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REGULAR ARTICLE

The Study of Singlet Biradical Character of the Benzene-lined Bisphenalenyl Molecule and the Anthracene-linked Bisphenalenyl Molecule

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Abstract: The ground and excited state properties of the benzene-linked bisphenalenyl (B-LBP) molecule and the anthracene-linked bisphenalenyl (A-LBP) molecule have been theoretically investigated by using the time-dependent density functional theory (TD-DFT) together with a set of extensive multidimensional visualization techniques. The results reveal that the singlet biradical character strongly influence the properties of the system, such as the aromatic stabilization energy and the second hyperpolarizability of the system increase with increasing the length of the linker, while with the increasing of the singlet biradical character, the strength of coherence and the ability of charge transfer decrease obviously. Consequently, the organic NLO coefficient of the system is controlled by adjusting the singlet biradical character.

AMS subject classifications: 74E40, 78M50

Key word: singlet biradical character, bisphenalenyl, Aromaticity, second hyperpolarizability, electron-hole coherence, charge transfer, organic NLO

Ⅰ Introduction

The rapid advances in fields such as high speed optical communication and Optical

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information processing play an active promoting role for study of organic nonlinear optical (NLO) materials in recent years [1-8]. Organic NLO materials，which have large nonlinear polarizability, high optical damage threshold, short response, molecular design at NLO responsive request and large potentiality in the matter of high speed integrated optical device, etc. properties, are more likely to be NLO materials [9-13]. The research on organic NLO property has attracted a lot of attention. The organic NLO property has been deeply research by Nakano, M et al [14]. They found that spin multiplicity, diradical character and electron correlation have effect on NLO coefficients. The organic NLO property of system is changed by adjusting spin multiplicity and diradical character, which lays a foundation for the further design of radical molecular.

Phenalenyl is a stable organic radical [15]. The phenalenyl radical and its derivatives have attracted a lot of attention for their significant conjugacy and delocalization, etc. properties. For example, the singlet biradical character and intermolecular covalent bonding interaction of bisphenalenyl Kekulé molecule were researched through experimental method by Akihiro Shimizu et al. [16, 17], the property of bisphenalenyl molecule was researched through theory method by Jingsong Huang et al [18]. Aromaticity, which is defined by the cyclic delocalization of 4n+2 π electrons, is associated with closed loop conjugated system, low energy and relatively stable of system [19].

In the present paper, quantum chemical calculation as well as visualized real-space analysis has been used to explore the nature of ground and excited state of the B-LBP molecule and the A-LBP molecule (such as singlet biradical character, charge transfer, electron-hole coherence and second hyperpolarizability). The paper is organized as follows: first, the theoretical approaches are described, and then calculated singlet biradical character (y), energy gap and bond length at the UB3LYP/6-31G** level are compared with the related experiment, respectively. Second, the excited-state properties of the B-LBP molecule and the A-LBP molecule are studied with the visualized 2D and 3D real space analyses [20]. Finally, the second hyperpolarizabilitys of the B-LBP molecule and the A-LBP molecule were calculated at the UB3LYP/6-31G** level. The results reveal that the length of the linker strongly influence aromatic stabilization energy, singlet biradical character and the charge transfer characters of these systems. The second hyperpolarizabilitys of these systems are controlled by adjusting the singlet biradical character.

Ⅱ Methods

All the quantum chemical calculations were done with Gaussian 09 software [21]. The geometries of the B-LBP molecule and the A-LBP molecule at ground state were fully optimized using the density functional theory (DFT) with B3LYP(UB3LYP) functional and

6-31G** basis set [22]. The optical absorption was calculated by the time-dependent density functional theory (TD-DFT) at the same level [23]. The hybrid qualities of B3LYP (UB3LYP) and the long-range correction were used in the ground and excited state calculations [24].

The recent research shows that the second hyperpolarizabilitys of the systems are controlled by adjusting the singlet biradical character [25]. Furthermore, the NLO coefficients are improved. Yamagnchi et al. proposed [26] that singlet biradical character(y) has been calculated by natural orbital method

$$y_i = 1 - 2T_i/(1 + T_i^2) \quad (1)$$

$$T_i = (n_{H-i} - n_{L+i})/2 \quad (2)$$

Where T_i is the orbital overlap of the paired orbitals; n_{H-i} and n_{L+i} are molecular orbital occupation number, which have been calculated by natural orbital method. In the present paper, singlet biradical character was estimated from the natural orbital occupation number (NOON) of the lowest unoccupied molecular orbital (LUMO) at the basis of UB3LYP/6-31G** calculations. The value of y is from 0 to 1. If y=0, the system is closed-shell system; if y=1, the system is pure radical system.

In this paper, the excited-state properties of the B-LBP molecule and the A-LBP molecule are studied with the visualized 2D and 3D real space analyses [27, 28]. The 3D cube representation of charge difference density indicates the result of intramolecular charge transfer during electronic transition, and the 2D site representation reveals the electron-hole coherence of electron-hole pairs on excitation. A study of charger transfer mechanism and coupling effect occurring in the charged linkers provides detailed insight into the excited state properties of the differently charged linkers.

Ⅲ Results and Discussion

1. Ground-State Properties of the B-LBP Molecule and A-LBP Molecule

Singlet biradical character (y) of the B-LBP molecule and the A-LBP molecule were estimated from the natural orbital occupation number (NOON) [29] of the lowest unoccupied molecular orbital (LUMO) at the basis of UB3LYP/6-31G** calculations. The y values increase with increasing the length of the linkers, as shown in **Table 1**. And the A-LBP molecule has longer length in the bond a (see **Figure 1** and **Table 1**) between the two bisphenalenyl molecules, which are in good agreement with the experimental reports. The length of the bond **a** is much sensitive to the contribution weight of the each canonical form, because the bond **a** has both single and double bond character in the Kekule′ form, whereas

only single bond character in the biradical form. The longer in the bond **a**, that is, the higher delocalization energy. Furthermore, in the biradical form, larger y values, that is, weaker coupling of two unpaired electrons [16], results in a smaller HOMO–LUMO energy gap, which was confirmed at the basis of UB3LYP/6-31G** calculations. The small HOMO–LUMO gap is an essential factor for a singlet biradical electronic structure [17]. These calculations thoroughly support that the singlet biradical character of the B-LBP molecule and the A-LBP molecule increase with increasing the aromatic stabilization energy in the linkers.

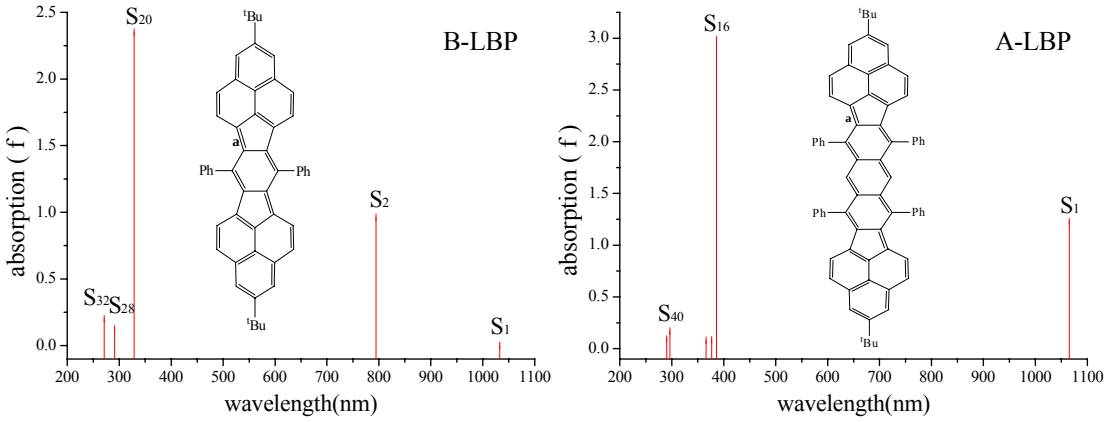


Figure 1: The Calculated Absorption Spectrum of the B-LBP Molecule and the A-LBP Molecule.

Table 1: Singlet Biradical Character (y), Length of Bond a and H-L Gap of the B-LBP Molecule and the A-LBP Molecule.

Compounds	y% (Exp)	y%	Length of Bond **a**/A (Exp)	Length of bond **a**/A	H-L gap (UV)/eV	H-L gap (CV)/eV	H-L gap /eV
B-LBP	30	30	1.457	1.449	1.64	1.20	1.2498
A-LBP	68	62	1.467	1.451	1.26	0.98	0.7755

2. Excited-State Properties of the B-LBP molecule and the A-LBP molecule

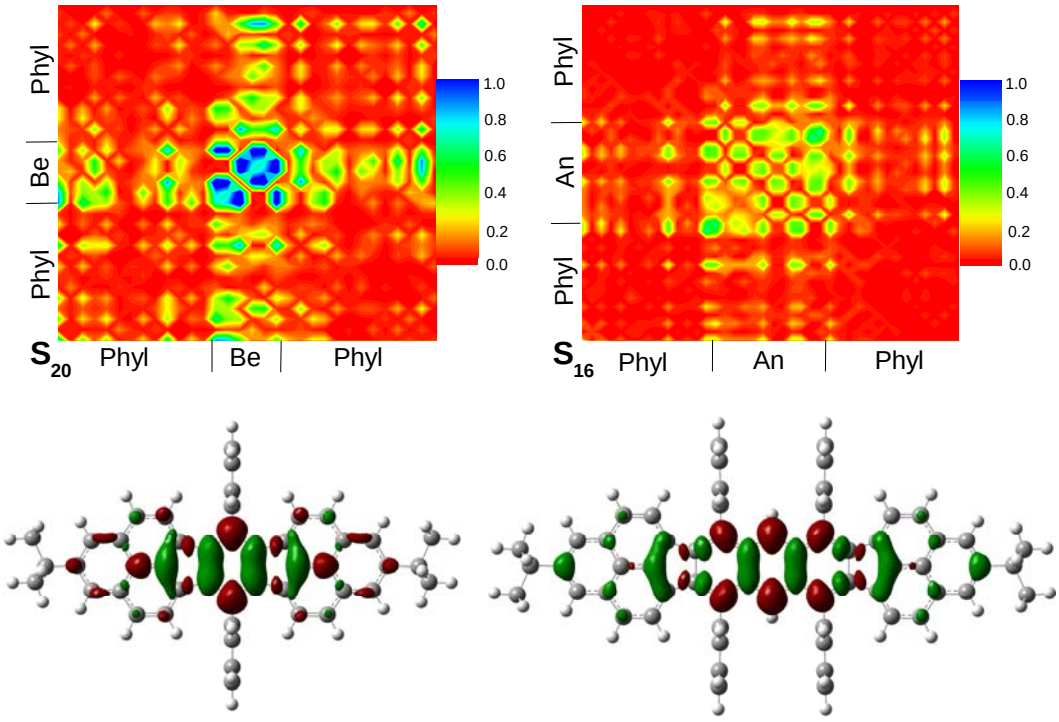
The results of low-lying electronic transitions were obtained at the TD-DFT with B3LYP functional and 6-31G** basis set level of theory. The transition energies and the oscillator strengths for the selected singlet excited states of the B-LBP molecule and the A-LBP molecule are summarized in **Table 2**, which states have the lowest energy or large oscillator strength (f≥0.08). The simulated absorption spectra of the B-LBP molecule and the A-LBP molecule are shown in **Figure 1** [20]. For the B-LBP molecule and the A-LBP molecule, the dominant orbital contribution to the electronic excitation originates from the HOMO to the

LUMO transition. As **Table 2** shows, the lowest energy excited state of the B-LBP molecule is found to be 1032.62nm with dipole-allowed electron transition, and which of the A-LBP molecule is located at 1065.47nm. For the B-LBP molecule, excited states with large oscillator strength (f≥0.1) correspond to S_2, S_{20}, S_{28} and S_{32} states, respectively, And S_1,S_{16} and S_{40} states for the A-LBP molecule. While for the B-LBP molecule and the A-LBP molecule, the largest absorption peak are S_{20} and S_{16} state, respectively.

Table 2: Transition Energies and Oscillator Strengths of the B-LBP molecule and the A-LBP molecule

	B-LBP			A-LBP	
	Eev (λnm)	f		Eev (λnm)	f
S_1	1.2007(1032.62)	0.0016	S_1	1.1637(1065.47)	1.2284
S_2	1.5609(794.31)	0.9630	S_{16}	3.2106(386.17)	2.9857
S_{20}	3.7735(328.57)	2.3519	S_{20}	3.2899(376.86)	0.0862
S_{28}	4.2581(291.17)	0.1259	S_{28}	3.3886(365.89)	0.0813
S_{32}	4.5709(271.25)	0.2026	S_{40}	4.1842(296.31)	0.1709
			S_{42}	4.2714(290.27)	0.0942

The excited states properties of the B-LBP molecule and the A-LBP molecule will be further explored by the 2D site (transition density matrix) and the 3D cube (charge difference density) representations, as shown in **Figure 2** [22]. From the 2D contour plots of transition density matrix of the B-LBP molecule and the A-LBP molecule, we can see that the electron hole cohere in the linker (shown with blue color for S_{20} of the B-LBP molecule and with green color for S_{16} of the A-LBP molecule), and with increasing the length of the linker the strength of coherence decreases obviously. After analyzing their visualized 3D real space (shown in **Figure 2**), we can clearly identify that the electron transfers from outside to inside, where the green and red stand for the hole and electron densities, respectively, because the excited electrons and holes reside on the edge of the molecule and centre of the molecule, respectively. Also the change of the static charge distribution caused by the photoexcitation is significantly influenced by the length of the linker. In other words, different aromatic compound in linkers has different contribution to the transition when the length of the linker is changed. This result is in accordance with the previous researches and again justifies that the larger y values, that is, weaker coupling of two unpaired electrons. So we can conclude that with the increasing of the singlet biradical character, the strength of coherence and the ability of charge transfer decrease obviously.



B-LBP A-LBP

Figure 2: The Contour Plots of 2D Site Representation (Transition Density Matrix) and the 3D Cube (Charge Difference Densities) of the B-LBP Molecule and the A-LBP Molecule. (Where Phyl is the abbreviation of the Phenalenyl; Be is the abbreviation of the benzene; An is the abbreviation of the anthracene.)

3. Second Hyperpolarizabilitys of the B-LBP Molecule and the A-LBP Molecule

The second hyperpolarizabilitys [30-32] of the B-LBP molecule and the A-LBP molecule were calculated, respectively, at the basis of UB3LYP/6-31G** calculations. The second hyperpolarizability components and their average values γ_s of the B-LBP molecule and the A-LBP molecule are listed in **Table 3**. For the average value γ_s of the second hyperpolarizability components, we define

$$\gamma_s = 1/5[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})] \quad (3)$$

As **Table 3** shows, the γ_{xxxx}, γ_{yyyy} and γ_{xxyy} values are much larger than other components. Consequently, for the B-LBP molecule and the A-LBP molecule, the dominant second

hyperpolarizability contribution originates from these three components. The results showed that all the average values γ_s are negatives, and negative second hyperpolarizabilitys can cause self-defocusing effect, therefore the two systems may be provided with property of self-defocusing effect. The second hyperpolarizability $|\gamma_s|$ of the A-LBP molecule is much larger than $|\gamma_s|$ of the B-LBP molecule (See **Table 3**), the results indicated that the second hyperpolarizabilitys increase with increasing the length of the linkers.

Table 3: Second Hyperpolarizability Components and their Average Value of the B-LBP Molecule and the A-LBP Molecule (Debye)

systems	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	γ_s
B-LBP	-48152.2294	-10547.6825	-1139.0342	-10372.7868	-9165.0073	-2032.7222	-20595.9957
A-LBP	-95467.1307	-18440.6063	-1720.2971	-19800.9304	-17877.2057	-3465.8207	-39583.1895

As shown in **Table 1** and **Table 3**, the results also indicated that the second hyperpolarizability of the system is dependent on singlet biradical character. The singlet biradical character (y) and second hyperpolarizability of the A-BLP molecule are larger than the B-LBP molecule, respectively. Consequently, the second hyperpolarizability increase with increasing the singlet biradical character of the system. So we can conclude that the second hyperpolarizability of the system is controlled by adjusting the singlet biradical character. Furthermore, the organic NLO coefficients are changed.

Ⅳ Conclusion

The ground and excited state properties of the B-LBP molecule and the A-LBP molecule have been theoretically investigated by using the time-dependent density functional theory at B3LYP(UB3LYP) functional and 6-31G** basis set. The charge transfer and electron-hole coherence of the B-LBP molecule and the A-LBP molecule were studied by the visualized 2D and 3D real space analyses. The conclusions are as follows: (1) The singlet biradical character of the B-LBP molecule and the A-LBP molecule increase with increasing the aromatic stabilization energy in the linkers. (2) With the increasing of the singlet biradical character, the strength of coherence and the ability of charge transfer decrease obviously, respectively. (3) The second hyperpolarizability increase with increasing the singlet biradical character of the system. Consequently, the organic NLO coefficient of the system is controlled by adjusting the singlet biradical character.

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