Chapter 1

Molecules Manifesting Magnetic Behavior

A general introduction of molecules manifesting magnetic behavior is presented in this chapter. A detailed literature survey along with the objectives of this thesis is systematically stated in this chapter.

1.1. Introduction

In recent years, research work on magnetism and magnetic materials has gained a tremendous momentum. Particularly synthetic magnetic molecules both of organic and inorganic origin have drawn a huge attention of researchers worldwide. One can have an idea of the volume of work that has already been done on this subject by the result of a Google search. Such a search in September 2012 gives around 18,100,000 http links in just 0.34 seconds with a keyword "magnetic molecules". Searching with a keyword "synthetic magnetic molecules" gave around 19,900,000 links on the subject. Several books have also been written on this topic.[1] A closer look on these articles reveals that the materials containing magnetic molecules with inorganic origin have some historical importance as many of the early magnetic materials is basically inorganic in nature. Nevertheless, in past few decades organic magnetic molecules have emerged as one of the most interesting topics in this line of research.[2] This field of study has numerous technological and biological applications. In a broader perspective the present thesis deals with the design, characterisation and application of molecular magnets of organic origin and in particular, of organic diradical systems. This chapter includes the background, objective and justification of the present research work.

1.2. Types of Magnetism

Although the initial discovery of magnetic phenomenon is not known; however, the word magnet is derived from the name of Magnesia province of Thessalia, where magnetite was found abundantly.[3] Depending on magnetic behavior, solids can be classified in different categories; say, diamagnetic, paramagnetic, ferromagnetic (FM), antiferromagnetic (AFM), ferrimagnetic, metamagnetic and so on. The genesis of these different types is due to the diverse coupling arrangements of electronic spin angular momentum in molecular and supramolecular arrays. So far, the most precious and rare class of materials from both theoretical and experimental point of view are ferromagnets. According to the first principle of magnetism, if spontaneous coupling between two equal spin moments occurs in parallel fashion then ferromagnetism arises leading to permanent magnetization. On the other hand, when two unpaired but equal spin moments are coupled in antiparallel fashion avoiding spin pairing then antiferromagnetism arises, leading to the lowering of magnetism. Both ferromagnetic and antiferromagnetic substances behave like paramagnetic substances beyond a certain temperature called Curie temperature (for FM) or Neel Temperature (for AFM) respectively. Paramagnetic substances show spontaneous magnetization under an external magnetic field but they loose that property in absence of such field. Diamagnetic substances contain spin paired electrons and do not show spontaneous magnetization under an external magnetic field. In ferrimagnetism unequal spin moments couple to give net magnetization. All these things are nicely discussed in different articles.[4]

1.3. Design, Characterisation and Application

Molecular designing is a creative process or strategy of finding new tailor made molecules having requisite characteristics. This is frequently done either by scratching or by creating intended variations in the known structures. Since 1960s the synthetic chemists are having continuous interest for designing of high spin magnetic molecules such as organic ferromagnets,[5] as ferromagnetic interactions are preconditioned to most attractive magnetic properties.[6] Thus the capability to design molecules or crystals with ferromagnetic exchanges in a balanced manner is significant and equally intellectually challenging.[7]

To design a molecule with desired magnetic properties it is essential to characterise the molecule with available theoretical tools. In characterising the magnetic molecules one must reveal its magnetic nature (ferro or antiferro) and its extent of magnetism. Magnetic systems are best characterised by magnetic exchange coupling constant (J) values. A positive sign of J, in which a situation of parallel spin is essential, is used to indicate a ferromagnetic interaction, whereas an antiferromagnetic interaction is indicated by a negative value, where a state of antiparallel spin is favored.[1] The high positive value of J indicates that the magnetic molecule is strongly ferromagnetic whereas less ferromagnetic character is observed for its low positive value.

It's being extremely essential to observe the applicability either in technologies or in biomedical sciences of the magnetic molecules after their design and characterisation.

Molecule based magnets are a class of compounds capable of showing interesting magnetic behavior. The first synthesis and characterisation of molecule-based magnet, a diethyldithiocarbamate-Fe(III) chloride complex, was credited to Wickman and co-workers.[8] Low density, mechanical flexibility, low-temperature processability, solubility, low environmental contamination, biocompatibility, high remanent magnetizations, low magnetic anisotropy, transparency, semiconducting properties and so on make these molecules suitable for the uses in different purpose.[4(b)] On the other hand, in biomedical field of research magnetic molecules can provide new opportunities including the improvement of magnetic resonance imaging, magnetic hyperthermia for cancerous cell and also in site specific drug delivery.[9]

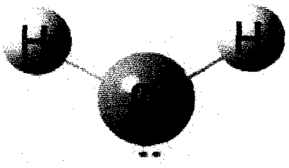
1.4. Background: The Essence of Interest

Magnetism in molecules has given rise to newer aspects of various interesting research areas both in the filed of Physics and Chemistry. In numerous studies the results are radiating. In the following subsections few gems are collected from the sea of knowledge which suit best to the present thesis work.

1.4.1. Molecule Based Magnetism

To be an effective building block of a synthetic magnetic molecule, the constituting magnetic sites must be stable enough. They can be prepared, isolated, and characterised with ease. It is known that stable organic radicals in pure state are the most suitable candidates for the building of various magnetically active substances. More specifically, stable diradical based organic ferromagnets are of primary interest to study the molecule based magnetism.[2] According to Borden and Davidson a diradical is "a molecule in which two electrons occupy a degenerate or nearly degenerate pair of orbitals".[10] In a more lucid version, diradical is a molecular species with two radical centers. One point should be noted here that there are two types of non-kekule diradical molecules, *disjoint* and *non-disjoint* type. This classification is based on the shape of their two non-bonding molecular orbitals (NBMOs). In case of non-disjoint molecules both NBMOs have electron density at the same atom; whereas, in the dis-

-joint molecules electron density resides on different atoms. Following Hund's rule, unpaired electrons in non-disjoint molecules are preferred to be in parallel orientation resulting in a triplet ground state. However, in case of disjoint molecules, the relative stability of the singlet ground state to the triplet ground state will be nearly equal even electrons can have anti parallel orientation resulting in a singlet ground state. The simplest examples of diradical is methylene $(CH_2)^{\cdot\cdot}$, but methylene **(1)** (Figure 1.1) is very reactive and unstable in nature.[11]



(1)

Figure 1.1. The simplest methylene diradical (**1**) (ref. 11).

1.4.2. Searching of Stable Radicals as Building Blocks for Magnetic Molecules

In molecular magnetochemistry nitroxide radical family is playing a prime role since long.[12] The first reported stable organic nitroxyl based ferromagnetic species was β-crystal phase of *para*-nitrophenyl nitronyl nitroxide (Figure 1.2). After its discovery by Kinosita and co-workers[13] in 1991, nitronyl nitroxide based diradicals with different couplers have been experimentally investigated and characterised by many group of researchers.[12] Zeissel *et al.* have extensively studied nitronyl nitroxide diradicals with ethylene coupler.[14]

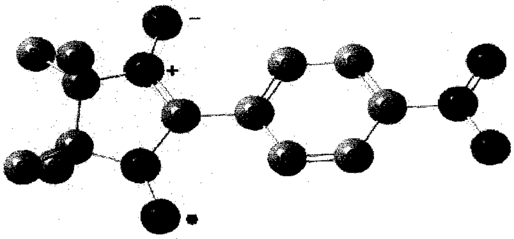
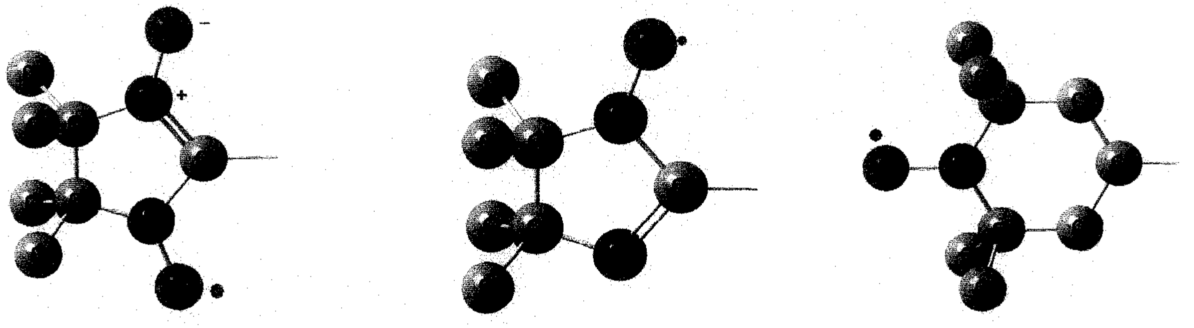


Figure 1.2. The *para*-nitrophenyl nitronyl nitroxide (ref. 13). Hydrogens are excluded for clarity.

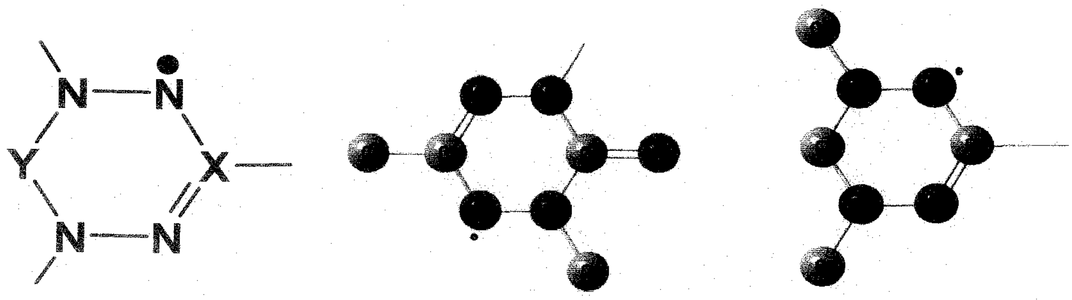
The excellent stability of nitronyl nitroxides (NN), imino nitroxides (IN), (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) (Figure 1.3) has made them mesmerizing to both synthetic and theoretical chemists.[13-19] The presence of strongly delocalized unpaired electrons in NN and IN make them perfect ferromagnetic precursor. Nonetheless, their excellent stability, lucid method of preparation, flexibility in coordination, and capacity to generate tailor made magnetic properties are the reasons for their wide study.[13-17] On the other hand, diradicals containing TEMPO as one of the radical centers have been synthesized and characterised.[18] TEMPO is well known class of stable organic radical which can be used in preparing molecule based magnetic materials, organomagnetic systems and so on. Charge transfer complexes, photo responsive devices can also be developed from TEMPO radicals.[19] Nonetheless; besides nitroxide family of radicals only few radical classes are used in preparing diradical based magnetic molecules due to their suitability in preparation, isolation, and characterisation. Following the trend, investigations were carried out to synthesize other radical species such as verdazyl, tetrathiafulvalene (TTF) etc. (Figure 1.4) which are suitable candidates for preparing organic diradical based ferromagnets at relatively higher temperature.[20-24]



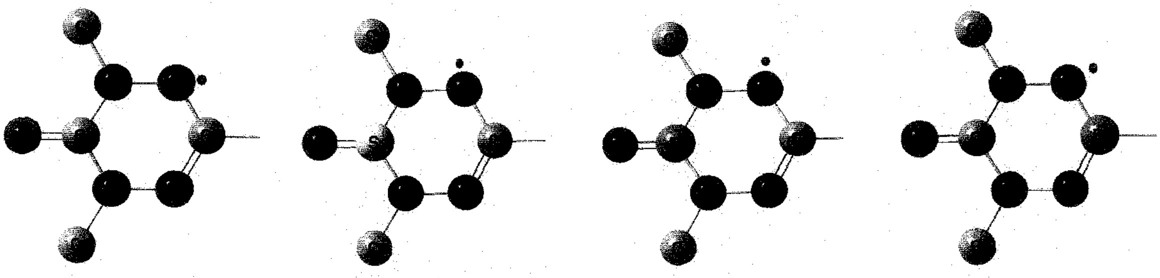
(NN-radical) (IN-radical) (TEMPO-radical)

Figure 1.3. NN, IN and TEMPO radicals, the building blocks of diradicals based magnetic molecules (ref. 28). Hydrogens are omitted for picture clarity.

The Verdazyl radical was discovered by Kuhn and Trischmann in early 1960s.[20] In recent years, a lot of effort is given to synthesize and characterise the "so-called" heteroverdazyl radicals incorporating different hetero atoms in place of nitrogen and carbon ring atoms at X or Y position or the both.[25] The most common heteroverdazyls are oxoverdazyl (OV), thioverdazyl (TV) and phosphaverdazyl (PV) and the last one is generally considered as the inorganic analogue of verdazyl radical (Figure 1.4). In the later case, spin leakage is prominent due to mixing of σ- and π-systems.[26] Spin leakage is the phenomena where the spin density of a particular atom at a definite site becomes lower than the expected spin density value. The spin leakage has an insightful effect on magnetic behavior of the concerned diradical. Different research groups have established the method of synthesis of the above mentioned different types of verdazyl radicals.[25–28]



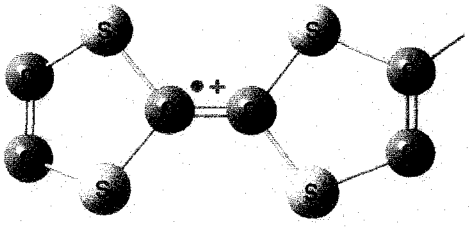
Heteroverdazyl radical   OV (N-linked)   Verdazyl (C-linked)



OV (C-linked)   TV (C-linked)   PV-Type I (C-linked)   PV-Type II (P-linked)

Figure 1.4. General schematic representation of heteroverdazyl radical, upon substitution of different atoms on X and Y positions yields different verdazyl analogues, such as OV (N-linked), Verdazyl (C-linked), OV (C-linked), TV (C-linked), PV-Type-I (C-linked), PV-Type-II (P-linked) which act as radical centers in different diradicals (ref. 28). Hydrogens are excluded for clarity.

Lahti and his co-workers have prepared azide substituted verdazyles.[29] Synthesis of carboxyl substituted verdazyl complexes of Ni(II) and Co(II) have been carried out in aqueous system as carboxyl substituted verdazyl radicals are highly soluble in water.[30] On the other hand, TTF has shown through bond and through space intramolecular ferromagnetic exchange interactions (Figure 1.5). TTF has also been used as building blocks for magnetic molecules having been used as supramolecular chemistry, molecular memories, organic conductors and so on.[31]

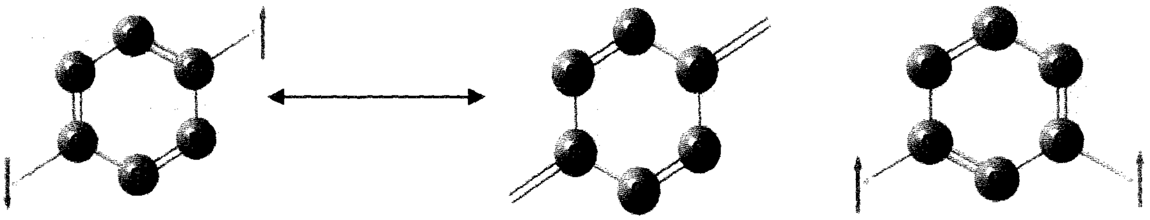


(TTF-radical cation)

Figure 1.5. TTF radical moieties used to develop different magnetic molecules (ref. 31). Hydrogens are excluded for simplicity.

1.5. Qualitative Methods: Ground State of the Diradical Based Magnetic Molecules

Qualitative prediction of the ground state of a magnetic molecule is a state of the art technique. Several methods are available for qualitative prediction of the ground spin state of diradicals. The first successful method of predicting the ground state of magnetic molecules was made by Longuet-Higgins.[32(a)] The method says, if there are total X number of carbon atoms with total Y maximum number of possible double bond then the number NBMOs can be calculated as $n = (X - 2Y)$. As an example, we predict the ground spin state of *para*-benzoquinodimethan (**2**). In case of *para*-benzoquinodimethan maximum four double bonds are possible. Hence the number of NBMOs is zero resulting in an antiferromagnetic interaction. Similarly for *meta*-benzoquinodimethan (**3**), there are two NBMOs and from Hund's rule, a triplet (S=1) ground state is estimated[32(b)] (Figure 1.6).

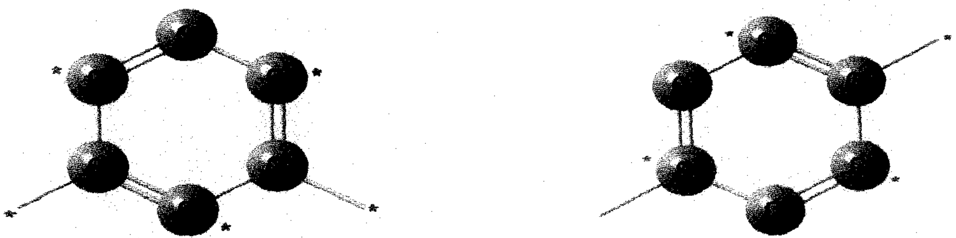


(2) (3)

para- benzoquinodimethan (S= 0) *meta*-benzoquinodimethan (S = 1)

Figure 1.6. Demonstration of ground spins state of *para-* (**2**) and *meta*-benzoquinodimethan (**3**) [ref 32(a)]. Hydrogen atoms are not shown in the picture for simplicity.

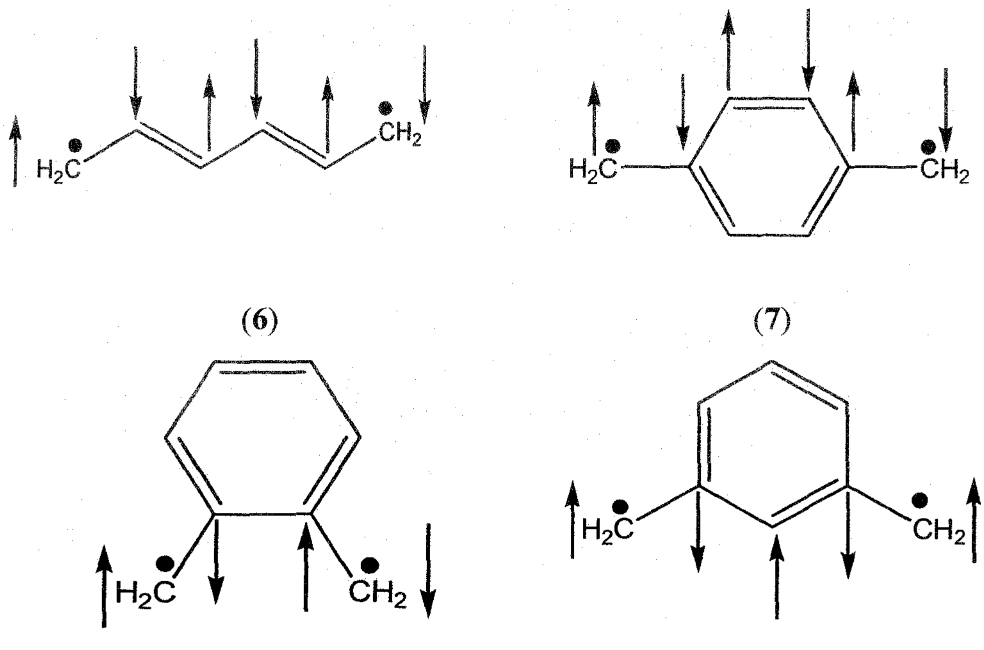
Another simple method was proposed by Ovchinnikov considering valence-bond formalism for planar alternate hydrocarbons.[32(c)] The method suggests that if the number of starred (K) and unstarred (K*) carbon atoms are not equal then the ground state spin S=|K*–K|/2 and the value is always nonzero. Applying the rule to previous examples of *meta-* (**4**) and *para-* (**5**) benzoquinodimethan one concludes that *meta* and *para* isomers have triplet and singlet ground spin states respectively (Figure 1.7). This model was further applied for the simplest case of trimethylenemethane (TMM) diradical, and triplet ground state was predicted and in addition confirmed by the experiment.[33]



(4) (5)

Figure 1.7. Determination of the ground spins state of *meta-* (**4**) and *para-* (**5**) benzoquinodimethan using starred/unstarred model by Ovchinnikov [ref. 32(c)]. Hydrogen atoms are not shown in the picture for simplicity.

The rule of spin alternation has been successfully explained and demonstrated in UHF treatment by Trindle et al.[32(h,i)] Heuristically, in a planar π-conjugated system the spin densities of a particular atom prefers opposite signs to that of its adjacent atoms. That is, the polarization of spins will follow an alternate $\alpha\beta\alpha\beta\alpha\beta$ pattern. The spin density alternation rule efficiently predicts the nature of exchange coupling interaction in almost every case (Figure 1.8). This rule states that, if the number of bonds through the coupler is odd in the coupling path, the exchange pattern is antiferromagnetic, whereas, exchange pattern is ferromagnetic if the number of bonds in the coupler is even between two π-conjugated magnetic sites. In the following figure, by using the rule, one can easily find the proper ground state of these diradicals with butadiene (**6**), *para*-phenylene (**7**), *ortho*-phenylene (**8**), and *meta*-phenylene (**9**) as couplers. They have antiferromagnetic ground state as the spin-spin coupling is transmitted through odd number of bonds. However, for the *meta*-phenylene (**9**) coupled diradicals ferromagnetic ground state is observed as the spin coupling is propagated through even number of bonds.



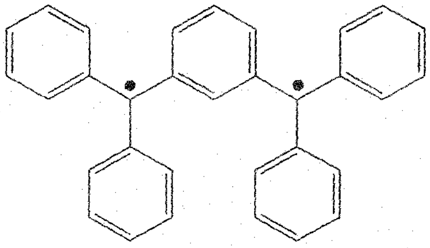
(**6**) (**7**)

(**8**) (**9**)

Figure 1.8. Spin alternation rule demonstrating the ground state ferromagnetic nature of *meta*-phenylene (**9**) coupled diradical with net two up spins in two magnetic centers; whereas the linear conjugated π-polyene (**6**), *para*-phenylene (**7**) and *ortho*-phenylene (**8**) coupled diradicals are antiferromagnetic in nature [ref. 32(h,i)].

1.6. Different Diradicals

In diradicals the magnetism arises mainly due to intramolecular interactions between two magnetic sites. The credit to synthesize and characterise the first stable ferromagnetic diradical (**10**) was accounted for Schlenk (Figure 1.9) in 1915.[34] In a diradical generally the spin polarization and spin delocalization play the major role for determining the magnetic coupling. A large number of works have been executed on this issue.[35,36] On the other hand, a great deal of theoretical works have also been done on organic molecule based magnetism. It must be noted that the first theoretical work to predict the high spin ground state had been attributed to McConnell.[5(a)]

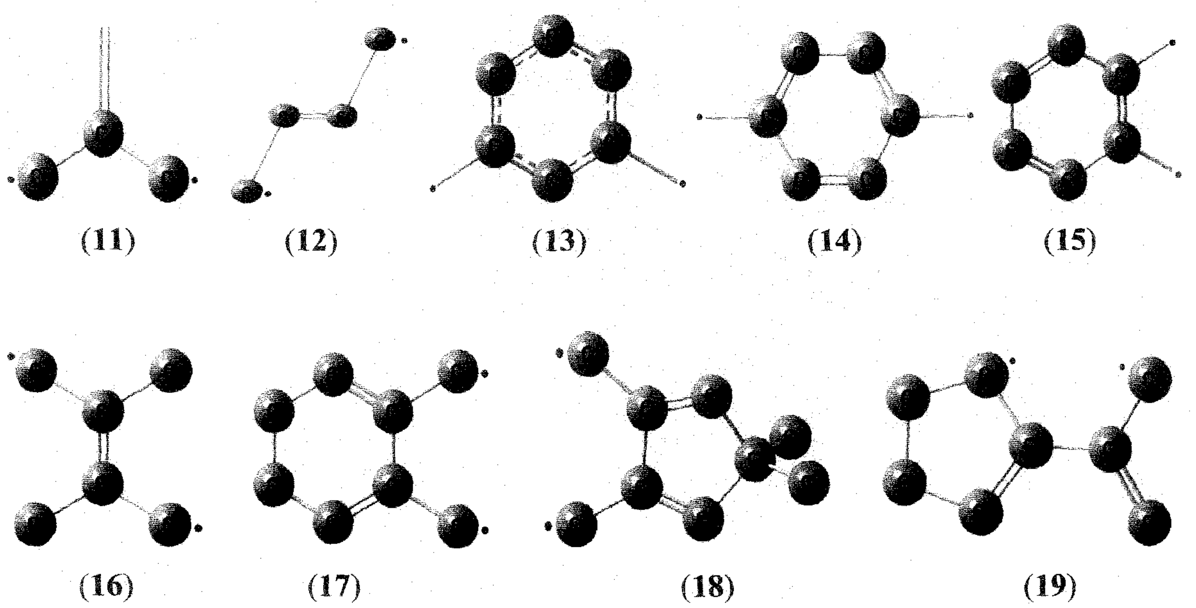


(10)

Figure 1.9. The Schlenk diradical (**10**) which is stable and remain in triplet ground state (ref. 34).

1.6.1. Simple Hydrocarbon Diradicals

Molecular topology and spin alignment in some simple hydrocarbon diradicals are interesting to understand their nature of magnetism in their ground state. Dowd[33] have first reported one of the most simple π-conjugated hydrocarbon diradical named trimethylenemethane diradical (**11**). This diradical has triplet ground state which can be proved both theoretically and experimentally. However, when two methyl radicals are attached in two different ends of ethylene (**12**), which is essentially a butadiene moiety, antiferromagnetism is observed. Benzene containing diradical *meta*-benzoquinodimethane (**13**) is strongly ferromagnetically coupled, whereas its *para* and *ortho* isomers (**14,15**) are antiferromagnetically coupled. It is to be noted here that ferromagnetic coupling is observed in non-kekulé molecules having non-disjoint nature,[37] that is, these MO's would be non-orthogonal and have overlapped at one or two atomic sites. There are other molecular structures where the simple hydrocarbon diradicals are disjoint in nature. Tetramethylene ethane (TME) (**16**), 2,3-bis(methylene)-1,3-cyclohexadiene (**17**), 2,2-dimethyl-4,5-bis(methylene)-1,3-cyclopentadiene (**18**), and 2-(1-methyleneethenly)cyclopentenyl (**19**) are such disjoint diradicals having triplet ground state (Figure 1.10). This fact has been attributed to the zero overlap between perpendicular π-systems. This phenomenon suggests that high spin ground state is also obtained in *para*-phenylene system when doped.[33]



(11) **(12)** **(13)** **(14)** **(15)**

(16) **(17)** **(18)** **(19)**

Figure 1.10. Molecular topology and spin coupling of some hydrocarbon diradicals (**11-19**). Hydrogen atoms are not shown in the picture for simplicity (ref. 33,37).

1.6.2. Biphenyl and Tetraphenyl Diradicals

Biphenyls have important uses in chemical synthesis and these are the potential linkers used as couplers for designing high spin organic molecules. Diradical species has been prepared and studied in frozen solutions with 3,3' and 3,4' biphenyl as spin coupling units.[38] Diradical (**20**) possessing 3,3'-biphenyl in its coupling unit, has antiferromagnetic ground state, whereas, its other isomer (**21**) has ferromagnetic ground state with 3,4'-biphenyl as coupling unit. This isomer (**21**) can be easily handled in low temperature in laboratory. However, there are examples where two different exchange coupling pathways (ECPs) are possible depending upon the structure of the coupler. A molecule having one ECP with 3,3'-biphenyl units (**22**) has the half exchange coupling constants in magnitude than the molecules with two ECPs with 3,3'-biphenyl units (**23**)[39] (Figure 1.11). If there are multiple parallel ECPs in a ferromagnetic coupled diradicals the magnetic exchange can be controlled with the increase or decrease of ECPs.

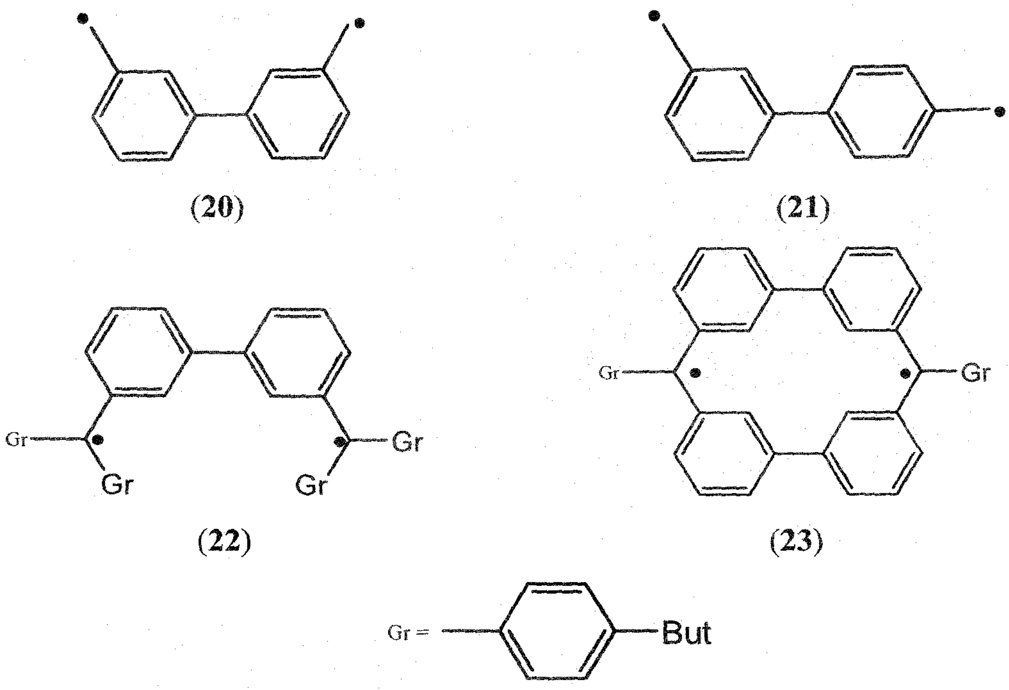
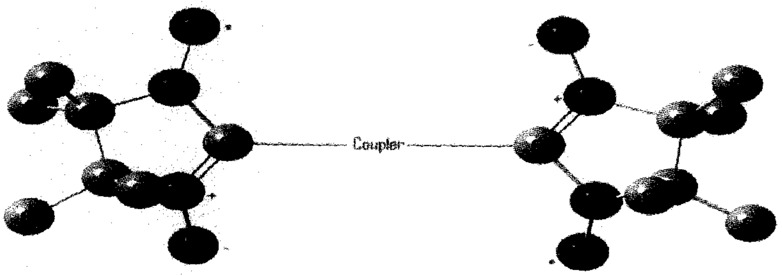


Figure 1.11. Synthesized biphenyl hydrocarbon diradicals with one ECP (**20,21,22**) and two parallel biphenyl units containing diradical (**23**) with two different ECPs (ref. 38,39).

1.6.3. Theoretically Designed Diradicals

Many researchers have studied theoretically intermolecular and intramolecular interactions, on which magnetic properties of diradical based systems depend. The degree of magnetism in magnetic molecules is best represented through intramolecular magnetic exchange coupling constant which depends on the structure and spin orientation of such systems. Previous knowledge about the magnetic characteristics of the designed diradicals is essential before synthesizing possible organic magnetic systems with desired magnetic nature. This has been successfully proven in many cases resulting in the discovery of several ferromagnetic molecules.[1] A development in this direction is discussed chronologically in the following:

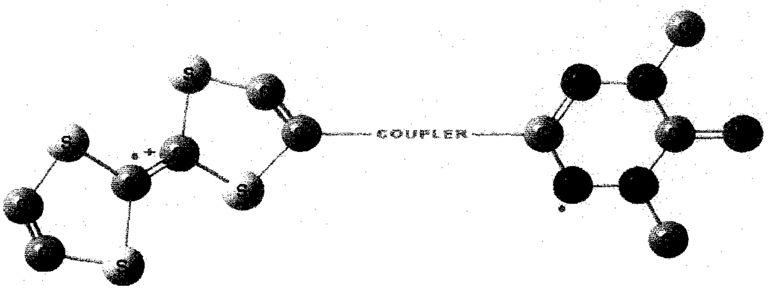
Diradical based magnetic molecules have been studied both with *ab-initio* or density functional theory (DFT) approach.[17,40] The spin states of some fused ring diradical systems[40(a)] along with some other diradical derivatives of IN and NN[40(b)] radicals have been investigated by *ab-initio* quantum chemical approach to calculate their singlet-triplet energy gap. At higher basis set it has been found that the calculated gas phase values are in excellent agreement with the solid state results.[17] Although, the *ab-initio* methods can give us accurate J value in principle but in actual practice it needs high level of computational resources. On the other hand, spin polarized DFT based broken symmetry (BS) approach in unrestricted formalism (BS-UDFT) is very suitable for evaluating J with less computational cost. Datta and co-workers have predicted the J values in different nitronyl nitroxide based diradicals **(24)** (Figure 1.12) using BS-UDFT approach.[40(c,d)] They have found that the ferromagnetic interactions prevail where *meta*-coupler is used, and for diradicals with linear couplers the antiferromagnetic interaction decreases as the length of the chain increases.[40(c)] In another work, molecular tailoring is executed to obtain the planarity of the molecules of trimethylenemethane-based nitroxide diradicals with the prediction of high positive J values due to larger delocalization of π–electrons.[40(d)]



(24)

Figure 1.12. Bis-IN diradical **(24)** with coupler. Hydrogens are omitted for clarity (ref. 40).

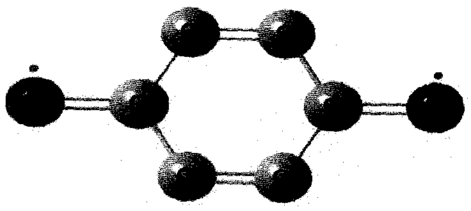
So far, we are confined in diradical based organic magnets with one particular monoradical in two different ends of the coupler; however, the diradicals with neutral OV radical and TTF radical cation as mixed magnetic sites (**25**) having different aromatic and nonaromatic linkers (Figure 1.13) have also been studied in the spin polarized BS-UDFT frame work by Polo and coworkers.[41] The OV and TTF are used as radical centers to prepare the cationic diradical based magnetic molecules. The obtained *J* values for the diradicals without coupler have been found to be very weak antiferromagnetic which is in good harmony with previous experimental work by Sugawara and coworkers.[42] Yamaguchi et al.[43] also have inspected mixed diradicals assembled from TTF and verdazyl with high positive magnetic exchange coupling constants. Nonetheless, in the work of Polo and coworkers,[41] the *J* values are explained in the light of planarity of the π–system, and in the presence of heteroatom in the spinning pathway as well as in the existence of different spin polarization paths instead of one. The novelty of this work is that, if these ferromagnetic materials are used in columnar staking one would get molecule based conducting ferromagnets.



(25)

Figure 1.13. OV and TTF cationic radicals based diradicals (**25**) with the couplers investigated by Polo and coworkers (ref. 41). Hydrogens are not shown in picture for simplicity.

Recently, magnetic interactions of some dinitrene systems (Figure 1.14) have also been investigated.[44] The *J* values for few unconjugated and their corresponding conjugated systems have been evaluated to compare the role of π-conjugation in such systems. A strong antiferromagnetic interaction is observed in investigated conjugated dinitrene systems [44(a)] (**26-28**). With the increase of chain length the magnetic interactions decrease for such systems. The corresponding unconjugated dinitrenes have weakly antiferromagnetic interactions (**28**). In another work,[44(a)] using the spin flip DFT, the positive J values in alkyl substituted cyclohexane diradicals (**29-30**) (Figure 1.15) have been evaluated. The dramatic change of J value is explained with positive inductive effect of the alkyl substituents.



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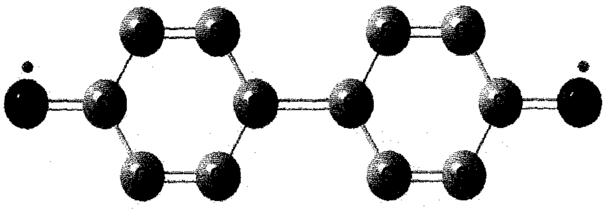

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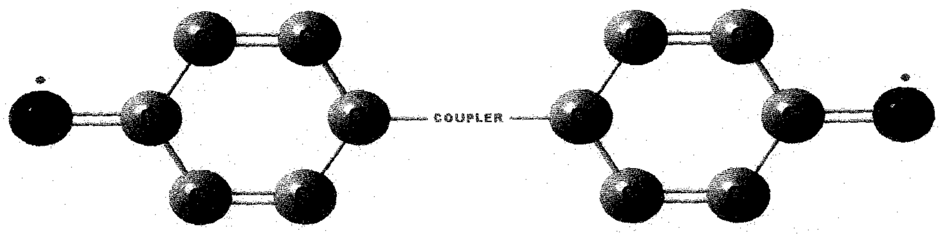
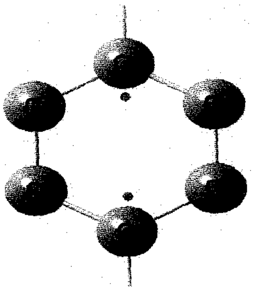


(**28**)

Figure 1.14. Investigated dinitrene systems (**26-28**) [ref. 44(a)]. Hydrogens are omitted for lucidity.



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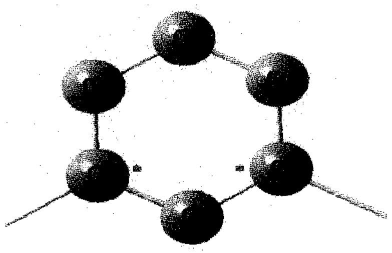
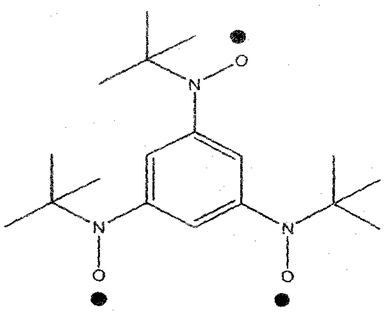


(**30**)

Figure 1.15. Alkyl substituted cyclohexane-1,4- (**29**) and -1,3-diyls (**30**) [ref. 44(b)]. Hydrogens are excluded for lucidity.

1.7. Organic Polyradicals and Polymer Magnets

Iwamura and co-workers have designed and characterised nitroxyl group containing triradical with ferromagnetic interactions having quartet ground state (**31**).[45] Rajca and co-workers have made significant progress in design and preparation of organic branched chain π-conjugated potential ferromagnets with strong intermolecular exchange coupling,[46] such as heptaradical (S=7/2) (**32**) and decaradical (S=5) (**33**) based on star branched topology.[46(a)] They have prepared magnetic polymer with large magnetic moment and magnetic order even at 10K.[46(b)] The credit of preparation and characterisation of dendritic polyradicals (**34**) and polymer magnets (**35**) with triplet ground state goes to the same group of researchers.[46(c-d)] Nonetheless, the presence of spin deficiencies in large systems is known as spin defects which has happened on a potential spinning site due to the non-generation of spins on the required site, and it causes the hindrance of spin propagation through the exchange coupling pathway. This problem can be overcome by designing multiple exchange coupling pathways in a single entity. One of such example is Calix[3]arene (**36**).[46(e)] Nonetheless, recently a computationally less rigorous technique has been developed so that one can estimate magnetic exchange between each two sites of the polyradicals following the Heisenberg model.[47] All the molecules are sketched in Figure 1.16.



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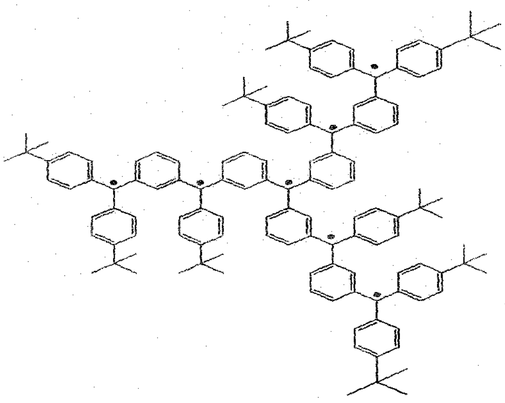
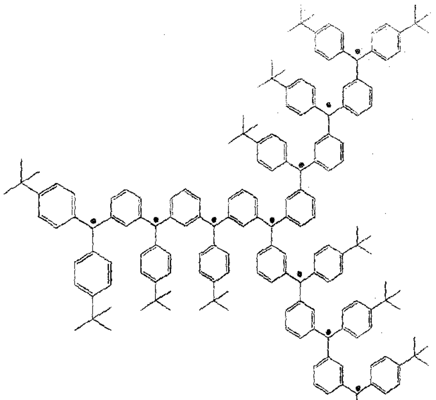
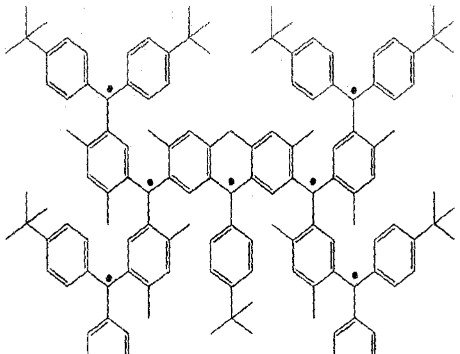


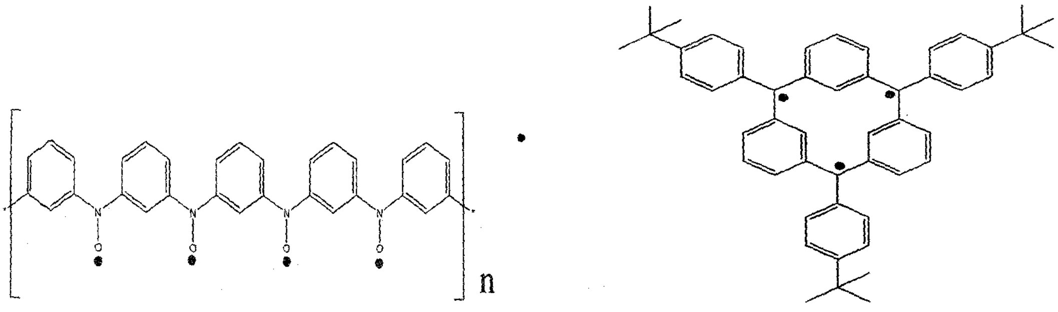
(32)



(33)



(34)



(35) **(36)**

Figure 1.16. Different types of synthesized polyradicals (ref. 45, 46).

1.8. Application of Diradical Based Magnetism

There are many uses of diradical based magnetic molecules. In technological applications[48] or in bio- medicines[9] they are in use. The organic diradicals are used as molecular junctions in spintronics.[48(a)] Apart from this role, they also serve as common intermediate in numerous chemical reactions and this is why they are very significant in chemical synthesis. However, the phenomena of magnetization reversal is important in the field of magnetic data storage, hard disk drives, and also in spintronic materials.[48(b)] The field induced magnetization reversal is difficult to execute,[48(c)] however, the photoinduced magnetic crossover is easy to accomplish and find wide applications in high density information storage devices, in superior resolution etc. [48(d)]

1.8.1. Earlier Photomagnetic Diradical Systems

If a photochromic moiety is used as a coupler between two magnetic sites then the nature of magnetic interaction of the resulting magnetic material can change upon photoirradiation of appropriate wavelength. In organic systems, electron spins can be conserved for longer time and distance than in conventional inorganic materials. In recent years, photomagnetism in organic compounds has engrossed generous attentiveness. Various photochromic spin couplers like diarylethene, azobenzene etc. have been synthesized and characterised with their magnetic properties by Matsuda and coworkers.[49]

Theoretically the photomagnetic behavior of nitronyl nitroxide, imino nitroxide and verdazyl derivatives of substituted dihydropyrene has been investigated.[50] The change of structural pattern from cyclophanediene to dihydropyrene can be obtained by the application of appropriate wavelength of electromagnetic radiation (Figure 1.17). When bis-IN or bis-NN are used as radical sites with these photochromic couplers the observed J values are very low.[50(a)] However, the J values are drastically increased when N-linked OV and NN are used as radicals with these couplers.[50(b)]

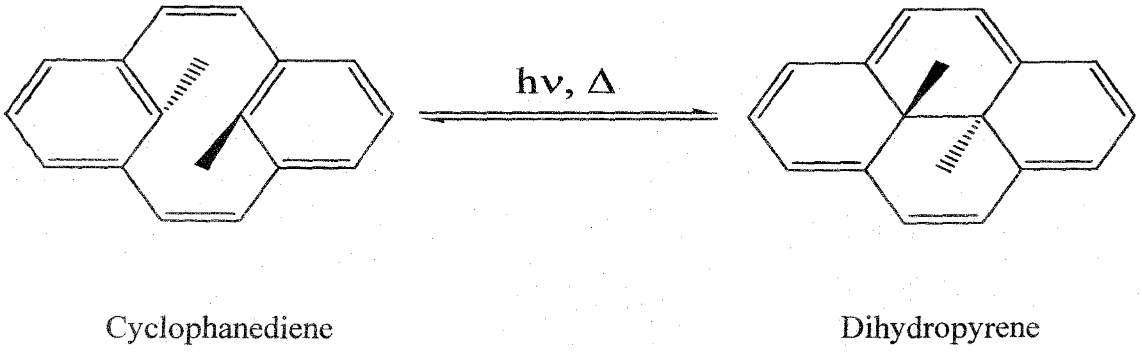


Figure 1.17. Photoconversion of cyclophanediene to dihydropyrene upon irradiation of appropriate wave length of light.

1.8.2. Photoinduced Antiferromagnetic to Ferromagnetic Crossover

The most interesting point of these previous systems is that only the change of magnitude of coupling constants is found yet the sign of coupling does not change. This leads to theoretical design and explore photomagnetic switch systems of organic origin, where magnetic crossover takes place when exposed to the light of a particular wave length,[51] (Figure 1.18) although different systems of inorganic origin, where such magnetic crossover takes place are already known.[52] Trans (a) and cis (b) azobenzene with bis-IN, bis-NN and bis-OV as radical sites (Figure 1.18) is used to design photomagnetic molecules which would likely to attract immediate attention of the experimentalists for their potential applications. It is needless to say that, in suitably crafted azobenzene molecules light can perform the magnetic crossover at nano second time scale which is more applicable in modern technology.

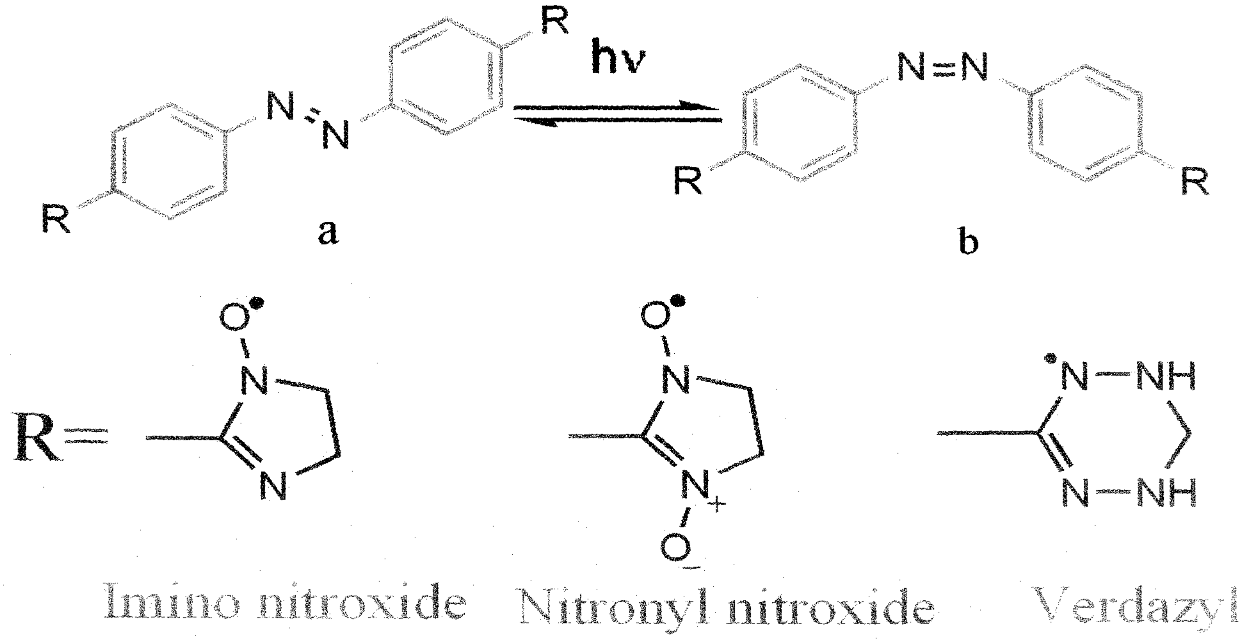


Figure 1.18. Conversion of trans azo-benzene diradicals to cis azo-benzene diradicals with the application of proper wave length of electromagnetic radiation (ref. 51).

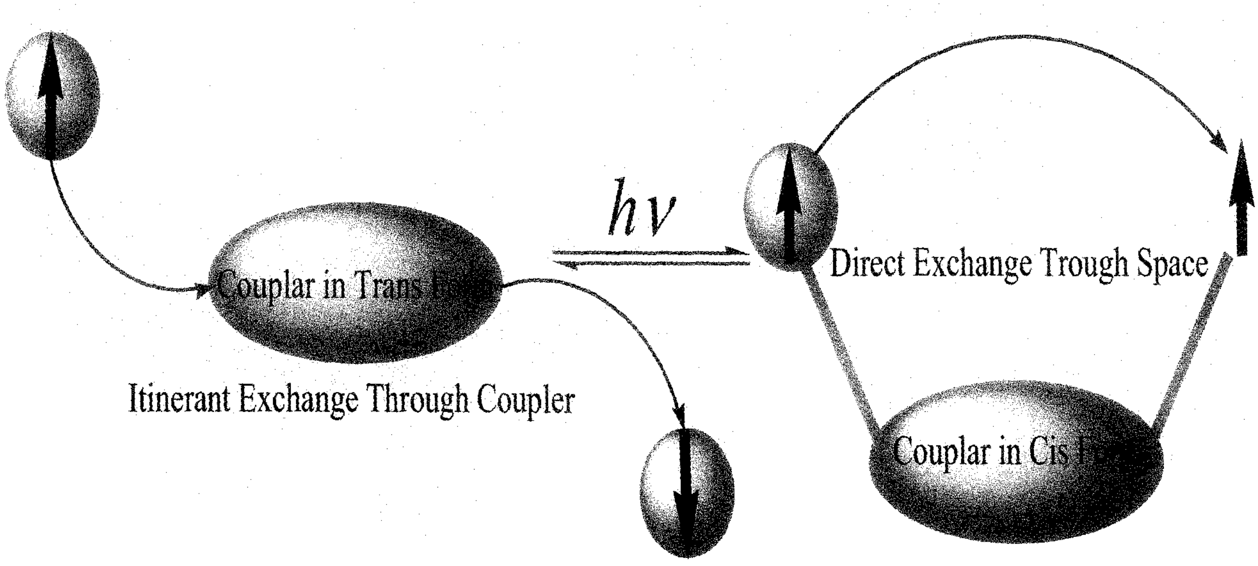


Figure 1.19. Pictorial representation of itinerant (through coupler) exchange and direct (through space) exchange in trans and cis geometric isomeric azobenzene (ref. 51) based diradicals showing anti parallel and parallel spin alignment respectively upon irradiation of light of appropriate wavelength.

In the azobenzene based work,[51] the J values of all three species in the trans forms are negative, but in the case of cis forms, J values are positive. Hence, from the basic principles of magnetism one may note that all trans forms have spins with opposite orientation (antiferromagnetic) in two spin sites and similarly all cis forms have spins with same alignment (ferromagnetic) in two radical centers (Figure 1.19). Accordingly, a magnetic crossover from antiferro (trans) to ferro (cis) would be noticed in all cases when the trans isomers undergo photoisomerization by the application of range 340–380 nm wavelength of light[51] (Figure 1.18).

1.8.3. Biologically Active Diradicals

Huge attention has been paid for the designing of tailor made biomedicines attached with magnetically active molecules for their site specific uses at the pathologic sites. Biocompatible multifunctional magnetic micro- and nano-particles are used to release specific drugs in the target by external or local control.[53] These magnetic particles find diverse biological applications such as in magnetic resonance imaging (MRI) contrast agents, hyperthermia treatment for malignant tumors, conveying medicines, gene delivery, fluorescent biological leveler, discovery of proteins, inquiring DNA structures, and so on, as discussed comprehensively in the review of Salata.[9] The use of target specific magnetic biodegradable materials reduces the inherent side effects through the local distribution of drugs. In MRI, the aminoxyl radicals are known as contrast agents.[54] Rajca and co-workers have made various attempts to synthesize many aminoxyl radicals with S=1 ground state.[55] Generally, gadolinium (Gd) complexes are used as MRI contrast agents, however they are nonspecific and the toxic nature of Gd^{+3} complexes causes renal failure in many cases. On the other hand, nitroxyls and aminoxyls are water soluble and can do the renal excretion with ease. Oppeneer and co-workers have theoretically investigated the effect of hydrogen (aminoxyl-water hydrogen) bonding ($NO^{\bullet}\cdots\cdots\cdots H_2O$) on J for different synthesized biologically active ferromagnetically coupled bis-aminoxyl diradicals.[56] However, the searching for biocompatible, easily renal excreable organic less toxic MRI contrast agents are still encouraging.

1.8.4. Molecular Spintronics

So far as the technological applications are concern the organic magnetic molecules are promising in the field of spintronic materials.[48(a)] Literally spintronics means spin based electronics, which is also called magneto electronics. One of the major advantages of the spintronic materials is that the nature of spin orientation makes them suitable candidate for making devices like memory storage, quantum computing, magnetic sensors etc.[57] Several experimental groups have reported the quantification of the current-voltage (*I-V*) characteristics of different organic molecules.[58] These developments have expanded the immense curiosity in modeling and understanding the capabilities of the molecular conductors from the basic scientific and applied point of view.[59] Recently, Sen and Chakrabarti have reported the smallest molecular spin filter which is essentially a ferromagnetically coupled cobalt-benzene-cobalt (CBC) system adsorbed on Au(III) surface with extraordinary spin injection coefficient.[60] In another work, it has been shown that the chemical and magnetic interactions of metalloporphyrenes and metallic substrates can be modified through the tuning of magnetic interactions between manganese porphyrenes and ferromagnetic Co substrates. The objective of the work was to tune the properties of molecular spintronic materials, that is, the adsorption of nano-magnetic molecules on metal surfaces by means of dedicated control of the molecule-surface interaction.[61] However, the field is in early stage, and the scientists are very keen to develop numerous spintronic nano- or micro-devices. Photoinduced spin valve effect has also been predicted in case of organic systems,[51] in azobenzene based diradicals examining density of states at Fermi level.

1.9. On Molecular Magnetism

The field of research where the magnetic properties of an isolated molecule as well as their assemblies are taken into consideration is the area of molecular magnetism. The molecules may have one or more magnetic centers. In case of assemblies of molecules residing in the solid state, the intramolecular magnetic interactions occur in between different magnetic entities. The similar type of interactions is observed among a single isolated magnetic entity where intermolecular magnetic interactions prevail. At this point it is really informative to mention that, in an extended isolated magnetic system strong magnetic interactions may be found which is responsible for bulk magnetic properties.

Over the time, as the science related to molecular magnetism is developing, the discovery of new magnetic building blocks as well as the way to assemble them in the solid state is increasing rapidly. It is to be noted that, the spin bearing entity is called as building block in such cases. There are different strategies by which one can assemble these unpaired spins in the molecular magnetic materials. The fundamental efforts are necessary to understand the structural and physicochemical features of these magnetic species to get the newly created molecular magnets.

In organic domain of molecular magnetism the organic radicals are used as spin active components. However, these radicals must be stable in air and moisture, isolated and characterised at room temperature. This limitation makes only a few organic radical classes to be useful for this purpose. It is found that the most active spin bearing site to be used as building block does not have much steric bulk. Hence, the radical approach to realize molecular magnet pays attention to nitroxides, verdazyls, heterocyclic thiazyl radicals etc.

As far as the applications of these materials are concerned their uses in domestic as well as high tech appliances are not overlooked. The increasing necessity of microelectronic devices with decreasing size finally reaches the molecular dimension. On the other hand, in biomolecular field of research molecule based magnetic materials can also find diverse uses. However, reaching the ultimate goal in the field of molecular magnetism in organic domain is still intellectually challenging.[27,62]

1.10. Objectives of the Thesis

The essence of magnetism is well known, however the design, characterisation and applications of molecular magnets are still fascinating. The main objective of my thesis is to examine molecular magnetic systems of organic origin. The magnetic character of a molecule is best quantified by the intramolecular magnetic exchange coupling constant (J).

Hence, the objectives of this thesis are to understand the magnetic features and applicability of different magnetic substances through quantification. These are systematically indentified in the following:

(1) To design different bis-oxoverdazyl based diradicals connected by various linkage specific aromatic ring couplers and to quantify their magnetic properties (**Chapter 3: Magnetism in Bis-Oxoverdazyl Diradicals Coupled with Different Linkage Specific Aromatic Ring Spacers**).

(2) To understand the magnetic nature and aromaticity of different high spin bis-oxo- and -thioxo-verdazyl based diradicals with linear polyacenes with varying length as couplers (**Chapter 4: Role of Linear Polyacene Spacers in Intramolecular Magnetic Exchange Coupling**).

(3) To find out a relation between the magnetic exchange coupling constant and different aromaticity index among different high spin and their corresponding low spin bis-heteroverdazyl diradicals having meta- and para-phenylene as couplers (**Chapter 5: Influence of Aromaticity on the Magneto Structural Property of Heteroverdazyl Diradicals**).

(4) To briefly investigate the antiferromagnetic to ferromagnetic crossover upon irradiation of appropriate wavelength of electromagnetic radiation in green fluorescent protein (GFP) chromophore coupled diradicals (**Chapter 6: Photoresponsive Magnetic Crossover**).

(5) To study computationally the possible biomedical uses, particularly as a potent candidates of magnetic resonance imaging contrast agents, of our designed different variants of GFP chromophore coupled diradicals (**Chapter 7: Possible Applications of Fluoro Protein Chromophore Coupled Photomagnetic Diradicals**).

1.11. References and Notes

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