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Research paper

Theoretical study of a novel imino bridged pillar[5]arene derivative

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ABSTRACT

In this paper, we report a novel imino bridged pillar[5]arene derivative (**P5N**) for the first time. Four conformers (**P5N0**, **P5N1**, **P5N12**, and **P5N13**, arising due to the different orientation of N—H bond of imino bridging group) are obtained by quantum chemical calculations at the CAM-B3LYP/6-31+G(d,p) level of theory. The geometries, energies, electronic structures, and absorption spectra of **P5N** conformers as well as pillar[5]arene (**P5**) are discussed in detail. The inclusion complexes of paraquat (**Pq**) with **P5N** and **P5**, respectively, are also obtained at the same level of theory. Compared to **P5**, **P5N** exhibits better performance in inclusion complexation toward **Pq**.

1. Introduction

As the new generation of supramolecular macrocyclic compounds, pillararenes have drawn great attentions in recent years [1–5]. Pillararenes are predicted to have application potentials in various areas such as supramolecular chemistry, materials science, and biomedicine [6]. Because of their rigid, columnar molecular skeleton, pillararenes can accommodate a number of guest molecules and cations within their pillar-shaped cavity with high selectivity [7,8]. To expand the application scope and improve application ability of pillararenes, a variety of chemical modifications are very important at the present stage. Therefore, the design, synthesis and characterization of novel pillararenes and their position-selective functionalization are the hot topic currently.

As may be seen in Scheme 1, there are three possible active sites of derivatization in the pillararene (**P[*n*]**) skeleton, (**a**) alkoxy group, (**b**) hydrogen on the benzene ring, and (**c**) bridging methylene. Most of derivatization of pillararene focuses on site (**a**) [9–14], a few cases on site (**b**) [15]. As far as we know, no derivatization on (**c**) maybe due to some difficulty in experimental synthesis. Theoretically, the derivatization on site (**c**) could fine-tuning the size of the pillararene cavity, affect the electronic properties of cavity, and finally affect the host-guest chemistry so that the supramolecular assemblies and applications of pillararene. Here, we want to report theoretically the first nitrogen heteroatom bridged pillararene, namely imino bridged pillar[5]arene (**P5N**), by using quantum chemical calculations.

Imino group is an isoelectronic species with methylene, and the replacement of methylene bridges by imino groups will not cause the collapse of the pillar[5]arene framework. Depending on the different orientation of N—H bond on imino bridges, **P5N** possess four conformers in sum (**P5N0**, **P5N1**, **P5N12**, and **P5N13**) (Fig. 1). In the case of **P5N0**, the orientations of five N—H bonds are all the same. One N—H bond is different from the other four ones in **P5N1**. Two adjacent and spaced N—H bonds are different from the other three ones in **P5N12** and **P5N13**, respectively. The electronic structure, relative stability as well as host-guest interactions of the four conformers may differ from each other. Moreover, the main differences on structure and properties between **P5N** and pillar[5]arene (**P5**) are very necessary to experimentally synthesize and characterize the novel pillar[5]arene derivative. The aim of this study is to characterize theoretically the structure and properties of **P5N** and exploring its potential applications based on host-guest interactions in supramolecular chemistry. As comparison, the structure and properties of **P5** are also presented in this work. The computational investigation into the first heteroatom bridged pillar[5]arene will be very important for the development of pillar[n]arene chemistry. The calculation results in this work will provide theoretical guidance for the synthesis and application of new pillar[n]arenes in the future.

2. Theoretical and computational details

Geometry optimization without symmetry constraints and then harmonic frequency calculations (no scaling) of the optimized structures are performed at the CAM-B3LYP method [16] along with 6-31+G(d,p) basis set. In order to verify the reliability of

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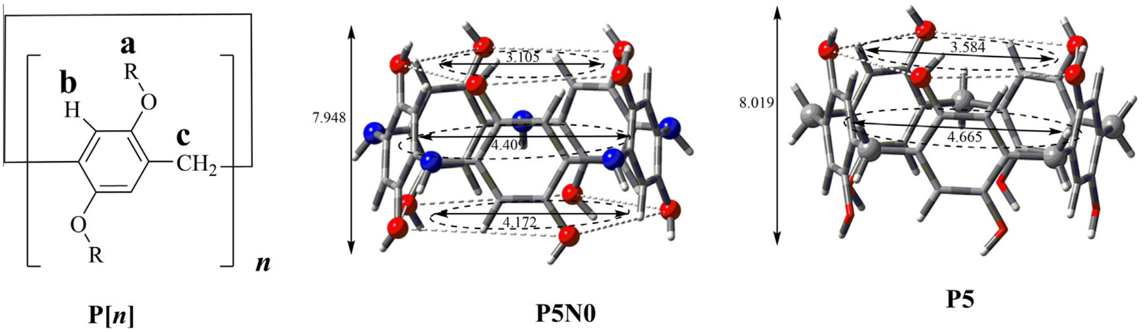

Scheme 1. Three active sites (a, b, and c) of derivatization of pillar[*n*]arene (**P[*n*]**), molecular skeletons of the imino bridged pillar[5]arene (**P5N0**) and pillar[5]arene (**P5**) along with the cavity diameter and height (distance in Å).

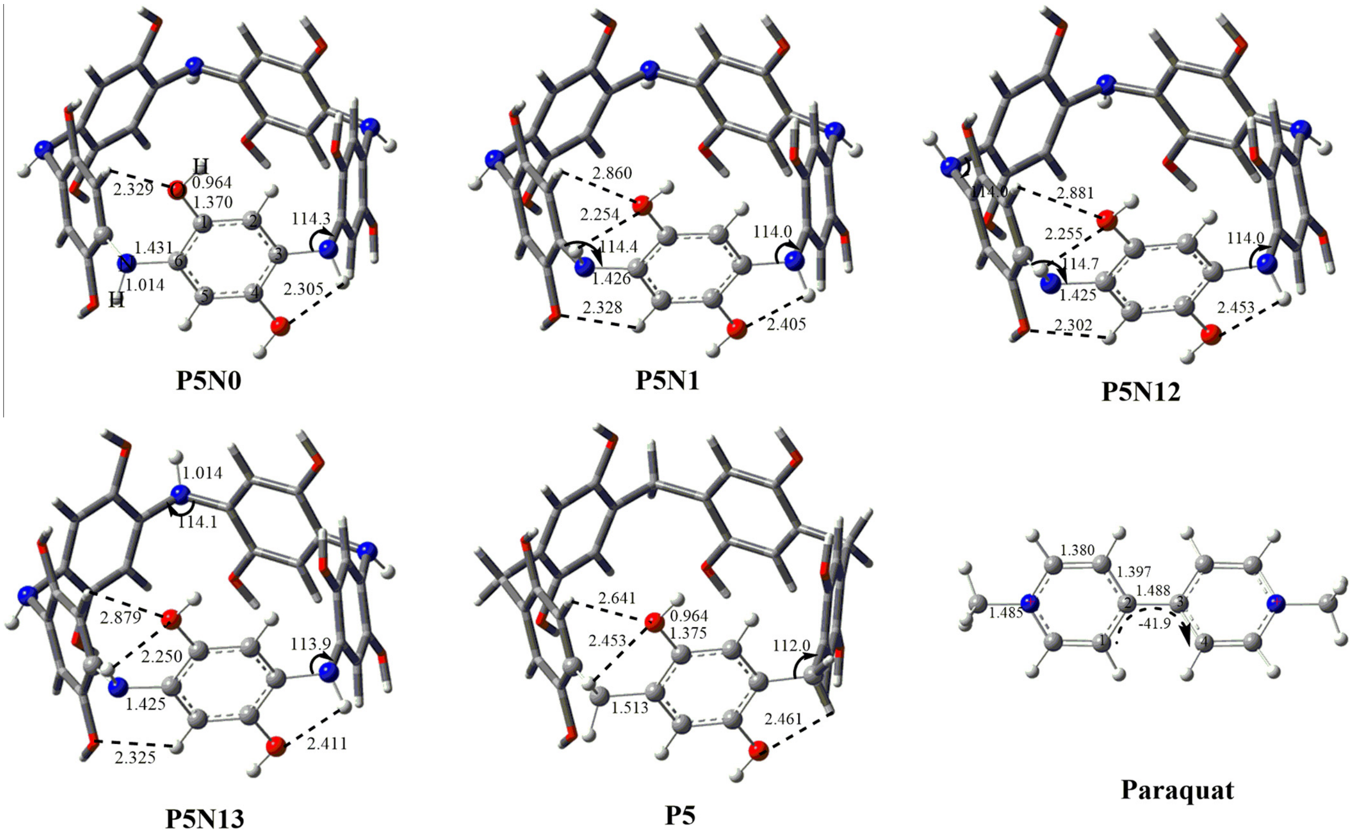

Fig. 1. Optimized geometries of four conformers of **P5N** (**P5N0**, **P5N1**, **P5N12**, and **P5N13**) as well as pillar[5]arene (**P5**) and Paraquat (**Pq**) calculated at the CAM-B3LYP/6-31+G(d, p) level of theory (bond length in Å and bond angle in degree).

CAM-B3LYP/6-31+G(d, p) calculation results, the CAM-B3LYP/6-311+G(2d, p) single-point calculations on CAM-B3LYP/6-31+G(d, p) optimized structures (denoted as CAM-B3LYP/6-311+G(2d, p)//CAM-B3LYP/6-31+G(d, p)) and the M06-2X/6-31+G(d, p) [17] re-optimizing for four P5N conformers are also performed. To understand the electronic features, the natural bond orbital (NBO) [18] analysis is carried out at the same level of theory for all optimized structures. Time-Dependent Density Functional Theory (TDDFT) [19] calculations at CAM-B3LYP/6-311+G(d, p) level of theory are carried out on optimized structures to obtain the absorption spectra [20,21]. All calculations are performed using Gaussian 09 suite of programs [22]. The UV–vis absorption spectra are derived from the SWizard program (revision 4.6) [23], in Gaussian line shape with a half-bandwidth of 3000 cm^{-1} (a typical half-bandwidth value for the molecules under consideration) [24].

3. Results and discussion

3.1. Geometry and energy analysis

The optimized structures of four **P5N** conformers obtained at the CAM-B3LYP/6-31+G(d, p) level of theory are given in Fig. 1 as well as selected hydrogen bond distances. Compared with the columnar pillar[5]arene (**P5**), strictly speaking, **P5N0** has a truncated cone shape possessing D_5 symmetry (Scheme 1). The intramolecular N—H⋯O hydrogen bonds (HBs) are formed between the NH group and phenolic hydroxyl in **P5N0** structure. The C—H⋯O HBs formed between benzene ring and phenolic hydroxyl surround the top and bottom rims. This HB framework stabilizes **P5N0** molecule. When one N—H bond turns to another orientation, the **P5N1** conformer forms with slightly structural