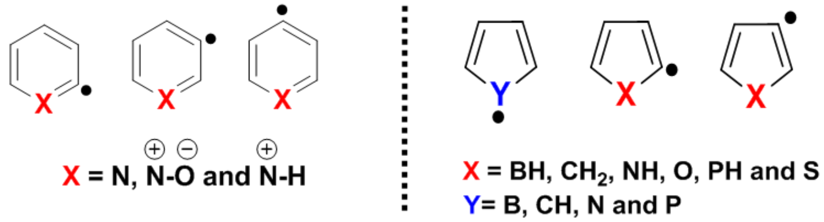
Abstract

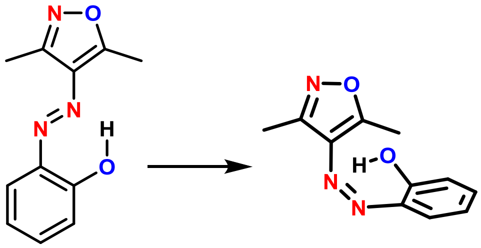
Free radicals are regarded as one of the important classes of highly reactive, short-lived intermediates containing an unpaired electron. The utility of these free radicals has been proposed by experimentalists and theoreticians in the field of organic synthesis, combustion chemistry, atmospheric chemistry, interstellar chemistry, and biological implications. Several approaches such as conjugation, spin delocalization, and introduction of heteroatoms have been adapted to enhance the stability as well as tuning the reactivity of radicals. In recent times, nitrogen-based heterocyclic radicals have gained immense importance for their various roles in reactive oxygen species (ROS), material chemistry, biofuels, and in constructing organic molecular-based magnets. Among the various heterocyclic radicals studied thus far, all of the radicals potentially resulted in two center-three electrons (2c-3e) interactions except for boryl and cyclopentadienyl radicals as shown in **Scheme A.1**.



Scheme A.1. Five-and six-membered heterocyclic radicals exhibiting (2c-3e) interactions [exceptions are boryl and cyclopentadienyl radicals].

In this regard, the detailed investigation of the electronic structure and reactivity aspects were carried out using quantum chemical calculations. Through space (TS) and through-bond (TB) interactions prevailing between lone-pair and the radical electron provided valuable information regarding the thermodynamic stability of the isomeric radicals. Whereas, spin density value played a crucial role in predicting the bond cleavage in unimolecular decomposition channels as

well as in explaining the reactivity trend. Moreover, attempts have also been made towards the experimental characterization of 2- and 3-dehydropyridine-*N*-oxide radicals using matrix isolation (MI) technique assisted with infrared spectroscopy and computations. Based on the observations under photochemical conditions, we were able to identify the formation of 3-dehydropyridine-*N*-oxide radical in an inert gas matrix at 4 K. However, our attempts were not successful in the generation of 2-dehydropyridine-*N*-oxide radical, but, we did observe a few interesting species due to photoirradiation.



Scheme A.2. 2-Hydroxyphenylazo-3,5-dimethylisoxazole (HPAI) undergoing *E*-*Z* photoisomerization in an argon matrix at 4 K.

Recently, azoheteroarenes have been intensely studied due to their excellent photoswitching properties and exceptional thermal stability of the photoswitched state. Typically, photoisomerization of azo compounds is well known in the solution phase but their studies are limited under cryogenic conditions in the rigid matrix. In this regard, we explored azoheteroarene based photoswitch (i.e. 2-hydroxyphenylazo-3,5-dimethylisoxazole, HPAI) and successfully confirmed the *E*-*Z* photoisomerization in an argon matrix at 4 K as shown in **Scheme A.2**. The sharp spectral features at low temperature in combination with computations allowed us to understand the conformations for both *E*- and *Z*-isomers.

Overall, theoretical insights on five-and six-membered heterocyclic radicals, and matrix isolation studies of 2- and 3-iodopyridine-*N*-oxide, 2-hydroxyphenylazo-3,5-dimethylisoxazole will be presented.