

## [18]Annulene : The Quest for a Definitive Equilibrium Structure Continues

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A definitive equilibrium structure for [18]annulene has remained elusive. A  $D_{6h}$  symmetry structure of this  $(4n+2)\pi$ -electron system appears compatible with unstrained carbon bond angles and modest repulsive interactions between the internal protons. Since the 1950's when Mislow used Van der Waals radii to argue that this repulsion would lead to non-planarity, the structure has been disputed. X-ray structures since 1965 have shown a lack of regular bond alternation alongside a slight deviation from planarity - with the deviation being typically ascribed to crystal packing.

In the late 20<sup>th</sup> century, electronic structure theorists took up the challenge. In retrospect, it is clear that many early attempts to compute the structure of [18]annulene were futile, as Hartree-Fock theory is completely inadequate. The inclusion of electron correlation is necessary to get *reasonable* results, but its effects are so large that it is just as easy to *overestimate* them.

Using the available theoretical armamentarium at the turn of the century, Wannere, Sattelmeyer, Schaefer, and Schleyer (*Angew. Chem. Int. Ed.*, **2004**) found a  $D_{6h}$  minimum (B3LYP) and a  $C_2$  minimum (KMLYP, BHLYP, SCS-MP2 via Grimme). Single-point energies favored  $D_{6h}$  (BLYP, BP86, MP2); or  $C_2$  (HF, CCSD(T)/DZ). They argued that NMR shifts were incompatible with a  $D_{6h}$  structure, while a more recent dynamical study argued the opposite (Kwan and Liu, *JCTC*, **2015**).

[18]annulene is iconic, but not anomalous. Analogous results have been obtained for the low-energy conformers of [10]annulene, as well as other conjugated  $\pi$ -electron systems. Determination of the global minimum and low-lying PES of [18]annulene will inform our understanding of bond-alternation, of aromaticity, of related materials such as acenes and graphenes, and also provide a highly sensitive test of theoretical methods.

We assail the problem of [18]annulene once again, and report a plethora of DFT and coupled-cluster results. Our single largest DF-FNO CCSD(T) energy computation with an aug-cc-pVQZ//aug-cc-pVTZ basis set places the  $C_2$  minimum lower than a  $D_{6h}$  transition state by 1.1 kcal/mol.