Revisiting the aromaticity concept: electrostatic effects are responsible for the stability of benzene towards ring distortions

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The concept of aromaticity lacks of a precise or general definition, even nowadays, due to the fact that is neither an observable quantity nor directly measurable. Furthermore, the question of which electrons are responsible for the stabilization of the D_{6h} structure of benzene is still matter of subject. For many decades delocalization of π electrons was pointed as the stabilizing factor responsible for stabilization of benzene, but recent works admit this effect is a by-product of the (C-C)σ frame's propensity to possess identical bond lengths [1]. This work revisits the aromaticity concept using the GPF-EP methodology [2] energy partitioning scheme that allows a proper evaluation of covalent and quasi-classical effects in different bonds and their role in the stability of the molecule. The method was applied to investigate how these contributions vary along vibration modes that distort the ring, including the b_{2u} mode that leads to a cyclohexatriene-like structure. The results show that, except for the symmetric breathing ring mode, quasi-classical effects are the main responsible for the stabilization of benzene towards distortion. For the b_{2u} mode, interference stabilizes a distorted structure (Figure 1A), while the partitioning of quasi-classical energy (Figure 1B) shows that the stability comes from the kinetic part of (C-C)σ and (C-C)π quasi-classical energies related to the polarization of the GVB orbitals associated to σ and π electrons. This shows that the σ and π electrons are equally important to the planarity and stability of the D_{6h} benzene – and therefore to aromaticity – but by quasi-classical effects, and not covalent ones.
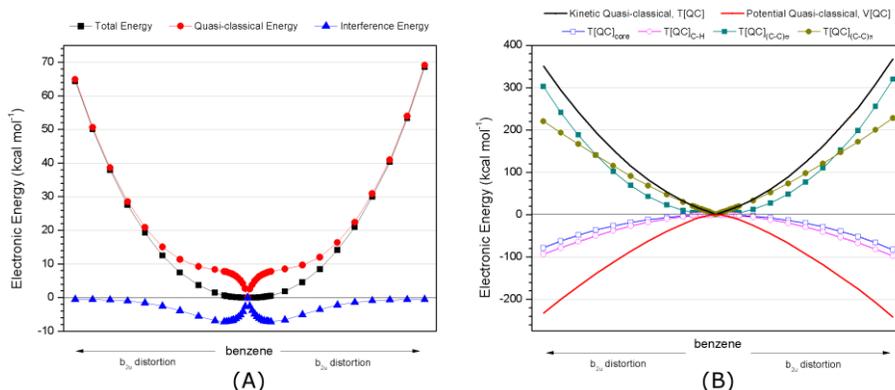

Figure 1 – Energy partitioning of benzene along the b_{2u} mode, obtained at the CASSCF(6,6)/cc-pVDZ level of calculation.

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