

阳离子- π 体系相互作用的理论研究 3: 碱金属阳离子-苯 复合物体系的量子 化学研究

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摘要 运用abinitioHartree-Fock从头算,微扰MP2

和密度泛函B3LYP方法在不同的基组水平上对碱金属阳离子-苯复合物体系的可能构型进行了自由优化,得到了复合物的能量最低构型为碱金属阳离子位于苯环平面的正上方,频率计算结果表明该结构为稳定结构.

复合物的键长、原子净电荷、分子轨道、前沿轨道能量、Mulliken键级等都表明,

碱金属阳离子和苯环碳原子之间的作用包含p- π 作用方式,

碱金属阳离子与苯结合时电子从苯环向碱金属阳离子转移,形成电荷转移复合物.

它们之间的结合方式和氢键的结合方式相似,

但计算得到的热力学参数表明复合物中碱金属阳离子与苯之间的结合强度远远大于典型的氢键,

尤其是锂离子-苯复合物的生成焓已和普通的化学键相当.复合物的红外特征振动频率位于 200cm^{-1} 附近,

对应于碱金属阳离子垂直于苯环平面的来回振动,同时形成复合物后,原来位于 3200cm^{-1} 的苯的C-H

振动红外活性消失.

关键词 [苯](#) [密度函数](#) [氢键](#) [从头计算法](#) [电荷转移](#) [碱金属](#)

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Theoretical studies on cation - π interactions 3: Quantum chemistry investigation on the configuration of and interactions in alkali metal cation -benzene complexes

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Abstract ab initio Hartree-Fock SCF,MP2 and density-functional theory B3LYP methods with different basis sets have used to optimize the possible geometries of the alkali metal cation-benzene ($M^+ \dots C_6H_6$) complexes. The calculation results show that the most stable geometries of alkali metal cation-benzene complexes are the configuration with C_{6v} symmetry axis,where the alkali metal cations are located above the benzene ring. The calculated IR spectrum show that these structures are reasonable.The bond lengths,total atomic charge,the coefficients of the molecular orbitals,frontier orbital energies,and Mulliken bonding population (MBP) of the complexes indicate that the interaction between alkali metal cations and benzene involve p- π interaction. On the other hand,electron is transfered from the benzene to the alkali metal cations,and thus gives charge transfer complexes.The calculated results also imply that the interaction characteristic of the alkali metal cation-benzene complexes are similar to hydrogen bonding. However,the theoretical thermodynamic parameters demonstrate that the interaction strength between the alkali metal cation and benzene is larger than that of the typical hydrogen bond,especially for the lithium cation-benzene,of which the formation enthalpy is as large as that for a chemical bond. The normal mode analysis of the predicted vibrational frequency shows that the characteristic vibration mode of the complex is located at about 200cm^{-1} ,which corresponds to the back and forth vibration of the alkali metal cations above the benzene ring plane.

Key words [BENZENE](#) [HYDROGEN BONDS](#) [AB INITIO CALCULATION](#) [CHARGE TRANSFER](#) [ALKALI METAL](#)

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