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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