Ab Initio Quantum Chemical Investigation of Intramolecular Magnetic Interaction in Some Diradical Derivatives of Imino Nitroxide and Nitronyl Nitroxide

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The magnetic properties of the monoradicals 2-(4-phenyl acetylene)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidozolyl-oxyl (**1**) and 2-(4-phenyl acetylene)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide (**2**) and the diradicals 2,2′-(1,2-ethynediyldi-4,1-phenylene)bis[4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidozolyl-oxyl] (**3**), 2,2′-(1,2-ethynediyldi-4,1 3,1-phenylene)bis[4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidozolyl-oxyl] (**4**), and 2,2′-(1,2-ethynediyldi-4,1 3,1-phenylene)bis[4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide] (**5**) are investigated by ab initio quantum chemical methods. The rule of spin alternation in the unrestricted Hartree−Fock (UHF) method clearly shows that the radical sites are antiferromagnetically coupled in **3** and ferromagnetically coupled in **4** and **5**, which is consistent with a previous experiment. The molecular geometries are optimized at Hartree−Fock levels. This is followed by single-point calculations using the density functional (UB3LYP) treatment and the multiconfigurational complete active space self-consistent field (CASSCF) methodology. Magnetic exchange coupling constants are determined from the broken-symmetry approach. The calculated *J* values, -3.60 cm^{-1} for **3**, 0.16 cm^{-1} for **4**, and 0.67 cm^{-1} for **5**, are in excellent agreement with the observed values. Because of the very large size of the diradicals **3**−**5**, the CASSCF (10,10) calculations cannot yield realistic *J* values. Nevertheless, the CASSCF calculations support the antiferromagnetic nature of the magnetic coupling in **3** and the ferromagnetic nature of the coupling in **4** and **5**. The existence of an intramolecular magnetic coupling in **3**−**5** is also confirmed through computations of the isotropic hyperfine coupling constants for monoradicals **1** and **2** as well as diradicals **3**−**5**.

1. Introduction

In the past few decades, the electronic, structural, and magnetic properties of diradical systems have attracted experimental, theoretical, and computational attention in the quest for organic ferromagnetic materials.[1] These studies are widely aimed at developing synthetic pathways to obtain materials with expected magnetic properties. In organic molecular magnetism, Ullmann-type diradicals (nitronyl nitroxides and imino nitroxides) are the most widely studied species. This is because of their exceptional stability, facile method of preparation, versatility in coordination, and ability to generate cooperative magnetic properties.[2] The first example of pure organic ferromagnets is based on the β-phase of the *p*-nitrophenyl-nitronyl nitroxide radical.[3] For these reasons, a large variety of imino nitroxides and nitronyl nitroxides have been investigated theoretically.[4] The first point to consider in designing novel organic magnets with more than one radical unit connected through a spacer or coupler is to gain a clear understanding of the intramolecular exchange interaction (*J*) between the radical fragments prior to their possible use as novel building blocks in a supramolecular network.[5] The objective of this work is to investigate the nature and magnitude of the intramolecular magnetic exchange coupling of a few derivatives of imino nitroxide (IN) and nitronyl nitroxide (NN) diradicals.

The monoradicals involved are 2-(4-phenyl acetylene)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidozolyl-oxyl (**1**) and 2-(4-phenyl acetylene)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide (**2**). The diradicals under investigation are 2,2′-(1,2-ethynediyldi-4,1-phenylene)bis[4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidozolyl-oxyl] (**3**), 2,2′-(1,2-ethynediyldi-4,1 3,1-phenylene)bis[4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidozolyl-oxyl] (**4**), and 2,2′-(1,2-ethynediyldi-4,1 3,1-phenylene)bis[4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide] (**5**). These radical species are shown in Figure 1. The diradicals **3**−**5** were synthesized by Wautelet et al.[6] These authors also characterized the diradicals by electron paramagnetic resonance (EPR), magnetic susceptibility measurements, and UV−Visible and IR spectra. The frozen-solution EPR measurement in a polystyrene glassy matrix followed by lyophilization in a benzene solution provides evidence of an intramolecular antiferromagnetic or ferromagnetic coupling between two monoradical units through π-conjugation, and the ground state was identified as singlet (S) for **3** and triplet (T) for **4** and **5**, with a very small absolute magnitude of S−T energy differences. In fact, the S ground state for **1** had been predicted earlier by the semiempirical AM1 calculations of Wautelet et al.[7] Also, the spin alternation scheme[8] shown in Figure 2 is in support of an S ground state for **3** and T ground states for **4** and **5**.

Organic diradicals are, in general, highly reactive because of the presence of degenerate nonbonding molecular orbitals (NBMOs).[9] Initially, different criteria were proposed to describe the nature of the ground state of such non-Kekulé hydrocarbons.[10] An S ground state results when the degeneracy of the NBMOs is spoiled.[11] A change of molecular symmetry or a variation of the electronegativity of the diradical termini can be used to control the spin multiplicity of the ground state.[12] The conformation of the molecule also plays an important role in determining the ground-state spin.[13] It is generally known

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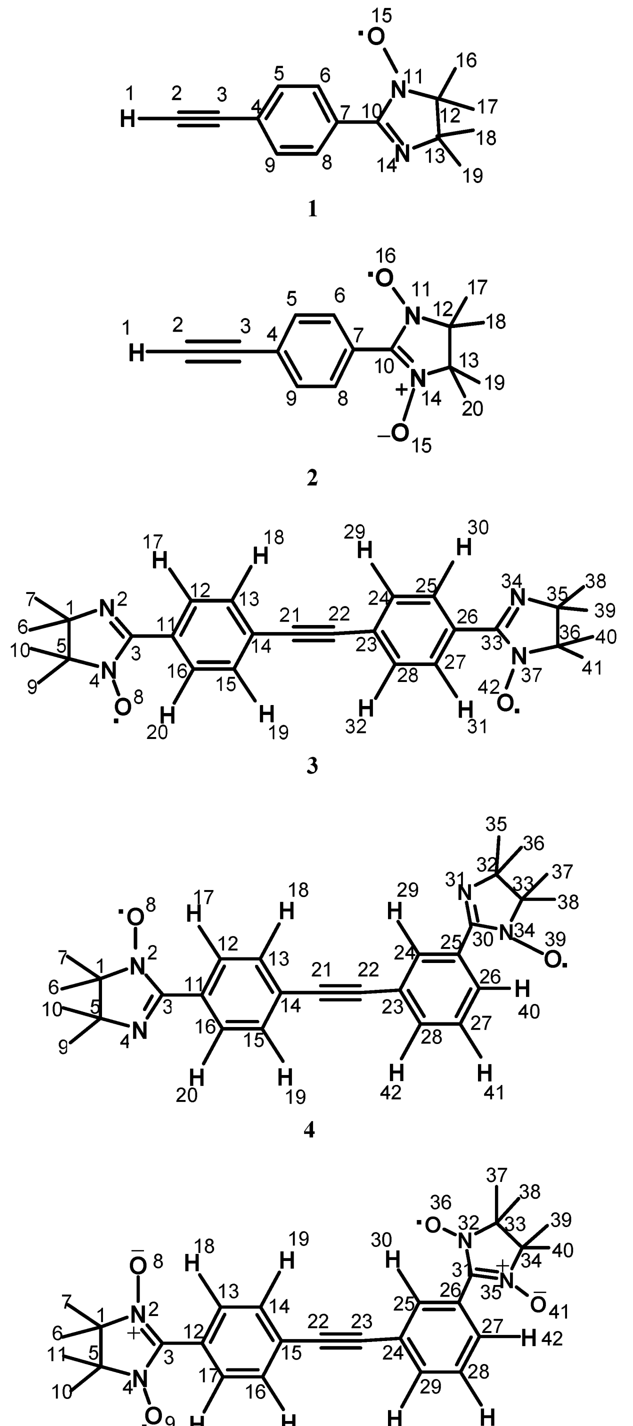

Figure 1. Species investigated in this work: (**1**) p-IN; (**2**) p-NN; (**3**) IN-2p-IN; (**4**) IN-pm-IN; (**5**) NN-pm-NN.

that an ab initio post-Hartree–Fock calculation with a large basis set can be used to predict the ground-state spin multiplicity.[14–18] Additionally, Klein and co-workers adopted the valence bond approach to extensively investigate a large number of free radicals.[19]

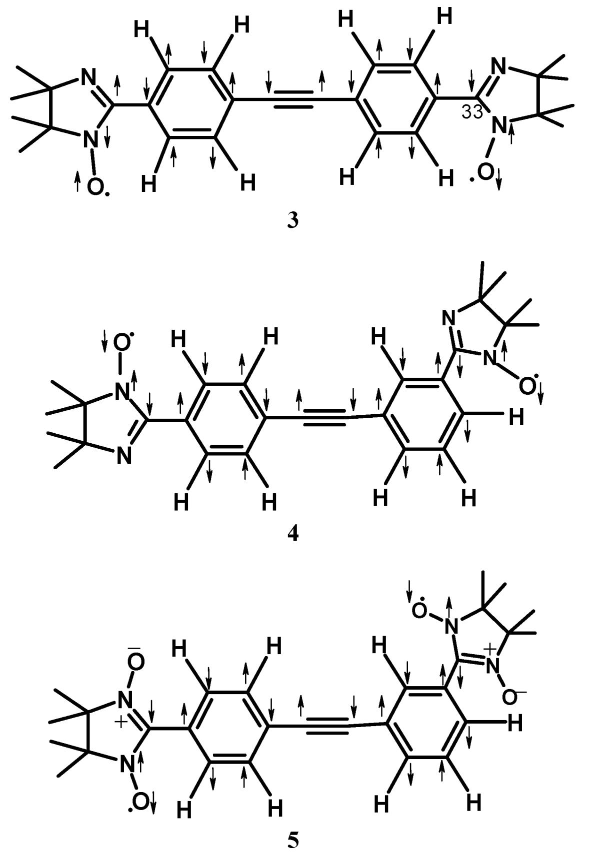

Figure 2. Spin alternation in the diradicals. **3** shows an S ground state, whereas **4** and **5** have T ground states.

In this work we adopt the computationally less expensive broken-symmetry (BS) approach and compare the broken-symmetry results with the post-Hartree–Fock and experimental results. The intramolecular magnetic coupling can be further confirmed by the calculation of hyperfine coupling constants (hfcc). To our knowledge, this work is the first report of ab initio results on the spin states of these species.

This paper is organized as follows: In section 2 we briefly discuss salient features of methodology. The computational strategies adopted in this work are discussed in section 3. Section 4 contains a discussion of the results, and a few concluding remarks are given in section 5.

2. Methodology

An accurate calculation of the magnetic exchange interaction between two magnetic units requires spin-polarized Hartree–Fock (HF) solutions. The unrestricted Hartree–Fock (UHF) method considers spin polarization by allowing two different orbitals for two different spins (α and β). But UHF calculations fail to produce the correct magnitude of magnetic interaction because the S (the lowest multiplet) state of a diradical cannot be correctly represented by a single-determinantal (SD) wave function.[20] Spin contamination is another factor in the failure of UHF. There are some techniques to annihilate the spin contamination effects, but these are difficult to implement and often do not provide unique solutions. As a consequence, UHF erratically produces an S–T energy gap.[20a] Of course, the restricted (open-shell) Hartree–Fock (ROHF) procedure is free from spin contamination effects, but the spin polarization is not adequately represented. These problems can be generally overcome by a multiconfigurational treatment. Post-HF calculations such as configuration interaction (CI) are certainly good candidates for this purpose. However, these are no longer computationally affordable once the size of the system increases.

Several new techniques based mainly on density functional theory (DFT) have been developed and applied to solve the problem of calculating multiplet energy levels. In this work,

TABLE 1: Single-Point Total Energy Calculated with the 6-311G(d,p) Basis Set for the Monoradicals in Their Doublet Ground States[a]

species	method	total energy (au)	$\langle S^2 \rangle$
1	UB3LYP	−766.6266	0.7716
	R(O)B3LYP	−766.6222	0.7500
2	UB3LYP	−841.8183	0.8267
	R(O)B3LYP	−841.8092	0.7500

[a] The molecular geometry for each radical was optimized via the 6-311G(d) basis sets at both restricted and unrestricted HF levels.

we adopt the BS approach proposed by Noodleman.[21] This has the important feature that only the calculation of the energy of SDs is needed to approximate the energies of all spin manifolds. Its main limitation is that the method is based on a pure Heisenberg−Dirac−van Vleck (HDVV) spin Hamiltonian, so non-Heisenberg systems will be described incorrectly. Magnetic interactions in organic diradicals are more or less isotropic in nature because of the weak spin−orbit interaction in a molecule containing only lighter elements.[22] Therefore, diradicals are like Heisenberg spin systems, and the BS approach appears to be very suitable for them.

The BS state is not a pure spin state but an artificial state of mixed spin symmetry and lower spatial symmetry. This is very useful for computational purposes. In fact the magnetic exchange coupling constant J can be expressed as[21]

$$E(S_{\max}) - E(\mathrm{BS}) = -S_{\max}{}^2 J \tag{1}$$

which is comparable to the exact relation

$$E(S_{\max}) - E(S{=}0) = -S_{\max}(S_{\max} + 1)J \tag{2}$$

For diradicals, the BS state corresponds to $\langle S^2 \rangle = 1$.

3. Computational Strategy

The monomer geometries of **1** and **2** are optimized in both restricted and unrestricted procedures at the HF level using 6-311G(d) basis sets. These optimized geometries are reoptimized in hybrid density functional methodologies, namely, UB3LYP and R(O)B3LYP (with Becke exchange functionals and the LYP correlation functionals), while the same basis sets are used. Single-point calculations are performed with the higher basis set 6-311G(d, p). Results are given in Table 1.

Molecular geometries of diradicals **3**−**5** are optimized first by the UHF/STO-3G method. These results are not shown here. Using the STO-3G optimized geometries, we carry out further optimizations by UHF/6-31G(d) methodology. Optimizations in the restricted formalisms with ROHF/6-31G(d) are also performed starting from the UHF/6-31G(d) optimized geometry. The computed total energy values are given in Table 2.

Borden, Davidson, and Feller[15] discussed that the ROHF calculations provide qualitatively correct molecular orbitals but in some cases fail to produce the accurate molecular geometry. They suggested the use of the UHF methodology for a reasonably correct description of T and open-shell S geometries. Furthermore, Illas et al. found that it is always good to start with correct molecular orbitals for finding the BS solution.[23] Hence, all the BS calculations are performed within the framework of the unrestricted formalism but using the ROHF/6-31G(d) optimized geometry and the corresponding guess values.

To calculate the magnetic interactions by the BS approach, single-point calculations are performed by the UB3LYP method with different basis sets. The increasing order of basis sets used are as follows: 6-31G(d), 6-31G(d, p), 6-31+G(d, p), 6-311G(d), and 6-311G(d,p). The computed energy values are given in Tables 3−5 for **3**, **4**, and **5** respectively.

TABLE 2: Optimization of Molecular Geometries of Diradicals 3−5 in Singlet and Triplet Spin States[a]

		total energy (au)		
system	method	singlet[b]	triplet $\langle S^2 \rangle$	E(S) − E(T) (kcal mol^{-1})
	UHF	−1446.0770	−1446.3270 *3.773*	156.9
3	ROHF	−1446.0770	−1446.2867 *2.000*	131.6
	UHF	−1446.0781	−1446.3171 *3.616*	149.9
4	ROHF	−1446.0781	−1446.2858 *2.000*	130.3
	UHF	−1595.6638	−1595.9259 *4.783*	164.5
5	ROHF	−1595.6639	−1595.8387 *2.000*	109.8

[a] The basis set used is 6-31G(d). [b] Numbers differ only in the fifth place after the decimal point, indicating that there is little difference between the UHF singlet and the ROHF singlet.

To compare the BS results with multiconfugurational results, post-HF ab initio calculations by the complete active space self-consistent-field (CASSCF) methodology are performed with 10 active electrons in 10 active orbitals and with 6-31G(d) and 6-311G(d, p) basis sets. The computed energy values are shown in Table 6. The 6-311G(d, p) calculations failed for **5**.

To investigate the hfcc, we use the B3LYP method along with the EPR−II[22c] and aug-cc-pvDZ basis sets for monoradicals **1** and **2** and only the EPR−II basis set for diradicals **3**−**5**. The optimized UHF/6-311G(d) geometries are used for the monoradicals, whereas the optimized UHF/6-31G(d) geometries are adopted for the diradicals. The calculated hfcc values for these radicals (in a vacuum) are listed in Table 7.

All of the calculations are performed with the Gaussian 98 quantum chemical code.[24]

4. Results and Discussion

The monomers **1** and **2** have doublet ground states. The single-point total energy values in Table 1 show that the unrestricted formalism provides slightly greater stability. This is the result of the spin polarization effect in the unrestricted formalism, but it comes at the expense of spin contamination as can be seen from the $\langle S^2 \rangle$ values in the same table.

Table 2 shows that, at the mean-field level, the T state is always far more stable than the S state for each diradical. The UHF method always yields a highly spin-contaminated T wave function. Consequently, the S−T energy gap is somewhat reduced in the ROHF calculations, but it is still too large, and the S ground state of **3** cannot be manifested at the HF level.

The UB3LYP total energies for the BS and T states of **3** are given in Table 3. The stability consistently increases with the basis size. We have considered basis sets up to 6-311G(d,p) because the T geometry was optimized at the 6-31G(d) level and a larger basis would not necessarily generate a good value for the energy difference ($E_{\mathrm{BS}} - E_{\mathrm{T}}$). Both the BS and the T wave functions suffer from spin contamination effects, but the difference in $\langle S^2 \rangle$ remains approximately equal to 1.0. The intramolecular magnetic exchange coupling constant J, calculated from eq 1, shows a smooth trend for all of the basis sets. Our best result, computed with the 6-311G(d,p) basis, is $J = -3.60$ cm^{-1}, which corresponds to the largest basis in Table 3 and a very small $\langle S^2 \rangle_{\mathrm{T}} - \langle S^2 \rangle_{\mathrm{BS}} - 1$ (1.36×10^{-4}). The

TABLE 3: Total Energy from UB3LYP Single-Point Calculations on 3 in Both Broken-Symmetry (BS) and Triplet (T) States Using Different Basis Sets

basis	E_{BS} (au) $\langle S^2 \rangle$	E_T (au) $\langle S^2 \rangle$	$E_{BS} - E_T$ (cal mol^{-1})	$(\Delta\langle S^2 \rangle - 1) \times 10^4$	J (cm^{-1})[a]
6-31G(d)	−1455.5299574 *1.022834*	−1455.5299586 *2.023165*	0.75	3.31	0.26
6-31G(d,p)	−1455.5768206 *1.022828*	−1455.5768137 *2.022475*	−4.33	−3.53	−1.52
6-31+G(d,p)	−1455.6213633 *1.024742*	−1455.6213548 *2.024146*	−5.33	−5.96	−1.87
6-311G(d)	−1455.8490083 *1.022876*	−1455.8489953 *2.022066*	−8.16	−8.10	−2.85
6-311G(d,p)	−1455.8948799 *1.022596*	−1455.8948635 *2.022732*	−10.29	1.36	−3.60
observed[b]					−3.37

[a] From eq 1. [b] Reference 6.

TABLE 4: Total Energy from UB3LYP Single-Point Calculations on 4 in Both Broken-Symmetry (BS) and Triplet (T) States Using Different Basis Sets

basis	E_{BS} (au) $\langle S^2 \rangle$	E_T (au) $\langle S^2 \rangle$	$E_{BS} - E_T$ (cal mol^{-1})	$(\Delta\langle S^2 \rangle - 1) \times 10^4$	J (cm^{-1})[a]
6-31G(d)	−1455.5310178 *1.023946*	−1455.5310264 *2.02445*	5.40	5.04	1.89
6-31G(d,p)	−1455.5778669 *1.024046*	−1455.5778774 *2.024745*	6.60	6.99	2.32
6-31+G(d,p)	−1455.6228021 *1.026287*	−1455.6228052 *2.026526*	1.95	2.39	0.68
6-311G(d)	−1455.8502143 *1.024004*	−1455.8502274 *2.024968*	8.22	9.64	2.87
extrapolated[b]					0.16

[a] From eq 1. [b] Figure 3a.

TABLE 5: Total Energy from UB3LYP Single-Point Calculations on 5 in Both Broken-Symmetry (BS) and Triplet (T) States Using Different Basis Sets

basis	E_{BS} (au) $\langle S^2 \rangle$	E_T (au) $\langle S^2 \rangle$	$E_{BS} - E_T$ (cal mol^{-1})	$(\Delta\langle S^2 \rangle - 1) \times 10^4$	J (cm^{-1})[a]
6-31G(d)	−1605.8625392 *1.078432*	−1605.8625728 *2.082158*	21.08	37.26	7.40
6-31G(d,p)	−1605.9099065 *1.082187*	−1605.9099236 *2.084283*	10.73	20.96	3.76
6-31+G(d,p)	−1605.9613842 *1.075813*	−1605.9613969 *2.076811*	7.97	9.98	2.8
6-311G(d)	−1606.2261714 *1.077158*	−1606.2262023 *2.080576*	19.39	34.18	6.79
extrapolated[b]					0.67

[a] From eq 1. [b] Figure 3b.

TABLE 6: Results from CASSCF (10,10) Calculations with Different Basis Sets for the Diradicals 3−5

		energy (au)			
molecule	basis set	singlet (S)	triplet (T)	$E_S - E_T$ (kcal mol^{-1})	J (cm^{-1})
3	6-31G	−1445.7448	−1445.7237	−13.24	−2323
	6-311G(d)	−1446.6345	−1446.6331	−0.88	−154.1
4	6-31G	−1445.7012	−1445.7788	48.69	8542
	6-311G(d)	−1446.5921	−1446.6342	26.42	4632
5	6-31G	−1595.2477	−1595.2859	23.97	4205
	6-311G(d)	convergence failure			

experimental J is -3.37 cm^{-1}. The difference may be attributed to the solvent effect, which is not considered in our computations, the slight difference of $\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}$ from 1, and the constraint of geometry optimization at the HF/6-31G(d) level. The magnetic coupling is manifestly antiferromagnetic, as predicted by the simple spin alternation rule (Figure 2). This is also consistent with the observation that linear diradical derivatives of IN with other couplers have S ground states.[25]

Results from UB3LYP single-point calculations on **4** and **5** are given in Tables 4 and 5, respectively. The coupling between the radical sites is manifestly ferromagnetic in each case, with positive J values. However, the calculated J values vary erratically among the basis sets. This is unlike the antiferromagnetic case in Table 4. Therefore, the calculated J values are plotted against $\Delta\langle S^2 \rangle - 1$, in which $\Delta\langle S^2 \rangle = \langle S^2 \rangle_T - \langle S^2 \rangle_{BS}$. These plots turn out to be surprisingly linear, and the best straight lines are shown in Figure 3a,b. The extrapolated values of J for $\Delta\langle S^2 \rangle = 1$ are 0.16 cm^{-1} for **4** and 0.67 cm^{-1} for **5**. From experiment, Wautelet et al. concluded that the J values for **4** and **5** are larger than the hfcc but extremely small in magnitude, being less than 1 K. The J values extrapolated here are consistent with the experimental observations.

In principle, the magnetic exchange coupling constant J can also be determined by the CASSCF methodology by using eq 2. In practice, however, an explicitly detailed CASSCF calculation can be performed only on very small species. For larger species, such as the diradicals **3**−**5**, one can carry out a CASSCF calculation with only a handful of active electrons in a handful of active orbitals. This limitation invariably results in a large value of the calculated energy difference between the spin states, and the J values cannot be accurately determined. In fact, Table

TABLE 7: (a) Isotropic Fermi Contact Coupling Constants for the Monoradicals[a] and (b) Isotropic Fermi Contact Coupling Constants Computed for the Diradicals Using the B3LYP Method with EPR−II Basis Sets[b]

(a)

species	atoms	B3LYP/EPR−II (in Gauss)	B3LYP/aug-cc-PVDZ	observed[c] (in Gauss)
1	N_{11}	4.33	7.05	4.22
	N_{15}	5.59	8.74	9.10
2	N_{11}	5.21	7.98	
	N_{14}	5.21	7.98	

(b)

species	calculated hfcc in Gauss[d]
3	2.14 (N2), 2.79 (N4), 2.14 (N34), 2.80 (N37)
4	2.94 (N2), 1.72 (N4), 2.92 (N34), 1.74 (N31)
5	2.71 (N2), 2.72 (N4), 2.68 (N32), 2.70 (N35)

[a] The optimized UHF/6-311G(d) geometries are chosen. [b] The optimized UHF/6-31G(d) geometries are chosen. [c] For the species solvated in CH_2Cl_2/xylene; ref 6. [d] The observed values for IN-3p-IN in CH_2Cl_2/xylene are 2.22, 4.53, 2.22, and 4.53 G; ref 6.

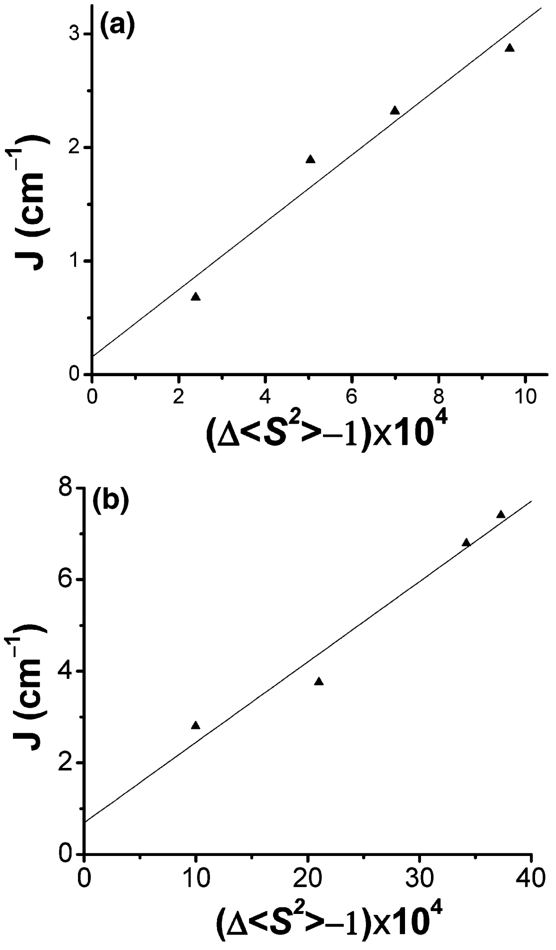

Figure 3. The best straight line plot of the computed J values against $\Delta\langle S^2\rangle - 1$. The final J is obtained by extrapolating the straight line to $\Delta\langle S^2\rangle = 1$. We get (a) $J = 0.16$ cm^{-1} for **4** and (b) $J = 0.67$ cm^{-1} for **5**. The standard deviations are (a) 0.25 and (b) 0.52 in cm^{-1}.

6 shows the results from the CASSCF calculations on diradicals **3**−**5** using 10 active electrons in 10 active orbitals. The spin state energy difference ($E_T - E_S$) is very large in every case, of the order of a few kcal mol^{-1}. Nevertheless, the CASSCF results definitely identify the ground-state spin. Table 6 clearly shows that **3** has an S ground state, whereas **4** and **5** have T ground states.

Isotropic hfcc. Akita et al.[26a] found hfcc's of 4.5 and 8.5 G for thieno[2,3-b]- and thieno[3,2-b]-thiophene derivatives of IN, respectively. Stroch et al.[26b] reported 4.28 and 9.20 G for the *p*-benzoic acid derivative of IN in benzene. Morita et al.[26c] obtained 4.19 and 9.33 G for the two nonequivalent nitrogen atoms of the 1,6-dithiopyrene derivative of IN in toluene. Wautelet et al.[6] observed hfcc's of 4.22 and 9.10 G for monoradical **1** in CH_2Cl_2/xylene. The experimental hfcc for a large number of derivatives of NN in different nonaqueous solvents was found to vary in the range 7.00−7.81 G.[27] D'Anna et al.[27a] found that the hfcc for the two equivalent nitrogen atoms in methyl, *o*-tolyl, and phenyl derivatives of NN are 7.66, 7.57, and 7.62 G, respectively, in ethanol solution, and 7.44, 7.31, and 7.47 G, respectively, in benzene. From these observations it is clear that the subtituents on the α-carbon of IN and NN do not play a significant role in determining the hfcc for the monoradical derivatives, whereas the nature of the solvent considerably affects the hfcc.

Cirujeda et al.[28] calculated the hfcc for several α-nitronyl aminoxyl radicals via the B3LYP method using EPR−II basis sets. They found similar hfcc's for the monoradicals with similar steric constraints between the two rings. This fact also supports the idea that the spin density distribution in the phenyl ring is not strongly dependent on the nature and position of substituents. The hfcc's calculated here for monoradical **1** (Table 7a) are comparable to the experimental hfcc's that were obtained for solvated species. We also find that the hfcc's calculated for **2** are approximately equal to those for **1**, which is consistent with the general conclusions reached by Cirujeda et al.[28]

Wautelet et al. found that the hfcc's for the nitrogen atoms in a different diradical, 2,2′-{[2,5-bis(dodecyloxy)-1,4-phenylene]bis(2,1-ethynediyl-4,1-phenylene)}bis[4,5-dihydro-4,4,5,5-tetramethyl-1*H*-imidazol-1-yloxy] (IN-3p-IN), are 2.22 and 4.53 G. These values are nearly half the values for monoradical **1**. This phenomenon occurs when the two monoradical units are joined through magnetic coupling units.[29a−c] In such systems, the electron−electron exchange coupling constant J is found to become greater than the hfcc a_N.[30] In the case of diradicals **3**−**5**, the hfcc's calculated here are nearly half the hfcc's calculated for the monoradicals **1** and **2** (Table 7). These results confirm that an intramolecular magnetic coupling exists through π-conjugation. As the spin alternation shows, the nature of the magnetic coupling for **3** is antiferromagnetic, whereas ferromagnetic coupling exists in **4** and **5**. The same conclusion is reached by the BS approach as well as by CASSCF calculations.

Deumal et al.[31] and Zakrassov et al.[32] showed that the hfcc computed by the DFT method drastically depends on the basis set, and even with a very large basis, significant differences occur from the observed values. The hfcc values calculated here (Table 7) follow the same trend. We have noticed that the UHF calculations overestimate the hfcc (data not given in Table 7), and DFT calculations underestimate it. The hfcc for a specific atom is proportional to the spin density on it. The lower values calculated by the EPR−II basis set can be attributed to a greater delocalization of spin density in the molecule. This effect is also responsible for the small difference between the hfcc calculated for the two nonequivalent nitrogen atoms in **1** (Table 7a) and **3** (Table 7b). There is a need for a methodology that can properly localize the spin density on different atoms in a molecule.

5. Conclusions

An accurate computation of the magnetic exchange coupling constant of an organic diradical species is extremely difficult to obtain because the magnetic interaction is very weak in these molecules. Computations at the HF level are far from being adequate. In principle, the CASSCF method can lead to an accurate J value. In practice, however, it fails because of the limitations of the calculations whenever the system is large. From a computational point of view, the density-functional-based BS approach is very suitable for calculating the J value.

The intramolecular magnetic exchange interaction between the radical units is antiferromagnetic, with $J = -3.60$ cm^{-1} for the diradical **3** and ferromagnetic for the diradicals **4** and **5,** with coupling constants 0.16 and 0.67 cm^{-1}, respectively. These calculated values are in excellent agreement with the experimental results.

The existence of the intramolecular magnetic coupling is also confirmed from the computed hfcc. The computed values for the N atoms in diradicals are approximately half the hfcc values computed for the N atoms in the monoradicals. This indicates that the electron spin is delocalized through the phenylene−ethynylene conjugated magnetic coupler.

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