

Excited State Aromaticity and Antiaromaticity: Scope, Limitations, Complications and Pitfalls

Henrik Ottosson

Department of Chemistry – Ångström Laboratory, Uppsala University, Box 523, 750 21 Uppsala, Sweden.

The usage of the excited state aromaticity and antiaromaticity concepts (ESA & ESAA) to rationalize excited state properties and processes has grown rapidly in recent years.[1,2] The concepts are often described through Baird's $4n$ and $4n+2$ rules for, respectively, aromaticity and antiaromaticity in the lowest $\pi\pi^*$ excited states, and they have been utilized to rationalize both new and old photoreactions,[3-5] to explore and design photofunctional molecules,[6-8] and to interpret fundamental excited state properties.[9-13] The concepts can likely find use in a very wide variety of areas, ranging from astrochemistry and organic synthesis to biophysics and photovoltaics.

Yet, as the concepts are applied within gradually more areas it is also important to explore the limitations, complications and pitfalls so as to hamper improper usage. A diatropic ring current in a T_1 state does not always indicate Baird-aromaticity. Indeed, there are molecules which are Hückel-aromatic in their excited states,[13,14] and some quinoidal compounds can be simultaneously Hückel- and Baird-aromatic in their lowest excited states.[15,16] Finally, heterocycles as well as macrocycles with tentative ESA character expose a number of complications, both computationally and conceptually.[17,18] Thus, simultaneously as we explore the scope of the ESA & ESAA concepts we also need improved knowledge on their limitations, complications and pitfalls. The talk will be dedicated to both of these aspects.

- [1] N. C. Baird, *J. Am. Chem. Soc.* **94**, 4941 (1972).
- [2] M. Rosenberg, *et al.*, *Chem. Rev.* **114**, 5379 (2014).
- [3] R. Mohamed, *et al.*, *J. Am. Chem. Soc.* **137**, 15441 (2015).
- [4] R. Papadakis, *et al.* *Nat. Commun.* **7**, 12961 (2016).
- [5] T. Slanina, *et al.*, *J. Am. Chem. Soc.* **142**, 10942 (2020).
- [6] M. Hada, *et al.*, *J. Am. Chem. Soc.* **139**, 15792 (2017).
- [7] O. El Bakouri, *et al.*, *J. Am. Chem. Soc.* **142**, 5602 (2020).
- [8] A. Pati, *et al.*, *Proc. Natl. Acad. Sci.*, **117**, 24305 (2020).
- [9] H. Ottosson, *et al.*, *Chem. Eur. J.* **13**, 6998 (2007).
- [10] M. Rosenberg, *et al.*, *Phys. Chem. Chem. Phys.* **13**, 12912 (2011).
- [11] Y. M. Sung, *et al.*, *Nat. Chem.* **7**, 418 (2015).
- [12] L. Karas, *et al.* *Chem. Sci.* **11**, 10071 (2020).
- [13] B. Uruganti, *et al.*, *Org. Lett.*, **19**, 4818 (2017).
- [14] W. Zeng, *et al.*, *Chem. Sci.* **12**, 6159 (2021).
- [15] K. Jorner, *et al.* *Chem. Eur. J.* **22**, 2793 (2016).
- [16] S. Escayola, *et al.* *Angew. Chem. Int. Ed.* **60**, 10255 (2021).
- [17] Y. Shoji, *et al.*, *Angew. Chem. Int. Ed.* **60**, 21817 (2021).
- [18] R. Ayub, *et al.*, *J. Phys. Chem. A*, **125**, 570 (2021).