
Chapter 3

Photoinduced Antiferromagnetic to Ferromagnetic Crossover in Organic Systems

In this chapter we have theoretically designed and investigated the photomagnetic property of azobenzene based diradical systems, where trans isomers convert into corresponding cis forms upon irradiation with light of appropriate wavelength. The coupling constant values have been estimated using broken symmetry approach in DFT framework. In each case, the trans isomer is found to be antiferromagnetic, while the cis form is ferromagnetic in nature. Therefore, photoinduced magnetic crossover from antiferromagnetic to ferromagnetic regime would be observed. This is a new observation in case of the systems of organic origin. Importance of such systems for photomagnetic switches, sensors, high density data storage, spin valves and semiconductor spintronic materials have also been discussed with support from density of state analysis, SOMO-SOMO energy gaps and spin density plots.

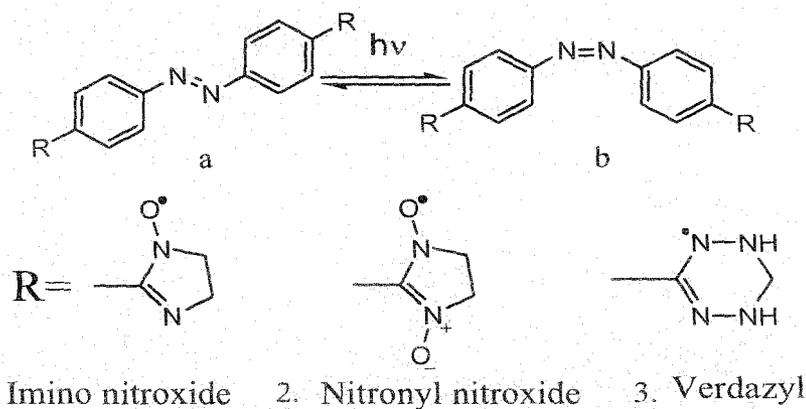
3.1 Introduction

Magnetization reversal in magnetic materials is a fundamental issue in magnetic data storage, occurrence of such process at nanosecond timescale is useful in technological improvements.^{1,2} In current devices, either a high magnetic field or a radiofrequency field in combination with a static field is required to reverse the magnetization, which is difficult to implement.¹ However, photoinduced magnetization reversal is easier to accomplish and likely to find wide applications.³ In organic systems, electron spins can be preserved for longer time scales and distances than in conventional inorganic materials, as a consequence, such materials are more useful in solid state devices.⁴

Photomagnetism in the compounds of organic origin has attracted substantial attention of experimentalists⁵⁻⁹ as well as theoreticians¹⁰ in recent years. In photomagnetic materials, sites with unpaired spins are connected by photochromic couplers, as a result the magnetic behavior changes when exposed to a particular external radiation. Among various photochromic spin couplers diarylethene, azobenzene, and so on have been isolated and characterized by Matsuda and coworkers.⁵⁻⁹ Ali and Datta have investigated theoretically the photomagnetic behavior of nitronyl nitroxide and imino nitroxide derivatives of substituted dihydropyrene.¹⁰ In these studies,⁵⁻¹⁰ it has been observed that magnetic coupling constants change their magnitude when exposed to electromagnetic radiation of right frequency.

Nevertheless, the most notable point is that the systems reported in the above mentioned investigations⁵⁻¹⁰ do not change the sign of the magnetic exchange coupling constant values by photoinduction, i.e., the very nature of magnetic interaction remains unaltered. This leads us to design and investigate systems of organic origin where photoinduced magnetization reversal occurs. To our knowledge, no such behavior in case of organic systems has been reported so far. It is needless to say that designability and ease of functionalization make such systems more suitable for technological applications.¹¹ The importance of materials with magnetization reversal for applications in spintronics has also been discussed by Thirion et al.¹ Inorganic systems in which magnetic crossover takes place are already known.¹² In suitably crafted azobenzene compounds light can reverse the magnetization at nanosecond time scale,¹³ such systems are more useful for applications in modern technology.^{1,2}

Substituted trans azobenzene converts into its cis isomer when exposed to light.¹⁴ Trans azobenzene is more stable than cis azobenzene, as a result, the trans isomer is easier to isolate. Radicals belong to imino nitroxide,^{15,16} nitronyl nitroxide,^{17,18} and verdazyl,^{19,20} families are known for their stability. In this work, we design six diradicals, (1) bis-imino nitroxide, (2) bis-nitronyl nitroxide, and (3) bis-verdazyl coupled through trans azobenzene and their cis isomers, which are illustrated in scheme 3.1, and predict the photoinduced magnetic behavior of them.



Scheme 3.1 Photoinduced antiferromagnetic to ferromagnetic crossover in organic systems

3.2 Theoretical Background

The interaction between two magnetic sites 1 and 2, is generally expressed by Heisenberg spin Hamiltonian

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \quad (3.1)$$

where \hat{S}_1 and \hat{S}_2 are the respective spin angular momentum operators and J is the exchange coupling constant. The positive value of J indicates the ferromagnetic interaction while the negative value indicates the antiferromagnetic interaction between two magnetic sites. For a diradical containing one unpaired electron on each site, J can be represented as

$$E_{(S=1)} - E_{(S=0)} = -2J. \quad (3.2)$$

The single determinantal wave function cannot adequately represent a singlet state of a diradical in the unrestricted formalism, which leads to spin contamination in such types of calculations.

Multiconfigurational approaches are suitable to describe pure spin states in an appropriate manner; however, these methods are resource intensive and not used in this work. Broken symmetry (BS) approach given by Noodleman^{21,22} in DFT framework is an alternative route to evaluate J , which is more useful due to less computational effort. The BS state is a weighted average of high and low spin states, which is not an Eigen state of the spin Hamiltonian. The BS solution is often found to be spin contaminated, and using spin projection technique one can overcome this problem. Many researchers²¹⁻²⁸ have developed different formalisms to evaluate J using unrestricted spin polarized BS solution, depending on the extent of magnetic interaction between two magnetic sites. The equation for evaluating J proposed by Ginsberg,²³ Noodleman²⁴ and Davidson²⁵ is applicable when interaction between two magnetic orbitals is small. On the other hand the expression proposed by Bencini^{26,27} and co workers and Ruitz et al.,²⁸ is applicable for large interaction. Nevertheless, the well known expression given by Yamaguchi²⁹ is applicable for both strong and weak overlap limits. Following the well established^{30,31} and widely applied method,³⁰⁻³⁵ we use the Yamaguchi²⁹ formula for evaluation of J in this work, which is given by

$$J = \frac{(E_{BS} - E_{HS})}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}} \quad (3.3)$$

where E_{BS} , E_{HS} and $\langle S^2 \rangle_{BS}$, $\langle S^2 \rangle_{HS}$ are the energy and average spin square values for corresponding BS and high spin states.

In any photoinduced process estimation of excitation energy is of extreme importance. In case of the photomagnetic couplers under investigation, the transition would take place from bonding-type to antibonding-type of π -orbitals in the azobenzene moiety. This $\pi \rightarrow \pi^*$ transition energy can be calculated through time dependent perturbative approach. Time dependent Hartree-Fock (TDHF) method is known to produce error in prediction of transition energy due to the problem of “near triplet instability”.³⁶ Prediction made by the post Hartree-Fock method are free from such errors, however, calculations involving such methods are computationally expensive and not being employed in this work. On the other hand, in time dependent DFT approach (TDDFT), which is essentially a response theory method, is known to produce less “near triplet instability” error.^{37,38} The TDDFT method to obtain excitation energies is based on

the fact that the dynamic polarizability $\alpha(\omega)$ of a system has poles at frequencies corresponding to its transition energies. If one obtains the frequency dependent polarizability from TDDFT calculations and substitutes in the sum-over-states relation,³⁶

$$\alpha(\omega) = \sum_l \frac{f_l}{\omega_l^2 - \omega^2} \quad (3.4)$$

where ω_l are the excitation frequency and f_l are corresponding oscillator strengths. Here, we calculate $\pi \rightarrow \pi^*$ transition energy in case of substituted trans azobenzenes following TDDFT method described above.

3.3 Results and Discussions

In this work, all the molecular geometries have been optimized using UB3LYP exchange correlation functional with 6-31G(d,p) basis set, with these geometries, single point calculations have been carried out with 6-31G(d,p) and 6-311++G(d,p) basis sets using GAUSSIAN 03W³⁹ quantum chemical package. Optimized structures of the molecules in trans form (1a, 2a, 3a) are planar. The singlet states of these molecules are more stable, i.e., the spins on individual radical sites are antiparallel to each other. In high spin states of planar trans isomers, the polarization of spin through azobenzene coupler is blocked (Figure 3.1);

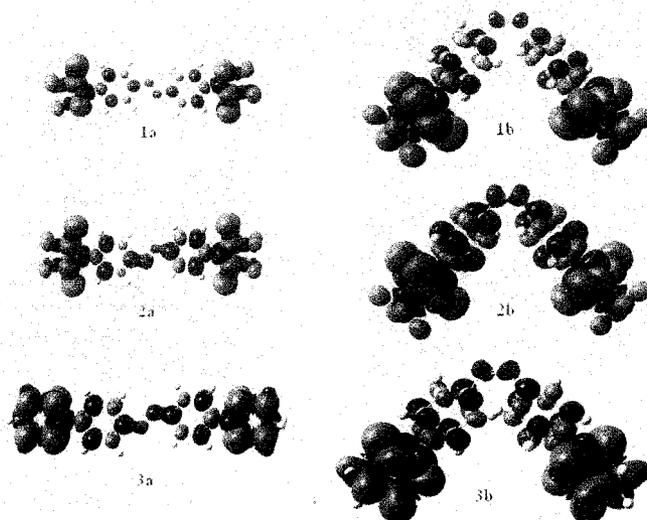


Figure 3.1 Spin density plots for the diradicals 1-3 in their high spin states; green colour indicates up spin and purple colour indicates down spin situations.

as a result, ferromagnetic states are less favourable in trans forms, which is also in agreement with the spin density alternation rule.⁴⁰ The geometries of the cis forms (1b, 2b, 3b) are nonplanar and the corresponding triplet states are more stable, and these molecules are found to be ferromagnetic. Dihedral angle between -N=N- plane and benzene ring in cis forms are 50.89°, 50.42° and 48.27° in 1b, 2b and 3b respectively. The itinerant exchange between unpaired electrons on radical sites through the coupler is forbidden due to their nonplanarity. In the crowded cis forms, the loss of planarity brings two magnetic sites closer in space; this allows the sites to participate in direct exchange. As J (Table 3.1) increases in the series 1b, 2b, 3b, it has been observed that spin density values in the benzene ring of the azobenzene coupler is increasing gradually, this may lead one to conclude that there is itinerant exchange through the π - network. However, itinerant exchange through π -network should eventually lead to antiferromagnetic interaction as seen in the trans forms (geometrical isomers), this is also supported by spin density alternation rule.⁴⁰ Nevertheless, to confirm the mechanism of magnetic interaction, we change the coupler in such a way that itinerant exchange through π -network becomes impossible (Figure 3.2). Here, also we find that there is a change in the spin density in the benzene ring as before, and still the molecules in cis forms are ferromagnetic in nature (J values are in Table 3.2). This observation in turn suggests that the coupling mechanism is direct exchange in case of cis isomers. Thus, change in spin density in the benzene ring is not connected with the mechanism of magnetic interaction in 1b, 2b and 3b, rather unpaired electron density on radical sites are to some extent dispersed on the benzene rings. The direct exchange usually favours the ferromagnetic coupling following the Hund's rule.⁴¹ Kanno et al.⁴² have shown that if the radical sites are close to each other, then the spin alternation is less pronounced, as illustrated by spin density plots (Figure 3.1).

Table 3.1 UB3LYP Level Absolute Energies in au, $\langle S^2 \rangle$, and Exchange Coupling Constants (J in cm^{-1}), Using 6-31G(d,p) and 6-311++G(d,p) Basis set for Diradicals 1-3

| Diradicals | | 6-31G(d,p) | | | 6-311++G(d,p) | | |
|------------|---------|-------------|-----------------------|---------------------|---------------|-----------------------|---------------------|
| | | Energy(au) | $\langle S^2 \rangle$ | $J(\text{cm}^{-1})$ | Energy(au) | $\langle S^2 \rangle$ | $J(\text{cm}^{-1})$ |
| 1a | Triplet | -1174.33982 | 2.040 | -2 | -1174.62103 | 2.041 | -7 |
| | BS | -1174.33983 | 1.042 | | -1174.62106 | 1.039 | |
| 1b | Triplet | -1174.31638 | 2.040 | 29 | -1174.59722 | 2.039 | 15 |
| | BS | -1174.31625 | 1.040 | | -1174.59715 | 1.038 | |
| 2a | Triplet | -1324.67654 | 2.134 | -53 | -1325.01057 | 2.119 | -31 |
| | BS | -1324.67678 | 1.147 | | -1325.01071 | 1.127 | |
| 2b | Triplet | -1324.65324 | 2.133 | 48 | -1324.98705 | 2.116 | 64 |
| | BS | -1324.65302 | 1.137 | | -1324.98676 | 1.122 | |
| 3a | Triplet | -1166.64501 | 2.069 | -20 | -1166.92512 | 2.064 | -47 |
| | BS | -1166.64510 | 1.077 | | -1166.92533 | 1.075 | |
| 3b | Triplet | -1166.64173 | 2.064 | 26 | -1166.92173 | 2.058 | 79 |
| | BS | -1166.64161 | 1.065 | | -1166.92137 | 1.057 | |

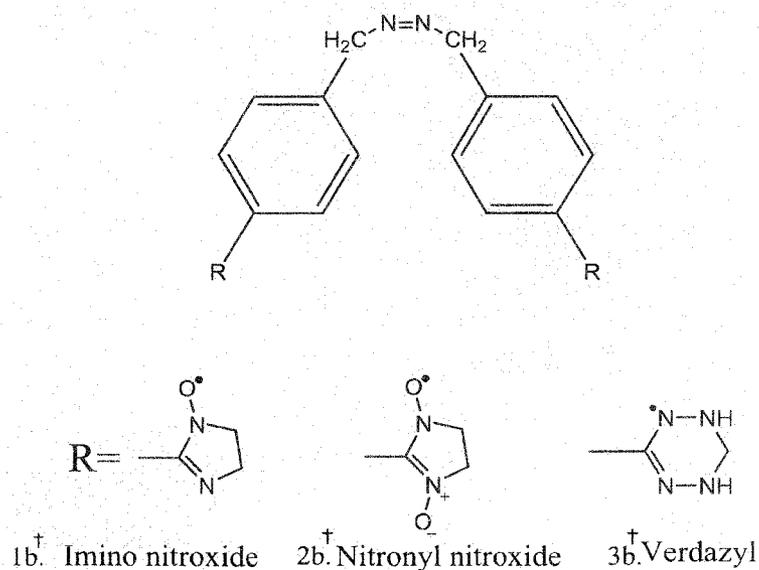


Figure 3.2 Diradicals with breaking pi conjugation.

Table 3.2 UB3LYP Level Absolute Energies in au, $\langle S^2 \rangle$ and Intramolecular Magnetic Exchange Coupling Constants (J , cm^{-1}) Using 6-31G(d,p) Basis Set, for cis Diradicals $1b^\dagger$ - $3b^\dagger$

| Diradicals | | 6-31G(d,p) | | $J(\text{cm}^{-1})$ |
|--------------|---------|---------------|-----------------------|---------------------|
| | | Energy(au) | $\langle S^2 \rangle$ | |
| $1b^\dagger$ | Triplet | -1252.9441239 | 2.04 | 5.38 |
| | BS | -1252.9440993 | 1.04 | |
| $2b^\dagger$ | Triplet | -1403.2808586 | 2.13 | 0.7 |
| | BS | -1403.2808554 | 1.13 | |
| $3b^\dagger$ | Triplet | -1245.2694019 | 2.06 | 57.47 |
| | BS | -1245.2691399 | 1.06 | |

We have calculated the value of J for all three systems in cis and trans forms. The energy and $\langle S^2 \rangle$ values for both triplet and BS states are reported in Table 3.1. Though the magnitude of J does change to some extent with different basis sets, the sign of it remains unchanged. So it is reasonable to accept that the magnetic behavior predicted by our investigation is authentic, and more reliable J values are those obtained with higher basis set. We observe that the J values of all three species in trans forms are negative, but in case of cis forms, J values come out as positive. Thus, a magnetic crossover from antiferro to ferro would be noticed in all three cases when the corresponding trans isomers are subjected to isomerization induced by appropriate external electromagnetic radiation. Ferromagnetic systems behave as bulk paramagnets above a temperature of J/k_B (where k_B is the Boltzmann constant), as a result, such systems would be more useful for practical applications below J/k_B .

Table 3.3 Energy of SOMOs in au and their Differences in eV at the UB3LYP Level Using 6-311++G(d,p) Basis Set for Diradicals 1-3

| Diradicals | $E_S(1)$, au | $E_S(2)$, au | ΔE_{SS} , eV |
|------------|---------------|---------------|----------------------|
| 1a | -0.21806 | -0.14240 | 0.21 |
| 1b | -0.19466 | -0.19466 | 0.00 |
| 2a | -0.18143 | -0.12288 | 0.20 |
| 2b | -0.18560 | -0.18551 | 0.0025 |
| 3a | -0.22648 | -0.15580 | 0.22 |
| 3b | -0.21057 | -0.21054 | 0.0008 |

Hoffmann⁴³ proposed that if the energy difference between two consecutive SOMOs is less than 1.5eV then to maximize the electrostatic repulsion between two degenerate orbitals, the parallel orientation of spins occurs. Constantinides et al.⁴⁴ showed that when the $\Delta E_{SS} > 1.3$ eV, antiparallel orientation of spins results, i.e., singlet state is the ground state. Zhang et al.⁴⁵ have shown that the critical value of ΔE_{SS} is different in different cases. Nevertheless, in our investigation the ΔE_{SS} value is greater for trans isomers than the corresponding cis forms, i.e., the ΔE_{SS} value is less for ferromagnetic interaction, which are given in Table 3.3.

Table 3.4 The π - π^* transition energy values in trans diradicals at UB3LYP(TDDFT) level using 6-31G(d,p) basis set

| Diradicals | E_{π} , au | E_{π^*} , au | Transition Energy(eV) |
|------------|----------------|------------------|-----------------------|
| 1a | -0.21807 | -0.09716 | 3.29 |
| 2a | -0.18143 | -0.06179 | 3.26 |
| 3a | -0.22644 | -0.09294 | 3.63 |

The photoisomerization reactions from a to b are initiated in each case by a π - π^* transition; therefore, we have calculated the transition energies in case of all three trans isomers in their ground states. The experimentally observed π - π^* transition energy of trans azobenzene in gas phase is 2.82 eV.⁴⁶ By DFT calculations, Fliegl et al.⁴⁷ have found that the transition energy of trans azobenzene is 3.29 eV. Results obtained by TDDFT method known to become less reliable for open shell molecules due to spin contamination.⁴⁸ Nevertheless, using TDDFT method, Radziszewski et al.⁴⁹ have calculated the transition energies for phenoxyl radical, Rinkevicius et al.⁴⁸ have investigated phenoxyl radical, tetrathiofulvalene cation radical and naphthalene cation radical, and Hirata et al.⁵⁰ have calculated the transition energies for aromatic hydrocarbon radical cations. They found that the calculated excitation energies are in close agreement with the experimental values. Thus, it has been logically put that the exceptional performance of the unrestricted TDDFT method for open-shell molecules are validated only from computational experience and lacks a solid theoretical background.⁴⁸ In our TDDFT calculations, we find that the transition energies for radical substituted trans azobenzenes in their ground states (Table 3.4), which are open-shell singlets, and the results obtained are in good

agreement with the previous calculations on azobenzene.^{46,47} That indicates, upon irradiation with electromagnetic radiation of 340 – 380 nm, all three trans isomers would be converted into the corresponding cis forms through photoisomerization process. As a result, magnetization reversal from antiferromagnetic to ferromagnetic regime would be observed.

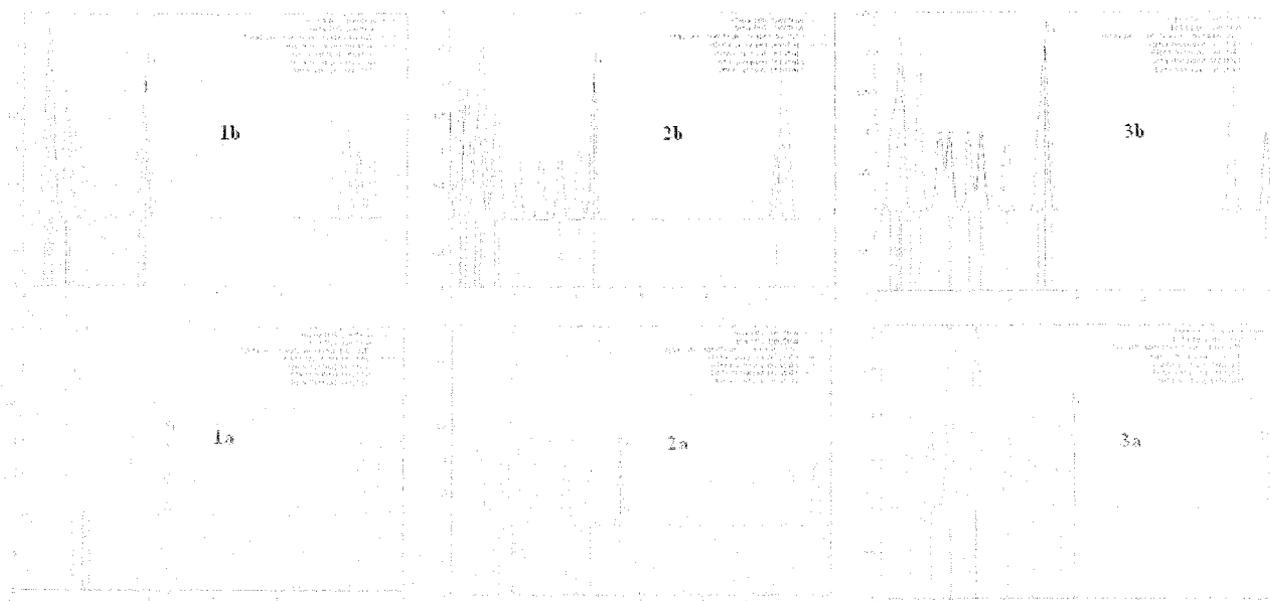


Figure 3.3 Density of states (DOS) vs. energy plots for the diradicals, corresponding Fermi levels are indicated as E_F .

The conductance through the molecule in ferromagnetic configuration is known to be much larger than in the antiferromagnetic arrangement.⁵¹ From the spin density plots (Figure 3.1), it is clear that the up spin density on both the radical sites are intense. When bias is applied, spin up electrons traverse the molecule from one magnetic site to another, while spin down electrons are blocked.⁵¹ The density of states (DOS) plots are evaluated from the Gaussian 03W output file of population analysis fitted to a Gaussian distribution with a full-width at half-maximum of 0.1 using Gausssum 2.1 software,⁵² which is being used widely by the scientific community.⁵³⁻⁵⁵ Calculated density of states (DOS) for ferromagnetic cis forms show that the spins are highly polarized at Fermi level (Figure 3.3), whereas in case of trans isomers there is no spin polarization (see supplementary information). Thus, the cis forms show spin valve effect.⁵¹ Another important point comes from the DOS analysis that the difference between DOS of up and down spins at Fermi level of ferromagnetic cis forms (1b 1.733; 2b 1.775; 3b 1.951) is proportional to the magnetic exchange coupling constant, hence ferromagnetic organic molecules

with higher J value will be more useful for technological applications. From the DOS plot of 3b it is noted that one beta HOMO resides 0.087 eV above the Fermi energy. This observation implies a non-Aufbau occupation of the molecular orbitals in this case. Westcott et al. show experimentally as well as theoretically that this non-Aufbau behavior in occasional cases is strongly favored by the electron-electron repulsion energies, regardless of electron relaxation energies with ionization, correlation energies, exchange energies, or other contributions.⁵⁶ Franceschetti and Zunger opine that the Aufbau principle can be violated due to a delicate balance between promotion energies, Coulomb repulsions, and exchange interactions.⁵⁷ The calculated HOMO-LUMO gaps of the molecules fall in the range 2.52 – 3.36 eV (1a 3.08 eV, 1b 3.36 eV; 2a 2.52 eV, 2b 2.83 eV; 3a 2.90 eV, 3b 3.31 eV) which is in the semiconducting region; as a result, ferromagnetic cis forms are active semiconductor spintronic molecules. The trans isomers are not spin polarized, however when isomerised by photoinduction, spin polarisation is observed. Thus, the molecular systems investigated here exhibit photoinduced spintronic behavior.

3.4 Conclusions

The phenomenon of photoinduced magnetization reversal is promising in the field of information storage devices, spintronics applications, photomagnetic switches, sensors, spin valves etc. Organic systems exhibiting such behavior are more attractive for these purposes. In this work, we predict some organic systems where magnetic crossover takes place upon irradiation with light. In all three systems investigated, antiferromagnetic trans isomers turn into ferromagnetic cis forms when exposed to light in the wavelength range 340 – 380 nm. The extent of magnetic interaction in all six molecules have been quantified in terms of the coupling constant (J) through broken symmetry approach in the framework of density functional theory. Analysis of density of states shows intense spin polarization in ferromagnetic cis isomers, which supports the usefulness of such systems for above mentioned applications. In ferromagnetic cis forms, difference in DOS of up and down spins at Fermi level is directly proportional to J values. Therefore, a system with higher value of exchange coupling constant would be more useful as spintronic material.

3.5 References

1. Thirion, C.; Wernsdorfer, W.; Maily, D. *Nat. Mater.* **2003**, *2*, 524.
2. Bauer, M.; Fassbender, J.; Hillebrands, B.; Stamps, R. L. *Phys. Rev. B* **2000**, *61*, 3410.
3. Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704.
4. Coronado, E.; Epstein, A. J. *J. Mater. Chem.* **2009**, *19*, 1670.
5. Matsuda, K.; Matsuo, M.; Irie, M. *J. Org. Chem.* **2001**, *66*, 8799.
6. Tanifuji, N.; Irie, M.; Matsuda, K. *J. Am. Chem. Soc.* **2005**, *127*, 13344.
7. Tanifuji, N.; Irie, M.; Matsuda, K. *Org. Lett.* **2005**, *7*, 3777.
8. Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195.
9. Hamachi, K.; Matsuda, K.; Itoh, T. Iwamura, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2937.
10. Ali, Md. E.; Datta, S. N. *J. Phys. Chem. A* **2006**, *110*, 10525.
11. Dediu, V. A.; Hueso, L. E.; Bergenti, I.; Taliani, C. *Nat. Mater.* **2009**, *8*, 707.
12. Gütllich, P.; Garcia, Y.; Woike, T. *Coord. Chem. Rev.* **2001**, *219*, 839.
13. Chen, E.; Kumita, J. R.; Woolley, G. A.; Kliger, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 12443.
14. Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915.
15. Lescope, C.; Luneau, D.; Rey, P.; Bussiere, G.; Reber, C. *Inorg. Chem.* **2002**, *41*, 5566.
16. Oshio, H.; Watanabe, T.; Ohto, A.; Ito, T. *Inorg. Chem.* **1997**, *36*, 1608.
17. Romero, F. M.; Ziessel, R.; Bonnet, M.; Pontillon, Y.; Ressouche, E.; Schweizer, J.; Delley, B.; Grand, A.; Paulsen, C. *J. Am. Chem. Soc.* **2000**, *122*, 1298.
18. Caneschi, A.; Ferraro, F.; Gatteschi, D.; Lirzin, A. L.; Rentschler, E. *Inorg. Chim. Acta* **1995**, *235*, 159.
19. Gilroy, J. B.; McKinnon, S. D. J.; Kennepohl, P.; Zsombor, M. S.; Ferguson, M. J.; Thompson, L. K.; Hicks, R. G. *J. Org. Chem.* **2007**, *72*, 8062.
20. Lemaire, M. T.; Barclay, T. M.; Thompson, L. K.; Hicks, R. G. *Inorg. Chim. Acta* **2006**, *359*, 2616.
21. Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737.
22. Noodleman, L.; Baerends, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 2316.
23. Ginsberg, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 111.
24. Noodleman, L.; Peng, C. Y.; Case, D. A.; Mouesca, J. M. *Coord. Chem. Rev.* **1995**, *144*, 199.
25. Noodleman, L.; Davidson, E. R. *Chem. Phys.* **1986**, *109*, 131.

26. Bencini, A.; Totti, F.; Daul, C. A.; Doclo, K.; Fantucci, P.; Barone, V. *Inorg. Chem.* **1997**, *36*, 5022.
27. Bencini, A.; Gatteschi, D.; Totti, F.; Sanz, D. N.; McCleverty, J. A.; Ward, M. D. *J. Phys. Chem. A* **1998**, *102*, 10545.
28. Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391.
29. Yamaguchi, K.; Takahara, Y.; Fueno, T.; Nasu, K. *Jpn. J. Appl. Phys.* **1987**, *26*, L1362.
30. Ali, Md. E.; Datta, S. N. *J. Phys. Chem. A* **2006**, *110*, 2776.
31. Ali, Md. E.; Datta, S. N. *J. Phys. Chem. A* **2006**, *110*, 13232.
32. Polo, V.; Alberola, A.; Andres, J.; Anthony, J.; Pilkington, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 857.
33. Bhattacharya D.; Misra, A. *J. Phys. Chem. A* **2009**, *113*, 5470.
34. Paul, S.; Misra, A. *J. Mol. Str (THEOCHEM)* **2009**, *37*, 970.
35. Paul, S.; Misra, A. *J. Mol. Str (THEOCHEM)* **2009**, *156*, 895.
36. Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439.
37. Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454.
38. Bauernschmitt, R.; Ahlrichs, R. *J. Chem. Phys.* **1996**, *104*, 9047.
39. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J. J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Ayala, P. Y.; Morokuma, K.; Voth, A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. GAUSSIAN 03W (Revision D.01), Gaussian, Inc.: Wallingford, CT, (2004).
40. Trindle, C.; Datta, S. N. *Int. J. Quantum. Chem.* **1996**, *57*, 781.
41. Sinha, B.; Ramasesha, S. *Phys. Rev. B* **1993**, *48*, 16410.

42. Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847.
43. Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.
44. Constantinides, C. P.; Koutentis, P. A.; Schatz, J. *J. Am. Chem. Soc.* **2004**, *126*, 16232.
45. Zhang, G.; Li, S.; Jiang, Y. *J. Phys. Chem. A* **2003**, *107*, 5573.
46. Anderson, J. A.; Petterson, R.; Tegner, L. *J. Photochem.* **1982**, *20*, 17.
47. Fliegl, H.; Köhn, A.; Hättig, C. Ahlrichs, R. *J. Am. Chem. Soc.* **2003**, *125*, 9821.
48. Rinkevicius, Z.; Tunell, I.; Salek, P.; Vahtras, O.; Agren, H. *J. Chem. Phys.* **2003**, *119*, 34.
49. Radziszewski, J. G.; Gil, M.; Gorski, A.; Larsen, J. S.; Waluk, J.; Mroz, B. *J. Chem. Phys.* **2001**, *115*, 9733.
50. Hirata, S.; Lee, T. J.; Gordon, M. H. *J. Chem. Phys.* **1999**, *111*, 8904.
51. Liu, R.; Ke, S. H.; Baranger, H.U.; Yang, W. *Nano Lett.* **2005**, *5*, 1959.
52. O'Boyle, N. M.; Tenderholt, A. L.; Langner, K. M. *J. Comput. Chem.* **2008**, *29*, 839.
53. Herlem, G.; Lakard, B. *J. Chem. Phys.* **2004**, *120*, 9376.
54. Vyas, S.; Hadad, C. M.; Modarelli, D. A. *J. Phys. Chem. A* **2008**, *112*, 6533.
55. Craig, I. M.; Duong, H. M.; Wudl, F.; Schwartz, B. J. *Chem. Phys. Lett.* **2009**, *477*, 319.
56. Westcott, B. L.; Gruhn, N. E.; Michelsen, L. J.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **2000**, *122*, 8083.
57. Franceschetti, A.; Zunger, A. *Europhys. Lett.* **2000**, *50*, 243.