

Effects of micro-solvation on the reaction dynamics of biphenyl cations following hole capture



Hiroto Tachikawa

Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

ARTICLE INFO

Article history:

Received 17 February 2017

In final form 24 March 2017

Available online 30 March 2017

Keywords:

Hydration

ab initio MD

Ionization

Friction effect

Hyperfine coupling constant

Hydrogen bond

Single molecule electronic device

Molecular modeling

ABSTRACT

Biphenyl (Bp) and its related compounds are widely applied in single-molecule electronic devices. In this study, the effects of micro-solvation on the hole capture (ionization) dynamics of Bp were investigated by means of direct ab initio molecular dynamics (AIMD) simulations. The micro-solvation of Bp was simulated using one and two water molecules (i.e., $\text{Bp}(\text{H}_2\text{O})_n$ ($n = 0-2$)). The reaction dynamics of $\text{Bp}^+(\text{H}_2\text{O})_n$ following hole capture were investigated via direct AIMD simulation. In the case without H_2O ($n = 0$), the twist angle of Bp^+ periodically vibrated without decay. In contrast, when water molecules were near Bp^+ , the amplitude of the twist angle vibration decayed periodically. The formation of hydrogen bonds between Bp^+ and water molecules prevents periodic vibration by generating friction. The electronic states and reaction mechanism were investigated based on the theoretical results.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The biphenyl molecule (Bp) and its related compounds are frequently used in electronic devices as polymer side chains because they can take on several structures depending on their electronic states [1–6]. The most obvious structural variation occurs in the twist angle between the two phenyl rings (ϕ). Experimental results [7–11] have confirmed that in the gas phase, the global minimum conformation appears at $\phi = 44.4 \pm 1.2^\circ$. In the radical anion, cation, and excited states, the two phenyl rings become coplanar [12,13]. Hence, Bp can be utilized as a single-molecule switching device that is dependent on the electronic state. For example, Solomon and Lang proposed the use of Bp as a single-molecule transistor based on density functional theory (DFT) calculations [14]. Because of the coupling between the two benzene rings, the electronic states become segregated into extended, current-carrying states and localized states.

The structure of Bp varies widely depending on its environment and electronic states. In solution, the twist angle ranges from 19 to 32° depending on the bulk solvent [15,16]. However, the origin of the effects of solvation on the structure and electronic states of Bp is not clearly understood.

Many theoretical calculations have been conducted to reproduce the value of the twist angle [17–29]. These investigations

mainly focused on the structure of Bp, especially its twist angle. However, no work has addressed the dynamical features of Bp following hole capture.

The electronic properties of devices are frequently affected by water molecules, and many are influenced by the presence of even a single water molecule. For example, a network of naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTCDA)–metal complexes can be broken by a water molecule; when this occurs, its electronic conductivity decreases strikingly. Therefore, studying the effects of micro-solvation on the electronic states of Bp is important to for the development of high-performance electronic devices [30–33].

In this study, the effects of micro-solvation on the hole capture (ionization) dynamics of Bp (Fig. 1) were investigated using direct ab initio molecular dynamics (AIMD) simulations [34–36]. In particular, we focus our attention on the effects of micro-solvation on the twist angle vibration of the Bp radical cation following hole capture.

2. Computational details

2.1. Static ab initio and DFT calculations

The structures of Bp and micro-solvated Bp (i.e., $\text{Bp}(\text{H}_2\text{O})_n$ ($n = 0-2$)) were fully optimized at the MP2/6-311++G(d,p) and (CAM)-B3LYP/6-311++G(d,p) levels of theory using Coulomb-attenuating methods [37]. The CAM-B3LYP functional provides

E-mail address: hiroto@eng.hokudai.ac.jp

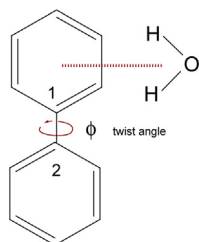


Fig. 1. Schematic of the micro-solvated biphenyl molecule studied here: $\text{Bp}(\text{H}_2\text{O})_n$ ($n = 0-2$). ϕ denotes the twist angle between the phenyl rings.

reliable results and is widely used to describe the intra- and intermolecular charge-transfer states of aromatic molecules [38]. The static ab initio and DFT calculations were conducted using the Gaussian09 program [39].

2.2. Direct AIMD calculations

First, the structures of $\text{Bp}(\text{H}_2\text{O})_n$ ($n = 0-2$) were fully optimized at the MP2/6-311++G(d,p) level. The trajectories of $\text{Bp}^+(\text{H}_2\text{O})_n$ ($n = 0-2$) following hole capture by $\text{Bp}(\text{H}_2\text{O})_n$ were calculated at the B3LYP/6-31G(d) level assuming vertical hole capture from the neutral state. The calculations of the trajectory of $\text{Bp}^+(\text{H}_2\text{O})_n$ were performed using the condition of constant total energy. The

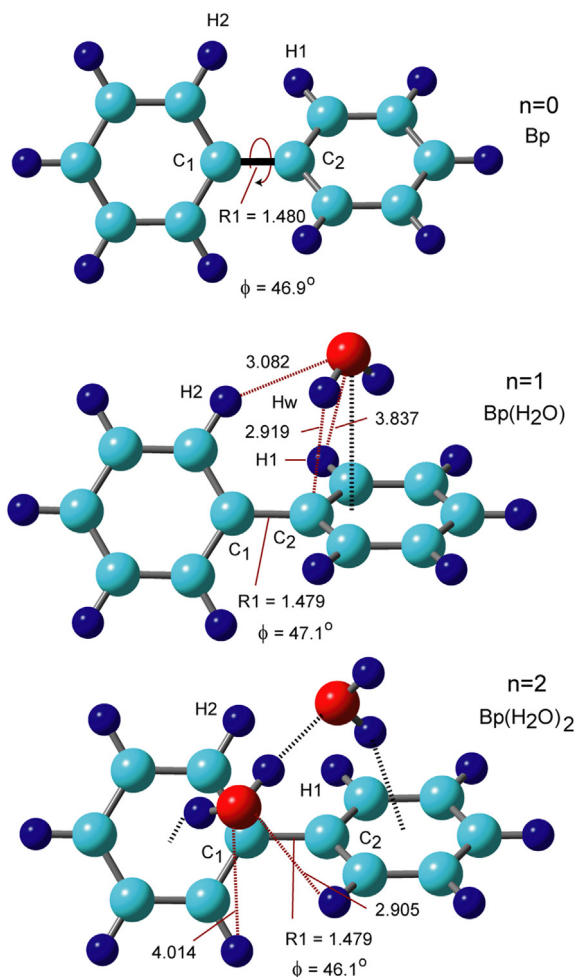


Fig. 2. Optimized structures of Bp ($n=0$) and $\text{Bp}(\text{H}_2\text{O})_n$ ($n = 1$ and 2). The calculations were conducted at the MP2/6-311++G(d,p) level. Distance and angles are in Å and degrees, respectively.

velocity Verlet algorithm was used with a 0.1-fs time step to solve the equation of motion of the system. The drifts of the total energies in all the trajectory calculations were less than 0.01 kcal/mol.

In addition to the MP2-optimized geometry of $\text{Bp}(\text{H}_2\text{O})_n$ ($n = 0-2$), five structures were randomly sampled from the Franck-Condon (FC) region of $\text{Bp}(\text{H}_2\text{O})_n$ ($n = 0-2$). Those generated around the equilibrium point were examined via the direct AIMD calculations of $\text{Bp}^+(\text{H}_2\text{O})_n$. The kinetic energy and angular momentum of each atom were assumed to be zero at time zero.

3. Results

3.1. Structures of $\text{Bp}(\text{H}_2\text{O})_n$ ($n = 0-2$)

Fully optimized structures of $\text{Bp}(\text{H}_2\text{O})_n$ ($n = 0-2$) are illustrated in Fig. 2. In free Bp ($n = 0$), the C–C bond length ($R1$) and twist angle (ϕ) were calculated to be $R1 = R(\text{C}1-\text{C}2) = 1.480 \text{ \AA}$ and $\phi = 46.9^\circ$, respectively. The angle calculated at the MP2/6-311++G(d, p) level is in good agreement with the experimental data ($\phi = 44.4^\circ$) [7–11].

When one water molecule interacts with the Bp molecule ($n = 1$), the dipole of the water molecule orients toward the π -electron of one of the benzene rings. Then, one of the protons of H_2O

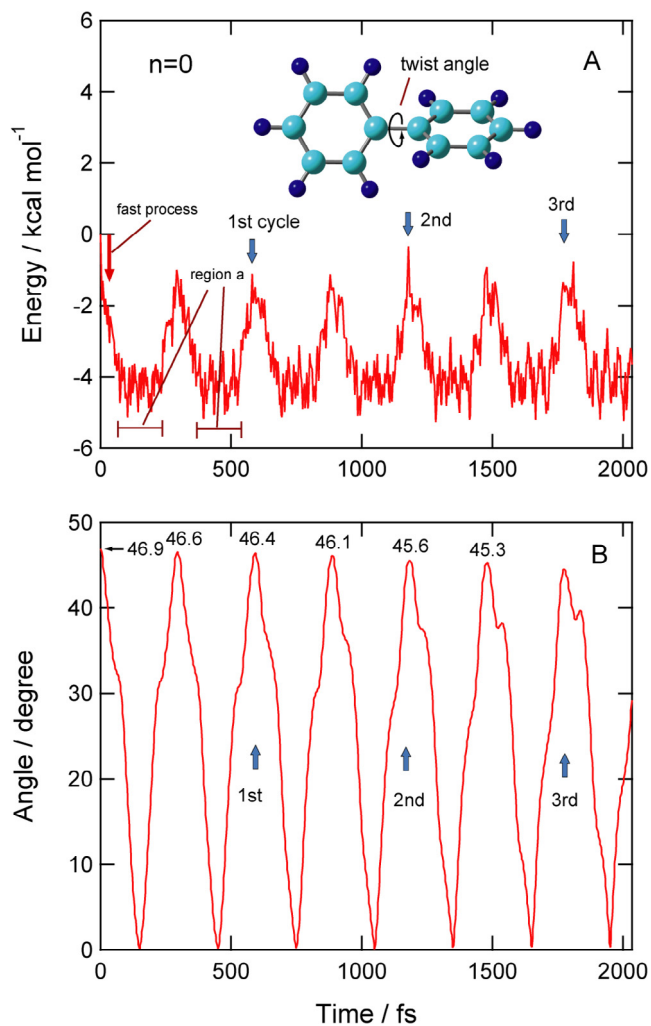


Fig. 3. Time evolutions of the potential energy (A) and twist angle (B) of Bp^+ following hole capture by Bp . Direct AIMD simulations were conducted at the B3LYP/6-31G(d) level. The MP2/6-311++G(d,p)-optimized structure was used as the initial structure of Bp at time zero.

Download English Version:

<https://daneshyari.com/en/article/5372643>

Download Persian Version:

<https://daneshyari.com/article/5372643>

[Daneshyari.com](https://daneshyari.com)