

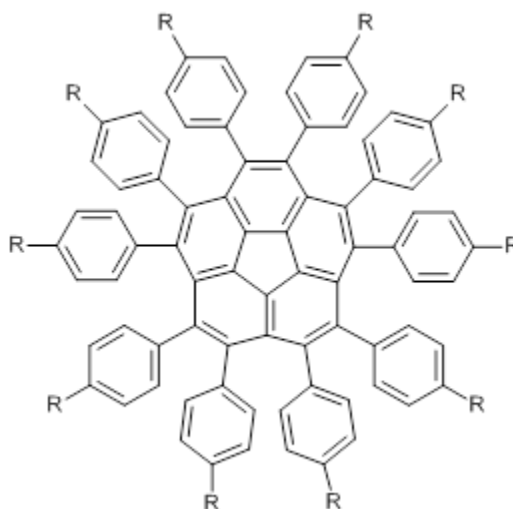
PALLADIUM-CATALYZED C–H ACTIVATION TAKEN TO THE LIMIT

Flattening an Aromatic Bowl by Total Arylation

Corranulene **1** is a bowl-shaped aromatic compound. It inverts through a planar transition state with a barrier of at 11.5 kcal mol⁻¹. What changes would be found if one *per*-phenylated corranulene, making **2**?



1



2a: R=H

2b: R=*t*-But

2c: R=Cl

Scott¹ has prepared **2a-c** by arylating corranulene using phenylboroxin and palladium acetate and repeating this arylation four times.

Amazing to me is that the yield of **2c** is 54%! The BMK/cc-pVDZ optimized structure of **2a** is shown in Figure 1. One can readily see that the bowl is nearly flat (click on the image to activate Jmol; the x-ray structure of **2b** has the bowl depth of only 0.248 Å, compared to a depth of 0.87 Å in **1**).

Interestingly, **2** inverts through a chiral TS (shown in Figure 1) so that inversion does not create the enantiomer! The computed barrier height is only 2.5 kcal mol⁻¹.

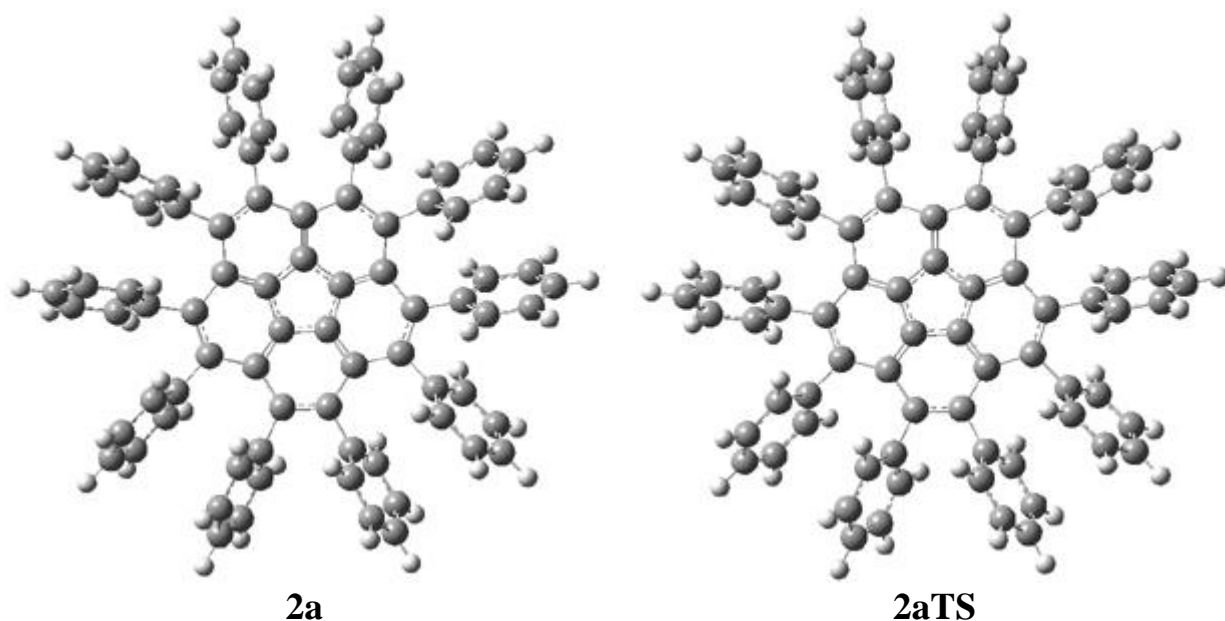
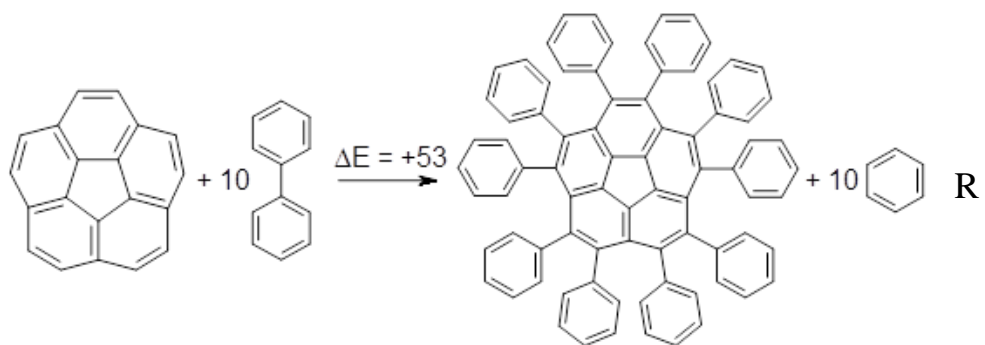


Figure 1. BMK/cc-pVDZ optimized structures of **2a** and the bowl inversion transition state **2aTS**.

The flatter bowl results in longer bonds and wider angles about the rim of **2** than in **1**. As one might expect, **2a** is very strained: the BMK/cc-pVDZ estimation is that **2** is 53 kcal mol⁻¹ more strained than **1**, using the homodesmotic Reaction 1. In total, this is a real nice study of using strain to alter shape.



Source: <http://www.compchemhighlights.org/2012/10/palladium-catalyzed-ch-activation-taken.html>