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Tetrahedron 59 (2003) 3499–3504

TETRAHEDRON

Substituent effect of the spin-coupling constant through *m*-phenylene in *m*-xylylene and its derivatives

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Received 2 January 2003; revised 28 February 2003; accepted 20 March 2003

Abstract—Density functional UB3LYP calculations with the broken symmetry approach and spin-projection method on *m*-xylylene diradical and its derivatives have been performed to investigate the dependence of the spin-coupling constant through *m*-phenylene on the number of phenyl substituents on the two radical sites. The results show that the coupling constant (or the singlet–triplet gap) steadily decreases on increasing the number of phenyl substituents on the two radical sites. This trend is ascribed to more spin delocalization into the phenyl substituents and the larger twist angle of the phenyl substituents out of the *m*-phenylene plane when the degree of phenyl substitution is increased. For Schlenk's hydrocarbon, the coupling constant J is 1.52 kcal/mol, only one quarter of that in the parent *m*-xylylene. © 2003 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the past decades, the design and synthesis of organic molecular ferromagnets have evoked continuing attention both experimentally and theoretically.[1–4] A useful strategy for designing these materials is to connect organic radicals by ferromagnetic coupling units (FCUs).[2,3] A large number of experimental and theoretical investigations[5–17] on diradicals with high-spin ground states have been conducted with the aim of estimating the strength of spin coupling through various FCUs, which is reflected in the energy gap between high-spin ground and lowest excited states. So far the best studied FCU is *m*-phenylene.[8,13–27] The prototypical structure is the diradical *m*-xylylene (**1**), which exhibits a substantial preference for the triplet ground state.[8,13–17] However, it is very unstable with respect to dimerization and reaction with oxygen. In contrast, its substituted derivatives have been successfully synthesized.[18–23] The simple methylene radicals ($\cdot CH_2$) of *m*-xylylene can be replaced by a wide array of spin-containing (SC) structures, and high-spin ground states are often produced. The most famous sterically shielded derivative of *m*-xylylene is Schlenk's hydrocarbon **6**, tetraphenyl-*m*-xylylene, which was first prepared in 1915[18] and established to have a triplet ground state in 1970.[19] Using Schlenk's hydrocarbon (or its derivatives) as building block moieties, stable ferromagnetic polymers and dendrimers can be rationally expected to be synthesized.[1,3,24] Because Schlenk's hydrocarbon **6** has such a strong triplet preference that thermal excitations at ambient temperature are not energetic enough to populate its first excited singlet state, the spin-coupling constant J of this molecule cannot be determined by susceptibility measurement.[20] However, in recent years it has become possible to estimate the singlet–triplet (S–T) energy differences (ΔE_{ST}) in diradicals by measuring photoelectron spectra of the corresponding radical anions.[6–8] However, this has not been reported for Schlenk's hydrocarbon. On the other hand, from the viewpoint of theoretical study, traditionally used quantum-chemical methods also have difficulties in obtaining the values of ΔE_{ST} reliably due to the large size of this molecule, although they have been quite successful for small diradicals.[14–17] A few semiempirical studies[3,10] have been undertaken to estimate the coupling constant in larger diradicals like Schlenk's hydrocarbon, but the obtained results are not quantitative. However, recently there has been increasing interest in employing various density functional theory (DFT) methods for studying the open-shell radicals[24–30] since they include appropriate treatment of electron correlation and can be applied to large molecules. Previous studies[24–30] on some radicals have shown that very good structural and magnetic properties can be attained by DFT methods, especially B3LYP with Becke's three parameter exchanges[31] and Lee–Yang–Parr correlation functionals.[32] For some diradiclas, UB3LYP calculations with the broken symmetry (BS) approach and spin-projection method give values of ΔE_{ST} within an accuracy comparable to the high level ab initio methods[25,14–17] such as UCCSD or UCCSD(T). Therefore we chose the UB3LYP method for both computational efficiency and accuracy.

Keywords: *m*-xylylene diradical; spin-coupling constant; UB3LYP; broken symmetry; spin-projection.

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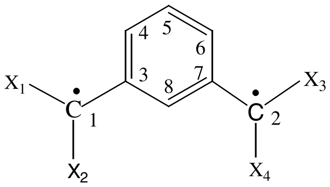
doi:10.1016/S0040-4020(03)00488-5



X_1	X_2	X_3	X_4	molecules[a]
H	H	H	H	**1**(0,0)
H	H	H	Ph	**2**(0,1)
H	Ph	H	Ph	**3**(1,1)
H	H	Ph	Ph	**4**(0,2)
Ph	H	Ph	Ph	**5**(1,2)
Ph	Ph	Ph	Ph	**6**(2,2)

[a] The number of phenyl substituents on each radical site given in the parentheses.

Figure 1. Selected diradicals (hydrogen atoms are omitted for clarity).

In this paper we study the substituent effect of the spin-coupling constant through *m*-phenylene by performing B3LYP calculations with the BS approach and spin projection procedure on *m*-xylylene and its derivatives **1**–**6** (Fig. 1). These structures are obtained by substituting one or more hydrogen atoms on radical sites with phenyl groups.

2. Method of calculation

For diradicals, the energies of their lowest singlet and triplet states are usually fitted to the energy levels of the Heisenberg model Hamiltonian $H=-2JS_a \cdot S_b$, where S_a and S_b are the spin operators on two radical centers. The spin-coupling constant J is related to the singlet–triplet energy gap, $\Delta E_{ST}=E_S-E_T$, by $\Delta E_{ST}=2J$. Here E_S and E_T are the energies of the pure singlet and triplet states, which can be estimated by performing calculations with various theoretical methods. Obviously, a positive value of J means a triplet ground state, and a ferromagnetic coupling between two spins; otherwise a negative J indicates a singlet ground state and an antiferromagnetic coupling.

Accurate theoretical calculations for open-shell singlet states are still challenging. The BS unrestricted DFT (or HF) solutions often have lower energies than the corresponding symmetrical solutions,[24–28,33] and thus are employed in calculating the open-shell singlet states. However, since UDFT (or UHF) wave functions for open-shell singlets are seriously spin-contaminated by triplet components, the energy of the UDFT singlet state should be corrected by removing triplet components. On the other hand, the UDFT triplet state is usually only slightly spin-contaminated, thus the UDFT triplet energy is often assumed to be the energy of the pure triplet. Therefore in calculations on diradicals the spin-projection procedure is usually required only for the open-shell singlet state to get the energy of a pure singlet state. There are several approximate ways[34–41] of doing this, each of which leads to a procedure for computing the spin-coupling constant J. In this work, we adopt an approximate spin-projection scheme advocated by Yamaguchi et al.[36–38] According to this scheme, the energies of the pure singlet (E_S) and the singlet–triplet energy gap (ΔE_{ST}) are given below, respectively (the UDFT triplet energy is assumed to be approximately equal to the energy of the pure triplet state),

$$E_S = E_{BS} + \frac{\langle \hat{S}^2 \rangle_{BS}}{\langle \hat{S}^2 \rangle_T - \langle \hat{S}^2 \rangle_{BS}} (E_{BS} - E_T) \tag{1}$$

$$\Delta E_{ST} = E_S - E_T = \frac{\langle \hat{S}^2 \rangle_T}{\langle \hat{S}^2 \rangle_T - \langle \hat{S}^2 \rangle_{BS}} (E_{BS} - E_T) \tag{2}$$

Where E_X and $\langle \hat{S}^2 \rangle_X$ (X=BS, T) in Eqs. (1) and (2) denote, respectively, the energy and the expectation of the square of total spin angular momentum for the BS singlet and triplet states. These formulas have been justified to be applicable to UDFT and UHF methods,[38–41] and post-UHF methods[36,37,39] such as UMP*n* (n=2–4) and UCCSD(T).

All the DFT computations have been performed using the GAUSSIAN-98 program.[42] We carry out full geometry optimizations with the unrestricted B3LYP (UB3LYP) method for both triplet and singlet states of all studied diradicals. For all atoms in studied molecules, the standard basis set 6-31G(d) has been used.

3. Results and discussion

First of all, to verify the reliability of the selected computational method, we carry out UB3LYP calculations for *m*-xylylene **1** and trimethylenemethane (TMM), which have been extensively studied experimentally and theoretically,[5,6,8,13–17,43] and compare our results with those calculated by UCCSD and CASPT2N methods with the same basis set. At the 6-31G(d) basis set, the UB3LYP calculations give ΔE_{BS-T}=6.72 kcal/mol for **1**, after approximate spin projection a value of ΔE_{ST}=13.15 kcal/mol is obtained, being very close to 11.7 kcal/mol calculated at the CASPT2N(8,8)//CASSCF(8,8) level by Borden et al.[16] and 13.42 kcal/mol estimated from UCCSD calculations with the approximate spin projection described above. For TMM, our UB3LYP calculations at the cc-pVDZ basis set give ΔE_{BS-T}=11.33 kcal/mol, after approximate spin projection we obtain ΔE_{ST}=23.05 kcal/mol, comparable to the value of 19.1 kcal/mol calculated with the CASPT2N(10,10) method by Cramer et al.[43] After including the zero-point energy and heat capacity corrections, our UB3LYP calculations with approximate spin projection give 12.92 kcal/mol for **1**, 21.28 kcal/mol for TMM, reasonably comparable to the corresponding experimental values of 9.6±0.2,[8] and 16.1±0.1 kcal/mol,[6] respectively. Thus, the combination of the BS UB3LYP approach and the approximate spin-projection procedure is a practical and reasonably reliable theoretical tool for describing the lowest singlet and triplet states of the selected diradicals.

Our calculations show that the selected diradicals from **1** to **6** all have triplet ground states. Table 1 displays the

Table 1. The energies of the triplet ground states E_{T} (a.u.), the BS singlet states E_{BS} (a.u.) the singlet–triplet gaps ΔE_{ST} (kcal/mol) (after spin projection) and spin-coupling constant J (kcal/mol) at the UB3LYP/6-31G(d) level for selected diradicals

Diradicals	E_{T} ($\langle \hat{S}^2 \rangle$)	E_{BS}($\langle \hat{S}^2 \rangle$)	ΔE_{ST} (ad)	ΔE_{ST} (ver)	J
1	−309.585129(2.071)	−309.574418(1.012)	13.15	14.11	6.58
2	−540.647837(2.075)	−540.640583(1.033)	9.07	10.17	4.54
3	−771.710256(2.077)	−771.705143(1.038)	6.41	7.24	3.21
4	−771.702199(2.069)	−771.697262(1.042)	6.24	7.79	3.12
5	−1002.765370(2.071)	−1002.761786(1.046)	4.55	5.51	2.28
6	−1233.819151(2.063)	−1233.816758(1.042)	3.03	3.99	1.52

calculated energies of triplet ground states and the BS singlets, the S–T energy gaps, ΔE_{ST}, and the spin-coupling constants J of all diradicals. The adiabatic transitions ΔE_{ST}(ad) were obtained for diradicals at their optimized geometries. The vertical transitions ΔE_{ST}(ver) were computed by assuming the lowest singlet state stays at the optimized geometry of the triplet ground state. Hereafter J means J(ad) for convenience. The UB3LYP spin contamination is very low for the triplet state with a deviation of $\langle \hat{S}^2 \rangle$ of at most 0.08 from the expectation value of 2, whereas a much higher spin contamination is obtained for BS singlets ($\langle \hat{S}^2 \rangle \approx 1.01 \sim 1.05$), indicating that the spin projection procedure is essential to obtain a good estimate of the energy of the pure singlet state.

From Table 1, we can see that the spin coupling constant J (or ΔE_{ST}(ad), and ΔE_{ST}(ver)) decreases steadily with the increase of the total number of phenyl substituents on two radical sites. The decreasing trend is clearly reflected in Figure 2. For Schlenk's hydrocarbon **6**, in which the two radical centers are disubstituted, the calculated ΔE_{ST}(ad) is only 3.03 kcal/mol, about one quarter of that in the parent *m*-xylylene **1**. Thus the spin coupling constant in **6** is calculated to be 1.52 kcal/mol. The adiabatic ΔE_{ST}(ad) are smaller by 0.83–1.55 kcal/mol than those vertical ΔE_{ST}(ver), indicating significant geometrical relaxation in the singlet state, as shown later in Table 2.

A simple interpretation to account for the substituent effect of the coupling constant is desirable. First, the steric repulsion due to the substitution of H with Ph group leads to a distorted structure of substituted *m*-xylylene, thus contributing to the decrease of the spin-coupling constant going from **1** to **6**. This point is reflected by optimized geometrical parameters for both triplet and singlets of studied molecules, as shown in Table 2. We note that the phenyl substituent is out of the *m*-xylylene plane by about 16–17° (triplet) and 21–26° (singlet) with one hydrogen substituted, and by about 31–33° (triplet) and 39–43° (singlet) with two hydrogens substituted, almost independent of the degree of substitution on another radical site. Actually, these geometries result from the combined effect of π-conjugation and steric repulsion. As we know, π-conjugation prefers a planar structure, but the steric repulsion between the bridged *m*-phenylene and the substituents, or between substituents, tends to introduce the non-planarity for the molecule. Obviously, if the twist angle is larger, the π-conjugation between the orbital on the radical site and orbitals on *m*-phenylene coupling unit is smaller, thus the bond linking the radical center and *m*-phenylene is weaker. Since each selected diradical can be approximately viewed as two radical sites interacted through *m*-phenylene, the strength of the bond connecting *m*-phenylene and one radical site is expected to be approximately proportional to the magnitude of the coupling constant of the diradical. Secondly, with the increase of phenyl substituents on two radical centers, the unpaired electrons on radical centers have less opportunity to delocalize into bridged *m*-phenylene because phenyl substituents are also accessible, thus the bond linking bridged *m*-phenylene and radical site becomes weaker, leading to a decrease of the coupling constant. As clearly shown in Table 2, the length of this bond becomes increasingly longer with the increase of the degree of substitution on the radical center, e.g. from 1.402 Å (unsubstituted) to about 1.430 Å (monosubstituted) and to about 1.460 Å (disubstituted) in the triplet ground state. Similarly, the corresponding bond in the singlet state is also elongated upon substitution, and is always longer than that in the triplet state for each diradical. We also note that phenyl substitution on one radical center has little effect on the bond linking another radical center and bridged *m*-phenylene in the triplet state, but slightly influences the corresponding bond in the singlet state. In summary, on increasing the number of phenyl substituents on two radical centers, the larger twist angle of phenyl substituents and wider delocalization of unpaired electrons result in smaller coupling constants.

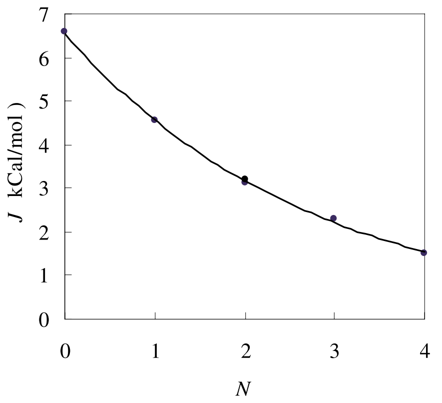


Figure 2. Plot of the coupling constant J vs the total number N of the phenyl substituents on two radical centers.

The above analysis can also be confirmed by examining the spin density distributions on radical centers or on *m*-phenylene coupling unit, which are tabulated in Table 3.

Here the spin density on *m*-phenylene is defined to be the sum of atomic spin densities of all the atoms in the *m*-phenylene unit including hydrogen. First, one can see that no obvious correlation between J (or ΔE_{ST}) and spin

Table 2. Optimized geometries for both triplet and singlets of studied molecules at the UB3LYP/6-31G(d) level

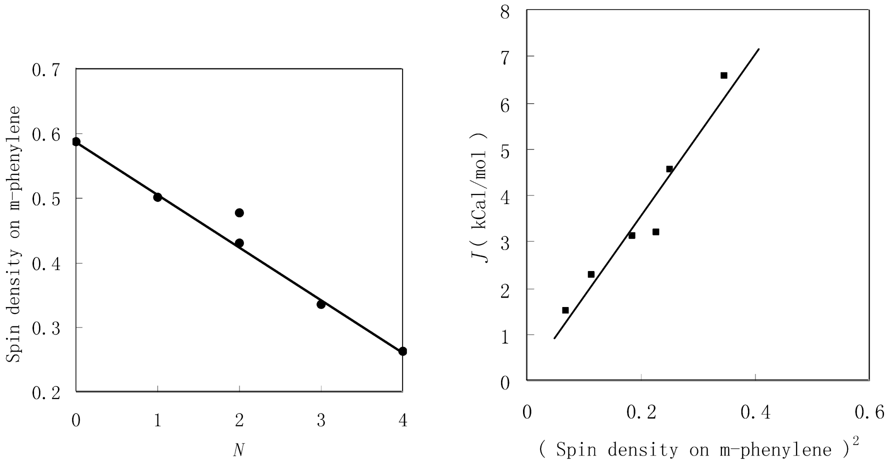
	1 (0,0)	**2** (0,1)	**3** (1,1)	**4** (0,2)	**5** (1,2)	**6** (2,2)
Triplet						
C1–C3	1.402	1.404	1.430	1.405	1.432	1.461
C2–C7	1.402	1.429	1.430	1.457	1.459	1.461
C3–C4	1.434	1.431	1.426	1.429	1.423	1.419
C3–C8	1.420	1.423	1.417	1.423	1.417	1.413
C4–C5	1.392	1.389	1.390	1.387	1.391	1.392
C5–C6	1.392	1.393	1.390	1.397	1.393	1.392
C6–C7	1.434	1.429	1.426	1.425	1.422	1.419
C7–C8	1.420	1.414	1.417	1.409	1.409	1.413
X1–C1–C3–C4	0.0	0.3	13.7	0.0	16.9	32.0
X2–C1–C3–C8	0.0	0.0	16.5	0.0	14.8	32.8
X3–C2–C7–C6	0.0	−14.2	−13.7	−30.7	−31.7	−32.0
X4–C2–C7–C8	0.0	−16.4	−16.5	−30.6	−31.4	−32.8
Singlet						
C1–C3	1.423	1.415	1.446	1.412	1.442	1.473
C2–C7	1.423	1.453	1.446	1.481	1.477	1.473
C3–C4	1.421	1.421	1.417	1.423	1.417	1.413
C3–C8	1.412	1.420	1.412	1.422	1.415	1.409
C4–C5	1.392	1.389	1.391	1.387	1.391	1.393
C5–C6	1.392	1.394	1.391	1.398	1.394	1.393
C6–C7	1.421	1.418	1.417	1.415	1.413	1.413
C7–C8	1.412	1.404	1.412	1.399	1.403	1.409
X1–C1–C3–C4	0.0	0.0	18.4	0.0	20.9	38.9
X2–C1–C3–C8	0.0	0.0	21.8	0.0	18.2	39.4
X3–C2–C7–C6	0.0	−22.9	−18.4	−43.0	−40.2	−38.9
X4–C2–C7–C8	0.0	−26.2	−21.8	−42.8	−40.0	−39.4

The number of phenyl substituents on each radical site given in parentheses. Bond lengths are in angstroms, and twisted angles in degrees.

Table 3. The spin densities on each radical site and *m*-phenylene of triplet ground states

Diradicals	Substitution	Radical site 1	Radical site 2	*m*-Phenylene
1	(0,0)	0.782	0.782	0.588
2	(0,1)	0.784	0.655	0.501
3	(1,1)	0.652	0.652	0.478
4	(0,2)	0.787	0.651	0.431
5	(1,2)	0.653	0.651	0.335
6	(2,2)	0.651	0.651	0.263

densities on two radical sites exists. For example, when one radical site is unsubstituted and the degree of substitution on the other radical site increases from 1 to 2, the $J(\Delta E_{\mathrm{ST}})$ decreases noticeably from 4.54(9.07) to 3.12(6.24) kcal/mol, but the spin density on the substituted radical site is almost unchanged, e.g. from 0.655 to 0.651. On the other hand, a good linear relationship between the spin density on *m*-phenylene coupling unit and the total number of phenyl substituents is found, as shown in Figure 3(a). This could be ascribed to the wider range of the spin delocalization, although the phenyl substituents on two radical sites are



(a) (b)

Figure 3. (a) Plot of the spin density on *m*-phenylene vs. the total number *N* of phenyl substituents on two radical centers; (b) The relationship between *J* and the square of the spin density on *m*-phenylene.

twisted to varying degrees out of the *m*-phenylene plane. Furthermore, we notice that an excellent linear correlation between J (or ΔE_{ST}(ad)) and the square of the spin density on *m*-phenylene holds, as reflected in Figure 3(b). This result rationalizes the postulation given by Rajca,[3,44] and it should be useful for roughly estimating J (also the adiabatic or vertical S–T gaps) of other structurally similar derivatives of *m*-xylylene based on the experimentally measured spin densities on *m*-phenylene coupling unit.

4. Conclusions

Unrestricted density functional UB3LYP calculations with the BS approach and spin-projection treatment on *m*-xylylene and its phenyl substituted derivatives **1–6** have been performed to investigate the dependence of the magnetic coupling constant J through *m*-phenylene on the number of phenyl substituents on two radical sites. Fully optimized structures of these diradicals at the triplet ground and lowest singlet states, and the corresponding singlet–triplet energy gaps are obtained at the UB3LYP/6-31G(d) level. The results show that the coupling constant decreases steadily on increasing the number of phenyl substituents on two radical sites. This trend could be ascribed to more spin delocalization into the phenyl substituents and larger twist angle of phenyl substituents out of the *m*-phenylene plane, when the degree of phenyl substitution is increased. We found an empirical linear correlation between the coupling constant J (or the S–T gap) and the square of the spin density on *m*-phenylene coupling unit, which could be useful for experimentalists to roughly evaluate the coupling constant for structurally similar derivatives of *m*-xylylene.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 20073020).

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