

## Polycyclic Compounds | Hot Paper |

## Bonding and Mobility of Alkali Metals in Helicenes

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**Abstract:** In this work, we analyze the interactions of alkali metal cations with [6]- and [14]helicene and the cation mobility of therein. We found that the distortion of the carbon skeleton is the reason that some of the structures which are local minima for the smallest cations are not energetically stable for  $K^+$ ,  $Rb^+$ , and  $Cs^+$ . Also, the most favorable complexes are those where the cation is interacting with two rings forming a metallocene-like structure, except for the largest cation  $Cs^+$ , where the distortion provoked by the size of the cation destabilizes the complex. As far as mobility is concerned, the smallest cations, particularly  $Na^+$ , are the

ones that can move most efficiently. In [6]helicene, the mobility is limited by the capture of the cation forming the metallocene-like structure. In larger helicenes, the energy barriers for the cation to move are similar both inside and outside the helix. However, complexes with the cation between two layers are more energetically favored so that the movement will be preferred in that region. The bonding analysis reveals that interactions with no less than 50% of orbital contribution are taking place for the series of  $E^+$ -[6]helicene. Particularly, the complexes of  $Li^+$  show remarkable orbital character (72.5–81.6%).

## Introduction

Helicenes are polycyclic aromatic compounds formed by ortho-fused aromatic rings. In 1956, Newman and Lednicher<sup>[1]</sup> synthesized phenantro[3,4-*c*]phenantrene and introduced the term hexahelicene (later [6]helicene), where the number in brackets indicates the number of rings in the helical backbone. The interest in these systems is due to their exceptional structural, chiroptical, and electronic properties.<sup>[2–5]</sup> Their distinctive helical structure emerges from the steric hindrance of the terminal rings, acquiring chirality even though they do not have chiral centers. However, studies revealed that this deviation from planarity does not represent a significant loss in aromaticity,<sup>[6]</sup> that is, the highly delocalized  $\pi$ -electron surface is preserved and the  $\pi$ - $\pi$  stacking interactions arise in helicenes with more overlapped layers. This  $\pi$ -cloud allows the interaction between

an helicene and a cation. Johansson and Patzschke, employing quantum chemical methods, predicted complexes formed by [6]- and [7]helicenes with Cr, Mo, W, and Pt and the feasibility of using these metals to fix the helicene to a specific atropisomer.<sup>[7]</sup> Recent studies by Makrlík and Vaňura<sup>[8–10]</sup> have confirmed the existence of the cationic complexes of [6]helicene with  $Tl^+$ ,  $Ag^+$ , and  $Li^+$  in the gas phase, which are characterized via electrospray ionization-mass spectrometry. Also, their computations for the  $Tl^+$ ,  $Ag^+$ , and  $Li^+$  complexes indicate that the most probable structure is a complex with the helicene acting as a molecular tweezer and the cation trapped amid the terminal rings.

Our group's recent interest in helicenes<sup>[11,12]</sup> and metallocenes<sup>[13–15]</sup> led us to ask the following questions: Are the structures with the cation on top of another ring energetically favorable? Is it possible to move the cation along the helicene? Is the mobility mechanism the same for all the alkali metals? If so, in which way would it move? Furthermore, these questions become even more relevant due to the importance of exploring carbon structures capable of adsorbing and releasing Li toward the development of Li-ion batteries.<sup>[16–18]</sup> To answer these questions and understand the relative stability and bonding of each cationic complex, we carry out a series of computations based on the density functional theory (DFT). Our most striking results include that smaller cations move

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