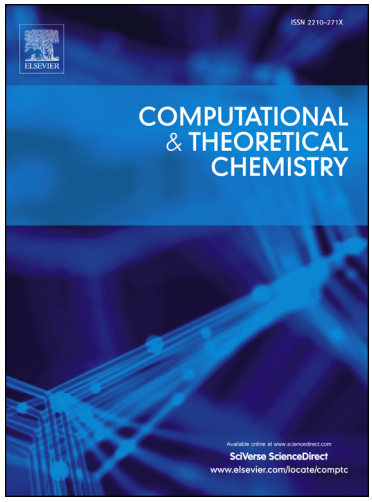

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Charge Distribution of Poly (p-phenylene benzobisoxazole) Investigated by Quantum Chemical Simulation

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ABSTRACT

The electrostatic potential fit (ESP) charges of the atoms of PBO model compound were evaluated by quantum chemical simulation. The geometry optimization with B3LYP functional and STO-3G, 6-31G(d), 6-311++G(2d,p), cc-pVTZ basis sets were applied, respectively. The charge distributions at these basis sets all indicate the N atoms to own the highest electronegativity, which are much stronger than that of O atoms. The result possesses successful representation of the electrostatic potential and deformation electron density. Moreover, the ESP charges fit well with the chemical trend exhibited by the protonation of PBO. Compared to the those derived from Mulliken, Hirshfeld and Natural Population Analysis (NPA) schemes, the charge distribution derived from electrostatic potential has the best performance both theoretically and experimentally.

KEYWORDS: Poly (p-phenylene benzobisoxazole); Charge distribution; Electrostatic potential; Deformation electron density.

1. INTRODUCTION

Poly (p-phenylene benzobisoxazole) (PBO) [1,2] is a rigid-rod heterocyclic polymer, which has gain extensive attentions for its high mechanical strength, thermal stability and distinctive photo-electronic properties [3-9]. Commercial fiber processed from PBO has been used in ropes, cables, body armor, space elevator research and some other fields. In recent years, PBO were often used as the polymer matrix of new composites [10-13]. In classical chemistry, atomic charge is the sum of the positive nuclear charge of an atom and its negative electron charge, which is a simple description of molecular electron distribution and can be used in the studies of reactivity, molecular structure and spectroscopy for PBO. But atomic charge cannot be directly determined by experiments. The simplest way to gain the charge distribution of a known molecule is the quantum chemical simulation. Based on Born-Oppenheimer approximation [14], the quantum mechanics has been used in physical models and experiments of chemical systems. The structures and characteristics of a molecule, such as the charge distribution, can be estimated from the electronic wave function or electron density.

The charge distribution of PBO has been calculated by various schemes and used in the analysis of other properties. Lukasheva et al. [15] used it in the study of the internal rotation of protonated PBO. They suggested that when the rotation potential is the minimum, the charge of N atoms is about 3 times as that of O atoms in Ph–Ht(2+) (one phenyl ring and one heterocyclic ring, in which the two N atoms are protonated) and Ht(2+)–Ph–Ht(2+) (one phenyl ring and two heterocyclic rings, in which all N atoms are protonated). Bhaumik et al. [16] calculated the charges of PBO and protonated PBO chains with the