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Inductive effects on cation–π interactions: Structures and bond dissociation energies of alkali metal cation–halobenzene complexes

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In honor of M.T. Bowers on the occasion of his 70th birthday, in thanks for his numerous contributions to gas-phase ion chemistry, ion mobility and mass spectrometry, and in appreciation for his scientific mentoring and friendship.

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ABSTRACT

The influence of halogenation on cation–π interactions is investigated both experimentally and theoretically. Bond dissociation energies (BDEs) of alkali metal cation–halobenzene complexes, $M^+(C_6H_5X)$, are determined using threshold collision-induced dissociation techniques in a guided ion beam tandem mass spectrometer, where $M^+ = Na^+$ and K^+, and X = Cl, Br, and I. The primary dissociation pathway for all systems is endothermic loss of the neutral halobenzene from the cation–π complex. In addition, minor production of the ligand exchange product, M^+Xe, is also observed. At elevated energies elimination of NaX is also observed for the $Na^+(C_6H_5Br)$ and $Na^+(C_6H_5I)$ systems. Ab initio calculations at the B3LYP/6-31+G* level of theory are used to determine the structures of the neutral π-ligands and cation–π complexes. Theoretical BDEs are determined from single point calculations at the MP2(full)/6-311+G(2d,2p) level using the B3LYP/6-31+G* optimized geometries. Good agreement between the theoretical and experimental BDEs is found in all cases. The trends in the BDEs of the $M^+(C_6H_5X)$ complexes are explained in terms of the varying magnitude of the electrostatic interactions in these complexes elucidated from a binding parameter model. Comparisons are also made to BDEs previously determined for the analogous $M^+(C_6H_6)$ and $M^+(C_6H_5F)$ complexes to examine the inductive effects of the halogen substituent on the strength of the cation–π interaction.

1. Introduction

As with hydrophobic interactions, van der Waals forces, and hydrogen bonds, cation–π interactions represent another type of noncovalent interaction that plays important roles in protein structure determination [1–4] and molecular recognition processes associated with the functions of ion channels and enzymes [5–11]. Cation–π interactions may occur between a cation and a neutral or anionic π-electron system; however cation–π interactions involving neutral π-electron systems are of greater relevance to biological processes [12]. To date numerous experimental studies have investigated cation–π interactions, and in particular have been devoted to the characterization of the strength of these interactions [13–31]. In addition, calculations of the structures and the bond dissociation energies (BDEs) of cation–π complexes [9,13–39] and electrostatic potential maps [29,31] have often been performed to complement the experimental work.

Most studies of cation–π interactions have been carried out in the gas phase or in a pseudo aqueous environment simulated by partial hydration of the cation. In these studies, it has been found that the more hydrated the metal cation, the less susceptible it is to a cation–π interaction [40]. Cabarcos et al. used such partial hydration studies to demonstrate ion selectivity in ion channels [41]. They attributed the selectivity for K^+ over Na^+ in potassium ion channels to differences in the energetics of solvation of these metal cations. Their studies showed that K^+ exhibits a greater binding affinity for benzene than water molecules in the first solvation shell. However, the sodium cation does not display such behavior, as the water molecules are not as readily displaced by benzene. This difference in their interactions confers selectivity for potassium cations over sodium cations [3]. Gas-phase studies also provide insight into the intrinsic contributions to the binding in cation–π interactions, which are dependent on both the specific metal cation and π-electron system. Studies in the gas phase provide a measure of the cation–π interaction in low polarity environments, which make up the bulk of cation–π interactions operative in biological systems.

The strength and specificity of cation–π interactions are determined by the electrostatic forces between the cation and π system involved, i.e., ion-dipole, ion-quadrupole, and ion-induced dipole interactions. Of these three, the ion-quadrupole interaction has been shown to dominate cation–π interactions in benzene systems [10,18–31,42]. However the relative contributions to the binding

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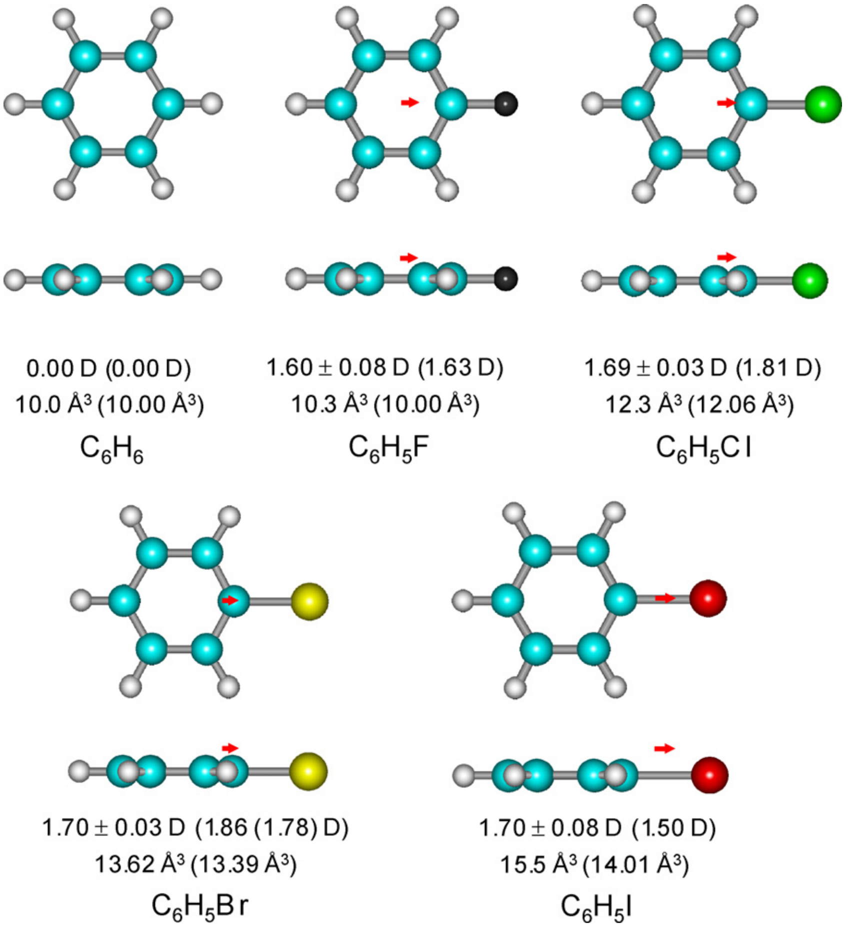

Fig. 1. Geometry-optimized structures of C_6H_6, C_6H_5F, C_6H_5Cl, C_6H_5Br, and C_6H_5I. Measured [45] (and calculated) dipole moments in Debye are shown. Properly scaled and oriented dipole moment vectors are shown as arrows as determined from the theoretical calculations. Measured [45] (and calculated) isotropic molecular polarizabilities in Å^3 are also shown.

are likely to be strongly influenced by substituents. Electropositive substituents enhance the cation–π interaction, while electronegative substituents tend to destabilize it [43]. Therefore, fundamental characterization of the factors that influence the strength and specificity of cation–π interactions is necessary and will prove useful in understanding the detailed roles these interactions play in biological systems and for optimization of technological applications that make use of cation–π interactions. The halobenzenes provide a simple deviation from the idealized symmetric structures of cation–π interactions between benzene and metal cations. In addition, halogen bonds occur naturally where they function as stabilizing intermolecular interactions in a C–X···O–Y bond fashion, where X is a halogen substituent, and O–Y a carbonyl, hydroxyl, charged carboxylate or phosphate group [44]. The electrostatic potential energy maps for the halobenzenes reveal that the strength of the X···O interaction should increase as the size of the halogen increases due to an increase in the polarizability [44], and to a lesser extent the dipole moment of the π system.

In this study, we explore the influence of inductive effects on cation–π interactions by examining cation–π complexes to several aromatic ligands containing electron-withdrawing substituents, the halobenzenes, C_6H_5X, where X = Cl, Br, and I. The alkali metal cations examined in the present study include Na^+ and K^+, which were selected due to their abundance and significance in biological systems. The present results are compared to the analogous benzene [16] and fluorobenzene [21] systems previously examined. In addition, a binding parameter analysis designed to elucidate the absolute and relative contributions that ion-dipole, ion-quadrupole, and ion-induced dipole interactions contribute to the binding is performed. In particular, the inductive effects of halogen substituents on the cation–π interaction are examined. The structures of benzene (C_6H_6), fluorobenzene (C_6H_5F), chlorobenzene (C_6H_5Cl), bromobenzene (C_6H_5Br), and iodobenzene (C_6H_5I) along with their measured [45] and calculated dipole moments and isotropic molecular polarizabilities are shown in Fig. 1.

2. Experimental and theoretical

2.1. Experimental protocols

Cross sections for collision-induced dissociation (CID) of six $M^+(C_6H_5X)$ complexes, where $M^+ = Na^+$ and K^+, and X = Cl, Br, and I are measured using a guided ion beam tandem mass spectrometer that has been described in detail previously [46]. The complexes are formed by condensation of the alkali metal cation and neutral halobenzene ligand in a flow tube ion source operating at pressures in the range of 0.5–0.8 Torr. These complexes are collisionally stabilized and thermalized by in excess of 10^5 collisions with the He and Ar bath gases such that the internal energies of the ions emanating from the source region are expected to be well described by a Maxwell–Boltzmann distribution at room temperature. The ions are effusively sampled, focused, accelerated, and focused into a magnetic sector momentum analyzer for mass analysis. Mass-selected ions are decelerated to a desired kinetic energy and focused into an octopole ion guide. The octopole passes through a static gas cell containing Xe [47–49] at sufficiently low pressure