

EXCITED STATE AROMATICITY AND ANTIAROMATICITY: OPPORTUNITIES FOR PHOTOPHYSICAL AND PHOTOCHEMICAL RATIONALIZATIONS

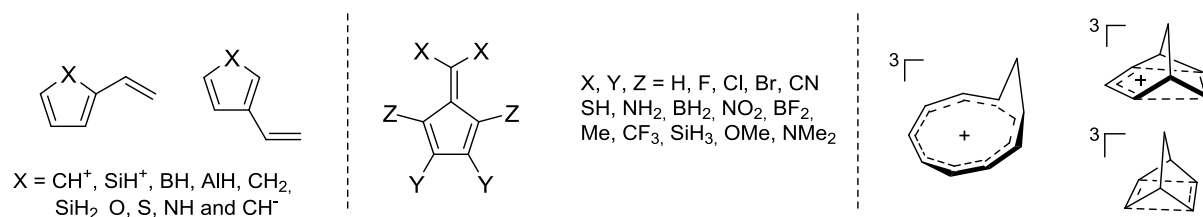
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Aromaticity is a key concept for chemistry in the electronic ground state (S_0), and reactions in which aromaticity is gained are normally highly favorable. Yet, despite that the rule for aromaticity in the lowest $\pi\pi^*$ excited triplet state (T_1) of annulenes was derived by Baird in 1972,^[1,2] it is very seldom applied to explain properties and processes in this state. The rule, Baird's rule, states that annulenes with $4n$ π -electrons are aromatic in T_1 and those with $4n+2$ are antiaromatic, *i.e.*, opposite to Hückel's rule for aromaticity in S_0 . Recently, it has been shown that the rule also applies to the first singlet excited state (S_1) of small annulenes.^[3,4] Indeed, it should be a powerful back-of-an-envelope tool for rationalization of photophysical and photochemical observations as well as for the design of new photoactive molecules.^[5]

Through a combination of quantum chemical calculations and experiments we earlier applied Baird's rule to explain (i) T_1 and S_1 state properties of fulvenes,^[6] (ii) the shapes of T_1 state potential energy surfaces for rotation about the C=C double bonds of annulenyl substituted olefins,^[7] and (iii) the magnitude reversals in proton and hydride affinities of annulenyl anions and cations when going from S_0 to T_1 .^[8] We have now analyzed to what extent there is a connection between a series of different T_1 state properties of substituted fulvenes and annulenyl olefins and the degree of (anti)aromaticity in the T_1 state as well as the changes in (anti)aromaticity upon excitation. The results in general reveal close relationships.

With Baird's rule in mind we have also searched for $4n\pi$ -electron compounds which display homoaromatic character in their T_1 states, thus being triplet state analogs to the well-established $(4n+2)\pi$ -electron species such as the homotropylium cation which are homoaromatic in S_0 .^[9] Indeed, our computations support T_1 state homoaromaticity, a finding which may provide deepened understanding of photochemical cycloaddition reactions.



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