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Microwave–Assisted Synthesis and Characterization of Carba– and Triazolehemiporphyrazines with Camphorapyrazine Fragments

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Dedicated to the memory of Prof. Larisa G. Tomilova

A series of new hemiporphyrazines bearing camphorapyrazine fragments were synthesized using microwave assisted solvent-free protocol by interaction of m-phenylenediamine, 1(H)- or 1-dodecyl-3,5-diamino-1,2,4-triazole with racemic mixture, R-(+)- or S-(-)-camphoradicyanopyrazines. The obtained macroheterocycles were characterized by mass spectrometry, UV-Vis, IR, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis data.

Keywords: Hemiporphyrazines, camphorapyrazine, microwave irradiation.

Микроволновый синтез и характеристика карба– и триазологемипорфиразинов с камфорапиразиновыми фрагментами

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Серия новых гемипорфиразинов, содержащих камфорапиразиновые фрагменты, была синтезирована с применением микроволнового излучения без использования растворителей, взаимодействием м-фенилендиамина, 1(H)- или 1-додецил-3,5-диамино-1,2,4-триазола с рацемической смесью, R-(+)- или S-(-)-камфорадицианопиразинами. Полученные макрогетероциклы были охарактеризованы данными масс-спектрометрии, электронной, ИК, ^{1}H и ^{13}C ЯМР спектроскопии, а также элементного анализа.

Ключевые слова: Гемипорфиразины, камфорапиразин, микроволновое излучение.

Introduction

Hemiporphyrazines (Hps) and carbahemiporphyrazines (cHps) are nonaromatic macroheterocycles in which two opposite faced isoindoline moieties are replaced by pyridine or phenylene units, respectively.[1–3] They can be prepared by crossover condensation of phthalonitriles with the corresponding diaminoheterocycle and diaminocarbocycle. Many practical interesting properties of Hps, such as optical limiting[4] and photophysical properties[5] have been described earlier. Furthermore, macroheterocyclic compounds of this type appear to be a suitable platform

for structural modification by selecting particular diamine derivatives and appropriate pyrrole-bearing subunits to assemble a macrocyclic framework, introducing adequate substituents at the periphery of macrocycle and metal-atoms into the coordination cavity.[6,7] Having an inner ring of 20 π-electrons, hemiporphyrazines demonstrate a non-aromatic character. It was found that in the case of Hp, pyridine subunits keep local aromaticity, which interrupts an extended conjugation over the macroring.[8] However, the destruction of the local aromaticity by introducing a carbonyl group in position 4 of 1,3-phenylene subunits induces the appearance of global aromaticity and transforms the corresponding cHp into a highly aromatic system with strong absorption in near infrared area.[9,10]

Triazolehemiporphyrazines (tHps), developed in our group, can be considered as structural analogues of Hps in which two pyridine rings are formally replaced by 1,2,4-triazole moieties.[11–13] The mesomorphic and non-aromatic properties of dodecyl-substituted tHps have been described.[14] Muranaka *et al*.[15] reported the structure of tHps using X-ray diffraction analysis and quantum-chemical calculations. It was shown that triazolehemiporphyrazine has a flat 20 π-electron system with a weak paramagnetic ring current. On the other hand, the use of substituted dinitriles based on pyrazine led to core modified macrocycles, which are characterized by the presence of additional nitrogen atoms, thus providing supplementary coordination abilitiy and a basic character of the macroheterocycle.[16,17] Optically active compounds based on tetrapyrazinoporphyrinoids have been obtained by introduction of camphor fragments in their structure.[18–21] Recently[22] we briefly reported on the synthesis of racemic and R-(+)-camphor substituted cHps, the last one being used as optically active dopant of a nematic mixture of cucurbit[6]uril (CB6). However, to the best of our knowledge, tHp having camphorapyrazines subunits have not been reported in literature so far.

Experimental

Racemic [(1'R,4'S)-(+)/(1'S,4'R)-(–)]-1',7',7'-trimethylbicyclo[2.2.1]heptano[2',3'-b]-2,3-dicyanopyrazine (**1a**), [(1'R,4'S)-(+)- (**1b**) and [(1'S,4'R)-(–)]-enantiomers (**1c**) have been prepared following the method described in the literature[23] by condensation of diaminomaleonitrile with racemic mixture, (1R)-(−)- or (1S)-(+)-camphorquinones in concentrated acetic acid. After recrystallization from ethanol and final drying at reduced pressure, at 150 °C for 3 hours, the compounds were obtained as white crystals in 60–70 % yield. *m*-Phenylenediamine (**2**) was recrystallizated from dichloromethane. 1(H)- (**3**) and 1-dodecyl-3,5-diamino-1,2,4-triazole (**4**) were prepared according to the method described in the literature.[13] The solvents were thoroughly dried before use according to standard procedures.[24]

All reactions were performed in the CEM-Discover monomode equipment with systems of continuous supply of microwave radiation (the power supplied is set by the operator in the range 0–300 W) and frequency of the magnetron 2455 MHz in open-vessels under solvent-free conditions. Temperature in the range 25–250 °C, evaluated by infrared detection, is maintained to be constant by modulation of emitted MW power. Column chromatography was conducted on silica gel Merck-60. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with aluminum oxide 60 F_{254} (Merck).

MALDI-TOF spectra on a Shimadzu Biotech Axima Confidence in positive ions field both without matrix and using dihydroxybenzoic acid (DHB) or *α*-cyano-4-hydroxycinnamic acid (CHCA) as matrixes, and the tests for carbon, nitrogen and hydrogen on a FlashEA 1112 CHNS–O Analyzer were recorded using the resources of the Center for collective use of scientific equipment of Ivanovo State University of Chemistry and Technology. ^{1}H NMR spectra were performed using Bruker DRX 500, Bruker Avance and Bruker Avance II (300 and 500 MHz) spectrometers on the base of Interdepartmental Investigation Service (SIdI) of Universidad Autónoma de Madrid.

*General procedure for synthesis of compounds **5–7**.* Mixtures of 0.24 g (1 mmol) of **1a**, **1b** or **1c** and 1 mmol of **2**, **3** or **4** were rigorously fine milled in agate mortar and placed into a 10 mL reactor. Microwave assisted synthesis was carried out using a Discovery LabMate focused microwave system with dynamic power not more 100 W in open vessels routine following the solvent-free protocol. The temperature and duration of the synthesis were selected individually for each compound. Purification of the target compounds was carried out depending on their individual properties.

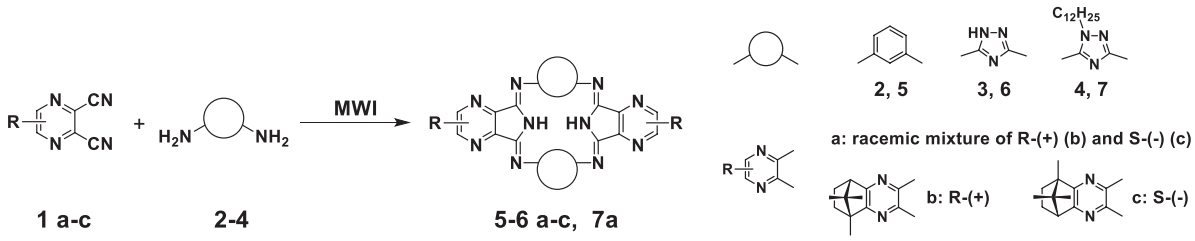
*5,26:13,18-Diimino-7,11:20,24-dimetheno-[c,n]-di(2,3-[(1'R,4'S)-(+)/(1'S,4'R)-(–)]- (**5a**), 5,26:13,18-diimino-7,11:20,24-dimetheno-[c,n]-di(2,3-[(1'R,4'S)-(+)]-(**5b**)and5,26:13,18-diimino-7,11:20,24-dimetheno-[c,n]-di(2,3-[(1'S,4'R)-(–)]-1',7',7'-trimethylbicyclo[2.2.1]heptano[2',3'-b]-pyrazino)-1,6,12,17-tetraazacyclodocosene-1,3,5,7,9,12,14,16,18,20-decene (**5c**).* Microwave synthesis of **5a-c** was carried out by the reaction of 0.24 g (1 mmol) **1a**, **1b** or **1c** and 0.11 g (1 mmol) of *m*-phenylenediamine **2** at a temperature of 150 °C for 20 minutes. The crude products were purified by column chromatography on silica gel (eluent mixture: dichloromethane:methanol:hexane 20:1:6). Products **5a–c** were obtained as yellow powders after recrystallization from ethanol and drying under reduced pressure at 130 ºC for 4 hours.

5a: Yield: 0.15 g (21 %). R_f = 0.61 (silica gel 60F_{254}, CH_2Cl_2:MeOH:C_6H_{14} (10:1:3)). IR (KBr) ν cm^{-1}: 3427, 3130, 2960, 2927, 2871, 2395, 1664, 1577, 1525, 1477, 1386, 1280, 1261, 1155, 1114, 1072, 952, 863, 688, 541. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H ppm: 10.59 (m, 1H, NH), 7.39 (s, 2H, CH_{ar}), 6.96 (m, 1H, CH_{ar}), 6.81 (s, 1H, CH_{ar}), 3.15 (s, 1H, CH), 2.31 (m, 1H, CH_2), 2.10 (m, 1H, CH_2), 1.37 (s, 3H, CH_3), 1.30 (s, 2H, CH_2), 1.09 (s, 3H, CH_3), 0.62 (s, 3H, CH_3). ^{13}C NMR (300 MHz, DMSO-d_6) δ_C ppm: 9.91, 18.29, 19.74, 23.92, 30.87, 52.36, 53.77, 55.74, 118.43, 130.00, 144.43, 149.12. *m/z* (MALDI-TOF, CHCA) Da: 659.4 [calcd. for $C_{40}H_{39}N_{10}^+$ $(M+H)^+$ 659.3], 681.4 [calcd. for $C_{40}H_{38}N_{10}Na^+$ $(M+Na)^+$ 681.3], 697.4 [calcd. for $C_{40}H_{38}N_{10}K^+$ $(M+K)^+$ 697.3].

5b: Yield: 0.17 g (25 %). R_f = 0.62 (silica gel 60F_{254}, CH_2Cl_2:MeOH:C_6H_{14} (10:1:3)). UV-Vis (C = 6.08·10^{-5} M, DMF) λ_{max} nm (A): 278 (1.24), 293 (1.30), 330 (0.86), 387 (0.50). IR (KBr) ν cm^{-1}: 528, 563, 681, 721, 782, 910, 1027, 1152, 1202, 1276, 1384, 1474, 1523, 1593, 1653, 2925, 2957, 3374. Found, %: C 67.38; H 6.52; N 19.05. $C_{40}H_{38}N_{10}\cdot 3H_2O$ requires, %: C 67.40; H 6.22; N 19.65. *m/z* (MALDI-TOF, CHCA) Da: 659.4 [calcd. for $C_{40}H_{39}N_{10}^+$ $(M+H)^+$ 659.3], 681.4 [calcd. for $C_{40}H_{38}N_{10}Na^+$ $(M+Na)^+$ 681.3], 697.4 [calcd. for $C_{40}H_{38}N_{10}K^+$ $(M+K)^+$ 697.3]. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H ppm: 7.16–7.02 (m, 1H, CH_{ar}), 6.97 (dd, J = 18.1, 10.4 Hz, 1H, CH_{ar}), 6.85 (s, 1H, CH_{ar}), 3.25 (s, 1H, CH), 2.36 (d, J = *10.1* Hz, 1H, CH_2), 2.10 (s, 1H, CH_2), 1.46–1.38 (m, 3H, CH_3), 1.31 – 1.28 (m, 2H, CH_2), 1.13 (s, 3H, CH_3), 0.69 (s, 3H, CH_3).

5c: Yield: 0.15 g (21 %). R_f = 0.58 (silica gel 60F_{254}, CH_2Cl_2:MeOH:C_6H_{14} (10:1:3)). *m/z* (MALDI-TOF, CHCA) Da: 659.4 [calcd. for $C_{40}H_{39}N_{10}^+$ $(M+H)^+$ 659.3], 681.4 [calcd. for $C_{40}H_{38}N_{10}Na^+$ $(M+Na)^+$ 681.3], 697.4 [calcd. for $C_{40}H_{38}N_{10}K^+$ $(M+K)^+$ 697.3]. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H ppm: 7.09 (d, J = 17.8 Hz, 2H, CH_{ar}), 6.90 (s, 2H, CH_{ar}), 3.24 (s, 1H, CH), 2.35 (s, 1H, CH_2), 2.11 (t, J = 9.2 Hz, 1H, CH_2), 1.47–1.37 (m, 3H, CH_3), 1.28 (d, J = *15.6* Hz, 2H, CH_2), 1.13 (s, 3H, CH_3), 0.69 (s, 3H, CH_3).

*5,24:12,17-Diimino-7,10:19,22-dinitrilo-8H,20H(21H)-[c,m]-di(2,3-[(1'R,4'S)-(+)/(1'S,4'R)-(–)]-(**6a**),5,24:12,17-diimino-7,10:19,22-*



Scheme 1.

*dinitrilo-8H,20H(21H)-[c,m]-di(2,3-[(1'R,4'S)-(+)]-1',7',7'- **(6b)** and 5,24:12,17-diimino-7,10:19,22-dinitrilo-8H,20H(21H)-[c,m]-di(2,3-[(1'S,4'R)-(–)]-1',7',7'-trimethylbicyclo[2.2.1]heptano [2',3'-b]-pyrazino)-1,6,11,16-tetraazacycloeicosene-1,2,4,9,11,12, 14,19-octene (**6c**).* Microwave synthesis was carried out by the reaction of 0.1 g (1 mmol) of 1*H*-3,5-diamino-1,2,4-triazole **3** and 0.24 g (1 mmol) of **1a-c** at 170 °C for 20 minutes. The crude products were purified by column chromatography on silica gel (eluent mixture: dichloromethane:methanol:heptane 100:1:6). Products **6a–c** were obtained as orange powders after recrystallization from ethanol and drying under reduced pressure at 130 ºC for 4 hours.

6a: Yield: 0.05 g (16 %). R_f = 0.35 (silica gel 60F_{254}, CH_2Cl_2:MeOH:C_6H_{14} (10:1:3)). UV-Vis ($C = 6.95 \cdot 10^{-5}$, DMF) λ_{max} nm (A): 296 (1.50), 344 (1.50), 368 (1.08), 387 (0.94). IR (KBr) ν cm^{-1}: 544, 587, 666, 764, 818, 856, 954, 1064, 1164, 1220, 1267, 1457, 1543, 1662, 2923, 2962, 3298, 3421. Found, %: C 54.06; H 5.71; N 30.00. $C_{32}H_{32}N_{16} \cdot 5H_2O$ requires, %: C 52.59; H 5.79; N 30.67. *m/z* (MALDI-TOF, DHB) Da: 641.3 [calcd. for $C_{32}H_{33}N_{16}^+$ $(M+H)^+$ 641.3], 663.4 [calcd. for $C_{32}H_{32}N_{16}Na^+$ $(M+Na)^+$ 663.3], 679.4 [calcd. for $C_{32}H_{32}N_{16}K^+$ $(M+K)^+$ 679.3].

6b: Yield: 0.06 g (20 %). R_f = 0.36 (silica gel 60F_{254}, CH_2Cl_2:MeOH:C_6H_{14} (10:1:3)). UV-Vis (THF) λ_{max} nm: 286, 341, 359, 381. *m/z* (MALDI-TOF, DHB) Da: 641.3 [calcd. for $C_{32}H_{33}N_{16}^+$ $(M+H)^+$ 641.3], 663.4 [calcd. for $C_{32}H_{32}N_{16}Na^+$ $(M+Na)^+$ 663.3], 679.4 [calcd. for $C_{32}H_{32}N_{16}K^+$ $(M+K)^+$ 679.3].

6c: Yield: 0.07 g (21 %). R_f = 0.35 (silica gel 60F_{254}, CH_2Cl_2:MeOH:C_6H_{14} (10:1:3)). UV-Vis (THF) λ_{max} nm: 287, 340, 358, 381. *m/z* (MALDI-TOF, DHB) Da: 641.3 [calcd. for $C_{32}H_{33}N_{16}^+$ $(M+H)^+$ 641.3], 663.4 [calcd. for $C_{32}H_{32}N_{16}Na^+$ $(M+Na)^+$ 663.3], 679.4 [calcd. for $C_{32}H_{32}N_{16}K^+$ $(M+K)^+$ 679.3].

*5,24:12,17-Diimino-7,10:19,22-dinitrilo-8,20(21)-di(dodecyle)-[c,m]-di(2,3-[(1'R,4'S)-(+)/(1'S,4'R)-(–)]-1',7',7'-trimethylbicyclo[2.2.1]heptano[2',3'-b]-pyrazino)-1,6,11,16-tetraazacycloeicosene-1,2,4,9,11,12,14,19-octene (**7a**).* Microwave synthesis was carried out by the reaction of 0.27 g (1 mmol) of 1-dodecyle-3,5-diamino-1,2,4-triazole **4** and 0.24 g (1 mmol) **1a** at the temperature of 170 °C for 20 minutes. The crude product was purified by column chromatography on silica gel (eluent mixture: dichloromethane:methanol:heptane 200:1:3) and gel permeation chromatography Bio Beads S-X1 (chloroform). After drying at reduced pressure at 100 ºC for 4 hours, product **7a** was obtained as orange powder.

7a: Yield: 0.05 g (17 %). R_f = 0.91 (silica gel 60F_{254}, CH_2Cl_2:MeOH:C_6H_{14} (10:1:3)). UV-Vis ($C = 4.61 \cdot 10^{-5}$, DMF) λ_{max} nm (A): 349 (1.19), 371 (0.99), 393 (0.72). IR (KBr) ν cm^{-1}: 544, 659, 759, 859, 963, 1017, 1072, 1112, 1166, 1263, 1370, 1467, 1666, 2852, 2923, 2955, 3292, 3357. Found, %: C 66.73; H 9.12; N 22.39. $C_{56}H_{80}N_{16} \cdot 2H_2O$ requires, %: C 66.37; H 8.36; N 22.11. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 15.59 (m, 1H, NH), 4.15 (m, 2H, NH_{ar}), 3.18 (m, 1H, CH), 2.21 (m, 1H, CH_2), 1.81 (m, 1H, CH_2), 1.38 (m, 3H, CH_3), 1.30 (s, 2H, CH_2), 1.02 (s, 3H, CH_3), 0.82 (s, 3H, CH_3). *m/z* (MALDI-TOF, DHB) Da: 977.8 [calcd. for $C_{56}H_{81}N_{16}^+$ $(M+H)^+$ 977.7], 1000.9 [calcd. for $C_{56}H_{80}N_{16}Na^+$ $(M+Na)^+$ 1000.8].

Results and Discussion

Earlier it was established that the reactions of 2,6-diaminopyridine or 1,3-phenylenediamine with phthalonitrile or 4-*tert*-butylphthalonitrile by microwave irradiation ran under solvent-free protocol with essential reduction in synthesis duration from 8–12 h to 20 min.[25] So, the compounds **5a**–**c**, **6a-c** and **7a** were obtained by cross-over condensation of racemic mixture of **1a**, R-(+)- **1b** or S-(–)- **1c**-camphoradicyanopyrazine and *m*-phenylenediamine **2** (at 150 °C for 20 minutes) or 1*H*-3,5-diamino-1,2,4-

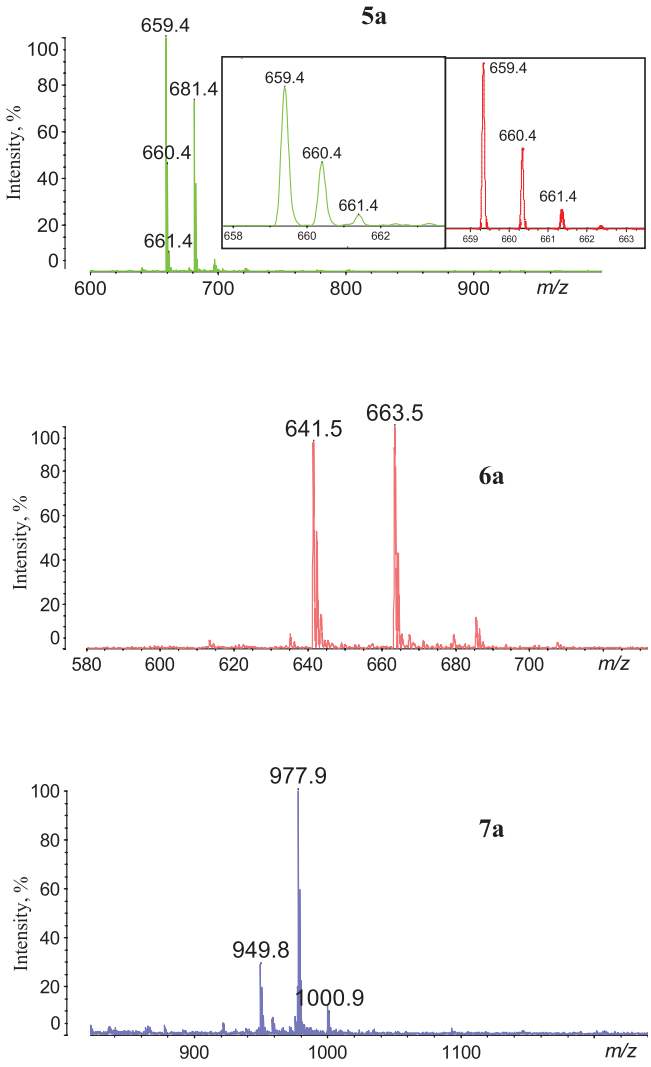


Figure 1. MALDI-TOF mass spectra of **5a** (spectrum (i) and its calculated isotopic distributions (ii)), **6a**, **7a** (DHB).

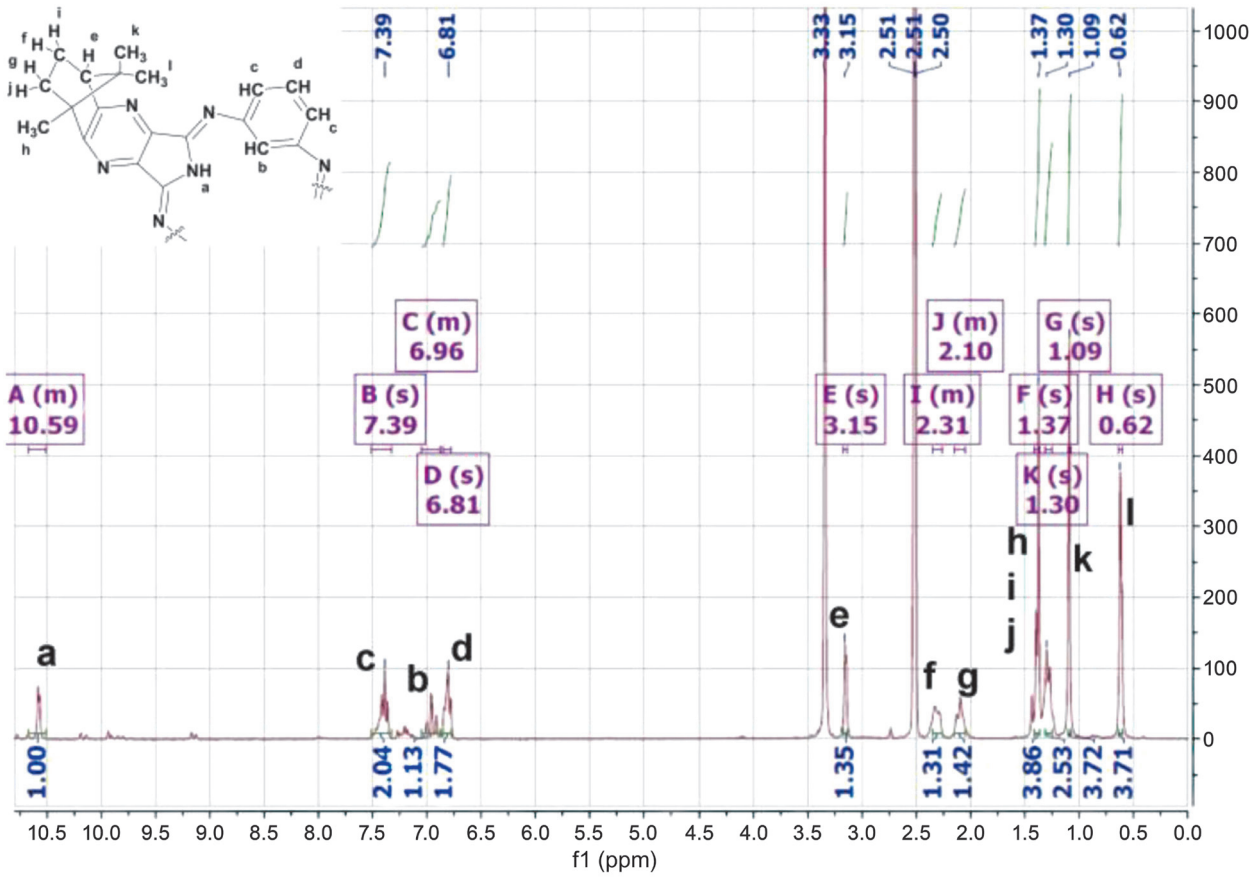


Figure 2. ^{1}H NMR spectrum of **5b** in DMSO-d_6.

triazole **3** or 1-dodecyl-3,5-diamino-1,2,4-triazole **4** (at 170 °C for 20 minutes) using the microwave system in open vessels following the solvent-free protocol (Scheme 1).

The crude products were purified by column chromatography on silica gel using the mixture: CH_2Cl_2:MeOH:C_6H_{14} (20:1:6) for **5a**–**c**, CH_2Cl_2:MeOH:C_7H_{16} (100:1:6) for **6a**–**c** and CH_2Cl_2:MeOH:C_7H_{16} (200: 1: 3) with final purification using gel permeation chromatography (Bio Beads S-X1, chloroform) for **7a** and finally recrystallization from ethanol for **5a**–**c**. All products were characterized by mass-spectrometry, UV-Vis, IR, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis data.

Based on the proposed synthetic scheme (Scheme 1), the resulting macroheterocycles are expected to be the mixtures of regioisomers which can differ by orientation of camphor fragments in **5–6 a–c** and **7a**, and mutual *cis*-/*trans*-orientations of H–N(1) or $C_{12}H_{25}$–N(1) groups in **6a–c** and **7a**. These mixtures could not be separated under the experimental conditions.

The peak at 659.4 Da in MALDI-TOF for **5a**–**c** (Figure 1) corresponds to $[M+H]^+$ ions. Good conformity of the calculated isotopic distributions with those taken from experimental data proves this assignment. The peak signal at 681.4 Da can be assigned to $[M+Na]^+$ ions.

In the MALDI-TOF mass spectra of **6a** and **7a**, along with the main peaks at *m/z* = 641.4 and *m/z* = 977.8 Da $[M+H]^+$, the peaks at *m/z*=663.4 and *m/z* = 999.7 Da, corresponding to the molecular ions with sodium $[M+Na]^+$ and peaks at *m/z* = 679.4 and *m/z* = 1015.7 Da corresponding to the molecular ions with potassium $[M+K]^+$ were detected (Figure 1). The peak at *m/z* = 948.8 Da of mass spectrum of **7a** corresponds to the molecular ion of undecyl-substituted triazolehemiporphyrazine and can be formed as a result of MALDI-TOF procedure.

The isomers **5a–c** revealed the same electronic absorption spectra within the region of 250–400 nm with characteristic maxima at 278, 293 and shoulders at 330, 387 nm (DMF at $C = 6.08 \cdot 10^{-5}$ M) which are consistent with observed for metal-free pyrazine containing hemiporphyrazine.[16] In the IR spectrum, bands of absorption were observed at 2960, 2927, 2871, 1477 and 1386 cm^{-1}, which were assigned to vibrations of the camphor fragments.[26] The bands at 3130 and 1577 cm^{-1} correspond to vibration of C-N bonds of pyrazine moieties.

In the ^{1}H NMR spectrum of **5b** (Figure 2), the singlets at 0.62, 1.09, 1.30 and 1.37 ppm induced by protons resonance of methyl groups of the camphor fragment are observed. Multiplets located at 2.10 and 2.31 ppm can be assigned to protons of methylene groups. The signal at 3.15 ppm corresponds to proton resonance of methyl group. The signals within the regions of 6.81–7.39 ppm are characteristic of proton resonance of 1,3-phenylene fragments. The signal at 10.59 ppm can be assigned to the protons of pyrrolic subunits.

The electronic absorption spectra of solutions of **5b** in ethyl acetate, chloroform, acetonitrile, tetrahydrofuran, methanol and dichloromethane are characterized by broadened intense bands with absorption maxima located at the region of

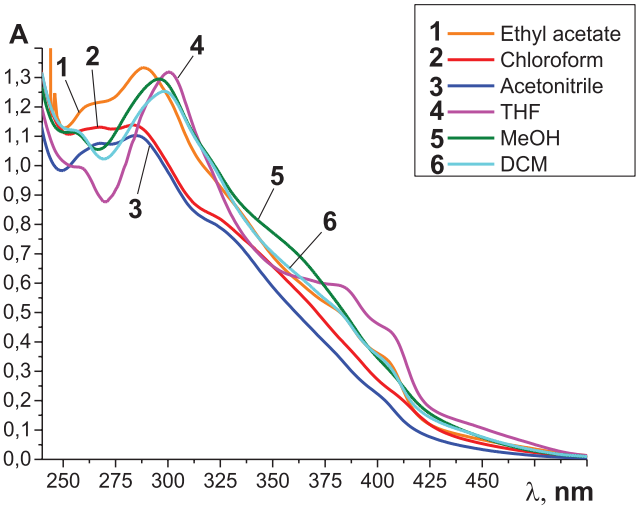


Figure 3. UV-Vis spectra of **5b** in ethyl acetate, chloroform, acetonitrile, THF, methanol and dichloromethane ($C = 3.4 \cdot 10^{-5}$ M).

250–400 nm, which correlates with the data published earlier for pyrazine-annulated carbahemiporphyrazine.[16]

A slight shift of the absorption bands to the long-wavelength region of UV-Vis spectrum was observed as solvents polarity decreases (Figure 3). So, a negative solvatochromic effect takes place,[27] which seems to be due to greater stabilization of the ground state compared with excited state induced by solvation when polar solvents are used.

Conclusions

In conclusion, we have been successful in the preparation of the first chiral bornane[2,3-b]pyrazino-fused carba- and triazolehemiporphyrazines by a crossover condensation of racemic, R-(+)- or S-(–)-bornane[2′,3′-b]-2,3-dicyanopyrazine and *m*-phenylenediamine, 1(H)- or 1-dodecyl-3,5-diamino-1,2,4-triazole. The racemic mixtures and the R-(+)- or S-(–)-enantiomers were characterized by mass spectrometry, UV-Vis, IR, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis data.

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