

EXPLORING PHOTOREACTIONS POTENTIALLY TRIGGERED BY EXCITED STATE ANTIAROMATICITY RELIEF

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Baird's rule tells that the electron counts for aromaticity and antiaromaticity in the first $\pi\pi^*$ triplet excited state (T_1) of simple annulenes are opposite to those in the ground state (S_0),^[1] and it has been shown that the rule also extends to the lowest singlet excited state (S_1).^[2,3] Motivated by this aromaticity/antiaromaticity switch we earlier labelled benzene as a molecular "Dr. Jekyll and Mr. Hyde".^[4] Now, to what extent is photoreactivity of S_0 state aromatic molecules triggered by relief of excited state antiaromaticity?

We recently showed in a combined experimental and computational study of cyclopropyl (cPr) substituted annulenes that the aptitude for cPr ring-opening in the T_1 state is strongly linked to the number of π -electrons of the annulene.^[5] T_1 state antiaromaticity in 6π -electron (hetero)cycles lowers the activation energy for cPr ring-opening by 3–8 kcal/mol when compared to cases with the cPr group attached to π -conjugated, yet, T_1 nonaromatic cycles. We will now present results revealing to what extent excited state antiaromaticity relief triggers various photoreactions that progress in the S_1 state instead of the T_1 state. Particular focus will be given to the photorearrangement of benzene to benzvalene and the photochemical formation of substituted bicyclo[3.1.0]hex-2-enes in protic nucleophilic media. In this context, we will also discuss the potential involvement of structures influenced by excited state homoaromaticity.^[6]

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