

THEORETICAL ASSESSMENT OF EIGHT RULES OF AROMATICITY

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Many of the quintessential aromatic compounds present high symmetry. Symmetry is one of the usual features of aromatic compounds. Although not all aromatic species are symmetric, the most archetypal aromatic compounds are highly symmetric and possess degenerate highest-occupied molecular orbitals. These orbitals can be fully occupied resulting in a closed-shell structure or can be same-spin half-filled. This closed-shell or same-spin half-filled electronic structure, which provides an extra stabilization, is the origin of several rules of aromaticity such as the Hückel $4n+2$ rule,¹⁻⁴ the lowest-lying triplet excited state $4n$ Baird rule,^{5,6} the Soncini and Fowler extension of the Baird rule,⁷ or the $4n$ rule followed by monocyclic conjugated hydrocarbons in a Möbius-type conformation.^{8,9} All these rules of (anti)aromaticity are nicely summarized in the so-called Ottosson's cube.¹⁰ In addition to the mentioned rules for the aromaticity of monocyclic annulenes, rules for polycyclic aromatic hydrocarbons like the π -sextet Clar rule¹¹ and for 3D aromaticity such as $2n+2$ Wade-Mingos' rule,^{12,13} the $2(n+1)^2$ Hirsch rule for spherical aromaticity¹⁴ or the $2n^2+2n+1$ ($S = n + 1/2$) rule for open-shell spherical aromaticity.¹⁵ Some examples of the applications of these rules performed in our group will be reviewed in the seminar. The validity of some of these rules will be assessed.

References

- (1) Hückel, E. *Z. Physik* **1931**, *70*, 104.
- (2) Hückel, E. *Z. Physik* **1931**, *72*, 310.
- (3) Hückel, E. *Z. Physik* **1932**, *76*, 628.
- (4) Hückel, E. *Z. Elektrochemie* **1937**, *43*, 752.
- (5) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941.
- (6) Ottosson, H. *Nat Chem* **2012**, *4*, 969.
- (7) Soncini, A.; Fowler, P. W. *Chem. Phys. Lett.* **2008**, *450*, 431.
- (8) Heilbronner, E. *Tetrahedron Lett.* **1964**, *5*, 1923.
- (9) Ajami, D.; Oeckler, O.; Simon, A.; Herges, R. *Nature* **2003**, *426*, 819.
- (10) Rosenberg, M.; Dahlstrand, C.; Kilsa, K.; Ottosson, H. *Chem. Rev.* **2014**, *114*, 5379.
- (11) Clar, E. *The Aromatic Sextet*; Wiley: New York, 1972.
- (12) Wade, K. *J. Chem. Soc. D: Chem. Commun.* **1971**, 792.
- (13) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

- (14) Hirsch, A.; Chen, Z.; Jiao, H. *Angew. Chem. Int. Ed.* **2000**, *39*, 3915.
- (15) Poater, J.; Solà, M. *Chem. Commun.* **2011**, *47*, 11647.