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A computational study of sulfur bridged cyclooctatetraenophanes

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Abstract

Calculations of several thiacyclooctatetraenophanes predicted, as part of their overall geometry, substantial flattening of the cyclooctatetraene (COT) structures relative to the tub conformation generally associated with the COT molecule. The COT structures were approximately parallel to each other and the interplanar distances were predicted to be within 2.787–2.803 Å at the DFT/UB3YLP level of calculation. DFT/UB3LYP optimized geometries afforded significant delocalization of the COT structures in each of the thiacyclooctatetraenophanes. Hartree–Fock (HF) methods and the semi-empirical Austin Model 1 (AM1) method deviated significantly from the DFT/UB3LYP optimized geometries. Cyclooctatetraenes can undergo reversible sizing by oxidation and reduction reactions to form the aromatic dication and aromatic dianion, respectively, which could then be used to prepare molecular backbones for polymeric organometallic molecular wires. The number of bridges and the introduction of the sulfur atom have been investigated to provide disparate synthetic routes.

Keywords: Cyclooctatetrene; Cyclophanes; B3LYP; Hartree–Fock; Semi-empirical; Delocalization

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1. Introduction

The ground state geometry for COT is a D_{2d} tub-shaped conformer with alternating single (1.43 Å) and double bonds (1.33 Å) [1]. It undergoes a variety of dynamic processes such as ring inversion, bond shifting and a plethora of isomerizations [2]. These processes make COT a mechanistically interesting molecule to study. The commonly recognized transition state for the process of ring inversion is a planar localized structure with D_{4h} symmetry [3–6] while the bond shifting mechanism passes through a transition state with D_{8h} symmetry [4–7].

A great deal of interest has been recently reported concerning 8π cyclic systems [8–13] and planar cyclooctatetraenes [3,14–16]. Isolation and characterization of perfluorotetracyclobutacyclo-octatetraene [17a–c] and Komatsu et al. synthesis of a planar cyclooctatetraene annelated with bicycle[2.1.1]hex-2-ene [18,19] are the best synthetic examples of proposed [20,21] planar delocalized diradicaloid cyclooctatetraenes. However, these synthesized cyclooctatetraenes utilize small annelating rings [18] to advance planarity. Although some delocalization occurs as shown by X-ray analysis [17a] of its bond lengths, small ring effects inhibit bond shifting in the planar COT derivatives. Therefore, it would be advantageous to construct a molecule with a geometry that has the propensity to be planar but does not suffer from these ring effects. We previously investigated the annelating effects on 4π cyclic systems [22] and herein extend these tools to 8π cyclic systems.

The thiacyclooctatetraenophanes **1**–**5** (Fig. 1) were investigated for the flattening and delocalization of their COT rings and interplanar distances between these rings. Several two-deck systems have been previously synthesized to investigate cyclophanes. Paquette and Kesselmayer [23] two-deck $[2_2](1,5)$cyclooctatetraenophane was synthesized from [6.3.3]-propellenediones and as expected, the COT units were in tub conformations. Two additional two-deck systems by Garbe and Boeckelheide [24] $[2_2](1,6)$cyclooctatetraenyl(1,4)cyclophane and $[2_4](1,2,5,6)$cyclooctatetraenyl(1,2,4,5)cyclophane, were found to have the familiar tub conformation as well.

The electron-rich cyclooctatetraenophanes molecules proposed herein will provide COT moieties with a high degree of flattening and delocalization. The purpose of this study is to find synthetically viable cyclooctatetraenophanes to be used as molecular wire backbones. Sansores and co-workers [25,26] provided several theoretical examples of superphanes with ring sizes

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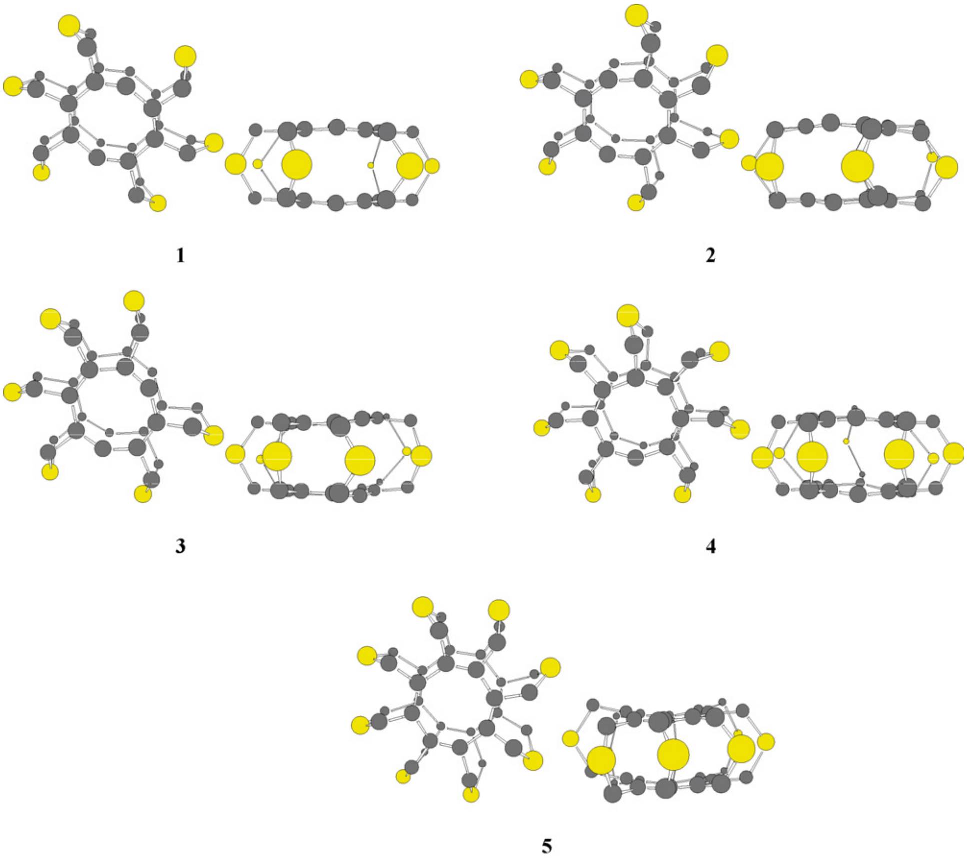

Fig. 1. Top and side views of DFT/B3LYP (6-31G(d,p)) optimized geometries for the thiacyclooctatetraenophanes (**1**–**5**).

from 3 to 7 adapting symmetric geometries and suggested their use as molecular wires. However, these superphanes are all synthetically difficult to prepare [25,26]. The cyclooctatetraenophanes investigated in this article possess sulfur bridges that provide an accessible entry to their assemblage. $[3_6]$(1,2,3,5,6,7)-Hexathiacyclooctatetraenophane **1**, exo-$[3_6]$(1,2,3,4,6,7)-hexathiacyclooctatetraenophane **2**, endo-$[3_6]$(1,2,3,4,6,7)-hexathiacyclooctatetraenophane **3**, $[3_7]$(1,2,3,4,5,6,7)-heptathiacyclooctatetraenophane **4** and $[3_8]$(1,2,3,4,5,6,7,8)-octathiacyclooctatetraenophane **5** vary in respect to the number and location of these sulfur bridges.

2. Methodology

The relative flattening (F_r) of each individual COT structure with respect to the tub conformation was calculated by first summing the absolute values of each bonded dihedral angle in the ring. Each bonded dihedral angle in the COT structures for **1**–**5** was measured and assigned to the variable D_{phane_i}, where $i = 1, 2, \ldots, 8$ and corresponds to the first carbon atom in the four carbons involved in the dihedral angle. The summation of the absolute values of the bonded dihedral angles was then:

$$\sum_{i=1}^{8} |D_{\mathrm{phane}_i}| = D_{\mathrm{phane}}$$

The same procedure was also performed on a COT molecule such that:

$$\sum_{i=1}^{8} |D_{\mathrm{cot}_i}| = D_{\mathrm{cot}}$$

The relative flattening could then be defined as:

$$F_r = \frac{D_{\mathrm{phane}}}{D_{\mathrm{cot}}}$$

Arithmetic mean values for the interplanar distance for each structure were calculated by averaging the distances between the corresponding atoms in the upper and lower rings. Standard deviations were calculated utilizing the biased standard deviation formula. The standard deviation of the interplanar distances for each compound gave an indication of the planarity of stacking since the individual rings were ostensibly flattened.

Semi-empirical Austin Model 1 (AM1) [27] and ab initio calculations at the levels RHF/6-31G(d) and RHF/6-31G(d,p) were performed using Spartan '04 Windows [28] and Gaussian '03 [29]. Density functional theory (DFT) [30] calculations employed the B3LYP method [31,32] with the 6-31G(d,p) basis set. All cyclooctatetraenophanes were optimized beginning from tub-shaped COT conformers. All structures were determined to be energetic minima from frequency calculations.