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The Influence of Chemical Surroundings on the Properties of α-Nitronyl Nitroxide Radicals in Solution. Its Relation with the Magnetic Properties in Solid State

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THE INFLUENCE OF CHEMICAL SURROUNDINGS ON THE PROPERTIES OF α-NITRONYL NITROXIDE RADICALS IN SOLUTION. ITS RELATION WITH THE MAGNETIC PROPERTIES IN SOLID STATE

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Abstract α-Nitronyl nitroxide radicals have been widely used for obtaining molecular magnetic materials. We report two characteristics of this radicals that are important in order to interpret their bulk magnetic properties in the solid state. On one hand, we describe the modification of the spin density distribution in the radical molecule caused by different chemical surroundings and by different substituents using the Linear Solvation Energy Relationship multiparametric approximation. On the other hand, we report the self-assembly of some hydroxylated α-nitronyl nitroxides in solution. The supramolecular aggregates, formed in solution, are found to be very similar than those present in the crystal structures. This fact allows to establish clear magneto-structural correlations that facilitate the interpretation of solid state magnetic properties.

INTRODUCTION

The research of purely organic molecular magnetic materials is an area of enormous activity since the discovery of the first example of a purely organic ferromagnet.[1,2] The main interest of this kind of materials is mainly due to the new and unexpected properties that they may exhibit. In this sense, the combination between a macroscopic magnetic property, like ferromagnetism, and the intrinsic properties of organic compounds (i.e. optical transparency, low density, or optical activity of chiral centres) may open the way to a fascinating world of new materials exhibiting unique properties.

Macroscopic physical properties of molecular materials, like the magnetic ones, are strongly related to two subjects: the intrinsic properties of their building blocks -open shell molecules- and the relative arrangement of these blocks in the solid state. A deep knowledge of both of them is necessary in order to interpret the experimental results or to design new materials with previously predicted properties. In the present paper we report some work done in solution which give insights to both of these aspects.

Intramolecular electronic properties of α-nitronyl nitroxide radicals, specially the spin density distribution, have been studied a lot in the last years with several techniques. [3,4] Although an overall view of such distribution is quite clear neither the reasons for the appearance of subtle modifications nor its consequences for the solid state behaviour are well understood. We report in the first part of this paper the use of the Linear Solvation Energy Relationship (LSER) multiparametric approximation in order to study the spin density distribution of a series of α-nitronyl nitroxide radicals in solution using different solvents. Using this approximation we will show that water changes drastically the spin density distribution of the aromatic ring of such radicals. On the other hand, the spin density of the α-nitronyl nitroxide ring shows less dependence on the chemical surrounding.

The strength of intermolecular forces that control the packing of purely organic neutral compounds in the solid state is rather small. Normally a complex and subtle combination of coulombic attractive forces,[5] hydrogen bonds,[6] π-π stacking[7] and van der Waals forces determine the intermolecular arrangement and, hence, the magnetic properties. In addition, organic compounds have usually a very low internal symmetry. For these reasons, it is extremely difficult to make any prediction of molecular arrangements in the solid state.[8] If strong hydrogen bonds are present, some structural features can be preestablished successfully. So, in a lot of cases hydrogen bonded supramolecular structures have been constructed in a very rational and predesigned way.[9] In the case of hydroxylated α-nitronyl nitroxides, we have reported previously [10] that certain crystalline features or motifs can be induced in a very satisfactory way by the proper design of the radical unit. Of course, the overall crystal packing remains a largely unknown variable until it is experimentally determined. Hydrogen bonded motifs appear clearly in the solid state and were called *secondary structure*, in analogy to biological

systems. These motifs are a clear consequence of the molecular structure and represent a first step in the search to control the crystal packing of molecular magnetic materials. In the second part of this paper we summarise the work done on the study of the aggregation of α-nitronyl nitroxide radicals in solution through hydrogen bonds stressing the similarity between these aggregates and the *secondary structures* in solid state.

THE INFLUENCE OF CHEMICAL SURROUNDINGS ON THE SPIN DENSITY DISTRIBUTION OF α-NITRONYL NITROXIDE RADICALS

The Linear Solvation Energy Relationship Approximation

A lot of multiparametric approximations are used in order to describe the effect of a given surrounding, as the solvent, on a given process in which a free enthalpy change is involved; e.g., EPR coupling constants, reaction rates, absorption frequencies, etc. A given chemical surrounding is described with several parameters so that the effect that it has on the studied process can be completely characterised with them. The intermolecular solvent-system interactions can be of specific (hydrogen bonds, acid-base interactions,...) or non-specific (dipole-dipole, dipole-induced dipole,...) nature. The parameters that describe these effects are determined empirically and used together in a general equation that ought to describe the experimental dependence of the studied process in different surroundings. We have used the LSER approximation [11] in order to study the dependence of the electronic structure, and in particular the spin density distribution of a series of α-nitronyl nitroxide radicals on the solvation. These characteristics are crucial in the interpretation of magnetic properties of bulk solids, since the actual spin distribution of radicals can largely be affected by a specific chemical surrounding and by other electronic interactions like electron-electron dipole or exchange. For this reason, any information about the different factors controlling the spin density distribution will permit to understand changes produced in the crystalline state.

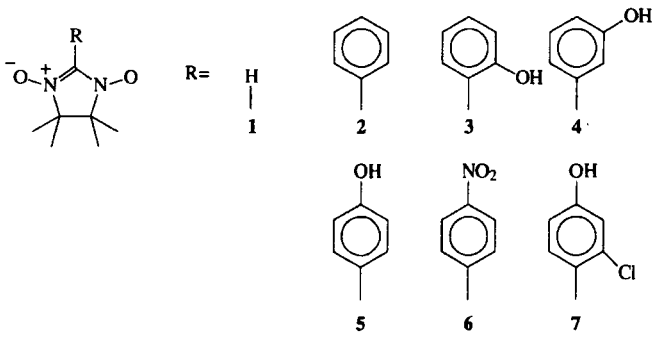
The general expression of the LSER approximation is:

$$XYZ = XYZ_0 + a \cdot \alpha + b \cdot \beta + s \cdot (\pi^* + d \cdot \delta) + c \cdot \Omega + \ldots \quad (1)$$

where XYZ represents the studied enthalpy dependent property, that depends on the intrinsic properties of the system and on the medium in which it is taking place. XYZ_0 is its value in a total absence of system-solvent interaction; being therefore at a first approximation its vacuum value. Each surrounding, usually a solvent or mixture of solvents, is described by the factors α, β, π^*, δ, Ω,etc., each of them describing one type of solvent-system interaction as will be explained later. The values a,b,s,c,... are the regression coefficients between the experimental XYZ values and the α, β, π^*, δ, Ω factors and consequently describe the sensitivity of the process to each one of the molecular interaction mechanisms described by the mentioned factors.

The meaning of the factors, also named solvatochromic parameters, are as follows: α and β describe the ability of the solvent to act, respectively, as hydrogen donor or acceptor, while π^* is a measure of polarity/polarizability of the solvent. δ is a correction parameter of π^*, used when a large variety of solvents are used. Finally, the cavitational parameter, Ω, is a measure of the internal cohesivity of the solvent or, in other words, is an indication of the difficulty of creating a cavity inside the solvent in order to introduce the studied system. The mentioned factors are determined by studying the dependence of a well known process in several solvents. Due to their definition, the solvatochromic factors, α, β, π^*, δ and the cavitational one, Ω, are almost orthogonal; i.e., not interdependent, and are usually scaled so that the regression coefficients can be used directly as a measure of the importance of a given solvent-system interaction.

While the EPR solvent dependence of some nitroxide radicals has been studied with the LSER approximation,[12] no such work has been carried out on α-nitronyl nitroxide radicals. For this reason, we measured the EPR spectra and the electronic absorption spectra of the series of seven α-nitronyl nitroxide radicals depicted below in 26 solvents, ranging from water to n-pentane[13].



Significant dependencies of both, the nitrogen coupling constants of the EPR and the maximum wavelength of the UV-Vis spectra with the solvent have been found. The LSER equation has been used to characterize both dependences and only the α, π* and δ factors were necessary to describe these correctly. An example of the behaviour of the experimental data and of the goodness of the description with the multiparametric LSER approximation, using the parameters α, β, π* and δ, is shown in Figure 1 where the experimental nitrogen coupling constant, a_N, of radical **1** is plotted against the calculated one.

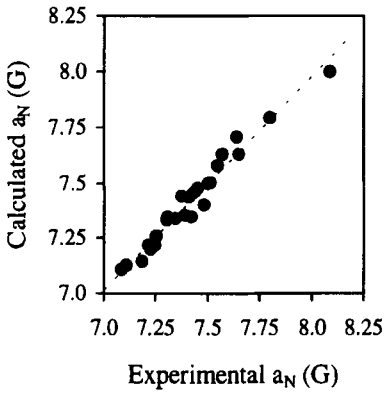
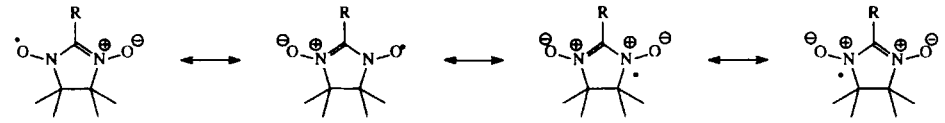


FIGURE 1 Experimental vs. calculated nitrogen coupling constants of **1** using the LSER approximation with 26 solvents.

As expected, larger a_N values were obtained by using polar and protic solvents, with the largest one, 8.09 G, obtained in water. This effect is ascribed to the stabilization

in this kind of solvents of the C and D mesomeric forms where the nitrogen atoms carry the unpaired electron and both oxygen atoms the negative charges.



A B C D

By contrast, in most of the non polar solvents low values are found, the lowest ones found for *n*-hexane and *n*-pentane (7.1 G). The XYZ_0 values of the seven studied compounds were quite similar (7.37 ±0.15 G) with exception of radical **1** (7.16 G), in which the absence of an aromatic substituent might be the cause of its specific behavior.

A graphic representation of the standardized coefficients a, b, s and d of equation 1, corresponding to the solvatochromic parameters α, β, π* and δ, for all the studied compounds are shown in Figure 2 for the case of the nitrogen coupling constants.

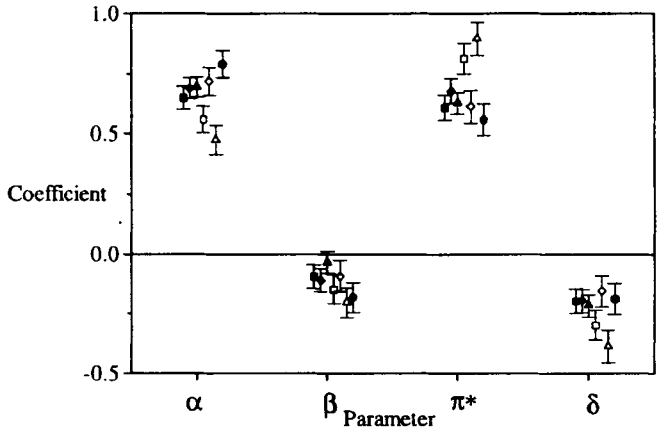


FIGURE 2 Standardized coefficients for the solvatochromic parameters in the LSER analysis of the nitrogen hyperfine couplings for radicals **1-7**. (**1**:■; **2**:◆; **3**:Δ; **4**:◊; **5**:▲; **6**:□; **7**:●)

The most remarkable result of these analyses is that both phenomena, the EPR coupling constants and the UV-Vis absorption bands are almost only dependent on the same parameters; i.e. the hydrogen bonding donor ability, α, and the polarity-polarizability, π* and δ, of the solvent. By contrast, β and Ω (not shown) are not significantly involved in the description of these phenomena. This result is coherent with

that previously found for nitroxide radicals in which the same parameters α, π* and δ were found to describe the a_N dependence.[12] Further, it is found that all the studied compounds behave in a very similar way; i.e., they show almost the same kind of interactions with the solvent.

These analyses also show that water has the strongest solvent radical interactions as revealed by the largest departure of the vacuum values. In a parallel way, the hyperfine coupling constants of all hydrogen nuclei of radicals **1-7** show in water significant lower values when compared with those found in other less polar solvents. The decrease of the coupling constants is specially large for *ortho* and *para* hydrogen atoms where a drop of about 30% of its value in non polar solvents is found. This effect is even more pronounced in the case of radical **3** because this compound shows under many conditions an intramolecular hydrogen bond that is very sensitive to changes on the surroundings affecting the molecular conformation and the conjugation between the α-nitronyl nitroxide moiety and the aromatic ring.

In conclusion, the most relevant interaction that controls the spin density distribution of α-nitronyl nitroxide radicals in solution are the hydrogen bonding ability and the polarity/polarizability of the surroundings. By analogy, the same intermolecular interactions are expected to control the spin density in solid state since such interactions are in many cases the driving forces of crystal packing of open shell molecules. [5,6]

AGGREGATION OF RADICALS IN SOLUTION VIA HYDROGEN BONDS.

In the analysis of the crystal structures of hydroxylated nitronyl nitroxides we have defined the supramolecular assemblies of radicals linked together in a very specific way by strong hydrogen bonds between the OH and NO groups as their *secondary structures*.[6b] In the present section we want to show that in solution similar arrangements of radicals occur and that they can be identified and characterized if convenient analytical techniques are used.

As already mentioned, radical **3** may show interesting effects caused by an intramolecular hydrogen bond. In its isomers **4** and **5** the change of the position of the

hydroxy group in the aromatic ring from *ortho* to *meta* or *para* positions may allow the formation of specific intermolecular hydrogen bonds, giving rise to supramolecular units in solution. These nanoscopic aggregates might exhibit in solution, if generated, a lot of interesting effects that are not observable in the crystalline solids. In addition, the information that can be extracted from the study of these entities can give valuable insights into electronic or magnetic intermolecular interactions, such as dipole-dipole or electron-spin exchange interactions.

We have been successful in the generation and study of discrete supramolecular assemblies of radicals **4** and **5**. Besides the analytical methods useful for the study of diamagnetic compounds (UV-Visible and IR spectroscopies, vapour pressure osmometry) we also used other more classical technique for paramagnetic compounds, like the EPR spectroscopy. Such technique permits to study a lot of intermolecular phenomena, such as electron dipole-dipole interactions, exchange effects, equilibrium rates and dynamic processes.[14]

Supramolecular Aggregates of Radical **4**

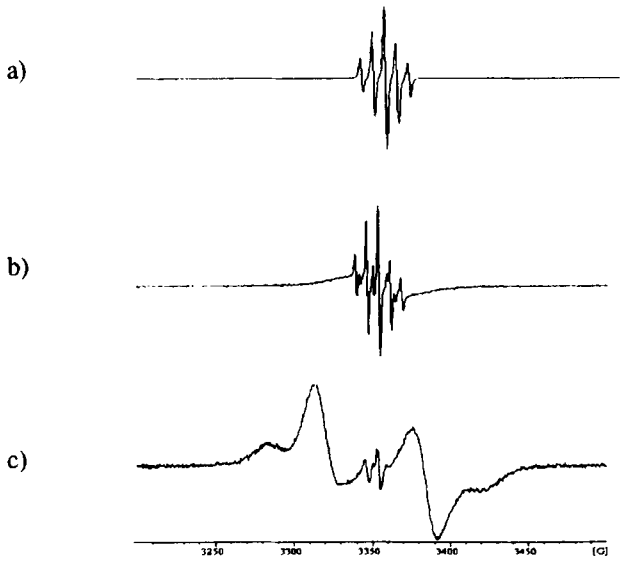
The *secondary structure* of radical **4** found in the solid state are the hydrogen bonded dimers.[6b] This result, together with other theoretical studies, such as the calculation of the molecular *electrostatic potential map*, strongly suggests that this radical ought also to form strong hydrogen bonded dimers in solution. A series of experimental techniques which are briefly reported as follows confirmed this expectation.

First of all, the IR spectrum of **4** in chloroform was followed at room temperature at different concentrations. The appearance of a wide band at about 3300 cm^{-1} upon increasing the concentration together with the simultaneous disappearance of a narrow peak at about 3620 cm^{-1}, that correspond respectively to the stretchings of a hydrogen bonded and a non hydrogen bonded OH group, were observed. This result clearly indicates the formation of hydrogen bonds in solution, but does not yield any information about the dimensionality, size or geometry of the formed species. One additional piece of information can be obtained from the VPO (Vapor Pressure Osmotic) measurements. A 3.5 mM solution of **4** in toluene at 45 °C shows a *number average molecular weight* of

303 ± 10 g/mol. The relatively small difference between the mean molecular weight and the formula mass (249 g/mol) indicates the presence of discrete, more than polymeric *supramolecular entities*. In addition, both MALDI-TOF MS (Matrix Assisted Laser Desorption Ionization - Time of Flight Mass Spectrometry) and Electrospray Mass Spectrometry show the presence of a peak with m/e=498, confirming the presence of a dimeric species of radical **4**. No peaks of higher degrees of polymerization of this compound were observable. Thermodynamics of the monomer-dimer equilibrium were first established by studying the temperature and concentration dependence of the UV-visible spectra of **4** in toluene solutions. Upon cooling or increasing the concentration of the solutions, a blue shift and a hyperchromic effect of all the absorption bands were observed. In addition, an isosbestic point at about 690 nm confirmed that the equilibrium takes place between exactly two different molecular species. The quantitative treatment of the spectral data according to the following equilibrium $2\,A \rightleftharpoons A_2$ yielded ΔH = -39 (± 1) kJ/mol and ΔS = -88 (± 4) J/mol K.

The most interesting features concerning this equilibrium were observed by means of EPR spectroscopy. This technique permits an unambiguous confirmation of the formation of dimers in solution and at the same time allows its structural and magnetic characterization. The temperature dependence of the spectrum of radical **4** in toluene (Figure 3) shows a typical behavior, which is characteristic of a monomer dimer equilibrium of two S=½ species. The observed phenomena and their interpretations are summarized in the following four points.

First, the intensity of the five lines diminishes remarkably with decreasing temperature. A "normal" behaviour for a classical free radical in solution implies the increase of its EPR line intensities upon cooling following the Curie law. Thus, in our case the disappearance of isolated radical species out of the medium is taking place. Together with the disappearance of these five main lines, that correspond to the isolated α-nitronyl nitroxide radicals, new lines appear upon cooling, located approximately at the middle of the original lines. (Figure 3b). Crystallization of the radicals, chemical transformations to diamagnetic compounds, or other phenomena must to be excluded because the overall signal intensity of the EPR spectra does not decrease at all and due to the reversibility of the phenomenon.



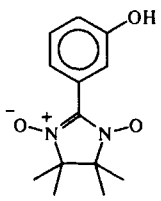


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FIGURE 3 Temperature dependencies of the X-Band EPR spectra of radical **4** in toluene at room temperature(a), at 210 K(b) and in glassy toluene at 120 K(c).

This phenomenon is caused by the presence of a magnetic exchange interaction between the two radical moieties of the dimeric species.[15] Generally speaking, the appearance of new lines in which the coupling constant is 1/n times the original ones indicates the existence of an exchange interaction between *n* radicals having exchange interactions of value *J* between them, which are much larger than the coupling constant *a*; i.e., $J>>a$. In the present case the new lines only appear with very small intensities and they apparently decrease upon further cooling probably because of the overlap of an emergent new broad signal (see below). This fact hinders their detailed analysis. Upon following the temperature dependence of the monomer EPR signal intensity, the extraction of the thermodynamic parameters of the involved monomer-dimer equilibrium is possible. The resulting data are ΔH = -38 (± 2) kJ/mol and ΔS = -70 (± 10) J/mol K which are in excellent agreement with those obtained with the electronic spectroscopy described previously.

Second, on further cooling, completely new and much broadened signals appear. The overall shape of these signals correspond to the typical fine structure, originated by the electron-electron dipolar magnetic field, of a rigid spectrum of an axial symmetric species with S=1 (Figure 3c). In addition to the fine structure, a signal at half-field, characteristic of a triplet species is observed. (Figure 4) Therefore, this result confirms unequivocally the presence of dimers of radical **4** in solution. Experiments performed with other non-polar solvents yield almost identical spectra under frozen conditions. By contrast, in polar solvents, either protic or non-protic, no dipolar field appears and the resulting spectra under frozen conditions are identical to those obtained for isolated α-nitronyl nitroxide radicals.[16] Thus, in polar solvents, intermolecular associations are suppressed, in accordance to the nature of the involved hydrogen bonds.

Third, the simulation of the spectrum[17] of the dimer under frozen conditions (Figure 4) allows the determination of its zero-field splitting parameters, |D'| and |E'|. In a rigid medium |D'| has a value of about 78 G while |E'| is less or equal to 2 G. It is well known that the |D'| value of a high-spin species reflects primarily the mean distance between the interacting electrons. By contrast, the |E'| value depends more on the symmetry of the spin density distribution of the open-shell species. Consequently, the study of both parameters provides information about the structure and electronic distribution of the dimers in solution.

Calculations of the |D'| and |E'| values using the dimer geometry found in the crystal structure and assuming different reasonable spin density distributions indicate strongly that the geometry of the dimer in frozen toluene solutions are experimentally undistinguishable with those found in the crystal structure of **4**.

And, fourth, the temperature dependence of the signal intensity of the half-field signal ($\Delta M_S=2$) allows the determination of the magnetic ground state of the dimeric species. This information allows to correlate a specific geometrical arrangement of radicals with the magnetic exchange interaction that is established between them.[18]

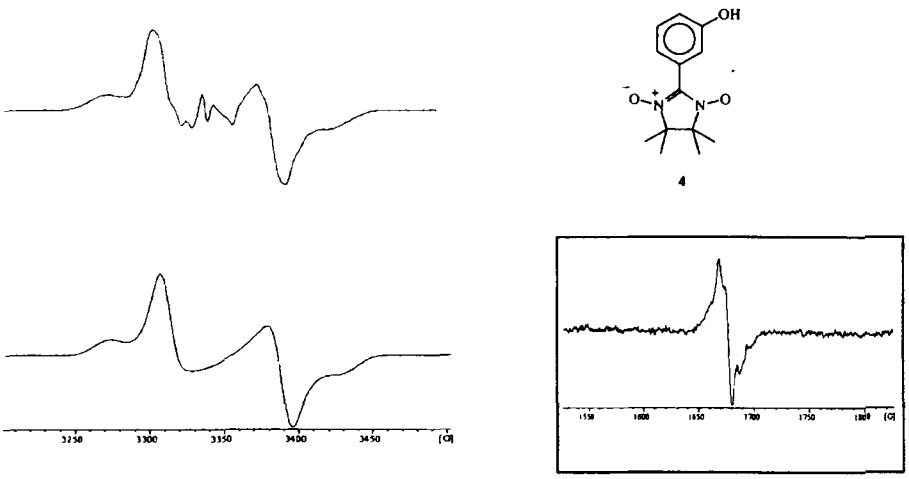


FIGURE 4 Experimental (a) and simulated (b) X-Band EPR spectra of glassy solutions of dimers of **4** in toluene. Insert: Signal at half-field, $\Delta M_S = 2$.

In the present case, the hydrogen bonded head to tail and side by side arrangement found in the dimers favors an antiferromagnetic interaction between the two radicals, the singlet being its magnetic ground state. Indeed, the signal intensity of the half-field signal of the dimers of **4** follows nicely a Bleaney-Bowers singlet-triplet model with J/k_B= -3.6(3) K. In compounds where this kind of geometric arrangement is present, similar values for the intermolecular exchange are found. [6b]

This result provides, thus, a clear magneto-structural correlation, indicating that the described dimeric arrangement leads always to an antiferromagnetic interaction between the involved radicals, either in the solid or in solution state. In addition, the hydrogen bond methodology provides a proper way for studying experimentally isolated *supramolecular aggregates*.

Supramolecular Aggregates of Radical **5**

Compound **5** shows a very specific behaviour in solution which is different from that expected for an isolated α-nitronyl nitroxide radical and is also originated by the

presence of hydrogen bonded supramolecular aggregates. In the solid state, radical **5** forms infinite linear chains linked through strong hydrogen bonds of N-O···H-O type. The comparison of this *secondary structure* with that of radical **4** shows three major differences. First, between two hydrogen bonded molecules of radical **5** only one hydrogen bond is formed, while in **4** two such bonds are established within each dimer. This means a *less favourable energetic situation* for the case of the linkage of two molecules of **5** than for the case of **4**. Secondly, while the dimers of **4** have almost no conformational degrees of freedom being very rigid, a much more complex behaviour might be expected for compound **5**. This *conformational flexibility* of the *supramolecular aggregates* of the latter compound are caused by several geometrical degrees of freedom of the involved hydrogen bonds. Finally, the linear arrangement of the secondary structure of radical **5** in the solid state opens the possibility of numerous types of aggregates in solution. Both, the formation of open chains or closed cyclic arrays are possible. For all these reasons, the spectral behaviour of compound **5** in solution is expected to be far more complex than the previously described one for the dimers of radical **4**.

The aggregation process of radical **5** in toluene solutions has been studied by means of their optical and EPR spectra. The obtained results are summarised in the following four points.

First, the temperature dependence of the visible spectra of toluene solutions of radical **5** shows upon cooling a hyperchromic effect and a blue shift for all the absorption bands. The appearance of an isosbestic point indicates further that we are dealing with an equilibrium between two species; at least between two kinds of species that have different optical spectra. The main difference with respect to the described behaviour of radical **4** is that in the present case the main effects are observed at far lower temperatures than for **4**. This fact indicate that the energetic requirements for the aggregation process of compound **5** are lower than for **4**.

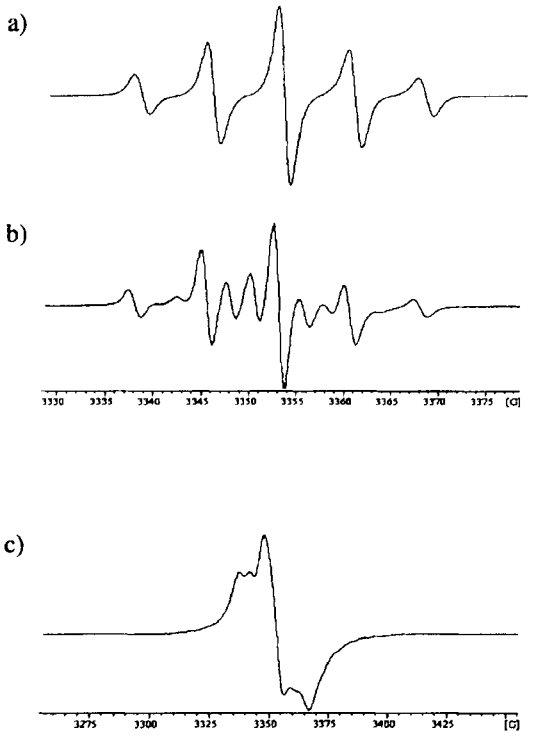
Second, a quite similar behavior in the EPR spectrum to that found in case **4** is recognized, as shown in Figure 5. Thus, on lowering the temperature, the intensity of the five 1:2:3:2:1 lines decreases gradually and at the same time two new lines appear between each pair of the initial ones, its intensity increasing upon cooling. This effect is

much more pronounced than in the previous case. This phenomenon can be interpreted assuming the formation of *supramolecular aggregates* of radicals in which the only relevant magnetic interactions take place between the next nearest neighbouring radicals and no interactions occur among the next neighbours. The assumption of the formation of a ring shaped species containing three radical units with S= 3/2 would be compatible with the observed spectra. Nevertheless, the formation of larger aggregates, either cyclic or linear, can not be completely excluded from this result assuming that each radical is magnetically sensitive only to its nearest neighbours. Geometry optimizations for a large number of clusters with either linear (n=2 to 9) or cyclic structure (n=3 to 9) at the empirical level[19] indicate that all of them are stable suggesting that, at least theoretically, a large number of different species, each of them having several distinct stable conformations might be present in solution. In addition, the electrostatic potential map of radical 5 does not indicate any favoured size or conformation for the *supramolecular aggregates*.

EPR spectra measured in the fast-tumbling regime do not provide any specific information about the aggregates of radical **5**, since only general structural characteristics can be inferred from these spectra. The absence of a field-shift of any of the observed new lines implies that we are dealing with supramolecular species in which their relative geometry is maintained; i.e., there are no changes in their geometries that would imply a modulation of the *J* value, since the *J/a* ratio is constant with temperature.[20] Most, probably, a simple displacement of the equilibrium between isolated free radicals and *supramolecular aggregates* is the cause for the observed EPR spectra.

Third, the X-Band EPR spectra of toluene solutions of radical **5** under frozen conditions show broad poorly resolved lines, regardless of the nature of the used solvent, as shown in Figure 5c. Such lines correspond to the fine structures of the high spin *supramolecular aggregates* present in solution. Its computer simulation implies the knowledge of several parameters, such as total spin number, hyperfine tensors of N nuclei, *g* tensor, etc., which are not known. In addition, the possibility that the observed spectrum is a superposition of several different aggregates should not to be ruled out. Consequently, these considerations obstructed the use of these poorly resolved EPR

spectra in order to determine the exact size and conformation of the supramolecular aggregates of radical **5** existing in solution.



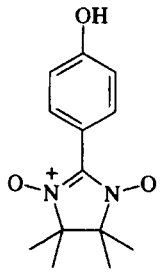


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FIGURE 5 X-band EPR spectra of a solution of radical **5** in toluene at room temperature(a), at 220 K(b) and in glassy toluene at 120 K(c).

And fourth, we have studied frozen toluene solutions of **5** through L-Band EPR spectroscopy, operating at 1.12 Ghz, that corresponds at a field of 430 G for g=2. The aim of this experiment was to simplifying the spectrum by averaging out the g factor anisotropy. The result is shown in Figure 6. As expected, the overall shape of the signal is highly symmetric when it is compared with the X-band result. It could be nicely simulated assuming the formation of a cyclic array with S= 3/2 as shown in Figure 6. The used parameters are |D'| = 13 G and |E'|=0 G.

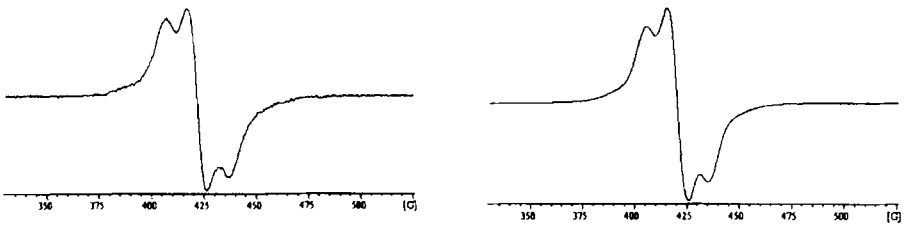

FIGURE 6 L-band EPR experimental (left) and simulated (right) spectra of a frozen toluene solution of radical **5**.

Although this result is not unequivocal, it should be interpreted as an indication that the trimeric cyclic arrangement of radical 5 in solution seems to be highly possible. Other techniques like Electron Spin Nutation should be used in order to get more precise information about the exact structure of the *supramolecular aggregates* present in frozen solutions.

In conclusion, radical **5** has shown to form aggregates in solution. Its geometry seems to correspond to cyclic trimers (S=3/2) as extracted from the EPR data. The main difference compared with its isomer **4** is that in the former case the secondary structure found in the crystal structure is maintained in solution while in **5** apparently the infinite chains are not present in solution state, but discrete, cyclic arrays are most probably formed. The numerous internal geometrical degrees of freedom of the involved hydrogen bond and entropic reasons might be responsible for this difference.

CONCLUSIONS

We have shown that the spin density distribution of α-nitronyl nitroxide radicals in solution is largely controlled by the chemical surrounding of the radical and, in particular, by its hydrogen bonding ability and polarity/polarizability. The same kind of

influence is also expected in the solid state for such free radicals. We interpret these behavior in terms of the different possible conformations of the radicals. The extend of the conjugation between the α-nitronyl nitroxide moiety and the aromatic ring is crucial for the spin distribution in the latter ring. In addition, polar and protic solvents rise the spin density located on the N nuclei. This fact can be rationalized in terms of the stabilization of some resonant canonical structures of the ONCNO moiety. Further, we have shown, that specific hydrogen bonded intermolecular arrangements of α-nitronyl nitroxide radicals that are found in crystal structures can be isolated in solution permitting the generation of high spin supramolecular aggregates. In this way the magnetic ground states of such aggregates can be identified being this information useful in the interpretation of the corresponding solid state magnetic properties.

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