Theoretical investigations on the geometric and electronic structures of polyacetylene molecule under the influence of external electric field

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Abstract. The geometric and electronic structures of all-trans polyacetylene (PA) molecule in neutral, cationic, and anionic states have been studied theoretically by density functional theory method at the B3LYP/6-31+G* level. The results show that both the geometric and electronic structures of the PA molecule are sensitive to the external electric field (EF). For neutral PA molecule, with the increase of EF, the carbon-carbon single bonds are shortened while the carbon-carbon double bonds are elongated. The energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (LUMO-HOMO gap) decreases with the EF increasing. For cationic PA molecule, the carbon-carbon single bonds and carbon-carbon double bonds on the high potential side are elongated and shortened, respectively. While, the carbon-carbon single bonds and carbon-carbon double bonds on the low potential side are shortened and elongated, respectively. Contrary to the neutral PA case, the LUMO-HOMO gap increases with the EF increasing. Contrast to the case of cationic PA, the evolution of carbon-carbon bond lengths for the anionic PA molecule under the external EF reverses. The LUMO-HOMO gap of the anionic PA molecule decreases with the increase of external EF. In addition, the spatial distributions of the HOMO and LUMO under the influence of external EF are also discussed for the PA molecule in neutral, cationic, and anionic states.

Keywords: modeling and simulation, density functional theory, polyacetylene, electronic structure, geometric structure

1. Introduction

π -conjugated polymers are the subject of recent fundamental and industrial research due to their novel properties and a variety of applications in the electronic devices, such as light-emitting diodes (LED) [1, 2], field-effect transistors (FET) [3, 4], and molecular electronic devices [5, 6]. The characteristic feature of all these substances is the conjugated double bond. Among these conjugated polymers, all-trans polyacetylene (PA) is the most prominent representative of this kind of material,

and many other conjugated polymers can, in principle, derived by the structure modification. Therefore, it has been studied intensively both experimentally [7–9] and theoretically [10–12]. Previous works [13–15] demonstrated that the properties of these polymers are critically dependent on the geometric and electronic structures of the molecules. Therefore, knowledge about these characters of the conjugated molecules is highly desired not only for understanding the packing model of molecules in solid, but also for designing or ration-

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alizing electronic devices. Although much information of the properties for this kind of materials has been obtained with the assistance of nuclear magnetic resonance (NMR) [16], X-ray analysis [17], and scanning tunneling microscopic (STM) investigation [18], the details of the molecular geometric and electronic structures as well as the structure/properties relationships are not very clear. Electric conductance is a bulk property. However, it does indeed take place over the single molecules [19]. Moreover, conjugated molecules are promising materials for electronic devices [1–6, 20], in which the molecules undergo a large external electric field (EF). Thus, in order to study, and eventually to be able to predict, electrical conduction of polymers made from organic monomers, it is important to understand the nature of the molecular response to an external EF both for neutral and charged species. However, there is no systematic report on these issues yet. The purpose of this work is to perform theoretical investigations on the evolution of the geometric and electronic structures of PA molecule in neutral and charged states by considering the influence of external EF.

2. Methods

Previous theoretical investigations of conjugated molecules have demonstrated the significance of correlation effects [21, 22]. In order to perform an accurate calculation on the geometric and electronic properties of a conjugated molecule, the computation of electron correlation effects by many-body perturbation theory should be carried out after the Hartree-Fock (HF) calculation. Alternatively, we can do density functional theory (DFT) calculation, in which the electron correlation is taken account. In the present work, all the calculations are performed at the B3LYP level with 6-31+G* basis set, which is widely used for calculations for conjugated molecules [22, 23], by using the GAUSSIAN 03 program [24].

Theoretical modeling has been achieved as follows. Prior to the introduction of EF, linear chain of all-trans PA (see Figure 1) was fully optimized at the B3LYP/6-31+G* level for both the neutral and charged states. All the geometric parameters were, then, optimized at the same level of theory in the application of uniform external EF. A uniform EF ranging from *zero* to $2.57 \cdot 10^9 \text{ V} \cdot \text{m}^{-1}$ and aligned

Figure 1. Scheme of the polyacetylene molecule studied in the present work. The external EF is aligned along the two terminal carbon-carbon inter-atomic vector C1–C12.

along the two terminal carbon-carbon inter-atomic vector was applied to the model molecules (see Figure 1), which may reasonably represent the working condition of organic electronic devices [19, 25].

3. Results and discussion

3.1. EF effect on the geometric structure

The equilibrium geometries of the neutral and charged all-trans PA without EF (*zero* EF) show a coplanar conformation with C_{2h} symmetry as expected. The carbon-carbon bond lengths along the backbone is one of the most crucial parameters in determining molecular properties, such as static electronic polarizability, second hyperpolarizability [26], nonlinear optical property [27], and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (abbreviated as LUMO-HOMO gap) in the conjugated molecules [28]. Figure 2 presents the bond lengths of the model PA in neutral state, cationic state, and anionic state. It

Figure 2. The bond lengths of PA molecule in neutral state, cationic state, and anionic state as a function of bond number (see chemical structures in Figure 1 for bond codes)

can be seen that the neutral PA shows biggest bond length alternation (BLA, the average of the difference in the length between the adjacent carbon-carbon bonds in the polyacetylene). When the PA gets charged, the BLA is decreased dramatically. In addition, the BLA of the anionic PA is somewhat smaller than that of the cationic PA. The carbon-carbon bond length is predominated not only by the nature of the molecule, but also the surroundings. Especially, when a considerable EF is applied, the carbon-carbon bond length is expected to vary [29]. In order to study, and eventually to be able to predict the properties of the conjugated molecule, it is important to understand how the carbon-carbon bond length responds to the external EF.

After the application of EF, the molecular symmetry is destroyed, although the coplanar conformation remains. Figure 3 gives the evolution of the bond length with respect to that of *zero* EF for the model molecule (see Figure 1) in neutral state. When EF increases, the carbon-carbon single bonds become shorter and the double bonds become longer, resulting in a decreased BLA. Similar result has also been observed for other conjugated molecules, such as polythiophene and oligo(phenylene ethylene), as reported by us [30, 31]. However, the EF dependence of the bond length is not identical for all the bonds. The bonds on the high potential side show more deviation than those on the low potential side of the model molecule. In addition, the maximum deviation occurs in the central part

Figure 3. Geometric deviation of the bond lengths of neutral PA molecule under various external EF (see chemical structures in Figure 1 for bond codes). The bond lengths under *zero* EF are referred to as *zero*.

Figure 4. Geometric deviation of the bond lengths of cationic PA molecule under various external EF (see chemical structures in Figure 1 for bond codes). The bond lengths under *zero* EF are referred to as *zero*.

for both the single and double bonds due to the chain end effect [29] and the better conjugation as compared to those toward the end of the molecule. When the molecules are under nonequilibrium conditions, the electronic state would be different and accordingly it is essential to investigate the charged state. Figure 4 presents the evolution of bond length with respect to that of *zero* EF for the model molecule in cationic state. When EF is introduced, all the bond lengths change. However, the bond length evolution is very different from that observed for the neutral PA. With the EF increasing, the single bonds and double bonds on the high potential side get longer and shorter, respectively; while the single bonds and double bonds on the low potential side get shorter and longer, respectively. Therefore, the application of external EF weakens the conjugation of the high potential side of the molecule and strengthens the conjugation of the low potential side of the molecule. Contrary to the case of neutral PA, the bonds in the central part of cationic PA exhibit minimum bond length deviation. Figure 5 shows the evolution of bond length with respect to that of *zero* EF for the model molecule in anionic state. In contrast to the case of cationic state, for the anionic PA, with the EF increasing, the single bonds and double bonds on the high potential side get shorter and longer, respectively; while the single bonds and double bonds on the low potential side get longer and

Figure 5. Geometric deviation of the bond lengths of anionic PA molecule under various external EF (see chemical structures in Figure 1 for bond codes). The bond lengths under *zero* EF are referred to as *zero*.

shorter, respectively. Thus, the application of external EF strengthens the conjugation of the high potential side of the molecule and weakens the conjugation of the low potential side of the molecule. Similar to the case of cationic PA, the bonds in the central part of the anionic PA exhibits minimum bond length deviation.

3.2. EF effect on the electronic structure

The energy levels of the molecular orbitals, especially the HOMO and LUMO, are excellent indicators of many molecular properties, such as chemical activity [32] and electrical performance [33]. Figure 6a gives the HOMO and LUMO levels for the model PA in neutral state calculated by B3LYP/6-31+G* method. It can be seen that with the increase of EF, both the energy levels of HOMO and LUMO decrease. When the EF increases from *zero* to $2.57 \cdot 10^9 \text{ V} \cdot \text{m}^{-1}$, the HOMO and LUMO are decreased by 1.66 and 1.90 eV, respectively. Figure 6b illustrates the LUMO-HOMO gap of the model PA in neutral state. Under *zero* EF, the LUMO-HOMO gap is 2.93 eV. With the EF increasing, the LUMO-HOMO gap decreases. By detailed analysis, it is interesting to find that the LUMO-HOMO gap decreases linearly with the square of EF (see the inset in Figure 6b). Figure 7a shows the HOMO and LUMO levels for the model PA in cationic state calculated by

Figure 6. (a) LUMO and HOMO energies for the neutral PA molecule under various external EF; (b) LUMO-HOMO gap for the neutral PA molecule under various external EF. The inset shows the linear relationship of the LUMO-HOMO gap and the square of EF.

B3LYP/6-31+G* method. Similar to that of neutral case, with the EF increasing, both the HOMO and LUMO decrease. When the EF increases from *zero* to $2.57 \cdot 10^9 \text{ V} \cdot \text{m}^{-1}$, the decrements of HOMO and LUMO are 1.74 and 1.67 eV, respectively. Figure 7b gives LUMO-HOMO gap of the model PA in cationic state. Under *zero* EF, the LUMO-HOMO gap is 2.58 eV, which is 0.35 eV lower than that of the neutral PA. Contrary to the case of neutral PA, with the EF increasing, the LUMO-HOMO gap of the cationic PA increases. A linear relationship between the LUMO-HOMO gap and the square of EF is also observed for the cationic PA (see the inset in Figure 7b). Figure 8a presents HOMO and LUMO levels for the model PA in anionic state calculated by B3LYP/6-31+G* method. With the EF increasing, both the HOMO and LUMO decreases. When the EF increases from *zero* to $2.57 \cdot 10^9 \text{ V} \cdot \text{m}^{-1}$, the decrements of HOMO

Figure 7. (a) LUMO and HOMO energies for the cationic PA molecule under various external EF; (b) LUMO-HOMO gap for the cationic PA molecule under various external EF. The inset shows the linear relationship of the LUMO-HOMO gap and the square of EF.

and LUMO are 1.91 and 1.94 eV, respectively. Figure 8b gives LUMO-HOMO gap of the model PA in anionic state. Under *zero* EF, the LUMO-HOMO gap is 2.42 eV, which is 0.16 and 0.51 eV lower than that of the neutral PA and cationic PA, respectively. When EF is less than $0.51 \cdot 10^9$ V·m⁻¹, the LUMO-HOMO gap seems not sensitive to the charges of EF. However, when the EF is higher than $0.51 \cdot 10^9$ V·m⁻¹, the LUMO-HOMO gap decreases dramatically. When EF increases from $1.02 \cdot 10^9$ to $2.57 \cdot 10^9$ V·m⁻¹, the LUMO-HOMO gap almost decreases linearly with the increase of EF. Compared to the cases of the neutral PA and cationic PA, the distortion of the linear relationship between the LUMO-HOMO gap and the square of EF for the anionic PA is possibly caused by the enhanced electron interaction from the additional electron.

Other than the energy levels of the molecular orbitals, one way to understand the molecular prop-

Figure 8. (a) LUMO and HOMO energies for the anionic PA molecule under various external EF; (b) LUMO-HOMO gap for the anionic PA molecule under various external EF

erties is to analyze the spatial distribution of frontier orbitals [34]. Table 1 compares the spatial distribution of the HOMO and LUMO for the model PA in neutral, cationic, and anionic states under various EF. At *zero* EF, both the HOMO and LUMO for the PA in neutral and charged states are fully delocalized on the whole molecular backbone. For the neutral PA, the introduction of EF tends to move the HOMO to the low potential side and the LUMO to the high potential side. Similar result has also been observed for other conjugated molecules, such as polythiophene and oligo(phenylene ethylene), as reported by us [30, 31]. While for the cationic PA, both the HOMO and LUMO are almost unchanged with the application of EF. For the anionic PA, the HOMO tends to shift to high potential side with the increasing of EF; The LUMO almost remains when the EF is less than $0.51 \cdot 10^9$ V·m⁻¹. However, further increasing EF leads the LUMO practically localize on the high potential end of the molecule.

Table 1. Spatial distribution of HOMO and LUMO of the PA in neutral state, cationic state, and anionic state under various EF

EF 10 ⁹ [V·m ⁻¹]	Neutral PA		Cationic PA		Anionic PA	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
0.00						
0.51						
1.54						
2.57						

4. Conclusions

B3LYP/6-31+G* calculations are performed to study the geometric and electronic characters of all-trans polyacetylene (PA) molecule in neutral, cationic, and anionic states under the influence of external electric field (EF). For neutral PA molecule, the carbon-carbon single bonds are shortened while the carbon-carbon double bonds are elongated with the EF increasing. The energy gap between the HOMO and LUMO is decreased with the interlocation of the external EF. For cationic PA molecule, the carbon-carbon single bonds and carbon-carbon double bonds on the low potential side are elongated and shortened, respectively. While, the evolution of carbon-carbon bond length on the high potential side reverses. Contrary to the neutral PA case, with the increase of EF, the LUMO-HOMO gap increases. When compared to the case of cationic PA, the evolution of carbon-carbon bond length of the anionic PA molecule under the external EF reverses. The LUMO-HOMO gap of the anionic PA molecule decreases with the increase of the external EF. Under *zero* EF, both the HOMO and LUMO of all-trans PA molecule in neutral, cationic, and anionic states are delocalized on the whole molecular backbone. Under the influence of external EF, the HOMO and LUMO for the neutral PA slightly shift to low potential side and high potential side, respectively. The introduction of EF has almost no effect on the spatial distribution of the HOMO and LUMO of the cationic PA. With the application of external EF, both the HOMO and LUMO of anionic PA shift to high potential side. In particular, under certain EF the LUMO of anionic PA practically localized on the high potential end of the molecule.

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