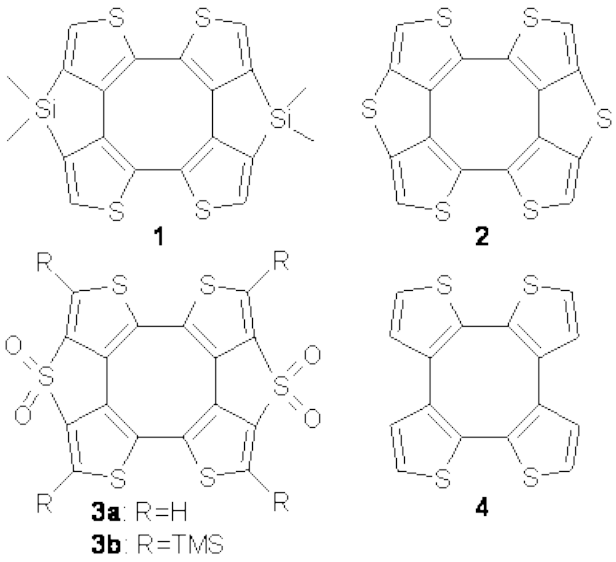
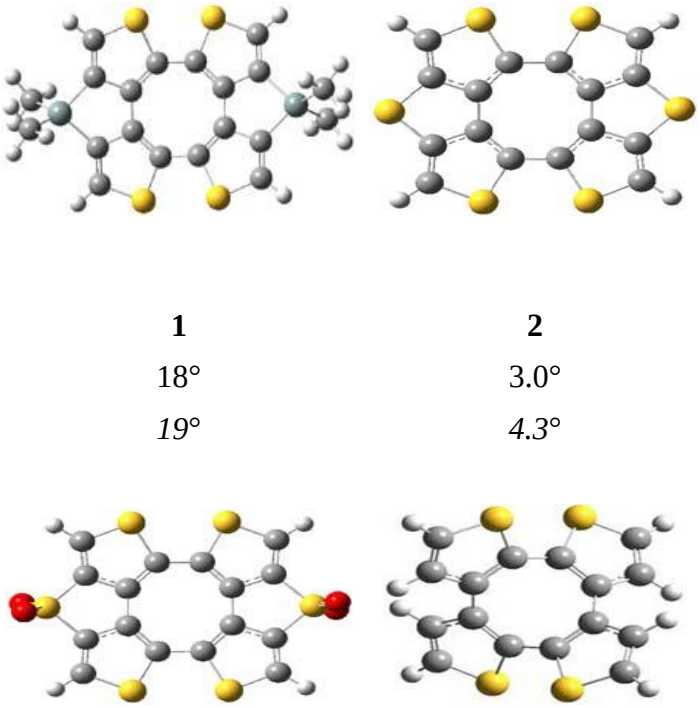
PLANAR CYCLOOCTATETRAENE?

Here's another attempt (almost successful!) in creating a planar cyclooctatetraene. Nishininaga and Iyoda have fused silicon and sulfur bridges to the COT framework, hoping to force the 8-member ring out of its preferred tub-shape into a planar structure.[1] They report the synthesis of **1**, **2**, and**3b** along with their x-ray structures. They also calculated the structures at B3LYP/6-31G (d,p) for **1**-4 , and these optimized structures are shown in Figure 1.





1	**2**
18°	3.0°
19°	*4.3°*

3a	**4**
7.0° (for **3b**)	39°
3.2° (for **3a**)	*40°*

Figure 1. B3LYP/6-31G(d,p) optimized geometries of **1-4**. The experimental (top) and computed (Bottom in italics) value of α are listed for each compound.[1]

The bent angle α is defined at the angle between the two planes that define the bottom of the tub and one of the sides. For COT itself, this angle is 40°, decidedly non-planar – as expected for a molecule avoiding the antiaromatic character it would have in its planar conformation. The computed and experimental values of α are shown in Figure 1. **4** is tub shaped.

The value of α for **1**is about 18° – still tub shaped but flattened. But **2** and **3** are nearly planar, with experimental values of α about 3° and the computed values are similar.

So what is the character of the 8-member ring in these compounds. The computed NICS(0) values are 3.8 ppm for **4**, the expected small value for a non-aromatic compound. (Note that the NICS value for COT is 2.9 ppm.) The values are much more positive for the other compounds: 12.7 ppm for **1**, 17.4 ppm for **2**, and 15.4 ppm for **3a**. These compounds therefore display *antiaromatic character* yet they are isolable compounds!

Source: http://comporgchem.com/blog/?p=741