



The Geometry, Electronic Structure and Response Properties of Trans Polyacetylene, a First Principle Study

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To cite this article:

Ying Ye, Qingxu Li. The Geometry, Electronic Structure and Response Properties of Trans Polyacetylene, a First Principle Study. *American Journal of Quantum Chemistry and Molecular Spectroscopy*. Vol. 7, No. 1, 2023, pp. 16-19. doi: 10.11648/j.ajqcms.20230701.13

Received: March 28, 2023; Accepted: April 12, 2023; Published: April 27, 2023

Abstract: Polyacetylene, as the simplest and the most typical conjugated polymer system with great potentials in electronics industry, was intensively studied both experimentally and theoretically in the recent decades. Many important issues about polyacetylene have been made clear, but there are still some important questions to be answered by further study. Quantum chemists often choose to extrapolate the oligomer properties to obtain the polymer properties, while the solid state physicists prefer to start with periodic boundary condition. In this article, the geometry, electronic structure and polarizability and the second hyper-polarizability of trans polyacetylene chain were studied with first principles calculations. Several commonly used functionals and basis sets were used in the study. Comparing with experimental results, the chemical model CAMB3LYP with 6-311G(d,p) basis set presents a good description for geometry, electronic structure and polarizabilities of trans polyacetylene. Response of trans polyacetylene to a longitudinal electrostatic field along the chain were obtained within the finite field scheme, and the polarizability and second hyper-polarizability were compared with those extrapolated from oligomers. It was found that the polarizability and the second hyper-polarizability of trans polyacetylene are much larger than those obtained through quadratic extrapolation from oligomer polyenes, as shows the computational study starting from periodic boundary conditions is essentially important.

Keywords: First Principles, Polyacetylene, Electronic Structure, Polarizability, Second Hyperpolarizability

1. Introduction

As a typical system of organic conjugated polymers, polyacetylene and its oligomer polyenes have been intensely studied by experimental and theoretical researchers for decades [1-5]. Also, polyacetylene and polyenes offer an ideal platform for computational scientists to testify their algorithms and computational codes, due to its simple structure and versatile physics.

Quantum chemists observe the properties of oligomer polyenes and try to find the rules of relation between properties and the size of the system studied, while the solid state physicists prefer to work with periodic boundary conditions. Many calculations about oligomers were reported, but much less reports on polyacetylene calculations with periodic boundary conditions are found in the literatures [6-13].

The geometry, electronic structure, polarizability and

hyperpolarizability of polyenes and polyacetylene are fundamental for understanding the opto-electronic properties of the systems [14-18]. Many important advances were reported now, however, some important issues are still unclear.

Polyacetylene is known a semiconductor with an optical bandgap of 1.5-1.8 eV [19-20], and electronic correlation plays an important role in quantitative calculations for conjugated oligomers and polymers [7-12]. Due to delocalized pi electrons of conjugated system, traditional functionals used in first principle calculations are found unable to give correct description for electronic structure and optical properties of conjugated systems [12-17]. Many new functionals have been proposed to achieve a better description for conjugated systems within the framework of Kohn-Sham density functional theory [19-22].

In this article, first principles calculations of trans polyacetylene, starting from periodic boundary condition, is presented. The optimized geometric parameters, electronic

energy bands, response properties to a longitudinal electrostatic field were evaluated and discussed in this study.

2. Computational Details

All calculations using projected augmented planes (PAW) were carried out with VASP [23], and all calculations using Gaussian basis sets were carried with Gaussian09 [24]. The finite field scheme [14] was used to obtain the polarizability and second hyperpolarizability of polyacetylene.

For a given chemical model (a chemical model refers to a functional plus a basis set, as used in Gaussian09), the optimized geometry was obtained firstly, and then the electronic structure was calculated.

As for response properties, the optimized geometry was obtained with a longitudinal electric field applied along the chain, and electronic structure was calculated. The finite field scheme then was used to evaluate the polarizability and second hyperpolarizability.

The formulae used for polarizability and second hyperpolarizability are the same to ref. 9. And the polarizability and second hyperpolarizability of polyenes are extrapolated to infinite unit cells with a quadratic extrapolation used in ref. 16.

3. Results and Discussions

The optimized geometric parameters are gathered in Table 1. It was found that CAMB3LYP could predict geometries of conjugated polymer very close to experiments [16], as is convinced here. The bond length and bond length alternation agree well with experiment. The bond-lengths predicted by CAM-B3LYP/6-311(g, d) of C-C and C=C bond lengths read 1.346 Å and 1.438 Å, resulting in a bond length alternation (BLA) about 0.092 Å. In contrast, the single and double bond length and BLA given by experimental results are 1.36 Å, 1.45 Å and 0.09 Å [25-26]. The following discussions will be made mainly based the calculations based on the chemical model CAM-B3LYP/6-311(g, d).

The response of polyacetylene to electric field was investigated by applying a longitudinal electrostatic field to the system along the chain, and the finite field scheme was used to evaluate the polarizability and second hyperpolarizability. The geometric relaxation of polyacetylene in the static field was considered. And the optimized structure obtained by CAMB3LYP/6-311(g, d) are presented in Table 2. It can be easily seen from the table that the bond-lengths and BLA decrease as the electric field get stronger. The important geometric parameter of polyacetylene with a longitudinal electric field, BLA, obtained with different chemical models are plotted in Figure 1. The popular functional B3LYP predicts a rather smaller BLA, as can be easily seen from Figure 1. As is well-known, B3LYP is unable to provide a correct description for conjugated oligomers and polymers [12], and CAMB3LYP has a significantly better performance in studying conjugated systems [16, 21].

It can be seen from Figure 2, as the electric field getting stronger, the energy of the lowest unoccupied crystal orbital (LUCO) increases, while the energy of the highest occupied crystal orbital (HOCO) and the HOCO-LUCO gap are found to have an opposite trend. As for CAMB3LYP/6-311G(d, p), the HOCO-LUCO gap decreases from 3.79 eV to 3.22 eV (in an electric field 0.0020 a.u.).

The electronic band of polyacetylene without and with longitudinal electrostatic field are plotted in Figure 3. Polyacetylene is found to be a direct bandgap semiconductor, agreeing well with experiment. And the bandgap reads 3.79 eV and 3.22 eV for polyacetylene without and with a longitudinal electrostatic field (0.0020 a.u.). The bandgap computed with exact change Kohn-Sham scheme (EXX) varies from 1.60 to 2.1 eV with various functionals [27]. The difference of the bandgap can be mostly owned to different geometry and the basis sets used in calculations.

The response properties, induced electric dipole moment, polarizability and second hyperpolarizability, evaluated with finite field scheme by CAMB3LYP/6-311G(d, p) are gathered in Table 3. It is apparently the polarizability and second hyperpolarizability of polyacetylene are both much less than those obtained through a quadratic extrapolation, as means calculations for properties of polymers starting from periodic boundary condition are significant and can't simply replaced by extrapolation from oligomers.

Table 1. The optimized bond lengths and bond length alternation (BLA) of PA (in Å).

| | $r_{C=C}$ | r_{C-C} | BLA |
|-----------------------|-----------|-----------|-------|
| PBE/PAW | 1.370 | 1.430 | 0.060 |
| PBE/6-311G(d,p) | 1.391 | 1.407 | 0.016 |
| HSE/PAW | 1.354 | 1.428 | 0.074 |
| B3LYP/6-31G(d) | 1.370 | 1.425 | 0.055 |
| B3LYP/6-311G(d,p) | 1.366 | 1.423 | 0.057 |
| CAMB3LYP/6-31G(d) | 1.350 | 1.440 | 0.090 |
| CAMB3LYP/6-311G(d, p) | 1.346 | 1.438 | 0.092 |
| HF/6-311G(d,p) | 1.332 | 1.456 | 0.124 |
| Exp. [1] | 1.360 | 1.450 | 0.090 |

Table 2. The optimized carbon-carbon bond lengths and bond length alternation (BLA) of polyacetylene with a longitudinal static electric field, using CAM-B3LYP/6-311G(d, p). (Electric field in a.u. and bond lengths in angstrom).

| Electric field | $r_{C=C}$ | r_{C-C} | BLA |
|----------------|-----------|-----------|-------|
| 0.0000 | 1.346 | 1.438 | 0.092 |
| 0.0005 | 1.345 | 1.436 | 0.090 |
| 0.0010 | 1.344 | 1.430 | 0.086 |
| 0.0015 | 1.342 | 1.419 | 0.077 |
| 0.0020 | 1.336 | 1.397 | 0.061 |

Table 3. The response properties of polyacetylene evaluated with finite field scheme ($\delta F = 0.0005$ a.u.), obtained by CAMB3LYP/6-311G(d, p) (in a.u.).

| | polarizability | polarizability |
|--|----------------|--------------------|
| trans polyacetylene | 3615 | 1.27×10^8 |
| Oligomers (extrapolation to infinite)* | 103 | 1.44×10^6 |

*The polarizability and second hyperpolarizability of polyenes and a quadratic extrapolation scheme in ref. 16 are used.

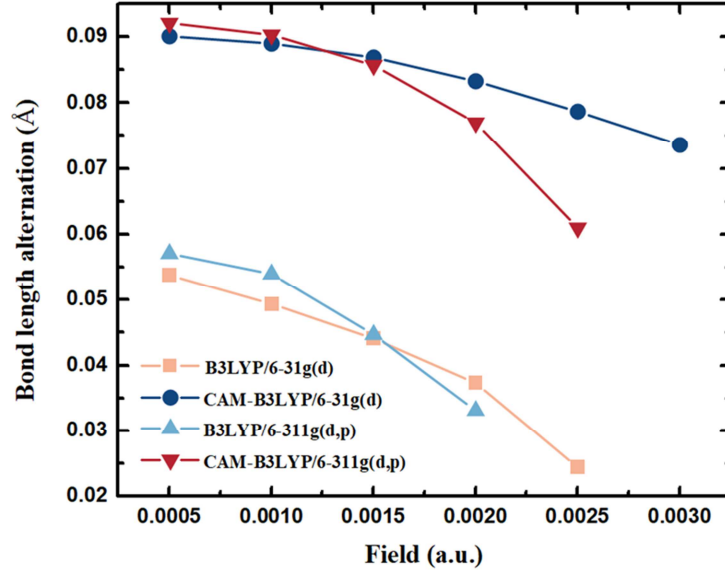


Figure 1. The optimized bond length alternation (BLA) of polyacetylene with longitudinal electrostatic field (in Å).

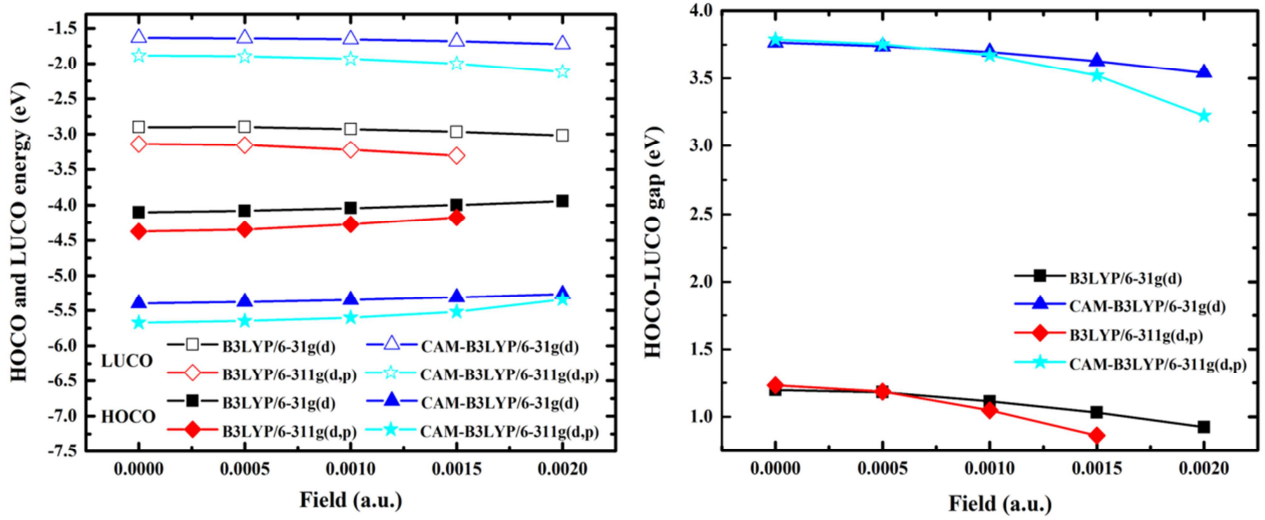


Figure 2. The HOCO, LUCO energies and HOCO-LUCO gap of polyacetylene in a longitudinal electrostatic field.

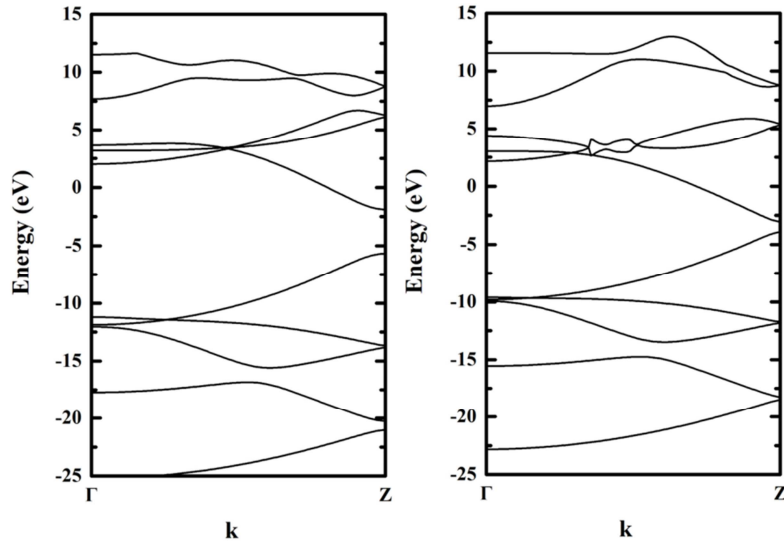


Figure 3. The electronic bands of polyacetylene without (left) and with (right) a longitudinal electric field.

4. Conclusions

A first principles study for geometry, electronic structure, response properties to longitudinal electrostatic field of trans polyacetylene is presented in this study. CAMB3LYP/6-311g(d,p) was found to be an appropriate chemical model for modelling the typical conjugated chains. An optimized geometry close to experimental results was obtained by the chemical model CAMB3LYP/6-311g(d,p).

The longitudinal electrostatic field has influences on the geometric parameters, electronic structure of polyacetylene. The bond length alternation, the HOCO-LUCO gap and the band-gap decrease as the electric field get stronger. Within the finite field scheme, one can find that both the polarizability and second hyperpolarizability of polyacetylene are much larger than those obtained by quadratic extrapolation from the response properties of the oligomer polyenes. The meaning of extrapolation from oligomers to polymer should be reconsidered, or new and more appropriate extrapolation scheme should be studied.

Acknowledgements

This work is supported by National Natural Science Foundation of China (NSFC: 20903123) and The Research Station Funding for Doctorial Faculty Members of Chongqing University of Posts and Telecommunications (A2008-16).

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