



Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Deltaarenes; novel macrocyclic molecules that are readily available from 1,4-benzoquinone and benzene dithiols

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ARTICLE INFO

Article history:

Received 1 March 2018

Received in revised form

18 April 2018

Accepted 20 April 2018

Available online xxx

Keywords:

Host-guest compounds

Supramolecular chemistry

Macrocyclization

Oxidative coupling

2-Sulfanyhydroquinone dimers

ABSTRACT

New types of macrocyclic compounds, deltaarenes, are prepared. The compounds were readily synthesized in three steps from an arenedithiol and benzoquinone, and the yields of the macrocyclization reaction reached up to 40% under high dilution conditions. X-ray crystallographic analysis revealed that the macrocycle has a relatively rigid trimeric structure with a unique triangular hole, the size of which was approximately 11 Å along each side. NMR data suggests that the ring has a C₃-symmetric structure. The X-ray analysis showed that the hole is large enough to capture one molecule of chlorobenzene. Use of a variety of dithiols allowed the synthesis of different types of deltaarene derivatives. MO calculations showed that the hole size depends on the dithiol unit. Deprotection of the twelve methoxyl groups was easily achieved by treatment with BBr₃ and yielded the free-OH deltaarene derivative.

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1. Introduction

Macrocyclic compounds have been of interest to organic chemists for their potential use as host molecules in supramolecular chemistry [1]. For example, cyclodextrins [2], crown ethers [3], calixarenes [4], and cyclophanes [5] have all played significant roles in the field. Recently, pillararenes, developed by Ogoshi and his coworkers, have opened new development in this field of chemistry [6]. Although there have been many reports on host-guest chemistry using various macrocyclic hosts, it is still desired to develop a new types of macrocyclic compounds that possess new and different physical and chemical properties.

Recently, we have successfully developed the chemistry of 2-sulfanyhydroquinone dimers that serve as new water-soluble fluorescent materials [7]. The compounds are readily prepared in three steps from commercially available 1,4-benzoquinone and thiols on the multi-gram scale, and their derivatization is easily achieved. During the course of our investigation, we wondered what compounds would be formed if the synthetic sequence

started from a dithiol instead of a simple thiol. With this question in mind, we started to examine the use of benzenedithiols and found that a new type of macrocyclic compound was readily prepared. In this paper, we report the synthesis and derivatization of novel macrocycles, deltaarenes, which have a unique C₃-symmetric triangular structure and a relatively large hole in the molecule.

2. Results and discussion

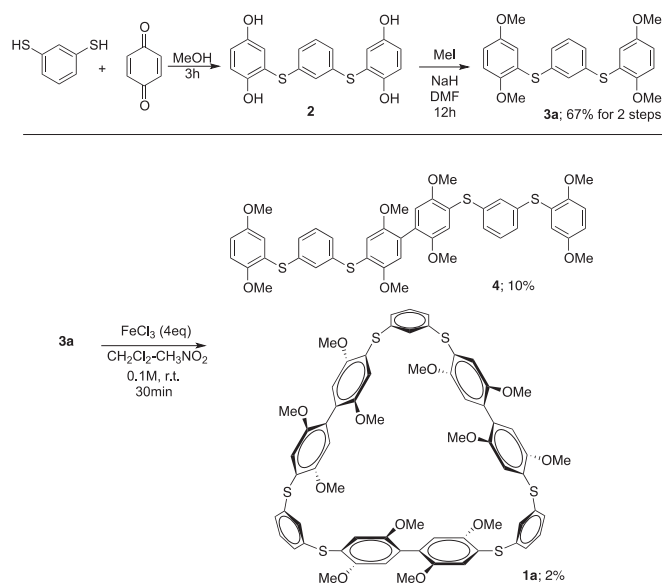
We firstly prepared the *m*-deltaarene **1a**, starting from the commercially available *m*-benzenedithiol and 1,4-benzoquinone (Scheme 1).

Treatment of *m*-benzenedithiol with two equivalents of 1,4-benzoquinone resulted in the formation of the 1:2 adduct **2a**, which was converted to the *O*-methylation product **3a** in 79% yield by simply protecting the four phenolic hydroxyl groups. We then examined the oxidative coupling reaction of **3a** by treatment with FeCl₃ (Scheme 1) [8]. The oxidative coupling reaction consumed all of the precursor **3a** smoothly, and we isolated two products from the reaction mixture by careful flash column chromatography.

One product, compound **4**, was obtained in 10% yield and showed 18 peaks in the aromatic region in its ¹³C NMR spectrum. The ESI-TOF mass spectrum of **4** showed the parent peak at

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Scheme 1. Preparation of *m*-deltaarene **1a**.

849.1660, supporting molecular formula of compound **4** as $C_{44}H_{42}O_8S_4$. These results clearly suggest that compound **4** is a linear dimer of the precursor **3a**. Since this type of coupling always progresses in a highly regioselective manner, we concluded the coupling only occurs at the para-position to the sulfur atom [7]. On the other hand, the other product, compound **1a**, was obtained in only 2% yield. It showed only 10 peaks in the aromatic region of its ^{13}C NMR spectrum, which clearly suggests that the compound has a very symmetrical structure. An ESI-TOF peak appears at 1259.2307, which suggests that the product is a cyclic trimer of precursor **3a**. Fortunately, compound **1a** gave good crystals from chlorobenzene-isopropanol solvent system, and its X-ray crystallographic analysis indicated that compound **1a** has a C3-symmetrical macrocyclic trimeric structure (Fig. 1) [9].

The structure of **1a**, was as expected, a cyclic trimer of compound **3a**, that is almost equilateral-triangular in shape with a relatively large central cavity. The three vertices of the triangle consist of the *m*-benzenedithiol units, and the biaryl units are positioned along the three sides. The distances between the C2 positions of the three *m*-benzenedithiol units were estimated to be 11.592, 11.671, and 11.892 Å, respectively. One chlorobenzene solvent molecule was located in the central hole. These results suggest that this new macrocyclic molecule has the possibility to act as a host molecule, which can encapsulate a small molecule. The benzene rings of the *m*-dithiol unit are tilting towards the inside of the hole. In the solution phase, all three biaryl units should be twisted in the same configuration, which fosters the C3 symmetric property of the molecule. This is strongly supported by the fact that only 10 peaks in the aromatic region of the ^{13}C NMR spectrum of compound **1a** were observed.

We have also obtained another crystal structure of **1a** from a different solvent system, hexane-EtOAc [10]. The obtained structure is shown in Fig. 2. Compound **1a** in this crystal includes one molecule of EtOAc in the central hole. Hence, the conformation of **1a** was slightly different to the structure obtained from chlorobenzene-isopropanol, shown in Fig. 1. For example, the crystal structure does not have C3 symmetry, as all of the benzenedithiol units were tilting in different ways. These results suggest that the structure of the macrocyclic trimer **1a** is relatively flexible, and the central space can adjust to fit a range of guest molecules.

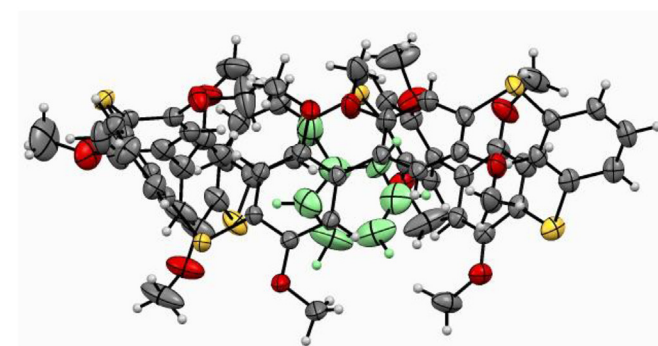
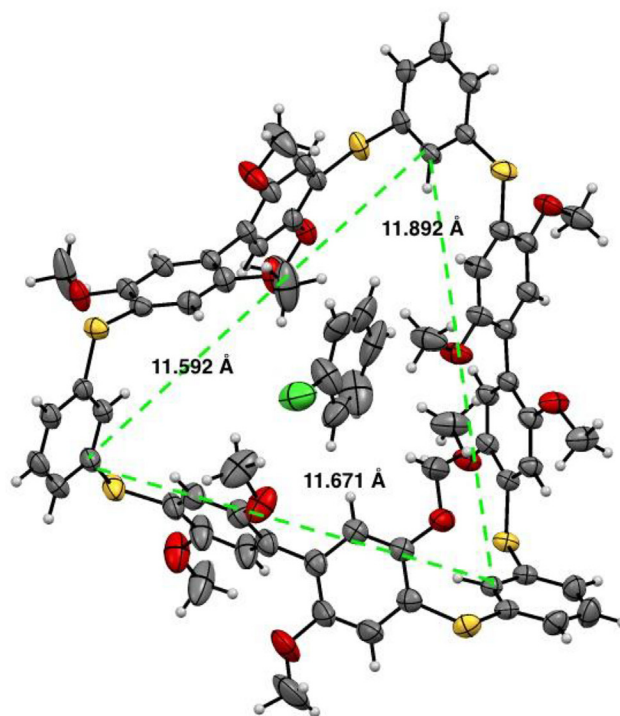


Fig. 1. Top-view (above) and side view (below) of X-ray structure of deltaarene **1a** crystallized from chlorobenzene-isopropanol (solvent molecules have been deleted except for one chlorobenzene shown in the cavity). Chlorobenzene in the side view is colored in light green.

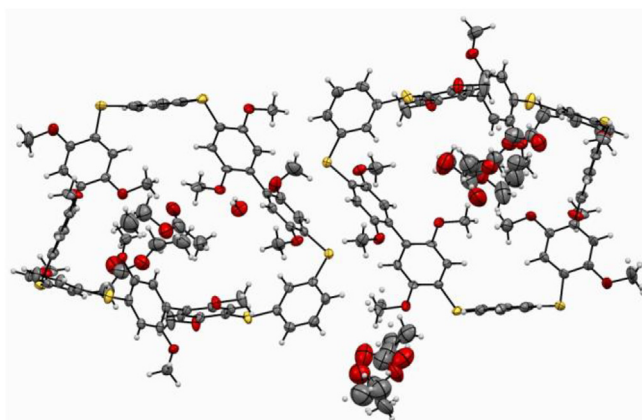


Fig. 2. X-ray structure of deltaarene **1a** crystallized from EtOAc-hexane.

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