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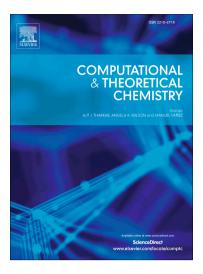
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Effect of counterion on the reactivity, stability, aromaticity and charge distribution in mono- and polyphosphacyclopentadienide ions - A Theoretical Investigation

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Graphical abstract

Highlights

The effect of counterion (Li⁺, Na⁺ and K⁺) on physicochemical properties of cyclopentadienide ion and its phospha-analogues has been investigated at the MP2 level

The distortion of the π -electrons cloud is mainly governed by the polarization effect of the cation Out-of-plane bending of hydrogen atoms is observed in all the M^+ - π complexes

The interaction energies of the Li⁺- π complexes are higher by $\sim 12-16$ kcal mol⁻¹

The CH/P exchange is accompanied by a decrease in the interaction energy

Nature of the counterion does not much affect aromaticity

Abstract

The effect of counterion (Li^+ , Na^+ and K^+) on π -charge distribution vis-a-vis aromaticity, chemical reactivity and stability of cyclopentadienide ion and its mono- and polyphospha-analogues has been investigated using the second-order Møller-Plesset (MP2) level of theory. The reactivity descriptors namely, chemical potential, electrophilicity index and chemical hardness based on LUMO, HOMO energy values are calculated at MP2/6-31++G(d,p) level. The aromaticity, thermochemistry, hydrogen-bending phenomena, Hirshfeld Population Analysis, Charge Model 5 (CM5) charges and electrostatic potential mapping are also computed at the same level of theory. All the results indicate greater stability of the Li^+ - π complexes in comparison to the Na $^+$ - π and K $^+$ - π complexes. The distortion of the π -electrons cloud is mainly governed by the polarization effect of the cation. Furthermore, the Nucleus-Independent Chemical Shift (NICS(1)zz) values indicate that the extent of aromaticity remains almost unaffected by complexation and the nature of the counterion.

Keywords

Counterion effect; Charge distribution; Cyclopentadienide ion; Mono-phosphacyclopentadienide ion; Polyphosphacyclopentadienide ion; Theoretical calculations

1. Introduction

Cation- π interactions between electron-rich aromatic rings and positively charged ions are non-covalent and electrostatic in nature and have emerged as one of the most fundamental interactions in material science, chemistry and structural biology [1-3]. The discovery of bis-

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