Supramolecular Regioselectivity of meso–Phenylporphyrin Sulfonation. Synthesis of 5,10,15–Tris(4′–sulfophenyl)porphine

Vladimir B. Sheinin, a,Dmitriy A. Ivanov, a and Oscar I. Koifman a,b

Dedicated to Academician Aslan Yusupovich Tsivadze on the occasion of his Birthday

aG.A. Krestov Institute of Solution Chemistry of Russian Academy of Sciences, 153045 Ivanovo, Russia
bIvanovo State University of Chemistry and Technology, 153000 Ivanovo, Russia
@Corresponding author E-mail: vbs@isc-ras.ru

The results of the prognostic computer synthesis of meso-phenylporphyrins H4P2+(Ph)n sulfo derivatives, which demonstrate the supramolecular nature of the porphyrins sulfonation regioselectivity in concentrated sulfuric acid and oleum, are presented. By means of DFT calculation it has been shown that regioselectivity of meso-phenylporphyrins sulfonation is due to host-guest complex formation of the diprotonated porphyrin platform with two hydrosulfate anions, [H4P2+(Ph)n(HSO4)2]. The guest anions control the reactivity of H4P2+(Ph)n. First, they activate H4P2+(Ph)n for electrophilic substitution by partial negative charge transfer to the diprotonated porphyrin. Second, the guest anions are the cause of a total charges redistribution on the carbon atoms of H4P2+ and the phenyl rings, thereby providing the regioselectivity of H4P2+(Ph)n sulfonation. The data from prognostic stage calculations and method of organic synthesis were used to obtain the new 5,10,15-tris(4′-sulfophenyl)porphine. The obtained results are comprehensive and applicable to other S E Ar reactions of porphyrins.

Keywords: meso-Phenylporphyrins, protonation, host-guest complexes, electrophilic substitution, supramolecular regioselectivity, sulfonation, sulfophenyl porphyrins.

Супрамолекулярная региоселективность сульфирования мезо–фенилпорфиринов. Синтез 5,10,15–трис(4′–сульфофенил) порфина

В. Б. Шейнин а,D. А. Иванов а, О. И. Койфман а,b

а Институт химии растворов им. Г.А. Крестова РАН, 153045 Иваново, Россия
б Ивановский государственный химико-технологический университет, 153000 Иваново, Россия
@ E-mail: vbs@isc-ras.ru

Приведены результаты прогностического компьютерного синтеза сульфопроизводных мезо-фенилпорфиринов H4P2+(Ph)n, которые демонстрируют супрамолекулярную природу региоселективности сульфирования порфиринов в концентрированной серной кислоте и в олеуме. Методом DFT показано, что региоселективность сульфирования мезо-фенилпорфиринов обусловлена образованием комплексов [H4P2+(Ph)n(HSO4)2] типа «хозяин-гость» дипротонированной порфириновой платформы с двумя гидросульфатными анионами. Анионы-«гости» контролируют реакционную способность H4P2+(Ph)n. Во-первых, они активируют H4P2+(Ph)n к электрофильному замещению путем частичного переноса отрицательного заряда на дипротонированный порфирин. Во-вторых, анионы-«гости» являются причиной тотального перераспределения зарядов на атомах углерода H4P2+ и фенильных колец, обеспечивая тем самым региоселективность сульфирования H4P2+(Ph)n. Прогностический этап и органический синтез были использованы для получения нового 5,10,15-трис(4′-сульфофенил)порфина. Полученные результаты имеют общий характер и могут быть распространены на другие S E Ar реакции порфиринов.

Ключевые слова: мезо-Фенилпорфирин, протонирование, комплексы «хозяин-гость», электрофильное замещение, супрамолекулярная региоселективность, сульфирование, сульфофенилпорфирин.
**Introduction**

Sulfonated derivatives of \( \text{meso-phenylporphyrins} \) generally are obtained by direct sulfonation in concentrated sulfuric acid (CSA), using the original Menotti procedure for \( 5,10,15,20 \)-tetraphenylporphyrin (\( \text{H}_2\text{P(Ph)}_4 \))\(^{[1]} \) or its variations. The only sulfonated derivatives currently described are these of \( 5,15 \)-diphenylporphyrins (\( \text{H}_2\text{P(Ph)}_2 \)) and \( \text{H}_2\text{P(Ph)}_4 \)^\(^{[2-10]} \).

![Figure 1. Nucleophilic centers in \( \text{H}_2\text{P(Ph)}_4 \) and \( \text{H}_2\text{P(Ph)}_2 \) molecules.](image)

There are a total of 28 nucleophilic centers (NCs) in the molecule of \( \text{H}_2\text{P(Ph)}_4 \), considering the porphyrin platform as well as all phenyl rings (Figure 1). However, when \( \text{H}_2\text{P(Ph)}_2 \) reacts with CSA, only 4'-sulfophenyl-derivatives are formed (Figure 2).

The fractional yields of \( \text{H}_2\text{P(Ph)}_4 \) 4'-sulfophenyl-derivatives depend on the reaction conditions (Table S1). It should be noted that no yield optimizations have been reported in the literature. The use of CSA allows to introduce only four sulfo groups into \( \text{H}_2\text{P(Ph)}_4 \). The product of its exhaustive sulfonation with CSA – 5,10,15,20-tetrakis(4'-sulphophenyl)porphine (\( \text{H}_2\text{P(PhSO}_3\text{H)}_4 \)) is the major product at 100 °C if the reaction time does not exceed 4 h. Lower temperatures and/or shorter reaction times result in greater fractional yields of lower sulfonated derivatives. Further sulfonation of \( \text{H}_2\text{P(PhSO}_3\text{H)}_4 \) is possible only in oleum. Treatment of \( \text{H}_2\text{P(Ph)}_4 \) with fuming sulfuric acid (2 h at ambient temperature) results in cross-linking of the adjacent respective 2 and 2'-positions of the porphyrin platform and a phenyl ring and affords a sulfone compound (Figure 2).\(^{[9]} \)

![Figure 2. Products of \( \text{H}_2\text{P(Ph)}_4 \) sulfonation in concentrated sulfuric acid and of \( \text{H}_2\text{P(PhSO}_3\text{H)}_4 \) sulfonation in oleum (sulfone).](image)
prognostic stage and organic synthesis were used to obtain a novel 5,10,15-tris(4’-sulfophenyl)porphine.

**Experimental**

All solvents and other chemicals were obtained from commercial sources and used as received without further purification. 5,10,15-triphenylporphine and 5,10,15,20-tetraphenylporphine were purchased from PorphyChem. A fiber-optic spectrofluorimeter Avantes AvaSpec-2048-2 was used to obtain spectral data. A Bruker Avance III 500 instrument was used for 1H NMR spectra (500.17 MHz operating frequency for 1H at 294 K). Mass spectra were obtained on a MALDI-TOF Shimadzu Biotech AXIMA Confidence mass-spectrometer. Geometry optimization was performed at the B3LYP/3-21G(d,p) level of density functional theory using Gaussian software package.[11]

5,10,15-Tris(4-sulfophenyl)porphine triple ammonium salt. A mixture of 100 mg (1.86·10⁻⁴ mol) H₃P(Ph)₃ and 3 mL concentrated sulfuric acid was sealed in a glass tube and subjected to sonication for 1.5 h at 50 °C. The tube was then heated in a boiling water bath for 6 h. The contents of the tube was cooled, poured onto ice and neutralized with concentrated aqueous ammonia. The obtained solution was evaporated to dryness on a water bath. Anhydrous ammonia salt H₂P(PhSO₃NH₄)₃ was obtained as the only product with a 69 % (127.3 mg) yield. 1H NMR (500 MHz, [D₆]DMSO) δ ppm: 10.60 (s, 1H, 20-H); 9.65 (d, 2H, 3_J=4.6 Hz, 2,18-H); 9.01 (d, 2H, 3_J=4.6 Hz, 3,17-H); 8.89 (m, 7,8,12,13-H); 8.22 (m, 6H, 2′,6′-H); 8.05 (m, 6H, 3′,5′-H); -3.16 (br.s, 2H, 21,23-H). MS (MALDI-TOF, MeOH), C₃₈H₂₆N₄O₉S₃ (H₂P(PhSO₃H)₃): calculated m/z 778.82; found 778.95

The Supporting Information is available free of charge on the www.macroheterocycles.isuct.ru website at DOI 10.6060/mhc170833s.

**Results and Discussion**

**DFT study of meso-phenylporphyrin sulfonation regioselectivity in sulfuric acid**

Reaction regioselectivity and pathways of meso-phenylporphyrin sulfonation were analysed using DFT/B3LYP/3-21G(d,p) theory level calculated charges of NCs (kinetic control) and total formation energies of sulfonated derivatives E₁ (thermodynamic control), based on four postulates:

1. The driving force of meso-phenylporphyrins dissolution in sulphuric acid is the formation of supramolecular complexes of doubly protonated porphyrinic platform H₄P₂⁺ which is an anion receptor[12-15] with two hydrosulfate anions (1).

$$\text{H}_2\text{P(Ph)}_{2+} + 2\text{H}_2\text{SO}_4 \rightarrow \left[\text{H}_4\text{P}^{2+}(\text{Ph})_2\right]\left(\text{HSO}_4^-\right)_2$$

(1)

2. Porphyrinic sulfoacids are non-electrolytes in CSA.[16]

3. Sulfonation of meso-phenylporphyrins in CSA proceeds via the S_EAr mechanism and is reversible due to acidic hydrolysis of the formed sulfoacids with residual water (2). The yields of sulfonation products are determined by the charges of nucleophilic centers (δ₁- and δ₂-) and the relative thermodynamic stability (ΔE₁) of competing isomers. If the reaction is carried out in oleum, it is irreversible.

$$\text{H}_2\text{P(Ph)}_{2\text{sol}} + 2\text{H}_2\text{SO}_4 \rightarrow \left[\text{H}_4\text{P}^{2+}(\text{Ph})_2\right]\left(\text{HSO}_4^-\right)_2$$

(2)

4. When CSA is used as the reaction medium, NCs with δ₀< −0.108 are active. This value corresponds to the maximal charge of NC in nitrobenzene, which does
not react with CSA. Nucleophilic centers with $\delta_1 \leq -0.108$ undergo sulfonation in oleum.

**Regioselectivity of 5,10,15,20-tetraphenylporphine sulfonation**

We initially performed regioselectivity DFT modeling for $H_P(Ph)_4$, which has the simplest molecular structure with no NCs in meso-positions of the porphyrinic platform (Figure 4).

The process of $H_P(Ph)_4$ dissolution in CSA (1) can be divided into two steps: double protonation of the porphyrin platform with the formation of an $H_2P_2^+(Ph)_4$ anionic receptor, followed by the formation of dihydrosulfate host-guest complex (3).

$$H_2P(Ph)_4 + 2H_2SO_4 \rightleftharpoons H_2P_2^+(Ph)_4 + 2HSO_4^- \rightleftharpoons \left[ H_2P_2^+(Ph)_4 \right] (HSO_4^-)_2$$

(3)

The starting molecule of $H_2P(Ph)_4$ has active NCs in 7, 8, 17, 18 positions of the main conjugation circuit of $H_2P$ and in 4' positions of the phenyl rings. Double protonation of $H_2P(Ph)_4$ leads $H_2P_2^+(Ph)_4$ to be completely inert in CSA due to a dramatic fall of $\delta_1$ charges on all NCs of the formed dication. Diprotonated $H_2P_2^+$ platform is an elastic 1,3-alternate with two pairs of opposite NH groups that are hydrogen bond donors. This, together with a circuit-delocalized positive charge, leading to the formation of twin bidentate coordination sites, pre-organized for a synergetic hydrogen and electrostatic bonding with contacting atoms of guest anions. An axial complex of the "double roost" type is formed as the result. The $H_2P_2^+(Ph)_4$ receptor possesses high complementarity towards the contacting atoms of $HSO_4^-$ anions. The mean value of hydrogen bond angles in $\left[ H_2P_2^+(Ph)_4 \right] (HSO_4^-)_2$ complex is $174.3^\circ$, which is close to the ideal value of $180^\circ$. Guest anions exhibit a strong and determining influence on the reactivity of $H_2P_2^+(Ph)_4$. First, they activate $H_2P_2^+(Ph)_4$ for electrophilic substitution by transferring a total of $-0.733$ unit charge to the macrocycle. The $\delta_1$ charges of NCs in 4' positions of phenyl rings of $\left[ H_2P_2^+(Ph)_4 \right] (HSO_4^-)_2$ are $-0.111$, that is equal to the value for benzene, which easily undergoes sulfonation in CSA even at 40 °C with a 90 % yield. Second, guest anions cause a total charge redistribution on carbon atoms of $H_2P_2^+$ which provides supramolecular-driven regioselectivity of sulfonation of $H_2P_2^+(Ph)_4$ in its dihydrosulfate complex. Meanwhile, positions 4' remain the only active NCs of the complexes during all stages of sulfonation in CSA, which is in complete accord with experimental data (Figure 5, Table P1).

All the formed 4'-sulfoacids $H_2P_2^+(Ph)_4$ afford dihydrosulfate complexes, which can exist in different isomeric forms with different positions of the two guest anions, namely AB, BC, CD, and AD types. The letter notation shows near which pyrrole rings the guest anions are localized (Figure 4). The isomeric complexes have different thermodynamic stability (Figure P1). Only the most stable isomers are shown.

![Figure 4](image-url)
in Figure 5, as intramolecular rearrangements of the isomers occur more rapidly than intermolecular sulfonation reaction steps. All 4'-position NCs are equal and independent until $\text{H}_2\text{P}(\text{Ph})_4$ is formed. The most stable isomer AB $\text{H}_2\text{P}(\text{PhSO}_3\text{H})_3(\text{Ph})(\text{HSO}_4^-)_2$ does not react with CSA, because it contains no NCs with $\delta_1 > -0.108$. In order to perform further sulfonation, an energy-demanding AB$\rightarrow$AD rearrangement is required. Moreover, the $\delta_1$ value of the active phenyl ring’s NC is lowered to $-0.110$. In practice, the above data should manifest in a quick build-up of AB isomer followed by its slow sulfonation into $\text{H}_2\text{P}(\text{PhSO}_3\text{H})_4(\text{Ph})(\text{HSO}_4^-)_2$. A paper by J. Winkelman et al. describes a slowdown effect for the step of $\text{H}_2\text{P}(\text{PhSO}_3\text{H})_3(\text{Ph})(\text{HSO}_4^-)_2$ formation. The authors subjected $\text{H}_2\text{P}(\text{Ph})_4$ to sulfonation is CSA at ambient temperature for 36 h and obtained a mixture.
of di-, tri-, and tetrasulfoacids with the respective yields of 19.6 %, 76.0 %, and 3.9 %. When we performed sulfonation of \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{H})_2 \) in CSA at 100 °C (using the procedure of C.A. Busby et al.\[5\]) we confirmed our DFT calculations data (Figure 6). Under such conditions, a mixture of mono- and disulfonated products is already formed after a 5 min heating of the reaction mixture (preliminary thoroughly ground in a mortar). After a 15 min period, most of the porphyrin was converted into the tri-sulfocacid, which then undergoes a relatively slow conversion into the final tetrasulfoacid. The tri-acid \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{H})_2 \) (Ph) was isolated with a 60 % yield when the reaction was interrupted after a 15 min period. The result is in accord with the mathematical model of \( \text{H}_2 \text{P}(\text{Ph})_2 \) sulfonation, the kinetic constants ratio is 1:(0.06:0.00014).

Sulfonation of meso-phenylporphyrins in CSA is reversible due to acidic hydrolysis of the formed sulfocacids (3), which leads to lowered yields.\[10\] The values of \( \delta_\gamma \) charges for all 4'-sulfoderivatives of \([\text{H}_2 \text{P}^{\text{P}}(\text{Ph})_2](\text{HSO}_4)_2\) and \([\text{H}_2 \text{P}^{\text{P}}(\text{Ph})_3](\text{HSO}_4)_2\) are in the range of \(-0.390 \div -0.393\), which is almost equal to the value of \(-0.393\) for benzenesulfoacid. Such \( \delta_\gamma \) values correspond to low hydrolysis rates, thus, the fractional yields of the products of exhaustive sulfonation of \( \text{H}_2 \text{P}(\text{Ph})_2 \) and \( \text{H}_2 \text{P}(\text{Ph})_3 \) in CSA are always the highest (Table P1). The experimental data shown in Figure 5 also demonstrate that sulfonation steps should be the same for \( \text{H}_2 \text{P}(\text{Ph})_2 \) in sulfuric acid and in oleum, until \([\text{H}_2 \text{P}^{\text{P}}(\text{PhSO}_3 \text{H})_2](\text{HSO}_4)_2\) is formed, which can be subjected to further sulfonation with oleum into a sulfone.\[9\]

**Using DFT calculations to predict the results of 5,10,15-triphenylporphine sulfonation**

The prognostic scheme of \( \text{H}_2 \text{P}(\text{Ph})_2 \), dissolution and sulfonation in CSA, including the calculated data, is shown in Figure 7.

A distinctive parameter of \( \text{H}_2 \text{P}(\text{Ph})_2 \) is a relatively high \( \delta_-\) charge (\(-0.150\)) on C-20 atom, which is significantly higher than the charges of other NCs of this molecule and \( \text{H}_2 \text{P}(\text{Ph})_3 \). The charge value for C-20 remains elevated on all steps of dissolution and sulfonation of \( \text{H}_2 \text{P}(\text{Ph})_2 \). The dihydrosulfocacid complex \([\text{H}_2 \text{P}^{\text{P}}(\text{Ph})_2](\text{HSO}_4)_2\), which is formed as the result of dissolution of \( \text{H}_2 \text{P}(\text{Ph})_2 \), in sulfonic acid, has three isomers: AB, BC, and AD (Figure P2). The most stable isomer BC exhibits a transfer of \(-0.742\) charge from guest anions onto the macrocycle and an averaged \( > \text{N}-\text{H} \cdots \text{O-SO}_3\text{H} \) hydrogen bond angle of 173.6°. The guest anions direct the electrophilic attack to position 20 of the porphyrin platform and positions 4’ of the phenyl rings on all steps of \([\text{H}_2 \text{P}^{\text{P}}(\text{Ph})_2](\text{HSO}_4)_2\) sulfonation. These competing NCs have different reactivity, which is determined by a combination of kinetic activity parameters (\( \delta_- \), \( \delta_- \)) and relative thermodynamic stability of the isomeric sulfocacids (\( \Delta \delta \)). Position 20 has significantly higher values of \( \delta_- (\sim 0.132 \div 0.135) \) and \( \delta_- (\sim 0.492 \div 0.474) \) compared to the corresponding values of positions 4’: \( \delta_- (-0.101 \div -0.111) \) and \( \delta_- (-0.392 \div 0.393) \). Thus, position 20 exhibits greater kinetic activity in both the direct sulfonation reaction and the reverse acidic hydrolysis reaction (2). Furthermore, the isomeric 20-sulfocacids possess lower thermodynamic stability compared to the 4’-sulfocacids. At substantially high hydrolysis rates of 20-sulfocacids, the corresponding 4’-sulfocacids should be the major products of \( \text{H}_2 \text{P}(\text{Ph})_2 \) sulfonation in CSA. Analysis of the calculated data shows that \( \delta_- \), \( \delta_- \), and \( \Delta \delta \) parameters of these two competing NCs depend on the number of meso-phenyl substituents connected to the porphyrinic platform. Therefore, sulfonation of positions 20 and 4’ in \([\text{H}_2 \text{P}^{\text{P}}(\text{Ph})_3](\text{HSO}_4)_2\) should proceed in CSA and oleum in a similar way it does for \([\text{H}_2 \text{P}^{\text{P}}(\text{Ph})_2](\text{HSO}_4)_2\) and \([\text{H}_2 \text{P}^{\text{P}}(\text{Ph})_3](\text{HSO}_4)_2\). High hydrolysis rates of porphyrinic meso-sulfocacids were reported by H. Garcia-Ortega and J.M. Ribo,\[10\] the authors demonstrated that vacant meso-positions in \( \text{H}_2 \text{P}(\text{Ph})_2 \), indeed undergo sulfonation only in oleum, while in CSA only 4’-sulfocacids are formed. We conclude that for \( \delta_- \approx -0.474 \) hydrolysis completely suppresses sulfonation of vacant meso-positions in phenylporphyrins and the final product, if the reaction of \( \text{H}_2 \text{P}(\text{Ph})_2 \), is carried out in CSA is only \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{H})_2 \). If oleum is used as the reaction medium, only direct sulfonation reaction dominates, which leads to a very rapid sulfonation of position 20 of the porphyrinic platform followed by a subsequent sulfonation of 4’ positions of three phenyl rings.

The prognostic capabilities of scheme shown in Figure 7 was demonstrated in this work by a synthesis of a novel watersoluble 5,10,15-tris(4-sulfophenyl)porphine, which was isolated as the only product of \( \text{H}_2 \text{P}(\text{Ph})_2 \) sulfonation in CSA.

**Synthesis of 5,10,15-tris(4-sulfophenyl)porphine triple ammonium salt**

A modified procedure of C.A. Busby et al.\[5\] was used to carry out sulfonation, purification and isolation of \( \text{H}_2 \text{P}(\text{Ph})_2 \) (see Experimental). was obtained as the only product with a 69 % (127.3 mg) yield. \( ^1\text{H} \) NMR spectrum of the sulfonated product is presented in Figure 8. In [D6]DMSO, which is a polar and basic solvent (\( \varepsilon=46.68 \); \( \text{DN}_{\text{H}_{2}\text{O}}=29.8 \)), the ammonium salt of porphyrin sulfocacid dissociates with the formation of \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{N})_3 \) trianion, which is not prone to aggregation in concentrated solutions used for NMR studies. This was further proved by recording an electronic absorption spectrum of a thin film of the solution on the inner surface of the NMR tube and a spectrum of the same solution diluted to about 10^4 M (Figure P3).

MS spectrum of \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{H})_2 \) is shown in Figure 9. Under spectrum registration conditions the salt \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{N})_3 \) loses ammonia and transforms into tri sulfonic acid \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{H})_3 \) with corresponding signal of main product. Two supplementary signals (m/z: 800.96 and 816.88) correspond to impurities of monosodium (+22.01) and monopotassium (+37.93) salts, which were obtained as a result of \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{H})_3 \) interaction with glass vessel.

**Optical spectroscopy**

A \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{N})_3 \) trianion is formed when \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{N})_3 \) is dissolved in water. The absorption and fluorescence spectra of an aqueous pH-neutral solution of \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{N})_3 \), are shown with key parameters in Figure 10. Aqueous solutions of \( \text{H}_2 \text{P}(\text{PhSO}_3 \text{N})_3 \), diluted to about 10^4 M and below, obey the Beer law \( A=\varepsilon c \) with a linearity coefficient not less than 0.999 (Figure 11).
Figure 7. A prognostic scheme of $\text{H}_2\text{P}(\text{Ph})_3$ sulfonation in sulfuric acid and oleum, including the DFT calculated data. Numbers denote the values of $\delta_1$ for the nucleophilic centers of sulfonation. Numbers in brackets denote the values of $\delta_2$ for the nucleophilic centers of acidic hydrolysis.
Supramolecular-directed Sulfonation Selectivity for meso-Phenylporphyrins

Figure 8. $^1$H NMR spectrum of $\text{H}_2\text{P(PhSO}_3\text{)}_3$ solution in [D$_6$]DMSO.

Figure 9. MALDI-TOF spectrum of $\text{H}_2\text{P(PhSO}_3\text{)}_3$ (without using matrix).
Conclusion

Regioselectivity of meso-phenylporphyrin sulfonation is supramolecular-directed. Understanding of the mechanism of this phenomenon allows the use of modern computational chemistry methods to explain the already accumulated experimental material on the synthesis of the corresponding sulfo-derivatives and for the purposeful preparation of 10,15-tris(4'-sulfophenyl)porphine. Since this regioselectivity is due to the properties of the diprotonated porphyrin platform anion complexes, this approach can be extended to other numerous electrophilic substitution reactions of porphyrins in acidic media (for example, nitration in the NaNO₂ – CF₃COOH system).[17]

Acknowledgements. Financial support by Russian Science Foundation (Project No. 14-23-00204-P). We thank the Centre for joint use of scientific equipment “The upper Volga region centre of physico-chemical research”. The authors are grateful to Dr. Viktor V. Aleksandriiskii and Dr. Alexander V. Zavialov for their help.

References

1. Menotti A.R. Doctoral Dissertation. Columbus: The Ohio State University, 1941.
2. Winkelman J., Slater G., Grossman J. Cancer Research 1967, 27(1), 2060–2064.
3. Fleischer E.G., Palmer J.M., Srivastava T.S., Chatterjee A. J. Am. Chem. Soc. 1971, 93, 3162.
4. Srivastava T.S., Tsutsui M. J. Org. Chem. 1973, 38, 2103.
5. Busby C.A., Dinello R.K., Dolphin D. Can. J. Chem. 1975, 53, 1554.
6. Rubires R., Crusats J., El-Hachemi Z., Jaramillo T., López M., Valls E., Farrera J.-A., Ribó J.M. J. Org. Chem. 1999, 85, 198–198.
7. Zhang Y.-H., Chen D.-M., He T., Liu F.-C. Spectrochim. Acta, Part A 2003, 59, 87–101.
8. Escudero C., El-Hachemi Z., Crusats J., Ribó J.M. J. Porphyrins Phthalocyanines 2005, 9, 852–863.
9. Cao Y., Gill A.F., Dixon D.W. Tetrahedron Lett. 2009, 50, 4358–4360.
10. Garcia-Ortega H., Ribó J.M. J. Porphyrins Phthalocyanines 2004, 564–568.
11. Frisch M.J., Trucks G.W., Schlegel H.B. et al., Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.
12. Sheinin V.B., Ratkova E.L., Mamardashvili N.Zh. J. Porphyrins Phthalocyanines 2008, 12, 1211–1219.
13. Sheinin V.B., Shabunin S.A., Bobritskaya E.V., Koifman O.I. Macroheterocycles 2011, 4, 80–84.
14. Sheinin V.B., Shabunin S.A., Bobritskaya E.V., Ageeva T.A., Koifman O.I. Macroheterocycles 2012, 5, 252–259.
15. Sheinin V.B., Bobritskaya E.V., Shabunin S.A., Koifman O.I. Macroheterocycles 2014, 7, 209–217.
16. Waddington Th.C. Non-Aqueous Solvent Systems. London: Academic Press, 1965. 408 p.
17. Kolodina E.A., Sheinin V.B., Semeikin A.S. In: Book of Abstracts of XII Youth Conference on Organic Chemistry, 2009, p. 405 (in Russ.) [Колодина Е.А., Шейнин В.Б., Семейкин А.С. Тез. Докл. XII Молодежн. конф. по органической химии, 2009, с. 405].

Received 26.08.2017
Revised 09.10.2017
Accepted 14.10.2017