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**Experimental and computational studies on C8H8** **radical cations**

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Valence isomers of annulenes, in particular the C8H8 group of compounds, continue to arouse the interest of the chemistry community by virtue of their interesting thermal, photochemical, and catalytic interconversions. Recently, the radical ions of several C8H8 hydrocarbons have become the target of (re)investigation by several of the research groups represented at this meeting. This contribution will cover some results obtained over the past few years through a collaboration between the Fribourg and Knoxville laboratories.

Two compounds will occupy a central position i.e. the radical cation of cyclooctateraene (**COT.**+) and the that obtained from semibullvalene (**BOD.**+) to which the former can be converted photochemically.



The interplay between the electronic and the molecular structure of **COT.**+ and **BOD.**+ as reflected in ESR and optical spectra as well as the properties of their excited states will be discussed in view of their photochemical reactivity. Special attention will be given to the question of possible localization of spin and charge in **BOD.**+ which serves as a simple model system for more complex radical ions which show this feature.1

The relation of the above two cations to other points on the C8H8**.**+ hypersurface, in particular the radical cation of the *syn* cyclobutadiene dimer and its decompositon products will be illustrated and the rich photochemistry leading from **BOD.**+ to tautomeric dihydropentalene cations will be mentioned.2

In a general sense, this contribution will revolve around the fruitful interplay between different types of experiments and between those and theory. Application of the latter may pose special problems in the case of radical ions. The present C8H8**.**+ examples serve to high­light some of these problems and to point the way to a judicious application of different quantum chemical models for the understanding of the molecular and electronic structure of radical ions.

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1 T. Bally, L. Truttman, S. Dai, F. Williams *J. Am. Chem.Soc.* **1995***, 117*, 7916

2 T. Bally, L. Truttmann, J. T. Wang, F. Williams, *J. Am. Chem. Soc.* **1995**, *117*, 7923