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Synthesis of *N*-Alkylthiadiazole-Containing Macroheterocyclic Compounds of ABBB Type

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Abstract—New substituted unsymmetrical macroheterocyclic compounds with a fragment of 1,3,4-thiadiazoline were obtained by condensation of 5-amino-2-imino-3-pentyl-1,3,4-thiadiazoline or 5-amino-3-dodecyl-2-imino-1,3,4-thiadiazoline with 1,1-dimethoxy-3-iminoisoindoline in methanol. The compounds obtained were characterized by the IR, electron and ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis.

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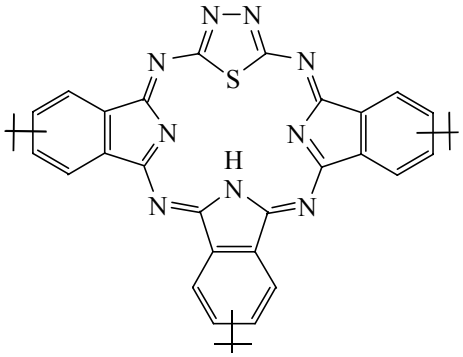
Currently non-centrosymmetric analogs of macroheterocyclic compounds of tetrapyrrole type with the ABBB-type azole fragments are the objects of intense research [1–4] because of their molecular structure and practically useful properties. These compounds exhibit interesting nonlinear optical [5–7], liquid crystalline [8], and semiconducting properties [9]. Because of the similarity of their structure with that of phthalocyanines the compounds containing triazole ring instead of one of isoindole fragments they were named triazolophthalocyanines [10].

The principal method of obtaining the ABBB-type metallocomplexes is the condensation of bis(1-imino-3-izoindolinylidenamino)azole with a substituted phthalonitrile in the presence of nickel salt or a complex compound of bis(1-imino-3-isoindilinyl-idenamino)azole with relevant phthalonitrile [11–13]. Recently Esperanza et al. [14] succeeded in the synthesis of metal-free triazolophthalocyanine, but the purification of this substance has proved to be very difficult.

Zinc and aluminum complexes of unsubstituted macroheterocyclic compound of ABBB type with 1,3,4-thiadiazole fragment were first described in [15]. The first report on the synthesis of metal-free *tert*-butyl-substituted macroheterocyclic compound **I** designated as thiadiazolophthalocyanine, that includes 1,3,4-thia-diazole fragment, appeared in 2001 [16]. This compound has been isolated in 15% yield as a byproduct in the synthesis of *tert*-butyl-substituted



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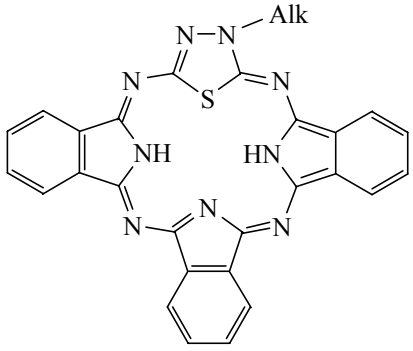


IIa, IIb

Alk = C_5H_{11} (**a**), $C_{12}H_{25}$ (**b**).

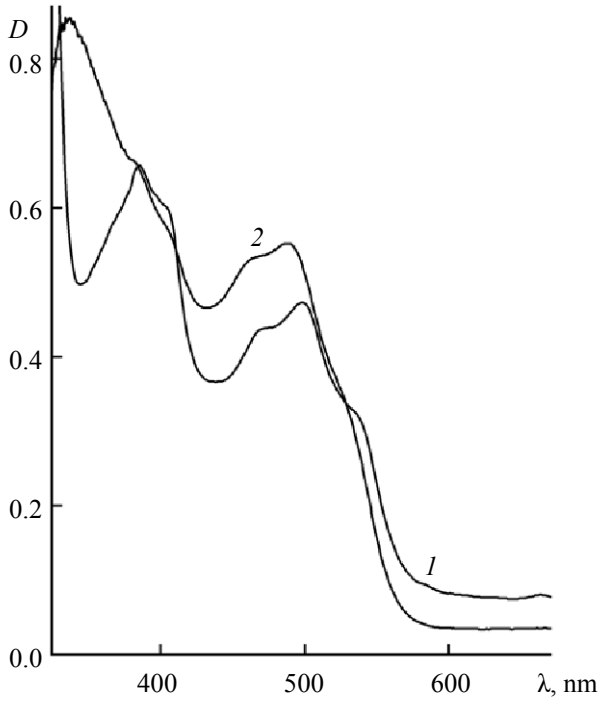


Fig. 1. Electron absorption spectra in MeOH: (*1*) compound **IIa,** concentration 1.25×10^{-4} mol l^{-1} and (*2*) compound **IIb**, concentration 1.14×10^{-4} mol l^{-1}.

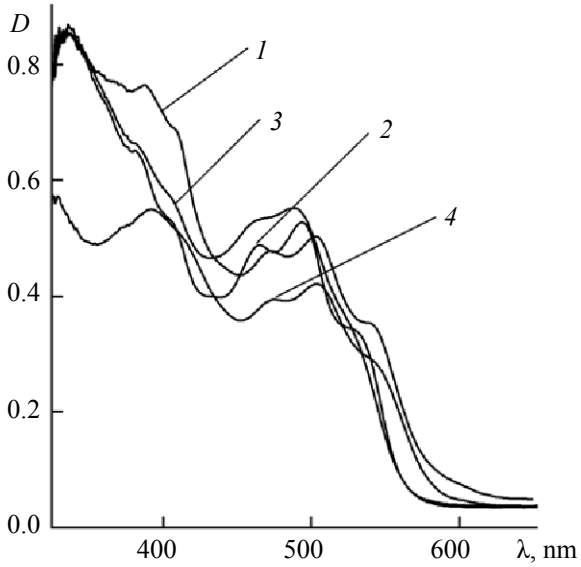
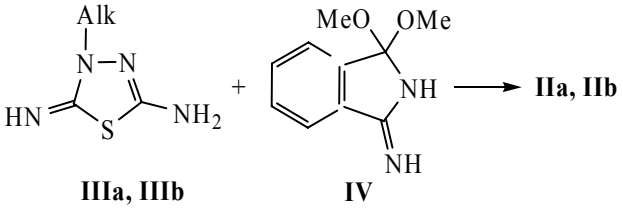


Fig. 2. Electron absorption spectra of compound **IIb** in various solvents: (*1*) C_6H_6, (*2*) $CHCl_3$, (*3*) MeOH, and (*4*) DMF.

macroheterocyclic compound of ABABAB type. The macrocyclic system of this compound includes 18π-electrons like the endocyclic system of phthalocyanine.

We obtained unsymmetrical macroheterocyclic compounds **IIa** and **IIb** by the reaction of respective 5-amino-3-alkyl-2-imino-1,3,4-thiadiazolines **IIIa** and **IIIb** with 1,1-dimethoxy-3-iminoisoindoline (**IV**) in 1:3 ratio in methanol at boiling for 15 h.



Alk = C_5H_{11} (**a**), $C_{12}H_{25}$ (**b**).

Yield of target products after chromatographic purification was 30% (**IIa**) and 35% (**IIb**), respectively.

The compounds were identified using electron, IR, and ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis.

The mass spectra of compounds **IIa** and **IIb** contain peaks of molecular ions $[M + H]^+$, which correspond to compound consisting of one alkylthiadiazoline and three isoindole fragments. The coincidence in molecular mass and isotope distributions of molecular ions with the calculated values confirms that these compounds are macroheterocycles of ABBB type.

The electron absorption spectra (Fig. 1) include a strong band in the visible region at 499 nm with shoulders at 538 and 490 nm for compounds **IIa** and **IIb**, respectively, and strong absorption bands at 386 and 337 nm. Long-wavelength absorption bands at 490 and 499 nm correspond to π–π*-electron transitions involving the highest occupied and lowest unoccupied molecular orbitals. With the increase of solvent polarity (benzene–$CHCl_3$–MeOH) a blue shift of the long-wave absorption band (504 → 493 → 489 nm) is observed as shown in Fig. 2 for the macroheterocycle **IIb**. Such a negative solvatochromic effect [17] has been observed previously [18] for triazolophthalocyanines.

As shows Fig. 3, the dilution of the solution of compound **IIb** (DMF) leads to the broadening of the absorption bands in the electron absorption spectrum, therewith, intensity of the solution absorption depends linearly on the solution concentration (Fig. 4). This is probably due to the effect of solvation of the studied

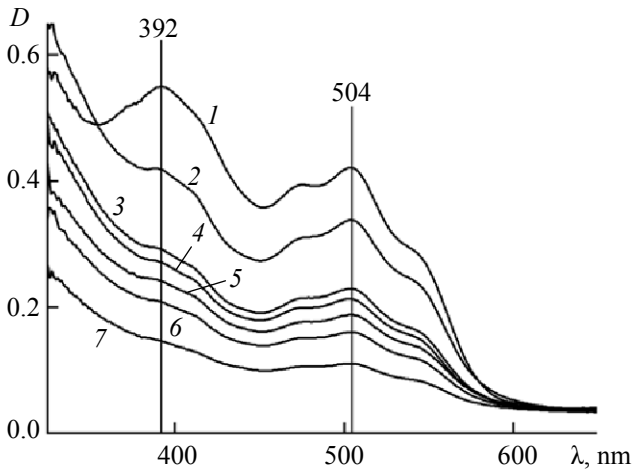


Fig. 3. Electron absorption spectrum of compound **IIb** in DMF at various concentrations, mol l^{-1}: (*1*) 4.71×10^{-4}, (*2*) 2.95×10^{-4}, (*3*) 2.69×10^{-4}, (*4*) 2.36×10^{-4}, (*5*) 1.89×10^{-4}, (*6*) 1.18×10^{-4}, and (*7*) 1.05×10^{-4}.

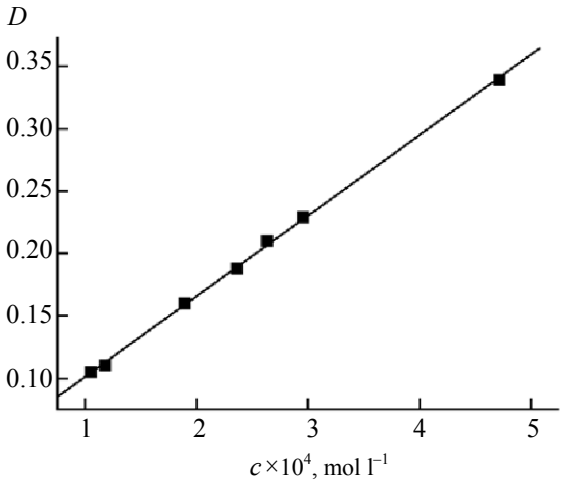


Fig. 4. The dependence of the optical density on the concentration of compound **IIb** (DMF, λ_{max} 504 nm). *Squares*: experiment, *line*: calculation by the least squares (± 0.001, the probability $P = 0.99$).

compounds in the concentration range of the tested solutions. The same dependence is observed for the solutions in chloroform and methanol. The nature of the spectra of macrocyclic ligands is similar to that of compound **I** [16].

The IR spectra of compounds **IIa** and **IIb** include a band at 3209 cm^{-1} characterizing stertching N–H vibrations in the isoindole fragments. A strong band at 1605 cm^{-1} can be attributed to the C=N vibrations. Intense bands at 2923 and 2852 cm^{-1} relating to the vibrations of C–H bond in the alkyl substituents indicate the presence of the latter in 1,3,4-thiadiazoline fragment.

EXPERIMENTAL

Electron absorption spectra in the visible and ultraviolet regions were recorded on a Hitachi U-2001 spectrophotometer using rectangular quartz cells of thickness 1–10 mm. The MALDI-TOF mass spectra were obtained on a Bruker Daltonics Ultraflex mass spectrometer in the positive ion mode using the reflection mode with the target voltage 20 mV. α-Cyano-4-hydroxycinnamic acid was used as the matrix. The samples were prepared by dissolving the examined compound in chloroform (concentration 10^{-4} to 10^{-6} mol l^{-1}) and mixed in a 1:1 ratio with the matrix solution (20 mg ml^{-1}) in 30% aqueous acetonitrile.

The ^1H NMR spectra were taken on an Avance spectrometer with operating frequency 500 MHz. The samples were prepared by dissolving examined compounds in $CDCl_3$. Chemical shifts (δ, ppm) were measured at T = 295 K using internal HMDS as reference (δ 0.037 ppm).

The IR spectra were recorded on an Avatar 360 FT-IR spectrometer. The samples for IR spectroscopy were tablets prepared by careful grinding a compound with KBr followed by pressing.

5-Amino-2-imino-3-pentyl-1,3,4-thiadiazoline (**IIIa**) and 5-amino-3-dodecyl-2-imino-1,3,4-thiadiazoline (**IIIb**) were prepared by the procedure we had developed earlier [19]. 1,1-Dimethoxy-3-iminoisoindoline (**IV**) was obtained by the method [20].

General methods of synthesis of macroheterocyclic compounds of ABBB type. A mixture consisting of 5-amino-3-alkyl-2-imino-1,3,4-thiadiazoline and compound **IV** in methanol was stirred at reflux for 15 h. During the synthesis the release of ammonia was monitored. The reaction mixture was then poured into 150 ml of water. The precipitate was filtered off and dried at room temperature. The target product was subjected to chromatography on a column filled with aluminum oxide, the eluent was a mixture of organic solvents. The product obtained was a crimson substance, insoluble in water and hexane and readily soluble in the most organic solvents.

1-Pentyl-18,23-imino-2,9,19-trinitrilo-2,25-thiotribenzo[*f,k,p*]-28*H*,30*H*-[3,8,13,18,20]pentaazacycloeicosene (IIa) was obtained along the general procedure from 0.013 g of compound **IIIa** and 0.0338 g of compound **IV**. As an eluent was used dichloro-

methane–methanol–hexane 10:1:3 mixture. Yield 12 mg (30%), mp 173–175°C. EAS (MeOH), λ_{max}, nm (log ε): 386 (3.72), 404 sh (3.68), 469 sh (3.54), 499 (3.57), 536 sh (3.41). IR spectrum (KBr), ν, cm^{-1}: 3394, 3209, (N–H), 2954, 2924, 2852 (C–H), 1699 (C=N), 1608, 1518 (C=C), 1471 , 1389, 1301, 1178, 1143, 1090, 1049, 722 (C–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 12.36 s (2H, NH), 7.78, 7.39, 7.25 m (4H, H-arom.), 4.48 t (4H, NCH_2), 1.87 s (4H, NCH_2CH_2), 1.25 m (12H, CH_2), 0.88 t (6H, CH_3). The MALDI-TOF spectrum, *m/z* 555 $[M]^+$. Found, %: C 66.86; H 4.47; N 23.05; S 5.34. $C_{31}H_{25}N_9S$. Calculated, %: C 67.01; H 4.53; N 22.69; S 5.77. *M* 555.65.

1-Dodecyl-18,23-imino-2,9,19-trinitro-2,25-thiotribenzo[*f,k,p*]-28*H*,30*H*-[3,8,13,18,20]pentaazacycloeicosene (IIb) was obtained along the general procedure from 0.29 g of compound **IIIb** and 0.50 g of compound **IV**. As an eluent was used dichloromethane–methanol–acetone–hexane–ethyl acetate mixture, 2:1:2:0.5:0.5. Yield 0.23 g (35%). EAS (MeOH), λ_{max}, nm (log ε): 337 (3.87), 382 sh, 462 sh, 489 (3.68). IR spectrum (KBr), ν, cm^{-1}: 3419, 3205, (N–H), 2954, 2922, 2851 (C–H, alk), 1613, 1605 (C=N), 1520, 1469, 1389, 1301, 1180, 1149, 1087, 1040, 721 (C–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 12.36 s (2H, NH), 7.78, 7.39, 7.25 m (4H, H-arom.), 4.50 m (4H, NCH_2), 1.9 s (4H, NCH_2CH_2), 1.25 m (40H, CH_2), 0.91 m (6H, CH_3). The MALDI-TOF spectrum, *m/z*: 654 $[M]^+$. Found, %: C 69.77; H 6.10; N 19.16; S 4.72. $C_{38}H_{39}N_9S$. Calculated, %: C 69.80; H 6.01; N 19.28; S 4.90. *M* 653.84.

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