

## Putting Baird's Rule on Excited State Aromaticity and Antiaromaticity into Action

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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 often described through Baird's  $4n$  and  $4n+2$  rules for aromaticity and antiaromaticity in the lowest  $\pi\pi^*$  excited states have, e.g., been utilized to rationalize new as well as 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 in gradually more areas it is also crucial 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 need improved knowledge on their limitations, complications and pitfalls. The talk will be dedicated to both of these aspects.

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# Tuning the Aromaticity of Excited Conjugated Rings

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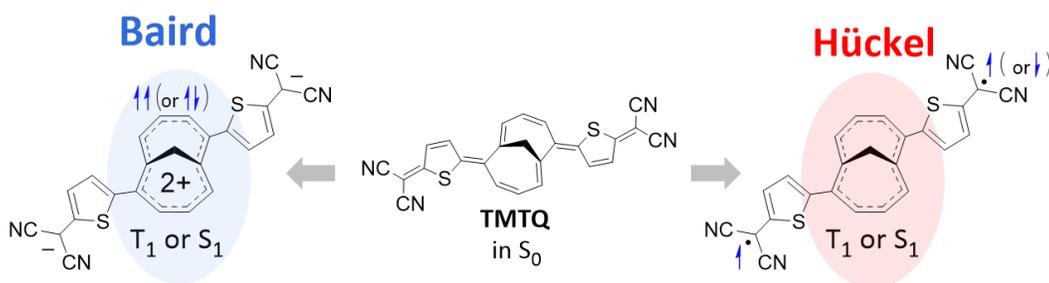
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**Abstract:** The excited state aromatic character of TMTQ, a quinoidal compound with a central 1,6-methano[10]annulene and two 5-dicyanomethyl-thiophene units, is controversial as it can be described as Hückel and/or Baird aromatic. The  $T_1$  state was earlier characterized as Hückel-Baird hybrid<sup>1</sup>, but recently it was claimed that  $S_1$  is Baird aromatic<sup>2</sup>. In light of the new experimental data, we reinvestigated TMTQ using (time-dependent) density functional theory methods and find that both  $S_1$  and  $T_1$  of TMTQ are only weakly Baird aromatic. Through comparison with related smaller compounds (neutral or charged), we provide guidelines on how to increase the excited state Baird aromaticity.



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