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| Title: | Does a Nitrogen Lone Pair Lead to Two Centered-Three Electron (2c-3e) Interactions in Pyridyl Radical Isomers? |
| Authors: | Sah, C. (/jspui/browse?type=author&value=Sah%2C+C.)<br>Venkataramani, Sugumar (/jspui/browse?type=author&value=Venkataramani%2C+Sugumar)<br>Jacob, Lilit (/jspui/browse?type=author&value=Jacob%2C+Lilit)<br>Saraswat, M. (/jspui/browse?type=author&value=Saraswat%2C+M.) |
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| Abstract: | Each of the three isomeric pyridyl radicals (2-, 3-, and 4-dehydropyridines) contains a lone pair and an unpaired electron. As a result, a potential two centered–three electron interaction between the radical electron and the lone pair through-space (TS) and/or through-bond (TB) can exist that may influence the stability of the radicals. Due to the change in geometrical positions relative to each other, the strength of interaction can be varied. In this study, we investigated the structural and stability aspects of pyridyl radical isomers with a major emphasis on the interaction of a nitrogen lone pair with the radical center. In order to obtain evidence for such interactions, protonated and N-oxide analogues of the corresponding isomeric pyridyl radicals have been considered in such a way to understand the consequences due to unavailability of the lone pair. Similarly, electron attachment and detachment energies at the radical center (vertical detachment energy, VDE, of corresponding anions and vertical ionization energy, VIE, of radical isomers) have been calculated to find out the interaction trend upon modification at the radical center. Different levels of theory including (U)B3LYP/cc-pVTZ, (U)M06/cc-pVTZ, CBS-QB3, single-point energy calculations at (U)CCSD(T)/cc-pVTZ, and multireference CASSCF/cc-pVTZ methods have been employed in this regard. A closer inspection of geometries, relative stability order, spin density, electrostatic potential, molecular orbitals, NBO analysis, and vibrational analysis have showed a strong and stabilizing TS interaction between the radical center and the lone pair in the case of the 2-pyridyl radical. On the other hand, the 4-pyridyl radical showed stabilizing interactions only via TB coupling, whereas the TS interaction is nonexistent. Despite the presence of both interactions in the case of the 3-pyridyl radical, their overall influence is less effective toward stability. |
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