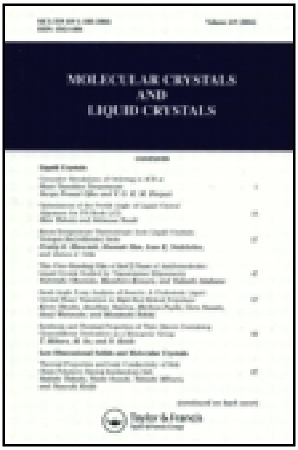

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Synthesis and Induction of Mesomorphic Properties of Tetrabenzoporphine Derivatives

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Synthesis and Induction of Mesomorphic Properties of Tetrabenzoporphine Derivatives

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Zinc complexes of meso-alkyl-substituted tetrabenzoporphines and their aza-derivatives have been synthesized using the interaction of phthalimide or its derivatives with zinc salts of the carboxylic acids. The porphyrin-ligands were obtained on the basis of the above mentioned compounds. The spectral and mesomorphic properties of the synthesized compounds were studied.

Keywords: mesomorphic properties; synthesis; tetrabenzoporphine derivatives

INTRODUCTION

Meso-substituted tetrabenzoporphines present one of the most important groups of synthetic analogs of natural porphyrines. By the present moment *meso*-arylsubstituted tetrabenzoporphyrines are more researched than others. These compounds are offered as dyes [1], photocromic filters [2], materials of photodynamic cancer therapy [3,4] and non-linear optics [5]. However of this the quantity of papers concerning the synthesis of *meso*-alkylsubstituted tetrabenzoporphines is rather restricted, though such compounds can present both theoretical interest and possibility for practical application.

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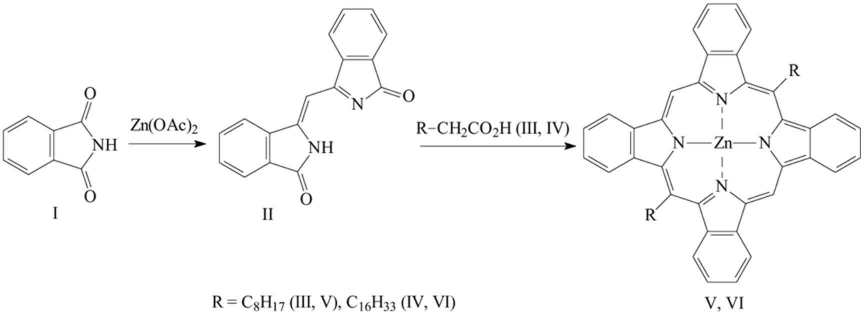


SCHEME 1 Synthesis of *meso*-alkylsubstituted tetrabenzoporphines.

EXPERIMENTAL

The organic soluble *meso*-alkylsubstituted tetrabenzoporphines were synthesized through the interaction of the phthalimide condensation product (**I**) with Zn acetate–3,3′-[1-(1-oxo-1*H*-izoindol-3-il)methylene]-2,3-dihydro-1*H*-izoindol-1-on (**II**), capric (**III**) and stearic (**IV**) acids in the presence of ZnO at 320°C during 30 minutes. In the result the following compounds were obtained respectively: *meso-trans*-dioctyltetrabenzoporphyrinate Zn (**V**) and *meso-trans*-dihexadecyltetrabenzoporphyrinate Zn (**VI**) (Scheme 1).

The isolation of complexes **V** and **VI** from the reaction mixture and their purification were carried out by column chromatography (Al_2O_3), the mixture CCl_4–dioxane (2:1) used as an eluent.

Meso-trans-dioctyltetrabensoporphyrine (**VII**) and *meso-trans*-dihexadecyltetrabensoporphyrine (**VIII**) were obtained by the metal complexes (**V**, **VI**) dissolving in the monohydrate of sulfuric acid during 2 hours at 20°C, and later recrystallization by water. The purification of ligands (**VII**, **VIII**) was carried out by the method of column chromatography.

^1H NMR spectra were obtained with a Bruker AC-200F spectrometer, using $CDCl_3$ as a solvent and TMS as the internal standard. Elemental analyses were carried out using a FlashEA 1112 CHNS-O analyzer. Mass-spectra were recorded with a Varian Saturn 2000R chromato-mass-spectrometer. A Hitachi UV-Vis model 2000 spectrophotometer was used to measure absorption spectra.

SYNTHESIS *MESO*-ALKYLSUBSTITUTED TETRABENZOPORPHINES

3,3-[1-(1-oxo-1H-izoindol-3-il)methylene]-2,3-dihydro-1H-izoindol-1-on (**II**) is synthesized according to the known method [6].

***meso-trans*-Dialkyltetrabenzoporphyrinates Zn** (**V**, **VI**). General techniques.

Mixture of 0.02 mol compound (**II**) and 0.04 mol acid (**III**) or (**IV**) and 0.4 g Zn oxide was heated up to 320°C during 30 minutes. The reaction mixture was cooled, dissolved in CCl_4 and purified by means of column chromatography (Al_2O_3, activity II according to Brockmann) (eluent: CCl_4–dioxane, 2:1), collecting the main green zone.

***meso-trans*-Dioctyltetrabenzoporphyrinate Zn** (**V**). It is obtained using general techniques with acid (**III**). The yield is 0.26 g (34%). The dark green powder is well-soluble in benzene, chlorophorm, CCl_4, and less soluble in hexane and acetone. The UV-Vis spectrum (CCl_4), λ_{max}, nm (lg ε): 403 (4,58), 427 (5,01), 579 (4,05), 626 (4,51). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 11,03 s (2H), 7,75–7,36 m (16H), 2,77 t (4H), 1,36 s (24H), 0,82 t (6H).

Microanalysis: Calcd for $C_{52}H_{52}N_4Zn$: C 78,23; H 6,56; N 7,02. Found: C 78,41; H 7,15; N 6,84.

***meso-trans*-Dihexadecyltetrabenzoporphyrinate Zn** (**VI**). It is obtained using general techniques with acid (**VI**). The yield is 0.23 g (37%). The dark green waxy substance, well-soluble in benzene, chlorophorm, CCl_4, hexane and less soluble in acetone. The UV-Vis spectrum (CCl_4), λ_{max}, nm (lg ε): 402 (4,59), 427 (5,02), 579 (4,03), 626 (4,50). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 11,12 s (2H), 7,77–7,41 m (16H), 2,75 t (4H), 1,33 s (56H), 0,85 t (6H).

Microanalysis: Calcd for $C_{68}H_{84}N_4Zn$: C 79,85; H 8,28; N 5,48. Found: C 80,22; H 8,76; N 5,12.

***meso-trans*-Dialkyltetrabenzoporphyrinates Zn** (**VII**, **VIII**). General technique. 0.1 g of metal complex **VI** or **V** was being dissolved in 10 ml of monohydrate sulfuric acid at 20°C for 2 hours, then the solution was diluted with 30 ml of water. The precipitated product was filtered off, washed by 50 ml of 20% ammonium, 100 ml of water and dried out. The residue was dissolved in CCl_4 and purified by column chromatography on Al_2O_3 activity II according to Brockmann (eluent: CCl_4–dioxane, 2:1), collecting the green zone.

***meso-trans*-Dioctyltetrabenzoporphyrine** (**VII**). It is obtained using general techniques with complex (**IV**). The yield is 0.07 g (78%). The dark green powder is well-soluble in benzene, chlorophorm, CCl_4 and less soluble in hexane and acetone. The UV-Vis spectrum (CCl_4), λ_{max}, nm (lg ε): 418 (4,87), 431 (4,91), 565 (4,14), 601 (4,35), 608 (4,38), 616 (4,35), 663 (4,27). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 11,05 s (2H), 7,76–7,33 m (16H), 2,76 t (4H), 1,32 s (24H), 0,84 t (6H)–2,41 s (2H).

Microanalysis: Calcd for $C_{52}H_{54}N_4$: C 84,97; H 7,40; N 7,62. Found: C 85,22; H 7,35; N 6,70.

***meso-trans*-Dihexadecyltetrabenzoporphyrine** (**VIII**). It is obtained using general techniques with complex (**V**). The yield is 0.06 g (67%). The dark green powder is well-soluble in benzene, chlorophorm, CCl_4, hexane and less soluble in acetone. The UV-Vis spectrum (CCl_4), λ_{max}, nm (lg ε): 419 (4,86), 433 (4,90), 565 (4,15), 603 (4,35), 608 (4,37), 616 (4,35), 663 (4,28). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 11,05 s (2H), 7,78–7,43 m (16H), 2,72 t (4H), 1,30 s (56H), 0,86 t (6H)–2,35 s (2H).

Microanalysis: Calcd for $C_{68}H_{86}N_4$: C 85,13; H 9,03; N 5,84. Found: C 85,20; H 10,12; N 4,62.

SYNTHESIS *MESO*-HEXADECYLSUBSTITUTED TETRABENZOAZAPORPHYRINATES

Complexes *meso*-hexadecylsubstituted tetrabenzoazaporphyrinates Zn (**X–XI**) Mixture of 6 mmol of compound (**IX**), 10 mmol of acid (**IV**) and 10 mmol of ZnO was kept at 280°C for 1 hour, then the reaction mixture was cooled, reduced to fine particles and the excess of carboxylic acid was removed by 10% KOH and water. The residue was dried out in the open air, dissolved in toluol and chromotographed in Al_2O_3 activity II according to Brockmann, eluting with toluol/ acetone mixture (20:1). As a result compounds **X** and **XI** of the green color were obtained.

***meso*-Tri(hexadecyl)tetrabenzomonoazaporphyrinate Zn** (**X**), the yield is 0.40 g (13%). The dark green waxy substance is well-soluble in benzene, chlorophorm, CCl_4, hexane. The IR-spectrum, ν, cm^{-1}: 3058, 2920, 2843, 1662, 1510, 1320, 758. The UV-Vis spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 648 (0,11), 625 (0,33), 575 (0,13), 454 (0,33), 425 (1,00), 402 (0,38). ^1H NMR spectrum (CCl_4), δ, ppm: 7,91–7,08 m (16H), 2,11 s (6H), 1,90 s (6H), 1,38–1,23 m (78H), 0,86 s (9H).

Microanalysis: Calcd for $C_{83}H_{115}N_5Zn$: C 79,87; H 9,29; N 5,61. Found: C 80,05; H 9,30; N 4,71.

***meso-trans*-Di(hexadecyl)tetrabenzodiazaporphyrinate Zn** (**XI**), the yield – 0.18 g (8%). The dark green waxy substance, well-soluble in benzene, toluol, chlorophorm, CCl_4. The IR-spectrum, ν, cm^{-1}: 3061, 2916, 2833, 1665, 1518, 1313, 733. The UV-Vis spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 669 (0,21), 642 (0,23), 626 (0,38), 579 (0,17), 458 (0,37), 426 (1,00), 402 (0,56). ^1H NMR spectrum (CCl_4), δ, ppm: 7,84–7,26 m (16H), 2,21 s (4H), 1,71 s (4H), 1,31–1,23 m (52H), 0,87 s (6H).

Microanalysis: Calcd for $C_{66}H_{82}N_6Zn$: C 77,35; H 8,07; N 8,20. Found: C 78,01; H 8,16; N 7,55.

Metal free *meso*-alkyl substituted tetrabenzoazaporphynes (**XII**, **XIII**). 0.05 g Zn complex (**X**, **XI**) were being dissolved in 10 ml of monohydrate at 20°C during 1 hour and poured out into 50 ml of water. The precipitated product was filtered off, washed by water, 10% ammonium and finally by water (pH ~ 7). The residue was dried out, dissolved in toluol and purified by means of column chromatography (Al_2O_3, activity II according to Brockmann) (toluol–acetone mixture, 20:1).

***meso*-Tri-(hexadecyl)tetrabenzomonoazaporphine** (**XII**), the yield – 0.04 g (85%). The dark green waxy substance, well-soluble in benzene, toluol, chlorophorm, CCl_4. The IR-spectrum, ν, cm^{-1}: 3210, 3028, 2933, 2847, 1661, 1511, 1313, 744. The UV-Vis spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 678 (0,07), 661 (0,23), 611 (0,22), 603 (0,27), 595 (0,28), 562 (0,01), 442 (0,26), 425 (1,00), 409 (0,94), 382 (0,36). ^1H NMR spectrum (CCl_4), δ, ppm: 7,92–7,12 m (16H), 2,10 s (6H), 1,95 s (6H), 1,33–1,22 m (78H), 0,86 s (9H)–1,72 s (2H).

Microanalysis: Calcd for $C_{83}H_{117}N_5$: C 84,14; H 9,95; N 5,91. Found: C 84,33; H 10,02; N 4,97.

***meso-trans*-Di(hexadecyl)tetrabenzodiazaporphyrine** (**XIII**), the yield – 0.03 g (65%). The dark green waxy substance is well-soluble in benzene, toluol, chlorophorm, CCl_4. The IR-spectrum, ν, cm^{-1}: 3212, 3055, 2928, 2844, 1660, 1517, 1334, 754. The UV-Vis spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 664 (0,57), 645 (0,30), 611 (0,27), 603 (0,30), 595 (0,30), 561 (0,17), 424 (0,93), 409 (1,00). ^1H NMR spectrum (CCl_4), δ, ppm: 7,82–7,22 m (16H), 2,33 s (4H), 1,98 s (4H), 1,38–1,29 m (52H), 0,88 s (6H),–2,02 s (2H).

Microanalysis: Calcd for $C_{66}H_{84}N_6$: C 82,45; H 8,81; N 8,74. Found: C 82,05; H 9,14; N 7,87.

The compounds (**V–VIII**), (**X–XIII**) are substances of the green color, well dissoluble in a wide range of organic solvents. Their structure was proved by thin-layer chromatography, elemental analysis, ^1H NMR and UV-Vis spectroscopy.

The ^1H NMR spectrum of the complex (**V**) exhibits signals of two *meso*-protons in the form of a singlet at 11.03 ppm in the weakest field, 16 protons resonance of isoindole fragments in the form of a multiplet is registered in the area of 7.75–7.36 ppm, the signal of 4 protons of two alpha-methylene groups of alkyl substituents was registered as a triplet at 2.77 ppm, the resonance of 6 protons of methyl groups as a triplet was registered at 0.82 ppm [7].

The ^1H NMR spectra of ligands (**VII** and **VIII**) are similar to the spectra of Zn complexes (**V** and **VI**) and differ by the presence of the signals in the stronger field, which correspond to the proton resonance within cyclic imine groups. For compound **XI** this signal in the form of

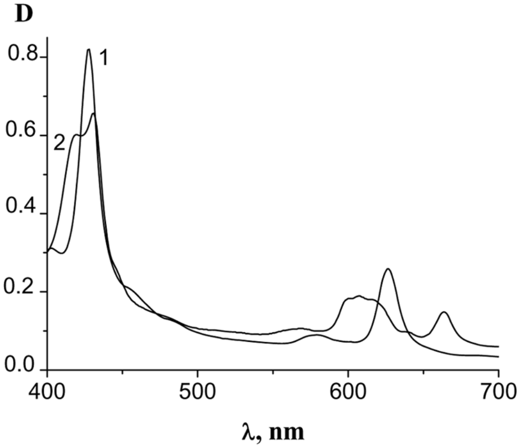


FIGURE 1 Absorption electronic spectra in CCl_4: 1 – compound **V**, 2 – compound **VII**, $C = 10^{-5}$ mol/l.

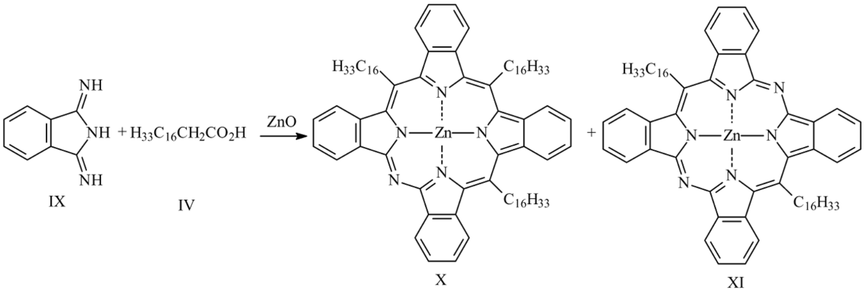
a singlet is found at 2.41 ppm, and in case of the ligand (**XII**) the signal is slightly shifted to the weak field up to 2.35 ppm.

The UV-Vis spectra of metal complexes (**V** and **VI**) and ligands (**VII** and **VIII**) (Fig. 1) are similar to the spectra of tetrabenzoporphyrines [8]. They possess two basic absorption bands in the visible spectrum part (bands Q and Soret). The bands position doesn't depend on the alkyl substituents length. For the complexes (**V** and **VI**) Soret band possesses maximum at 427 nm, Q-band at 626 nm, so both bands are located in the same area as in the spectrum of Zn tetrabenzoporphirinate. As for the ligands (**VII** and **VIII**) there is a slight batochromic shift of the absorption bands (5–6 nm) compared to the tetrabenzoporphyrine spectrum.

Aza-derivatives of *meso*-alkyl substituted tetrabenzopophyrines were synthesized with the purpose to determine the influence of nitrogen atoms in *meso*-positions of the tetrabenzoporphyrine macrocycle on the physico-chemical properties of porphyrines.

The synthesis of such compounds is carried out by the interaction of 1,3-diiminoizoindoline (**XI**) with the acid (**IV**) in the presence of Zn oxide at 280°C for 1 hour. As a result a mixture of Zn complexes of *meso*-tri(hexadecyl)tetrabenzomonoazaporphyrine (**X**) and *meso-trans*-di(hexadecyl)tetrabenzodiazapophyrine (**XI**) was obtained according to the following Scheme 2.

Compounds (**X**, **XI**) are evolved out of the reaction mixture by the method of column chromatography. Metal free azaporphyrines (**VII**,



SCHEME 2 Synthesis of *meso*-alkylsubstituted tetrabenzoazaporphyrines.

VIII) were synthesized through their treatment with concentrated sulfuric acid. They were also purified by means of column chromatography.

Meso-hexadecyltetrabenzoazaporphyrines (**X–XIII**) present green waxy substances, well-soluble in a wide range of organic solvents. Their structure is established on the basis of the elemental analysis data, IR-, ^{1}H NMR and absorption spectroscopy.

In the ^{1}H NMR spectrum of Zn complexes of *meso*-tri(hexadecyl)tetrabenzomonoazaporphine (**X**) two basic groups of signals are registered. In the weak field at 7.91–7.08 ppm there is a multiplet corresponding to the resonance of 16 benzene rings protons of isoindole fragments. In the strong field the resonance of mesoalkyl substituents protons is revealed. The singlet at 2.11 ppm corresponds to the

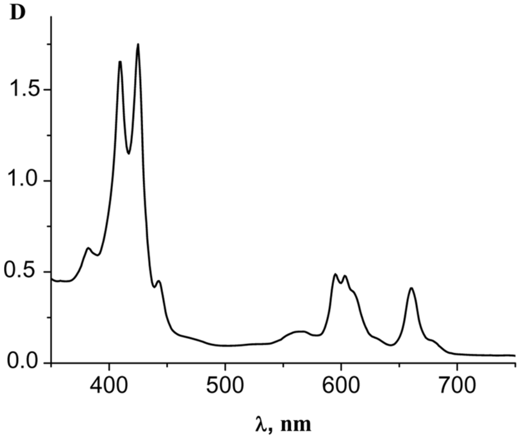


FIGURE 2 Absorption electronic spectra of compound (**XII**) in chlorophorm, $C = 10^{-5}$ mol/l.

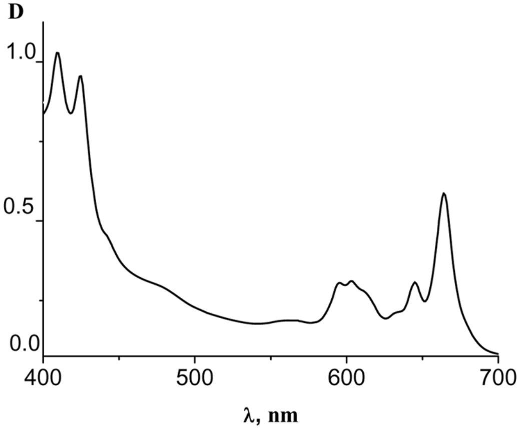
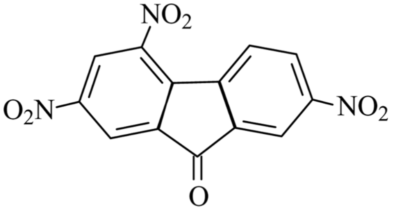


FIGURE 3 Absorption electronic spectra of compound (**XIII**) in chlorophorm, $C = 10^{-5}$ mol/l.

resonance of 6 protons of α-CH_2 groups, the singlet at 1.90 ppm characterizes the resonance of 6 protons of β-CH_2 groups, the multiplet at 1.38–1.23 ppm characterizes the resonance of 78 protons of the remaining methylene groups, and finally the singlet at 0.86 ppm corresponds to the resonance of 9 protons of 3 methyl end groups. The ^1H NMR spectrum of compounds (**XI**) is similar to the spectrum of compound (**X**) in terms of the position and signal character and differs by the increase of the relative intensity of protons signal in the weak field.

The UV-Vis spectrum of compound (**XII**) contains split Q- and Soret bands, characteristic to metal free porphyrines (Fig. 2). Nonsymmetric azasubstitution leads to the complication of the spectrum compared to tetrabenzoporphyrines. In case of the ligand (**XIII**) the increase of the relative intensity of the Q-band is noticed (Fig. 3).



TNF

FIGURE 4 The structure of TNF.

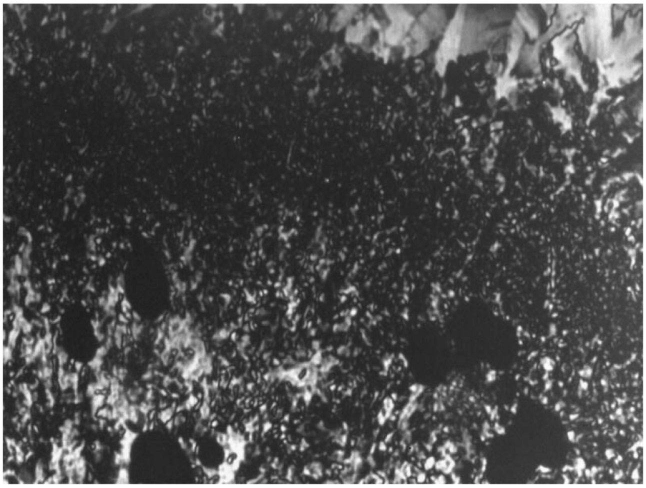


FIGURE 5 Polarizing optical micrograph of compound **VII** with TNF CT-complex on cooling, contact preparation, at 24.0°C, × 250.

Mesomorphic properties were determined using an optical polarizing microscope Leitz Laborlux 12 Pol in conjunction with a hot stage Mettler FP 82. The texture microphotos were taken with a $24 \times 34\,\mathrm{mm}^2$ microscope camera and a Photoautomat Wild MPS51. Lyotropic properties were investigated by means of contact preparations with organic solvents such as toluol, benzene, chloroform and DMF.

RESULTS AND DISCUSSION

The mesomorphic properties of were studied by means of optical polarizing microscopy. It has been shown, that synthesized compounds (**V–VIII**, **X–XIII**) possess neither thermotropic nor lyotropic (in binary systems with organic solvents, such as chloroform, benzene, toluol, DMF, etc.) mesomorphism.

Mesomorphic state can be induced or stabilized through the CT-complexes formation between disc-like molecules and organic electron acceptors, for instance, 2,4,7-trinitro-9-fluorenone (TNF) (Fig. 4) [9].

In this way, mesomorphic state in compounds **VII**, **X** and **XI** with TNF was obtained. The isotropic state of compound **VII** transfers to mesophase on cooling (61.1°C) and vitrifies at 37.2°C, retaining the mesophase texture (Fig. 5). For compounds **X** and **XI** mesophase is formed with TNF also on cooling from the isotropic state at 34.4°C and 44.8°C correspondingly. The mesophase texture in these compounds retains till ambient temperature.

Considering the texture characteristics and disc-like shape of porphine derivatives symmetrically substituted in two positions, the columnar or columnar-lamellar mesophase type of a CT-complex can be supposed.

CONCLUSION

- The synthesis methods were elaborated and 8 new meso-alkylsubstituted tetrabensoporphyrines and their aza-analogues were synthesized.
- The structure of synthesized compounds was confirmed by the data of elemental analysis, NMR-, IR-, electronic and mass-spectroscopy.
- The LC properties of synthesized compounds were investigated by means of thermopolarizing microscopy. It has been established that 8 *meso*-alkylsubstituted tetrabensoporphyrines and their aza-analogues reveal neither thermotropic nor lyotropic mesomorphism (in binary system with organic solvents such as chloroform, benzene, toluol).
- Mesomorphic state was induced in 3 compounds by complex formation with charge-transfer between discogens and organic electrons acceptor of 2,4,7-trinitro-9-fluorenone (TNF).

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