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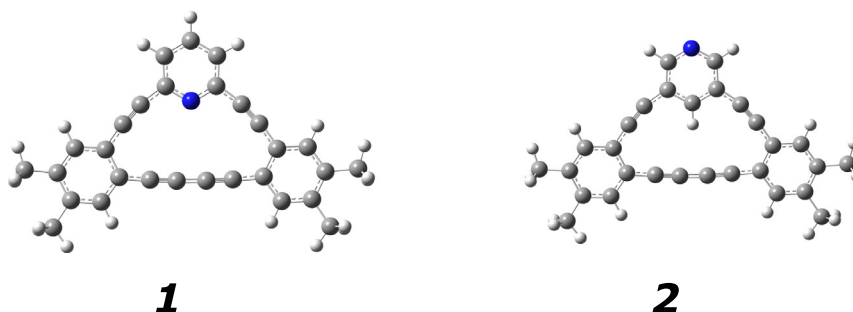
## Experimental and theoretical study of the cation binding properties of macrocyclic dehydrodibenzopyrido[15]annulenes

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## HIGHLIGHTS

- Dehydrodibenzopyrido[15]annulene protonation confirmed experimentally and theoretically.
- Inclusion of proton leads to significant thermal stabilization of dehydroannulene ring.
- The metal binding potential of dehydrodibenzopyrido[15]annulenes is greater than expected.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The UV/Vis titration measurements, vibrational and NMR spectroscopy of isomeric dehydrodibenzopyrido[15]annulenes (DBPA) **1** and **2** clearly show that under proper conditions these macrocycles can achieve fast, quantitative and unselective binding of metal ions. The macrocycle **1** is an example of a hindered amine 2,6-bis(R)pyridine and its isomer **2** of a non-hindered amine 3,5-bis(R)pyridine. The protonation stoichiometry for both **1** and **2** was assumed to be DBPA:H<sup>+</sup> = 1:1 and the formation constants logK = 4.77 ± 0.02 for **1**, and logK = 6.78 ± 0.08 for **2** were obtained that well agree with those obtained under similar conditions for a macrocycle containing bipyridine units. The protonation of **2** gave the estimated stoichiometry of 2:H<sup>+</sup> = 1:1 while the stoichiometric protonation of macrocycle **1** could not be achieved and the lower stability of the ion pair containing **1H**<sup>+</sup> is most likely due to the inaccessibility of the nitrogen atom of **1** to the counterions and solvent molecules. The structures and electronic absorption spectra of **1** and **2**, as well as the structures and spectra of **1H**<sup>+</sup> and **2H**<sup>+</sup>, i.e. the species formed by protonation of the pyridine nitrogen, were calculated with the time-dependent DFT method with a B3LYP functional and a 6-31+G(d) basis set. The solvent effects were incorporated by means of the polarizable continuum model (PCM). The agreement of the calculated absorption data for the parent and protonated species with the observed spectra is rather satisfactory. Vibrational IR and Raman spectra of **1**, **2**, **1H**<sup>+</sup> and **2H**<sup>+</sup> in vacuo were calculated at the B3LYP/cc-pVTZ level of theory. Macrocycles **1** and **2**, and their products protonated by trifluoromethanesulfonic acid (**1HOTf** and **2HOTf**) were also characterized by temperature-dependent FTIR technique known as two dimensional IR correlation analysis. Quite large difference in degradation temperature between macrocycle **1** and **2** and their protonated complexes was measured, indicating that inclusion of proton leads to significant thermal stabilization of dehydroannulene ring.

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## Introduction

Dehydroannulene macrocycles have been attracting attention due to their remarkable conjugated π-electron system

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encompassing a ring cavity up to several nanometers size. By combining such an annulenic core ring with arene groups, one can obtain shape-persistent macrocycles with vast biological, chemical and physical potential. Therefore, facilitated by the synthetic accessibility of acetylenic compounds the chemistry of dehydroannulenes rapidly expanded in the last decade. Many experiments showed that these macrocycles have the capacity of forming carbon-rich polymers and also unusual electronic, magnetic and photonic materials [1,2].

A new group of compounds known as dehydrobenzopyridoannulenes (DBPA) are dehydroannulene macrocycles that incorporate azaarene units [3–7]. Due to the presence of nitrogen atoms they are expected to serve as receptors for various species, above all for metal ions. The selective recognition and binding can hopefully be fine tuned having in mind that the prevailing factors in complexation of such macrocycles with metal ions are: (1) the position of nitrogen atoms of the azaarene unit that can be endoannular or exoannular with respect to the annulenic ring and (2) the annulenic ring size. The complexation of macrocycles with outer N-atoms could lead to metal-ion induced supramolecular assemblies with the final result in the form of carbon-rich 2D networks [8]. The extended conjugation of the central ring in such annulenes might also serve as an electron delocalization pathway, as already seen in donor/acceptor functionalized dehydrobenzoannulenes [9–14]. As a result, materials incorporating metal-ion complexes of arene-azaarene dehydroannulenes are predicted to display utilizable properties such as electrochemical, photochemical, magnetic, optical, catalytic, mechanical and sensory abilities. Despite the fact that only a few of arene-azaarene dehydroannulenes were fully characterized and tested to metal binding properties [15–20], review articles on these macrocycles have already appeared due to wide interest [1,2,21,22].

In continuation of our research regarding dehydroannulenes [9], we report here on the spectroscopic and theoretical characterization of an isomeric pair of dehydrodibenzopyrido[15]annulenes **1** and **2** (Scheme 1). The same ring moiety but functionalized with  $-t\text{-Bu}$  and  $-\text{NBu}_2$  groups were first synthesized by Haley et al. [23,24]. The compounds **1** and **2** are here considered as potentially good candidates for a thorough metal-binding study of the whole group of arene-azaarene dehydroannulenes because they have: (1) quite small and hence possibly selective central cavity, (2) shape persistent property, and (3) only one preferential binding place (a pyridine nitrogen with its lone pair of electrons). The

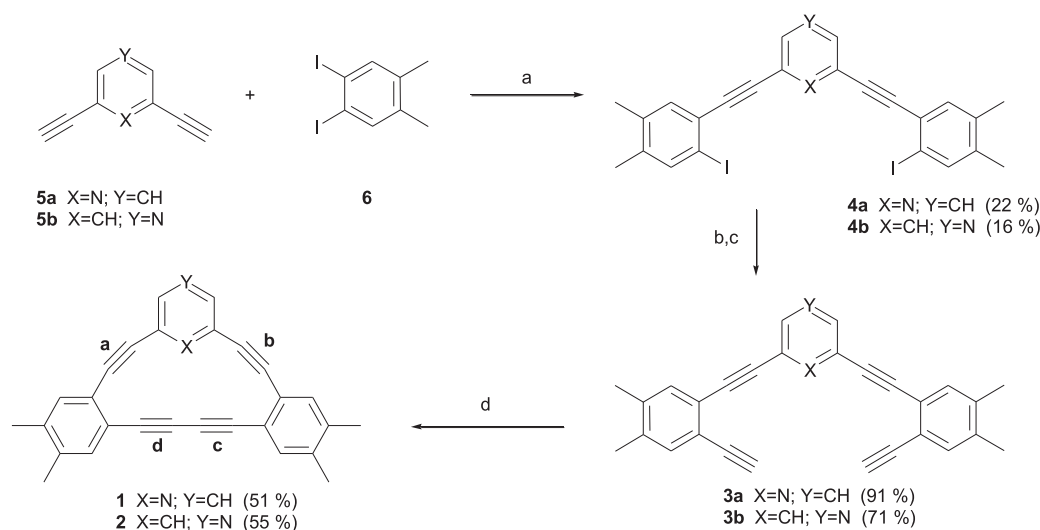
pyridine-containing macrocycles can have abilities to serve as host molecules and accommodate a guest molecule by hydrogen bonds. Although the importance of investigation of isomeric dehydropyridoannulenes is generally acknowledged, this work presents the first systematic attempt to clarify differences in ion-binding properties within an endoannular–exoannular isomeric pair. The study covered the UV/Vis, NMR and IR spectroscopic responses of **1** and **2** to protons and metal ions, including measurements in the solid state. The study revealed the crucial role of solvent media on the ion-binding properties of the DPBAs. The special emphasis has been given to the protonation of **1** and **2**. The possibility of  $1\text{H}^+$  being a case of proton complexation with a proton hydrogen-bonded to the  $\pi$ -systems of the  $\text{C}\equiv\text{C}$  bonds has been examined. Such a complex is certainly expected to have quite a different vibrational spectrum than any of the monomers. Vibrational analysis of dehydrodibenzopyrido[15]annulenes can hopefully be used as a reference when interpreting the spectrum of the complex. The results and the interpretation thereof related to metal cations are part of the [Supplementary Information \(SI\)](#) in order to enable more focused and detailed description of the macrocycle protonation.

## Experimental

### Synthesis

Synthesis of compounds **1** and **2** is based on unimolecular homocoupling reaction between terminal alkynes. Sonogashira reaction of 2:1 stoichiometric amounts of diyne **5a** and diiodide **6** gave diiodide **4a**, as well as larger diiodide with two pyridyl and three phenyl groups. This method was selected due to ease of separation of these two compounds, which are both valuable precursors for DBPAs. Once diiodide **4a** has been obtained, the subsequent synthesis was quite simple with Sonogashira reaction of **4a** with ethynyltrimethylsilane, desylation to **3a** and finally Eglinton oxidative homocoupling of diyne resulting in macrocycle **1**. Likewise, starting with **5b**, and through **4b** and **3b**, we obtained macrocycle **2**.

Ring closure of **3a** and **3b** to **1** and **2**, respectively, creates characteristic spectroscopic features in the spectra of **1** and **2**. The most noticeable are the disappearance of the acetylenic  $-\text{C}\equiv\text{C}-\text{H}$  stretching vibration at around  $3280\text{ cm}^{-1}$  in the IR spectra, twofold increase of the UV/Vis molar absorption coefficients at  $\lambda_{\text{max}}$  that is downshifted by 13 nm in both cases (from 253 nm to 230 nm) and



**Scheme 1.** Synthesis of DBPAs **1** and **2**: (a)  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ ,  $\text{CuI}$ , DIPA,  $55\text{ }^\circ\text{C}$ ; (b)  $(\text{CH}_3)_3\text{SiC}\equiv\text{CH}$ ,  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ ,  $\text{CuI}$ , DIPA,  $\text{CH}_2\text{Cl}_2$ ,  $50\text{ }^\circ\text{C}$ ; (c)  $\text{NaOH}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{MeOH}$ ; (d)  $\text{Cu}(\text{OAc})_2$ , pyridine.

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