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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 ( $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) on physicochemical properties of cyclopentadienide ion and its phospho-analogues has been investigated at the MP2 level  
 The distortion of the  $\pi$ -electrons cloud is mainly governed by the polarization effect of the cation  
 Out-of-plane bending of hydrogen atoms is observed in all the  $\text{M}^+-\pi$  complexes  
 The interaction energies of the  $\text{Li}^+-\pi$  complexes are higher by  $\sim 12\text{-}16 \text{ kcal mol}^{-1}$   
 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 ( $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) on  $\pi$ -charge distribution vis-a-vis aromaticity, chemical reactivity and stability of cyclopentadienide ion and its mono- and polyphospho-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  $\text{Li}^+-\pi$  complexes in comparison to the  $\text{Na}^+-\pi$  and  $\text{K}^+-\pi$  complexes. The distortion of the  $\pi$ -electrons cloud is mainly governed by the polarization effect of the cation. Furthermore, the Nucleus-Independent Chemical Shift (NICS(1)<sub>zz</sub>) 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- $\pi$  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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