

# Aromaticity on the fly: cyclic transition state stabilization at high temperature

András Stirling

*Chemical Research Center of the Hungarian Academy of Sciences, Budapest, Hungary*

We study the transition state of pericyclic reactions at elevated temperature with unbiased ab initio molecular dynamics. We find that the transition state of the intramolecular rearrangements for barbaralane and bullvalene remains aromatic at high temperature despite the significant thermal atomic motions. Structural, magnetic and electronic properties of the dynamical transition state show the aromatic character. Free energy calculations also support the validity of the transition state theory for the present rearrangement reactions. The calculations indicate that cyclic delocalization represents a strong force to synchronize the thermal fluctuations for the concerted bond rupture and formation processes.

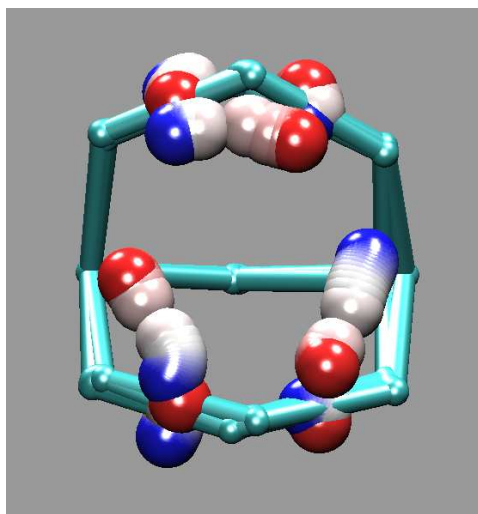


FIG. 1: Characteristic pattern of an electrocyclic reaction traced out by the Wannier centers of the delocalized electrons.