Chapter 12

High spin molecules directed towards Molecular Magnets

Martin Baumgarten,

Max Planck Institute for Polymer Research, Mainz, Germany

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Abstract: EPR has often been used to define spin states of high spin molecules. This chapter outlines some meaningful considerations for the classification of interacting radicals and the determination of their ground spin multiplicity. Then a review on different classes of high spin molecules follows, sorted by their spin state, summarizing the application of EPR in that domain.

1. INTRODUCTION

Molecular magnetism is a part of material science chemistry, which strongly developed over the last 20 years. It may be viewed as a frontier research among inorganic and organic structures and their hybrid solids. Milestones include the detection of bulk ferromagnetism in the molecular complex of decamethylferrocene-tetracyanoethylene Fe^{III}(C_{5}(CH_{3})_{5})_{2}[TCNE] in 1987 by Miller and Epstein\(^1\) and the first pure organic ferromagnet of p-nitrophenyl-nitronylnitroxide in 1991 by Kinoshita.\(^2\) Besides use of inorganic metal complexes for molecular magnets large efforts went into the controlled synthesis of new stable organic high spin moieties and their in depth characterization. Therefore, by now a huge number of organic bi- and oligo-radicals of very different nature concerning their radical sites and the connectivity between them are available. Some of them are fairly old and are known since the beginning of the last century: ones like the Schlenk hydrocarbon\(^3\) and Tschitschibabin’s\(^4\) or Yang’s\(^5\) and Coppinger’s\(^6\) biradicals

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(Fig.1). Many more were just added over the last twenty years and most of them were synthesized and characterized or trapped as intermediates to clarify their electronic structure and ground state spin multiplicity. This has been performed especially in order to gain further insight into the factors controlling spin alignment and their possible use as building blocks for organic materials with magnetic ordering.

![Some classical biradicals]

Figure 1. Some classical biradicals

Triplet state molecules, on the other hand, also play an important role as intermediates in bio-organics and bio-physics. In order to define the basic structure of this chapter we may first consider the classification of bi- and oligoradicals (see Fig. 2 for the energy levels of two spin systems in a magnetic field). While a monoradical is just represented by the spin up/spin down energy levels which lose their degeneracy in a magnetic field, a biradical can be described in many different ways: if there is a large distance ($d \geq 1$ nm) and no conjugation between the radical sites the exchange coupling $J$ is zero and the biradical may either be presented as two independent monoradicals or as an equilibrium mixture of a triplet and a singlet state (Fig. 2b,c).

If we deal with the excited states of neutral organic precursors as aromatic compounds, then the lowest triplet often is below the lowest photoexcited singlet state and can be accessed by intersystem crossing from the latter. Such highly activated triplet states will not be considered in this review, although it might be an intriguing task to find even higher than triplet spin multiplicities after photoexcitation, e.g. by considering two phenyl bridged naphthalenes, where a quintet state may become accessible.
Figure 2. Different kinds of the biradicals and their energetic states compared to a) monoradical, b) or c) biradical with distant radical centers d) photoexcited triplet state, e) ground state triplet, and f) ground state singlet with thermally accessible triplet, and g) ground state triplet with thermally accessible singlet. According to K. Scheffler, H.B. Stegmann in “Elektronenspinresonanz” Springer, Heidelberg 1970.

In this vein it was demonstrated very recently that quartet and quintet states are amenable upon photoexcitation of a 9,10-Diphenyl-anthracene situated between stable nitronyl nitroxide or oxo-verdazyl radicals.

In the discussion we can delineate three cases in order of decreasing high-spin stability: i) a triplet ground state where no thermal activation to the excited states is possible under ambient laboratory conditions (Fig.2e); ii) a ground-state triplet with thermally accessible singlet state, and iii) thermally activated triplet state above a singlet ground state. While biradicals at large distance connected through saturated spacers may easily be classified as b) or c) and photo excited triplet states d) are rarely long lived stable species, the last three groups (Fig. 2e, f, g) deserve more intimate characterization in order to define their ground state spin multiplicity unambiguously. This also holds for even higher spin states in discrete molecules and the method of choice to do that certainly is EPR spectroscopy.
1.1 Determination of the spin states and ground state multiplicities of high spin molecules

Over the last decade EPR has often been applied to identify many ambiguous spin states in high spin molecules and for characterizing new molecules. This was performed in order to fully understand the conditions and prerequisites for obtaining high spin molecules or parallel spin alignment in extended polymers with radical sites in the main or side chain with linear, branched, dendritic, or hyperbranched extensions. The basis for these approaches was the clean experimental elucidation of the spin states of the molecular building blocks by EPR spectroscopic methods and their theoretical understandings. Continuous wave X-band EPR and sometimes ENDOR studies have most often been employed, besides the use of high field high frequency and FT-pulsed EPR techniques. The latter especially transient nutation experiments developed fast during the last 10 years.\cite{6,11}

The basic parameters for characterization of more than one unpaired electron are the electron electron spin-spin interactions $\mathcal{H}_{SS}$, consisting of the isotropic exchange $J$ and the dipolar exchange described by tensor $D$. The latter are also referred to as fine structure or zero field splitting (ZFS) parameters. The spin Hamiltonian $\mathcal{H}_{\text{spin}}$ for describing high spin molecules is then expressed by eq.(1), including further the electron spin orbit and electronic Zeeman $\mathcal{H}_{\text{LS}} + \mathcal{H}_{\text{ZE}}$ and the hyperfine interaction $\mathcal{H}_{\text{SI}} = S \cdot I$, while higher order terms for nuclear Zeeman $\mathcal{H}_{nZ} = - g_n \beta_n I \cdot B$ and quadrupolar interactions $\mathcal{H}_{II} = I \cdot P \cdot I$ are often neglected.

$$\mathcal{H}_{\text{spin}} = \mathcal{H}_{\text{LS}} + \mathcal{H}_{\text{ZE}} + \mathcal{H}_{\text{SS}} + \mathcal{H}_{\text{SI}} \left[ + \mathcal{H}_{nZ} + \mathcal{H}_{II} + \ldots \right] =$$

$$\mathcal{H}_{\text{spin}} = \beta B \cdot g \cdot S + S \cdot D \cdot S + J S \cdot S + S \cdot A \cdot I \left[ - g_n \beta_n I \cdot B + I \cdot P \cdot I + \ldots \right]$$

(1)

In solid state EPR the dipolar exchange (ZFS) is dominating, while the isotropic exchange $J$ contributes a common constant to the energy of each high spin state. Since $D$ is traceless, the fine structure is usually described by two energetic parameters $D$ and $E$, which are $D = 3D^z/2$ and $E = (D_x - D_y)/2$, expressed in cm$^{-1}$ as $D' = D/\hbar c$ and $E' = E/\hbar c$ or in magnetic field units $D' = D/g_e \beta$ and $E' = E/g_e \beta$. The EPR spectral analyses for isolated triplet state molecules are well established and described in standard textbooks.\cite{12}

For high spin molecules usually it is assumed that the $g$ anisotropy is small and that the zero field splitting $|D|$ is not larger than the microwave transition energy (high field approximation), but exceeds the hyperfine interaction, which can then be considered as perturbation.

$$\mathcal{H}_{\text{spin}} = \beta B \cdot g \cdot S + D(S_z^2 - S(S+1)/3) + E(S_x^2 - S_y^2)$$

(2)
This approximation has been encountered most widely in bridged bi- and oligoradicals leading to the “typical” high spin patterns with a maximum of 2Sx3 allowed fine structure transitions (Δm_S = 1). In addition Δm_S = 2 and sometimes Δm_S = 3 forbidden transitions can be observed. One should note that the relative intensities of the Δm_S = 1, Δm_S = 2, and Δm_S = 3 transition obey the ratio 1:(D'/Bo)^2:(D'/Bo)^4, respectively. A typical spectral simulation for a quartet state (S = 3/2) at X-band is shown in Figure 3.

Figure 3: Simulated X-band EPR spectrum for S = 3/2 with D' = 0.01075 cm\(^{-1}\), E' = 0.00019 cm\(^{-1}\), and g = 2.003 at 9.4 GHz. (B_res = 335 mT).

Very complex patterns and additional absorption lines have been identified and analysed for high spin molecules with very large zero field splittings (e.g. carbenes and nitrenes) where \( \mathcal{H}_{SS} \geq \mathcal{H}_{ZE} \). Such spectra were a true puzzle in the early 60’s, when Wassermann et al. reported about new powder spectra for meta-phenylene bridged dicarbenes and dinitrenes. They could not be explained until 1967, when Itoh submitted a single crystal study on meta-phenylene-bis(phenyl-methylene) 2.

The breakdown of the perturbation approach in cases of very large zero field splitting parameters \( |D| \geq \hbar \nu \) was pointed out carefully by Takui et al. leading to off axis extra absorption peaks. Those can be simulated by direct diagonalization of the spin Hamiltonian but not directly extracted from the observed spectra, which led to spurious documentation on spin-quintet dinitrenes.
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Figure 4: Simulated EPR spectra at X-band a) and at W-band b) for very large ZFS parameters $D' = 0.200 \text{ cm}^{-1}$, $E' = 0.0314 \text{ cm}^{-1}$. Broad star marks highest z-field component, the sharp arrows some extra absorption lines.

If these measurements, on the other hand, would be performed in W-band at 94 GHz, where the high field approximation still holds, they will give the “usual” pattern for a $S = 2$ spin state (Fig. 4a, b). The standard cw EPR application is limited to discrete spin systems since with increasing number of spins the number of allowed transitions grows rapidly, producing high spectral density in the center with extremely weak intensity of the outermost signals. This was found already for a hexaradical in a septet state and can be further demonstrated for an $S = 5$ state with $D' = 0.0060 \text{ cm}^{-1}$ and $E' = 0.0002 \text{ cm}^{-1}$ (Fig. 5).

Another problem in determining the fine structures by EPR may occur when they are smaller or equal to the hyperfine splitting. In some cases with well defined hyperfine couplings as in phosphinyl radicals ($^3\text{P} A_\parallel = 850 \text{ MHz}, A_{\text{iso}} = 297 \text{ MHz}$ while $D' = 260 \text{ MHz}$), shown by Janssen et al., the well resolved transitions can still be fully analysed. Otherwise this situation may lead to unresolved EPR spectra in the $\Delta m_S = 1$ region but also to weak signals for the $\Delta m_S = 2$ transition due to small $D'$-value. In such cases high resolution ENDOR experiments can be very helpful to analyze hyperfine and sometimes exchange interaction.
They have been applied for the identification of multispin states in solution and in rigid media,\textsuperscript{19,20} but hardly for the identification of the ground state multiplicity itself. However, additional information on the hyperfine coupling scheme and thus spin density distribution can be obtained. If the absolute signs of the hyperfine coupling constants are determined, e.g. from isotopic labelling and triple resonance, the sign and the size of the isotropic exchange coupling $J$ and of the dipolar ZFS component $D'$ can be deduced as well.\textsuperscript{20}

Other hurdles may be faced in large molecular or polymeric spin systems where the observed spectra are often composed of mixtures of different spin states and also conformers rendering the analysis very difficult. New FT-EPR methods based on transient nutation therefore seem to be very promising for elucidating such spin states.\textsuperscript{9,10} The transient nutation spectroscopy provides an extremely high resolution for spin multiplicities and magnitudes of ZFS parameters. It is based on the precession or nutation of the magnetization vector $\mathbf{M}$ around the effective magnetic field $\mathbf{B}_{\text{eff}}$ summed by the static field $\mathbf{B}_s$ and the microwave field $\mathbf{B}_1$ described in the rotating frame. In the rotating frame under microwave irradiation this precession is no longer the Larmor frequency as in the laboratory frame but called “transient nutation”, since the signal is observed for a finite time only after turning on the microwave radiation until a steady state is reached. When the excitation pulse is turned off, $\mathbf{M}$ undergoes the free induction decay (FID). The effective nutation frequency $\omega_{\text{eff}}$ for a doublet spin $S=1/2$ with an isotropic $g$ value is described in the rotating
frame $\omega_{\text{rot}}$ as typical Larmor precession $\omega_s = g\beta_B / \hbar$ and the additional precession about the microwave field $\omega_1 = g_1 \beta_B / \hbar$ (here $g_1$ is related to the laboratory frame as described by equation 3.4.17 in reference 10).

$$\omega_{\text{eff}} = \left[ (\omega_s - \omega_{\text{rot}})^2 + \omega_1^2 \right]^{1/2} \quad (3)$$

In the resonant case $\omega_s = \omega_{\text{rot}}$ and $\omega_{\text{eff}} = \omega_1$. That is the resonant magnetization nutates with $\omega_1$ around the rotating x-axis, whereas the off resonance magnetization nutates with frequency $\omega_{\text{eff}}$ around the effective field vector, which is deflected from the z-axis by the angle $\theta$. The description of the spin nutation about the effective field follows the Hamiltonian including their spin states.

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 = (\omega_s - \omega_{\text{rot}})S_z + \omega_1 S_x \quad (4)$$

In case of high spin molecules the nutation frequency is directly depending on the contributing spin states. The transition amplitudes depend on the spin quantum number $S$. If the microwave radiation excites only a single transition in the weak extreme limit, the nutation frequency for the transition between the two states characterized by the magnetic quantum numbers $m_S$ and $m_S + 1$ is given by $\omega_{\text{nut}}$:

$$\omega_{\text{nut}}(m_S, m_S + 1) = \omega_1 \sqrt{S(S+1) - m_S(m_S+1)} \quad (5)$$

where $\omega_1$ includes the microwave $B_1$ field (see eq. 4) which can be determined separately in a calibration experiment for a standard as DPPH, where $g = g_1 = 2.0037$. If the microwave excitation is not transition sensitive, as in strong microwave field limit where all transitions are excited, a nutation of the magnetization along $\omega_1$ is observed, which is independent of the spin states ($\omega_{\text{nut}} \sim \omega_1$). For the intermediate situations the interpretation of
the spectra may be more or less complicated. The various limits are well described by Takui et al.\textsuperscript{9,21} Finally the Nutation experiments can be conducted by either observing the FID or the electron spin echo, and the latter has most often been applied for characterizing high spin molecules.\textsuperscript{9,21}

In order to define the ground state spin multiplicities and to separate them from thermally activated ones, the most usual characterization is to follow the temperature dependent variation of signal intensities of the given spin state. If the intensity changes linearly with the temperature (I-T = const) the behavior is Curie like and the exchange interaction is either very large or very small. The activation energy for experimental determination is usually limited to the temperature range 2 - 300 K (~ 4 - 600 cal/mol) or even lower due to the thermal stability of the radicals or their matrix.

Especially for the standard cw-techniques, complications in the ground state determination for the bi- and oligoradicals may arise from overlapping signal contamination of other spin states, and very different saturation effects. Therefore these measurements should be checked for reversibility, temperature errors, and saturation effects, which become most important at lowest accessible temperature range. A deviation from linear dependence of signal intensity versus square root of microwave power showing the saturation effect may easily be implied upon lowering the temperature.

Besides experimental techniques for determining ground state spin multiplicities, where also magnetic susceptibility measurements have been applied, many molecular systems have been considered theoretically in order to obtain a deeper understanding and further confirmation. Such quantum chemical studies on high spin states also enable the prediction of ground state multiplicities for molecules so far unknown as a guiding design.

Discrepancies between experimental results and theoretical predictions have spurred more accurate characterisation of old or synthesis of novel high spin candidates. A number of high spin molecules have been designed from standard radicals attached to coupling units (CU) providing spin exchange by topological or geometrical control. Thus in the following paragraph we will pass through the common rules and exceptions, in order to get a more complete picture on the molecular level. Since this book focuses on EPR spectroscopy and its application, we will sort this chapter by the spin states and not by the type of radicals. A few exceptions may be apologized, for very closely related molecules. Research has been focused mainly on bi-, tri-, and tetra-radicals, while higher spin states have only been dealt with in a few cases.
Since the number of biradicals is huge we have to limit this outline to a choice of importance. For a more complete overview on all available organic high spin molecules and extended molecular based magnets further textbooks and review articles may be considered.22,31

2. BIRADICALS – THE TRIPLET STATE

The most often used approach for high spin molecules is the control of through bond exchange in conjugated molecules leading to so called non-Kekulé structures as in \textit{m-Xylene} (1,3-Dimethylene-benzene), where no double bond between the unpaired electrons can be formed. In difference thereto, the \textit{para} and \textit{ortho} derivatives usually undergo spin pairing to the more stable quinoid structures in the Kekulé forms.

![Non-Kekulé vs. Kekulé structures](image)

The number of non bonding MO’s (NBMO’s) and thus the number of unpaired electrons \(S\) can easily be predicted by the rules of Longuet Higgins\textsuperscript{32} \([n\text{NBMO} = (N-2T)]; S = 0.5 (N-2T)\) with \(N\) number of \(\pi\)-centers and \(T\) number of double bonds] or according to the rule of Ovchinnikov\textsuperscript{33} based on spin polarisation, by subtracting the number of starred and unstarred \(\pi\)-centers \(S = 0.5 (n^*-n^0)\). The spin polarisation is thus used to explain high spin ground states for Schlenk’s and Yang’s biradicals, but low spin ground state for Tschitschibabins and Coppingers biradicals (Fig. 1).

The \textit{m-phenylene} as coupling unit (CU) to connect radical sites has therefore been used in many high spin molecules with common radical sites as given in Fig. 7. Some of them are very stable and can be handled even in solution at room or higher temperatures (\text{NIT, IN}..). Others are moisture and air sensitive as the ketyl anion or aromatic radical anions and cations. The usual nitrenes and carbenes are very reactive and only stable below 100 K. Over the last years a major breakthrough was made with triplet carbenes being stable up to room temperatures. They could be synthesized with halides in the \textit{o-phenyl}-positions close to the carbene as
perchlorodiphenylcarbene, 2,2′,4,4′,6,6′-hexachlorodiphenylcarbene, or 2,2′,6,6′-tetrabromo-4,4′-ditert-butyldiphenylcarbene.\textsuperscript{34,35,11}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{radical_sites.png}
\caption{Common radical sites, nitronyl nitroxide \textbf{NIT}, iminonitroxide \textbf{IN}, tert.-but.-nitroxide \textbf{NO}, phenoxide \textbf{ArO}, ketyl radicals, triphenylmethyl \textbf{TPM}, verdazyl \textbf{VZ}, Dithiadiazyl, nitrenes, carbenes, Triphenylamin cation \textbf{TPA} or aromatic radical cation and anions like naphthalene.}
\end{figure}

In the 90s there were already known several exceptions of high spin states in non-Kekulé hydrocarbon structures, which were then addressed as “Violations of Hund’s Rule in Non-Kekulé Hydrocarbons”.\textsuperscript{36} It was shown and predicted earlier by Borden\textsuperscript{37,38} that another classification of non-Kekulé molecules is very important, e.g. the separation of molecules into those possessing non-disjoint and those possessing disjoint non-bonding MO’s. Most easily it can be demonstrated by comparing Trimethylenemethane (\textbf{TMM}) and Tetramethylenethane (\textbf{TME}). In TMM the NBMOs are distributed over the whole molecule (non-disjoint) while in TME and in the more rigid 2,3-Dimethylenecyclohexane-1,4-diyl (\textbf{DMC}) the NBMOs are

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spin_states.png}
\caption{a) Structure and spin state of TMM, TME, and DMC, b) the NBMO’s of TMM and TME.}
\end{figure}
localized on two subparts as separate moieties (disjoint). Thus spin polarization already predicts ground state singlets for TME and DMC.

Experimentally Dowd could access all 3 molecules in frozen matrices showing similar biradical behavior concerning their EPR fine structure with ZFS’s of $D' = 0.024 \text{ cm}^{-1}$ (TMM), and $D' = 0.025 \text{ cm}^{-1}$ (TME) and $D' = 0.024 \text{ cm}^{-1}$ (DMC). Although irradiations for nitrogen extrusion of the precursors were performed at 10 K, Curie like temperature dependence of EPR signal intensities was only plotted down to 20, 15, and 16 K, respectively, suggesting ground spin triplets for all three of them. While for TMM there were no doubts about, the ground spin multiplicities of TME and DMC were heavily discussed for quite some time, and many further theoretical calculations with different geometries and basis sets resulted in contradictory descriptions of TME and DMC. In 1996 Iwamura’s group unambiguously evidenced that the ground state for DMC and TME is singlet, nearly degenerate with a thermally excited triplet above 10 K. The final experiments was even more important, since there exists a large number of similar biradicals and substituted derivatives which can be grouped into the “families” of TMM and TME possessing the same spin interaction core.

![Diagram of biradicals](image)

The “TMM family” has been widely tested for all kinds of radicals attached to 1,1'-ethenyl (3). It comprises also cyclic structures like dihydropentafulvenes 4 and cyclobutenes 5-7. Different symmetric and asymmetric substitutions $R_1, R_2$ have been used for 4 and for all of them the ground state was triplet. Just the ZFS values were largest for electron donating groups like methoxy, while electron acceptors or extension of the π-system leads to a decrease of the zero field splitting. For the Cyclobutadion-diyl 7 only, no biradical could be found and a singlet state is predicted, also argued from the strong contribution of dipolar resonance structures, as shown below.

Within the “TME family” as for TME itself, there occurred many ambiguous papers, while theory predicts singlet ground states for them, even
more in the cyclic planarized forms. For 8-10 first triplet states were assumed, then Berson studied the tetramethylenebenzene 8 in more detail demonstrating ground state singlet. Therefore it must be assumed that also Cyclopentadienes 9 and 10 should be further requested. Closely related is the cyclopentane-1,3-diyl 11 where a triplet ground state has been established.

![Molecules](image)

But the singlet triplet splitting should be small, since the two competing pathways through $\sigma$ bond yield opposite signed spin polarization presented by $\alpha$ and $\beta$ spin (or spin up and spin down) as given schematically.

```latex
\begin{array}{c}
\alpha \beta \alpha \\
\text{CH}_2 \text{CH}_2 \text{CH}_2
\end{array} \quad \begin{array}{c}
\alpha \beta \alpha \\
\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2
\end{array} \quad \begin{array}{c}
\alpha \beta \alpha \\
\text{CH}_2 \text{CH}_2 \text{CH}_2 \\
\beta \alpha \beta \alpha
\end{array}
```

*Figure 9. Spin polarisation through methylene and ethylene*

The heteroatomic substitution in the five membered ring systems leading to Dimethylenethiophene 12, Dimethylenefurane 13, and Dimethylenepyrrol 14, destabilizes the triplet state to such an extent that all of them are biradical singlets, even without thermal activation of the triplet state. Partially zwitterionic forms must be considered. One exception seems to be the tosylated pyrrole 15 where a stable triplet was reported with thermally activated components of only 19 cal/mol. This exception was explained with long lived spin isomerism and shown to be dependent on the excitation wavelength for nitrogen extraction leading to different species.

Also several exceptions for meta-phenylene bridging without high spin ground state multiplicities have been found in the 90’s. While for a typical meta-phenyl bridged bisnitroxide 16 the triplet state was witnessed, for the tris-methylated bisnitroxide 17 two isomers were found in their singlet state and the triplet excitation was reported to be in the range $2J = -(66 – 81)$ K. This was also the first case where it could be shown that a corresponding para-phenylene bridged biradical is more stable triplet with $2J/k=-35$K or ca 70 cal/mol than its meta form. A very similar finding of thermally excited
triplet bisnitroxides was reported by Iwamura\textsuperscript{63} using methoxy groups neighboring the nitroxides 18 and yielded $2J/k = -7.0$K for a diluted sample in solid PVC, where the intermolecular exchange is negligible, and $-73.8$ K for a crystalline material, where strong antiferromagnetic intermolecular interactions are enclosed. Thus not surprisingly also the three spins in a trisnitroxide with one more nitroxide radical between the methoxy groups are coupled antiferromagnetically to a doublet ground state.\textsuperscript{64}

The reason for this unusual singlet ground states of 17 and 18 was further discussed by Borden.\textsuperscript{65} On the basis of ab initio calculations considering twisted radical sites, singlet states for angles of torsion between 70- 90° were unequivocally predicted. A surprise was found for a bis-trifluormethyl derivative 19 reported by Rajca et al.\textsuperscript{66} demonstrating that rapid cooling of the biradical leads to a singlet state, which slowly converts to its ground state triplet. Different temperature dependent conformer preferences were assumed to be responsible for the observed changes.

Other exceptions of $m$-phenylene acting as ferromagnetic CU’s when strong steric hindrances are involved were manifested by the diphenothiazine and diphenoxazine dication derivatives.\textsuperscript{67,68} The zero field splittings of the biradical \textit{para}-, \textit{meta}-, and \textit{ortho}- derivatives (20-25) formed in sulfuric acid nicely reflected their distance dependence with $D' = 0.0043$, 0.0060, and 0.0204 cm\textsuperscript{-1} (20-22) corresponding to $r \sim 0.84$, 0.76, and 0.50 nm, respectively. This dipolar approach with $D' \sim 3g_\beta^2\beta_e^2/4r^3$ estimation can be refined for distributed spin densities in delocalised biradicals, as well. The above finding is one of the very rare cases, where \textit{o}-phenylene bridging gave EPR active species, what is based on the strong twisting and stabilization of the dication through the sulphonate counterion. In case of the phenoxazines the ZFS components are slightly larger, due to the higher spin density on the connecting nitrogens and lower charge on the oxygen compared to sulfur in phenothiazines. The temperature dependence indicated a singlet ground state for 21 with $2J = -28$ cal/mol and here again more stable triplet states with Curie like behavior were identified for the corresponding \textit{p}-phenylene bridged biradicals 20.
In principle strict orthogonal alignment of radicals may also open a way to high spin ground states (geometrical vs. topological approach).\textsuperscript{23} In an early approach this was tested by Veciana et al.\textsuperscript{69} with the perchlorobiphenyl- dication 26, where the large chloro-substituents lead to a strong twisting of the biphenyl unit and also decrease the oxidation potential. But later it was shown that the biradical had singlet ground state. Since Bianthryl 27 is aligned perpendicularly and can be oxidized with SbCl\textsubscript{5} to the biradical dication (D' = 0.00225 cm\textsuperscript{-1}) or reduced with alkali metal to the biradical dianion (D' = 0.00177 cm\textsuperscript{-1}), also oligo(anthrylenes) 27-29 and the corresponding polymer were studied for this purpose.\textsuperscript{70} Temperature dependent studies of the zero field splittings (zfs) in the frozen solution EPR spectra evidenced that the charged oligo(9,10-antihrylenes) 27-29 persist in low spin ground states. The low temperature measurements of the bianthryl dianion additionally revealed that the average orthogonal alignment is lost upon lowering of the temperature, with a clear orthorhombicity of the zero field splitting parameters D' = 0.00182 cm\textsuperscript{-1} and E' = 0.0010 cm\textsuperscript{-1} at 20 K which correlates to an angle \( \theta \) of 81° derived from the two extremes \( E_{\min} = 0 \)
$(\theta = 90^\circ)$ and $E_{\text{max}} = D/3$ $(\theta = 0^\circ)$. Also in other asymmetric biaryles with strong to orthogonal hindrance only thermally activated triplet states were found.\textsuperscript{71}

Another way to overcome the standard topological rule was excellently demonstrated by Iwamura and Inoue\textsuperscript{72,73} using asymmetric radical sites in \textsuperscript{30, 31}. Then spin polarisation leads to stable triplet ground state biradicals with strong intramolecular ferromagnetic coupling.

In a similar way the topological rules for exchange coupling may be overcome upon use of delocalized radicals and radical ions.\textsuperscript{74,75} A necessary property is large sign-alternating spin densities along the periphery, well known for the neutral phenalenyl- (\textsuperscript{32}) and pyrenyl (\textsuperscript{33}) cation or anion radicals. Bridging through so called antiferromagnetic CU’s as single bond, 1,2-ethenyl, or $p$-phenylene will then lead to high spin formation if the radical ions are connected through positions of opposite signed spin densities. While the bridged 1,2’-biphenalene \textsuperscript{34} was just considered as model theoretically\textsuperscript{74} the 1,2’-bipyrene \textsuperscript{35} and 2-(9-anthryl)-pyrene \textsuperscript{36} \textsuperscript{75} should also form high spin ground state entities and were synthesized and charged to their biradical dianion.\textsuperscript{76}

A third opportunity to obtain high spin molecules besides topology and geometry, is based on high symmetry. It has long been established for molecules having threefold or higher symmetry, that they possess doubly degenerate HOMO’s or LUMO’s which can be charged, leading to triplet biradicals. Classical examples are the pentadienyl cation \textsuperscript{37}\textsuperscript{77} and some cations of substituted derivatives\textsuperscript{78,79} as well as the benzene dianion \textsuperscript{38,80} so called antiaromatic annulenes. The perphenyl substituted derivatives \textsuperscript{37, 38}, on the other hand, yielded singlet ground states or paramagnetic contributions only.\textsuperscript{81,82} For hexaphenylbenzene \textsuperscript{38} even a one step dehydrocyclization to hexabenzocoronene \textsuperscript{46} is well established.\textsuperscript{83}
Therefore also 1,3,5-triphenylbenzene 39 dianion and dication,\textsuperscript{84} triphenylene dianion 40,\textsuperscript{85} and the dication of donor substituted derivatives 41,\textsuperscript{86} 42\textsuperscript{87} yield triplet ground states. Suitable derivatives with lowered reduction/oxidation potentials as 42\textsuperscript{88} and hexaazahydrocoronene 43\textsuperscript{89} were also deemed as building blocks for organic magnets by Breslow\textsuperscript{88-92} in alternating donor acceptor stacks, in line with McConnell model II.\textsuperscript{93} For 43 more detailed studies revealed the singlet ground state\textsuperscript{94,95} which was also found for the dianion (D’ = 0.054 cm\textsuperscript{-1}, \(\Delta E_{ST} = 2.3\) kcal/mol)\textsuperscript{96} and dication (D’ = 0.0591 cm\textsuperscript{-1}, \(\Delta E_{ST} = 1.4\) kcal/mol)\textsuperscript{97} of coronene 44. Due to Jahn-Teller distortions also other fused hydrocarbons like corannulene 45\textsuperscript{98} and hexabenzocoronene 46,\textsuperscript{99} loose their high symmetry upon charging, yielding singlet ground state dianions. For 46, however the thermal activation of the triplet state is extremely small, nearly degenerate with the singlet (\(\Delta E_{st} = 15\) cal/mol). For higher charged molecules the use of an additional independent method besides EPR spectroscopy to characterize the charging process like optical absorption or potentially controlled generation has shown to be very powerful in many occasions. The latter holds also for the reduction of [60]fullerene which even possesses threefold degenerate LUMO’s in the neutral form. Only for the dianion of C\textsubscript{60} new large thermally excited ZFS components were measured, being lost at trion formation, additionally evidenced by absorption spectroscopy\textsuperscript{100} and potentiometric control.\textsuperscript{101}
Without such control in higher concentrated samples even triradicals and higher spin states could be found, while the single crystal study of the trianion supported its doublet state.

3. **TRIRADICALS - THE QUARTET STATE**

Many triradicals have been evidenced by EPR spectroscopy, since the early work by Brickmann and Kothe on a triradical in the quartet state and the full analysis of its powder spectra. At first glance some ambiguities from cw-EPR spectral analysis may easily occur, since the ZFS in the \( \Delta m_S = 1 \) region itself can be very similar to a mixture from mono- and biradicals. Additional information then come from the possible identification of a \( \Delta m_S = 3 \) forbidden transition and splittings of the size of \( D' \) in the \( \Delta m_S = 2 \) region (e.g. Figure 3). Further hints can be derived in cases of stepwise formation upon charging and control of the relative signal intensities as well as by comparison with similarly structured triradicals.

![Diagram of triradicals](image)

In 1992 a triradical trication of *Trisphenylaminobenzene* (49) was reported, but the ZFS components were very small (\( D = 0.0012 \text{ cm}^{-1} \)), and the 5 line solution spectrum for three equivalent nitrogens unexplained. This forced Blackstock to fully characterize the charging of the hexa-anisyl (50) derivative. The electron donating methoxy groups certainly support the trication formation, where cyclic voltammetry at low temperature (-78 °C) yielded 3 reversible oxidation waves. The liquid solution EPR spectrum of the trication showed 10 lines for strong exchange coupled nitrogens. In frozen state a typical spectrum of a quartet was found (5 lines) with \( D' = 0.0046 \text{ cm}^{-1} \). This value is very close to the one given for the isoelectronic hexaphenyl-trimethylenebenzene (48) (\( D' = 0.0049 \text{ cm}^{-1} \)) and further supported the correct quartet state assignment. Thus it was assumed that in the earlier report some dimerization might have occurred, which can easily be found for triphenylamines and triphenylmethylenes.
The ground state quartet of 50 was further evidenced by 2D-ESTN spectroscopy,\textsuperscript{111} where in a well defined trication no hint of contributing excited doublet states was found.

\[ R_1 \leftrightarrow R_2 \]

The problems of dimerization can also be overcome in extended oligo(m-p-N-phenylaniline)s 51-56 reported by Janssen et al.\textsuperscript{112-114} They indicated quartet ground state for all of them, but certainly with much smaller ZFS ($D' = 0.0026, 0.0029 \text{ cm}^{-1}$ 51, 52) than for 50 due to the larger delocalisation. As seen from the D’ values, the exchange of each phenyl group by a donating methyl substituent still does not strengthen much dipolar interactions.

Comparable triradicals with triazine skeleton obtained by Blackstock,\textsuperscript{115} on the other hand, were found to deviate from Curie like behavior at low temperatures, and a low spin ground state was assumed. This is somewhat in contrast to other reports, claiming the disubstituted 1,3-triazenes or trisubstituted 1,3,5-triazenes to be a more favourable CU than substituted...
1,3- or 1,3,5-benzenes.\textsuperscript{116,117} The s-triazines have also been shown to support high spin ground states for dinitrenes.\textsuperscript{118}

Many more stable quartet triradicals have been reported, synthesized by attaching radical sites to topologically controlled positions of a $\pi$-network. Only a few will be discussed here focusing on EPR studies.

Triradicals with nitroxides as spin carrying units have been synthesized extensively by Iwamura et al.\textsuperscript{119-122} Here the quartet states were proven for the phenylene bridging between the radical sites in 59-61. They have also been established as valuable stable building blocks for molecular magnets upon further ligation with metal complexes through the nitroxide unit.\textsuperscript{123} This is inherently combined with the need of very clean oligo-radicals (100%).

If a methyl center is used (62) a triplet ground state results, while for a central amine in 63 or borane in 64 only doublet ground states were found.\textsuperscript{124,125} This was reasoned by electron excess in case of the amine leading to superexchange between two spin sites, and by electron deficiency in borane, stabilizing degenerate doublet states below the quartet.

Similarly, many nitronyl-nitroxides (NIT) and iminonitroxides (IN) have been attached to aromatic cores and used also in mixtures with nitroxide radicals and as building blocks for molecular magnets.\textsuperscript{126} Typical
examples are the 1,3,5-tris-NIT-benzene (65) by Shiomi et al.\textsuperscript{127} and the tris-NIT-diphenylacetylene 66 by Turek et al.\textsuperscript{128}

\begin{center}
\includegraphics[width=\textwidth]{chemical Structures.png}
\end{center}

While many publications just treated symmetrical radical sites with a 1,3,5-phenylene bridging, Matsuchita and Itoh et al.\textsuperscript{129} tried to charge dicarbenes to the monoanion 67 and monocation 68. First some deviation from Curie type behavior in the very low temperature range \(\sim 5\) K was reported, but since there was no obvious reason for spin frustration of the quartet state, the work was redone carefully also with \(^{13}\text{C}\) labelling of the methylene.\textsuperscript{130} The quartet ground state was evidenced thereby for both, 67 and 68.\textsuperscript{131}

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\includegraphics[width=\textwidth]{chemical Structures 2.png}
\end{center}

Several other triradicals in the quartet state were also obtained by using mixtures of different radical sites - so called “heterospin molecules” - and modified topology as for instance nitrenes in combination with NIT or nitroxides.\textsuperscript{132,133} Although a quinoid structure can be formed in 69 it remains a non-Kekulé form with 3 unpaired electrons and quartet ground state. The ZFS value (\(D' = 0.277\) cm\(^{-1}\), \(E'\sim 0\)) is smaller than for the \(m\)-isomer 70 (\(D' = 0.347\) cm\(^{-1}\), \(E' = 0.0045\) cm\(^{-1}\)) which was found to be a general criterion for a range of different radicals, e.g. the nitroxide 71 (\(D' = 0.336\) cm\(^{-1}\), \(E' = 0.0045\) cm\(^{-1}\)) yields nearly identical ZFS components as the NIT 70. This similarity for the ZFS still makes sense although 70 actually should be low spin ground state judged from the topology (it was only reported at 77 K) while 71 should have high spin ground state.

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Chapter 12

The features of the nitrenes coupled with NIT or nitroxide radicals are structurally very close to those found earlier by Matsuda and Iwamura\textsuperscript{134,135} for carbenes mixed with NIT \textsuperscript{72} (D = 0.113 cm\textsuperscript{-1}, E = 0.006 cm\textsuperscript{-1}) or nitroxide \textsuperscript{73} (D' = 0.118-0.125 cm\textsuperscript{-1}, E' = 0.006 cm\textsuperscript{-1}). Just in the case of carbenes, conformational isomers occur again and the spin is partially delocalised in the outer phenyl ring.

As shown for the trisnitroxide \textsuperscript{59} one diphenyl-nitroxide can also be used as bridging unit between radical sites. This was extended to bis-NIT \textsuperscript{74}, bis-IN \textsuperscript{75} and their mixed structure \textsuperscript{76}.\textsuperscript{136} Here the EPR spectra yielded no resolved ZFS components, only a strong central signal and some shoulders, together with non resolved $\Delta m_s = 2$ signal. The magnetic measurements further proved the quartet state and were fitted with nearly twice as large exchange coupling for the bis-NIT \textsuperscript{74} ($J = 231$ cm\textsuperscript{-1}) than for bis-IN \textsuperscript{75} ($J = 127$ cm\textsuperscript{-1}). For the asymmetric \textsuperscript{76} an even more complex analysis yielded one very strong and a weak interaction. The elucidation of these effects on a cleanly separated sample seems worthwhile, since NIT can easily be contaminated with IN upon sample preparation.

Sugawara demonstrated that the attachment of two NIT units to thianthrene in \textsuperscript{77,78} regardless of the substitution position in 2,7 or 2,8 lead to quartet ground states upon one electron oxidation of the thianthrene.\textsuperscript{137}
The ZFS components also are nearly identical for both isomers $D' = 0.012(5)$, $E' = 0.0009 \text{ cm}^{-1}$. The independence of the topology was reasoned by equally signed spin densities on the 7 and 8 position of the thiophene cation. Several other redox switchable high spin molecules based on stable radicals and easily oxidized $\pi$-systems like tetrathiafulvalenes or triarylamines have been prepared by Sugawara et al.\textsuperscript{138,139}

### 4. TETRARADICALS - THE QUINTET STATE

Many tetraradicals in the quintet state have been evidenced by EPR. Classical examples are the $m$-phenylene bridged dicarbenes and dinitrenes mentioned in the introduction and a 3,6-Dimethyleneanthracenediyl-1,7-dioxy 80 in its quintet state.\textsuperscript{140} The carbenes and nitrenes have been applied as spin sources with many different CU’s.

In 1991 Iwamura\textsuperscript{141} evidenced that quintet spectra are formed for the diphenylacetylene and diphenyldiacetylene dinitrenes 81-84. But stable ground state entities resulted from the $m,p'$ isomers 81, 82, only. The quintet $m,m'$-isomers 83, 84 gave maximum intensity at 50 and 28 K, according to antiferromagnetic exchange with $J \approx -30$ (83) and $J \approx -14 \text{ cal/mol}$ (84), respectively. The exchange couplings were derived from the fit of the intensity of the quintet state by assuming standard thermal excitation with $\Delta E_{\text{Qan,S}} = 6J$ and accounting for the intermediate triplet state $\Delta E_{\text{S,T}} = 2J$.

\[ I \cdot T = C \cdot \frac{\exp(6J/RT)}{1+3\exp(2J/RT) + 5\exp(6J/RT)} \] (6)
From the ZFS \(D' = 0.169 \text{ cm}^{-1}, E' = 0.040 \text{ cm}^{-1}\) it was concluded that the Z-isomers should be preferred. The overall result is similar to the reports of ground state singlets for the dicarbenes \(^{85}\) and ground state quintet for \(^{86}\). Several years before it had been shown that a meta-para linkage at a stilbene unit yields quintet ground states for \(^{87}\).

Further diphenyldinitrenes with 1,1-ethenyl\(^{145,146}\) or carbonyl\(^{146}\) bridges were also studied for obtaining deeper insight into the spin coupling mechanism. The \(p,p'\)-isomers \(^{88,91}\) were shown to be the only one to form ground state quintets, while for the \(m,m'\)- and \(m,p'\)-isomers \(^{89,90}\) thermally activated quintet states were defined.

While spin polarization accounts for the low spin state of the \(m,p'\)-isomer it does not in case of the \(m,m'\)-isomer. The latter was concluded by Iwamura to be explained as a “doubly-disjoint” structure on basis of Borden’s classification. A comparison with nitroxide spin centers instead of nitrenes at the same positions shown above, yielded the same signs for the exchange interaction, even though the dinitroxides lead to weaker spin polarization into the bridging units. Based on the nitrene results and Itoh’s model\(^{147}\) for weakly interacting triplets, the ZFS \(D_q\) of a quintet was estimated from the two triplets \(D_t\) from centers \(a\) and \(b\) (eq. 7). Lahti\(^{148,149}\) proposed a vector model to explain the angular dependence of the ZFS in bridged dinitrenes. Thereby it clearly came out that a decent approximation is obtained but that it is still limited to planarized spin centers and \(\pi\)-network\(^{149}\). Overall the topology determines the ground state multiplicity as long as no large geometrical demands (strong torsions) occur.

\[
D_q = \frac{(D_t^a + D_t^b)}{6} + \frac{D_{ta}}{3}
\]  

(7)

In an elegant work using the TMM-approach with 2-alkylidene-1,3-cyclopentanediyl, Dougherty\(^{92-95}\) tested the spin interaction through various spacers \(^{92-95}\). Even saturated CU’s as cyclobutanediyl, cyclopentanediyl, and adamantyl were included. For each system Kekulé forms can be drawn towards the inner/outer units, indicating the bridging of triplets directly connected to the spacer. In \(^{92}\) different \(R\) were also applied demonstrating
the ability to control the interaction. For \( R = \) methyl still sufficient coupling to the quintet was found, but no longer for \( R = \) tert.-butyl where only triplets can be measured since the biradicals are twisted out of conjugation and become separated moieties.

93 and 94 were shown to possess quintet ground states, with \( D' = 0.021 \) and 0.018 cm\(^{-1}\), respectively. For 94 thermally activated triplet components appeared around 40 K in the temperature dependent study, suggesting a small quintet triplet gap \( \Delta E_{QT} = 200 \) cal/mol (\( \Delta E_{QT} = 4J, J = 50 \) cal/mol). For the adamantane derivative 95 containing a 1,3-cyclohexanediyl fragment, no quintet was found upon photolysis of the diaza-precursor. This showed that the interaction between the triplet sites depends sensitively on the through bond coupling, the bond angle, and the distance.

Heterocycles have been considered further as substitutes for benzene, e.g. the aforementioned triazine\(^{118}\) and pyridine.\(^{151-154}\) Dougherty\(^{151}\) described stable quintet ground state for all three pyridine isomers \( 96-98 \). Only small changes in \( D' \) were found for the neutral tetraradicals and as assumed from model calculations, \( 96 \) is closest to \( 92 \), since the nitrogen is substituted in a so called “inactive” position (unstarred). Additional formation of the pyridinium cation by protonation led to singlet ground state for the 2,6-isomer \( 99 \) as predicted, but surprisingly not for the protonated 2,4-isomer \( 98 \), where also an active position is involved.

Using phenyl carbenes as radical sites, other authors\(^{152}\) suggested that only 3,5-pyridine bridging should yield high spin quintet states, while for the 2,6- and 2,4-pyridine bridging, the disturbance of active sites by heteroatomic substitution should lead to ground state singlets. This is somewhat contradictory to other reports where the 2,6-pyridine bridging is well acknowledged for high spin formation.\(^{153,154}\) Also Lahti et al.\(^{155}\) tested the interaction of di- and trinitrenes through 2,6-, and 2,4-, and 2,4,6-substituted pyridines. They further supported the finding of high spin ground
states by ab initio and DFT calculation with 6-31G* basis sets. The pyridine seems thus to act as coupling unit very similar to benzene.

Rajca\textsuperscript{156} synthesized and characterized many \textit{oligoarylmethanes} which were used to get further control of spin interaction but also directed towards use in larger arrays, where a defect on one spin site would not hinder interaction between the others. One of these examples is the cyclic tetraradical \textit{100}, which has been used as a core or a building block in many other polyradicals. The ZFS components of \textit{100} (D$' = 0.0033$ cm$^{-1}$) are only slightly larger than those for the branched tetraradical \textit{101}\textsuperscript{157}.

\begin{center}
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\end{center}

A small central peak was attributed to half integral spin (S=1/2, 3/2) impurities estimated to contribute less than 10%. No thermally excited low spin components were envisaged up to 80 K, which are a problem for the even further extended high spin states.

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\end{center}

Finally it should be mentioned that in a very different approach well defined tetraradical formation could be proven for diketyl radical dimerization through metal bridging.\textsuperscript{158,159} Based on very early examples of
triplet formation in benzophenone anions were shown to persist in their quintet ground state.

5. HIGHER SPIN STATES, \( S \geq 5/2 \)

Just a handful of papers are dealing with spin state detection by EPR of even higher spin multiplicities than the quintet, with the majority of reports for the heptet state. Two pentaradicals with \( S=5/2 \) state based on NO as in 103 and arylmethyl 104 radical sites of very similar structure have been identified. They were found in their sextet ground state from temperature dependent studies. As expected from further spin delocalisation into the outer aryl units in 104 the ZFS parameters are smaller (\( D' = 0.0027 \text{ cm}^{-1}, E' = 0.0009 \) ) than for the oligonitroxide 133 (\( D' = 0.0039, E' = 0.0013 \text{ cm}^{-1} \)).

The heptet state was considered most often, since it is accessible through threefold 1,3,5-benzene substitution with \( S=1 \) radical units. The first prepared hexaradical of this type was a tricarbene reported in 1973 soon after the understanding of the dicarbene spectra. Further preparations on extended linear carbene 105, 106 followed. They were studied by single crystal EPR spectroscopy and shown to persist in \( S = 4 \) and \( S = 5 \) state. The oligocarbones are much more difficult to characterize in powders, since the number of possible conformers increases, all giving rise to somewhat different ZFS parameters.

Adam et al reported the hexaradical 107 based on the 1,3-cyclopentane-diyl unit as a spin carrier. It was shown that nitrogen extrusion takes place in a stepwise fashion, leading to a triplet, a quintet and finally a heptet ground state. The intermediately formed bi- and tetraradicals were shown to be identical to the ones found earlier 108, 109. The difficulty in analysing the hexaradical was its incomplete formation (yield \( \sim 35\% \)). Although the identification with ZFS components of \( D' = 0.00907 \text{ cm}^{-1} \) and
a small $E' = 0.000187 \text{ cm}^{-1}$ was possible$^{166,167}$ such molecules then can not be considered as building blocks for organic magnets, since incomplete formation is a major problem in all extended organic high spin systems.

In the early 90s Rajca$^{167}$ synthesized and characterized by cw-EPR spectroscopy star shaped polyarylmethylradicals 110, 111 achieving $S = \frac{7}{2}$ ($D' = 0.00163$, $E \sim 0$) and $S = 5$ ($D' = 0.0012$, $E \sim 0$), which could still be resolved due to symmetry ($E \sim 0$) and quite clean preparations of the spin states with only small contributions from lower spin moieties. Similar carbene structures with $S = 6$ (112) and $S = 9$ (113) were reported,$^{168,169}$ which at that time have been the highest spin states from organic high spin molecules. However EPR spectroscopy was applied only up to $S = 6$.

The comparison of different hexacarbenes was made including cyclic and further branched derivatives 114-116$^{171,172}$. Different fine structures were observed and shown to follow Curie behaviour but no complete analysis of the complex spectra was given. A critical behaviour was found for the further extended branched nonacarbenes 114, which did not yield the anticipated $S=18/2$ spin state, but $S = 7$. Subsequent sample analysis
indicated a loss of two active centers most probably due to chemical bond formation between the outer carbenes which should be spin allowed.\textsuperscript{172} Since such unsubstituted carbenes generally suffer from high reactivity and destruction at ambient temperatures new halide substituted derivatives, as mentioned for the radical sites, are very promising. An example for such an extended stable hexaradical 117 was given by Tomioka et al.\textsuperscript{11}

Upon the search of stable building blocks with very high spin, Rajca extended manifold the structures of polyarylmethyl radicals.\textsuperscript{157,173} One major goal was to establish substructures where even a defect does not hinder the interaction between all remaining spins. He achieved that perfectly using Calix[4]arene rings like 118, and many more. For such well defined molecules full cw-EPR spectral analysis is possible. For 118 the ZFS components were determined to be $D' = 0.00127 \text{ cm}^{-1}$, $E' \sim 0$. 
Some remarkable resolutions of high spin states in polymers by 2D-ESTN were achieved, where standard cw-EPR just showed a single broad line.\textsuperscript{9,21,174} High spin components in the polymer 119 were identified as having $S = \frac{1}{2}-4$ from their different nutation frequencies. Many more polyradicals like 120, 121 with phenoxy, nitroxy and other radical sources attached under topological control to conjugated linear polymer chains or to star shaped, dendritic or hyperbranched structures were still published in the 90’s.\textsuperscript{175-181} The overall problem as in many other polymeric materials is the complete conversion of all active precursors to the radical sites without defects or a “soft” polymerisation with the radicals as shown nicely by Miura et al.\textsuperscript{179} Therefore usually only relatively low spin concentrations of 0.2-0.9 per repeat unit are found, displayed by an average of discrete $S$ states, and no ferromagnetic domains are formed.

So far the only way towards very high spin pure organic molecules and polymers is based on Rajca’s extension\textsuperscript{182,183} of ladder type and star-branched polymers with multiple pathways of spin interacting moieties. Intriguing example are the ladder type structures 122 ($S = 12.4/2$ measured instead of $S = 14$) and the cyclic branched molecule 123 ($S = 10$ measured instead of $S = 12$) which have further been extended to polymers accessing high spin states of $S=50, 100$ or now even several 1000’s.\textsuperscript{184} However EPR does no longer represent a useful technique for the identification of these spin states.
6. CONCLUSION AND OUTLOOK

The highest spin states in organic molecules determined by EPR spectroscopy so far do not exceed the $S = 6$ state and it remains an open question whether even with new developed and extended pulsed techniques they will become identifiable. Therefore, the inherent usefulness of the EPR methods seems to be based on identification of oligoradicals and their ground state multiplicities. Manifold applications of magnetic susceptibility measurements have shown to be useful and superior for identification of real high spin states ($S > 10/2$) or magnetic probes and can be used in addition.

From the outlines above it should be clear that application of EPR to high spin molecules is very fruitful and an important characterization. As mentioned in the introduction most of the work is directed towards organic magnets. Although it is already an intellectual task to add new building blocks of high spin ground state by design, magnetic ordering desires bulk spin alignment. In order to use the molecules further as building blocks for
organic magnets, the molecules in their high spin state should be well defined and very clean, not contaminated partially by lower spin states. Since 1991 a large progress has been made and many more examples of organic ferromagnets became available. Earlier reported ones were shown to be unrepeatable and most probably due to impurities, especially those from ill defined polymers. Some of the newly developed organic ferromagnets are based on stable organic mono- or biradicals and their 3-dimensional ordering. For instance after the nitrophenyl-NIT ordering at 0.7 K, Chiarelli and Rassat showed an organic ferromagnet with a ferromagnetic transition temperature of $T_c = 1.48$ K and Banister et al. succeeded in the alignment of a dithiadiazolyl derivative with a much higher $T_c = 36$ K.

Also pure organic [60]fullerene charge transfer compounds have been found to exhibit ferromagnetic ordering besides high superconductivity. Already in 1991 Wudl et al. realized a C60/TDAE complex with $T_c = 16$ K and prompted further studies for understanding this phenomenon from pure $S = \frac{1}{2}$ spin systems.

Inorganic organic hybrids have shown to become very promising and resulted in magnetic ordering at much higher temperatures than for pure organic molecules. For instance Gatteschi mixed hexafluoroacetylacetonato-Mn(II) with NIT and found magnetic transition at $T_c < 8$ K. This approach was further used extensively with NO and NIT radicals as mentioned earlier.

Certainly the inorganic complexes prepared by Verdaguer based on iron exchange in Prussian blue by V and Cr ($V[Cr(CN)6]$, $T_c = 315$ K) and those of Miller, complexes vanadocene with tetracyanoethylene under loss of the benzenes ($V(TCNE)x(CH2Cl2)y$, $T_c \sim 400$ K) result so far in much higher $T_c$'s. However the organic and inorganic/organic hybrid solids based on organic high spin molecules are still a very promising field of material science research and many more interesting results are anticipated from them in the near future.
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