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| Title: | Deciphering Stability of Five-Membered Heterocyclic Radicals: Balancing Act Between Delocalization and Ring Strain |
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| Abstract: | Computational studies on five-membered heterocycles with single heteroatom and their isomeric dehydro-borole 1a–1c, cyclopentadiene 2a–2c, pyrrole 3a–3c, furan 4b–4c, phosphole 5a–5c, and thiophene 6b–6c radicals have been carried out. Geometrical aspects through ground state electronic structures and stability aspects using bond dissociation energies (BDE) and radical stabilization energies (RSE) have been envisaged in this regard. Spin densities, electrostatic potentials (ESP), and natural bond orbital (NBO) analysis unveiled the extent of spin delocalization. The estimated nucleus-independent chemical shifts (NICS) values revealed the difference in aromaticity characteristics of radicals. Particularly the heteroatom centered radicals exhibit odd electron π-delocalized systems with a quasi-antiaromatic character. Various factors such as, the relative position of the radical center with respect to heteroatoms, resonance, ring strain and orbital interactions influence the stability that follows the order: heteroatom centered > β-centered > α-centered radicals. Among the influences of various factors, we confirmed the existence of a competition between delocalization and the ring strain, and the interplay of both decides the overall stability order. |
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