Strength of Spin Coupling in High-Spin Organic Molecules

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The effective valence bond (EVB) model proposed by Malrieu and Maynau is exactly solved to calculate the strength of spin coupling in a large number of high-spin conjugated di- and polyradicals with up to 22 π-electrons. In terms of simple concepts such as spin-coupling unit, spin-coupling path, etc., we carefully analyze the topological dependence of the calculated coupling constants in these high-spin molecules. For diradicals, our calculations indicate that the strong ferromagnetic coupling often requires short topological distance, numerous spin-coupling paths, and large delocalization interaction provided by spin coupling units. Besides this, the connectivity of two radical sites also plays a significant role in determining the coupling strength in diradicals. When extending diradicals to their homologous higher polyradicals, the coupling constant through vinylidene is found to decrease appreciably from the diradical to the "linear" and "circular" triradicals and to approach the corresponding value in related one-dimension infinite spin system at different rates; the spin coupling through *m*-phenylene in the diradical is predicted to be reduced by about 2 and 4 times in linear and "star-branched" macroscopic-size systems, respectively, while the 2,3′-connected biphenyl coupling unit has a stronger coupling ability in the linear triradical than in the diradical.

Introduction

The design and preparation of high-spin organic molecules for use in organic molecular-based ferromagnets is a rapidly developing area.[1−4] In recent decades, a number of theoretical chemists have worked on predicting the type (ferromagnetic/antiferromagnetic) of spin coupling in π-conjugated molecules.[5−13] Under the guidance of proposed theoretical models, many di-, tri-, and polyradicals with high-spin ground states have been synthesized and characterized.[14−18] But until now, an understanding of the strength of spin coupling in these systems, reflected in the energy gap between high-spin ground and lowest excited states, has been seriously hindered by the limitations of experimental measurements and theoretical computations. Experimentally, magnetization/magnetic susceptibility measurements are only applicable to those species in which energy gaps are somewhat narrow and on the order of a few hundred calories/mole as exemplified in several persistent di- and triradicals.[19,20] Whereas in light of theoretical methods, high-level ab initio calculations involving large basis sets, geometry optimization, and extensive configuration interaction (CI) would presumably provide the most reliable evaluations to this problem. For some small molecules such calculations have been reported;[21−26] however, they are still impractical for larger molecules. Although in some cases limited CI calculations are employed to give a rough estimate of the spacing between high-spin and lower spin states,[27−30] the size-consistency dilemma of this method prevents its useful application to the comparison of the strength of spin coupling in molecules of different size. Fortunately, for pure organic conjugated radicals the renewed interest in valence bond (VB) theory[31−35] brings us a unique chance to avoid this problem. Recently, we have made a preliminary investigation of the ferromagnetic interactions in a series of di- and polyradicals by means of the classical (Pauling−Wheland) VB and nonempirical VB models.[36,37] Considering that only nearest-neighbor interactions are included in these two models, the effective valence bond (EVB) theory proposed by Malrieu and Maynau,[31] implementing fourth- and sixth-order corrections based on the classical VB theory, should be more appropriate for more elaborate investigation of magnetic coupling in conjugated radicals. In fact, for some smaller diradicals, Malrieu and Maynau's work has demonstrated that singlet−triplet separations calculated with this more complicated VB model are in good agreement with those derived from the full CI PPP calculations.[9,31] It should be noted that fourth-order corrections enable the EVB model to include the second-nearest-neighbor interactions and four-body cyclic contributions, which constitute the main modifications to the classical VB theory. Therefore, we choose the EVB model containing up to fourth-order corrections as our theoretical model in subsequent calculations for the purpose of computational simplicity.

By use of the EVB model, we calculate the strength of spin coupling in a number of conjugated di- and polyradicals with up to 22 π-electrons, many of which are model compounds of some synthesized high-spin molecules. All these species have high-spin ground states predicted theoretically by the disjoint NBMO analysis[8] and the Ovchinnikov formula.[7] In the present work, we focus our attention to two important problems involving magnetic coupling in high-spin molecules and molecular-based ferromagnets: (1) How do the topological characteristics of π-networks of diradicals affect the spin coupling between two spin sites? (2) To what extent is the spin coupling through ferromagnetic coupling units in diradicals maintained in their homologous polyradicals and even related ferromagnetic polymers? In addition, the coupling strength in some known high-spin species without available experimental measurements is estimated in terms of the results obtained from corresponding model compounds.

Methodology

Effective Valence Bond (EVB) Hamiltonian. By projecting the Hubbard Hamiltonian onto the subspace of neutral determinants in which every spatial atomic orbital is singly occupied, Malrieu and Maynau[31] have derived the effective valence bond (EVB) Hamiltonian including various order corrections via the quasi-degenerate many-body perturbation theory. The second-order effective Hamiltonian is essentially the well-known Pauling−Wheland VB model, being equivalent to the Heisen-

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berg model of solid-state theory, as shown in eq 1[38]

$$H^{(2)} = J\sum_{i,j}\left(2S_iS_j - \frac{1}{2}\right) \tag{1}$$

where S_i is the spin operator for site i, J is an (positive) exchange parameter, and $i-j$ denotes nearest-neighbor sites. For alternant hydrocarbons discussed in this paper, there are no odd-order terms.[31] Some computations show that in the absence of squares the fourth-order correction can be written in the spin operator form as follows[39]

$$H^{(4a)} = J'\sum_{i,j}[-4b_{ij}(4S_iS_j - 1) + c_{ij}(4S_iS_j - 1)] \tag{2}$$

where b_{ij} is 1 if the ith and jth atoms are nearest neighbors and otherwise is 0, while c_{ij} is the number of other atoms which are simultaneously bonded to the ith and jth atoms. In the presence of four-membered rings, another term should be included[39]

$$H^{(4b)} = J'\sum_{i,j,k,l} d_{ijkl}\Big\{10[(S_iS_j)(S_kS_l) + (S_iS_l)(S_jS_k) - (S_iS_k) \times (S_jS_l)] - \frac{1}{2}[S_iS_j + S_jS_l + S_iS_k + S_jS_k + S_lS_k + S_iS_l] + \frac{1}{8}\Big\} \tag{3}$$

where

$$d_{ijkl} = \begin{matrix} 1 & \text{if } b_{ij}b_{jk}b_{kl}b_{il} = 1 \\ 0 & \text{otherwise} \end{matrix}$$

As expected, through fourth-order corrections the EVB model introduces the second-nearest-neighbor magnetic coupling for any molecule, with four-body interactions being crucial for those systems containing four-membered rings. It is worthwhile pointing out that the inclusion of sixth-order corrections will improve to a certain extent the accuracy of the EVB model especially for those molecules with benzene nuclei,[31] but the increasing complexity of the model will make it difficult to treat relatively larger molecules. Hence the EVB model up to fourth-order corrections will be adopted in this present work for simplicity. Also worthy of remark is the determination of the exchange parameters J and J' appearing in the above three equations. It is well-known that the degenerate many-body perturbation expansion actually would diverge when applied to conjugated systems;[31,40] namely, the theoretical estimates of J and J' will result in a nonconvergent behavior of the perturbation expansion. However, Malrieu and Maynau have demonstrated that this problem may be avoided by fitting the values of these two parameters to the full CI PPP results for a series of small conjugated hydrocarbons.[31] In this way, they gave the values of J and J' to be 1.95 and 0.0282 eV, respectively, which will be used in our subsequent calculations.

Despite the fact that this model has a more complicated form than the classical VB model, it also acts on the space of covalent VB structures, whose number exponentially increases with the number of atoms. Although spin symmetry can be utilized to simplify the solution of the EVB model, a powerful algorithm for the diagonalization of large matrices is still desirable. Our recent works[35−37] have demonstrated that the Lanczos method is applicable to this problem. Some details of our calculations will be given below.

Details of the Calculations. The details of the Lanczos method have been introduced elsewhere.[41] The central idea of this method is to transform a general symmetric matrix to a tridiagonal matrix by exerting a specially chosen transformation on basis functions. After an initial state in a specified spin subspace is selected, the recursion procedure will yield a tridiagonal matrix. Due to the special characteristics of the produced basis sets, a few recursion steps are enough to give an excellent approximation to the low-lying eigenvalues of the EVB model in this subspace.[42] In our previous treatments,[35−37] the lowest energy determinants in various S_Z subspaces were taken as starting states to obtain the low-lying states in these subspaces. It should be noted that this selection is not unique. We can also choose the common eigenvectors of S^2 and S_Z as the initial state as shown below

$$\Phi_k = \frac{1}{\sqrt{N!}}\sum_P (-1)^P P[\Omega(r_1,r_2,...,r_N)\Theta_k(S_1,S_2,...,S_N)] \tag{4}$$

where

$$\Theta_k(S_1,S_2,...,S_N) = \prod_{i-j}\frac{1}{\sqrt{2}}[\alpha(i)\beta(j) - \alpha(j)\beta(i)]\prod_l \alpha(l) \tag{5}$$

$$\Omega(r_1,r_2,...,r_N) = \chi_1\chi_2...\chi_N \tag{6}$$

Here χ_i denotes the ith carbon p_z orbital. $\Omega(r_1,r_2,...,r_N)$ is the spatial wave function of the considered system, and $\Theta_k(S_1,S_2,...,S_N)$ is the common eigenvectors of S^2 and S_Z operators with the same eigenvalue S. Obviously, the total wave function Φ_k is a linear combination of some neutral determinants. With this type of wave function as a starting state, the low-lying eigenstates in various S subspace can be directly obtained. In this way, we have calculated the high-spin ground and first excited states for all di- and polyradicals by using the standard Lanczos method, which has been given in ref 35. As done in other semiempirical π-electron theories, all molecules are assumed to be planar in our calculations. We have carried out these calculations on an SGI R8000 workstation. In comparison with other techniques,[33,34] the Lanczos method seems simpler and requires less storage.

Results and Discussion

Diradicals. The singlet−triplet energy separation (ΔE_{ST}) of diradical species is not only closely related to their chemical reactivity but also reflects the coupling strength between two unpaired electron sites. There have been a number of reports of theoretical calculations of this quantity for small molecular systems.[9,21−23,25−30] Firstly, this section aims to ascertain the influence of topological features between two radical sites on the spin coupling in diradicals. Accordingly the calculated singlet−triplet gaps for four typical sets of diradicals as shown in Figure 1 are provided in Table 1. To analyze the spin coupling in these diradicals conveniently, we prefer to resort to the concept of spin coupling unit and spin-coupling path.[4] Diradicals may be viewed as systems containing “localized” spin sites which are linked via the spin-coupling unit. A spin-coupling path is defined to the array of bonded atoms (orbitals) between two radical sites. The topological distance then means the number of bonds in the shortest spin-coupling path.[29] To visualize the results in Table 1, Figure 2 shows the correlation of singlet−triplet energy gap with the topological distance for each listed molecule.

Set a consists of open-chain branched molecules, α,ω-dimethylenepoly(vinylidene), where the first member is trimethylenemethane (TMM, **1**). The radical sites at the ends are coupled through a unique spin-coupling path. It can be observed

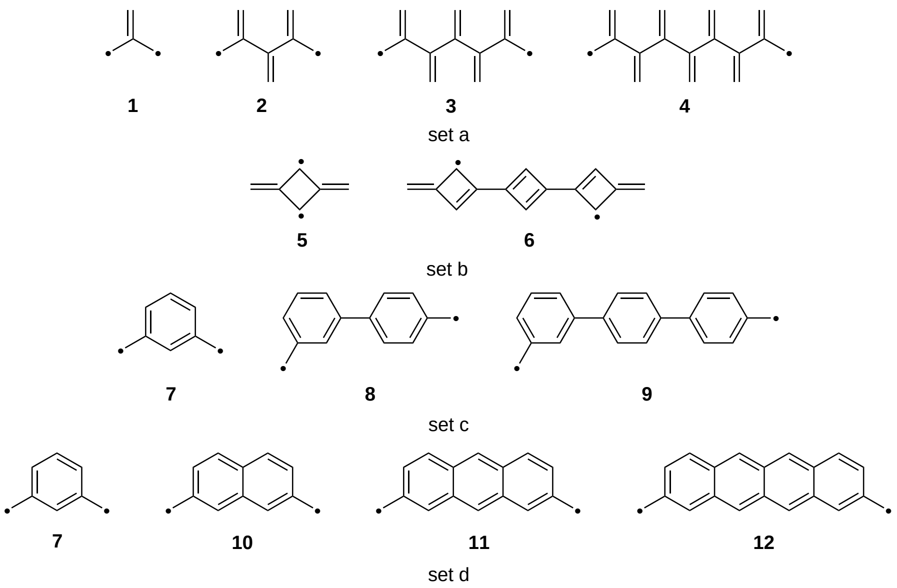


Figure 1. Selected four sets of diradicals.

TABLE 1: Singlet−Triplet Energy Gaps ΔE_{ST} (eV) for Selected Diradicals in Figure 1

set	compd	ΔE_{ST}	set	compd	ΔE_{ST}
a	**1**	1.555	c	**7**	1.146
	2	0.146		**8**	0.380
	3	0.029		**9**	0.147
	4	0.006	d[a]	**10**	0.842
b	**5**	1.492		**11**	0.634
	6	0.248		**12**	0.487

[a] Species **7** is also the first member of set d.

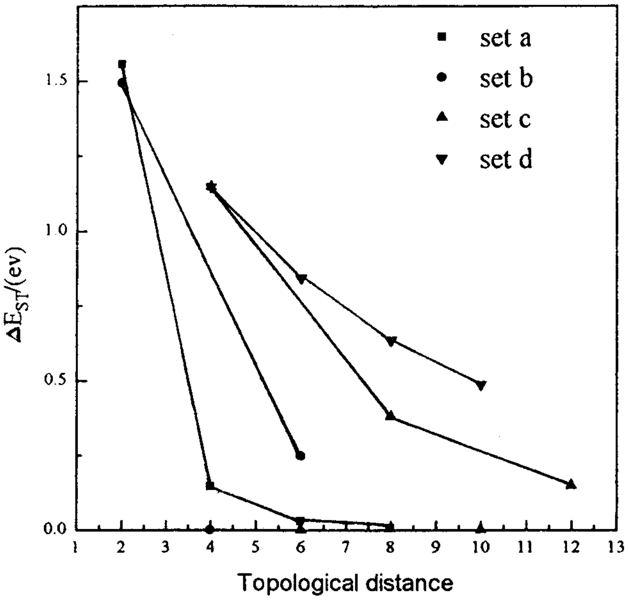


Figure 2. Variation of ΔE_{ST} with the topological distance between two radical sites.

that the singlet−triplet gap decays drastically with increasing topological distance as in going from 2 to 6 along this series. In fact, a nearly degenerate ground state is expected for the last one (**4**) of set a.

Set b starts from 2,4-dimethylene-1,3-cyclobutanediyl (**5**). This species, elsewhere termed as “non-Kekule benzene”, has been synthesized, characterized, and also theoretically studied.[17a,b,26b] Since there exists a parity rule on the ground multiplicity of non-Kekule acenes,[28] the first and third members of this series, which have triplet ground states, are chosen for our investigation. From Figure 2, the trend of decay of the spin-coupling strength with the topological distance is displayed for this set. There are 2^n spin-coupling paths with n being the number of four-membered rings, so that it is plausible that in this set there seems to be a slower decay rate of spin coupling compared to the situation in set a.

Set c consists of polyphenylenes with methylene groups at the ends. The first member of this series, *m*-quinodimethane (**7**), has been well studied experimentally and theoretically to estimate the ferromagnetic coupling efficiency of *m*-phenylene coupling unit.[17f,22,30,43] Apparently, the magnitude of the spin coupling decreases along this series as in set a and set b, but in a smoother manner. Interestingly, the coupling through sequential connection of three benzene rings is still appreciable.

In set d, aromatic polyacenes play the role of the ferromagnetic coupling units. We find that the decrease of the magnetic coupling with the topological distance becomes slower in this set than in previous sets. This may be attributed to the fact that aromatic polyacenes provide stronger π-electron’s spin polarization than corresponding ferromagnetic coupling units in set b and set c, respectively. The results obtained from this set also suggest that the smaller members of the polyacenes can be used as potential spin-coupling units to build very high spin molecules and magnetic polymers.

Summarizing the above discussions, we conclude that the strong ferromagnetic coupling often emerges in those diradicals with short topological distance, numerous spin-coupling paths, and large delocalization effect presented by spin-coupling units.

In theoretical research on diradicals, another aspect that should be particularly noticed is the correlation of connectivity of radical centers with spin-coupling constant J ($\Delta E_{ST} = -2J$). For example, as a sterically hindered derivative of *m*-quinodimethane, Schlenk’s hydrocarbon **16** is a representative of stable diradicals with triplet ground states. Similar to this molecule, several stable di- and polyradicals have been prepared and studied.[14−16] Moreover, it is expected that pure organic ferromagnetic polymers can be built from this stable monomer. Because the Schlenk hydrocarbon has a strong triplet preference so that thermal excitations at room temperature are not energetic enough to populate its first excited singlet state, spin-coupling parameter J of this molecule cannot be determined by susceptibility measurements.[14b] On the other hand, various theoretical approaches have difficulty in obtaining this quantity reliably

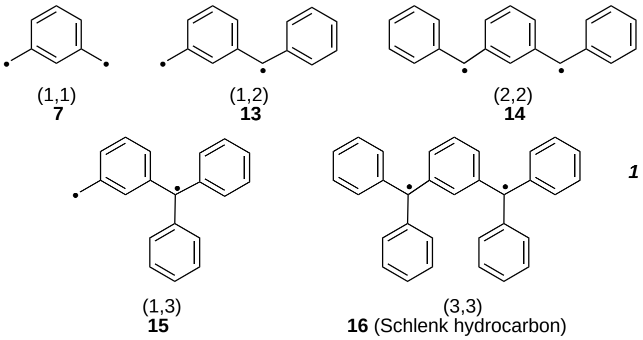
TABLE 2: Coupling Constants (eV) in Four Diradicals (shown in *1*)[a]

compd	connectivity	coupling constant ($-J$)
7	(1,1)	0.573
13	(1,2)	0.366
14	(2,2)	0.273
15	(1,3)	0.301

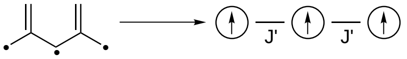
[a] The respective connectivity of two radical centers in each molecule is also given for analysis.

due to the size of this molecule. In order to estimate the coupling strength in larger diradicals like the Schlenk hydrocarbon, we consider several smaller diradicals similar to the Schlenk hydrocarbon (*1*) as model systems to study the relation between the connectivity of radical sites and spin-coupling constants. On the basis of extrapolation, the coupling constant in the Schlenk hydrocarbon may be estimated.

In Table 2, we list the calculated coupling constants for four diradicals in *1*. Let's analyze the respective connectivities of two radical sites in each molecule with respect to the coupling constant J. Clearly, when one fixes one radical center of species (1,1) and increases the connectivity of the other one from 1 to 3, the value of J decreases by a factor of 47.5%. Similarly, the spin coupling is further weakened by 25.4% from (1,2) to (2,2) species. We may ascribe the reduction of J to smaller and smaller polarization of the π-electrons on the m-phenylene coupling units with increasing connectivity of two radical centers. Combining this idea with the value of J in the (1,3) diradical, we predict that J in the Schlenk hydrocarbon which can be signified as (3,3) is about one-fourth of that in the parent diradical (1,1). This value is in good agreement with the empirical estimate given by Rajca.[4]


(1,1)
7
(1,2)
13
(2,2)
14
(1,3)
15
(3,3)
16 (Schlenk hydrocarbon)
1

Polyradicals. It has been recognized that a high-spin molecule can be built up from two elements: the spin-containing unit (SCU) and the ferromagnetic coupling unit (FCU).[17d−f] The SCU is simply any structure that possesses the unpaired electrons, and the FCU is a structural unit that ferromagnetically couples any two or more SCUs. By adopting this strategy, experimental chemists have synthesized many high-spin tri- and polyradicals.[14b−e,15d,16,17d−f] However, the knowledge of the strength of the spin coupling in these polyradicals are relatively rare compared to diradicals.[4,19] To simplify the treatment on these larger polyradicals, chemists usually assume that a polyradical is composed of many "unpaired" electrons coupled through spin-coupling units with different coupling constants.[4] Theoretically, this type of "renormalization" process can actually be derived by applying a cluster expansion technique.[10a] For example, tetramethylenepropane (TMP) can be represented by the reduced "molecule" (*2*), in which J' is the ferromagnetic coupling constant through vinylidene (J' is a negative value).



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By using the classical VB model, one can easily determine the value of J' from the relation $\Delta E_{DQ} = -J'$ (ΔE_{DQ} is the energy separation between the ground quartet and lowest doublet states). It should be mentioned that the coupling constant J' through vinylidene in the triradical TMP may be different from that in the corresponding diradical. This problem stimulates the following question concerning the spin coupling in polyradicals: To what extent is the ferromagnetic coupling constant through FCU in diradicals maintained in their homologous polyradicals and even related ferromagnetic polymers? To answer this question, three classes of di- and polyradicals are selected as our model systems. As done in TMP, the energy gap between the high-spin ground and lowest excited states is firstly calculated within the EVB model for these species, and then ferromagnetic coupling constants in each molecule are obtained by the application of the classical VB theory. In the following we discuss our results according to different FCUs.

(a) Vinylidene. Two series of polyradicals based on vinylidene as the FCU, **17**−**19** in a "linear" arrangement and **20**−**24** in a "closed loop" arrangement (*3*), are employed to study the variation of the coupling constant through vinylidene with the increase of radical sites. It is necessary to point out that in linear polyradicals **18** and **19** the coupling parameter through the terminal FCU may differ from that through the middle FCUs. An approximate treatment is to suppose that the coupling parameter through the terminal FCU in **18** and **19** has the same value as that obtained from the triradical **17**. On the basis of this assumption, the coupling constant through the middle FCU in **18** and **19** can be derived from the calculated energy gaps, respectively. We summarize the calculated energy gaps and coupling constants for these polyradicals in Table 3. For comparison, the corresponding value in the TMM diradical is also included. For the linear series, we observe that the coupling constant decreases appreciably from the diradical to the triradical and then stays constant in tetra- and pentaradicals. Surprisingly, the middle and terminal FCUs in **18** and **19** have the same coupling ability. This indicates that in these two molecules unpaired electrons basically localize on the radical sites we assume. As expected, we verify that the energy gap of the pentaradical is also exactly fitted by using this coupling constant, implying that the coupling constant in the related one-dimension polymer is also near to that in the tetraradical.

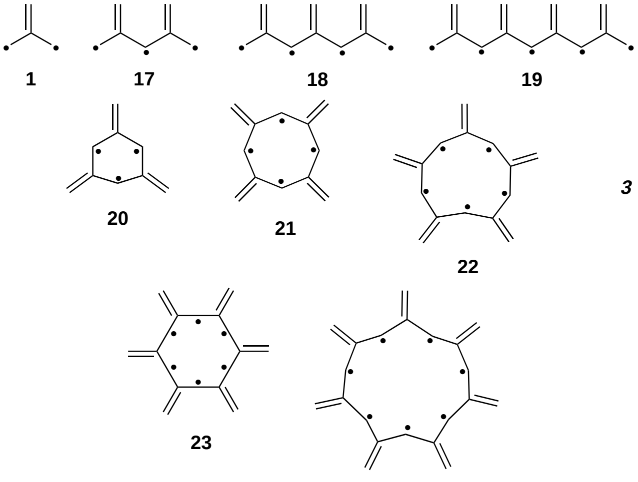

1
17
18
19
20
21
22
23
24
3

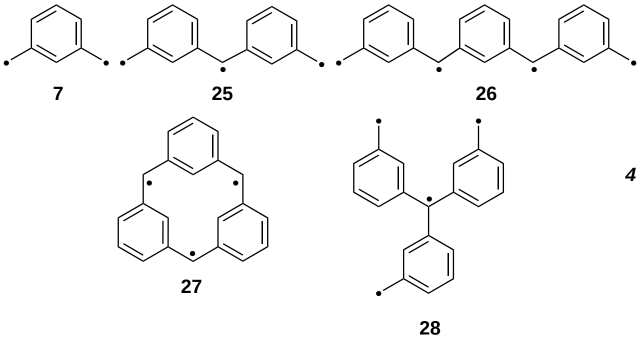
TABLE 3: Energy Gaps (eV) between the Ground and Lowest Excited States and Coupling Constants (eV) through Vinylidene for All Molecules Shown in *3*[a]

compd	ΔE	coupling constant ($-J$)	ratio
1	1.555	0.777	0.71
17	0.552	0.552	0.71
18[b]	0.324	0.552	0.71
19[b]	0.212	0.552	0.49
20	1.137	0.379	0.55
21	0.863	0.431	0.59
22	0.641	0.463	0.62
23	0.486	0.486	0.65
24	0.378	0.503	

[a] The ratio of coupling constant between polyradicals and diradical is also listed for comparison. [b] The coupling constant through the central vinylidene is given.

Let's turn to the "circular" series. The drastic drop of coupling strength from the diradical to the triradical is still observed, but in the circular triradical the spin coupling is relatively weak compared to that in the linear triradical, reflecting the effect of end groups. When extending the circular triradical to higher polyradicals, a novel feature of spin coupling appears. It can be seen that the coupling constant gradually increases from **20** to **24**. However, we may anticipate that in a sufficiently large molecule with more FCUs the coupling constant will no longer increase, approaching the corresponding value in the linear infinite system mentioned above.

(b) *m*-Phenylene. The intramolecular spin coupling through the *m*-phenylene coupling unit in small molecules has been extensively studied via a variety of theoretical methods.[9,22,30,36−37] Numerous experiments have also been designed to characterize the effectiveness of *m*-phenylene as a FCU.[16b,17f,19,20,43] By far *m*-phenylene has been proven to be the best FCU for synthesizing very high spin molecules and truly practical magnetic materials. As a result, an understanding on the magnetic coupling in these polyradicals constructed from the *m*-phenylene coupling unit is very desirable. Toward this goal, the following molecules depicted in *4* are investigated. With a similar strategy as addressed above, we obtain the coupling parameters through *m*-phenylene in these systems which are tabulated in Table 4. The data indicate that about two-thirds of the coupling constant in diradical **7** is maintained in the linear triradical and one-half in the circular triradical. Here we would like to mention the related experimental results obtained by Ishida and Iwamura.[16b] In their experiments, nitroxide groups are introduced as radical centers in species **7** and **25**. They found that the ratio between J in the diradical and that in the triradical is about 1/2, basically consistent with our estimates for model systems **7** and **25**. In addition, this estimate is slightly lower than our previous results based on nonempirical VB model.[37]



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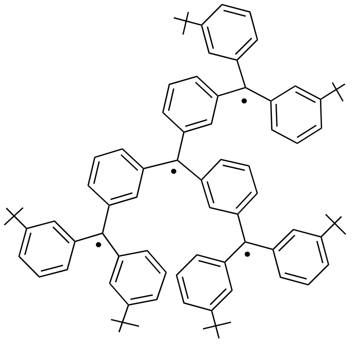
As expected, the magnitude of the coupling constant through the central *m*-phenylene in the tetraradical **26** is lower than that through the terminal *m*-phenylene, consistent with the relation between spin coupling and the connectivity of radical sites described in the previous section. On the other hand, the calculated coupling constant in **27** is very close to that through the central *m*-phenylene unit in **26**, again verifying that the spin coupling through the *m*-phenylene primarily depends on the connectivity of two radical sites. On the basis of this rule, the coupling constant through the central FCU in the linear tetraradical **26** should be a rather good approximation to that in infinite poly(*m*-phenylmethyl) system. For the remaining species **28**, we note that this molecule and diradical **15** have close coupling constants. This can be interpreted as that the addition of two radical sites at ends has small influence on the spin coupling in diradical **15**. Now we consider a known molecule **29**[14d] analogous to species **28**. Combining the result of **28** with the preceding spin-coupling/connectivity relation, we infer that the coupling parameter in the planar conformation of this molecule may be around 0.17 eV (3.9 kcal/mol). If we extend high-spin molecule **29** to a two-dimension magnetic solid, the corresponding J in this infinite system may also approach this value.

TABLE 4: Energy Gaps (in eV) between the Ground and Lowest Excited States and Coupling Constants (eV) through *m*-Phenylene for All Molecules Shown in *4*[a]

compd	ΔE	coupling constant ($-J$)	ratio
7	1.146	0.573	
25	0.383	0.383	0.67
26[b]	0.200	0.310	0.54
27	0.905	0.302	0.53
28	0.339	0.339	0.59

[a] The ratio of coupling constant between polyradicals and diradical is also listed for comparison. [b] The coupling constant through the central *m*-phenylene is given.



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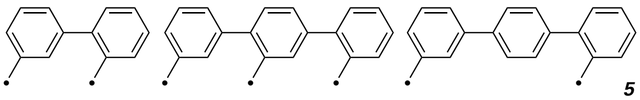
(c) Biphenyl. The variation of coupling strength through the 2,3′-connected biphenyl in extending diradical **30** to triradical **31** is also worth investigating. This FCU can be used to design a class of linear polyradicals which can illustrate to some extent the impact of defects formed at spin sites.[4]



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For instance, when experiments fail to generate an unpaired electron in the central radical site of **31**, in place of **31** one can obtain a diradical **32**, which is still a weakly coupled triplet molecule. If similarly for **17** experiment failed to generate the central radicaloid site, then **17** is divided into two uncoupled parts each with lower spin $S = {}^1/_2$. Therefore for designing linear spin systems, the topological character possessed by **31**

TABLE 5: Energy Gaps (eV) between the Ground and Lowest Excited States and Coupling Constants (eV) through 2,3′-Connected Biphenyl for Three Molecules Shown in 5

compd	ΔE	coupling constant ($-J$)
30	0.409	0.204
31	0.256	0.256
32	0.156	0.078

and its analogues is very important to obtain very high spins because there is a significant probability for the formation of defects in generating unpaired electrons in polyradicals. Table 5 shows us the quantitative variation of coupling constants from **30** to **32**. Interestingly, we find that the coupling constant through the 2,3′-connected biphenyl in the triradical is slightly amplified compared to that in the diradical. This is understandable because the connectivity of neighboring radical sites does not change when extending **30** to **31**, and the weak ferromagnetic coupling between two terminal radical centers increases to some extent the spin-polarization effect in 2,3′-connected biphenyl coupling units. The "amplifying" effect of spin coupling reported here and in our previous work[37] widens our recognition of spin coupling in extended systems. On the basis of the same inference, we predict that this effect will rapidly disappear in homologous higher polyradicals of species **31**. As to the effect of a defect on the spin coupling in **31**, J in **32** indicates that the spin coupling between two terminal radical sites is still not negligible.

Concluding Remarks

This paper presents a systematic investigation on the quantitative aspect of spin coupling in high-spin conjugated molecules. The theoretical model we used is more elaborate than the traditional Pauling−Wheland VB theory. It seems that various di- and polyradicals can be well studied by this spin model. In terms of simple concepts such as spin-coupling units, spin-coupling paths, etc., we carefully analyze the calculated coupling constants in these ferromagnetically coupled organic molecules. For diradicals, our calculations indicate that the strong ferromagnetic coupling often requires short topological distance, numerous spin-coupling paths, and significant delocalization of the π-electrons in the intervening spin-coupling units. Besides this, we demonstrate that the connectivity of two radical sites also plays a significant role in determining the coupling strength in diradicals. From the results obtained for polyradicals, we gain important insight into the variation of spin coupling through different FCUs in extending diradicals to their homologous higher polyradicals. Firstly, it is found that the coupling constant through vinylidene decreases appreciably from the diradical to the linear and circular triradicals and approaches the corresponding value in related one-dimension infinite spin system at different rates. Secondly, the spin coupling through *m*-phenylene in the diradical is predicted to be reduced by 2 and 4 times in linear and star-branched macroscopic-size systems, respectively. Thirdly, the 2,3′-connected biphenyl unit is found to have stronger coupling ability in the linear triradical than in the diradical. In addition, the predictions of coupling constants in two known high-spin molecules are made as a direct application of our investigation.

Although significant progress toward understanding spin coupling in high-spin organic molecules has been made in this paper, the direct verification of these results still needs much work by experimental chemists. In order to obtain experimentally the strength of spin coupling in those strongly coupled high-spin molecules, a feasible approach is to synthesize some extended systems with more unpaired electrons derived from those molecules, which may have narrow energy gaps suitable for experimental measurements. Then the measurement of spin coupling in these extended systems can be employed to derive the corresponding values in their parent systems by extrapolation. Finally, the results we obtain are also of considerable use for experimentalists to synthesize strongly coupled high- spin molecules and organic molecular-based ferromagnets with high T_C temperatures.

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