Synthesis and Properties of Macroheterocyclic Compounds of ABAB–Type with *tert*–Butylpyrrolepyrazine Fragments⊗

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New representatives of macroheterocyclic compounds of ABAB-type were synthezised by condensation of m-phenylenediamine or 2,6-diaminopyridine (A) with 5-tert-butyl-2,3-dicyanopyrazine (B) in ⁿBuOH. These compounds were characterizised by UV-vis, IR, ¹H NMR spectroscopies, mass-spectrometry and elemental analysis.

Keywords: Macroheterocyclic compounds, *m*-phenylenediamine, 2,6-diaminopyridine, 5-*tert*-butyl-2,3-dicyanopyrazine, hemiporphyrazine.

Introduction

Macroheterocyclic compounds (Mc) of ABAB-type can be represented as structural analogues of phthlocyanine, where two opposite isoindole moieties (B) are replaced by aromatic rings (A) derived from aromatic diamines. Since their discovery,[1] these compounds called by Campbel "hemiporphyrazines"[2] are the objects of continuous interest due to their structure particularities[3,4] as well as attractive properties revealed recently: optical limiting, fluorescence, catalysis, devices for keeping information and so on.[5-7]

For the moment a number of representatives of this series was synthesized,[8,9] but macrocycles containing pyrazine fragments (B) and those of six-membered aromatic diamines (A) are studied not enough completely. The first two representatives of nonsubstituted macroheterocyclic compounds of this type were described earlier.[10] These compounds were characterized by IR and UV-vis spectroscopies as well as elemental analysis data. Their serious imperfection is a low solubility in common organic solvents, what makes their refinement to be little tedious and constricts a number of methods which could be applied to study their structures and properties. It was established that introduction of bulky *tert*-butyl groups led to increase of solubility of Mc. [11] Hence the subject of this work is synthesis of Mc of ABAB-type bearing *tert*-butylpyrazine rings incorporated into macrocyclic core as units (B).

Experimental

General procedure. A mixture of 5-*tert*-butyl-2,3-dicyanopyrazine (1 mmol) and *m*-phenylenediamine or 2,6-diaminopyridine (1 mmol) in butanol (10 ml) was stirred at 80 ^{0}C for 6 h and then refluxed for 23 h. The solvent was removed under vacuum, and the crude product was washed with MeOH and then extracted with $CHCl_3$ in Soxhlet's apparatus. After solvent evaporation, the product was purified by column chromatography on silica gel ($CHCl_3$:MeOH:C_6H_{14} = 10:1:5). The solvents were removed and the solids were dried under vacuum.

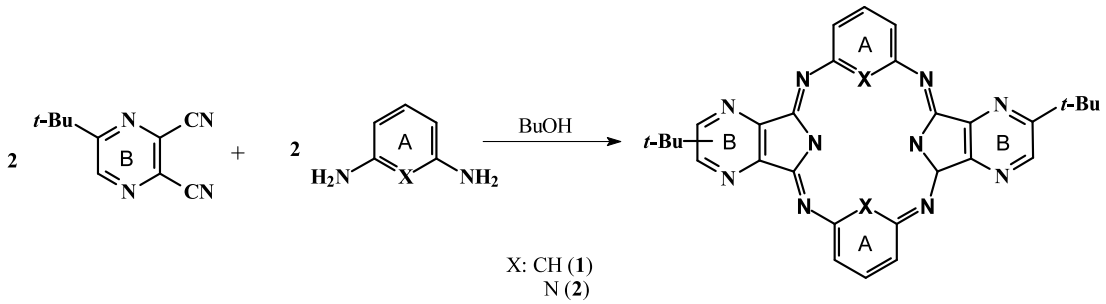
2,15-Di(tert-butyl)-5,26:13,18-diimino-7,11:20,24-dimetheno-[c,n]-dipyrazino-[1,6,12,17]-tetraazacyclodocosen-[1,3,5,7,9,12,14,16,21,23], ***1***. It was synthesized following the general procedure by interaction of 5-*tert*-butyl-2,3-dicyanopyrazine with *m*-phenylenediamine as a dark orange powder. Yield: 36 mg (26 %). UV-vis ($CHCl_3$) λ_{max} nm (lg ε): 361 (3.82), 383 (3.82). IR (KBr) ν cm^{-1}: 3424, 2922, 2852, 1636, 1464, 1254, 1157. MS (MALDI-TOF) *m/z*: 555 [$(M+H)^+$]. Found: C 68.51, H 5.34, N 25.17 %. $C_{32}H_{30}N_{10}$ requires C 69.30, H 5.45, N 25.25 %.

2,15-Di(tert-butyl)-5,26:13,18-diimino-7,11:20,24-dinitrilo-[c,n]-dipyrazino-[1,6,12,17]-tetraazacyclodocosen-[1,3,5,7,9,12,14,16,21,23], ***2***. It was synthesized following the general procedure by interaction of 5-*tert*-butyl-2,3-dicyanopyrazine with 2,6-diaminopyridine. The target product represents a dark red powder. Yield: 13 mg (9 %). UV-vis ($CHCl_3$) λ_{max} nm (lg ε): 379 (3.96), 425 (3.96). IR (KBr) ν cm^{-1}: 3327, 2927, 2856, 1746, 1640, 1465, 1250, 1165. ^{1}H NMR ($CDCl_3$) δ ppm: 15.09 (s., 2H), 8.9 (s., 2H), 7.6 (tr., 2H), 7.1 (d., 2H), 6.3 (d., 2H), 1.55, (18H, -C*H*$_3$). MS (MALDI-TOF) *m/z*: 556 [$(M+H)^+$]. Found: C 64.41, H 4.89, N 29.63 %. $C_{30}H_{28}N_{12}$ requires C 64.72, H 5.03, N 30.21 %.

Results and Discussion

A general way to gain access to the Mc of ABAB-type is the interactions of alkoxy- or diiminoisoindolines with aromatic diamines. But phthalonitrile itself and substituted phthalonitriles are able to react directly with diamines without previous transformation into corresponding isoindoline derivatives.[12,13] It is worthy to note that presence of nitrogen atoms in dicyanoconstituent makes this reaction easier to go.[13] So we succeed in synthezising of Mc **1, 2** by direct condensation of 5-*tert*-butyl-2,3-dicyanopyridine with 1.3-phenylenediamine or 2,6-diaminopyridine in ⁿBuOH.

⊗ This contribution is dedicated to professor Vasilij Fedorovich Borodkin on the occasion of his 100th Anniversary.
⊗ Статья посвящена 100-летнему юбилею профессора Василия Фёдоровича Бородкина.



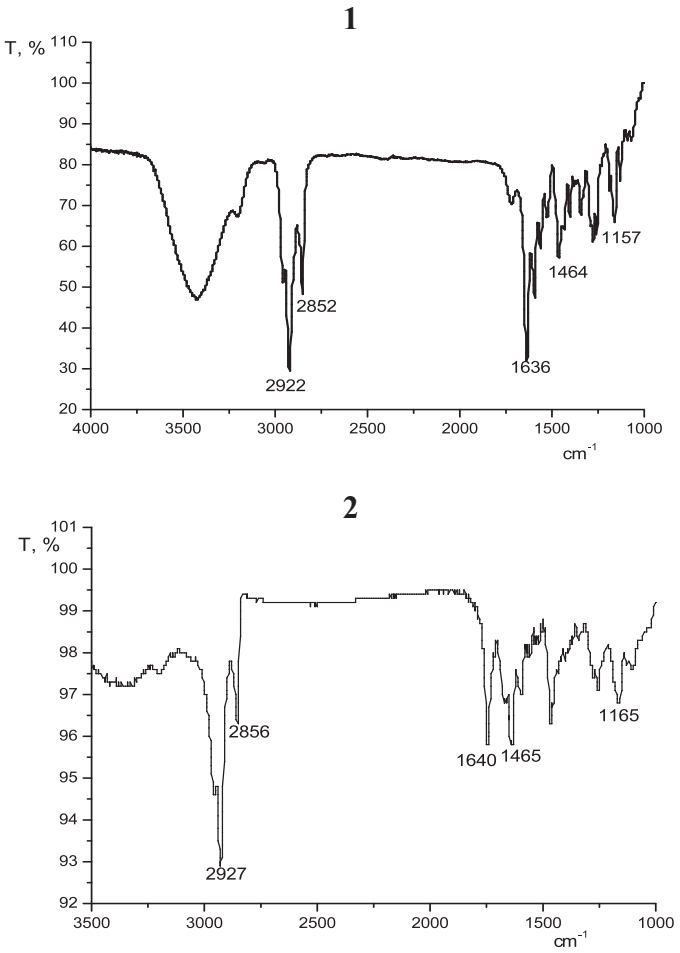


Figure 1. IR spectra of compounds **1** and **2.**

The reactions were monitored by TLC along with NH_3 separation. After solvent elimination, the residues were purified by extraction of topic products by $CHCl_3$ in Soxhlet extractor with following column chromatography using silica-gel.

The compounds **1, 2** were characterized by UV-vis, IR, ^{1}H NMR spectroscopies, mass-spectrometry, and elemental analisys.

The signals at 555 and 556 *m/z* which are in good agreement with molecular ions $[M+H]^+$ of **1** and **2** correspondingly were detected in MALDI-TOF. There are three groups of signals in the ^{1}H NMR spectra of **1** and **2**. So, in spectrum of **2**, two series of signals located at 0.8 – 1.8 and 6.0 – 9 ppm are induced by resonance of the protons of *tert*-butyl groups and those of aromatic systems correspondingly. The signals (~15 ppm) of **1** and **2** are due to the resonance of iminogroup protons and their position at a such low field shows that these compounds have no aromatic macrocycles at the base of their sceletons.

UV-vis spectra of **1** and **2** in chloroform contain the broad bands of absorbance with maxima located at 383 and 425 nm, correspondingly. A longer wavelength shift observed on going from **1** to **2** is most probably due to more plane structure of the central core of Mc **2** if compared with **1**.

IR-specra of compounds **1** and **2** (Figure 1) are very similar to each other. So, the strong bands at 2925 and 2855 cm^{-1} are due to the symmetric and asymmetric valance vibrations of C-H bonds belonging to *tert*-butyl groups. The bands at 1640 and 1465 cm^{-1} can be put in concordance with deformations of C=C and C=N bonds, correspondingly.

Conclusions

tert-Butylsubstituted azaanalogues of hemiporphyrazines were obtained by direct condensation of 5-*tert*-butyl-2,3-dicyanopyridine with *m*-phenylenediamine or 2,6-diaminopyridine in boiling *n*-butanol. Sufficiently high solubility in organic solvents allows to apply the column chromatography for their purification. Their structures were established on the base of UV-vis, IR, ^{1}H NMR spectroscopies, mass-spectrometry and elemental analisys data.

Acknowledgements. This work was supported by Federal Principal Program "Research and research-pedagogical staffs of innovative Russia for 2009-2013" (№ 02.740.11.0106).

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Received 10.11.2009
Accepted 15.03.2010
First published on the web 20.03.2010