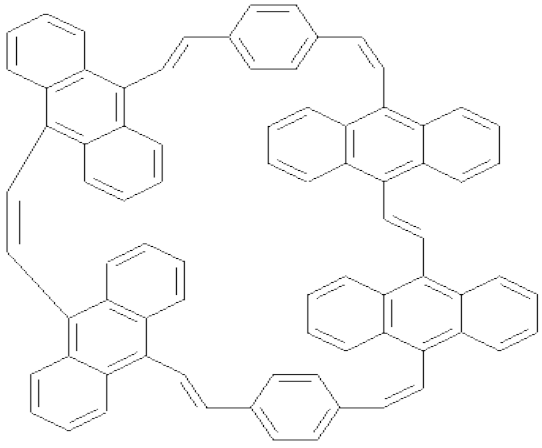
[36]-ANNULENE

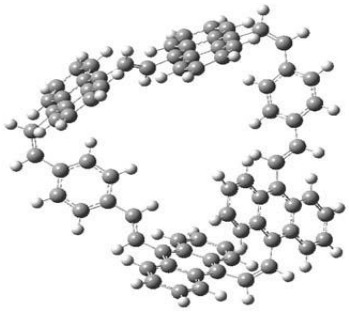
Annulenes can twist, and I have blogged about a number of examples (cations and neutrals). The twist can be portioned into a twist associated with the dihedral angle as one progresses around the compound and writhe which is associated with distortion of the annulene into a third dimension.[1]

Herges has prepared the 36-annulene **1** where the anthracenyl units were introduced to force the loop out of plane.[2] Four different conformations of **1** where isolated by crystallization out of different solvents. **1a** and **1b** were produced in benzene, and they differ by having two half-twists (L_k=2) and one half-twist (L_k=1), respectively. **1c** was isolated from DMF, with one half-twist. **1d**was isolated from Et_2O/CH_2Cl_2.

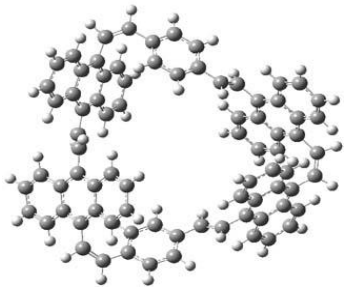


1

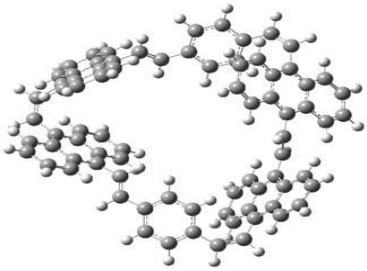
Computations at the B3LYP/6-31g* level identified 10 low lying conformations, and the ones corresponding to the experimentally observed forms are shown in Figure 1. The computed conformer that matches with **1d** differs form the experimental version by a rotation about one single bond, and the computed version has a different topology than the experiment. One item of note is that all of the 10 computed conformers are dominated by the twist (T_w) and have very small writhe.



1a

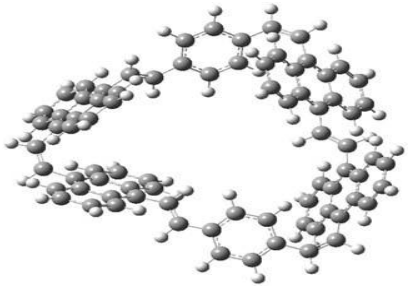


1b



1c

1d



1e

Figure 1. B3LYP/6-31G* optimized structures of **1a-e**.

Though not isolated in experiment, one of the low lying conformers has three half-twists (L_k=3) and is also shown in Figure 1 as **1e**. Identification of this highly twisted species would be quite interesting.

Source: http://comporgchem.com/blog/?p=1192