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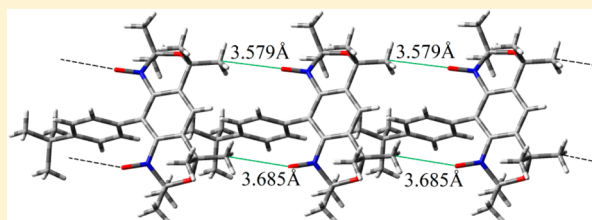
Metaphenylene-Based Nitroxide Diradicals: A Protocol To Calculate Intermolecular Coupling Constant in a One-Dimensional Chain

Tumpa Sadhukhan, Shekhar Hansda, Iqbal A. Latif, and Sambhu N. Datta*

Department of Chemistry, Indian Institute of Technology—Bombay Powai, Mumbai 400 076, India

S Supporting Information

ABSTRACT: Intramolecular magnetic exchange coupling constants are determined for seven isolated metaphenylene-based dinitroxide diradicals by unrestricted density functional methodology (UDFT) using a number of hybrid functionals such as B3LYP, B3LYP-D3, M06-2X, HSE, and LC- ω PBE. Geometry optimizations for both triplet and broken symmetry solutions are performed with the 6-311G(d,p) basis set for all the molecules. In all cases, B3LYP somewhat overestimates the coupling constant, and M06-2X produces a more realistic value. The range-separated HSE and LC- ω PBE functional yield large deviations from experiment. The nature of spin coupling agrees with the spin alternation rule and the calculated spin densities, in conjunction with the McConnell rule. It can also be explained in terms of the nondisjoint Single Occupied Molecular Orbital effect. Furthermore, it correlates with the calculated NICS(1) isotropic and *zz* and hyperfine coupling constants. We also put forward a method for the determination of the intramolecular (*J*) and intermolecular (*J'*) coupling constants from quantum chemical calculations on a one-dimensional chain of weakly bound diradicals. Two expressions are derived for the energies of different spin states in terms of *J* and *J'*. Exemplary UDFT computations are done on the *N*-mers (*N* = 2–6) of two diradicals for which the crystal coordinates are available. The intramolecular and intermolecular coupling constants are determined from the calculated UDFT energies. These are indeed in general agreement with the measured coupling constants.



INTRODUCTION

Organic molecular magnetic materials can have diversified properties that can be achieved by a careful arrangement of the building blocks. Ferromagnetic interaction among the electron spins in organic diradicals and radical crystals is of increasing interest for the development of different electronic devices.¹ Nitroxides are as such quite reactive, but when they are linked to large residues including aromatic rings their stability increases. Stable solvated diradicals with ground state spin *S* = 1 have naturally attracted attention in biomedical applications as markers.^{2–6} In particular, nitroxide radicals are in vivo radioprotector and paramagnetic; hence, they can be used as T1 contrast in magnetic resonance imaging (MRI) and electron paramagnetic resonance imaging (EPRI).^{6,7} Many of the stable *S* = 1 diradicals reported so far are based on *tert*-alkylnitroxides that are cross-conjugated through the *m*-phenylene group. These diradicals may have a singlet–triplet (*S*–*T*) energy gap (*2J*) greater than or equal to *kT* at room temperature. However, in highly polar aqueous solution, the nitroxyls are often found to be twisted out of the plane of the *m*-phenylene coupler,^{8–10} which weakens their paramagnetic nature.

The first aim of this work is to theoretically verify the large intramolecular magnetic exchange coupling constants (*J*) of some of the molecules that are known as suitable for biomedical applications. In this work, we have investigated seven diradicals that are based on *m*-phenylene dinitroxide, as shown in Figure 1. Diradical 1 was prepared by Calder et al.¹¹ It changes into an

isomeric aminoquinone imine *N*-oxide in a few hours in solution.^{11,12} Curie studies^{12,13} and EPR spectrum^{11,14} showed that it has a triplet ground state. The EPR spectrum and magnetic properties for diradical 2 showed a triplet ground state.^{15,16} The spin alteration rule^{17,18} shows that bis-nitroxide diradicals that are cross-conjugated through the *m*-phenylene coupler generally have intramolecular ferromagnetic coupling, that is, a triplet ground state (Figure 2). Using density functional (DF) treatment, we show that these diradicals indeed have large and positive coupling constants. The 2,4,6-trimethyl derivative of the diradical 1 was prepared¹⁹ and separated in crystalline form. This is diradical 3. From EPR spectrum and Curie studies, it was found to be antiferromagnetically coupled.¹⁹ Diradical 4 provides another example of the deviation of the rule that *m*-phenylene serves as a robust ferromagnetic coupler. Its synthesis, EPR spectra, and magnetic properties measurements were reported by Iwamura et al.²⁰ Annulation of the ligands attached to the nitroxide moieties constrains the latter to become coplanar with the *m*-phenylene coupler. Thus, one may get nitroxyl diradicals with large singlet–triplet energy gap, such as 5 and 6.²¹

The second objective of this work is to determine the intermolecular coupling constant (*J'*) for these compounds in

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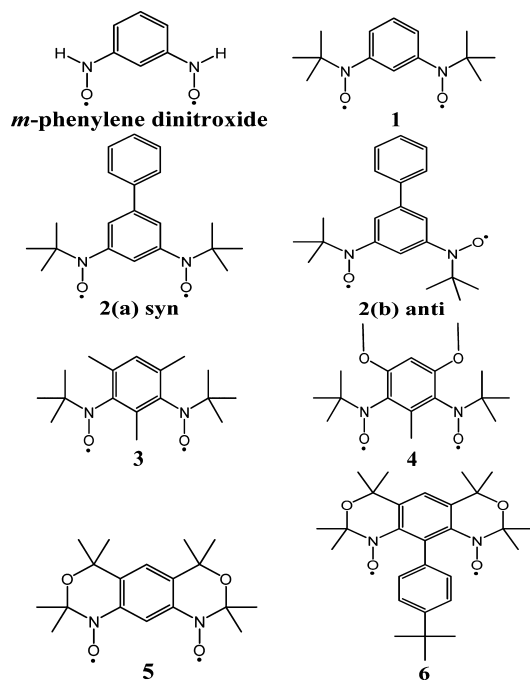


Figure 1. Structure of the diradicals investigated here: 1,3-*N,N'*-di-*tert*-butyl-*m*-phenylene dinitroxide (1), biphenyl-3,5-diylbis(*tert*-butyl nitroxide) (2), *N,N'*-di-*tert*-butyl-2,4,6-trimethyl-*m*-phenylene dinitroxide (3), 4,6-dimethoxy-1,3-phenylene-bis(*N-tert*-butyl nitroxide) (4), 2,2,4,4,6,6,8,8-octamethylbenzobis(1,3-oxazine) *N,N'*-dioxide (5), and 2,2,4,4,6,6,8,8-octamethyl-10-[4-(1,1-dimethylethyl)phenyl]-benzobis(1,3-oxazine) *N,N'*-dioxide (6).

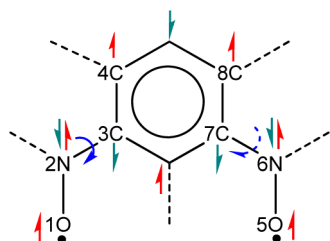


Figure 2. Illustration of spin alteration rule and dihedral angles.

solid state from quantum chemical calculations. This will shed light on the nature of coupling—ferromagnetic or antiferromagnetic—in solid phase. As a first guess, one would think that an antiferromagnetically coupled chain would have spins in a successively up and down orientation and it would correspond to a low spin state that would be difficult to obtain from an unrestricted calculation. A second thought tells us that the spin alternation merely causes a state of low S_z , and in fact all possible S states would be represented with this low S_z . The coupling constant can be unequivocally determined from the high- S calculations. Therefore, we have prepared a theoretical formalism for the spin states and coupling constants for a one-dimensional molecular chain.

Next, we have examined two known one-dimensional polymers of diradicals 5 and 6 by quantum chemical calculations. These polymers were prepared and studied by Rajca et al.²¹ and are shown in Figure 3. Though diradicals 5 and 6 have triplet ground states in solution, they were found to form antiferromagnetically coupled one-dimensional chains. From our analysis, we have shown that indeed the diradicals in these chains are very weakly coupled to each other, the

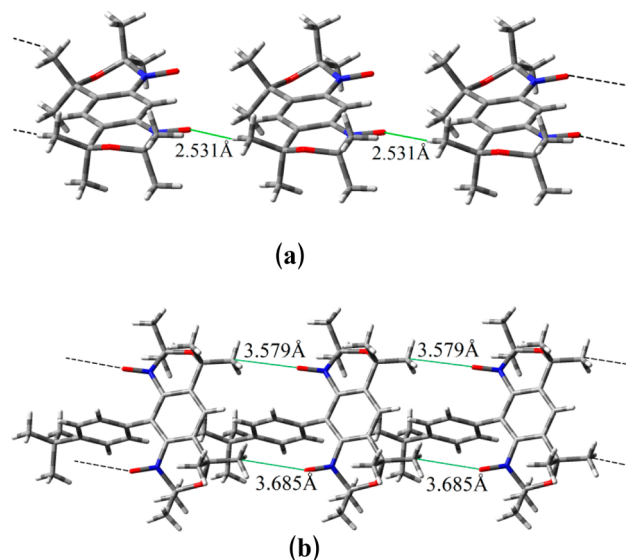


Figure 3. Representation of 1D polymer chain prepared from the crystallographic data in ref 21: (a) polymer of diradical 5 with $\text{N}\cdots\text{H}-\text{CH}_2-$ distance 2.531 Å; (b) polymer of diradical 6 with $-\text{H}_3\text{C}\cdots\text{O}-\text{N}<$ distances 3.579 and 3.685 Å.

corresponding magnetic exchange coupling constants being small and negative, comparable to the observed values.

THEORY

Intramolecular Coupling Constant. The restricted open shell Hartree–Fock (ROHF) method needs a large basis set and a subsequent post-Hartree–Fock treatment to produce correct relative energies and geometries for singlet and triplet diradicals, though it is known to yield qualitatively correct molecular orbitals for a species with two open shell electrons.^{22–24} It is also known that the unrestricted Hartree–Fock (UHF) methodology can be used for a reasonably accurate description of triplet ($S = 1$) geometries while requiring a vastly reduced computational effort.^{22–24} Unfortunately, the UHF is based on a single determinant wave function that is not capable of describing an open-shell singlet. To circumvent this lapse, Noodleman proposed the broken-symmetry (BS) methodology^{25–28} that can eventually lead to an estimate of the energy of the diradical singlet.

For a diradical, the effective spin Hamiltonian is written as

$$h_{\text{eff}} = -2JS_1 \cdot S_2 \quad (1)$$

This Hamiltonian commutes with S^2 where $S = S_1 + S_2$, the total spin angular momentum for the two unpaired electrons. The energy eigenvalues are $E(S = 0; S) = 3J/2$ and $E(S = 1; T) = -J/2$ such that the energy difference between singlet and triplet states is twice the magnetic exchange coupling constant (J). When J is negative, the singlet is lower in energy, and the intramolecular coupling is said to be antiferromagnetic. A positive value of J is representative of a ferromagnetic interaction in the diradical and a triplet ground state. The ideal BS state is an equal mixture of the singlet and the triplet, and has an M_S equal to zero. The ideal triplet (T) state has an S^2 eigenvalue of 2, whereas $\langle S^2 \rangle = 1$ in the ideal BS state that is accompanied by $E(\text{BS}) - E(\text{T}) = J$. In actual calculation, however, approximate $\langle S^2 \rangle$ values are obtained, thereby showing a spin-state contamination. Therefore, the calculated coupling constant needs to be corrected. This was pointed out

by Yamaguchi^{29–33} who showed that the coupling constant corrected for contamination can be written as

$$J = \frac{E_{BS} - E_T}{\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}} \quad (2)$$

This expression is used by us to determine the intramolecular coupling constant for the isolated diradical species.

Intermolecular Coupling Constant. Hamiltonian. A one-dimensional chain of N weakly bound diradical species is considered here. Each diradical unit has two radical centers. Radical centers in the i th unit have spin angular momentum operators labeled as S_{2i-1} and S_{2i} and the total spin $S_i^{\text{tot}} = S_{2i-1} + S_{2i}$. The total exchange Hamiltonian can be written as

$$H = H^{(0)} + H' \quad (3)$$

In the above, $H^{(0)}$ represents the exchange Hamiltonian for the noninteracting diradicals,

$$H^{(0)} = \sum_{n=1}^N h_{\text{ex},n} \quad (4)$$

where $h_{\text{ex},n}$ is, as in 1, the intramolecular Heisenberg exchange interaction in the n th diradical

$$h_{\text{ex},n} = -2J S_{2n-1} \cdot S_{2n} \quad (5)$$

and J is the intramolecular exchange coupling constant. The operator H' stands for the weak interspecies magnetic interaction

$$H' = -2J' \sum_{(m < n)} S_m^{\text{tot}} \cdot S_n^{\text{tot}} \quad (6)$$

where J' is the intermolecular magnetic exchange coupling constant, and the bracket indicates that m and n are nearest neighbors.

Zeroth Order Energy. For any isolated diradical, say, the n th one, there are four ground states, one with $S_n^{\text{tot}} = 0$ (singlet) and three with $S_n^{\text{tot}} = 1$ (triplet). The corresponding state vectors are written as $|S_n^{\text{tot}} = 0, M = 0\rangle$ and $|S_n^{\text{tot}} = 1, M = 0, \pm 1\rangle$, and the eigenvalues of $h_{\text{ex},n}$ are

$$E_n^{(0)}(S_n^{\text{tot}}) = \left(\frac{3}{2} - 2S_n^{\text{tot}} \right) J \quad (7)$$

It is to be observed here that S_n^{tot} is the spin number (0 or 1) for the n th unit. The eigenstates of $H^{(0)}$ are written as

$$|S_1^{\text{tot}}, M_1; S_2^{\text{tot}}, M_2; \dots S_N^{\text{tot}}, M_N\rangle = \prod_{n=1}^N |S_n^{\text{tot}}, M_n\rangle \quad (8)$$

with eigenvalues

$$E^{(0)} = \left(\frac{3}{2}N - 2S^{\text{tot}} \right) J \quad (9)$$

In the above, S^{tot} is the sum of spin numbers for N individual monomers (diradicals),

$$S^{\text{tot}} = \sum_{n=1}^N S_n^{\text{tot}} \quad (10)$$

and not to be confused with the total spin angular momentum operator for the polymer.

Conceptual Background. The triplet diradicals are anti-ferromagnetically coupled in a one-dimensional chain, but the

binding between any two neighboring units is weak. One obtains a number of multiplet states with S^{tot} varying as 0, 1, 2, ..., N . The number of states (N) with the same M value is given by

$$N_{N-2m} = \sum_{p=0}^m \binom{N}{p} \binom{N-p}{2(m-p)} \\ N_{N-(2m+1)} = \sum_{p=0}^m \binom{N}{p} \binom{N-p}{2(m-p)+1} \quad (11)$$

From this result, it is possible to calculate the number of multiplets (N) with a specific S :

$$N_S = N_S - \sum_{p=0}^{N-S-1} N_{N-p} \quad (12)$$

These numbers satisfy the sum rules

$$N_0 + 2 \sum_{M=1}^N N_M = 3^N \\ \sum_{S=0}^N (2S+1)N_S = 3^N \quad (13)$$

A list of the number of multiplets with different spin S is given in Table 1. In principle, the ground state of a weakly bonded

Table 1. Number of Multiplets with Different Spin for the N -mer

N	$S = 0$	$S = 1$	$S = 2$	$S = 3$	$S = 4$	$S = 5$	$S = 6$
1	0	1					
2	1	1	1				
3	1	3	2	1			
4	3	6	6	3	1		
5	6	15	15	10	4	1	
6	15	36	40	29	15	5	1

and finite antiferromagnetic chain should correspond to $M = 0$ when N is even and $M = \pm 1$ when N is odd because of the negative value of the intermolecular coupling constant.

In contrast, unrestricted quantum chemical calculations normally yield the highest spin state with the largest M value. Thus, from an unrestricted calculation on the N -mer of triplet diradicals, one would obtain a state with $S^{\text{tot}} = N$ such that $\langle S^{\text{tot}2} \rangle = N(N+1)$ and $M = N$. Since we are considering a collection of open-shell species, the lower spin states with $M = N-1, N-2$, and so forth, would not be achieved in a spin-pure form from the unrestricted methodology. Instead one would obtain the spin-contaminated “broken symmetry” (BS) solutions.

For a specific multiplet state (such as a particular triplet state), and in the absence of a magnetic field, any (antiferromagnetically coupled) state of a low $|M|$ value is, of course, degenerate with the states of all other M , in particular the $M = S^{\text{tot}}$ state belonging to the same multiplet. The ideal broken symmetry state is also a linear combination of two or more well-defined states. Therefore, a quantum chemically determined energy difference for two spin states, such as those with $S^{\text{tot}} = M = N$ (highest spin state) and $M = N-1$ (broken symmetry), remains valid for the energy difference between two

Table 2. Calculated Magnetic Exchange Coupling Constant Using Different Functionals^{a,b}

system	<i>J</i> , cm ⁻¹					
	UB3LYP	UB3LYP-D3	UM06-2X	UHSE	ULC- <i>ω</i> PBE	obsd
<i>m</i> -phenylene dinitroxide	527.9	531.92	413.4	646.06	900.76	541 ^c
1[T]	463.6	480.61	384.6	572.75	805.87	347.5 ^d
2(a)[T]	387.0	409.61	312.2	549.73	639.74	FM ^e
2(b)[T]	504.8	471.81	294.6	579.67	644.21	FM ^e
3[BS]	-25.8	-34.45	-18.5	-30.98	-13.46	-26.2 ^f
4[BS]	-5.3	3.07	-1.5	-3.29	1.97	-2.5 ^g
5[T]	486.5	466.78	372.7	588.14	845.74	>69.5; ^h 556; ⁱ 485 ^j
6[T] ^k	321.0	316.43	238.6	408.95		>69.5; ^h 382 ⁱ

^aThe molecular geometry has been optimized in every case using the 6-311G(d,p) basis set. We have used 1 au = 219474.6 cm⁻¹. ^bSinglet molecular geometry optimization has reduced to a BS solution in UB3LYP calculation. BS optimization is carried out starting from optimized triplet geometry in UM06-2X, UB3LYP-D3, UHSE, and ULC-*ω*PBE calculation. ^cDDCI2/6-311G(d), refs 53 and 54. ^dIn solution, ref 13. ^eDiscussed to be ferromagnetically coupled, refs 15 and 16. ^fIn *n*-hexane/ethyl acetate 3:1, ref 19. ^gIn PVC, ref 20. ^hIn EtOH, ref 21. ⁱUB3LYP/6-31G*, ref 21. ^jM06-2X, ref 55. ^kBS convergence failure for diradical 6 in ULC-*ω*PBE/6-311G(d,p) methodology.

corresponding spin states for an antiferromagnetically coupled chain.

Quantum Chemical Wave Function. The quantum chemical wave functions are discussed in detail in Appendix I. The highest spin state available from a quantum chemical calculation on the *N*-mer is

$$|\Psi_N\rangle = |(11)_1; (11)_2; \dots; (11)_{N-1}; (11)_N\rangle \quad (14a)$$

It is an eigenfunction of $S^{\text{tot}2}$ with

$$S^{\text{tot}} = N$$

$$M = N$$

$$E^{(0)} = -NJ/2 \quad (14b)$$

and

$$E^{(1)} = -2(N-1)J'$$

From Appendix I, we notice that single determinant broken symmetry solutions of $M = N - 1$ can be written as

$$\begin{aligned} |\text{BS}\rangle &= |(11)_1; (11)_2; \dots; (11)_{N-1}; \frac{1}{\sqrt{2}}[(00)_N + (10)_N]\rangle (\text{terminal}) \\ |\text{BS}\rangle &= |(11)_1; (11)_2; \dots; \frac{1}{\sqrt{2}}[(00)_i + (10)_i]; \dots; (11)_{N-1}; (11)_N\rangle (\text{insider}) \end{aligned} \quad (17)$$

In both cases, $\langle S^{\text{tot}2} \rangle = N(N-1) + 1$, and $\langle H^0 \rangle = -NJ/2 + J$. However, $\langle H' \rangle = -2(N-2)J'$ for the terminal BS and $\langle H' \rangle = -2(N-3)J'$ for the insider one. When J' is negative, the insider BS is more stable.

Coupling Constant. To summarize, we find for the terminal BS, $E_{\text{BS}} - E_{\text{HS}} = J + 2J'$ and for the insider BS, $E_{\text{BS}} - E_{\text{HS}} = J + 4J'$. In both the cases, $\langle S^{\text{tot}2} \rangle_{\text{HS}} - \langle S^{\text{tot}2} \rangle_{\text{BS}} = 2N - 1$. Considering the fact that the exact $\langle S^{\text{tot}2} \rangle$ value is generally not obtained from an unrestricted calculation, we may even apply the contamination restriction due to Yamaguchi, and write

$$\begin{aligned} J + 2J' &= (E_{\text{BS}} - E_{\text{HS}}) \\ &(\text{without Yamaguchi correction}) \\ J + 2J' &= (E_{\text{BS}} - E_{\text{HS}}) \frac{(2N-1)}{\langle S^{\text{tot}2} \rangle_{\text{HS}} - \langle S^{\text{tot}2} \rangle_{\text{BS}}} \\ &(\text{with Yamaguchi correction}) \end{aligned} \quad (15)$$

for the dimer. When $N > 2$, the more stable BS solution gives

$$\begin{aligned} J + 4J' &= (E_{\text{BS}} - E_{\text{HS}}) \\ &(\text{without Yamaguchi correction}) \end{aligned}$$

$$\begin{aligned} J + 4J' &= (E_{\text{BS}} - E_{\text{HS}}) \frac{(2N-1)}{\langle S^{\text{tot}2} \rangle_{\text{HS}} - \langle S^{\text{tot}2} \rangle_{\text{BS}}} \\ &(\text{with Yamaguchi correction}) \end{aligned} \quad (16)$$

These relations can be exploited to determine unique values for J and J' .

METHODOLOGY

We have used spin-polarized unrestricted DFT with the time-tested B3LYP^{34,35} functional as well as the more modern M06-2X^{36,37} hybrid functional and 6-311G(d,p) basis set for optimizing the molecular geometry in triplet as well as broken symmetry states of each diradical species. It is known that B3LYP overestimates the coupling constants.³⁸ We have still used this functional for two reasons, for comparison, and for calculating a number of molecular properties other than the coupling constant. Moreover, the Grimme D3 correction^{39,40} has also been included in B3LYP so as to incorporate dispersion effect.

Results of higher accuracy can be expected for the range-separated functional, such as HSE^{41,42} and LC-*ω*PBE.⁴³ They have also been used along with the 6-311G(d,p) basis set. For other properties, single-point calculations at the UB3LYP/6-311++G(d,p) level have been used to obtain the spin-density plots and the Single Occupied Molecular Orbital (SOMO) diagrams. The same basis set was used for the calculation of the nucleus-independent chemical shift at a location 1 Å above the ring center (NICS1). Hyperfine coupling constants (hfcc) have been determined in different media from the optimized result using the UB3LYP/EPR-III methodology. For *m*-phenylene dinitroxide, hfcc is calculated in gas phase, and for all other diradicals, PCM calculation has been carried out in different solvents. The B3LYP functional is known to produce an overestimated J value. Hence, the M06-2X functional has also been taken into consideration to estimate the coupling constants.

The magnitude of $J_{\text{UM06-2X}}$ decreases from that of J_{UB3LYP} when there is a large contribution from dispersive effects. To determine the intermolecular coupling constant in a one-dimensional chain of diradicals (prepared from the crystallographic data given in ref 21), we carried out single-point

Table 3. Dihedral Angles (deg) of the Diradicals in More Stable Optimized State^a

system	B3LYP		M06-2X	
	C4–C3–N2–O1 (φ_1)	C8–C7–N6–O5 (φ_2)	C4–C3–N2–O1 (φ_1)	C8–C7–N6–O5 (φ_2)
<i>m</i> -phenylene dinitroxide	–180.0	180.0	–180.0	–180.0
1 [T]	180.0	180.0	–180.0	–180.0
2(a) [T]	168.2	168.7	–155.6	170.0
2(b) [T]	10.9	173.0	20.6	164.7
3 [BS]	–79.2	80.0	–83.3	82.9
4 [BS]	–101.3	110.9	–103.2	112.7
5 [T]	179.0	179.0	178.6	178.6
6 [T]	–153.7	153.7	–159.9	160.2

^aSpin states are indicated.

calculations using UB3LYP and UM06-2X methodologies with 6-311++G(d,p) as the basis set.

All calculations were done using the Gaussian 09 (G09) suite of programs.⁴⁴

RESULTS AND DISCUSSION

Intramolecular Interaction. Molecular geometries of *m*-phenylene dinitroxide as well as the seven diradicals under investigation have been optimized by both UB3LYP and UM06-2X methods using the 6-311G(d,p) basis set, for both triplet and BS states. The optimization process for the singlet state in UB3LYP has led to the BS solution with $\langle S^2 \rangle$ value approximately equal to 1. In the UM06-2X calculations, however, the BS geometry optimization has been carried out starting from the optimized triplet geometry. Computed total energies and $\langle S^2 \rangle$ values are given in Tables S1–S5 of Supporting Information. The optimized molecular geometries are shown in Figure S1, Supporting Information. Coupling constants calculated from eq 2 for the isolated molecules are given in Table 2. The M06-2X functional has consistently produced a reduced—and more realistic—magnitude for the coupling constant. These are quite comparable to the experimentally determined *J* values.

It is well-known that the *m*-phenylene group normally acts as a ferromagnetic coupler. The general results obtained here are consistent with this observation, although we take this opportunity to pinpoint a few examples of deviation from the normal trend, as discussed in the following.

Coupling Constant and Dihedral Angle. It is well-known that the magnetic exchange coupling constant depends on the orientation of the molecule; that is, the dihedral angle plays an important role in determining the singlet–triplet energy gap.^{45–50} The molecule *m*-phenylene dinitroxide has a high *J* value. When the hydrogens are replaced by the *tert*-butyl group (as in diradical 1), the *J* value decreases but still remains high. The distance between the two oxygen atoms decreases from 5.062 Å in UB3LYP and 4.996 Å in M06-2X (for *m*-phenylene dinitroxide) to 4.515 Å in UB3LYP and 4.504 Å in M06-2X (for diradical 1). The diradicals 2(a) and 2(b) are known to be ferromagnetically coupled. Our calculations show that both forms have large and positive *J* values. Both the molecules become slightly nonplanar, with important dihedral angles given in Table 2. As a general rule, the coupling constant decreases with increased deviation from planarity. This becomes manifest in diradicals 3 and 4, which have N–O bonds almost perpendicular to the plane of the phenylene ring and consequently have singlet ground states with negative *J* values. These diradicals are the exceptions from the usual trend of ferromagnetic coupling observed for *m*-phenylene couplers.

The dihedral angles at the two radical centers are –79.2° and +80.0° for diradical 3 and –101.3° and +110.9° for diradical 4 (Table 3).

Table 2 also shows the effect of using the D3 correction by Grimme^{39,40} to the B3P calculations and also the effect of range-separated functionals such as HSE^{41,42} and LC- ω PBE.⁴³ While the dispersion correction leads to a slight change from the original B3LYP coupling constants, the range-separated functionals clearly gives rise to larger coupling constants. The latter trend for the range-separated functionals has always been noticed from our earlier calculations on organic diradicals such as stilbene-coupled⁴⁹ and *m*-xylylene. These functionals are nevertheless known to yield good results for transition metal complexes.^{51,52} The most likely reason is the presence of the 25% Hartree–Fock short-range exchange. With the 54% Hartree–Fock exchange, the M06-2X functional yields realistic values for the coupling constants.

In general, the annulated aminoxide diradicals 5 and 6 show large and positive *J* values. In particular, the M06-2X functional yields for 6 a coupling constant of 239 cm^{–1} that is in the experimentally observed range.²¹ The nitroxide radicals in 5 are constrained to remain in the plane of the benzene ring, while the bulky aryl group in 6 causes non-zero dihedral angles (Table 3), leading to a reduction in the coupling constant (Table 2). Because of the environmental protection, these two radicals are more stable in solution. From Table 2, it transpires that in general the geometry that increases conjugation between the radical centers and the benzene ring leads to a diradical with a higher *J* value. Comparing ref 21, we note that a small basis like 6-31G* deviates the *J* value by 15–20%.

Spin Density, Spin Alternation, and SOMO Effect. The calculated *J* values show that all the diradicals barring 3 and 4 possess a magnetic nature as predicted from the spin alternation rule [12]. See Figure 2 for spin alternation, giving rise to a ferromagnetic coupling. This becomes more transparent in the spin density plots in Figure S2, Supporting Information. Spin alternation rule is not applicable to 3 and 4 as they are not conjugated through spacer. As the spin density plots reveal, the spins in these two species are more or less localized on the nitroxide fragments, and only a small spin polarization is observed on the phenylene ring. Of course, the N–O moieties are almost perpendicular to the phenylene ring. There is through-space interaction between the two N–O moieties, and McConnell's rule^{56,57} becomes operative. The *C*_{2v} local symmetry leads to the stabilization of the singlet state, and the nature of spin coupling is antiferromagnetic.

According to Borden and Davidson,⁵⁸ if the orthogonal linear combinations of the SOMO wave functions can be made disjoint then the ground state will be a singlet, and if these are

always nondisjoint then the ground state is triplet. The SOMO plots for 3 and 4 in Figure 4 can be made disjoint, while for the

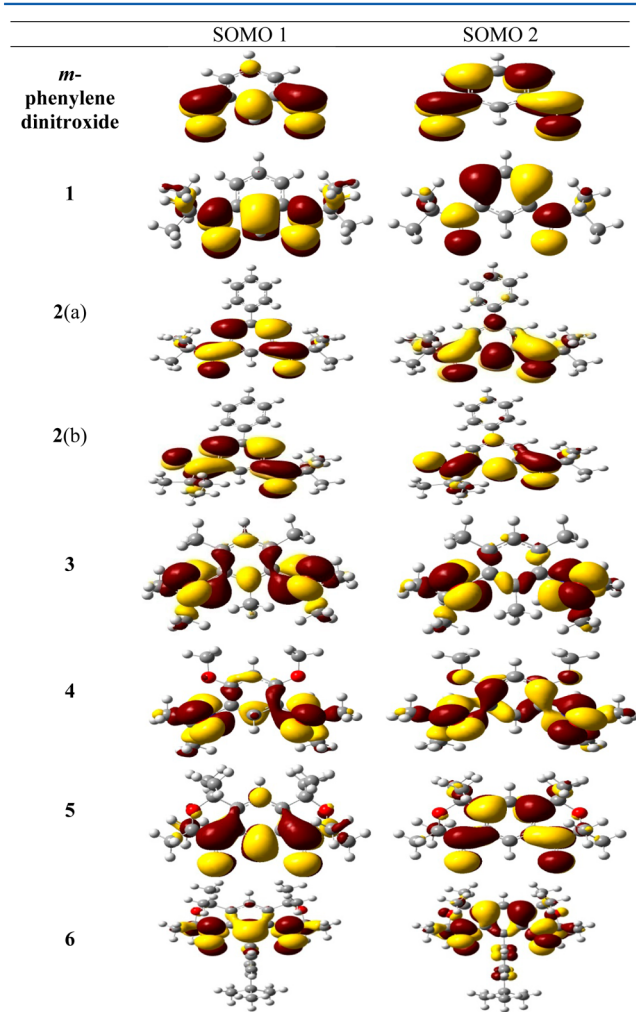


Figure 4. SOMO of the diradicals obtained from UB3LYP method using 6-311G++(d,p) basis set single point calculations.

other diradicals the SOMO combinations always remain nondisjoint. Thus the SOMO effect can explain the nature of spin coupling even when the dihedral angles are large, whereas spin alternation rule (for planar, conjugated species) and

McConnell's rule (for large dihedral angles) need to be used in a complementary fashion.

Nuclear-Independent Chemical Shift (NICS). The nucleus-independent chemical shift (NICS) was developed by Schleyer and his co-workers⁵⁹ as a reliable criterion for aromaticity. The NICS values at the ring center of benzene [NICS(0)] and 1 Å above it [NICS(1)] are −8.0 and −10.2 ppm, respectively, at the GIAO-B3LYP/6-311+G**/B3LYP/6-311+G* level. These are often taken as standard. A large NICS implies an increase in aromaticity. Aromaticity is accompanied by increased conjugation, stability, and a lowering of radical behavior. The reported values in Table 4 have a maximum deviation of 2.87 ppm. The changes are too small to be interpreted as an increase in antiaromaticity. Nevertheless, the decrease in aromaticity enhances the diradical character and gives rise to a larger J value. In Table 4, we report NICS(1) calculated at the UB3LYP/6-311++G(d,p) level. It is observed that all the *m*-phenylene dinitroxide derivatives have NICS(1) smaller than that for benzene. Therefore, these molecules are obviously less aromatic. Compared to *m*-phenylene dinitroxide, derivatives 1, 2a, 2b, 5, and 6 have slightly smaller NICS(1), indicating that they would have the same order of the magnetic exchange coupling constant. Species 3 and 4 have larger NICS(1): their J values are substantially reduced and actually negative.

The NICS(1) data in Table 4 were obtained from UB3LYP calculations. The M06-2X functional was also used for all the diradicals with the same basis set [6-311++G(d,p)] and they are reported in Supporting Information (see Table S6). The M06-2X NICS(1) values exhibit a minor change. More modern and reliable approaches to determine the degree of aromaticity of a compound exist. These have been discussed by Jusélius et al.⁶⁰ and Fliegl et al.⁶¹

Hyperfine Coupling Constant. Two types of hyperfine coupling constants (hfcc) have been calculated—isotropic, which arises from Fermi contact interaction, and anisotropic, evolving from spin dipolar coupling. To determine hfcc in the solvent medium, the Polarizable Continuum Model (PCM) optimization has been carried out on the triplet state using the B3LYP functional and the EPR-III basis set. The values are given in Table 5. The calculated anisotropic hfcc excellently agrees with the observed values. Both isotropic and anisotropic hfccs become large when the intramolecular interaction is antiferromagnetic. This is because with disjoint SOMOs the radical centers are less spread out, leading to a greater unpaired electron density near the nitrogen nuclei.

Table 4. NICS(1) Values of the Diradicals from the UB3LYP Method Using the 6-311++G(d,p) Basis Set on the Optimized Geometry of the More Stable State^a

system	calculated NICS1		Δ NICS1 ^b		Δ NICS1 ^c		J , cm ^{−1}	
	isotropic	zz	isotropic	zz	isotropic	zz	UB3LYP	UB3LYP-D3
benzene	−10.25	−29.36	0.0	0.0	−2.21	−13.09		
<i>m</i> -phenylene dinitroxide	−8.04	−16.27	2.21	13.09	0.0	0.0	527.9	531.92
1[T]	−7.86	−18.73	2.39	10.63	0.18	−2.46	463.6	480.61
2(a)[T]	−7.33	−17.76	2.92	11.60	0.71	−1.49	387.0	409.61
2(b)[T]	−7.39	−17.10	2.86	12.26	0.65	−0.83	504.8	471.81
3[BS]	−9.08	−19.23	1.17	10.13	−1.04	−2.96	−25.8	−34.45
4[BS]	−8.68	−18.58	1.57	10.78	−0.64	−2.31	5.3	3.07
5[T]	−7.84	−14.20	2.41	15.16	0.20	2.07	486.5	466.78
6[T]	−7.56	−17.72	2.69	11.64	0.48	−1.45	321.0	316.43

^aNICS1 value of benzene = −10.2, ref S9. ^bWith respect to benzene. ^cRelative to *m*-phenylene dinitroxide.

Table 5. Isotropic and Anisotropic hfcc Values of the Diradicals Obtained from the Optimized Results Using the UB3LYP/EPR-III Methodology on the Triplet State

system	medium	hyperfine coupling constant (G)			
		isotropic		anisotropic	
		calcd	calcd	obsd	ref
<i>m</i> -phenylene dinitroxide	gas phase	2.6	9.2		
diradical 1	toluene	3.8	10.5		
	ethanol	4.0	10.9		
diradical 2(a)	benzene	4.0	11.0	20 ^a	15
diradical 2(b)	benzene	4.0	10.8		
diradical 3	ethanol	5.1	13.4		
diradical 4	toluene	5.0	12.7	14.2	20
diradical 5	ethanol	4.2	10.0	10.8	62
diradical 6	ethanol	4.2	10.8	10.9 ^b	21

^aPeak-to-peak line width. ^bOnly yy.

Intermolecular Coupling Constant. We now turn our attention to the one-dimensional polymers of diradical **5** and **6** as shown in Figure 3, the $N = 2$ to $N = 6$ structures for calculation have been generated from the crystallographic data in ref 21. Again, both the B3LYP and the M06-2X functional have been used. The computed total energy and $\langle S^2 \rangle$ values are given in Table 6. The detailed calculation for each individual N has been shown in Supporting Information (Table S7–S10). In general, these show a converging trend, with a few results to be discarded. We have made an average of $(J + 4J')$ for $N > 2$. From these results, we have determined the coupling constants J and J' using eqs 15 and 16. These constants are shown in Table 7.

From the $N = 5$ and $N = 6$ total energies for the higher spin states in Table 6, one can calculate the average monomer energy (E_m) and average binding energy per pair (B) in the chain. Thus $E(N = 5) = 5E_m + 4B$ while $E(N = 6) = 6E_m + 5B$.

This gives $E_m = 5E(N = 5) - 4E(N = 6)$ and $B = 5E(N = 6) - 6E(N = 5)$. For polymer **5**, we have obtained $B = -4.9$ kcal mol⁻¹ (B3LYP), -9.2 kcal mol⁻¹ (M06-2X); for polymer **6**, $B = -18.1$ kcal mol⁻¹ (B3LYP), -25.3 kcal mol⁻¹ (M06-2X). These results indicate that the monomer units are weakly bound in the chain, the binding energy being comparable to that for a few hydrogen bonds.

As discussed earlier for the diradicals in gas phase, B3LYP overestimates the intramolecular coupling constant. In any case, the calculated intramolecular coupling constant lies in the experimental range. For polymer **5**, the calculated J is greater than that for the corresponding monomer, while for polymer **6**, it is less. This kind of variation is of course an outcome of different multipolar interactions in the chain and the variation of the lattice constant.

A more striking observation is that the B3LYP functional produces an antiferromagnetic (negative) intermolecular coupling constant that is comparable to the experimental result. The good agreement regarding B3LYP might be due to a fortitious error cancellation. The J' values were also calculated using the UB3LYP-D3 functional to take care of dispersion interaction, but the values were nearly equal to that obtained from the UB3LYP functional (see Table S11–S13, Supporting Information). The results obtained from UHSE and ULC- ω PBE for monomers are not satisfactory; hence, these functionals are not considered for polymers. The J' calculated from the M06-2X functional is not optimum: for polymer **5**, it has more than doubled compared to the observed value (ref 21), while for polymer **6**, it has become very small, in the range of 0.13 to -0.18 cm⁻¹. One possible reason is that the polymer geometry has not been optimized by us, but kept static at the unit cell level. A second reason is that the vibrational contributions to total energy have not been considered. Since J' is exceedingly small, 2.2 cm⁻¹ being approximately equal to 10^{-5} hartree, any of these reasons can easily change the

Table 6. Computed Total Energy (and $\langle S^2 \rangle$ in Parentheses) in Atomic Units for Polymers of Diradicals 5 and 6 from Single Point Calculations Using 6-311++G(d,p) as the Basis Set

number of units	multiplicity	polymer 5		polymer 6	
		UB3LYP	UM06-2X	UB3LYP	UM06-2X
2	5	-2223.8011562 (6.071409)	-2222.8844942 (6.075730)	-3000.2639280 (6.050195)	-2999.0236083 (6.052152)
	3	-2223.7987368 (3.035315)	-2222.8822989 (3.048136)	-3000.2626986 (3.030024)	-2999.0225712 (3.037386)
3	7	-3335.7051603 (12.10753)	-3334.3331998 ^a (12.114183)	-4500.3955840 ^a (12.075393)	-4498.5406929 (12.078630)
	5	-3335.7027576 (7.068193)	-3334.2716962 ^a (6.075904)	-4500.3943583 ^a (7.055874)	-4498.5396577 (7.063591)
4	9	-4447.6106303 ^a (20.143522)	-4445.7838076 (20.152474)	-6000.5368146 (20.100606)	-5998.0674490 (20.104736)
	7	-4447.6081343 ^a (13.106705)	-4445.7817140 (13.125344)	-6000.535595 (13.080683)	-5998.0664130 (13.090245)
5	11	-5559.51483 (30.179764)	-5557.2329908 (30.191081)	-7500.6781327 (30.126303)	-7497.5942806 ^a (30.131351)
	9	-5559.5124697 (21.14014)	-5557.2308869 (21.163651)	-7500.6769139 (21.105679)	-7497.5932419 ^a (21.116112)
6	13	-6671.4193571 (42.216018)	-6668.6825140 (42.229702)	-9000.8195124 (42.152132)	-8997.1211956 (42.156944)
	11	-6671.4169992 (31.176366)	-6668.6803080 (31.201629)	-9000.8182958 (31.131635)	-8997.12016040 (31.142218)

^aResult not considered because of large deviation from other sets of data.

Table 7. Calculated Coupling Constants (cm⁻¹) for One-Dimensional Chains of Diradical 5 and 6

system	functional	$(J + 2J')_{\text{chain}}^a$	average $(J + 4J')_{\text{chain}}^b$	J		J'	
				calcd	obsd ^c	calcd	obsd ^c
5	with Yamaguchi correction						
	B3LYP	524.69	518.20	531.2		−3.2	
	M06-2X	477.42	467.00	487.8		−5.2	
	without Yamaguchi correction				$\gg 104.3^d$		-2.3^d
	B3LYP	531.00	520.95	541.1		−5.0	
	M06-2X	481.81	468.47	495.1		−6.7	
6	with Yamaguchi correction						
	B3LYP	268.02	266.77	269.3		−0.63	
	M06-2X	226.51	226.78	226.2		0.13	
	without Yamaguchi correction				$\sim 139\text{--}278^d$		-1.3^d
	B3LYP	269.82	267.39	272.3		−1.2	
	M06-2X	227.62	227.26	228.0		−0.18	

^aFrom eq 15. ^bFrom eq 16. ^cReference 21. ^dIn solid state.

calculated value of J' . The overwhelming agreement of the sign and the order of magnitude of the calculated J' with the experimental data in Table 7 confirm the antiferromagnetic coupling in the chain.

CONCLUSIONS

We have used quantum chemical calculations to determine intramolecular coupling constants (J) of seven nitroxide based diradicals in gas phase, and both intra- and intermolecular coupling constants (J and J') of two diradicals in solid state. For the isolated molecule, J has been calculated from the standard formula due to Yamaguchi. A theoretical formalism has been done to express the coupling constants in a one-dimensional polymer with the quantum chemically calculated energy values, and J and J' have been determined from eqs 15 and 16.

Density Functional methodology has been used to study these nitroxide based diradicals. We have used the time-tested hybrid B3LYP and relatively modern M06-2X functionals in the unrestricted formulation. We have also used Grimme D3 correction in B3LYP and range separated functional like HSE and LC- ω PBE. Molecular geometry has been optimized for the triplet and broken symmetry solutions of individual diradicals using the 6-311G(d,p) basis set. The 6-311++G(d,p) basis set and more stable optimized geometry has been used to study spin density plots, SOMO diagrams and NICS. EPR-III basis set has been used to estimate hfcc. Large and positive J values have been observed for *m*-phenylene dinitroxide and diradicals 1, 2(a), 2(b), 5 and 6, whereas small and negative J value have been calculated for diradicals 3 and 4. Large dihedral angles and McConnell's rule explain this discrepancy. Our analysis confirms the experimental findings that diradicals 5 and 6 form weakly antiferromagnetic one-dimensional chains. The calculated intramolecular as well as intermolecular coupling constants are in the range of the observed values.

APPENDIX I

Quantum Chemical Wave Function

The highest spin state available from a quantum chemical calculation on the N -mer is

$$|\Psi_N\rangle = |(11)_1; (11)_2; \dots; (11)_{N-1}; (11)_N\rangle \quad (14a)$$

It is an eigenfunction of $S^{\text{tot}2}$ with

$$\begin{aligned} S^{\text{tot}} &= N \\ M &= N \\ E^{(0)} &= -NJ/2 \end{aligned} \quad (14b)$$

and

$$E^{(1)} = -2(N-1)J'$$

The next highest spin state can be written as

$$|\Psi'_{N-1}\rangle = |(11)_1; (11)_2; \dots; (11)_{N-1}; (00)_N\rangle \quad (1.1)$$

It is an eigenfunction of $S^{\text{tot}2}$ with eigenvalue $(N-1)N$ such that

$$\begin{aligned} S^{\text{tot}} &= N-1 \\ M &= N-1 \\ E^{(0)} &= -NJ/2 + 2J \end{aligned} \quad (1.2)$$

and

$$E^{(1)} = -2(N-2)J'$$

An insider singlet like

$$|\Psi'_{N-1}\rangle = |(11)_1; (11)_2; \dots; (00)_i; \dots; (11)_N\rangle \quad (1.3)$$

also has

$$\begin{aligned} S^{\text{tot}} &= N-1 \\ M &= N-1 \\ E^{(0)} &= -NJ/2 + 2J \end{aligned} \quad (1.4)$$

but the first order correction to energy is given by

$$E^{(1)} = -2(N-3)J'$$

Each of these states with $S^{\text{tot}} = N-1$ is a two-determinant configuration that cannot be obtained from the single determinant approach of unrestricted methodologies.

Another type of two-determinant open-shell functions can be written down:

$$|\Psi''_{N-1}\rangle = |(11)_1; (11)_2; \dots; (11)_{N-1}; (10)_N\rangle \quad (1.5)$$

$$|\Psi''_{N-1}\rangle = |(11)_1; (11)_2; \dots; (10)_i; \dots; (11)_N\rangle \quad (1.6)$$

These are not eigenfunctions of $S^{\text{tot}2}$. It is easy to show that $\langle S^{\text{tot}2} \rangle$ for these functions equals $N^2 - N + 2$, although $M = N$

– 1 is still an eigenvalue of S_Z^{tot} . The $\langle S^{\text{tot}2} \rangle$ value is a combination of $(N - 1)N$ for the (11) units together, and 2 for (10) unit.

A single determinant broken symmetry solution of $M = N - 1$ should be a linear combination of functions of type $|\Psi'_{N-1}\rangle$ and $|\Psi''_{N-1}\rangle$:

$$|\text{BS}\rangle = |(\text{11})_1; (\text{11})_2; \dots; (\text{11})_{N-1}; \frac{1}{\sqrt{2}}[(\text{00})_N + (\text{10})_N]\rangle(\text{terminal})$$

$$|\text{BS}\rangle = |(\text{11})_1; (\text{11})_2; \dots; \frac{1}{\sqrt{2}}[(\text{00})_i + (\text{10})_i]; \dots; (\text{11})_{N-1}; (\text{11})_N\rangle(\text{insider})$$

(1.7)

In both cases, $\langle S^{\text{tot}2} \rangle = N(N - 1) + 1$ and $\langle H^0 \rangle = -NJ/2 + J$. However, $\langle H' \rangle = -2(N - 2)J'$ for the terminal BS and $\langle H' \rangle = -2(N - 3)J'$ for the insider one. When J' is negative, the insider BS is more stable.

■ ASSOCIATED CONTENT

■ Supporting Information

Log files of all calculations and full ref 44. This information is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sndatta@chem.iitb.ac.in.

Notes

The authors declare no competing financial interest.

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