Density Functional Theory Prediction of Enhanced Photomagnetic Properties of Nitronyl Nitroxide and Imino Nitroxide Diradicals with Substituded Dihydropyrene Couplers

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We predict the photoswitching magnetic properties of four substituted dihydropyrenes from density functional broken-symmetry calculations. The magnetic exchange coupling constants differ up to 9.44 cm^{-1}. The intramolecular exchange interactions are ferromagnetic in nature. The calculated coupling constants are much larger than those reported earlier for photomagnetic organic molecules.

Photochromism is the reversible photon-induced transition of a chemical species between two different forms having different absorption spectra. Photochromic materials change their geometries and physical properties with irradiation. They are useful in potential photoswitching. If a photoswitchable molecule is used as a spin coupler between two magnetic units, the magnetism of the resulting species can change upon irradiation.[1]

Perfluorocyclopentene is one of the widely studied photochromic spin couplers. Matsuda et al. have synthesized a large number of nitronyl nitroxide diradicals with perfluorocyclopentene.[1] In these diradicals, the intramolecular exchange interaction is very weak, and the coupling constant J is of the order of the hyperfine coupling constant (hfcc). The J value differs nearly 150-fold between the open- and closed-ring isomers. Its absolute magnitude is generally found to be <10^{-3} cm^{-1} for open ring isomers and ~10^{-2} cm^{-1} for closed ring isomers except for NN diradicals with 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene where J equals −0.76 and −4.03 cm^{-1}, respectively.[1b,d,g] As |J| is very small in the ground state, the photomagnetic properties of these molecules are not expected to find a great usage. This has led to the investigation of photoexcited states of diradicals. Teki et al. have investigated the magnetic properties of excited states of nitronyl nitroxide diradicals with diphenylanthracene coupler.[2] Huai et al. have also investigated similar excited states by theoretical means.[3]

The substituted pyrene molecule exists in two different forms, namely, cyclophanediene (CPD) and dihydropyrene (DDP), as shown in Figure 1.[4] The restricted lifetime of CPD limits the utility of these molecules. The thermal return of CPD to DDP belongs to the category of Woodward−Hoffmann orbital symmetry *forbidden* processes. Nevertheless, the barrier created from the correlation of the occupied reactant orbitals with the virtual product orbitals and vice versa is not too high for CPD → DDP conversion. Recently, Williams et al. have found that proper substitutions can increase the activation barrier to hinder the thermal conversion.[5]

In this work, we have investigated the ground-state photomagnetic properties of nitronyl nitroxide diradicals and imino-
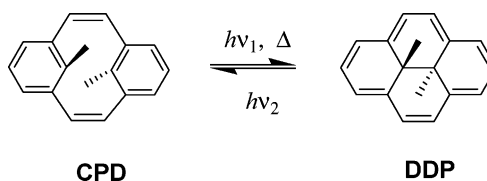

Figure 1. Conversion of CPD to DDP.

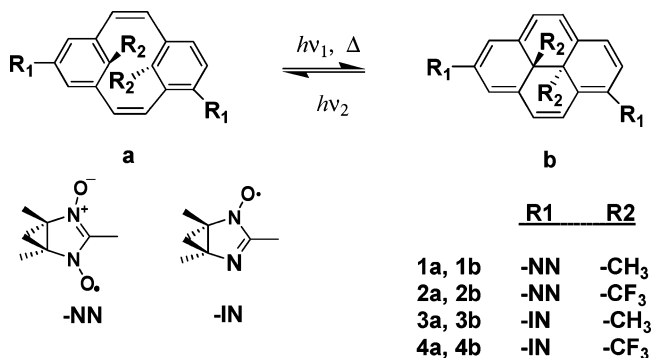|	R1	R2
1a, 1b	-NN	-CH$_3$
2a, 2b	-NN	-CF$_3$
3a, 3b	-IN	-CH$_3$
4a, 4b	-IN	-CF$_3$

Figure 2. Diradicals under investigation.

nitroxide diradicals with substituted pyrene couplers. The four sets of diradicals are illustrated in Figure 2. One novelty of this work is in the choice of the coupler. To our knowledge, these molecules have not been synthesized so far. The J values of the isomers differ by 4.7−9.6 times for each pair. The magnitude of J for the closed ring isomers is significantly large, which constitutes the second novelty. Besides, the points of attachment of the NN and IN groups are decided from the rule of spin alternation[6] such that the resulting diradicals are ferromagnetic in nature.

The theoretical evaluation of the magnetic exchange coupling constant has been performed using broken-symmetry (BS) density functional (DFT) methodology proposed by Noodleman.[7] The exchange interaction J between two magnetic sites 1 and 2 is normally expressed by the Heisenberg effective spin Hamiltonian $\hat{H} = -2J\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2$ where $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ are the respective spin angular momentum operators. A spin-polarized, unrestricted formalism and a broken-symmetry solution is needed for the lowest spin state in the BS method.[8] The BS state is not an

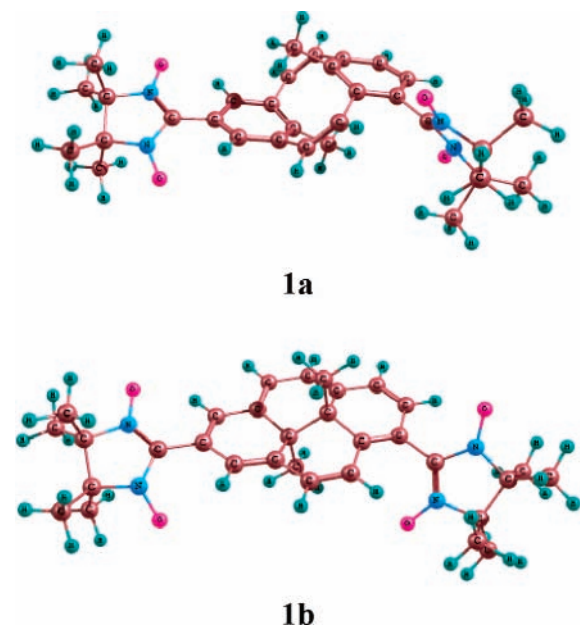* Corresponding author. E-mail: sndatta@chem.iitb.ac.in.

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Figure 3. Optimized geometries for **1** in two different states.

eigenstate of $\hat{H}$, but an equal mixture of singlet and triplet states. The coupling constant can be written as $J = (E_{BS} - E_{ET'})/(1 + S_{ab}^2)$, where S_{ab} is the overlap integral between the two magnetic orbitals a and b. The quantity E_{BS} is the energy of the broken-symmetry solution, and $E_{T'}$ is the triplet energy in the unrestricted formalism using the BS orbitals. In a single-determinantal approach, $E_{T'}$ can be approximated by the triplet energy E_T that is achieved from a direct computation ($E_{T'} \approx E_T$) because of the very less spin contamination in the high-spin state. In contrast, the BS state is often found to be spin-contaminated. Therefore, spin-projected methods have been applied to eliminate the effect of the spin contamination from the energy of the BS state. The magnetic exchange coupling constant can be calculated by the so-called Ginsberg,[9] Noodleman,[7] and Davidson[10] (GND) spin projected equation, $J^{GND} = (E_{BS} - E_T)/S_{max}^2$, when the overlap integral S_{ab} is very small and the spin contamination in the BS solution is negligibly low. Similar expressions have also been obtained by Ruiz et al.,[11] Bencini et al.,[12] and Illas et al.[13] The Bencini–Ruiz formula gives J^{BR} that is the half of J^{GND} and is applicable to highly degenerate systems. Yamaguchi et al.[14] have also derived a general expression, $J^Y = (E_{BS} - E_{T'})/(\langle S^2 \rangle_T - \langle S^2 \rangle_{BS})$.

The molecular geometries of all the eight species (**1**–**4a,b**) are optimized at the ROHF/6-31G(d,p) level using Gaussian 03 software.[15] The optimized molecular geometry for **1a** and **1b** are shown in Figure 3. The magnetic exchange coupling constants, which are calculated at UB3LYP/ 6-311+G(d,p) level, are given in Table 1 for all the species.

We show only J^{GND} and J^Y in Table 1. These are almost equal to each other in every case. It is observed that NN radicals are much more strongly coupled to each other than the IN radicals. This is due to the larger spin density on the carbon atoms of the O–N–C–N–O fragments in NN diradicals. The spin density on the carbon atoms of N–C–N–O fragments in IN diradicals is much less.

The J value is greater for the –CF$_3$ substituents than that for the –CH$_3$ groups in the closed form, and smaller in the open form. This is due to the bulkier group restricting the angle of rotation (Φ) of the nitronyl nitroxide rings from the coupler plane. The average Φ follows the orders **1** > **2** and **3** > **4**. A smaller Φ gives a greater conjugation. The intra-ring C–C

TABLE 1: Calculated Exchange Coupling Constants (J) and Total Energies at UB3LYP/6-311+G(d,p) Level^a

species	E_B (au) $\langle S^2 \rangle$	E_T (au) $\langle S^2 \rangle$	J^{GND} (cm^{-1})	J^Y (cm^{-1})
1a	−1762.3338519 *1.0670*	−1762.3338619 *2.0679*	2.20	2.20
1b	−1762.3569120 *1.0750*	−1762.3569596 *2.0805*	10.43	10.37
2a	−2357.9438295 *1.0700*	−2357.9438367 *2.0707*	1.58	1.58
2b	−2357.9639160 1.0784	−2357.9639662 2.0847	11.02	10.95
3a	−1611.9511192 *1.0727*	−1611.9511208 *2.0235*	0.34	0.34
3b	−1611.9723107 *1.0242*	−1611.9723196 *2.0253*	1.95	1.95
4a	−2207.5623297 *1.0243*	−2207.5623308 *2.0245*	0.22	0.22
4b	−2207.5831239 *1.0250*	−2207.5831336 *2.0263*	2.13	2.13

^{a} The J values are calculated using the GND and Yamaguchi equations.

distances are more or less same in the four closed species. Therefore, J exhibits the reverse orders, **1** < **2** and **3** < **4**. The calculated intra-ring C–C distance and dihedral angles are given in Supporting Information.

The opposite effect is found for the open form. The reason is that the substitution of a bulkier group increases the intra-ring C–C distance by about 0.065 Å, and the bridging C–C bond lengths also increase. This causes the phenyl rings that are no longer coplanar in CPD to move further away from each other, thereby weakening the magnetic interaction.

The difference between the magnetic properties of **a** and **b** species are not due to the angle Φ, as the average value of Φ always follows the order **b** > **a**. The stronger magnetism in the **b** species is evidently an outcome of the shorter route for the transmission of magnetic interaction and the planarity of the coupler.

The total energy difference between the **a** and **b** species in the triplet state are nearly the same for **1-4**. The ratio J^b/J^a is largest in case of **4**, but species **2** is undoubtedly the best photomagnetic molecule. The ($J^b - J^a$) for substituted dihydropyrenes is clearly much larger than those for the diradicals based on perfluorocyclopentene.

In conclusion, we predict that species **1-4** would be good photomagnetic molecules with J varying by a few cm^{-1} upon irradiation. Besides, the species are all ferromagnetically coupled. The **a** forms (CPD) have very small singlet–triplet energy differences and would be faintly magnetic. The **b** isomers (DDP), however, would retain a fairly considerable magnetic character at a low temperature, and possibly also in an inert matrix.

Supporting Information Available: Table of calculated J at UB3LYP/6-311G(d,p), intra-ring C–C distances, NN/IN-coupler dihedral angles, complete ref 15 and the coordinates of all eight optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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