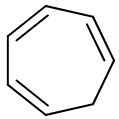
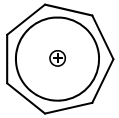
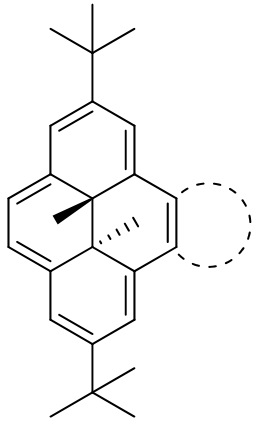


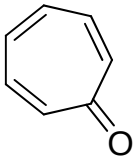


# Experimental verification of the Homoaromaticity of 1,3,5-Cycloheptatriene and Evaluation of the Aromaticity of Tropone and the Tropylium Cation by Use of the Dimethyldihydropyrene Probe

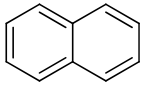

Richard Vaughan Williams,* W. Daniel Edwards
*University of Idaho, United States*
Pengrong Zhang, David J. Berg and Reginald H. Mitchell*
*University of Victoria, Canada*

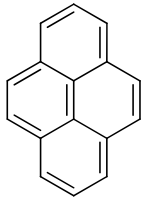



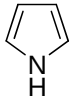

*J. Am. Chem. Soc., 2012, 134 (40), pp 16742–16752*


University of Victoria

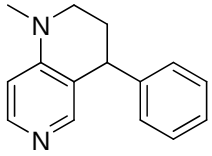


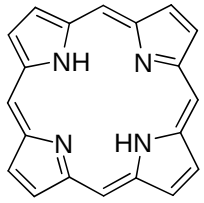


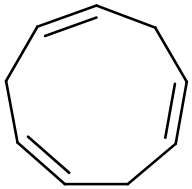


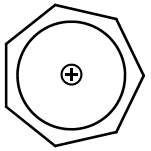

**Aromaticity:**

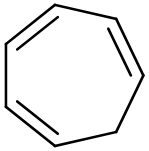
- delocalised conjugated $\pi$ system
- coplanar system
- contributing atoms in one (or more) rings
- 4n+2 $\pi$ electrons (n being an integer number)

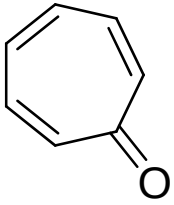



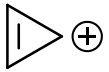






**Homoaromaticity:**
aromaticity in which conjugation is interrupted by a single $sp^3$ hybridized carbon atom.





No experimental evidence of cycloheptatriene aromaticity

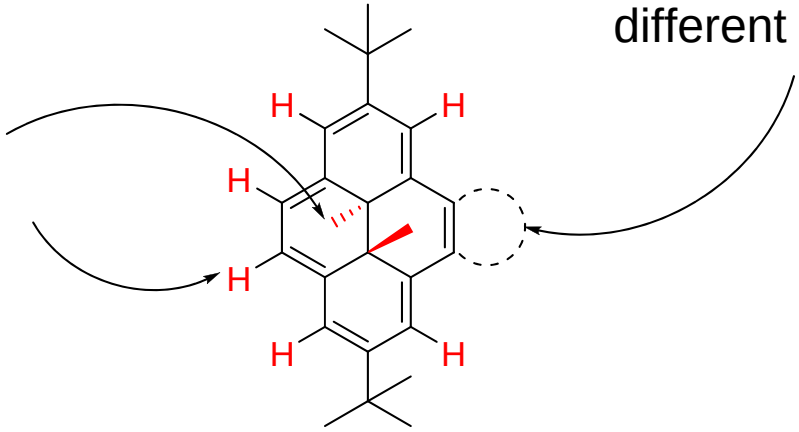
2011: first neutral compound to be proven homoaromatic (semibullvalene)
Griffiths, P. R.; Pivonka, D. E.; Williams, R. V. *Chem. Eur. J.* **2011**, *17,* 9193-9199

# The DMDHP probe

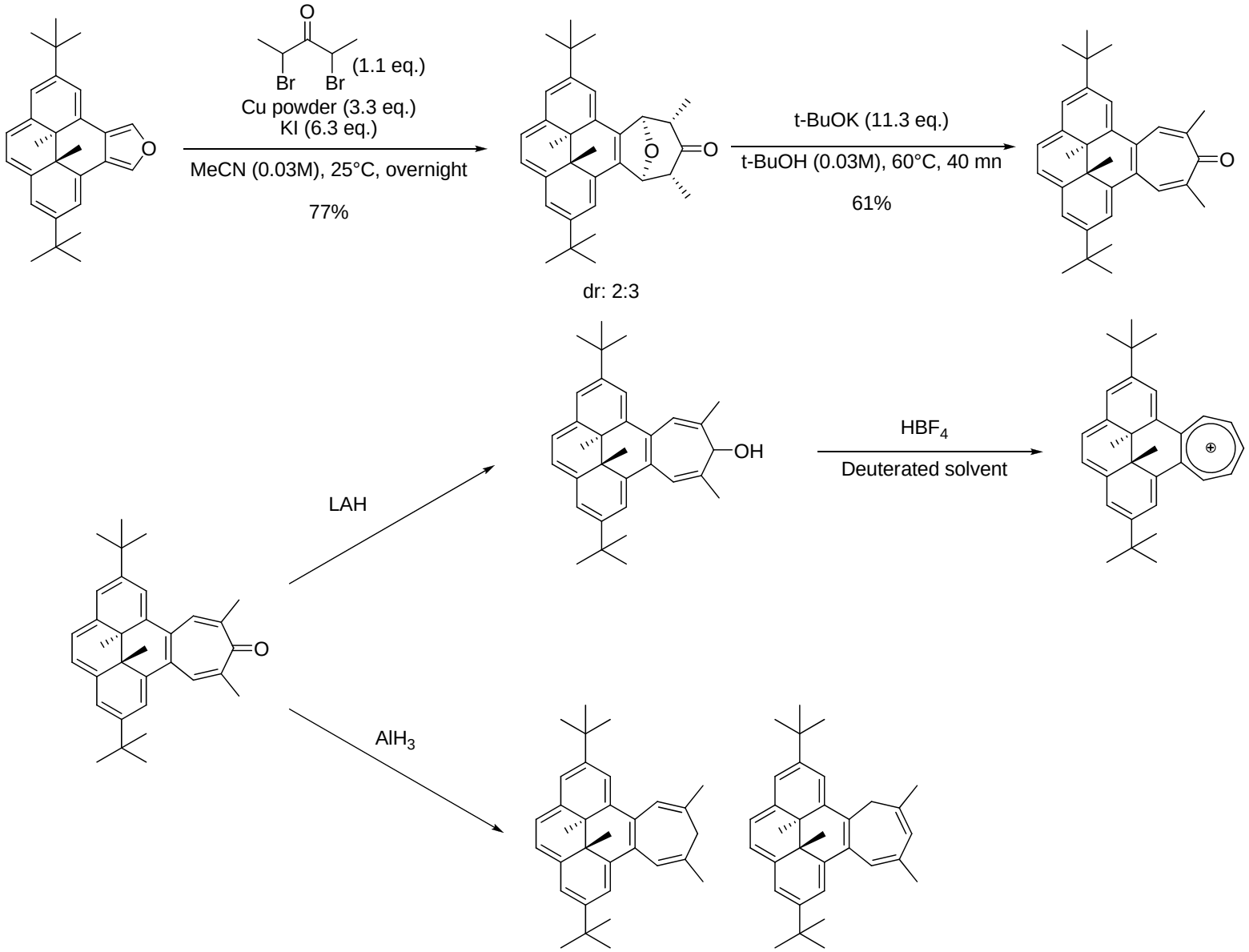
Enables comparing molecules

Synthesize DMDPH with different aromatic moieties

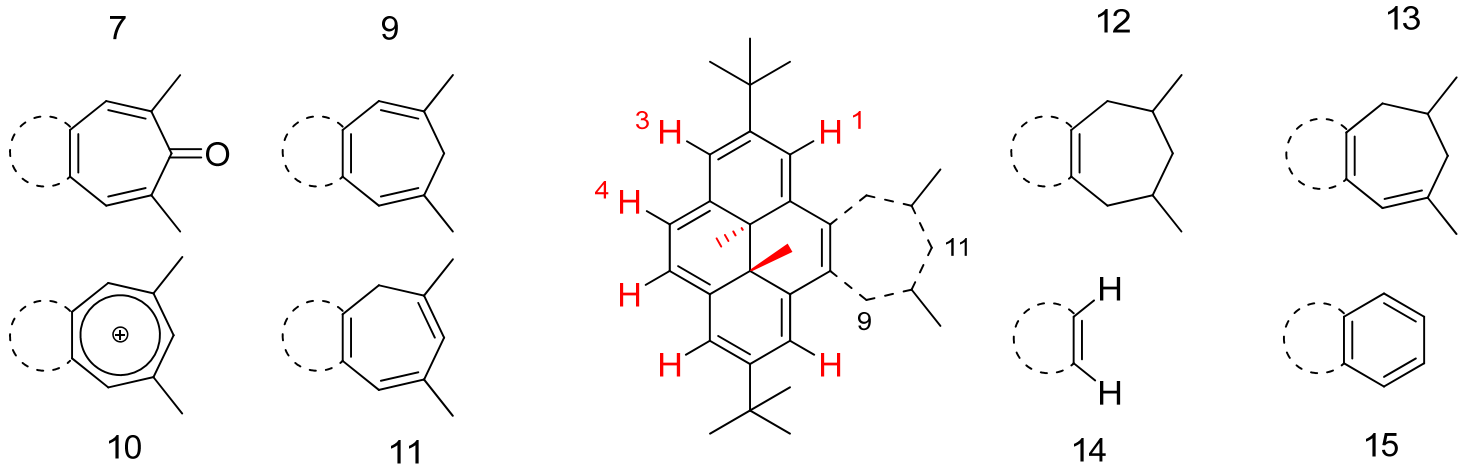
Study the H and Me NMR shifts



# DHP synthesis

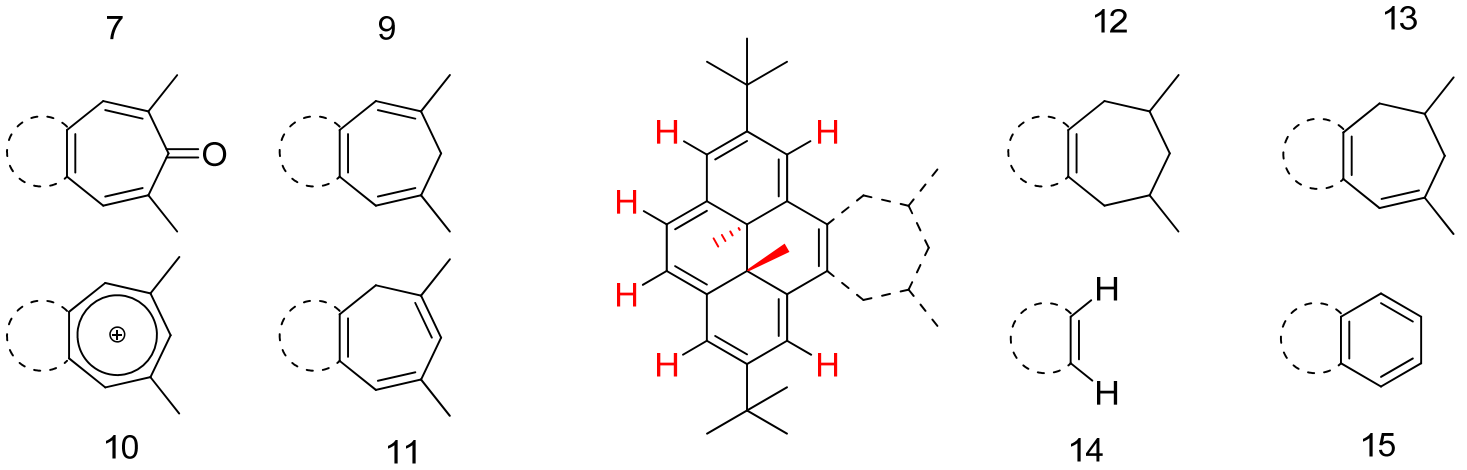


# « Aromaticity » data based upon 1H NMR spectra




| Shift (ppm, CDCl3) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| proton | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| 1 | 9.16 | 8.59 | 9.60 | 8.80 | 8.72 | 8.60 | 8.58 | 8.28 |
| 3 | 8.41 | 8.16 | 8.45 | 8.36 | 8.43 | 8.43 | 8.58 | 7.35 |
| 4 | 8.26 | 8.00 | 8.23 | 8.24 | 8.34 | 8.31 | 8.46 | 7.13 |
| 9 | 9.27 | 7.46 | 10.45 | 8.27 | | | | |
| 11 | | | 8.81 | 5.91 | | | | |
| Int-Me | -3.56 | -3.32 | -2.79 | -3.65/ -3.89 | -4.00 | -3.87 | -4.06 | -1.58 |

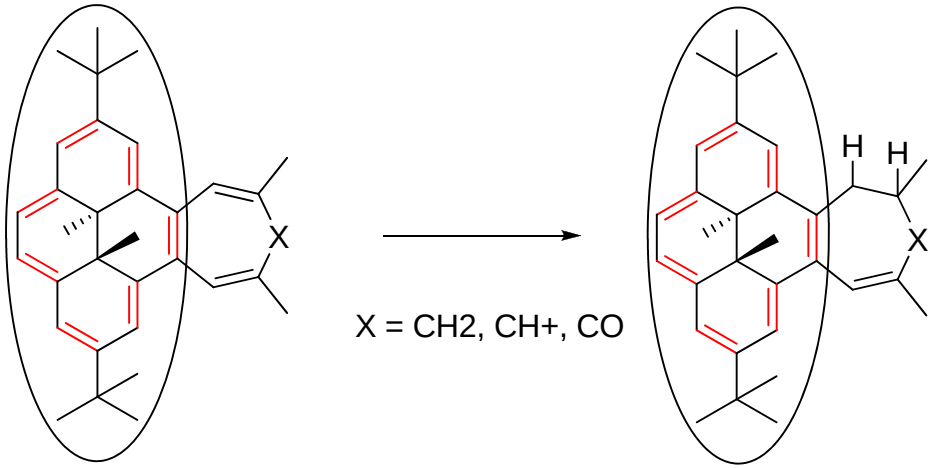
# « Aromaticity » data based upon 1H NMR spectra




$$\text{Aromaticity} = 100*(\delta_{DDPmolecule} - \delta_{DDP})/(\delta_{DDPbenzene} - \delta_{DDP})$$

| Shift (ppm, CDCl3) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| Int-Me | -3.56 | -3.32 | -2.79 | -3.65/ -3.89 | -4.00 | -3.87 | -4.06 | -1.58 |
| Aromaticity | 20% | 30% | 51% | 12% | 2% | 8% | - | 100% |

# Nucleus-independant chemical shift




**NICS:**

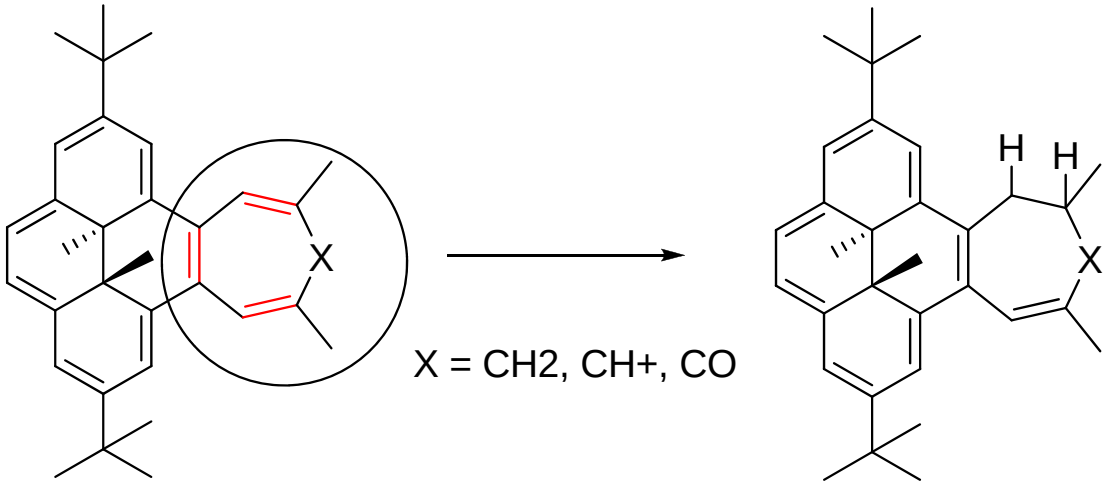
Nucleus-independant chemical shift

Evaluates the absolute magnetic shielding at the ring center

**$NICS_{avg}$:**

average of NICS values calculated at the centroids of the four 6-membered rings constituting the DDPN

# Nucleus-independant chemical shift



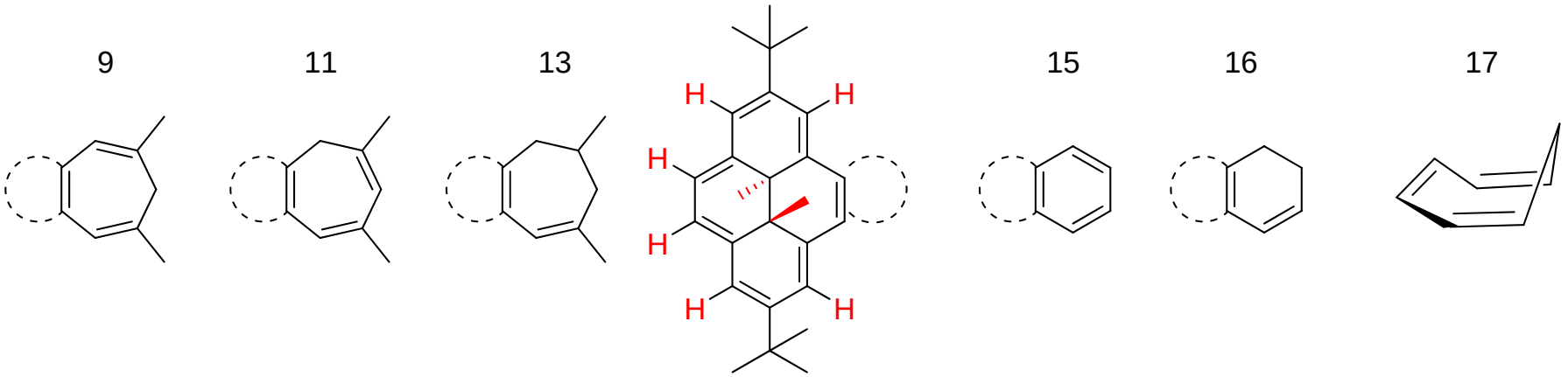

**$NICS_{Ann}$:**

NICS of the branched ring

NICS > 0 ⇔ anti-aromaticity

NICS < 0 ⇔ aromaticity

# « Aromaticity » data based upon DFT Computational studies

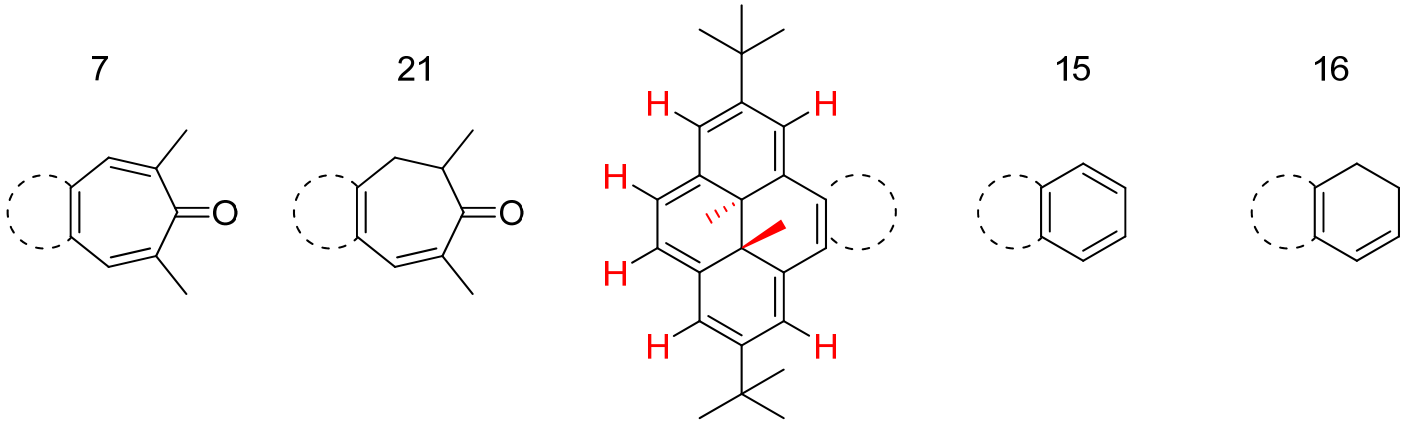



$$Aromaticity_{DFT} = 100*(NICS_{avg\ DDPmol} - NICS_{avg\ DDPmolH2})/(NICS_{avg\ DDPbenz} - NICS_{avg\ DDPbenzH2})$$

| | 9 | 11 | 13 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|
| **$NICS_{avg}$** | -11.08 | -12.96 | -14.89 | -4.64 | | -16.06 |
| **$NICS_{Ann}$** | -1.19 | -1.83 | -1.25 | -10.80 | -5.69 | |
| $Aromaticity_{DFT}$ | 33% | 17% | | | | |
| $Aromaticity_{NMR}$ | 30% | 12% | | | | |

**<u>Model shortcoming</u>:** Differences between 9 and 11 probably due to geometry

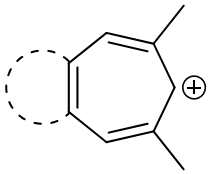
# « Aromaticity » data based upon DFT Computational studies



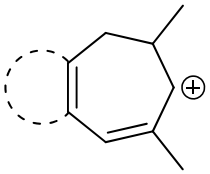

| | 7 | 15 | 17 | 21 |
|---|---|---|---|---|
| **$NICS_{avg}$** | -11.90 | -4.64 | -16.06 | -14.67 |
| **$NICS_{Ann}$** | | -10.80 | | |
| $Aromaticity_{DFT}$ | 24% | | | |
| $Aromaticity_{NMR}$ | 20% | | | |

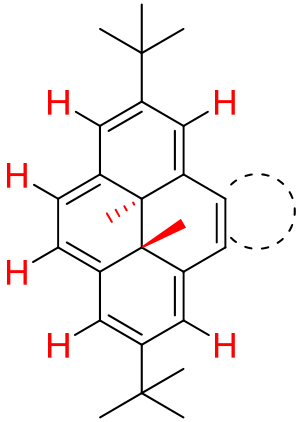
« Aromaticity » data based upon DFT Computational studies

10

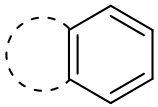


23

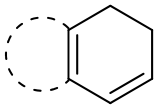





15



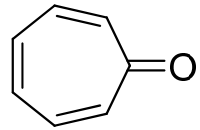
16

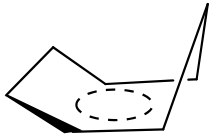


| | 10 | 15 | 17 | 23 |
|---|---|---|---|---|
| **$NICS_{avg}$** | -8.57 | -4.64 | -16.06 | -3.25 |
| **$NICS_{Ann}$** | | -10.80 | | |
| $Aromaticity_{DFT}$ | 47% | | | |
| $Aromaticity_{NMR}$ | 51% | | | |

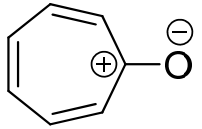
**<u>Model shortcoming</u>:** the positive charge delocalises on the pyrene ring

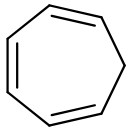
- Cycloheptatriene first proven homoaromatic !

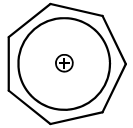


- DHP probe evaluates tropone and cycloheptatriene are (homo)aromatic
    - ~ 30% of the benzene aromaticity for one cycloheptatriene model
    - ~ 15% for the other model
    - ~ 20% for the tropone





- Results support tropylium cation is homoaromatic but model probably underestimates its value (~50%)