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Synthesis of Tri(4−tritylphenoxy)− and Hexa(4−methylphenoxy)−Substituted Hemihexaphyrazines

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New representatives of hemihexaphyrazines bearing bulky substituents were synthesized by condensation of 2,5-diamino-1,3,4-thiadiazole with products derived in situ from interaction of 4-(4-tritylphenoxy)- or 4,5-bis(4-methylphenoxy)phthalonitriles with sodium alkoxides in methanol-butanol mixture. Target compounds purified by column chromatography were characterized by elemental analysis, UV-vis, IR, ^{1}H NMR spectroscopy and mass spectrometry.

Keywords: Porphyrinoids, hemihexaphyrazine, aryloxy-substituted phthalonitriles.

Introduction

Porphyrinoids are the structural analogues of porphyrin macroheterocyclic system of which consists of 5 or more pyrrole subunits. In contrast to porphyrin, the porphyrinoids possess an extended inner cavity and therefore they are able to coordinate metal cations of large ionic radius. For instance, complexes of lanthanides are considered to be attractive for photodynamic therapy and virology,[1] whereas those of actinides can be recommended for analytics determination of radioactive impurities.[2] Structural peculiarities of macrocyclic core determine the capability of porphyrinoids to absorb the anions and to transport them through membranes.[3] Moreover like natural tetrapyrrolic macrocycles, porphyrinoids[4-7] show the light absorption in visible region at high level [8] what stimulates searching of new photoactive materials on their basis.[9-11]

Immense capabilities of both core and peripheral modification[12-15] allow to realize directional synthesis of new compounds[16-18] with expended coordination cavities which are different in dimensions, composition and number of atoms included.

Following this strategy, structural modification of hexaphyrin core by substitution of pyrrole subunits (B) by residues of aromatic diamines (A) led to the discovery of macroheterocyclic compounds of ABBABB, ABBAAB and ABABAB-types.[19-25]

If compared with various aza-analogues of porphyrinoids, macroheterocyclic compounds of ABABAB-type are the most scrutinized now. Their macrocyclic core is formed by alternation of three 1,3,4-thiadiazole and three pyrrole subunits connected with each other via aza-bridges. The structures of *tert*-butyl- and 3,6-hexapentoxysubstituted Mc both in gas phase and solid states were established by gas-phase electronography[22-24] and X-ray[25] methods correspondingly. It was shown that the macrocyclic core of their molecules is plane and thiadiazole subunits are oriented by such way that their S-atoms are outside of inner cavity. This configuration is stabilized by three tricentered intramolecular hydrogen bonds.

This work is considered to be a continuation of our recent research[22,26] and its main objective is synthesis and properties of new representatives of tri- and hexasubstituted hemihexaphyrins bearing the bulky substituents on their periphery.

Experimental

2,5-Diamino-1,3,4-thiadiazole was obtained following the procedure proposed by us.[27]

4-(4-Tritylphenoxy)phthalonitrile (**1**) was obtained by the known procedure,[28] 4,5-bis(4-methylphenoxy)phthalonitrile (**2**) was provided by Prof. I.G. Abramov.[29]

General procedure. Nitrile **1** or **2** was added into solution of sodium alkoxides prepared previously by dissolution of metallic sodium in methanol-butanol mixture and reaction mass was stirred at room temperature for 7 hours. Then ammonia chloride was added 3 hours later, 2,5-diamino-1,3,4-thiadiazole was added and reaction mass was stirred for 2 hours at 80 °C and then refluxed for 30 hours. Reaction proceeding was monitored by thin layer chromatography.

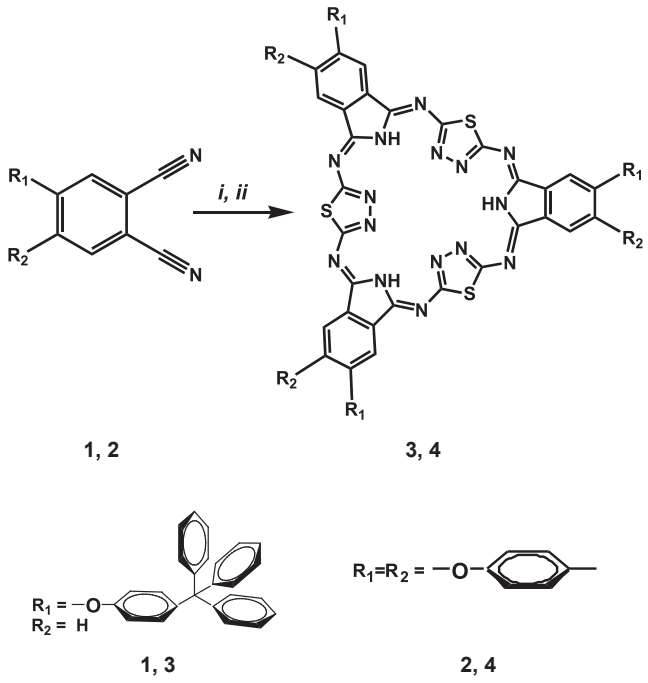
2,14(15),26(27)-tri(4-tritylphenoxy)-5,36:12,17:24,29-triamino-7,10:19,22:31,34-trithio-[f,p,z]-tribenzo-1,2,4,9,11,12,14,19,21,22,24,29-dodecaazaccyclotriacontene (**3**) was synthesized following general procedure from 4-(4-tritylphenoxy)phthalonitrile (**1**) (2.00 g, 4.0 mmol) and 2,5-diamino-1,3,4-thiadiazole (0.46 g, 4.0 mmol) in dried BuOH (45 ml), MeOH (5 ml) and 6.0 mg-equivalent of metallic sodium with use of NH_4Cl (0.32 g, 59.0 mmol). Yield: 1.61 g (65.8 %). **3** doesn't found up to 300 °C. Found: N 12.10 %. $C_{105}H_{69}N_{15}O_9S_3$ requires N 12.48. IR (KBr) ν_{max} cm^{-1}: 3440, 3103, 2968, 2927, 2360, 1747, 1615, 1477, 1430, 1329, 1275, 1234, 1100, 1031, 933, 876, 744, 704, 633. UV-vis (benzene) λ_{max} nm (lgε): 398 (4.91), 419 (4.92), 513 (4.21).[30]

2,3,14,15,26,27-Hexa(4-methylphenoxy)-5,36:12,17:24,29-triimino-7,10:19,22:31,34-trithio-[f,p,z]-tribenzo-1,2,4,9,11,12,14,19,21,22,24,29-dodecaazaccyclotriacontene pentadecaene (**4**) was synthesized following general procedure

from 4,5-bis(4-methylphenoxy)phthalonitrile (**2**) (0.615 g, 1.81 mmol) and 2,5-diamino-1,3,4-thiadiazole (0.21 g, 1.81 mmol) in dried BuOH (5 ml), MeOH (0.2 ml) and 0.267 mg-equivalent of metallic sodium with use of NH_4Cl (0.16 g, 0.267 mmol). The solvents were evaporated and the solid was triturated with methanol. Suspension obtained by this way was filtered and washed by MeOH. Further purification was made by means of column chromatography on alumina using dichloromethane as eluent. Yield: 0.143 g (18 %). Found: C 63.75; H 4.39; N 17.87; S 8.23; O 4.39 %. $C_{90}H_{87}N_{15}O_6S_3$ requires C 63.98, H 4.56, N 18.65, S 8.54; O 4.26 %. *m/z* (MALDI-TOF, dithranole) 1126.4 $[M+H]^+$. IR (KBr) ν_{max} cm^{-1}: 3229, 2922, 2850, 1627, 1473, 1373, 1223, 1089, 1033, 838, 777, 735, 713, 689. UV-vis (CH_2Cl_2) λ_{max} nm (lgε): 393 (4.85), 414 (4.87), 468 (sh), 502 (4.18).^{1}H NMR ($CDCl_3$) δ_H ppm: 12.34 (s., NH), 7.77, 7.39, 7.05 (m., H-arom), 1.25 (s., CH_3).

Results and Discussion

Hemihexaphyrazines **3** and **4** were synthesized by condensation of 2,5-diamino-1,3,4-thiadiazole with the products derived *in situ* from interaction of 4-(4-tritylphenoxy)phthalonitrile **1** or 4,5-bis(4-methylphenoxy) phthalonitrile **2** with sodium alkoxides in methanol-butanol mixture following the Scheme:



i = BuONa, MeOH, BuOH, 7 h, 20-25 ^{0}C;
ii = NH_4Cl, 2,5-diamino-1,3,4-thiadiazole, 3 h, 30 °C; refluxing, 24 h

The reaction run has been monitored by TLC and UV-vis spectroscopy.

Due to the presence of bulky substituents, hemihexaphyrine **4** was found to be soluble in organic solvents quite enough to apply column chromatography for its purification. The macrocycle **3** was obtained with high yield hence its purification by extraction allows to get sufficiently pure substance. These compounds were characterized by elemental analysis, and UV-vis, IR, ^{1}H NMR spectroscopy mass spectrometry.

Intense picks of molecular ion $[M+H]^+$ corresponding to the ABABAB-structure were detected in mass-spectra of **4**. A coincidence of experimentally observed molecular masses and isotopic distributions of molecular ions with calculated values prove the structure of this compound as Mc of ABABAB-type.

In the IR spectrum of compound **3**, there are absorption bands corresponding to stretching vibrations of the bonds: C_{Sp2}-H (3103-3049 cm^{-1}), C-C (1615 and 1430 cm^{-1}), as well as C-O and C-O-C (1275-1031 cm^{-1}). The absorption band corresponding to N–H stretching vibrations of imino groups is observed at 3103 cm^{-1}. It is noteworthy that stretching vibrations of C–O–C bonds are observed at 1272-1223 cm^{-1} region in the IR spectra of the both Mc **3**, **4** and initial nitriles **1**, **2**.

^{1}H NMR spectra of compound **4**, measured in $CDCl_3$, reveal a signal at 1.25 ppm, which can be assigned to the protons of methyl groups. The multiplets at 7.77–7.05 ppm are induced by the resonance of the protons of benzene rings, and the singlet at 12.34 ppm characterises the absorbance of the protons of imino groups. The presence of these signals in the low field highlights the non-aromatic character of ABABAB macrocycle.

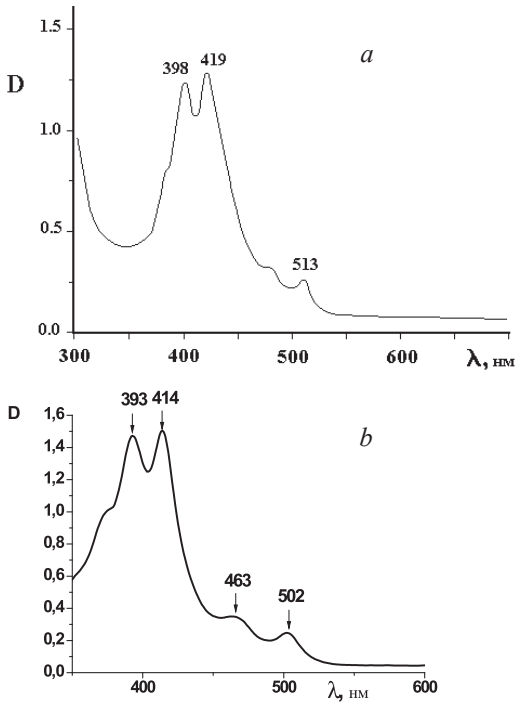


Figure 1. UV-vis specra of Mc's *a* - **3** (benzene, c = 1.514 ·10^{-5} mol·l^{-1}); *b* - **4** (CH_2Cl_2, c = 2.023 ·10^{-5} mol·l^{-1}).

The character of UV-vis spectra of compounds **3** and **4** shown in Figure 1 is similar. Thus, the strong absorbance bands at 398 and 419 nm (**3**) and at 393 and 414 nm (**4**) dominate in the spectra of both compounds while the bands of lower intensities are located at about 450–505 nm. These spectra are similar to the spectrum of substituted macroheterocyclic compound of ABABAB-type,[26,31] and it can evidence the similarity of their chromophore systems.

Conclusion

It was shown that introduction of bulky substituents doesn't lead to any noticeable changes of optical properties of hemihexaphyrazines possessing a large inner cavity.

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