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Synthesis and spectral properties of new substituted diazepinoporphyrazine compounds as optical materials

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Synthesis of new diazepinoporphyrazine containing eight styryl fragments in the periphery of the macrocycle — tetrakis-2,3-{5,7-bis[(E)-2-phenylvinyl]-6H-1,4-diazepino}porphyrazine and its magnesium complex was reported. The composition and structure of the compounds obtained was determined by means of ^{1}H NMR, IR, electronic spectroscopy and elemental analysis. The optical properties of the synthesized compounds were investigated in toluene and DMSO.

Сообщается о синтезе новых диазепинопорфиразинов, содержащих восемь стирильных фрагментов на периферии макроцикла — тетракис-2,3-{5,7-бис[(E)-2-фенилвинил]-6H-1,4-диазепино}порфиразина и его магниевого комплекса. Состав и строение полученных соединений установлены методами ПМР, ИК, электронной спектроскопии и элементным анализом. Исследованы оптические свойства синтезированных соединений в толуоле и ДМСО.

1. Introduction

Macroheterocycle systems such as porphyrins, tetrabenzoporphyrazines and their aza analogues are interesting objects of extensive studies and practical applications in a lot of fields of science and industry for the last years [1]. Porphyrazines with annulated six-membered aromatic rings and with or without metal-atom as the central atom have attracted intent attention of scientists due to their unique physico-chemical properties: catalytic, photoconductive, nonlinear optical and others [1–5].

One area of possible development of new porphyrazine materials is introduction of the various substituents in the periphery of macrocycle. The formation of phthalocyanine-like macrocycles is achieved by replacement of the benzene rings present in phthalocyanine skeleton by heterocyclic rings, for example, annulated diazepine rings [6, 7]. Porphyrazine macrocycles containing annulated diazepine rings are investigated insufficiently [6–8]. Tetrapyrrolic macrocycles with seven-membered heterocyclic rings annulated to the pyrrol rings of the central porphyrazine core, in contrast to phthalocyanines and its aza analogues having planar molecular geometry, are far from entirely planarity [8] that have influence on their electronic and hence physical and chemical properties [6, 8]. Introduction of substituents in the periphery of the macrocycle leads to change spectral, optic and other physical chemical properties too. The nature of the introducing groups affects on the electronic structure of the system [9–11]. In addition, tetrakis-2,3-(5,7-dimethyl-6H-1,4-diazepino)- porphyrazine (Me_8DzPzH_2) and its metal complexes have not been synthesized, at the same time, the presence of two peripheral phenyl groups in the starting monomer leaded to the possibility of tetra-

merisation [9] and tetrakis-2,3-(5,7-diphenyl-6H-1,4-diazepino)porphyrazine (Ph_8DzPzH_2) and its metal complexes have been synthesized [6–8]. It can be explained by the participation of the phenyl groups in the π-conjugation that decreases the energy of the transition state and stabilizes of the macrocycle.

Our investigation is devoted to synthesis of new derivatives of diazepinoporphyrazine containing eight styryl fragments attached to the diazepine rings ($Styr_8DzPzH_2$ and $Styr_8DzPzMg$) and determination of the general physical chemical characteristics of the obtained compounds.

2. Experimental

All reactions were carried out under atmospheric conditions (Fig. 1).

Benzene, 1-propanol, acetic acid, pyridine, dimethylsulfoxide (DMSO) and reagents (2,4-pentandione, diaminomaleonitrile, Mg turnings, benzaldehyde, piperidine and oxalic acid) were obtained commercially and used without further purification (Aldrich, Merck).

IR spectra were recorded on a Specord M-80 spectrometer in KBr pellets. ^{1}H NMR spectra were recorded on a Varian (300 MHz) spectrometer (DMSO-d_6/TMS). The UV-vis absorption spectra were obtained on a Specord M-40 in DMSO and toluene (l = 10 mm).

Synthesis of 5,7-dimethyl-6H-1,4-diazepine-2,3-dicarbonitrile. 0A mixture of diaminomaleonitrile (10 mmol), 2,4-pentandione (10 mmol) and oxalic acid (30 mg) in benzene (50 ml) was refluxed for 3 h in a flask equipped with a Dean-Stark trap to remove generated water. The mixture was cooled to room temperature and benzene was removed in vacuum. The residue was triturated with water and filtered. Then obtained product was crystallized from methanol. Yield: 57 %, mp: 158–159°C; ^{1}H NMR δ ppm ($CDCl_3$) 4.42 (2H, s, CH_2), 2.13 (6H, *d*, $2CH_3$). Anal. calcd. for $C_9H_8N_4$: C-62.78, H-4.68, N-32.54; found C-63.17, H-4.73, N-31.88. IR (cm^{-1}): 2240s (C≡N), 1600s, 1590sh, 1560sh, 1495m, 1440s, 1430sh, 1330m, 1260s, 1225m, 1210m, 1200m, 1135m, 1060m, 1050m, 1025w, 1000m, 980m, 940m, 850m, 755m, 640s.

Synthesis of 5,7-bis[(E)-2-phenylvinyl]-6H-1,4-diazepine-2,3-dicarbonitrile (compound I). A mixture of 2,3-dicyano-5,7-dimethyl-6H-1,4-diazepine (10 mmol), benzaldehyde (20 mmol) and several drops of piperidine in benzene (50 ml) was refluxed for 6 h in a flask equipped with a Dean-Stark trap to remove generated water. The mixture was cooled to room temperature and benzene was evaporated. The precipitate was collected, dried and crystallized from chloroform. Yield: 49 %, mp: 238–239°C; ^{1}H NMR δ ppm (DMSO) 8.12–8.07 (d., 2H, -HC=CH- *trans*), 7.75 (m., 4H, $-C_6H_5$), 7.41 (m., 6H, $-C_6H_5$), 7.15–7.10 (d., 2H, -HC=CH- *trans*), 5.41 (s., 1H, $-CH_2-$), 2,06 (s., 1H, $-CH_2-$). Anal. calcd. for $C_9H_8N_4$: C-79.29, H-4.63, N-16.08; found C-79.03, H-4.73, N-16.18. IR (cm^{-1}): 2230s (C≡N), 1625s, 1600sh, 1580m, 1520s, 1495sh, 1350m, 1315m, 1290m, 1275m, 1240m, 1210–1200d m, 1180s, 1155m, 1140w, 1110m, 1100w, 1075w, 1050sh, 1000s, 985s, 970s,

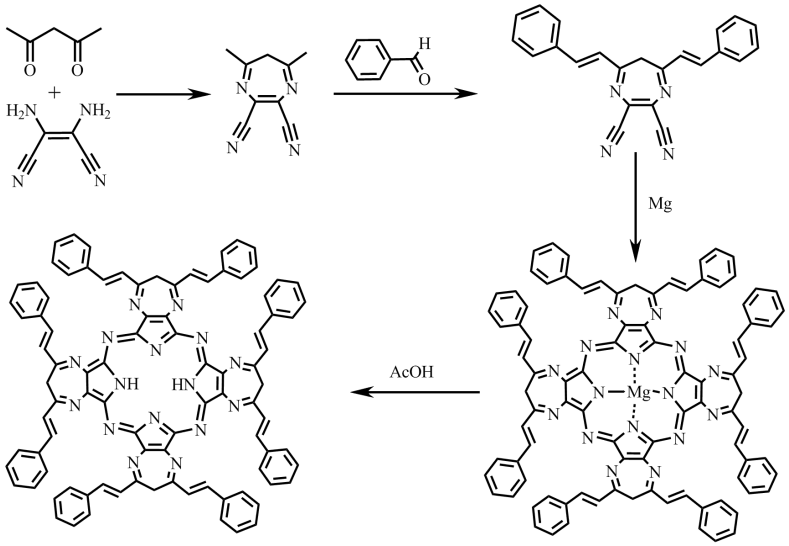

Fig. 1. Scheme of the synthesis of $Styr_8DzPzMg$, and $Styr_8DzPzH_2$.

930w, 890w, 860w, 845w, 750s, 690s, 670w, 645w. UV/Vis (DMSO): λ_{max} = 356 and 434 nm; (toluene): λ_{max} = 355 and 428 nm.

Synthesis of {5,7-bis[(E)-2-phenylethenyl]-6H-1,4-diazepino}porphyrazinatom agnezium (II) (compound II) A suspension of Mg turnings (2.0 mmol), one small crystal of iodine and *n*-propanol (5 ml) was heated at reflux for 8 h. The reaction mixture was then cooled to room temperature, and 2,3-dicyano-5,7-bis[(E)-2-phenylethenyl]-6H-1,4-diazepine (8 mmol) was added in one portion. The reaction mixture was quickly reheated to reflux for 30 min. The reaction mixture was kept at 110°C during 6 h and changing of color from bright yellow to dark green was observed. The mixture was cooled and obtained precipitate was filtered, washed by methanol and water and dried. Yield: 34 %, Anal. calcd. for $C_{92}H_{64}MgN_{16}x10H_2O$: N-14.02, C-69.15, H-5.30; found: N-14.48, C-68.95, H-5.53. Thermogravimetric analysis revealed a featureless loss of ten water molecules for this sample in the temperature range 25–250°C (found 10.91 %, calculated for 10 molecules of H_2O 11.17 %). ^{1}H NMR δ ppm (DMSO) 8.31–8.20 (d., 8H, -HC=CH- *trans*), 7.89 (m., 6H, -C_6H_5-), 7.79 (m., 18H, -C_6H_5), 7.58–7.49 (d., 8H, -HC=CH-*trans*), 7.31 (m., 16H, -C_6H_5), 6.17 (s., 4H, NH), 4.93 (s., 4H, -CH=). IR (cm^{-1}): 3500–3200 ww (H_2O), 1650w, 1625s, 1600w, 1580m, 1520s, 1500w, 1340m, 1320m, 1270m, 1210m, 1175s, 1115s, 1030s, 1000w, 970s, 850w, 780m, 765m, 750s, 690s. UV/Vis (DMSO): λ_{max} = 373 and 692 nm; (toluene): λ_{max} = 373, 664 and 701 nm.

Synthesis of {5,7-bis[(E)-2-phenylethenyl]-6H-1,4-diazepino}porphyrazine (compound III) Solvated magnesium complex I (322 mg, 0.20 mmol) was suspended in 25 % aqua solution of acetic acid (15 ml) and the mixture was refluxed for 8 h. After cooling, the dark green precipitate was filtered and washed abundantly with water and dried under vacuum at 60°C. Yield: 84 %, Anal. calcd. for $C_{92}H_{66}N_{16}x4H_2O$: N-15.27, C-75.29, H-5.08; found: N-15.44, C-74.95, H-5.23. Thermogravimetric analysis revealed a featureless loss of four water molecules for this sample in the temperature range 25–250°C (found 4.80 %, calculated for 4 molecules of H_2O 4.90 %). ^{1}H NMR δ ppm (DMSO) 8.33–8.25 (d., 8H, -HC=CH- *trans*), 7.99 (m., 6H, -C_6H_5), 7.79 (m., 18H, -C_6H_5), 7.58–7.49 (d., 8H, -HC=CH- *trans*), 7.31 (m., 16H, -C_6H_5), 6.88 (s., 2H, -NH), 6.18 (s., 2H, -CH=), 4.91 (s., 2H, -CH). IR (cm^{-1}): 3500–3300 ww (H_2O), 3220m (NH), 1655w, 1620s, 1605w, 1580m, 1520s, 1505w, 1345m, 1320m, 1270m, 1210m, 1175s, 1115s, 1030s, 1000w, 975s, 850w, 780m, 765m, 755s, 690s. UV/Vis (DMSO): λ_{max} = 383, 656 and 696 nm; (toluene): λ_{max} = 381, 659 and 701 nm.

3. Results and discussion

Fluorescent chromophores have been generally known to have a planar and rigid π-conjugation system, for example: stilbene, coumarin, perylene and others. Recently, it was reported about the synthesis of styryldiazepine fluorescent dyes and their spectral properties [12]. Their absorption and fluorescent spectral properties were correlated with their non-planar molecular structure [12]. Although 5,7-bis[(E)-2-phenylvinyl]-6H-1,4-diazepine-2,3-dicarbonitrile was described but the attempts to use it as precursor for the synthesis of porphyrazines has not been made. This precursor was obtained by two step reaction (Fig. 1) of the commercially available diaminomaleonitrile with 2,4-pentandione subsequent condensation of product with benzaldehyde. The template tetramerization of 5,7-bis[(E)-2-phenylvinyl]-6H-1,4-diazepine -2,3-dicarbonitrile (compound I) was carried out in the presence of magnesium propylate and {5,7-bis[(E)-2-phenylethenyl]-6H-1,4-diazepino}porphyrazinatomagnezium (II) complex ($Styr_8DzPzMg$) (compound II) was formed as a hydrated bluish-green solid material (Fig. 1). The introduction of two styryl fragments in position 5, 7 of diazepine ring in the starting monomer leads to the redistribution of the electron density and promotes of the aromatization of the seven-member cycle that increases reactive ability of the nitrile groups and, as a result, the tetramerization reaction takes place.

The Mg complex II can be demetallated to the metal-free macrocycle $Styr_8DzPzH_2$ (compound III) in boiling 25 % aqua solution of acetic acid. The use of glacial acetic acid leads to the formation of the metal-free macrocycle immediately at room temperature. The use of stronger acids such as trifluoroacetic or 96 % sulfuric acids leads to demetallation at first and following by destruction of the macrocycle.

Table. The data of UV-vis spectroscopy of 5,7-bis[(E)-2-phenylvinyl]-6H-1,4-diazepine-2,3-dicarbonitrile, $Styr_8DzPzMg$, and $Styr_8DzPzH_2$

Compound	Solvent	λ, nm (log ε)	
		B-band	*Q*-band
I	DMSO	356 (4.57), 434 (4.13)	–
	toluene	355 (4.68), 428 (4.35)	–
II	DMSO	373 (4.63)	656 (4.18), 692 (4.33)
	toluene	373 (4.60)	664 (4.14), 701 (4.19)
III	DMSO	383 (4.72)	656 (4.50), 696 (4.50)
	toluene	381 (4.80)	659 (4.56), 700 (4.40)

The ^{1}H-NMR spectrum of starting 5,7-bis[(E)-2-phenylvinyl]-6H-1,4-diazepine-2,3-dicarbonitrile shows the presence of two doublets with J = 16.5 and 16.1 Hz, corresponding four protons of two (-HC=CH-) groups in *trans*-configuration of the styryl fragments in the low field region (δ = 8.12–8.07 and 7.15–7.10 ppm); two multiplets of the phenyl protons at δ = 7.75 and 7.41 ppm and two singlets for the $-CH_2-$protons are observed at δ = 5.41 and 2.06 ppm.

The ^{1}H-NMR spectrum of the Mg complex II in DMSO-d_6 contains nonresolved multiplets of the phenyl protons (δ = 7.89; 7.79; 7.31 ppm), doublets of eight (-HC=CH-) group protons (δ = 8.31–8.20; 7.58–7.49 ppm) and two broad signals at 6.17 and 4.93 ppm. The intensity ratio of these signals to the signals of the phenyl protons is 1 : 1 : 10, which allows to assign the signal at 4.93 ppm to the methine -CH= proton and another signal at 6.17 ppm to NH group protons. The NH-groups located close to the aromatic porphyrazine macrocycle should be deshielded by its π-electron ring current and on the other hand this group is joined with π-conjugated styryl fragment. The similar signal positions of the CH and NH group protons were described for tetrakis-2,3-(5,7-diphenyl-6H-1,4-diazepino)porphyrazine [8].

The UV-vis spectra of starting compound I recorded in DMSO and toluene exhibit strong absorption in the ranges 300–450 nm. The UV-vis spectra of the macrocycle compounds II and III recorded in the same solvents show in addition to strong absorption in the ranges 300–450 (Soret region) the band at 650–710 nm (*Q*-band region) (Table, Fig. 2). The UV-vis spectra of compound I have two absorption bands in Soret region in both solvents and no absorption presents in *Q*-band region. At the same time, *Q*-band appears in UV-vis spectra of

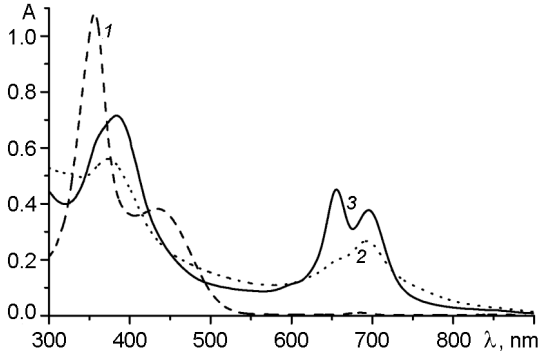

Fig. 2. UV-vis spectra of 5,7-bis[(E)-2-phenylvinyl]-6H-1,4-diazepine-2,3-dicarbonitrile (*1*), $Styr_8DzPzMg$ (*2*) and $Styr_8DzPzH_2$ (*3*) in toluene.

compounds II and III that is evidence of the macrocycle formation and certainly attributes to the allowed HOMO-LUMO intraligand $\pi-\pi^*$ transitions and similar to the usual spectra observed for the class of phthalocyanine species. This implies an overall like electronic distribution and an extensive π-electron delocalization throughout the skeleton of the new diazepinoporphyrazine macrocycle. Presumable, the peripheral diazepine fragment, although not coplanar with the central porphyrazine core, are at least partly involved in some kind of structural and π-electron rearrangement. Moreover, peripheral styryl fragments involve structural and π-electron reorganization too. In the case of Mg complex II *Q*-band is broad both in DMSO and toluene (Fig. 2) that can be explained by molecular association in solution too. The UV-vis spectrum of the metal-free ligand III shows the split *Q*-band (because of its lower symmetry, i.e. D_{2h}) which also can be observed for free-metal phthalocyanines and macrocyclic compounds like to diphthalocyanine systems [13].

Furthermore, the introduction of the styryl substituents in the periphery of diazepinoporphyrazine macrocycle influences considerable on position of *Q*-band in the UV-vis spectroscopy. In the spectra of Ph_8DzPzH_2 and $Ph_8DzPzMg$ *Q*-band is situated at $\lambda_{max} = 639–677$ nm and $\lambda_{max} = 639–680$ nm, respectively [8, 14], whereas, in the spectra of $Styr_8DzPzH_2$ and $Styr_8DzPzMg$ *Q*-band is at $\lambda_{max} = 656–698$ nm and $\lambda_{max} = 656–700$ nm, respectively. So, the bathochromic shift (≈20 nm) of the *Q*-band is observed. It is known that the shift of the *Q*-band in the longer wavelength region is mostly due to the destabilization of the first HOMO or the stabilization of the first LUMO [15]. Therefore, the introduction of the eight styryl substituents in the periphery of diazepinoporphyrazine macrocycle leads to extension of the π-conjugated system taken as a whole that, in one's turn, promotes to the stabilization of the first LUMO.

4. Conclusions

The new diazepinoporphyrazine containing eight styryl fragments in the periphery of macrocycle-tetrakis-2,3-{5,7-bis[(E)-2-phenylvinyl]-6H-1,4-diazepino}porphyrazine ($Styr_8DzPzH_2$) — and its magnesium (II) complex ($Styr_8DzPzMg$) have been synthesised in the first time. The introduction of two styryl fragments in position 5, 7 of diazepine ring in the starting monomer leads to the re-distribution of the electron density that allows to occur the tetramerization reaction. The data of ^1H NMR, IR, UV-vis spectroscopy and elemental analysis have confirmed composition and structure of the synthesized compounds. The introduction of the styryl substituents in the macrocycle leads to the bathochromic shift of the *Q*-band, that can be explained by the stabilisation of the first LUMO.

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Синтез та спектральні властивості нових заміщених діазепінопорфіразинових сполук як оптичних матеріалів

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Повідомляється про синтез нових діазепінопорфіразинів, що містять вісім стирільних фрагментів на периферії макроциклу — тетракіс-2,3-{5,7-біс[(Е)-2-фенілвініл]-6Н-1,4-діазепіно}порфіразину і його магнієвого комплексу. Склад і будову отриманих сполук встановлено методами ПМР, ІЧ, електронної спектроскопії та елементним аналізом. Досліджено оптичні властивості синтезованих сполук в толуолі та ДМСО.