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Title: Computational Studies on Five Membered Heterocyclic Open-Shell Systems and Setting up of Matrix Isolation IR Spectroscopy

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**Abstract:** Computational studies of five membered mono-heteroatom containing heterocyclic radicals have been performed. Isomeric dehydro- pyrrole, furan, thiophene and borole radicals have been investigated. (Scheme 1a) These systems have been chosen to understand the effect of heteroatom in structural, stability and reactivity aspects of radicals. In this regard, we explored the ground state electronic structures and their geometrical parameters to get insights in to the structural aspects. Isodesmic reactions have been performed in order to get the radical stabilization energy (RSE) and overall stability order of the related radical species. Spin density and electrostatic potentials (ESP) have been computed in order to understand the localization of spin at the radical center and to get an overview of the electrostatic charges, respectively. Multiconfigurational CASSCF calculations and natural bond orbital (NBO) analysis have been performed for obtaining semi-quantitative information on the interaction between lone pair(s) of the heteroatom and radical electron. This information will be very useful in the fundamental point of view to understand whether such interactions provide stabilizing or destabilizing effects and also the mode of operation. In this regard, different levels of theory including (U)B3LYP/cc-pVTZ, (U)M06/cc-pVTZ, (U)MP2/cc-pVTZ and single point energy calculations at (U)CCSD(T)/cc-pVTZ and multireference CASSCF/cc-pVTZ methods have been used. Reactivity of dehydropyrrole radicals have also been investigated. In this regard, 1, 2 H-shift and unimolecular decomposition pathways have been calculated at (U)B3LYP/cc-pVTZ level of theory. Based on above electronic structural and reactivity informations, we found out that nitrogen centred radical is the most stable among all possible isomeric radicals that we investigated. The reason is delocalization of radical electron in the ring that result in a p-character of SOMO. After this significant result, where we obtained a  $\pi$ -radical when the radical centre is created at nitrogen atom, we shifted our attention to create the spin interaction upon creation of another radical centre at carbon centres. In this regard, we extended this study to understand the ground state spin multiplicities of all possible didehydropyrrole biradicals. (Scheme 1b) Both singlet and triplet states for each pyrrole biradicals have been investigated in order to predict the ground electronic states. In this regard, we estimated the geometrical parameters, spin density, biradical stabilization energy, singlet-triplet energy gap, bond dissociation energy and natural bond orbital (NBO) at (U)B3LYP/cc-pVTZ level of theory. All these results show that all the biradicals with one of the radical centres at nitrogen atom are found to have triplet ground states. This provides an excellent chance for exploring new types of high spin systems.


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