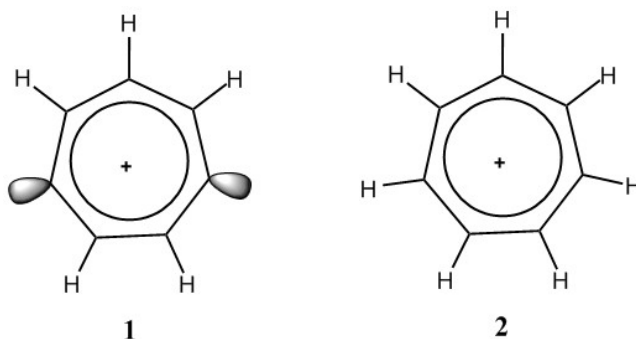


## A Multi-Reference Study of the Tropylium Cation

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The study of polyradicals such as the tropylium cation can not only reveal fundamental characteristics about this type of molecule but can also contribute to our understanding of the Bergman cyclization, responsible for transforming enediyenes into cancer warhead drugs. *Ab initio* methods have been performed on molecule **2** but not molecule **1**, which contains  $6\pi$  delocalized electrons.



**Figure 1.** Two variations of the tropylium cation

The focus of this work was to characterize the tropylium cation (**1**). A starting geometry was obtained using single reference CCSD/cc-pVDZ. Molecular orbitals were assigned to irreducible representations under  $C_{2v}$  symmetry. A CAS(8,9) approach was used for MCSCF on this aromatic cation with active space orbitals  $1b_1$  ( $\pi_1$ ),  $2b_1$  ( $\pi_2$ ),  $1a_2$  ( $\pi_3$ ),  $9b_2$  ( $\sigma^*1$ ),  $12a_1$  ( $\sigma_1$ ),  $2a_2$  ( $\pi^*4$ ),  $3b_1$  ( $\pi^*5$ ),  $4b_1$  ( $\pi^*6$ ), and  $3a_2$  ( $\pi^*7$ ). High level multi-reference methods on the Columbus software package were then used with cc-pVDZ and cc-pVTZ basis sets to run geometry optimizations on the lowest energy singlet and triplet states. We were able to determine the electronic structure and the geometry of the tropylium cation at its  $^1A_1$  ground state and at its  $^3B_2$  state.

Across all methods the singlet state was consistently lower energy, indicating through-bond coupling. Small adiabatic gaps and minimal geometry differences suggest near-degeneracy between states.