Probing Aromaticity In Intermediates And Transition States Along Non-Traditional Reaction Paths.

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Abstract

For chemists, the tryst with aromaticity began with the dream and subsequent works by Kekulé. Gradually with the advent of quantum chemistry, aromaticity was given a strong theoretical foundation, the Hückel’s rule being the most prominent of them. Yet the problem of quantification of aromaticity remained unresolved. This problem was interfaced with the phenomenon of magnetically induced ring current and quantification of aromaticity was linked with NMR chemical shifts. Nuclear Independent Chemical Shift (NICS methods) and more recently Magnetically Induced ring Current density (MICD) have been used to quantify aromaticity. NICS has been employed majorly, due to its computational simplicity, to investigate the implication of aromaticity in chemical reactions, by quantifying aromaticity of transition states, in pericyclic reaction in particular. MICD has seen some very few recent applications. Chances for isolation of transition states are nil and aromaticity of intermediates of chemical reactions have rarely been investigated. The work presented in this thesis is concerned with the investigation of aromaticity property for intermediates involved in the non-traditional mechanistic pathways of simple chemical reactions. This thesis is composed of two major types of work/findings. Firstly the attempt has been to establish unusual mechanistic pathways for simple chemical reactions. This thesis reconciles different facets of quantum chemistry like static computation, for structure determination and property calculation, coupled with the reaction dynamics, in condensed phase, under one common roof. Secondly, computation and quantification of aromaticity, using NICS and MICD in particular, for intermediates along the non-traditional reaction paths has been addressed. The chemical reactions investigated span from oxidation reaction and photo-redox process to excited state photochemical reaction.

Four-center-two-electron (4c-2e) bond is a more recently discovered bonding pattern. Aromaticity of paradigmatic cases of 4c-2e bond like TCNE$_2^{2-}$ and four-sulfur-two-electron bonded complex have been thoroughly investigated. An unusual 4c-2e bonded intermediate has been found in the mechanistic pathway for oxidation of hydrazine. The aromaticity of this intermediate has also been investigated.

Excited state aromaticity has been addressed using MICD technique for the first time. While investigating the photo-dissociation of N$_2$ from 5-Phenyl-Tetrazole, an interlink between photo-induced charge transfer and drastic changes in excited-state aromaticity has been established.

Additionally, a prebiotic photo-redox reaction has been studied. Dimerization of two dipole-bound-anions was found to be a crucial step in the mechanism for the photo-reduction process. Despite the coulombic repulsion, the dimerization was found to be facile due to the gain in the aromatic stabilization of the dianionic intermediate formed.

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