

Cation– π interaction in potassium–polyene complexes and the fate of potassium ion: A theoretical study

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Abstract

Ab initio studies have been done at B3LYP/6-31G* level of theory to determine the structural changes on the substitution of potassium to odd-numbered all-trans conjugated polyenes ranging from C_5 to C_{13} . The results show that potassium is always positioned in the form of K^+ above an odd carbon other than the terminal carbons and that the stablest structural isomer is the one with K^+ lying above the central odd carbon. If a central odd carbon does not exist (as in C_{11} -system), then K^+ will be positioned above the odd carbon nearest to the central carbon to achieve maximum stability. The difference in the binding energies of the isomers is generally small and it becomes insignificantly small as the carbon chain length increases so that under suitable conditions K^+ ion may be made to move between the ends of the polyene. The metal–polyene complexes are seen to have a considerably reduced HOMO–LUMO gap. Further, the interaction of potassium with the polyene not only caused a total rearrangement of the bond lengths, bond angles and dihedral angles, but also induced a bend (warping) to the polyenic fragment that pockets K^+ . The structural changes and stability of the metal–polyene complexes are explained in terms of electrostatic interaction and cation– π cloud interaction.

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Keywords: Computational studies; Polyenes; Potassium; Warping of carbon skeleton; Electrostatic interaction; Cation– π interaction

1. Introduction

There is considerable interest in the theoretical study of cation– π interaction due to its prominence in a wide range of systems such as host–guest complexes, protein structures, catalytic systems, and functional materials [1–6]. However, there have been very few studies on interactions involving cations with non-aromatic systems such as polyenes [7]. Such studies may bring out the possible influence of the cation– π interaction in the mechanism of transition of semiconducting polymers to perfect conductor, which is a fundamental problem of conductive polymer research. A theoretical understanding of the electronic and structural changes occurring due to the presence of the cation may provide valuable information in this regard. We have thus taken up a systematic theoretical investigation on the interactions between metallic species and conjugated polyenyl systems, and we report some interesting features of K-complexes.

2. Methodology

We have chosen odd-numbered all-trans conjugated polyenes (C_nH_{n+3}) ranging from C_5 to C_{13} as our samples for this theoretical investigation. For convenience, the carbon atoms in the polyenes are numbered after setting the sp^3 -carbon as C1 (Fig. 1). All hydrogen atoms except the two on the sp^3 -carbon lie in the plane of the carbon skeleton. In order to model polyenyl potassium complex ($C_nH_{n+2}K$), potassium was substituted at the terminal sp^3 -carbon (C1) of the polyene by replacing one of the non-planar hydrogens. The resulting structure was fully optimized using density functional theory (DFT) with B3LYP hybrid functional and standard split valence plus polarization 6-31G* basis set. To determine whether the optimized structure corresponded to a local minimum on the potential energy surface or a transition state, the force constant matrix was constructed, which on diagonalization yielded the normal mode vibrational frequencies. By examining the number of negative eigenvalues of this matrix, decision regarding local minimum or transition structure was made. Full geometry optimization was also carried out on all systems using second order Moller–Plesset perturbation theory (MP2)

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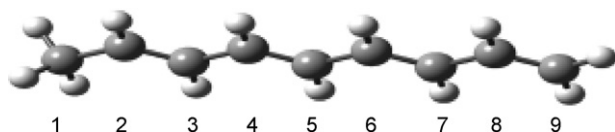


Fig. 1. Labeling of the carbon atoms in odd-numbered all-trans polyenes (shown for C_9H_{12}). The terminal sp^3 -carbon is labeled as carbon-1 (C1). The other terminal carbon (here, C9) is always sp^2 -hybridized.

with 6-31G* basis set. Further, for selected samples, full geometry optimization was carried out by B3LYP and MP2 methods using the higher basis set 6-311+G* to test for any difference in the trend observed with 6-31G* basis set. All calculations were made using Gaussian 03 programme package [8].

3. Results

On substituting potassium on the terminal sp^3 -carbon (C1) and optimizing, we found that the metal never stayed on C1, but C1 changed to sp^2 -hybridized state and the metal shifted and positioned in the form of cation above the carbon C3 to produce the complex $C_nH_{n+2}K(3)$, the numeral in parentheses indicating the carbon above which the cation is positioned in the optimized geometry. This is equivalent to doping the planar polyenic anion $(C_nH_{n+2})^-$ with K^+ over the carbon C3. To explore the possible existence of other structural isomers with K^+ positioned at different locations above the carbon skeleton, K^+ was doped on different carbons of the polyenic anion and geometry optimizations were done. This procedure revealed the existence of several stable isomers differing slightly in energy

with K^+ positioned above different carbons. Both B3LYP and MP2 methods gave similar results.

The binding energy (E_b) of potassium–polyene complex $C_nH_{n+2}K$ was taken as the negative of the energy of formation of the complex and was determined by subtracting the energy of the optimized potassium–polyene complex from the sum of the energies of K^+ and the polyenic anion $(C_nH_{n+2})^-$.

The total energy (E) of the isomer, binding energy of the isomer (E_b), distance of K^+ from the n^{th} carbon above which it is stationed (R_n), Mulliken charge of the cation (Q_{cat}), and HOMO–LUMO gap of the isomer (ΔE_{isomer}) and of the corresponding polyene ($\Delta E_{\text{polyene}}$) are given in Table 1. In Table 2, the distance R_n is compared with the distances R_{n-1} and R_{n+1} of K^+ from the $(n-1)^{\text{th}}$ and $(n+1)^{\text{th}}$ carbons. Table 3 shows the angle made by K^+ with the n^{th} carbon and the n^{th} hydrogen ($KCnHn$) and also the angle with the n^{th} and $(n+1)^{\text{th}}$ carbons ($KCnCn-1$). Further, the dihedral angles $Cn-1CnCn+1Cn+2$ and $Cn-2Cn-1CnCn+1$ are also included in Table 3. The Mulliken charges (Q) on different carbons in C_{13} -systems are given in Table 4.

The results show the following features:

- (i) K^+ is always positioned above an odd carbon other than the terminal carbons, i.e., C3, C5, C7, etc. and C1 undergoes a change of hybridization to sp^2 . For instance, the C_{13} -system gave three stable structural isomers $C_{13}H_{15}K(3)$, $C_{13}H_{15}K(5)$ and $C_{13}H_{15}K(7)$. (Note that R_{n-1} and R_{n+1} are almost equal and larger than R_n (Table 2); further, the angle made by K^+ with Cn and Hn is about 90° for all the three isomers (Table 3), suggesting that K^+ is located vertically above Cn .)

Table 1
Selected parameters of the structural isomers of different metal–polyene systems optimized at B3LYP/6-31G* and MP2/6-31G* levels

Metal–polyene system	Method	Stable isomer ^a	E (hartree)	E_b (kcal/mol)	R_n (Å)	Q_{cat} (a.u.)	ΔE_{isomer} (hartree)	$\Delta E_{\text{polyene}}$ (hartree)
C_5H_7K	B3LYP	$C_5H_7K(3)$	−794.59862	118.50	2.7807	0.58958	0.06954	0.20248
	MP2	$C_5H_7K(3)$	−793.16404	122.41	2.7625	0.69827	0.19015	0.43709
C_7H_9K	B3LYP	$C_7H_9K(3)$	−872.00842	107.71	2.7772	0.64391	0.06293	0.16240
	MP2	$C_7H_9K(3)$	−870.31811	112.18	2.7712	0.73515	0.18083	0.37884
$C_9H_{11}K$	B3LYP	$C_9H_{11}K(3)$	−949.41836	100.47	2.7816	0.66000	0.05942	0.13765
		$C_9H_{11}K(5)$	−949.41799	100.44	2.7755	0.69512	0.05941	0.13765
	MP2	$C_9H_{11}K(5)$	−947.47212	105.61	2.7702	0.76685	0.17347	0.34264
		$C_9H_{11}K(3)$	−947.47152	105.23	2.7751	0.74612	0.17421	0.34264
$C_{11}H_{13}K$	B3LYP	$C_{11}H_{13}K(5)$	−1026.82776	95.24	2.7830	0.70611	0.05779	0.12079
		$C_{11}H_{13}K(3)$	−1026.82749	94.89	2.7854	0.67142	0.05782	0.12079
	MP2	$C_{11}H_{13}K(5)$	−1024.62543	100.79	2.7783	0.77400	0.16865	0.31720
		$C_{11}H_{13}K(3)$	−1024.62393	99.85	2.7795	0.75324	0.16934	0.31720
$C_{13}H_{15}K$	B3LYP	$C_{13}H_{15}K(7)$	−1104.23727	91.29	2.7895	0.71474	0.05652	0.10855
		$C_{13}H_{15}K(5)$	−1104.23677	90.99	2.7879	0.71426	0.05599	0.10855
		$C_{13}H_{15}K(3)$	−1104.23621	90.46	2.7880	0.67906	0.05593	0.10855
	MP2	$C_{13}H_{15}K(7)$	−1101.77857	97.29	2.7838	0.77943	0.16506	0.29909
		$C_{13}H_{15}K(5)$	−1101.77777	96.80	2.7836	0.77892	0.16486	0.29909
		$C_{13}H_{15}K(3)$	−1101.77586	95.59	2.7830	0.75788	0.16589	0.29909

^a The numeral in parentheses corresponds to the carbon above which the metal is stationed.

Table 2

Distance (Å) (B3LYP/6-31G* values) of the cation from the carbons of the warped segment

Isomer	R_{n-1}	R_n	R_{n+1}
C ₁₃ H ₁₅ K(7)	2.9658	2.7895	2.9658
C ₁₃ H ₁₅ K(5)	3.0061	2.7879	2.9302
C ₁₃ H ₁₅ K(3)	2.9566	2.7880	2.9644

(ii) The stablest isomer is always the one with K⁺ lying above the central odd carbon. If central odd carbon does not exist (as in C₁₁-system), then K⁺ will be positioned above the odd carbon nearest to the central carbon to achieve maximum stability. Accordingly, in C₁₃-system K(7) isomer is the stablest, whereas in C₁₁-system K(5) isomer is the stablest (Table 1). Thus, K⁺ shifts towards the center of the polyene to achieve more and more stability as shown in Fig. 2.

(iii) The interaction of K⁺ not only causes a total rearrangement of bond lengths, bond angles and dihedral angles, but also induces a dramatic bend (warping) to the polyenic fragment that pockets the cation. Fig. 2 illuminates this phenomenon. Also note from Table 3 that the angle KCnCn–1 is much less than 90° indicating the bend of the carbon skeleton. Deviation of the dihedral angles from 180° also demonstrates clearly the warping phenomenon.

(iv) The HOMO–LUMO gap of the polyene is reduced by about 50% by potassium doping (Table 1). The odd carbons of the polyenic chain possess considerably higher negative charge than the even carbons, the charges on the terminal odd carbons being the highest (Table 4).

Optimization after substituting K by replacing the planar hydrogen on any sp² carbon resulted in a geometry in which K remained in the carbon plane attached to the same carbon where it was substituted. Planar substitution on the sp³-carbon (C1) resulted in a transition state. (A planar substitution is indicated by adding *p* to the numeral in the label. Thus, C_nH_{n+2}K(5p) indicates that K⁺ is attached to C5 and lies in the carbon plane.)

Table 3

Selected bond angles and dihedral angles (°) (B3LYP/6-31G* values) at the warped segment

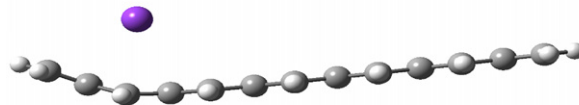
Isomer	KC _n H _n	KCnCn – 1	Cn – 1CnCn + 1Cn + 2	Cn – 2Cn – 1CnCn + 1
C ₁₃ H ₁₅ K(7)	92.75	82.89	–157.70	157.71
C ₁₃ H ₁₅ K(5)	92.45	84.61	157.64	–157.71
C ₁₃ H ₁₅ K(3)	90.33	82.35	156.21	–152.33

Table 4

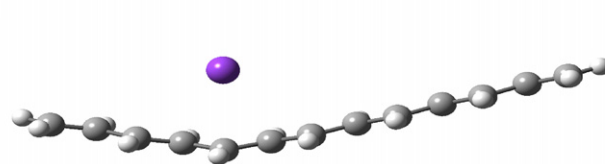
Mulliken charges (*Q*) (B3LYP/6-31G* values) on the carbons in C₁₃H₁₆, (C₁₃H₁₅)[–] and C₁₃H₁₅K

System	<i>Q</i> (a.u.)												
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
C ₁₃ H ₁₆	–0.357	–0.060	–0.124	–0.122	–0.125	–0.123	–0.125	–0.123	–0.126	–0.123	–0.100	–0.105	–0.491
(C ₁₃ H ₁₅) [–]	–0.409	–0.048	–0.162	–0.116	–0.166	–0.115	–0.165	–0.115	–0.166	–0.116	–0.162	–0.048	–0.409
C ₁₃ H ₁₅ K(3)	–0.448	–0.099	–0.251	–0.160	–0.204	–0.118	–0.153	–0.121	–0.143	–0.120	–0.137	–0.057	–0.372
C ₁₃ H ₁₅ K(5)	–0.392	–0.056	–0.193	–0.163	–0.252	–0.168	–0.206	–0.119	–0.153	–0.121	–0.142	–0.057	–0.378
C ₁₃ H ₁₅ K(7)	–0.380	–0.058	–0.149	–0.120	–0.199	–0.167	–0.250	–0.167	–0.199	–0.120	–0.149	–0.058	–0.380

(a):



(b):



(c):

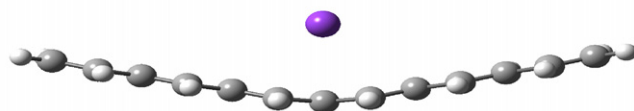


Fig. 2. Optimized structures of the stable isomers of C₁₃H₁₅K, showing the shifting of the cation (K⁺) towards the central odd carbon. The K(7) isomer (c) has the maximum stability. Note the warping of the polyenic fragment that pockets the cation: C₅ in (a), C₉ in (b) and C₁₃ in (c).

It is evident from Table 1 that the isomers obtained by non-planar substitution have reasonably high binding energy and that the energy difference between the isomers of the same system is very low. For example, C₉H₁₁K(3) and C₉H₁₁K(5) differ in energy by 0.233 kcal/mol (B3LYP). However, the isomers obtained via planar substitution, for example, C₉H₁₁K(5p) and C₉H₁₁K(9p) possess energies –949.38870

and -949.38647 hartree (1 hartree = 627.509 kcal/mol), which are higher than that of the non-planar isomer $C_9H_{11}K(3)$ by 19.17 and 20.01 kcal/mol (B3LYP), respectively. Thus, planar substitution complexes are generally less stable, and are not further pursued.

4. Discussion

The preferential affinity of K^+ towards an odd carbon (C3, C5, C7, etc.) rather than an even carbon may be generally explained in terms of the higher negative charge possessed by the odd carbon (see Table 4) and the resulting stronger attractive Coulombic interactions (*Type I interaction*) with K^+ . However, this simple model is insufficient, since K^+ doped at the terminal odd carbon (C1) carrying the maximum negative charge, never sticks on to it, but always moves towards C3 carrying a lesser charge. The role of other factors contributing to stability is thus apparent.

It is easy to see that the odd carbon above which K^+ is stationed is the central carbon of the polyene itself or of a fragment of the polyene. For instance, C7 is the central odd carbon in $C_{13}H_{15}K$, C5 is the central odd carbon of the C_9 -fragment in $C_{13}H_{15}K$ and C3 is the central odd carbon of the C_5 -fragment in $C_{13}H_{15}K$. Similar relationships can be easily established in all the other K -polyene complexes. In other words, K^+ always seeks a location above the central odd carbon (i.e., C3, C5, C7, etc.) of a polyenic fragment consisting of 5 carbons and 6 π -electrons, or 9 carbons and 10 π -electrons, or 13 carbons and 14 π -electrons, etc., producing stable isomers with a dramatic bend (warping) at the polyenic fragment that pockets K^+ . Fig. 2 illuminates this interesting phenomenon. Further, a 9-carbon fragment is obtained by the fusion of two pentadienyl groups, a 13-carbon fragment is obtained by the fusion of three pentadienyl groups and so on. Thus, in all its complexes K^+ formally interacts with a polyenic fragment

carrying a cloud of $(4n + 2)$ π -electrons (n = number of pentadienyl groups fused together in the polyenic segment) and this interaction produces a warping of the carbon skeleton. The earlier proposal [7] that “the isomers containing 3-carbon 4 π -electron interaction sites appear favored”, is thus not true with K -complexes. Our results suggest that for potassium the stability appears to be associated with an interaction between the cation and $(4n + 2)$ π -electrons rather than 4 π -electrons. Higher the value of n , higher is the stability. In other words, K^+ moves towards the central odd carbon of the polyene itself to attain maximum stability for the complex (see Fig. 2). If the central carbon is even as in $C_{11}H_{14}$, then K^+ will be positioned above the odd carbon closest to the central even carbon (C5 in C_{11} -system) (see Table 1). Therefore, in addition to the Coulombic interaction (*Type I*), the number of interacting π -electrons, in other words the size of the π -electron cloud, also holds the key to the stability of the K -complexes. The reduction in the charge of K^+ in the complex to a value noticeably less than the original value of +1 (see Table 1) is indicative of this cation- π -cloud interaction (*Type II interaction*). Thus, π -electrons of the polyenic system tend to ‘flow’ towards the cation resulting in an interaction between the cation and the π -cloud attributing stability to the complex.

The MP2 binding energies of the isomers of all the polyenic systems studied are in accordance with the above model. It is the case with the B3LYP values too, but for $C_9H_{11}K$ (see Table 1). The model suggests that the stablest isomer of $C_9H_{11}K$ is $C_9H_{11}K(5)$ in agreement with MP2 result, whereas B3LYP calculation showed that $C_9H_{11}K(3)$ is the stablest. However, B3LYP also gave the expected result for $C_9H_{11}K$ on the use of the higher basis set 6-311+G* resolving the only contradiction (see Table 5).

As the length of the polyene increases, the number of stable isomers also increases. Based on the above model, it is easy to predict all of them. For instance, there should exist six stable

Table 5
Effect of basis sets on the binding energies of some selected systems

Method	Stable isomer	Basis set	E (hartree)	E_b (kcal/mol)	R_n (Å)	Q_{cat} (a.u.)	ΔE_{isomer} (hartree)
B3LYP	$C_5H_7K(3)$	6-31G*	-794.59862	118.50	2.7807	0.58958	0.06954
		6-311+G*	-794.69138	109.92	2.7255	0.89059	0.08507
MP2	$C_5H_7K(3)$	6-31G*	-793.16404	122.41	2.7625	0.69827	0.19015
		6-311+G*	-793.60479	115.78	2.7234	0.93866	0.19489
B3LYP	$C_7H_9K(3)$	6-31G*	-872.00842	107.71	2.7772	0.64391	0.06293
		6-311+G*	-872.11817	101.25	2.7325	0.92055	0.07938
MP2	$C_7H_9K(3)$	6-31G*	-870.31811	112.18	2.7712	0.73544	0.18075
		6-311+G*	-870.81421	107.71	2.7338	0.9615	0.1864
B3LYP	$C_9H_{11}K(3)$	6-31G*	-949.41836	100.47	2.7816	0.66000	0.05942
		6-311+G*	-949.54478	95.05	2.7411	0.92988	0.07622
	$C_9H_{11}K(5)$	6-31G*	-949.41799	100.44	2.7755	0.69512	0.05941
		6-311+G*	-949.54480	95.18	2.7421	0.94375	0.07600
MP2	$C_9H_{11}K(3)$	6-31G*	-947.47152	105.23	2.7751	0.74612	0.17425
		6-311+G*	-948.02281	101.82	2.7419	0.96997	0.18052
	$C_9H_{11}K(5)$	6-31G*	-947.47212	105.61	2.7702	0.76685	0.16830
		6-311+G*	-948.02368	102.37	2.7436	0.97689	0.18060

isomers for the complex $C_{25}H_{27}K$ with K^+ above C3, C5, C7, C9, C11 and C13 and that the isomer $C_{25}H_{27}K(13)$ should be the stablest. In fact, geometry optimizations confirmed this prediction (data not included). Further, as can be verified from Table 1, the isomers differ in energy only slightly and further this difference decreases as the chain length increases. The small difference in energies among the isomers, especially of a complex involving a long chain polyene, may have a far-reaching implication, viz., the possibility of transformation of one isomer to another by tunneling from one potential well to another, leading to the oscillation of K^+ from one end of the chain to the other. This novel phenomenon may find application in the preparation of new materials with interesting electronic, electrical, magnetic and optical properties. The substantial decrease in the HOMO–LUMO gap (red shift) of the K-complexes (see Table 1) may be a pointer to the above speculation.

5. Summary and conclusions

Non-aromatic π systems also exhibit considerable cation– π interactions like aromatic π systems. In all the stable isomers of $C_nH_{n+2}K$ complexes, the sp^3 -carbon undergoes a change of hybridization to sp^2 and the metal exists as K^+ above an odd carbon other than the terminal carbons. The isomer achieves maximum stability when K^+ is positioned above the odd carbon at or close to the center of the polyene. The polyenic fragment that pockets K^+ undergoes warping. The major interactions that stabilize the metal–polyene complex include Coulombic interaction and interaction between the cation and the π -cloud spread over the polyenic pocket. The small difference in the energies of the isomers of a complex suggests that the cation is likely to wander from one end of the polyene to the other and back, which can impart novel changes in the properties of the complex. Further, the structural changes including the phenomenon of warping can evoke substantial deviations in the physico-chemical behavior of the polyenic ligand, which may be of use in the catalysis involving organometallics.

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