The attractive isomers of 1,1′-bis(verdazyl)ferrocene diradical on structure-property relationship

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ABSTRACT

In 2006, the interesting π-stacks diradical 1,1′-bis(verdazyl)ferrocene (2_0) with two-electron multicenter (2e/mc) bonding were synthesized and investigated (*J. Am. Chem. Soc.* **2006,** *128*, 690–691). Based on the 2_0, two attractive isomeric complexes(3_{19} and 4_{144}) are designed by a piece of radical rotating along iron-Cp axis about 19° and 144°, respectively. Among these three diradicals, a unique two-electron eight-center (2e/8c) $\pi-\pi$ bonding is obtained in the 2_0 due to the overlap of SOMOs of the two pieces of radicals, the 3_{19} has a σ-covalent bonding, and two separate radicals are shown in the 4_{144}. Further, the UV-visible absorption spectrum of 2_0 and 3_{19} arise a new absorption feature at 566 and 530 nm, respectively, which may be assigned to π-π stacking (2_0) and σ-covalent (3_{19}) bonding of two pieces of radicals, although this absorption feature not exist in experimental UV-visible absorption spectrum. Fortunately, the UV-visible absorption spectrum of 4_{144} is similar to experimental results, which demonstrate that the 2_0 with 2e/8c bonding may transform to be 4_{144} with two separate radicals in solution. These three diradicals may transform to each other, which is beneficial to understanding their magnetic properties in solution and crystal and designing new complexes with excellent magnetic property.

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1. Introduction

Radicals with open-shell electron configurations have attracted increased interest, due to the rapid development of radicals field in potential magnetic materials [1–4] and conducting materials [3,5–12]. Among these radicals, the radical electron for some radicals with π-symmetry are delocalized over several atoms such as oxygen, carbon or nitrogen in the singly occupied molecular orbital (SOMO). In this case, the two-electron multicenter (2e/mc) bonding is formed in radical dimer through the overlap of SOMOs [13–23]. For example, the phenalenyl (PLY) is open-shell radical, so its SOMO is delocalized over the six carbon atoms of the PLY. The two-electron twelve-center bonding is formed by two PLY monomers staggered stacking [24,25]. Although a variety of features can suppress dimerization by the presence of charge on the radical [3,26], steric protection [3,27] and resonance delocalization [3,28]. For these π-dimers with non-covalent bonding has admirable

effect in charge transport and magnetic properties [3,29]. Many theoretical and experimental chemists invest a lot of efforts on the designing and synthesizing these complexes with 2e/mc bonding. Such as point that the biphenalenyl with two-electron twelve-center bonding has excellent magnetic property [2], and the charge transport of $[TCNE]_2^{2-}$ with two-electron four-center bonding has been investigated by Juan N. Novoa [17,30–32]. We found that two radical monomers are only linked by 2e/mc bonding and the interaction between these radical dimer is weaker than conventional covalent bond [3,16].

Ferrocene was discovered in 1951. Due to the stability of the ferrocenyl group, the accessibility of a variety of derivatives, and the favorable electrochemical properties, the ferrocenyl compounds have attracted increased interest. The compound has found many applications in materials science including sensors, catalysts, electroactive and optical materials [33–36]. Such as six novel ferrocene-based compounds were designed and investigated that the compounds have potential nonlinear optical applications by Yu W. group [37], and ferrocene chromophores were investigated that the compounds are used to valuable nonlinear optical materials by Kaur S. group [38].

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In 2006, the attracting diradical 1,1′-bis(verdazyl)ferrocene that two radical verdazyl are linked by ferrocene (so two pieces of radical can be restricted rotate around iron-Cp axis) were synthesized and investigated by Bryan D. K. group [3]. They demonstrate that the structure of diradical may change in solid phase and solution phase through contrast solution absorption spectrum and solid state diffuse reflectance spectra in experiment. So two radical monomers are linked by "Fe-bridge" for this diradical 1,1′-bis(verdazyl)ferrocene, these interesting structures excited our interest. To detailed investigate this structures-properties relationships, some lower energy points are obtained by scan around an axis (Fe-bridge). In which three diradicals (2_0, 3_{19}, 4_{144}) are selected and optimized by density functional method. Significantly, we found that three diradicals have different bonding due to the different location of two pieces of radical monomers: the 2e/8c bonding for 2_0, σ-covalent bonding for 3_{19} and non-bonding for 4_{144}.

2. Computational details

Firstly, four functional methods (B3LYP, PBE0, M06L and M06-2X) are used to optimize the structure of synthesized π-stacks diradical 1,1′-bis(verdazyl)ferrocene (2_0) [39]. Among these methods, the geometric parameters of B3LYP are close to that of experimental crystal (see Table S1). So the B3LYP method with basis sets (LANL2DZ (Fe) and 6-31 + G (d, p) (C, H, O)) is chosen to optimize the structures of four complexes **1**, 2_0, 3_{19}, 4_{144}. Results show that three isomeric diradicals 2_0, 3_{19} and 4_{144} with all real frequencies are obtained by the rotation of a piece of radical along iron-Cp axis about 0°, 19° and 144°, respectively. Further, their spin density surfaces are analyzed to show the location of the two radical electrons. And then the diradical characters are calculated using the spin-unrestricted B3LYP method and basis sets (LANL2DZ (Fe) and 6-31 + G (d, p) (C, H, O)) to study the interaction of the two pieces radical.

The diradical character y_i (related to the HOMO - i and LUMO + i) is defined by the weight of the doubly-excited configuration in the
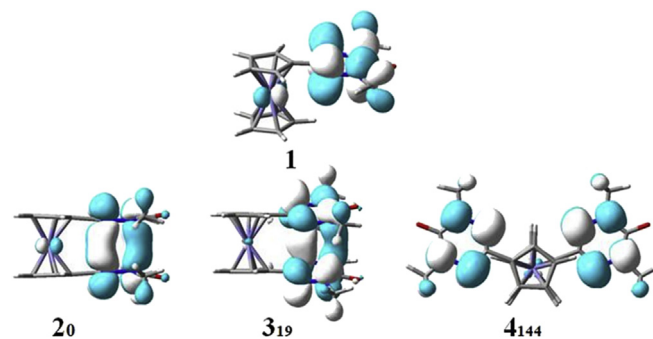

Fig. 2. The HOMO of four complexes (**1**, 2_0, 3_{19}, 4_{144} isovalue = 0.02 a.u.).

multi-configurational (MC)–SCF theory and is formally expressed in the case of the spin-projected spin-unrestricted Hartree–Fock (PUHF) theory as

$$y_i = 1 - \frac{2T_i}{1+T_i^2} \tag{1}$$

where T_i, the orbital overlap between the corresponding orbital pairs, and can be expressed in terms of the occupation numbers (n_i) of the UHF natural orbitals (UNOs):

$$T_i = \frac{n_{HOMO-i} - n_{LUMO+i}}{2} \tag{2}$$

The y_i takes a value between 0 and 1, which correspond to closed-shell and pure diradical states, respectively [40–43].

On the other hand, the B3LYP method is used to calculate the UV-visible absorption spectrum. All calculations were performed by the Gaussian 09 program package [44].
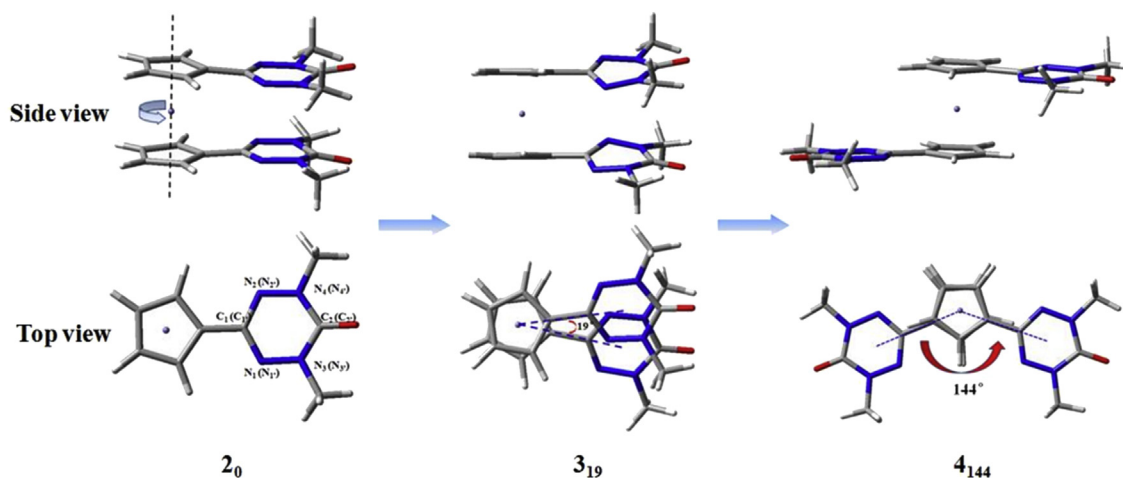

Fig. 1. The optimized structures of three complexes (2_0, 3_{19}, 4_{144}).

Table 1
The selected geometric parameters (Å) for the studied complex (2_0, 3_{19}, 4_{144}).

	N1-C1	N2-C1	N3-C2	N4-C2	N1-N1′	N2-N2′	N3-N3′	N4-N4′	N1-N2′	N3-N4′
2_0	1.337	1.337	1.392	1.392	2.969	2.969	2.935	2.935		
3_{19}	1.372	1.308	1.399	1.384					2.372	2.719
4_{144}	1.335	1.335	1.392	1.390						