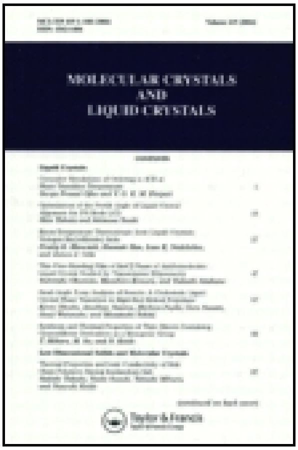

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A Chiral Hydrogen-Bonded α-Phenyl Nitronyl Nitroxide in the Solution and Solid States

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A new phenyl α-nitronyl nitroxide (*R*)-4LNN bearing a chiral substituent has been synthesized with the aim of combining in the near future the magnetic properties of this kind of radical with the optical properties endowed by the chiral group. This optically active carboxylic acid forms hydrogen bonds between the COOH and NO groups which control the solid state structure, and consequently the magnetic properties. We present both the solid state structure and the magnetic susceptibility curve of this radical, as well as its solution properties, where it shows interesting aggregation phenomena owing to the noncovalent interaction of the carboxylic acid moiety with the NO groups.

Keywords: hydrogen bonds; α-nitronyl nitroxide; chirality; electron spin resonance; magnetism

INTRODUCTION

Purely organic molecule-based magnetic materials have attracted increasing interest in recent times,[1] as their properties can be subtly modified by adequate selection of substituents. Substitution of the phenyl ring of α-nitronyl nitroxides with functionalities which are able to form hydrogen bonds to the NO groups is a very interesting way to control the relative arrangement of the radicals, both in the solid state[2] and in solution.[3] For example, mono- and bis- hydroxyphenyl α-nitronyl nitroxides have crystal structures in which hydrogen bonds control the packing of the compounds,[4] thereby endowing the resulting molecular materials with very interesting magnetic behaviours. One of the most pertinent examples of this situation is the radical 2OHNN (the 2-hydroxyphenyl derivative), which orders ferromagnetically in the solid state below 0.4 K because of the establishment of a three dimensional network of weak hydrogen bonds.[5] The presence of these intermolecular hydrogen bonds in solution can lead to the formation of dimers, trimers and larger cyclic aggregates.[3] These phenomena offer the possibility of studying magnetic interactions between radicals in small, and well-defined supramolecular organizations.

The combination of magnetic properties and a chiral medium is a subject of much current interest[6] because, in principle, an additional effect should arise when the two are active. With this aim in mind, we seek to combine optical and magnetic properties in the same molecule, and therefore we have embarked on a research programme whose primary aim is to introduce chiral substituents on the phenyl ring of an α-nitronyl nitroxide radical. Chiral nitronyl nitroxides have already been prepared in the 70's, in order to study the non-equivalence of the methylene protons of the chiral substituent linked directly to the carbon atom of the ONCNO unit,[7] although no magnetic properties have been reported. Kahn and coworkers recently described the structure and magnetic properties of a chiral nitronyl nitroxide designed to act as a metal-ion ligand.[8]

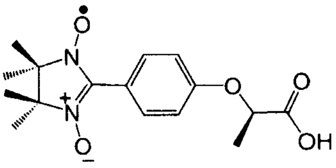

FIGURE 1. Radical *(R)*-4LNN.

As the chiral substituent, we chose the lactic acid group due to its availability, cheapness and easy processability. The carboxylic function of this group was expected to form hydrogen bonds with the oxygen atoms of the ON group, thereby controlling the solid state organization,[9] and it was also expected to form some kind of aggregate in solution. Following this design, we have prepared and studied the chiral radical *(R)*-[4-(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide)phenoxy]-2-propionic acid (*(R)*-4LNN, Figure 1), whose most important properties are presented.

RESULTS AND DISCUSSION

Synthesis

The chiral radical *(R)*-4LNN was prepared as follows. 4-Hydroxy-benzaldehyde was condensed with *(L)*-butyl lactate using a Mitsunobu protocol.[10] The chiral aldehyde thus obtained was used to form the corresponding α-nitronyl nitroxide, first by condensation with 2,3-dihydroxylammonium-2,3-dimethylbutane sulfate and subsequent oxidation of the condensation adduct with sodium periodate following the classic procedure of Ullman et al.[11] The resulting butyl ester of the radical, which is an oil, was saponified using aqueous sodium hydroxide in ethanol, leading to the carboxylic acid derivative *(R)*-4LNN, which is a dark blue solid. Crystals suitable for X-ray diffraction were obtained by slow evaporation from a dichloromethane/hexane solution. Satisfactory elemental analysis and mass spectrum were obtained.

Characterization in solution

The ESR spectrum at room temperature of a 0.1 mM solution of *(R)*-4LNN in CH_2Cl_2/toluene (1:1) (Figure 2) shows the five groups of lines corresponding to the coupling of the unpaired electron with two equivalent nitrogen nuclei (I=1). Each of these five groups of lines shows the hyperfine structure corresponding to the coupling of the electron with the hydrogen nuclei of the four equivalent methyl groups and with the four aromatic protons. The coupling constants obtained by simulation of the spectrum are: a_N=7.590 G, a_{Me}=0.202 G, a_{orto}=0.461 G, a_{meta}=0.202 G, and the isotropic Landé factor is 2.0060.

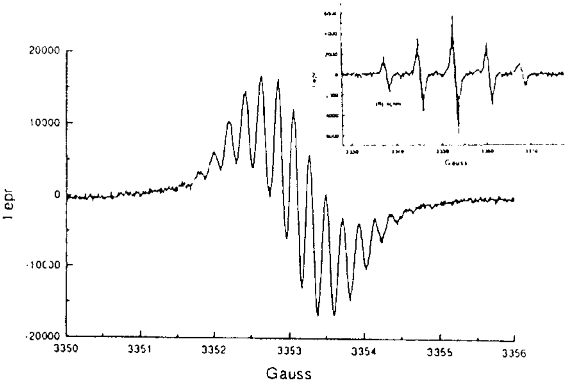

FIGURE 2. Room temperature ESR spectrum of the radical*(R)*-4LNN (inset) and expansion of the central line (M_I=0).

In frozen solution (CH_2Cl_2/toluene (1:1), Figure 3a), the spectrum of *(R)*-4LNN consists of the sum of the spectra corresponding to isolated radicals and to dimeric aggregates with S=1. The zero field splitting parameter *D'* of the dimer is 22 G. The presence of dimers of *(R)*-4LNN is evidenced by the existence of a half-field signal (Figure 3b) which shows the typical fine structure of α-nitronyl nitroxides due to the anistropies of *g* and the hyperfine coupling tensor under these conditions. The dependence of the intensity of this half-field signal with temperature has also been evaluated, proving that the ground state of this dimer is the triplet and that the two unpaired electrons are *ferromagnetically coupled* with J/k_B=+4.5 K.

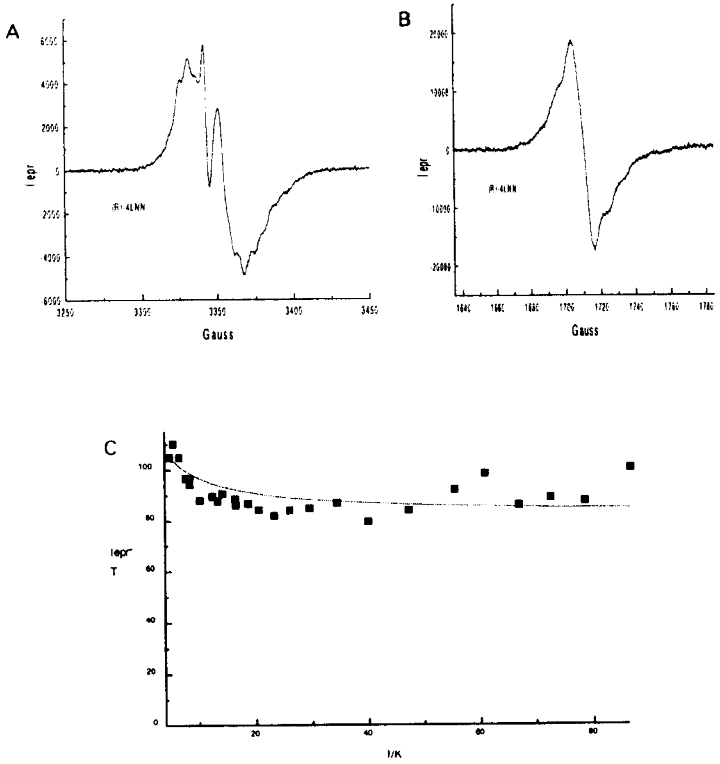

FIGURE 3. a) ESR spectrum recorded at 160 K; b) half-field signal at 160 K and c) fitting of the product between the intensity of the half-field signal and temperature plotted against temperature.

The propensity of this radical to form hydrogen bonded aggregates has also been confirmed by MALDI-TOF mass spectrometry recorded using neat samples, as shown in Figure 4, where peaks in two separate regions corresponding to the dimeric aggregate and the trimeric aggregate are observed, along with those arising from the isolated radical.

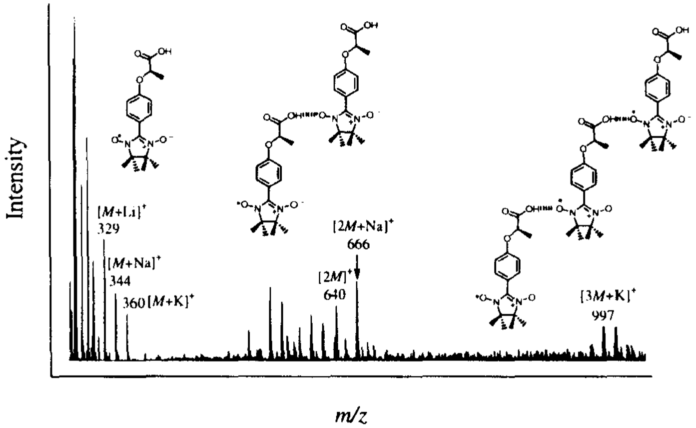

FIGURE 4. MALDI-TOF mass spectrum of *(R)*-4LNN (monomer m/z=321, dimer m/z=642). Note: The carboxylic acids fly together with alkali metal ions of the holder (Li:7, Na:23, K:39), accounting for the peaks of larger mass than the molecular ion in the spectrum.

Differences in the aggregation phenomenon observed by ESR and by MALDI-MS could be ascribed to the low energy requirements for changes of the conformation in the chiral acidic group. By rotation of the ArO-C* bond, the chiral group is able to adopt different conformations, as shown schematically in Figure 5. One of these conformations might favour the formation of cyclic dimers in solution, as evidenced by ESR, while other conformations might favour the linear chains of molecules observed by MALDI-MS and in the solid state.

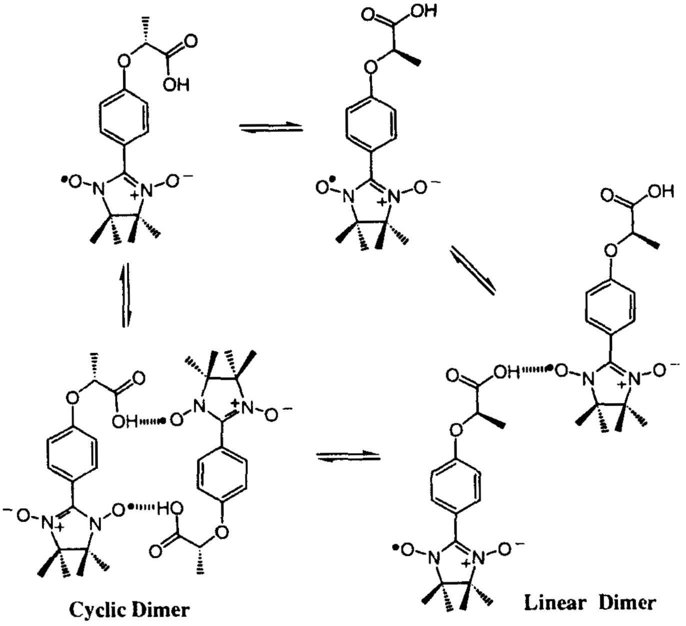

FIGURE 5. Possible conformations of the chiral group, leading to linear and cyclic aggregates.

Characterization in solid state

Solid state structure

This radical crystallises in the orthorhombic non-centrosymmetric space group $P2_12_12_1$. The asymmetric unit consists of one α-nitronyl nitroxide molecule. As a consequence, all the molecules present the same torsion angle between the planes of the ONCNO moiety and the aromatic ring which is of -29°. The heterocyclic ring presents an NCCN torsion angle of +28°. The sign of the torsion angle defining the puckering of the imidazolyl ring is most likely to be influenced by the intermolecular hydrogen bonds involving the substituent methyl groups, instead of by the remote chiral group within the molecule, since the energy barrier for any conformational change is lower than 0.6 kcal/mol.[12] It is also remarkable that the N-O distances of the two NO groups are very different (N1-O1=1.276(4) Å and N2-O2=1.301(4) Å), which is a consequence of the strong hydrogen bond formed between the O2 atom and the carboxylic acid of the next molecule.

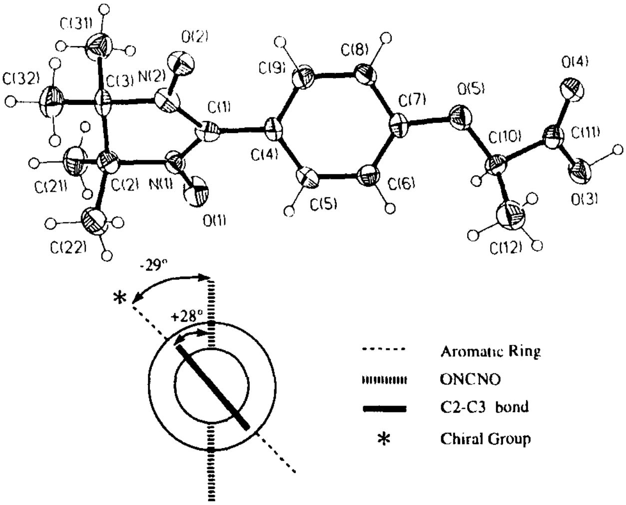

FIGURE 6. View of the solid state structure of the radical *(R)*-4LNN and a representation of the helicity of the rings.

Molecules of *(R)*-4LNN pack forming chains along the *c* axis (Figure 7), linked by strong hydrogen bonds between the carboxylic group of one molecule and the NO moiety of the next one, the neighbours being related by a two fold screw axis. The resulting molecular chains are linked to each other by weak hydrogen bonds along the *b* direction established between the free oxygen of one NO group and the aromatic hydrogen atom at the *meta* position of molecules belonging to the neighbouring chain. Another weak hydrogen bond that seems to participate in the crystal packing propagates along the *b* direction, formed between CH_3 groups and the oxygen atom of the chiral group of a molecule located in the contiguous chain. These three sets of hydrogen bonds give rise to corrugated molecular sheets in the *bc* plane, which are piled up along the *a* axis. In Table I, the [H···O] distances and [X-H-O] angles for the hydrogen bonds relevant to the crystal packing are given.

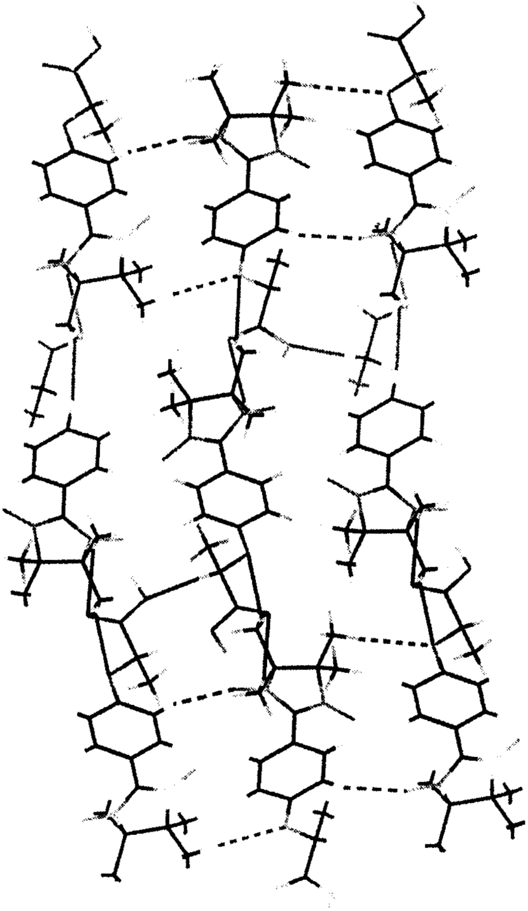

FIGURE 7. View of the *(R)*-4LNN molecules along the *bc* plane.

TABLE I Relevant parameters of the hydrogen bonds of *(R)*-4LNN

Type of H-bond	[H···O] (Å)	[X-H-O] angle (°)
O3-H···O2	1.627	159.2
C31-H···O4	2.738	148.2
C32-H···O4	2.619	153.0
C22-H···O5	2.784	176.6
C6-H···O2	2.331	155.5

As a consequence of the large corrugation of these planes, the shortest NO···ON distance (4.07 Å) found is that between NO groups located on neighbouring chains that belong to different corrugated planes. These short contacts are probably related with the observed magnetic behaviour in the solid state.

Magnetic properties

The magnetic susceptibility curve of the radical *(R)*-4LNN shows a deviation from the Curie law as the temperature is lowered indicating low dimensional antiferromagnetic interactions.

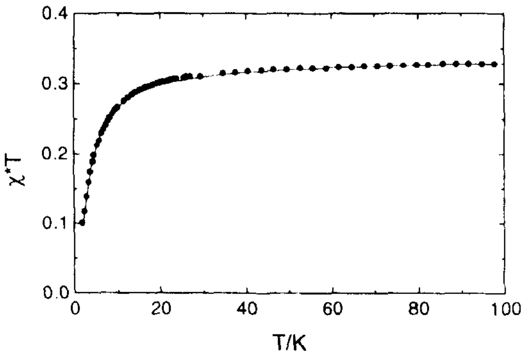

Figure 8. χT vs T plot of the radical *(R)*-4LNN.

This magnetic behaviour is completely reproduced by a one dimensional antiferromagnetic Heisenberg spin chain (S=1/2) model, with $J/k_B = -2.0$ K (Figure 8), supporting the hypothesis that the short contacts between the NO groups are responsible for the observed antiferromagnetic interaction.

Conclusions

The new chiral nitronyl nitroxide reported possesses a sterogenic centre which influences the conformation of the molecule as a whole, at least in the crystal. We have observed interesting aggregation phenomena in solution by using ESR spectroscopy. The cyclic dimers have been found to have a triplet ground state in frozen solution. This ferromagnetic interaction is not sustained in the crystal, where the radical exhibits 1-D antiferromagnetic behaviour since it is comprised of chains of radicals which interact antiferromagnetically between themselves. The thermodynamically-favoured, and more interesting magnetic situation that pertains in solution has thus been lost upon crystallisation. Investigation of possible magneto-optical effects in this and other related chiral radicals is underway in our laboratory.

Acknowledgements

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