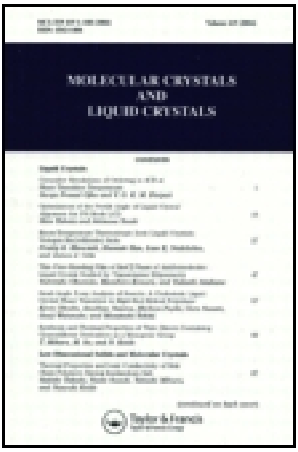

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The Hydrogen Bonding Strategy. A New Approach Towards Purely Organic/ Molecular Ferromagnets

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THE HYDROGEN BONDING STRATEGY. A NEW APPROACH TOWARDS PURELY ORGANIC/MOLECULAR FERROMAGNETS

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Abstract The variation of the number and position of OH substituents at the phenyl ring of α-phenyl nitronyl nitroxide radicals yields different H-bonded molecular self-assemblies in the solid state but do not change essentially their molecular spin density distributions. In accordance with the distinct structural dimensionalities, the obtained radicals show a large variety of magnetic behaviors, being the mono *ortho* substituted isomer the most remarkable one since it shows a 3-D network of weak H-bonds exhibiting a *bulk ferromagnetic* transition below 0.45K.

INTRODUCTION

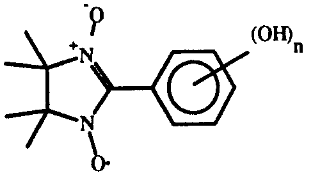
The macroscopic physical properties of purely organic molecular crystals are a consequence of the molecular electronic properties and the intermolecular electronic interactions present in the solid state. Therefore, both molecular electronic characteristics and crystal packings play a critical role in the magnetic properties of purely organic molecular solids built-up with open-shell molecules. Consequently, there is a challenge for the development and study of ***crystalline design elements*** able to control the crystalline molecular arrangements and, at the same time, to transmit strong intermolecular ferromagnetic (FM) interactions along pre-determined spatial directions.[1]

Self-complementary hydrogen bonding groups can be considered as efficient ***crystalline design elements*** since they permit to control the relative molecular layouts in the solid state. In fact, they are responsible of the self-assembly of several complicated and non-covalent structures from simpler molecular building blocks that contain two or more groups that act as complementary H-bond donor and acceptor groups.[2] Two different types of hydrogen bonds are normally observed in such organic molecular aggregates: the strong Y-H···X bonds, formed between an electronegative atom (X = O or N) and a H atom bonded to an heteroatom (YH = OH or NH_2), and the weaker C-H···X bonds, where the H atom belongs to an alkyl or an aromatic group.[3] Regardless of their different strength, both types of H-bonds show a high degree of directionality, which depends mainly on the hybridization of the X atom.[4] This characteristic makes both types of H-bonds appropriate for the generation and transmission of intermolecular ferromagnetic interactions along pre-established spatial directions.[5] Indeed when these H-bonds are settled between hydrogen donor and acceptor groups of radicals with alternating spin densities, it could occurs an overlapping of regions with opposite spin signs and, therefore, a FM coupling of the neighboring spins could be produced, in accordance with theoretical predictions.[6]

Very recently some of us have found evidences about both types of H-bonds are able not only to control certain aspects of the crystal packing of open-shell molecules but also to generate and propagate FM interactions.[7,8,9] Thus, the hydroxylated phenyl α-nitronyl nitroxide radicals **1** and **2** give rise to 2-Dimensional self-assemblies via networks of strong and weak H-bonds. Accordingly with their own structural characteristics, the radical **1** shows ferromagnetic interactions along the 2 dimensions of the molecular self-assembly,[7] while a coexistence of anti- and ferromagnetic intermolecular interactions is observed for radical **2**.[8] Very recently it has also been reported that the crystal structure of the dihydroxylated radical **3** is controlled by strong H-bonds and that this radical shows a bulk ferromagnetic transition at 0.43K.[10]

All these interesting results prompted us the question of how the number and the relative positions of the OH groups in hydroxylated phenyl α-nitronyl nitroxide radicals influence their spin density distributions and their molecular self-assembling processes and, therefore, how these molecular structural changes affect their macroscopic magnetic properties.

Herein we present a study addressed to answer such questions, that includes some new members of this family of free radicals as the monohydroxylated radicals **4** and **5** and the dihydroxylated derivative **6**.



1; n = 1, *para*
2; n = 2, *meta, para*
3; n = 2, *orto, meta'*
4; n = 1, *orto*
5; n = 1, *meta*
6; n = 2, *meta, meta'*
7; none

As it will be shown later, the change of the number and position of the OH groups in the hydroxylated phenyl α-nitronyl nitroxide radicals does not produce any significant alteration of their spin density distributions. By contrast, such changes influence notably in the crystal packings determining the resulting macroscopic magnetic properties. The distinct structural dimensionalities of the H-bonded molecular self-assemblies achieved for each one of the studied radicals clearly exemplify the benefits of the hydrogen-bonding strategy in controlling and extending the dimensionality of the intermolecular magnetic interactions. Worthy of remark is the 3-Dimensional network of weak H-bonds shown by the radical **4** which seems to be the origin of the bulk ferromagnetic transition observed at 0.45K.[9]

EXPERIMENTAL

The radicals were synthesized following the usual procedure described by Ullman et al.[11] Single crystals were grown by slow evaporation of concentrated solutions. X-ray intensity data were collected with an automated four-circle diffractometer at 298 K. Cell parameters are listed in Table I. EPR measurements were performed on a Bruker ESP 300E spectrometer operating in the X-Band with a rectangular TE102 cavity and equipped with a frequency-field lock accessory and a built-in NMR gaussmeter. Computer simulations of the EPR spectra were carried out on a commercial personal computer using a least-square fit procedure based on Monte Carlo methods.[12] The nitrogen coupling constants, a(N), were obtained simulating the entire spectra while the hydrogen coupling constants, a(H), were obtained by simulating only the highly resolved center line of each spectrum.

TABLE I Summary of crystallographic data of radicals **1-6** with standard deviations in parenthesis.

	1[7]	**2**[8]	**3**[10]	**4**	**5**	**6**
	Pca2_1	*P*2_1*/a*	*P*2_1*/n*	*Pbca*	*C*$_2$*/c*	*P*2_1*/n*
a/Å	11.765(3)	15.905(3)	15.142(3)	12.957(8)	25.08(1)	6.988(1)
b/Å	12.726(4)	11.927(3)	12.320(1)	13.584(9)	8.313(1)	19.820(2)
c/Å	17.601(4)	7.598(1)	7.196(1)	14.772(9)	12.841(7)	9.809(1)
β°	90	111.83(1)	99.18(2)	90	105.34(3)	108.03(1)
V/Å^3	2635(1)	1338(3)	1325.3(4)	2600(1)	2582(2)	1292(3)
Z	8	4	4	8	8	4

RESULTS AND DISCUSSION

Electronic Structure of Substituted Phenyl α-Nitronyl Nitroxides

One of the most important features of the electronic structure of the α-nitronyl nitroxide radicals is their characteristic spin density distribution. Although the unpaired electron is distributed mainly along the two NO groups and the α-carbon atom between them, a small but significant amount of spin density is also present on the rest of the nuclei of this kind of radicals.[13,14]

We have determined the spin density distributions of radicals **1,2,5-7** by means of their free tumbling solution EPR spectra. The EPR spectra of these radicals present in all cases five main lines, with relative intensities of 1:2:3:2:1, due to the coupling of the free electron with two equivalent nitrogen (I=1) nuclei. An enhancement of the spectral resolution enables to detect very complex patterns for each of those five main lines due to additional couplings with several hydrogen (I=1/2) nuclei; as is shown in Figure 1 for radical **6**.

The different complex patterns observed for each one of the studied radicals are obviously caused by the distinct substitution patterns of their phenyl ring, allowing therefore their assignment. The computer simulation of all these complex patterns yields the absolute value of the hyperfine coupling constants with the 12 equivalent H nuclei of the 4 methyl groups and with other non-equivalent sets of H nuclei belonging to the aromatic rings.

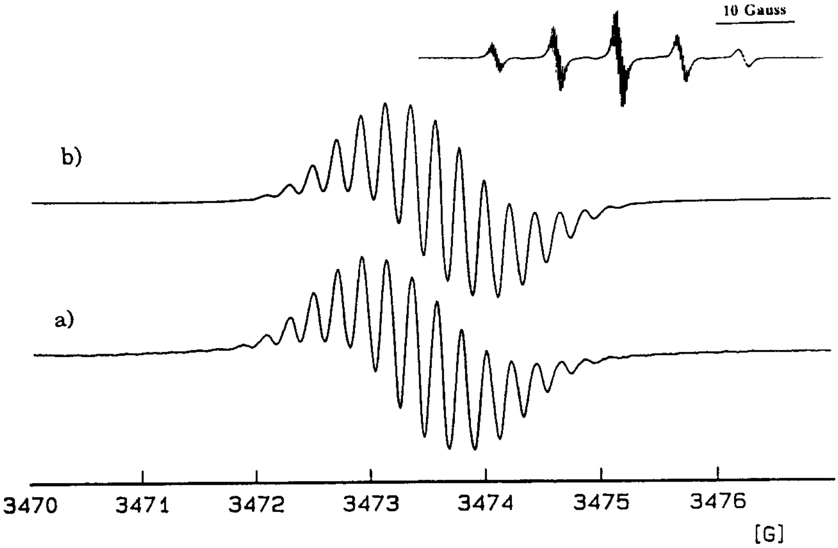


FIGURE 1 Experimental (a) and simulated (b) EPR spectra of radical **6**. The main figures correspond to the enlarged central lines of both spectra and the insert to the complete experimental EPR spectrum.

The assignment of the last coupling constants to the *ortho*, *meta*, and *para* H atoms of the aromatic rings was done in order to achieve a global coherence of the simulated coupling constants in the whole series of studied radicals and it should be considered moreover as unequivocal. The results of the computer simulation and assignments for radicals **1,2,5-7** are summarized in Table II.[15] By comparing the hyperfine coupling constants of the studied radicals we can observe that the spin distribution along the whole molecule (aromatic ring, methyl groups and N atoms) is not largely affected by the different number and position of the OH groups on the *meta* and *para* positions of the aromatic ring. Only in radicals **2** and **5** a slight non equivalent *ortho* H atoms can be observed as a consequence of the asymmetric substitution at the *meta* positions of the aromatic rings in these radicals. It should be stressed out, that the spin density distribution found for the unsubstituted radical **7** is in agreement with the reported ones determined independently either by NMR[13] or ENDOR[16] spectroscopies.

In conclusion, the studied substituted phenyl α-nitronyl nitroxide radicals show, independently of the substitution pattern, accessible molecular contours formed by O and H atoms with positive and negative spin densities that are very similar to those of the unsubstituted derivative 7.[13,14,16] This fact is of great importance in order to understand how hydrogen bonds can propagate efficiently the intermolecular FM interactions through C-H···O-N contacts, since the O atoms of N-O groups always support large positive spin densities while some of the aromatic H atoms (*ortho, para*) and all of the H atoms of the CH_3 groups support small, but not negligible, negative spin densities.

TABLE II Simulated coupling constants (in Gauss) of radicals with the estimated standard deviation in parenthesis.

Radical	a (H_{methyl})	a (H_{ortho})	a (H_{meta})	a (H_{para})	a (N)
1	0.207(1)	0.499(1)	0.177(3)	-	7.507(2)
2	0.210(1)	0.479(1); 0.550(1)	0.172(3)	-	7.527(2)
5	0.210(2)	0.499(2); 0.519(2)	0.187(7)	0.421(7)	7.445(2)
6	0.205(2)	0.469(1)	-	0.392(4)	7.645(2)
7	0.209(1)	0.495(1)	0.173(2)	0.421(5)	7.435(2)

Hydrogen Bond Self-assemblies of Hydroxylated Phenyl α-Nitronyl Nitroxides

In radical **5**, the presence of two self-complementary strong H-bonding groups at the same side of the molecule promotes a dimerization in a side-by-side and head-to-tail fashion through two identical strong intermolecular H bonds. These dimers are linked to each other through several weak H-bonds established between the two vicinal CH_3 groups of a molecule and the intradimer NO group of a neighboring dimer giving rise to chains of dimers along the *c*-axis. These chains are meshed between the O atoms of the free NO groups of one chain and the H atoms at the *para* positions of the phenyl rings of neighboring chains forming a herringbone pattern of molecules. This self-assembly therefore gives rise to weakly H-bonded 2-D layers of dimers along the *bc* plane (Figure 2).

The same structural self-complementarity of H-bonding groups observed in radical **5** is also present in **6** since its two OH groups are located at *meta* positions. Nevertheless, in this radical each molecular unit has an equal number of strong H-bonding donor and acceptor groups which promote an increase of the dimensionality from 0-D (dimers) to 1-D (chains) of the resulting molecular self-assembly builded by the strong H-bonds. The resulting molecular ribbons are linked together through two simultaneous weak H bonds settled between two CH_3 groups of one radical and both O atoms of the two OH groups of another radical pertaining to a neighboring ribbon. In such a way single corrugated planes of molecules, linked by a 2-D network of strong and weak H-bonds, are formed (Figure 3).

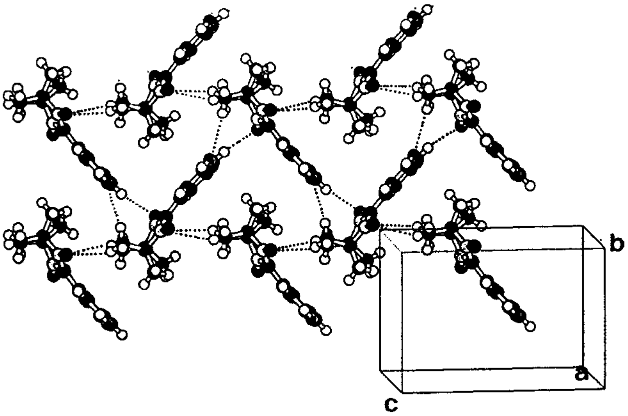


FIGURE 2. Projection on the *bc* plane of the 2-D molecular self-assembling formed by means of weak H-bonds (dotted lines) of dimers of radical **5**. Only one radical of each dimer is represented for clarity.

Crystal packing of radical **1** shows that radical molecules form 2-D hydrogen-bonded networks parallel to the crystallographic (*a*,*b*) plane. Within each 2-D network, the radicals are packed in such a way that one of its two NO groups forms a strong H-bond with the OH group of a neighboring molecule giving rise to zigzagged chains along the *a*-axis. Each one of these chains is meshed with the two translationally related chains along the *b*-axis through weaker H-bonds between the O atoms of the free NO groups of one chain and the H atoms belonging to two vicinal CH_3 groups of the two neighboring chains (Figure 4).

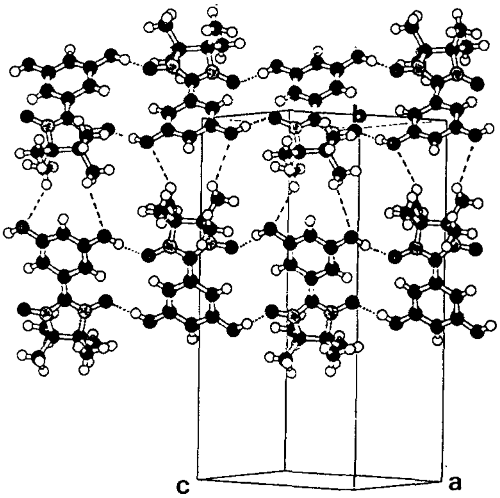


FIGURE 3. Projection of the crystal structure of radical **6** showing the single corrugated planes.

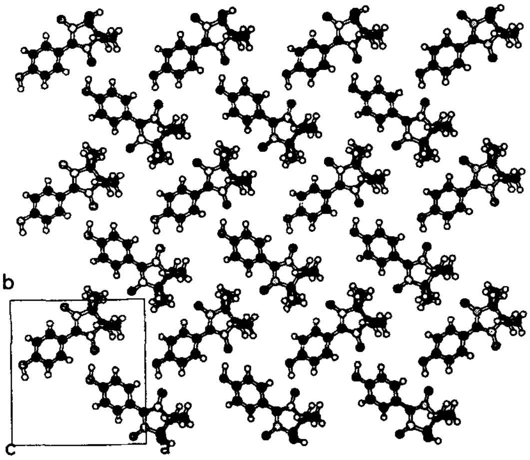


FIGURE 4. 2-D hydrogen-bonded network of radical **1** molecules viewed along the *c* axis.

The dihydroxylated radical **2** has its two OH groups located at the same positions as those of radicals **1** and **5** and, as a consequence, its crystal packing is governed by two types of strong H-bonds that are similar to those observed for these monohydroxylated radicals. The *meta* OH group is responsible for the formation of dimers which are linked to each other through strong H bonds formed by the *para* OH and the remaining NO groups. In such a way, double corrugated layers of dimers are formed (Figure 5).

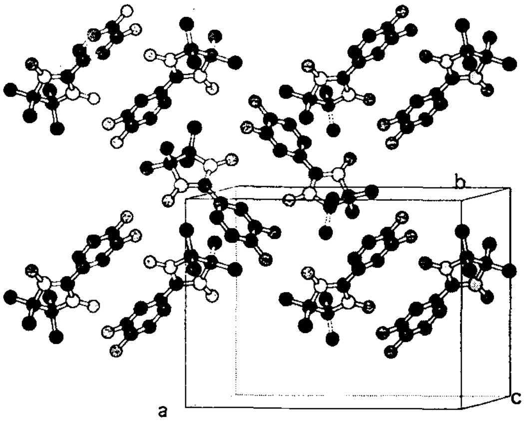


FIGURE 5. Crystal structure of radical **2**. View of a 2-D corrugated layer parallel to the *ab* plane.

In the monohydroxilated radical **4** the location of the OH group at the *ortho* position favors the settlement of a strong intramolecular H bond which gives rise to a seven-membered ring. The resulting crystal packing is therefore only governed by several types of intermolecular weak H-bonds (Figure 6). The bonds established between the non-intramolecularly bonded NO groups and the H atoms of two vicinal CH_3 groups of a neighboring molecule, that link the molecules in chains along the crystallographic *a* direction in a herringbone fashion, and those between the two NO groups of a molecule and the *meta* and *para* hydrogens of neighboring aromatic rings that assemble the chains together along the *b* and *c* directions. Thus, a molecular self-assembly through a 3-D network of weak H-bonds is achieved.

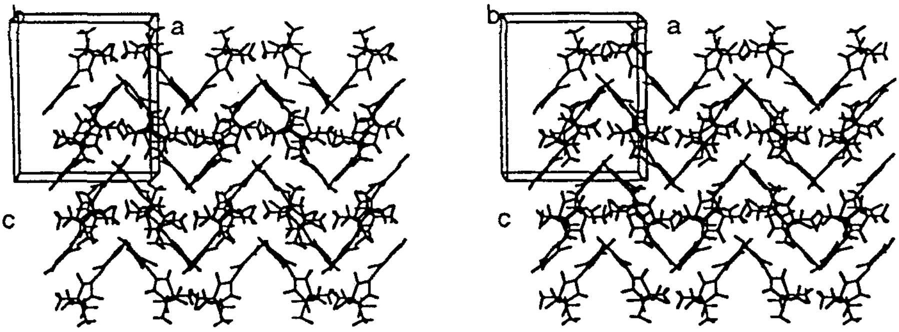


FIGURE 6. Stereoview of the crystal packing of radical **4** in which the radicals are linked through a 3-D network of weak H-bonds.

In order to confirm that both strong and weak H-bonds are the main grounds for the molecular self-assembling observed in the solid state, we performed for each radical an *ab-initio* computation, using the UHF method and a 3-21G basis set, of its molecular electrostatic potential (MEP) map. This kind of maps are important for analyzing the collective actions of H-bonds in a given molecule since it is well known that the electrostatic component described by each MEP map is one of the most important contributions to H-bonds. The computed MEP maps explain fairly well the observed relative orientations of molecules found in the solid state confirming the important role of the H-bonds on the crystalline structures of this family of radicals. Quantitative calculations of the energies involved in all the studied structures are in progress and will be published elsewhere.

Magnetic Properties of Substituted Phenyl α-Nitronyl Nitroxides

As a consequence of their different crystal packing, the macroscopic magnetic properties of the studied molecular solids are notably affected by the number and relative positions of the H-bonding acceptor and donor groups. Thus, radical **1** shows 2-D *ferromagnetic interactions*,[7] while radical **5** presents mainly *antiferromagnetic* intermolecular interactions.[9] In radicals **2** and **6** a coexistence of *anti-* and *ferromagnetic* interactions is observed.[8,9] Radical **4**, with a 3-D self-assembling of weak H bonds, shows a *3-D ferromagnetic ordering* at 0.45 K.[9] So, in accordance with the mechanisms generally used to explain the magnetic properties of α-nitronyl nitroxide radicals -the so-called *McConnell I mechanism*[6] and the *Charge Transfer mechanism involving frontier orbitals*[17]- those crystal engineering elements that favor the presence of side-by-side and head-to-tail molecular arrangements will develop *antiferromagnetic* intermolecular interactions. By contrast, those elements that avoid such arrangements and instead promote another kinds of contacts, in particular those of C-H···O-N type will induce *ferromagnetic* intermolecular interactions. The last kind of magnetic interactions can be extended, under favorable circumstances, into the three spatial dimensions yielding a *bulk ferromagnet*.

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