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Theoretical study of conformational effect on electronic structure and charge transfer in silabiphenyl system

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ABSTRACT

Conformational effect on electronic structure and charge transfer of silabiphenyl system has been investigated at several different levels of theory. The rotational potential energy curves as a function of torsion angle show that conjugation effect makes the system favor planar structure whereas steric effect facilitates it to prefer perpendicular one. The competition between these two effects results in a gauche and a trans conformer. Full geometric optimization, frequency analysis, and disassociation energy calculation indicate that the characteristic buckling distortion occurs and the trans conformer is more stable than the gauche. Moreover, conjugation and steric effects on geometric parameters, HOMO and LUMO energies, and electron populations of Si atoms have been evaluated and the results provide more aspects to understand these two effects. Furthermore, the linear dependence of charge transfer on the square of the cosine of torsion angle has been observed on the basis of natural charge population analysis and interpreted by effective π-orbitals coupling model. The present study shows possible manipulation on charge transport by changing the conformations in silabiphenyl system.

1. Introduction

It is generally recognized that organic π-conjugated molecules are good candidates for molecular electronics applications [1–8]. Thus a lot of theoretical and experimental studies have been carried out for molecular junction based on organic π-conjugated molecule [9–17]. These studies have revealed that the transport properties of molecular junction depend on many factors, such as molecular conformation and length, the nature of electrodes, and the relative position of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gap to the Fermi level of electrodes. Among these factors, molecular conformation is intrinsic and possesses a fundamental determination to transport property of molecular junction. Therefore, in recent years, great efforts have been made to investigate conformational effect on electronic structure and charge transport property of organic π-conjugated molecules [12–17].

Biphenyl system, one typical group of these organic π-conjugated molecules, has attracted more attentions due to its peculiar structure with two conjugated phenyl rings linked by a C–C bond [14–24]. The studies on biphenyl system indicate that the conformations are mainly determined by two factors [18–24]. One is conjugation effect and the other is steric effect. The influences of these two effects on geometric and electronic structures were extracted by changing the torsion angle between the two phenyl rings [18–24]. Conjugation effect makes biphenyl system more stable through π-electrons delocalization and the system facilitates to be planar, while steric effect makes it favor perpendicular structure. Because conformational effect can be manipulated by changing the torsion angle, the charge transport properties of molecular junctions based on biphenyl system have been studied extensively [14–17]. These studies show that the conductance of molecular junction is roughly proportional to the square of the cosine of the torsion angle. More importantly, the charges of transport property of molecular junction are not only intrinsically determined by the molecular conformations such as the torsion angle, but also complicated by the nature of contacts between molecule and electrodes. Investigating charge transfer in molecular system with different conformations facilitates to understand intrinsic conformational effect on charge transport in the corresponding molecular junction.

Besides carbon-based molecules of biphenyl system, in recent years, more attentions have been paid to silicon-based molecules and nanostructures for their exceptional electronic properties [25–36]. Like biphenyl system, in silabiphenyl system conjugation and steric effects should be sensitive to conformation changes and play crucial roles on determining their electronic structure.

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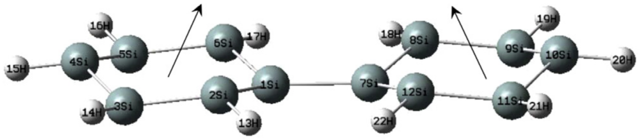
Therefore, silabiphenyl system may be significant molecular models to investigate conjugation and steric effects. However, as far as we know, there are no theoretical and experimental studies on silabiphenyl system up to now. The recent studies on silicene have indicated that it has buckling geometric structure due to the presence of sp^3 hybridization in Si atoms, being different from the carbon-based molecules and nanostructure such as biphenyl and graphene [28–36]. In order to understand the buckling distortion in silicene, geometric and electronic structures of hexasilabenzene were theoretically studied by Jose and Datta [34]. They found that the sufficiently strong coupling between the unoccupied molecular orbitals and the occupied molecular orbitals leads to the pseudo-Jahn–Teller distortion and the stable D_{3d} structure with the characteristic buckling in hexasilabenzene [34]. Considering the buckling structure in hexasilabenzene and silicene, one may expect that electronic structure and charge transport property of silabiphenyl system are more interesting. Therefore, inspired by the previous fruitful studies on hexasilabenzene, silicene, and biphenyl system, in the present work, geometric and electronic structures of silabiphenyl system have been studied. Moreover, in order to explore conformational effect on charge transport property, charge transfer in molecular system of silabiphenyl has been investigated rather than charge transport in the molecular junction with electrodes.

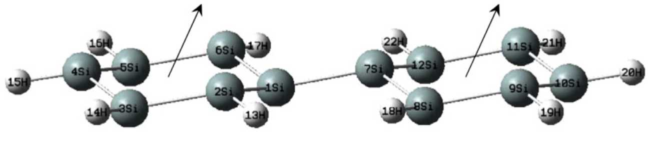
The present work was organized by three steps as follows. Firstly, the rotational potential energies were calculated at several different levels of theory for silabiphenyl system with the different torsion angle φ_0 (defined as the dihedral angles of Si2–Si1–Si7–Si12 and Si6–Si1–Si7–Si8 in Scheme 1). Combined with the calculated potential curves, two stable conformers were characterized according to full geometric optimization, frequency analysis, and disassociation energy calculation. To further understand conjugation and steric effects from more aspects, secondly, the dependences of some typical geometric parameters, natural atomic orbital populations, and HOMO and LUMO energies on torsion angle φ_0 were studied. Finally, charge transfer through the central Si$-$Si bond was investigated by charge population analysis for a substituted silabiphenyl system.

2. Computational details

The partial geometric optimizations were carried out by the HF, MP2, BLYP [37], and B3LYP [38,39] methods with the 6-31G(d) and cc–pVTZ basis sets for silabiphenyl system with the different torsion angle φ_0. At the same theoretical levels, the rotational potential energies were calculated for the above partially optimized structures. Electron exchange and correlation effects, which are correlated to electron delocalization, were considered at the different theoretical levels. To evaluate steric effect from the aspect of electrostatic interaction, the partial geometric optimization and the energy calculation for silabiphenyl system with different torsion angle φ_0 were performed by Coulomb method, in which electron exchange and correlation effects are skipped and only electrostatic coulomb interaction is considered.



(a) cis conformer



(b) trans conformer

Scheme 1.

In light of the rotational potential energy curves, full optimizations for possible stable structures of silabiphenyl system were performed by the B3LYP method with the 6-311G, 6-311G(d, p), and cc–pVTZ basis sets. Harmonic vibrational frequencies and disassociation energies were also calculated at the above levels of theory to ensure the optimized structures to be minimum and stable. The dissociation energy was calculated as the differences in the energies of silabiphenyl and the two constituent silaphenyl rings and corrected by zero point energy. The basis set superposition error (BSSE) was avoided by using counterpoise procedure (CP) of Boys and Bernardi [40]. In order to further investigate conjugation and steric effects, on the one hand, the changes in some typical geometric parameters, such as the central Si1–Si7 bond length and the dihedral angle $\varphi_{7,1,2,6}$, were extracted from a series of geometric structures with the different torsion angle φ_0 optimized at the B3LYP/cc–pVTZ level. On the other hand, the natural atomic orbital populations and the HOMO and LUMO energies were calculated at the same level for the above structures. The listed HOMO and LUMO energies were taken from their eigenvalues.

Like biphenyl system, great attentions from physics, chemistry, and molecular electronics have been paid to the investigation of charge transport property [14–17]. In the present work, we studied the direct influences of molecular conformations on charge transfer in silabiphenyl system rather than charge transport in the corresponding molecular junction. To do this, a substituted silabiphenyl system, denoted by 4,10–Na–F–silabiphenyl, was employed, in which one Na and one F atom substitute the two H atoms at the two sides of silabiphenyl, respectively. The geometric optimization and the corresponding frequency calculation for 4,10–Na–F–silabiphenyl were conducted. The introduction of Na and F atoms gives different chemical potentials to the two silaphenyl rings. Therefore, charge transfer through the central Si–Si bond occurs from one silaphenyl ring to the other. In order to investigate the conformational effect on the charge transfer, the partial optimizations were performed for 4,10–Na–F–silabiphenyl system with the different torsion angle φ_0, and the natural population analysis was subsequently done for all above optimized structures. The changes of charge populations for either silaphenyl ring, i.e., charge transfers through the central Si–Si bond, were obtained. All above calculations were performed with the GAUSSIAN 09 suite of programs [41]. The natural atomic orbital population analysis was executed by using natural bond orbital (NBO) version 3.1 program [42,43] embedded in the GAUSSIAN 09 package.

3. Results and discussion

3.1. Rotational potential energy curves

The dependence of rotational potential energies on the torsion angle φ_0 for silabiphenyl system has been studied by the Coulomb, HF, MP2, BLYP, and B3LYP methods with the 6-31G(d) and cc–pVTZ basis sets. The Coulomb method was described in details in the above section. The rotational potential energy curves were presented in Fig. 1. For comparisons, all curves were normalized to zero at $\varphi_0 = 0°$.

As shown in Fig. 1, with the increases of torsion angle φ_0, the rotational potential energies calculated by the Coulomb method decrease drastically in the angle range from 0° to 50°, maintain almost constant from 50° to 90°, and increase slowly from 90° to 180°. The rotational potential energy at $\varphi_0 = 0°$ is a litter larger