Molecular Tailoring and Prediction of Strongly Ferromagnetically Coupled Trimethylenemethane-Based Nitroxide Diradicals

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We have investigated the magnetic properties of four recently synthesized stable TMM-type nitroxide diradicals. Four new diradicals are proposed by tailoring one of the species in such a way that both conjugation and planarity increase. As a remarkable consequence, the intramolecular ferromagnetic exchange interaction was found to be quite high in the proposed radicals. The calculated coupling constants were in the range of +102 to +140 cm^{-1}. The MO and spin density analysis are provided to interpret the exchange interactions. We observed the existence of intramolecular $\pi-\pi$-interactions for the species **2**. This slightly increased the J value by shortening the length of the spacer between the two spin sources.

Introduction

Diradicals with strong intramolecular ferromagnetic coupling constitute one of the prerequisites for the design of organic molecular magnets. Thermal stability of the building blocks (or long-term persistence at room temperature) is a desired property, and the structure of the diradical has to accommodate π-conjugation in the system for an effective transmission of spin wave. The design and synthesis of such diradical building blocks of strong ferromagnets remain a challenge. Numerous efforts have been devoted to obtain such organic magnetic materials.[1]

Trimethylenemethane (TMM) is a widely studied diradical in this area. It was first isolated by Dowd et al.[2a−c] It is known to be ferromagnetically coupled but very unstable. The impact of TMM has been significant, resulting from the synthesis and studies of numerous derivatives that are stable at cryogenic temperatures and the fact that the molecular geometry can be tailored to obtain desired molecular properties.[3,4] Recently, Shultz and co-workers have synthesized stable TMM analogues **1**−**4** and investigated their magnetic properties.[5a−c] These are shown in Figure 1. Observation of the magnetostructural properties in these molecules prompted Shultz et al.[5b] to correlate exchange parameters with phenyl-ring torsion angles (φ) in accordance with a simple Karplus−Conroy-type relation: J (cm^{-1}) = 44 $\cos^2 \varphi - 17$. The magnetic characterization of these molecules was performed using solid-state magnetic susceptibility measurements and by EPR spectra in fluid and frozen solutions.

The first objective of this work was to calculate the magnetic exchange coupling constant of the four isostructural diradicals **1**−**4** by a broken symmetry (BS) density functional method. We aimed to validate the computational methodology on these systems by comparing them with available experimental data. The second objective was to propose similar structures that would have a greater conjugation and were at the same time strongly ferromagnetically coupled. Species **4** is more rigid than the others, as the internal dihedral angles φ_1 and φ_2 are nearly zero (Scheme 1), and has the highest ferromagnetic J value. The structure of **4** was tailored without disturbing the magnetic centers and the principal exchange pathway, except for increasing the planarity of −NO with respect to the phenyl rings. We obtained four new molecules **5**−**8** (Figure 2) that were expected to gain in electronic conjugation and have a strong intramolecular ferromagnetic exchange interaction.

Computational Methodology

The magnetic exchange coupling constant was calculated here by the so-called Ginsberg,[6] Noodleman,[7] and Davidson[8] (GND) spin projected formula, $J^{GND} = (E_{BS} - E_T)/S_{max}^2$, when the overlap integral S_{ab} was very small and the spin contamination in the BS solution was negligibly low. Similar expressions have also been obtained by Ruiz et al.,[9a] Bencini et al.,[9b] Illas et al.,[10] and Yamaguchi et al.[11] The detailed theoretical aspects have been discussed elsewhere.[12]

Crystal geometries were used here to investigate the molecules **1**−**4**, with appropriate structural features. The J values calculated at the UB3LYP/6-311+G(d,p) level using Gaussian 03[13] software are given in Table 1. Molecular geometries of species **5**−**8** were optimized at the UB3LYP/6-311G(d,p) level. The final computations were performed at the UB3LYP level with a 6-311+G(d,p) basis set. Results are given in Table 2.

Results and Discussion

There was an intramolecular anti-ferromagtic interaction in **1**, while the ferromagnetic interaction was involved in molecules **2**−**4** (Table 1). The magnetic exchange coupling constant for **1** obtained from the EPR Curie plot was −24 cm^{-1}. The calculated J value was in agreement with the value obtained from EPR data. Shultz et al. were not able to fit the solid-state magnetic susceptibility data for **2**. They reported a J value of −5.75 cm^{-1} in PVC film with 74% purity. Here, we find a J value of 7.43 cm^{-1}. An excellent agreement between calculated and observed values was again obtained for **3.** It was noticeable that the crystal of **3** was of 100% purity. For **4**, however, the J value was measured from susceptibility data of crystals with 80−96% purity.[5b] The deviation of the calculated J value from the observed one for **4** can be attributed to it.

We notice that not only the phenyl twist angles[5b] (φ_1 and φ_2) but also the nitroxide twist angles (θ_1 and θ_2) were instrumental in controlling the J value. The J value increased

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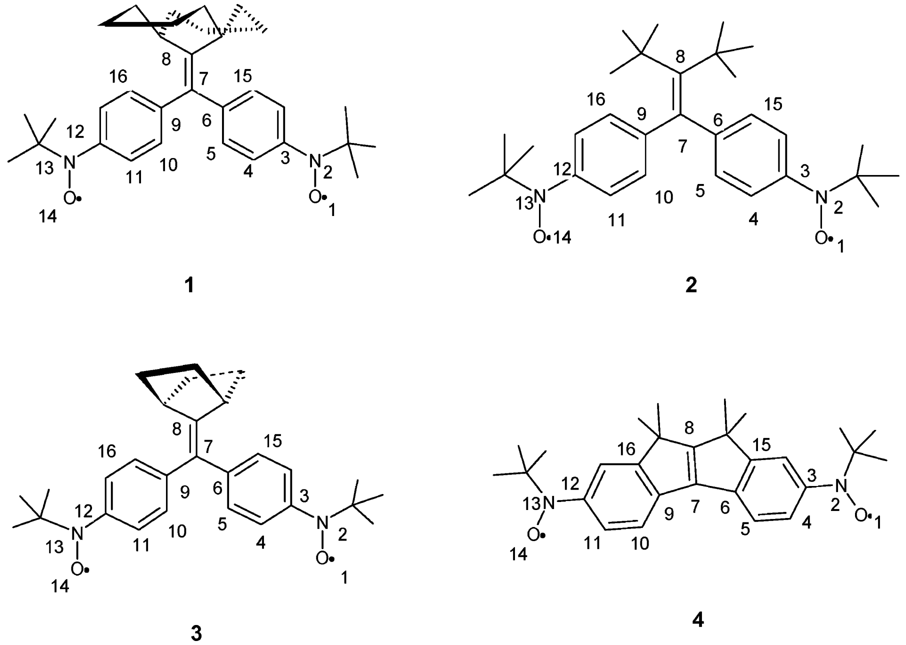


Figure 1. Recently synthesized TMM analogue stable diradicals.

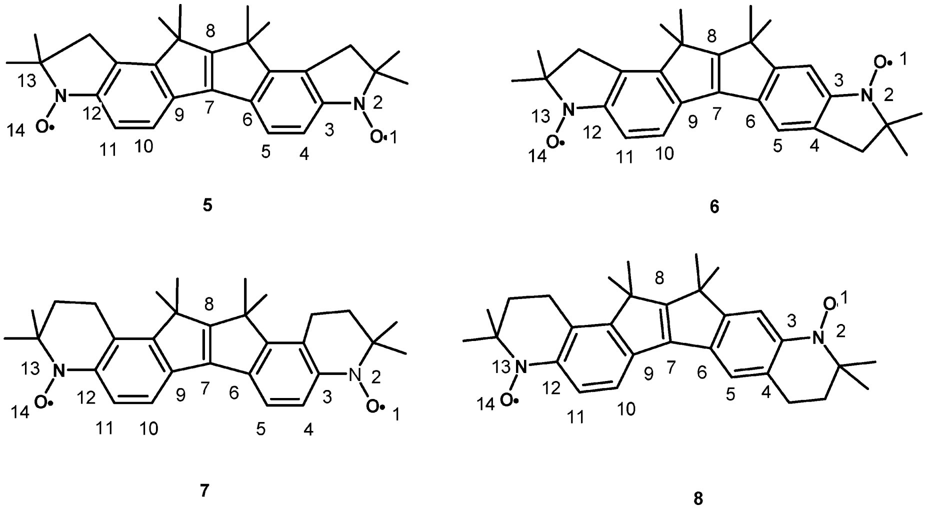
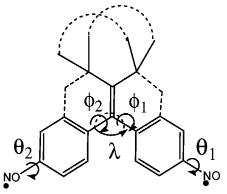


Figure 2. Proposed diradicals (**5**−**8**) with strong ferromagnetic interactions.

SCHEME 1: Specification of θs and φs in 1−8 Diradicals



with a decrease of the phenyl−NO twist angles θ_1 and θ_2. We have also calculated J for **4** by setting $\theta_1 = 0$ and $\theta_2 = 0$ instead of $\theta_1 = 45.8$ and $\theta_2 = 43.3$ as reported in the CIF file (ref 5b), while keeping φ_1 and φ_2 intact at nearly zero values. The J value remarkably increases to +33.09 cm^{-1}. This shows the sensitivity of the J value toward the θ values.

A geometric comparison of all the species is given in Table 3. Crystal impurity always makes it difficult to estimate J from the experimental susceptibility data. This occurrs because of improper accounting of paramagnetic impurities in the theoretical model. For species **1**, the susceptibility measurement for a crystal with an impurity yields a J value of only −12 cm^{-1}, half the correct J value measurable from EPR.[5b] In any cases, our calculations show that either the CIF file reported for **4** is not the correct one or that the estimated J value is incorrect because of the lack of purity of the sample.

TABLE 1: Calculated Magnetic Exchange Coupling Constant (J) Using Crystal Geometries

diradicals	E_B (au) ⟨S^2⟩	E_T (au) ⟨S^2⟩	J (cm^{-1})	J^{exp} (cm^{-1})
1	−1498.38607147 *1.0208*	−1498.38594640 *2.0219*	−27.40	−24.00[a] −12.00[b]
2	−1429.38235299 *1.0222*	−1429.38238676 *2.0257*	7.43	NA
3	−1348.41626916 *1.0189*	−1348.41629762 *2.0209*	6.13	6.79
4	−1348.45559411 *1.0109*	−1348.45563557 *2.0129*	8.98[c]	26.35

[a] From EPR Curie plot. [b] From susceptibility. [c] J value increases to +33.09 cm^{-1} using $\theta_1 = \theta_2 = 0$.

The spin alternation rule[14] (spin polarization) predicts all the species to be ferromagnetic in nature. The spin density plots are shown in Figure 3. A node of the spin density was found on C_7 that orients the spins on the two spine sources in two opposite directions, which results in an antiferromagnetic

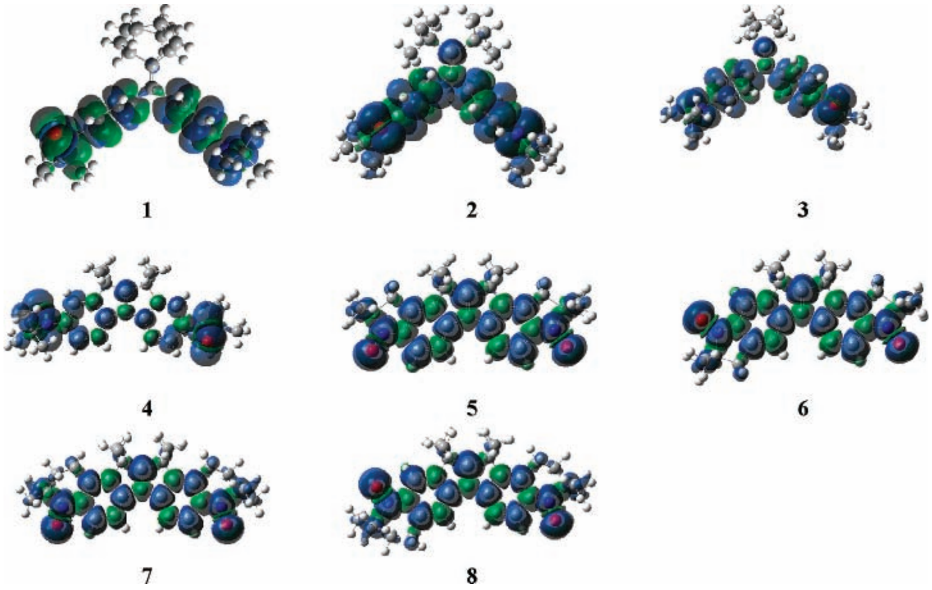


Figure 3. Plot of spin density for **1**−**8** species.

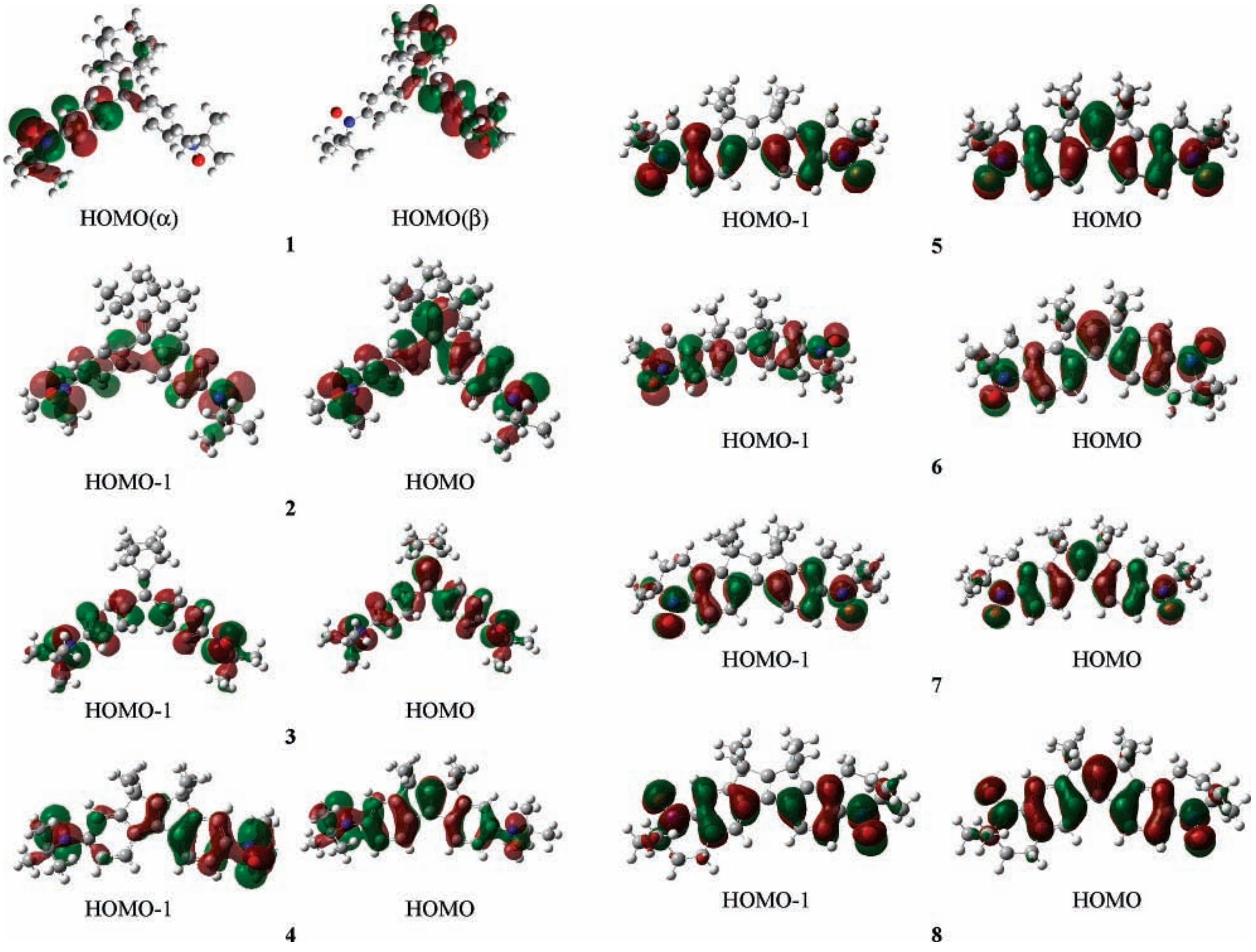


Figure 4. Magnetic orbitals in the ground state for all species.

interaction in **1**. The main reason for the antiferromagnetic interaction in **1** is that the phenyl rings as well as the NO groups are largely rotated (Table 3). In fact, the torsion angles θ_1, θ_2, φ_1, and φ_2 are quite high also for **2**− **4**, thereby making the latter weakly ferromagnetically coupled. The plot of spin densities shows the normal trend in all the other cases **2**−**8**. The spins on all the alternate atoms and on the −NO groups were oriented in parallel fashion in these cases.

To restrict the free rotation of the -NO− group, that is, to reduce angles (θ_1 and θ_2) and to decrease the φ_1 and φ_2 angles, we have tailored molecule **4**. The modeled diradicals **5**−**8** are planar molecules with facile π-conjugation between the radical centers. The conjugation increase corresponds to a slight increase in Wiberg[15] bond orders (index) in Table 4, which were calculated using natural bond orbital (NBO) analysis at the UB3LYP/6-311+G(d,p) level. The increase in planarity was

TABLE 2: Calculated Magnetic Exchange Coupling Constant (J) for Optimized Geometries in Vacuum

diradicals	E_B (au) $\langle S^2 \rangle$	E_T (au) $\langle S^2 \rangle$	J (cm^{-1})
5	−1346.45223672 *1.0301*	−1346.45286613 *2.0499*	138.12
6	−1346.45515415 *1.0294*	−1346.45579535 *2.0512*	140.72
7	−1425.09230912 *1.0271*	−1425.09277573 *2.0445*	102.41
8	−1425.09905362 *1.0267*	−1425.09952026 *2.0449*	102.42

TABLE 3: Geometric Comparison of Crystal Structures for 1−4 and Optimized Geometries for 5−8

	torsion angle				
molecule	θ_1	θ_2	ϕ_1	ϕ_2	l
1	40.68	23.14	65.92	82.37	112.62
2	9.80	11.23	54.30	55.50	109.56
3	31.40	3 1.30	43.19	50.84	115.71
4	30.10	28.40	1.90	1.80	139.33
5	0.000	0.004	−0.001	0.001	138.351
6	−0.133	−0.266	0.003	0.022	138.520
7	−7.599	−7.250	−0.390	−0.368	138.350
8	−6.923	−7.997	0.131	0.028	138.695

TABLE 4: Calculated Wiberg Bond Index (Order) at UB3LYP/6-311+G(d,p) Level

	bond order						
molecule	O_1-N_2	N_2-C_3	C_6-C_7	C_7-C_8	C_7-C_9	$C_{12}-N_{13}$	$N_{13}-O_{14}$
1	1.2891	1.0527	0.9896	1.8267	0.9850	1.0320	1.2776
2	1.2844	1.0562	1.0245	1.7773	1.0126	1.0437	1.2849
3	1.2745	1.0358	1.0130	1.7634	1.0201	1.0292	1.2763
4	1.2638	0.9853	1.0763	1.6209	1.0816	0.9876	1.2727
5	1.2974	1.0912	1.0780	1.6124	1.0780	1.0912	1.2974
6	1.3000	1.0947	1.0846	1.6048	1.0813	1.0905	1.2966
7	1.2869	1.0695	1.0787	1.6175	1.0776	1.0694	1.2869
8	1.2859	1.0758	1.0792	1.6139	1.0790	1.0709	1.2864

manifest from computed torsion angles given in Table 3. In these optimized structures, φ_1 and φ_2 were almost zero, and θ_1 and θ_2 were significantly low. The configurational isomers **5** and **6** are in the syn and anti forms, respectively. Similarly, **7** and **8** are configurational isomers. The calculated J values are much larger than the J values for the parent molecule. All the species were ferromagnetically coupled, indicating that these molecules can serve as viable molecular magnets.

MO Analysis for Magnetic Exchange Interaction. The shape of the magnetic orbitals in the ground sate [HOMO(α) and HOMO(β) for the broken symmetry state of **1** and HOMO(α) and HOMO(α) − 1 for triplet states of **2**−**8**] are shown in Figure 4. The magnetic orbitals HOMO(α) and HOMO(β) of **1** are clearly disjointed, showing the antiferromagnetic nature of magnetic exchange. The contribution of σ orbitals arising from the C_6-C_7 and C_7-C_9 bonds to the HOMOs was significantly large. The calculated bond order was less than 1.00 for the C_6-C_7 and C_7-C_9 bonds (Table 4).

The ground-state magnetic orbitals (HOMO and HOMO − 1) are non-disjointed in nature for all the ferromagnetic species. The λ (angle between the two phenyl rings) value was the smallest for **2** among the species studied (Table 3), which resulted from the spatial overlap between the p_z orbitals of C_6 and C_9 (Figure 4). This facilitated the π-conjugation, and **2** was slightly more strongly ferromagnetically coupled as compared to **3**. In species **4**, the θ angles were high (∼28°). We also found that there was a considerable amount of mixing between σ and π for **4** (Figure 4). The mixing was the reason for the lower π-conjugation and hence lower magnetic exchange interaction. The calculated lower (<1.00) Wiberg bond index for N_2-C_3 and $C_{12}-N_{13}$ in **4** was also in support of a lower conjugation.

In the predicted cases, we made both θ and ϕ angles very small, which reduced σ- and π-overlap in the HOMOs. The magnetic orbitals plotted for **5**−**8** were pure π-orbitals, reflecting strong conjugation and higher ferromagnetic interactions. The negligible contributions in the spin densities and in the magnetic orbitals (HOMO and HOMO − 1) of fragments $-CH_2-$ (in **5** and **6**) and $-CH_2-CH_2-$ (in **7** and **8**) added to **4**, indicated no additional path for the exchange interaction for higher J values in **5**−**8**.

Conclusion

In conclusion, we observed that calculated J values matched with experimental J values only when the crystal had high purity. Also, four new ferromagnetically coupled molecules were obtained by tailoring diradical **4** such that the planarity of the molecules increased, simultaneously facilitating a strong ferromagnetic interaction. The J value was very high for **5**−**8**, in a range of 102−142 cm^{-1}. The intramolecular $\pi-\pi$-interaction existed for species **2**. This slightly increased the J value by shortening the length of the spacer between the two spin sources. The larger J values for species **5**−**8** were solely due to the proper exploitation of the structural parameters instead of any new conjugation pathways.

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Supporting Information Available: Optimized geometries for **5**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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