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INTRAMOLECULAR LONG RANGE ELECTRONIC SPIN EXCHANGE COUPLING IN DIRADICALS: A NEW MAGNETIC COUPLING UNIT.

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Abstract A phenyl diethynyl bridge is used as a magnetic coupling unit (MCU) between two iminonitroxide π-radicals. The ethynyl moiety is attached to the central phenyl ring either in the para or in the meta position. The magnetic properties of the resulting bis-imino nitroxide diradicals (*p*-BIN and *m*-BIN) are investigated both at the molecular scale and in the condensed phases. An intramolecular through bond spin coupling is observed at an unusual long distance (about 20 Å) in both derivatives. However, the ground state is found to be a singlet spin state in both compounds. The results suggest an interplay between the spin polarization and the spin delocalization (π-conjugation). An intermolecular weak antiferromagnetic spin coupling is occuring in both compounds.

INTRODUCTION

The prediction of the high-spin magnetic ground state in purely organic molecules, such as π-conjugated oligomers and/or polymers, is mainly based upon the early topological models.[1] Given the difficulty in the art of building such topologically branched polyradicals,[2] it is of utmost interest to synthesize and to characterize new through bond magnetic coupling units (MCU), whose main interest would be the ferromagnetic coupling. Although the theoretical predictions lead to the proposal of numerous MCU's,[3] it is worth mentioning that only a few ones have been synthesized up to now. Within this frame, we have previously reported on diradicals based on stable aryl ethynyl compounds bearing galvinoxyl and phenoxy radicals.[4] Our goal is to design and to characterize such linear or broken rod molecules with the aim to find out some of the relevant parameters governing the intramolecular magnetic behavior. This procedure is

expected to allow the synthesis of i) higher polyradicals, and ii) materials with potential magneto-optical properties.

We report here on the characterization of two phenyl diethynyl diradicals with the imino nitroxide radical (p-BIN and m-BIN, Figure 1a,b).[5]

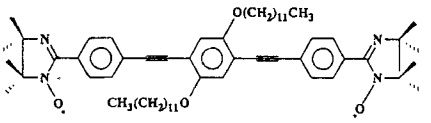

FIGURE 1a. p-BIN molecule

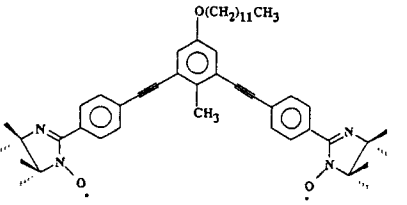

FIGURE 1b. m-BIN molecule

The magnetic properties are investigated mainly with the help of the EPR technique (9 GHz, 4K-300 K) both in solution and in the solid state (single crystal and powder). The studies within the solid state provide additional informations about the intermolecular magnetic interactions. Semiempirical MO calculations have been performed in order to predict the magnetic properties and in particular to get the spin density distribution over the molecules. The aim of these investigations is two-fold: i) to check the efficiency of the MCU, and ii) to get the molecular magnetic ground state.

THE RIGID ROD p-BIN

Crystal structure[5]

The crystal structure of p-BIN (Figure 2) has been determined by X-ray diffraction at 110 K.

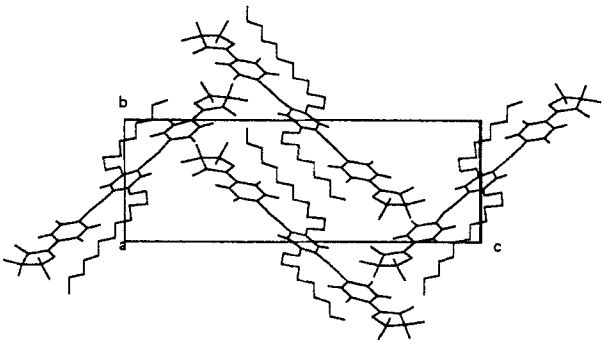

FIGURE 2. p-BIN crystal structure: projection along the a*-axis.

The alignment of the OC_{12} paraffinic chains along the rigid rod skeleton of the molecule is to be noticed. The intramolecular distance between both the NO groups is about 21 Å and the molecule is almost perfectly flat. This points towards an efficient π-conjugation throughout the whole molecule.

The crystal lattice is monoclinic with the space group P21/c whose parameters: are a=9.337 Å; b=11.956 Å; c=24.788 Å; ß=99.912°. Given the present assignment for the position of the NO group, the shortest intermolecular distances are observed between the side H of the central phenyl ring and O from the nitroxide group NO: $d_{O\text{-}H}$=2.909 Å. The relevance of such intermolecular contacts for a weak ferromagnetic coupling has been already stressed in the case of the ferromagnetic ß-phase of the nitrophenyl nitronyl nitroxide derivative.[6,7] However, the relevance of this mechanism depends upon the efficiency of the spin polarization mechanism in order to enable relevant spin densities on the phenyl ring. The molecular packing results in distorted sheets of square connected molecules within the (bc) plane (Figure 2). These sheets are stacking along the a-axis without well defined interplane contacts.

EPR studies.

EPR study of the molecule into solution. The EPR spectrum recorded at room temperature for a 10^{-3} M solution of p-BIN within a 1:1 mixing of CH_2Cl_2 and p-xylene is reported in Figure 3.

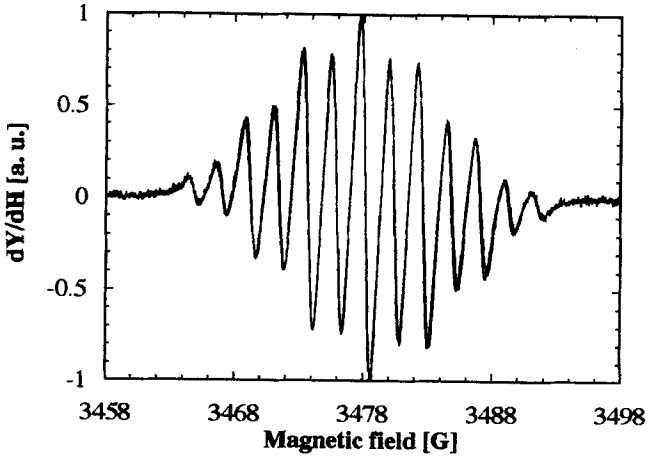

FIGURE 3. EPR spectrum of a solution of p-BIN at 295 K (the simulated spectrum is superimposed).

A susceptibility calibration has been performed upon comparison with a standard sample. The number of radical spins (N_S) in p-BIN is estimated to be N_S=1.8±0.3 spins

1/2 per molecule. The most important feature arising from the study of Figure 3 is that the radical spins within the diradical p-BIN must be described as interacting within the strong exchange limit ($|J| >> |A|$; J=intramolecular exchange interaction, A=hyperfine interaction). This is very unusual, since one would expect the isolated spins in this diradical owing to the large distance between them (c.a. 20 Å). The present experiment shows that the phenyl diethynyl bridge must be considered as a through-bond MCU, although we expect a weak coupling. The following set of hyperfine coupling constants for the two non equivalent ^{14}N nuclei (a_{N1}, a_{N2}) and individual Gaussian line widths (ΔB) is estimated from the simulated spectrum: a_{N1}=4.45 G; a_{N2}=2.22 G; ΔB=0.85 G. However, neither the sign nor the strength of the intramolecular spin-spin interaction may be estimated from the present results.

For this purpose, the EPR study of the solution has been performed in the glassy state from 160 K down to 4 K (Figure 4).

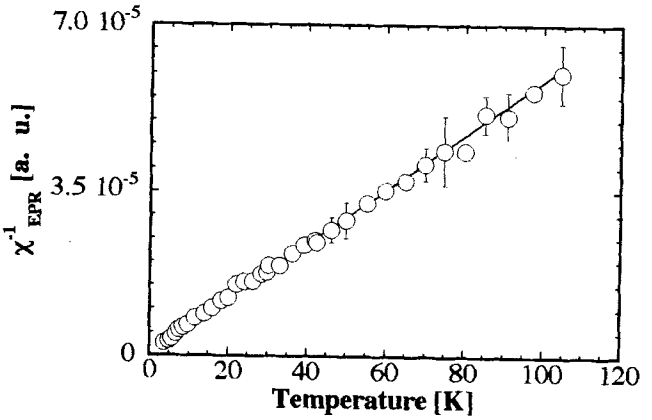

FIGURE 4. Reciprocal EPR integrated intensity as a function of temperature for a glassy 10^{-3} M solution of p-BIN within 1:1 CH_2Cl_2 and p-xylene. Continuous line: fit of the experimental data with $(T-\theta)/C$; θ=-1.31 ± 0.16 K.

The temperature dependence of the reciprocal EPR susceptibility is well represented by a Curie-Weiss law with an extrapolated θ=-1.31 K. In the present case of isolated diradicals, this corresponds to the limit $k_BT>>J$ of a Bleaney-Bowers law with a singlet ground state and a singlet-triplet energy gap of 2.6 K.[8] Neither the half-field signal ($\Delta M_s=\pm 2$) nor the fine structure were observed for this thermally populated triplet state.

The observation of nearly degenerate singlet and triplet states is in agreement with the results of the MO calculations (see below). Assuming the unexpected intramolecular spin exchange coupling, the stabilization of the singlet ground state could be predicted

by a simple rule of the alternation of the sign of the spin densities. Thus, following such a simple scheme the results of geometrical modifications might stabilize the triplet ground state.

Solid state EPR. The temperature dependence of the EPR susceptibility is reported for a single crystal between 4 K and 150 K in Figure 5. The temperature dependence of the reciprocal EPR susceptibility is well represented by a Curie-Weiss fit between 4 K and 150 K yielding an intermolecular weak antiferromagnetic coupling with an estimation of θ =-0.6±0.1 K. Such a weak intermolecular magnetic coupling was expected from the previous analysis of the crystal structure, since no short intermolecular contacts were found between molecular sites with a high spin density.

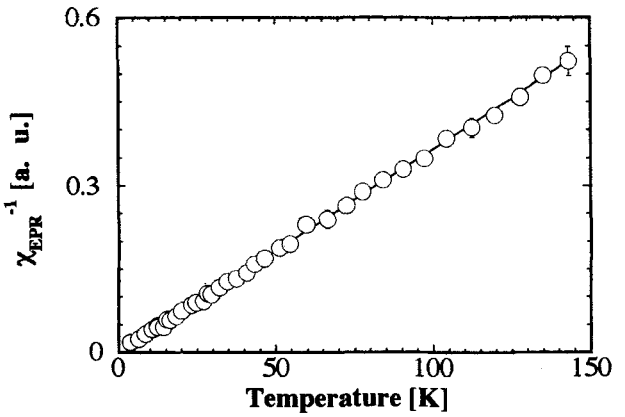

FIGURE 5. Reciprocal EPR susceptibility of a single crystal of p-BIN versus temperature. Solid line: Curie-Weiss fit; θ =-0.6±0.1 K.

Spin densities from semi-empirical MO calculations.

The semiempirical calculations are performed in two successive steps, namely i) the geometry optimization, and ii) the evaluations of the spin density. The calculations were carried out using the program package MOPAC 6.0.[9] In this work, both AM1 and PM3 approximation schemes were used. The geometries were obtained within the unrestricted Hartree-Fock method. For p-BIN, a perfectly planar geometry is obtained for the unsubstituted compound, which is in close agreement with the geometry observed in the crystal structure. Lowering the symmetry upon substitution in the meta position (m-BIN) results in a twist of the five-member ring (25°-30°) without relevant modifications of the spin distribution. In general, the MOPAC program yields very poor results for the spin densities;[10] for this reason, the INDO approximation has been used to compute the spin densities.[11,12] The spin densities were calculated for the molecules in the triplet state. The full discussion of the results of the MO calculations will be

reported in a forthcoming publication[13] and we summarize here only the results about the spin densities.

As previously reported, the MOPAC program gives the correct qualitative trend for the spin polarization but largely enhanced (S(S+1)>3).[14] The eigenvalue of S^2=S(S+1) after spin annihilation in the triplet state is very close to the theoretical value, namely S(S+1)=2.001. The spin densities ($\rho_S \times 10^4$) over the $O_1N_1CN_2$ imino nitroxide fragment are as follows: 6698 (O_1); 2349 (N_1); -1096 (C); 2077 (N_2). As expected, the spin density is strongly localized on the NO fragment. It is worth noting that not only the sign but the order of magnitude are well reproduced as compared to a recent spin density determination by polarized neutron diffraction and *ab initio* calculations for another imino nitroxide derivative.[15] The spin density falls off very rapidly after the nearest six-member ring. The values obtained on the C-C triple bond are less than 10^{-2} μ_B, and they are less than 10^{-3} μ_B on the central phenyl ring. The ground state is found to be a singlet spin state.

The overall picture of p-BIN is that of a diradical with exchange coupled spins having a singlet ground state and nearly degenerate singlet and triplet states. The weak intermolecular antiferromagnetic coupling results from the crystal packing. The most important fact is the unusual through-bond spin exchange interaction at a distance of 20 Å. Given the occurrence of through-bond exchange coupling, it is interesting to introduce a geometrical modification of the p-BIN molecule in order to check the possible resulting intramolecular ferromagnetic coupling yielding a triplet ground state. The following section deals with such a molecule named m-BIN, since the phenyl ethynyl bridge are now in the meta position of the central phenyl ring (Figure 1b).

THE BROKEN-ROD m-BIN

The main modification introduced by the meta connection to the central phenyl ring corresponds to an even number of bonds between the radical sites instead of an odd one in the p-BIN molecule (Figure 1a,b). Therefore, assuming the alternation of the sign of the spin densities the spin polarization would result in a parallel alignment of the radical spins. The crystal structure of m-BIN is unknown, since an amorphous state is observed at room temperature and no single crystals could be grown.

EPR studies.

The same route is followed than the one reported for the p-BIN material. The study of the molecule into solution yields the nature of the diradical, i.e. isolated spins vs. interacting spins. The low temperature study of the signal of a glassy solution then

allows the determination of the magnetic ground state.

EPR study of the molecule into solution. The EPR spectrum recorded at room temperature for a 10^{-3} M solution of m-BIN within a 1:1 mixing of CH_2Cl_2 and p-xylene is reported in Figure 6. The number of radical spins (N_s) in m-BIN is estimated to be N_s=1.6±0.3 spins 1/2 per molecule. It is clear that the radical spins are not isolated. The 13 lines expected for the interacting spin system are well observed (see Figure 3 for p-BIN). However, there is a strong asymmetry of the different components. The 1:2:5:6:10:10:14:10:10:6:5:2:1 sequence of the amplitudes is no longer obeyed. This may originate from: i) a weaker exchange in m-BIN than in p-BIN, i. e. the intermediate range may be considered[16,17] , or ii) the difference in the molecular motion,[18] e. g. the rotation correlation time is very different for these large molecules. Although the MO calculations presented below suggest a greater efficiency of the spin polarization in m-BIN than in p-BIN, the π-conjugation may be less efficient in this case.

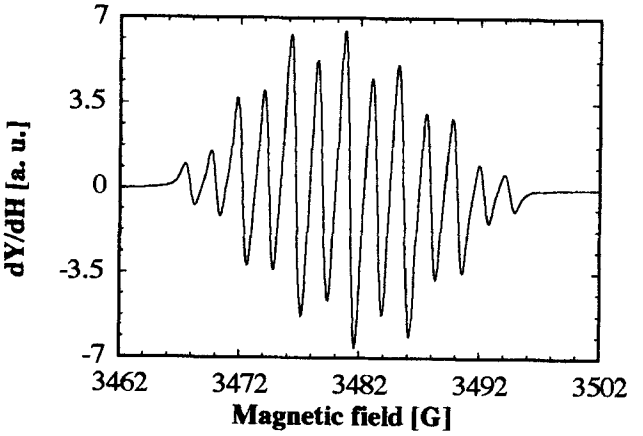

Figure 6. EPR spectrum of m-BIN in solution at room temperature

The results of the EPR study of the glassy solution of m-BIN are presented in Figure 7. The temperature dependence of the reciprocal EPR integrated susceptibility is represented by a Curie-Weiss law with an extrapolated θ=-0.87±0.05 K. As for p-BIN this corresponds to a diradical with interacting spins. The magnetic ground state is the singlet state. The excited triplet state is separated from the ground state by c.a. 1.7 K. The remarks made for p-BIN concerning the half-field signal and the fine structure hold for m-BIN. The observation of nearly degenerate singlet and triplet states is in agreement with the theoretical prediction. However, the stabilization of the singlet ground state rather than the "topologically expected" triplet ground state in m-BIN must rely on more subtle mechanisms which cannot be described by the simple application of

the alternation rule for the spin densities. The interplay (positive or negative) between the different mechanisms for intramolecular spin coupling in π-conjugated diradical having butadiene as a MCU has been discussed theoretically in the frame of ferromagnetic or antiferromagnetic coupling.[19] Both the spin polarization and the π-conjugation mechanisms are required for the present materials to behave as MCU's.

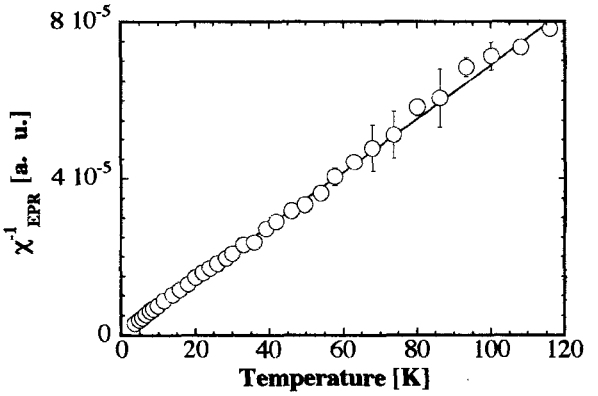

FIGURE 7. Reciprocal EPR integrated intensity as a function of temperature for a glassy 10^{-3} M solution of m-BIN within 1:1 CH_2Cl_2 and p-xylene. Continuous line: fit of the experimental data with (T-θ)/C; θ=-0.87 ± 0.05 K.

Solid state: EPR , SQUID The existence of an amorphous state at room temperature in the solid state of m-BIN is suggested by the observation of the thermal behavior of powder material under the polarized light microscope. Preliminary DSC scans show a weak peak of enthalpy by c.a. 320 K. The sensitivity of the EPR technique allowed a clear determination of the temperature of transformation. However, the nature of this transformation is still unclear: crystallization process, ... The jump of the peak-to-peak amplitude of the absorption derivative is well observed in Figure 8 at 320 K. It is worth noting that the degradation of the sample is observed at temperatures higher than 350 K. This yields irreversibility and the loss of radical spins. The lack of observation of any change in the line width within the experimental accuracy (0.1 G) emphasizes the high disorder suggested by the results obtained from DSC and microscopy.

The susceptibility of a powder sample has been determined as a function of the temperature within a field of 0.1 T using a SQUID susceptometer. The susceptibility follows a Curie-Weiss law with C=0.741±0.005 emu.K/mole and θ=-0.98±0.04 K. The intermolecular antiferromagnetic interactions are within the same range than for the p-BIN material.

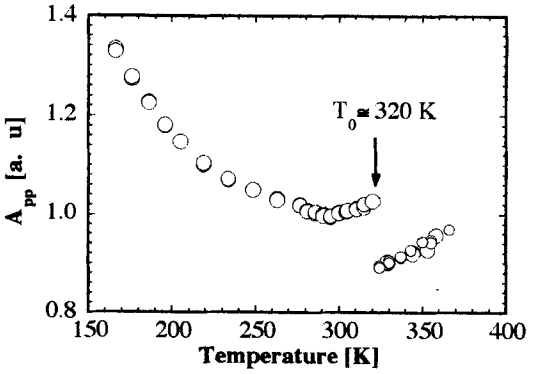

FIGURE 8. Temperature dependence of the peak-to-peak amplitude of the first derivative of the EPR absorption signal of a "powder" of m-BIN.

Spin densities from semi-empirical MO calculations.

The procedure summarized for p-BIN is followed for m-BIN. The step of the geometry optimization is actually important, since no crystal structure is available. The OC_{12} chain has been simulated by an $0C_2$ fragment. A twist angle of the terminal five-member rings, namely 25.6° and 27.3°, is found with respect to the phenyl ethynyl moieties. The spin densities ($\rho_S \times 10^4$) over the $O_1N_1CN_2$ imino nitroxide fragment are : 6777 (O_1); 2372 (N_1); -1003 (C); 1857 (N_2) respectively. It is worth noting the larger effect of the spin polarization in m-BIN than p-BIN. The ground state is found to be a singlet state. The singlet and triplet spin states are considered as nearly degenerate.

SUMMARY

The radical spins within the diradicals p-BIN and m-BIN are shown to couple magnetically. This result is much attractive, given the long through-bond MCU that the phenyl diethynyl bridge may represent. However, both compounds exhibit a singlet ground state with a small singlet-triplet energy gap. Whereas this result could be predicted from a crude application of the topological rules in the case of p-BIN, the same scheme would predict the triplet ground state for the m-BIN molecule. The present MO calculations reproduce correctly the spin polarization effects within these imino nitroxide derivatives. The nearly degeneracy of the singlet and triplet states was also estimated. The important role of the spin polarization mechanism has been emphasized for the setting up of either the intermolecular ferromagnetic coupling[20,21] or the intramolecular high spin ground state.[22] The present work points to the subtle interplay between spin polarization and π-conjugation. At the present stage neither the through

bond spin coupling in both compounds nor the stabilization of the singlet ground state in m-BIN could be predicted.

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