starting compounds. It was established that the introduction of sulfo groups into bi-functionally substituted phthalocyanine molecules with 1-benzotriazolyl and cyclohexylphenyl fragments leads to a decrease of the solubility of the synthesised compounds, decrease of the maximum temperature of the mass loss and the inability of the compounds to form a mesophase. All mentioned above can be explained by strengthening of intermolecular interactions between central parts of the molecules. The introduction of octadecylsulfamoyl substituents also contributes to the absence of mesomorphism, which, in our opinion, can be connected with sterical hindrance of liquid crystalline molecular packing.

The performed work for the first time revealed that introduction of bulky sulfo or alkylsulfamoyl fragments into *ortho*-position with respect to the oxygen atom of aryloxy group excludes manifestation of liquid crystalline properties. While substitution by the same fragments in *para*-position leads to formation of mesophase. It was shown that the presence of donor and acceptor fragments in mix-substituted phthalocyanines is important [4] but not determining factor for mesophase formation of disc-like molecules.

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