

1003-7713/2002/02-093-4

# A Theoretical Study on the Structures of the Cation- $\pi$ Complexes Formed by Ethylene, Benzene with $\text{Li}^+$ , $\text{Na}^+$ , and $\text{K}^+$ \*

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**Abstract** The structures of the cation- $\pi$  complexes between ethylene, benzene and  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  were studied systematically in detail for the first time. It was found that though the C-H bond of ethylene is elongated upon complexation as expected, the C-H bond of benzene is unexpectedly shortened upon complexation especially with lithium cation. Such a behavior might have the same physical origin as that in the recently found blue-shift hydrogen bonds.

**Key words** *ab initio*, Cation- $\pi$  interaction, C-H bond shortening

**CLC number:** O643      **Document code:** A

## 1 Introduction

With the development of supramolecular science, theoretical studies on non-covalent interactions have attracted more and more attention recently<sup>[1]</sup>. In fact, such studies have become so effective that sometimes the unexpected chemical behaviors could be predicted by theory at first and then verified by experiment subsequently. For example, in recent studies it was established that contrary to the traditional hydrogen bond  $\text{X}-\text{H}\cdots\text{Y}$  in which X-H is elongated upon the complexation, the so-called improper blue shifting hydrogen bond also exists where X-H bond length decreases upon hydrogen bond formation<sup>[2]</sup>.

Herein, we reported another unexpected X-H shortening behavior, which however, takes place in cation- $\pi$  interaction. As known, such an interaction has been found very important in molecular recognition and biochemistry, though its physicochemical details have not been sufficiently well characterized<sup>[3]</sup>.

## 2 Methods

All the calculations were performed with Gaussian 98<sup>[4]</sup>. Methods including HF/3-21G\*, HF/6-31G\*, HF/6-311G\*\*, B3LYP/6-31G\*, B3LYP/6-311G\*\*, MP2/6-31G\*, MP2/6-311G\*\*, and MP2/6-311++G(2d,2p) were used. After geometry optimization with a method, frequency calculation with the same method was done to verify that the geometry was an energy minimum. The systems studied included the ethylene and benzene cation- $\pi$  complexes with  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ .

## 3 Results and discussion

In Fig. 1 are shown the geometries of the cation- $\pi$  complexes, whose corresponding structural parameters are listed in Table 1 and Table 2. From the Tables, it can be seen that Hartree Fock methods predict smaller C-C and C-H bond lengths than those by DFT and MP methods. However, the results of different

\* Project supported by the National Natural Science Foundation of China.

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Received date: 2001-06-12.

theoretical methods are basically in agreement with each other, indicating the reliability of the optimizations. It is also interesting to see that in HF method the C-H bond lengths of the ethylene and benzene lengthen with the larger basis sets used, while they decrease with the larger basis sets in DFT and MP methods. This phenomenon is not observed concerning the C-C bond lengths.

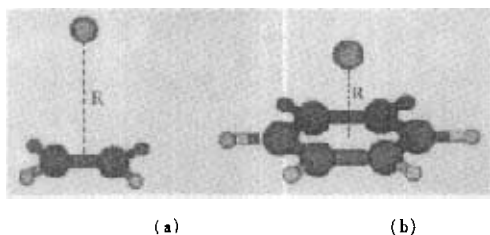


Fig. 1 The geometries of the ethylene (a) and benzene (b) cation- $\pi$  complexes with alkali-metal cation

As expected, the distance from the  $\pi$  system to the cation R increases in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$  for ethylene as well as benzene. Such a behavior is caused by the fact that the electrostatic force plays a very important role in the cation- $\pi$  interaction<sup>[5]</sup>. Therefore, the larger the radius of the cation, the smaller the interaction energy and the larger the distance R was shown.

Interestingly, all the methods predict that the C-C bond length will increase upon the formation of a cation- $\pi$  complex compared with that of a free ethylene or benzene molecule. Such a behavior might not be surprising, because it could be anticipated that a small amount of charge transfer might take place from the bonding orbitals of the  $\pi$  systems to the empty orbitals of the cations in the cation- $\pi$  complexes, resulting in the weakening of the C-C bond and a concomitant increase of its length.

In fact, similar argument was also used to explain the usual X-H elongation in X-H...Y hydrogen bonding, which however, cannot account for the X-H shortening in blue shifting hydrogen bonds<sup>[2]</sup>. Herein, if the above explanation were correct, it can be anticipated that the C-H bond should also be elongated, or at least remain unchanged upon the cation- $\pi$  complexation. Indeed, such a behavior is observed for the complexation of ethylene with  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ .

However, the change in the C-H bond length of benzene is unexpected. For  $\text{Na}^+$ , and  $\text{K}^+$  complexes, different theoretical methods do not agree with each other on whether the C-H bond length increases or decreases upon complexation. Nevertheless, for  $\text{Li}^+$  complex, the C-H bond is always definitely shortened upon complexation, which is also verified with higher-level methods such as MP2/6-311++G(2d,2p).

Table 1 The structural parameters of the ethylene complexes with  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  (Å)

Complex	HF/6-31G*	HF/6-311G**	B3LYP/6-31G*	B3LYP/6-311G**	MP2/6-31G*	MP2/6-311G**	MP2/6-311++G(2d,2p)
R							
Li <sup>+</sup>	2.3533	2.3177	2.2867	2.2700	2.3105	2.2870	2.3004
Na <sup>+</sup>	2.7273	2.7403	2.6392	2.6605	2.6710	2.6962	2.7148
K <sup>+</sup>	3.2743	3.2923	3.1643	3.1733	3.1585	3.1283	3.1448
C-C							
Li <sup>+</sup>	1.3332	1.3307	1.3462	1.3408	1.3505	1.3499	1.3445
Na <sup>+</sup>	1.3298	1.3276	1.3440	1.3387	1.3477	1.3471	1.3420
K <sup>+</sup>	1.3254	1.3237	1.3399	1.3348	1.3442	1.3441	1.3396
Free	1.3170	1.3163	1.3309	1.3269	1.3363	1.3372	1.3341
C-H							
Li <sup>+</sup>	1.0777	1.0785	1.0900	1.0875	1.0883	1.0882	1.0821
Na <sup>+</sup>	1.0773	1.0780	1.0893	1.0867	1.0876	1.0874	1.0814
K <sup>+</sup>	1.0769	1.0776	1.0888	1.0863	1.0869	1.0867	1.0810
Free	1.0760	1.0767	1.0875	1.0850	1.0852	1.0852	1.0794

Table 2 The structural parameters of the benzene complexes with  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  (Å)

Complex	HF/6-31G*	HF/6-311G**	B3LYP/6-31G*	B3LYP/6-311G**	MP2/6-31G*	MP2/6-311G**	MP2/6-311+G(2d,2p)		
R	$\text{Li}^+$	1.9443	1.8890	1.8806	1.8452	1.9234	1.8689	1.8696	
	$\text{Na}^+$	2.4534	2.4751	2.3775	2.4068	2.3925	2.4254	2.4582	
	$\text{K}^+$	2.9780	2.9835	2.8776	2.8765	2.8452	2.8058	2.8327	
C - C	$\text{Li}^+$	1.3954	1.3936	1.4062	1.4024	1.4065	1.4076	1.4036	
	$\text{Na}^+$	1.3933	1.3917	1.4041	1.4007	1.4043	1.4056	1.4015	
	$\text{K}^+$	1.3912	1.3899	1.4020	1.3987	1.4020	1.4039	1.4003	
Free		1.3862	1.3854	1.3966	1.3939	1.3968	1.3991	1.3961	
	C - H	$\text{Li}^+$	1.0744	1.0746	1.0860	1.0837	1.0872	1.0861	1.0803
		$\text{Na}^+$	1.0749	1.0751	1.0864	1.0839	1.0875	1.0865	1.0809
$\text{K}^+$		1.0752	1.0753	1.0867	1.0842	1.0876	1.0866	1.0811	
Free		1.0757	1.0756	1.0870	1.0844	1.0874	1.0864	1.0809	
	$\text{C}_6\text{H}_6^{++}$	—	—	1.0864	1.0822	—	—	—	

On the other hand, this unexpected behavior might be of importance in that: (1) The shortening of C - H bond might be accompanied with a corresponding blue shift in the infrared spectroscopy, whose detection could provide much information for such a non-covalent interaction. (2) The difference in C - H bond length change between ethylene and benzene complexes indicates that the two cation- $\pi$  complexes have certain subtle differences, which have not been noticed before. (3) The shortening here might have the same physical origin as that in the blue shifting hydrogen bonds.

It should be mentioned that the origin of the blue shifting hydrogen bonds has not been fully understood. Nevertheless, recently Hobza *et al.* proposed that in the blue shifting hydrogen bonds, instead of the charge transfer from the proton acceptor Y to the X - H bond, charge transfer happens from Y to the remote part of the proton donor molecule. This remote charge transfer causes the proton donor to reorganize its structure resulting in the shortening of X - H bond<sup>[2]</sup>. However, from Hobza's study it has not been known how and why the structural reorganization happens.

In the present systems, it is clear that the C - H bond shortening cannot be caused by the charge transfer from the C - H bonding orbitals to the cation. Never-

theless, there must be some charges transfer from benzene to the cation, which can be viewed to be from the remote part of the donor molecule relative to the C - H bond. As an extreme spot, when the benzene donates a full electron to the cation resulting in benzene radical cation, the C - H bond length is found shortened according to B3LYP calculations (see Table 2). Thereby, the charge transfer from the remote part could cause C - H contraction. In other words, this behavior has a similar mechanism with the blue shifting hydrogen bond, although here we have also found why and how the structural reorganization could happen.

## 4 Conclusion

From high-level theoretical studies, we found that in the benzene complexes with lithium cation, the C - H bond is shortened upon the complex formation. This is a novel phenomenon, and may be useful for the spectroscopic study of the noncovalent complexes. We propose that the mechanism for the C - H shortening is the remote charge transfer, which is confirmed by the calculations on the benzene radical cation. Thereby, the finding is related to the recently found blue shifting hydrogen bond in that they may have the same mechanism. Clearly, such studies on the effects of noncovalent

lent interactions on the geometry of the molecules create an interesting new field.

Acknowledgement: This work was supported by the National Natural Science Foundation of China.

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## 乙烯、苯与 $\text{Li}^+$ 、 $\text{Na}^+$ 、 $\text{K}^+$ 形成的阳离子- $\pi$ 复合物结构的理论研究\*

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**摘要:** 系统地研究了乙烯、苯与  $\text{Li}^+$ 、 $\text{Na}^+$ 、 $\text{K}^+$  形成的阳离子- $\pi$  复合物的结构. 发现在乙烯与  $\text{Li}^+$ 、 $\text{Na}^+$ 、 $\text{K}^+$  阳离子形成的复合物中, 乙烯分子的 C-H 键与形成复合物前相比伸长了, 然而, 在苯的阳离子- $\pi$  复合物中, 苯分子的 C-H 键却出乎意料地变短了(特别是在锂离子- $\pi$  复合物中). 这种现象可能与最近由 Hobza 等人发现的蓝移氢键现象有相同的机理.

**关键词:** *ab initio*; 正离子- $\pi$  相互作用; C-H 键缩短

**中图分类号:** O643      **文献标识码:** A

\* 国家自然科学基金资助项目.

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