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Synthetic Metals 152 (2005) 269–272
SYNTHETIC METALS
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Theoretical investigation of electronic structure and spectroscopic properties of functionalized bis-silicon-bridged stilbene homologue

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Abstract

Electronic structures of bis-sillicon-bridged trans-stilbene homologues were theoretically analyzed from the viewpoint of electronic effect occurring from geometrical difference in the vicinity of the stilbene bridged moiety using DFT B3LYP method. Absorption and emission energies were reported on the basis of TD-DFT and ZINDO approaches, establishing good agreement with experimental data. As compared with the carbon analogue, the absorption and emission maxima of silicon-bridged stilbene analogues have substantial red shifts. These significant red shifts are attributable to the electronic contribution of the silicon bridges. EL peak was predicted to be about 393 and 483 nm for them. The effects of hole and electron injection are clarified by the ionization potentials (IPs) and electron affinities (EAs) calculations.It is suggested that bis-sillicon-bridged trans-stilbene homologue should be more efficient at trapping the electron than carbon species.

Keywords: Trans-stilbene, Silicon-bridge, Density functional calculations, Excitation spectra calculations

1. Introduction

Organic π-conjugated systems have shown to exhibit a broad spectrum of extremely desirable electrical, optical, and photoelectrical properties, which have application as organic semiconductors, sensors and nonlinear optical (NLO) devices, optical storage, liquid crystals and organic light emitting diodes (OLEDs) materials [1-3]. Preparing new small band gap conjugated frameworks of enhanced stability and performance is one of highlight research issue up to date, and intensive works have been undertaken. Siloles are a group of Si-containing conjugated rings with novel molecular structures and unique electronic properties that differ vastly from those of well-studied polythiophene or polyaniline, and so on [4]. Siloles exhibit an unusually high electron affinity associated with the σ*–π* conjugation arising from an interaction between the butadiene π*(b_1) orbital and the silylene σ*(b_1) orbital resulting in a significant lowering in LUMO energy levels [5]. In addition, the rapid growth of chemistry of other Si-containing compounds has stimulated interest amongst both experimental and theoretical chemists. Aromatic building blocks have also been widely used and p-phenylenevinylenes (PPVs) are probably the most studied conjugated π-systems [6]. More recently, Yamaguchi et al. successfully synthesized the silicon-bridged stilbene homologues by a new intramolecular reductive double cyclization method [7]. These compounds show an obvious bathochromic shift relative to stilbene species experimentally. However, the theoretical investigations on the photophysical properties of them have not been performed. In this work we characterized the electronic structure effects of bis-silicon-bridged stilbene derivative **2** comparing with bis-methylene-bridged stilbene derivative **1** on the absorption and emission properties by theoretical investigations.

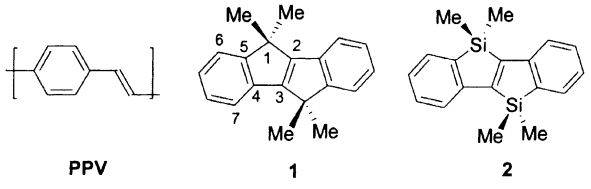

Fig. 1 PPV, bis-methylene-bridged stilbene derivative (**1**) and bis-silicon-bridged analogue (**2**).

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0379-6779/$ – see front matter
doi:10.1016/j.synthmet.2005.07.102

2. Theoretical methodology

The ground state geometries of **1** and **2** are optimiazed with C_1 and C_{2h} symmetry using hybrid B3LYP functional with the 6-31G(d) basis set. Excitation energies and oscillator strengths are determined by means of Zerner's intermediate neglect of differential overlaps (ZINDO) method [8] and time-dependent density functional theory (TD-DFT) [9] with B3LYP/6-31g(d) level based on above structures. Additionally, we have employed a Hartree–Fock single-excitation configuration interaction (CIS) method [10] for the optimization of the lowest excited state geometries. The transition energies of emission energies were calculated by TD-DFT. Electroluminescence (EL) spectrum were predicted by the vertical transition energy from the optimized structure of the anion ground state using TD-DFT/6-31G(d) level.

3. Results and discussion

3.1. Ground state and excited state structures

Two geometrical optimizations in ground states were performed with C_1 and C_{2h} symmetry for compounds **1** and **2**, respectively. The very similar results were obtained from two symmetry geometries, which all possess highly coplanar structure. To discuss conveniently, C_{2h} geometries were used for the following discussion. The selected optimized bond lengths and angles of model compounds **1** and **2** are listed in Table 1. The optimal Si(1)-C(2) distance of **2** is 1.891 Å and is significantly longer than the C(1)-C(2) distance of **1** by 1.517 Å. It is noteworthy that the difference of bond angles of C(2)-C(Si)(1)-C(5) were estimated to be 8.8° between **1** and **2**. Although the experimental value of the compound 2 is so far unknown, the optimal value of **2** is almost the same as the experimental value of the related tetrakissilicon-bridged derivative (91.2° vs. 91.1°) [7]. Although there has obviously change in bond length between **1** and **2**, they have the planar backbone, the dihedral angle between the two terminal benzene rings is 0°. It can be identified with contribution from rigidity of the silicon bridges. This fact suggests that the π-conjugation is effectively extended over the entire molecule. The geometrical parameters that computed at the CIS levels in the lowest singlet excited state are shown in Table 1. No significant out-of-plane displacement in the backbone is revealed. This table suggests that it has same change regularity for geometries of two compounds in going from the ground state to the lowest singlet excited state. the C(Si)(1)-C(2), C(3)-C(4), and C(5)-C(6)bond lengths of 1(2) are decreased by about 0.003(0.016), 0.061(0.060), and 0.011(0.0) Å, respectively, while the C(2)-C(3), C(4)-C(5) and C(4)-C(7) bond lengths are increased by about 0.066(0.077), 0.018(0.013) and 0.023(0.019) Å. Geometry relaxation leads to a quinoid structure for the lowest singlet excited state.

Table 1
Optimized Bond Lengths (Å) and Angles (°) of Model Compounds **1** and **2** in S_0 and S_1 Electronic States

	1		**2**	
	S_0	S_1	S_0	S_1
Bond lengths				
C(Si)1-C2	1.517	1.514	1.891	1.875
C2-C3	1.357	1.423	1.373	1.450
C3-C4	1.457	1.396	1.475	1.415
C4-C5	1.420	1.438	1.424	1.437
C5-C6	1.387	1.376	1.393	1.393
C4-C7	1.397	1.420	1.400	1.419
Bond angles				
C(Si)1-C2-C3	112.3	111.8	109.0	110.2
C2-C3-C4	110.0	109.7	116.7	114.5
C2-C(Si)1-C5	100.0	99.1	91.2	89.6
C3-C4-C5	107.0	108.0	115.2	115.9

3.2. Frontier molecular orbitals

The HOMO and LUMO patterns of **2** show that characteristics of orbital profile are similar to that of **1** in Fig. 2. As seen in the electronic structure of compounds above-metioned, the orbital interaction between the σ^* orbital of the Me_2Si moiety and the π^* orbital of the stilbene framework effectively decreases the LUMO level. Orbital energy level calculations indicated that the LUMO of **2** is lower than that of carbon analog **1** by 0.46 eV, while the slight decrease in the HOMO level from **1** to **2** is only 0.14 eV, in accordance with the result of Ref. 7 calculations at the HF/6-31G(d) level, 0.55 and 0.19 eV, respectively. As a consequence, the silicon analogue **2** has a smaller HOMO-LUMO energy gap than **1** (4.13 eV for **1** and 3.81 eV for **2**). The extended conjugation with the silicon bridge strongly affects LUMO level, but slight effects on the HOMO level, and thus diminishes HOMO-LUMO gaps. It is proposed that silicon bridges not only rigidize the stilbene skeleton but also contribute to the electronic structure through orbital interaction.

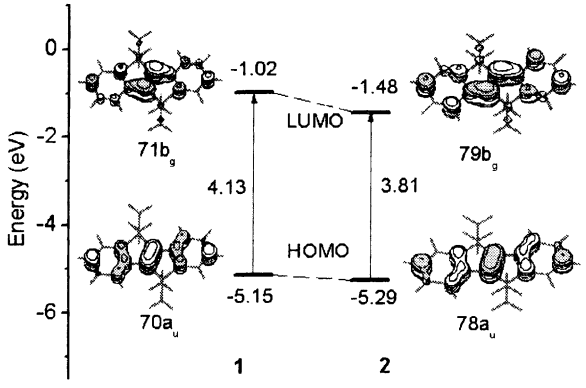

Fig. 2 HOMO and LUMO energy levels of the model compounds **1** and **2** based on the B3LYP/6-31G(d) calculations.