ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 7, pp. 1441–1446. © Pleiades Publishing, Ltd., 2008.
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Phthalocyanines and Related Compounds: XLVI.[1] [4+2]-Cycloaddition of Tetraazaporphine to Dienes of the Cyclopentadiene Series

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Received December 20, 2007

Abstract—The [4+2]-cycloaddition reaction of unsubstituted tetraazaporphine as the dienophile with a series of dienes of the cyclopentadiene series gave novel norbornene-condensed tetraazachlorins, tetraazabacteriochlorins, and tetraazaisobacteriochlorins. It was shown that, depending on the type of the diene, the reagent ratio, reaction time, and temperature mono- or bis-adducts are formed. The compounds obtained were characterized by the elemental analyses, electronic absorption spectra, ^{1}H NMR spectra, and mass spectra.

DOI: 10.1134/S1070363208070281

Tetraazaporphine derivatives hydrogenated by the quasi-isolated double bonds of the pyrrole fragments, such as tetraazachlorins, tetraazabacteriochlorins, and tetraazaisobacteriochlorins strongly absorb in the red and near-IR spectral range. Due to that they present a significant interest as a new class of photosensitizers for photodynamic cancer therapy [2]. Alkyl derivatives of tetraazachlorins were first synthesized in 1958 [3], but detailed studies on their structure and properties were initiated in the past decade.

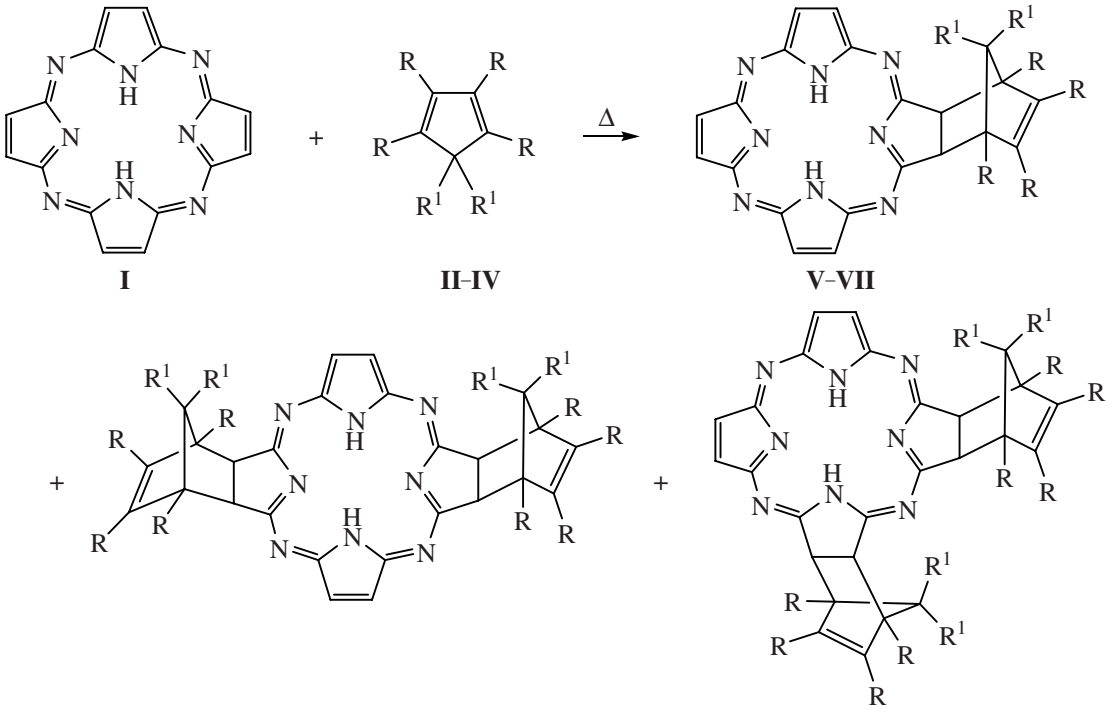
Our laboratory has developed new methods for preparing tetraazachlorins and previously unknown tetraazabacteriochlorins and tetraazaisobacteriochlorins and investigated their spectral, electrochemical, photophysical, and some other properies necessary for practical use of these compounds as new functional materials. One of the methods for preparing of hydrogenated tetraazaporphyns is based on the addition of tetraazaporphines by peripheral double bonds of the macroring. Hence, the [4+2]-cycloaddition reaction of unsubstituted tetraazaporphine with dienes of the anthracene series we prepared dibenzobarrelene-substituted tetraazachlorins and tetraazabacteriochlorins [4, 5] and studied their spectral and luminescent properties [6–11].

In the present work we have studied the Diels–Alder reaction of unsubstituted tetraazaporphine (**I**) as the dienophile with dienes of the cyclopentadiene series, such as cyclopentadiene (**II**), 1,2,3,4,5,5-hexachloro- (**III**), and 1,2,3,4-tetra-chloro-5,5-dimethoxypentadiene (**IV**). Depending on the activity of the diene, reagent molar ratio, and reaction temperature, either monoadducts (norbornene-condensed tetraazachlorins **V–VII**) or bis-adducts with substituents in opposite (norbornene-condensed tetraazabacteriochlorins **VIIIa, VIIIb, IXa**, and **IXb**) or neighboring pyrrole fragments (norbornene-condensed tetraazaisobacteriochlorins **X, XI)** are formed (see scheme).

The reaction progress was followed by the disappearance of the absorption bands at 617 and 542 nm, belonging to compound **I**, in the electronic absorption spectrum of the reaction mixture. The reaction of **I** with cyclopentadiene at a 1:30 molar ratio and 150–155°C for 3 h gives chlorin **V** in 45% yield. With freshly distilled cyclopentadiene **II** and dienophile:diene molar ratio 1:60, the reaction time is 1 h and the yield of chlorin **V** is 65%.

As known, hexachloro-substituted diene **III** exhibits a higher activity in [4+2]-cycloaddition reactions as compared to diene **III** [12]; the same was also observed in our described reaction. The reaction of

[1] For communication XLV, see [1].



I **II–IV** **V–VII**

VIIIa, VIIIb–IXa, IXb **X, XI**

R = R^1 = H (**II, V**); R = R^1 = Cl (**III, VI, VIIIa, VIIIb, X**); R = Cl, R^1 = OMe (**IV, VII, IXa, IXb, XI**).

compound **I** with diene **III** at a 1:10 molar ratio and 130°C for 8 h gave chlorin **VI** in 10.7% yield. A little starting compound **I** was recovered, and a profound destruction of the macroring was observed. When this reaction was carried out with a 30-fold excess of diene **III** in an inert atmosphere for 3 h, absorption bands of starting compound **I** disappeared completely from the electronic absorption spectrum of the reaction mixture, and the yield of chlorin **VI** increased to 47%. Performing the reaction at 220°C decreases the reaction time to 0.5 h, and, together with chlorin **VI** (34%), *cis*- and *trans*- (depending on the mutual location of substituents with respect to the macroring plane) bacteriochlorins **VIIIa** (3.7% yield) and **VIIIb** (3.3%), as well as a small amount of isobacteriochlorin **X** (~0.5%) were also isolated. The formation of only one of the two theoretically possible geometric isomers (evidently, *trans*) in the case of isobacteriochlorin **X** can be explained by a significant steric strain in the *cis* isomer. The formation of bisadducts **VIIIa, VIIIb**, and **X** in this reaction provides evidence showing that compound **III** is a more active diene than **II** which does not form such products at all. Diene **III** is also more active than anthracene involved previously in an analogous reaction. The latter forms bacteriochlorin only under catalysis with $AlCl_3$ [4,5].

According to [13], dimethoxy-substituted diene **IV** is more reactive in Diels–Alder reactions compared to diene **III**. It reacts with various dienophiles under fairly mild conditions. The cycloaddition of diene **IV** in the reaction under study, too, proceeded much easier. Hence, in the reaction of compound **I** with **IV** at a 1:10 molar ratio and 220°C no absorption bands of **I** were observed in the spectrum of the reaction mixture already within 20 min. Along with chlorin **VII** (32.9%), two isomeric bacteriochlorins **IXa** (10%) and **IXb** (17.8%) and a small amount of isobacteriochlorin **XI** were formed.

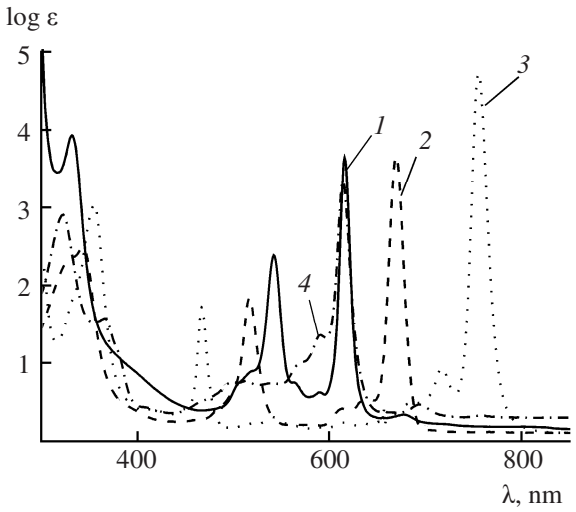
Except for chlorin **V**, the compounds obtained all are readily soluble in usual organic solvents due to the presence of bulky substituents deviating from the macroring plane. The products were separated and purified by chromatography on silica gel. Compound **V** was eluted with chloroform, **VIII–XI**, with methylene chloride, and **VI, VII**, with a 10:1 methylene chloride–ethanol mixture.

The structures of compounds **V–XI** were established by their elemental analyses and mass, ^{1}H NMR, and electronic absorption spectra. The mass spectra of **V–VII** contain molecular ions related to monoadducts, and the spectra of **VIII–XI**, molecular

ions related to bisadducts. Due to the great amount of chlorine atoms in the compounds obtained, ^{37}Cl contributes significantly in the isotope distributions. For example, the mass spectrum of bacteriochlorin **VIIIa** contains the following isotope peaks of the molecular ion, *m/z*: 853 $[M - H]^+$ (16%), 855 $[M - H + 2]^+$ (59%), 857 $[M - H + 4]^+$ (92%), 859 $[M - H + 6]^+$ (100%), and 861$[M - H + 8]^+$ (87%). The observed isotope abundances are in a good agreement with calculation, *m/z*: 854 $[M]^+$ (12%), 856 $[M + 2]^+$ (50%), 858 $[M + 4]^+$ (91%), 860 $[M + 6]^+$(100%), and 862 $[M + 8]^+$ (74%).

The ^1H NMR spectra show well-resolved signals from different proton groups, confirmatory of the structure of the compounds obtained. Hence, the ^1H NMR spectrum of chlorin **VII** shows two signals at 3.78 and 4.05 ppm from methoxy protons and a signal 5.71 ppm from methine protons. The β-pyrrole proton signals are located downfield and look like a singlet at 8.9 ppm and two doublets at 9.0 and 9.2 ppm. The proton signal of the central imino group is observed at –1.19 ppm. The integral intensity ratio of these signals is 3:3:2:6:2, which is in a good agreement with the structure of chlorin **VII**. The ^1H NMR spectrum of bacteriochlorin **VIIIa** with two hydrogenated double bonds in the opposite pyrrole fragments of the macroring contains one methine proton signal at 5.79 ppm and one sinal at 8.88 ppm from β-pyrrole protons, which confirms equivalence of protons in these two groups. By contrast, in the spectrum of isobacteriochlorin **X** one should expect two signals for each type of protons. The imino proton signal is located at –1.35 ppm. The integral intensity ratio of the signals of bacteriochlorin **VIIIa** is 2:2:1, what is in a good agreement with its structure.

We studied the electronic absorption spectra of compounds **V–XI** in organic solvents in the range 300–1100 nm. In the long-wave range of the Absorption spectra of chlorins **V–VII** and bacteriochlorins **VIIIa, VIIIb, IXa**, and **IXb**, a strong *Q*-band consisting of two components of different intensity is observed. Hence, in the case of chlorin **VI** (Fig. 1, curve *2*), this band has two maxima at 668 and 516 nm, and in the case of bacteriochlorin **VIIIa** (Fig. 1, curve *3*), maxima at 756 and 466 nm. Hence, in going from tetraazaporphine **I** to chlorins **V–VII**, that is hydrogenation of β positions of one of the pyrrole fragments, the long-wave band Q_1 shifts bathochromically by 51–57 nm (depending on substituent) and the Q_2-band shifts hypsochromically by 23–29 nm.



Electronic absorption spectra of compounds (*1*) **I**, (*2*) **VI**, (*3*) **VIIIa**, and (*4*) **X** in methylene chloride.

Hydrogenation of the β positions of two opposite pyrrole fragments, that is transfer from tetraazaporpine **I** to bacteriochlorins **VIIIa, VIIIb, IXa**, and **IXb**, causes still stronger batochromic shift of the Q_1-band (by 138–148 nm) and hypsochromic shift of the Q_2-band (by 77–80 nm). The splitting of the *Q*-band for the chlorins reaches 4400 cm^{-1} and for the bacteriochlorins, about 8400 cm^{-1}, which is larger than the corresponding splitting for tetraazaporphine (2140 cm^{-1}) 2 and 4 times, respectively. The intensity ratio of the Q_1- and Q_2-bands increases in going from tetraazaporphine **I** to chlorins **V–VII** and bacteriochlorins **VIIIa, VIIIb, IXa**, and **IXb**. The electronic spectra of *cis*- and *trans*-bacteriochlorins are identical. Hence, location and intensity of the absorption bands do not depend on the spatial arrangement of substituents in relation to the macroring plane.

In the long-wave range of the absorption spectra of isobacteriochlorins **X, XI**, there is a strong unsplit *Q*-band with maxima at 614 and 618 nm, respectively. In the short-wave range, a weaker *B* band similar to the Soret band of porphyrins is observed. This band undergoes almost no shifts in going from tetraazaporphine **I** to monoadducts **V–VII** and bisadducts **VIII–XI**.

EXPERIMENTAL

The electronic absorption spectra were measured on a Hewlett Packard 8453 spectrophotometer in 10-mm quartz cells and the concentrations of the solutions of

about 10^{-5} M. The ^{1}H NMR spectra were taken on a Bruker WM-250 (250.13 MHz) in $CDCl_3$. The mass spectra were obtained on a Finnigan LCQ/Electrospray spectrometer. The purity of the compounds synthesized was controlled by TLC on Silufol UV-254 plates in methylene chloride for **VIII–XI** and in methylene chloride–ethanol (10:1) for **V–VII**.

Tetraazaporphine [14], cyclopentadiene [15], and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene [16] were obtained by published procedures.

Norborn-5'-eno[*b*]tetraazachlorine (V). *a. Dienopile:diene molar ratio 1:30*. Compound **I**, 0.05 g, was dissolved at elevated temperature in 10 ml of trichlorobenzene and 0.3 ml of cyclopentadiene dimer were added. The reaction mixture was stirred at 150°C under argon for 3 h and then cooled to room temperature and chromatographed on silica gel. First trichlorobenzene and excess diene were eluted with hexane and then **V** was eluted with a 10:1 methylene chloride–ethanol mixture (violet fraction, R_f 0.3). Yield 0.025 g (45.3%). Electronic absorption spectrum (*o*-dichlorobenzene), λ_{max}, nm (log ε): 678 (4.90), 643 (4.00), 619 (4.05), 520 (4.55), 349 (4.61), 333 (4.61). Mass spectrum (ES/MS), *m*/*z* (I_{rel}, %): 379 $[M - H]^+$ (53), 313 $[M - H - C_5H_6]^+$ (100). Found, %: C 64.51, 64.62; H 4.35, 4.37; N 26.86, 26.84. $C_{21}H_{16}N_8 \cdot C_2H_5OH$. Calculated, %: C 64.78; H 5.16; N 26.29.

b. Dienophile:diene molar ratio 1:60. Compound **I**, 0.05 g, was dissolved at elevated temperature in 10 ml of trichlorobenzene. The solution was cooled to 40°C, and 0.8 ml of compound **II** was added. After that the reaction mixture was slowly heated to 150–155°C and stirred at this temperature for 1 h under argon, allowed to cool, and chromatographed on silica gel as described in procedure *a* to obtain 0.038 g (63%) of compound **V**.

1',4',5',6',7',7'-Hexachloronorborn-5'-eno[*b*]tetraazachlorin (VI), bis(1'4'5'6'7'7'-hexachloronorborn-5'-eno)[*b,l*]tetraazabacteriochlorin (VIIIa, VIIIb), and bis(1'4'5'6'7'7'-hexachloronorborn-5'-eno)[*b,g*]tetraazaisobacteriochlorin (X). *a. Dienophile:diene molar ratio 1:10*. Compound **I**, 0.02 g, was dissolved at elevated temperature in 10 ml of chlorobenzene, and 0.2 ml of diene **III** was added.The reaction mixture was refluxed with stirring under argon for 8 h, cooled, and chromatographed on silica gel. First chlorobenzene and excess diene were eluted with hexane and then a 10:1 methylene chloride-ethanol mixture was used to elute two violet fractions. The first contained 0.003 g (10.7%) of compound **VI**, and the second, 0.005 g of starting compound **I**.

b. Dienopile:dienel molar ratio 1:30. Compound **I**, 0.088 g, was dissolved at elevated temperature in 15 ml of chlorobenzene, and 1.32 ml of diene **III** was added. The reaction mixture was refuxed with stirring under argon for 3 h, cooled, and chromatographed on silica gel as described above. The violet fraction was collected to obtain 0.071 g (47.38%) of compound **VI**.

c. Dienophile:diene molar ratio 1:30. Compound **I**, 0.1 g, was dissolved at elevated temperature in 10 ml of trichlorobenzene, and 1.5 ml of diene **III** was added. The reaction mixture was refluxed with stirring under argon for 30 min, cooled, and chromatographed on silica gel first in hexane and and then with methylene chloride. Three fractions were collected. The first was green (R_f 0.46) and contained 0.01 g (3.7%) of compound **VIIIa**. The second one was light blue (R_f 0.22) and contained 0.001 g (5%) of compound **X**. The third fraction was green (R_f 0.03) and contained 0.009 g (3.3%) of compound **VIIIb**. The fourth fraction was eluted with a 10:1 methylene chloride–ethanol to obtain 0.015 g (33.7%) of compound **VI**.

Tetraazachlorin VI. Electronic absorption spectrum, λ_{max}, nm (log ε): 668 (4.83), 638 (3.98), 612 (3.77), 516 (4.50), 345 (4.69). ^{1}H NMR spectrum, δ, ppm: –1.75 s (2H, =NH), 5.8 s (2H, –CH), 8.81 s (2H, =CH), 8.95 d (2H, =CH), 9.1 d (2H, =CH). Mass spectrum (ES/MS), *m*/*z*: 583 $[M - H]^+$ (48%), 585 $[M - H + 2]^+$ (100%), 587 $[M - H + 4]^+$ (73%), 589 $[M - H + 6]^+$ (28%). Found, %: C 42.34, 42.40; H 2.26, 2.47; N 17.30, 17.42. $C_{21}H_{10}C_{l6}N_8 \cdot C_2H_5OH$. Calculated, %: C 43.60, H 2.52, N 17.70.

Tetraazabacteriochlorin VIIIa. Electronic absorption spectrum, CH_2Cl_2, λ_{max}, nm (log ε): 7.56 (4.86), 7.18 (4.18), 467 (4.45), 3.55 (4.60), 301 (4.51). ^{1}H NMR spectrum, δ, ppm: –1.35 s (2H, =NH), 5.79 s (4H, –CH), 8.88 s (4H, =CH). Mass spectrum (ES/MS), *m*/*z*: 853 $[M - H]^+$ (16%), 855 $[M - H + 2]^+$ (59%), 857 $[M - H + 4]^+$ (92%), 859 $[M - H + 6]^+$ (100%), 861 $[M - H + 8]^+$ (87%). Found, %: C 35.53, 35.76; H 1.35, 1.48; N 13.57, 13.84; $C_{26}H_{10}Cl_{12}N_8$. Calculated, %: C 36.32, H 1.17, N 13.03.

Tetraazabacteriochlorin VIIIb. Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (log ε): 755 (4.84), 717 (4.09), 468 (4.37), 356 (4.63), 300 (4.49). ^{1}H NMR spectrum, δ, ppm: –1.35 s (2H, =NH), 5.79 s (4H, –CH), 8.88 s (4H, =CH). Mass spectrum (ES/

MS), *m/z* (I_{rel}, %): 8.55 $[M - H + 2]^+$ (59), 857 $[M - H + 4]^+$ (67), 859 $[M - H + 6]^+$ (100), 861 $[M - H + 8]^+$ (84).

Tetraazaisobacteriochlorin X. Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (rel. intensity): 614 (1.0), 591 (0.4), 514 (0.23), 499 (0.22), 366 (0.47). Mass spectrum (ES/MS), *m/z* (I_{rel}, %): 855 $[M - H + 2]^+$ (58), 857 $[M - H + 4]^+$ (76), 859 $[M - H + 6]^+$ (100), 861 $[M - H + 8]^+$ (88).

1',4',5',6'-Tetrachloro-7',7'-dimethoxynorborn-5'-eno[*b*]tetraazachlorin (VII), bis(1',4',5',6'-tetrachloro-7',7'-dimethoxynorborn-5'-eno)[*b,l*]tetraazabacteriochlorin (IXa,b), bis(1',4',5', 6'-tetrachloro-7',7'-dimethoxynorborn-5'-eno)[*b,g*]tetraazaisobacteriochlorin (XI). Compound **I**, 0.1 g, was dissolved at elevated temperature in 20 ml of trichlorobenzene, and 0.55 ml of the diene **IV** was added. The reaction mixture was refluxed with stirring under argon for 20 min, cooled, and chromatographed on silica Gel first in hexane and then in methylene chloride. Two green fractions were collected. The first (R_f 0.26) contained 0.009 g (10%) of compound **IXa** and the second (R_f 0.19) contained 0.016 g (17.8%) of compound **IXb**. The third, violet fraction was eluted with a 10:1 methylene chloride–ethanol mixture to obtain 0.029 g (32.8%) of compound **VII**.

b. Dienopile:diene molar ratio 1:30. Compound **I**, 0.1 g, was dissolved at elevated temperature in 15 ml of trichlorobenzene, and 1.68 ml of diene **IV** was added. The reaction mixture was refluxed under argon for 20 min and then treated as decribed in procedure *a*. Three fractions were isolated. The first (R_f 0.26) was green and contained 0.08 g (5.97%) of compound **IXa**. The second (R_f 0.22) was light blue and contained 0.003 g (0.71%) of compound **XI**. The third (R_f 0.19) was green and contained 0.01 g (7.57%) of compound **IXb**. The fourth fraction was eluted with a 10:1 methylene chloride–ethanol mixture to obtain 0.024 g (26.08%) of compound **XI**.

Tetraazachlorin VII. Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (logε): 670 (4.83), 640 (4.01), 614 (3.89), 582 (3.60), 517 (4.54), 343 (4.67), 329 (4.64). ^{1}H NMR spectrum, δ, ppm: –1.19 s (2H, =NH), 3.78 s (3H, OCH_3), 4.05 s (3H, OCH_3), 5.71 s (2H, –CH), 8.9 s (2H, =CH), 9.0 d (2H, =CH). Mass spectrum (ES/MS), *m/z*: 575 $[M - H]^+$, 577 $[M - H + 2]^+$, 579 $[M - H + 4]^+$. Found, %: C 47.80, 47.92; H 3.11, 2.81; N 18.04, 17.92. $C_{23}H_{10}Cl_4O_2$. Calculated, %: C 47.77, H 2.79, N 19.38.

Tetraazaisobacteriochlorin IXa. Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (log ε): 762 (4.82), 724 (4.07), 686 (3.51), 466 (4.37), 414 (3.89), 355 (4.56), 300 (4.47). Mass spectrum (ES/MS), *m/z*: 842 $[M + 4]^+$, 844 $[M + 6]^+$, 846 $[M + 8]^+$. Found, %: C 47.43, 47.25; H 3.64, 3.40; N 11.20, 11.19. $C_{30}H_{22}C_{l8}N_8O_4 \cdot C_6H_{14}$. Calculated, %: C 46.58; H 3.91; N 12.07.

Tetraazabacteriochlorin IXb. Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (log ε): 765 (4.85), 726 (4.09), 682 (3.47). 465 (4.38), 415 (3.80), 355 (4.57). Mass spectrum (ES/MS), *m/z*: 840 $[M + 2]^+$, 842 $[M + 4]^+$ 844 $[M + 6]^+$.

Tetraazaisobacteriochlorin XI. Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (rel. intensity): 618 (1.0), 591 (1.05), 379 (shoulder), 367 (shoulder), 322 (1.30). Mass spectrum (ES/MS), *m/z*: 840 $[M + 2]^+$, 842 $[M + 4]^+$, 844 $[M + 6]^+$.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 04-03-32533).

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