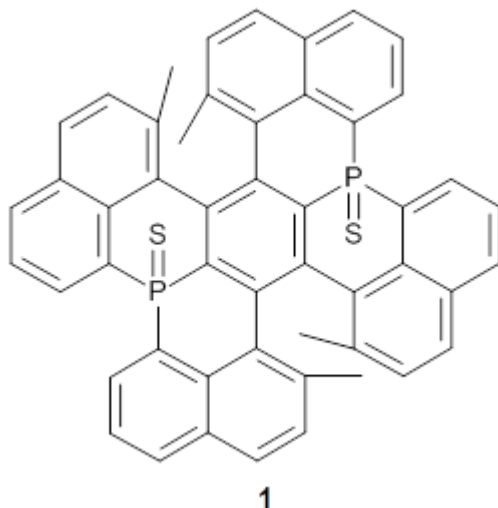


# TWISTING A BENZENE RING

Here's another cruel and unusual punishment applied to the poor benzene ring.

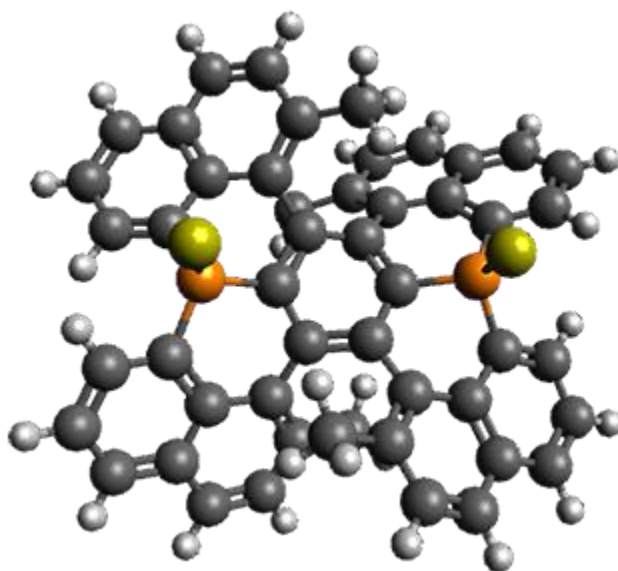
Hashimoto, et al. have created a molecule that is a fused double helicene, where the fusion is about a single phenyl ring.<sup>1</sup> Compound **1** has two [5]helicenes oriented in opposite directions. This should provide a twist to the central phenyl ring, and the added methyl groups help to expand that twist.



They prepared **1** and its x-ray crystal structure is reported. The compound exhibits  $C_2$  symmetry. The twist (defined as the dihedral of four consecutive carbon atoms of the central ring) is  $28.17^\circ$ , nearly the same twist as in [2]paraphenylene.

The B3LYP/6-31G(d) structure of **1** is shown in Figure 1. This geometry is very similar to the x-ray structure. The calculated NICS value for the central ring is -4.9

(B3LYP/6-311+G(d,p)/B3LYP/6-31G(d)) and -4.3 (B3LYP/6-311+G(d,p)/x-ray structure). This diminished value from either benzene or  $C_6(PSH_2)_2(CH_3)_4$  indicates reduced aromaticity of this central ring, presumably due to the distortion away from planarity. Nonetheless, the central ring of **1** is not oxidized when subjected to MCPBA to oxidize to the bis phosphine oxides.



**1**

**Figure 1.** B3LYP/6-31G(d) optimized structure of **1**.

Source: <http://comporgchem.com/blog/?p=3432>