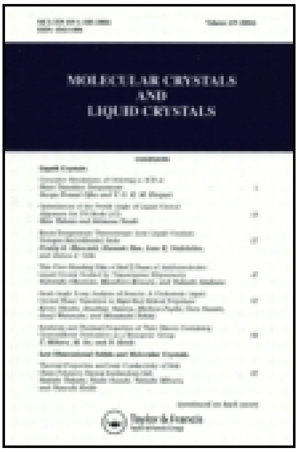

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MOLECULAR AND CRYSTAL ENGINEERING IN THE DESIGN OF ORGANIC SOLIDS WITH FERROMAGNETIC INTERMOLECULAR INTERACTIONS

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Abstract A brief account on organic solids showing ferromagnetic (FM) intermolecular interactions is given, paying special attention to the crystal design involved. In addition, new crystal engineering approaches are proposed in order to obtain FM couplings between organic free radicals.

INTRODUCTION

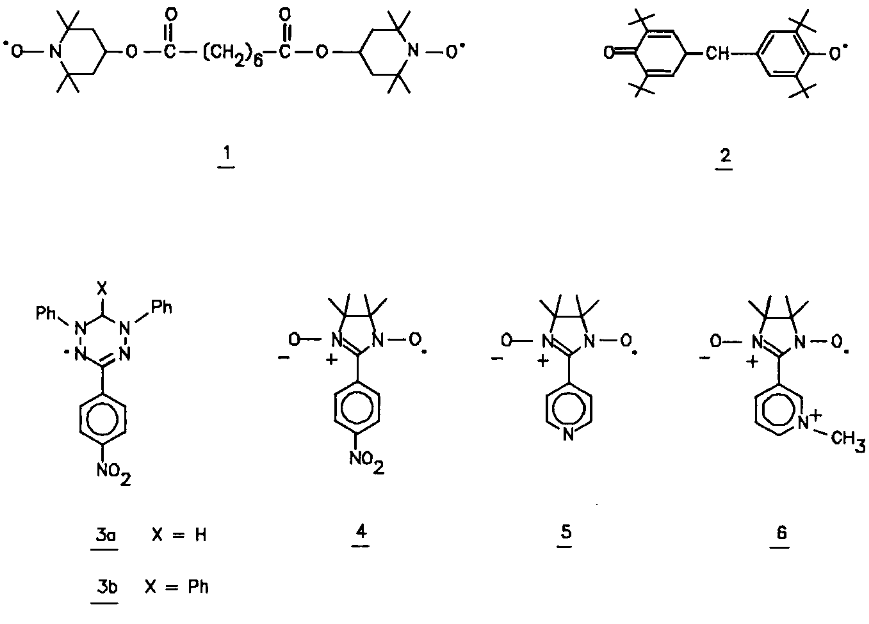
The quest for a purely organic molecular ferromagnet has been the subject of intensive research activity during the last years.[1] The development of such new materials is still a very important topic, both from the standpoint of basic research as from its potential technological applications.

Bulk ferromagnetism with a spontaneous magnetization below a critical temperature, T_c, is generally a three-dimensional phenomenon; in certain special conditions it can be a two-dimensional one, but it will never occurs in a one-dimensional system.[2] In addition, from a thermodynamic point of view, the observation of ferromagnetism at zero applied field requires three major conditions: 1) the system has to possess molecules with a magnetic moment; 2) intermolecular interactions between magnetic moments have to tend to align them parallel with respect to each other; and 3) the correlation lenght has to become infinite below T_c. If only the two first conditions are fulfilled the molecular material will exhibit interesting magnetic behaviour (due to short range FM exchange interactions) but it will not be a ferromagnet.

Consequently, the design of a molecular ferromagnet involves mainly two steps. First, the selection of a proper theoretical model predicting intermolecular FM interactions between organic radicals. And, second, *molecular and crystal engineering tools*, that is, the synthesis of chemically and electronically stable open-shell organic compounds, with the structural and/or electronic properties necessary to achieve FM interactions between neighboring molecules in the crystal lattice, and to extend these interactions along the three directions of space.

At this point, it is necessary to emphasize that although the principles of covalent organic synthesis are now well established and constitute a powerful tool for the molecular chemist, crystal engineering is still in its first infancy. Nevertheless, and as it will be shown later, the conjunction of crystal engineering with proper theoretical models allows in some cases successful design of the magnetic interactions in a lattice.

In this paper we will focus on the small, but continuously growing, number of open-shell organic molecules with crystal phases exhibiting FM intermolecular exchange interactions (shown in Figure 1), paying special attention to those cases which result from a successful molecular and/or crystal design. In addition, we will present our own approaches to this field and the latest results we have obtained.



1

2

3a X = H

3b X = Ph

4

5

6

FIGURE 1: molecular structure of organic free radicals with crystal phases exhibiting FM intermolecular exchange interactions.

FERROMAGNETIC INTERMOLECULAR INTERACTIONS IN ORGANIC MOLECULAR CRYSTALS. A CRYSTAL DESIGN APPROACH

The magnetic properties of Tanol Suberate 1 have been extensively studied. For a long time it was considered to be the first purely organic ferromagnet, but recent experimental results show that, in the absence of any applied magnetic field, **1** is an antiferromagnet, and presents a metamagnetic transition at ca. 100 Oe.[3,4] The crystal structure of this substance consists of layers of symmetrically related NO radical groups in the *ac* plane, stacked along the *b* axis. The antiferromagnetic (AFM) structure corresponds to a ferromagnetic coupling between the magnetic moments located within the same layer and to an antiferromagnetic coupling between layers.

Galvinoxyl radical **2** is known from the earlier work of Mukai[5] to exhibit FM intermolecular interactions in the crystalline state. However, galvinoxyl undergoes a first-order phase transition at 85K and most of its paramagnetism disappears, preventing a detailed study of FM interactions. Kinoshita et al. have shown that the phase transition can be supressed by preparing mixed crystals of galvinoxyl and hydrogalvinoxyl (the corresponding closed-shell compound).[6] The details of the FM interactions can now be studied at low temperatures in these mixed crystals.[6,7,8,9] This is a rather peculiar but completely successful example of crystal engineering, in which a compound with a closely related molecular and crystal structure is introduced as an impurity in the lattice of a host compound, in order to modify its solid state behaviour and, indirectly, modulate its magnetic properties.

The crystal packing of the verdazyl radical **3a** consists of stacks of molecules in which the tetraazapentadienyl moieties overlap extensively. Since these are the regions of maximum spin density, McConnell's model I[10,11] predicts AFM intermolecular exchange interactions, as were in fact observed.[12] According to Wudl et al. "if the molecules within a stack could be slid relative to one another in the *b* direction (perpendicular to the stacking axis), then regions of high spin density would overlap regions of nodes in adjacent molecules. The McConnell model would then predict intrastack ferromagnetic interactions".[12] Wudl et al. reasoned that placement of a phenyl ring in the 6-position could produce the desired effect. Verdazyl **3b** was subsequently synthesized, showing the predicted packing pattern and exhibiting FM intermolecular interactions.[12,13] To our knowledge, this is the most beautiful example of molecular and crystal engineering in the field of molecular magnetism.

However, in spite of the presence of intermolecular FM interactions in the crystals of compounds **1**, **2** and **3b**, none of them becomes a bulk ferromagnet, due to the fact that the interactions are restricted to one (compounds **2** and **3b**) or two (compound **1**) directions in the lattice, while in the other directions either there exist no interactions or these are predominantly AFM. These results clearly demonstrate the importance of extending the FM interactions in the three spatial directions.

A first approach in the design of lattices exhibiting extended magnetic interactions involves the use of highly symmetric organic molecules able to establish interactions in the three directions of space. A paradigmatic example of such compounds is provided by the C_{60} molecule, which possesses a spherical shape and is known to be readily reduced by organic donors, yielding stable anion-radical charge-transfer complexes. In fact, the 1:1 complex of C_{60} with the strong organic donor tetrakis(dimethylamino)ethylene exhibits "soft" ferromagnetism below 16.1K.[14,15,16]

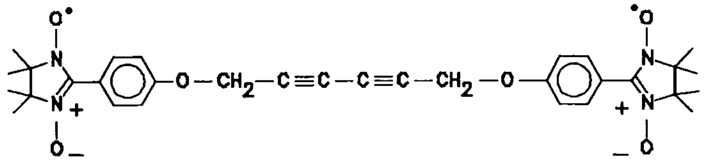
Another system in which the extension of the FM interactions in more than one dimension is possible is provided by the α-nitronyl nitroxide free radicals family.[17] α-Nitronyl nitroxide **4** is known to exist in four different crystal modifications, and all of them exhibit weak FM intermolecular exchange interactions[18-23]. It must be emphasized that crystals of phases β and γ display bulk ferromagnetism at about 0.6K,[24,25] *providing the first known examples of purely organic ferromagnets, consisting only of the light elements C, H, N, O and having well defined chemical and crystal structure.*

The magnetic properties displayed by crystals of compound **4** has been explained within the theoretical framework developed for galvinoxyl,[9] and based on a charge transfer mechanism involving the frontier orbitals.[26] The FM coupling has its origin in the SOMO-NHOMO and/or SOMO-NLUMO contacts, while SOMO-SOMO contacts lead to AFM coupling in these crystals. Semiempirical MO calculations show that in α-nitronyl nitroxides with an aromatic substituent in the α position, the SOMO is localized in the O-N-C-N-O moiety, while NHOMO and NLUMO are mainly localized in the aromatic substituent.[20] These facts, together with the strong electronic polarization of the $N^{\delta(+)}$-$O^{\delta(-)}$ bond, provides the basis for the application of crystal engineering tools in these systems.[27] α-Nitronyl nitroxide radicals **5** and **6** are two smart examples of successful crystal design based on mechano-quantical calculations and the theoretical models explained above.[28,29] The cation radical **6**, for instance, was designed to get a large intermolecular overlap between the N-O group (where the SOMO is localized) and the pyridinium ring (where NHOMO and NLUMO are mainly localized) due to the Coulombic attraction force between the positive charge on the pyridinium ring and the negative charge polarized on the O atom of the NO group. In fact, a lattice with the designed contacts was obtained, exhibiting FM intermolecular exchange interactions.

The development of well established strategies in order to achieve three-dimensional FM interactions and the discovery of new ones is obviously demanded. In the following, we will present two attempts to achieve this goal.

DIACETYLENES AS A CRYSTAL ENGINEERING TOOL

Diacetylenes (DAs) of general formula R-C≡C-C≡C-R display packing patterns characterized by the formation of parallel stackings of individual molecules along a given crystallographic direction.[30] The lattice is stabilized by a close packing of the diacetylene units along the stack and by intermolecular contacts between side groups R of adjacent stacks. It appeared to us that placement of stable open-shell organic molecules as side groups R could provide the possibility to modulate the interaction of magnetic centres in the lattice, allowing a favourable overlap of the radicals along the stack. In addition, the contacts between side groups of parallel adjacent stacks could allow the extension of the interactions in other spatial directions. To test these hypothesis, we synthesized the DA diradical **7**



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The design of this DA was based on the fact that DAs with -CH_2OAr side groups (Ar being a substituted phenyl) are known to exhibit packing patterns resembling those described at the beginning of this section.[31] The election of α-nitronyl nitroxide as the open-shell moiety was made according to the theoretical considerations previously exposed.

The magnetic properties of a phase of DA **7**, in the temperature range 5-200 K, have been given in a preceding paper,[32] and were rationalized as indicative of the presence of small AFM interactions (Weiss temperature θ=-2.3K). However, we have recently reexamined such magnetic properties in a wider temperature range (2-300 K). The obtained results point towards the coexistence of FM and AFM intermolecular interactions in the lattice. The study of the crystal structure provides the clues for the understanding of this behaviour. A view of the crystal packing in the *ac* plane is shown in Figure 2. Crystals of DA **7** obtained by slow evaporation of a saturated chloroform solution belong to the C2/c, monoclynic, space group: a=16.57(2) Å, b=16.116(2) Å, c=13.10(1) Å, β=123.05(4)°; V=2931(4) $Å^3$, Z=4, D_{calc}=1.30g/cm^3; R=9.2%, Rw=11.6%.

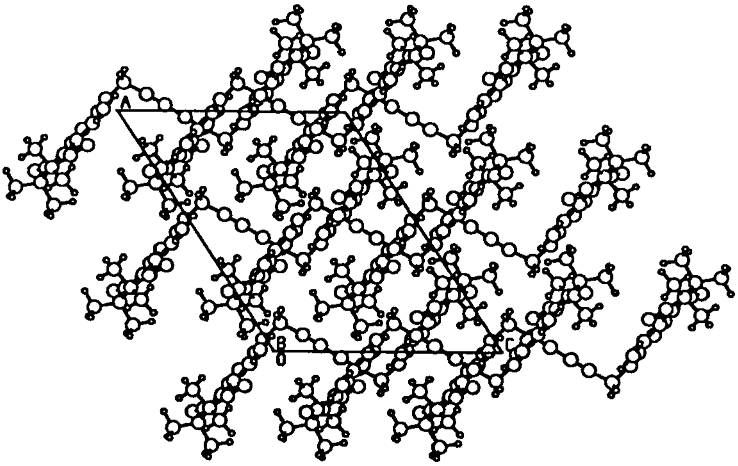


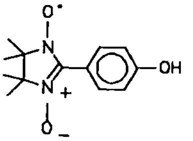
FIGURE 2: Packing pattern of DA **7** viewed in the *ac* plane.

Although the individual molecules are stacked along the *a* direction, the magnetic centres are not properly disposed to overlap extensively in that direction. Instead, the individual radical centres are disposed head to tail and side by side along the *c* crystallographic axis, giving rise to alternating magnetic chains. Along the chains there is an alternation of FM and AFM couplings. A detailed study of this exotic magnetic behaviour is under progress, and will be reported in a forthcoming paper.

Although FM couplings are operative in the crystals of DA **7** and the systems displays a rather interesting magnetic behaviour, we have not succeeded in the control of the magnetic interactions through the packing of the diacetylenic units. We adscribe these disappointing results to the fact that the intermolecular interactions involved in the crystal (essentially of Van der Waals type) are very weak. In this situation, the packing pattern is mainly determined by the intramolecular conformation adopted by the molecules. Consequently, in order to perform successful crystal engineering, it seems necessary to use stronger and more directional intermolecular interactions.

HYDROGEN BONDING AS A CRYSTAL ENGINEERING TOOL

Hydrogen bonding has been extensively demonstrated to be a powerful tool for the design of crystal architectures.[33] To our knowledge, the only molecular crystal in which the magnetic interactions are transmitted through a hydrogen bonding network is that formed by Tanol (2,2,6,6-tetramethyl-4-hydroxypiperidine-1-Oxyl), but in this case the interactions are AFM.[34,35] However, it was our feeling that hydrogen bonding network design, guided by proper theoretical considerations, could lead to lattices exhibiting FM interactions. With this purpose, we chose α-nitronyl nitroxide **8**[17], hereafter referred to as pHPNN, as a model compound.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The rationale for the selection of this compound was based on the fact that it possesses two hydrogen bonding acceptor groups (NO groups) and one hydrogen bonding donor group (OH group) in a non colinear fashion. Semiempirical MO calculations showed, as expected, that the SOMO is localized in the O-N-C-N-O moiety, while NHOMO and NLUMO are mainly localized in the *p*-hydroxiphenyl substituent. Thus every hydrogen bond in the lattice could give rise to SOMO-NHOMO and or SOMO-NLUMO contacts, which, according with the previously described theory,[9] would result in FM coupling. In addition, the existence of two hydrogen bonding acceptor groups per structural unit allows the extension of the magnetic interactions in different spatial directions.

Static magnetic susceptibility measurements on a microcrystalline sample of pHPNN are shown in Figure 3. The paramagnetic susceptibility data can be fitted in the temperature range 10-300K to the Curie-Weiss law, $X_{para}=C/(T-\theta)$, with C=0.37emuK/mol and $\theta=+0.4K$. So, the designed lattice displays the expected FM coupling. Below 10K the data deviates from the Curie-Weiss law, but is well described in terms of an 1D Heisenberg ferromagnetic chain.[36] Figure 4 shows the magnetization of the same sample of pHPNN as a function of the applied magnetic field at three different temperatures. The experimental points deviate upwards from the theoretical curves obtained for an ideal S=1/2 paramagnet (with g=2.006). However, an excellent fit is obtained when a Molecular Field correction is introduced in the Brillouin function for an ideal S=1/2 paramagnet. The best fit is obtained for $\theta = +0.4$ K.[37] Thus, magnetization measurements confirm the operation of FM couplings in the crystals. In order to test if FM couplings take place in more than one dimension in the lattice, low temperature magnetic measurements (in the mK region) are in progress. Also, molecular and crystal structure determination is being carried out with the aim of correlating the magnetic behaviour with the crystal packing.

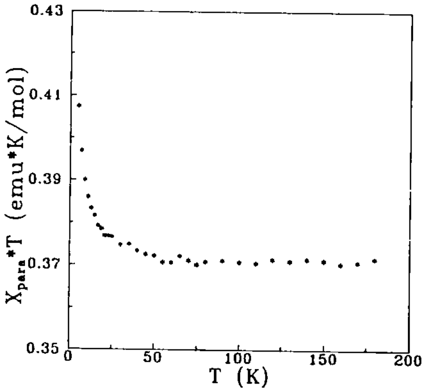

FIGURE 3: Temperature dependence of $X_{para}T$ of pHPNN radical measured at an applied fiel of 10kOe in the temperature range of 5-200K.

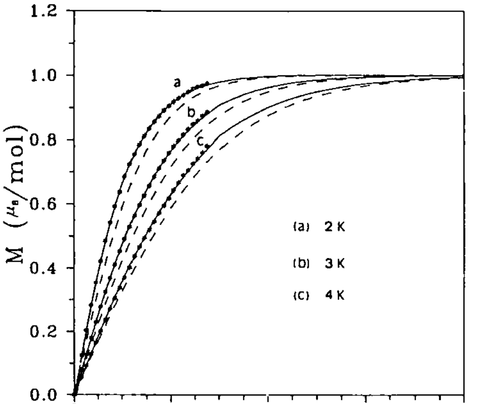

FIGURE 4: Magnetization of pHPNN as a function of applied magnetic field at three different temperatures. *, experimental points; ---, theoretical Brillouin function for S=1/2, g=2.006; —— , theoretical Brillouin function corrected with the Molecular Field Theory to account for FM interactions: S=1/2, g=2.006, θ=+0.4K.

To summarize, crystal engineering guided by proper theoretical models allow successful magnetic interactions design in crystal lattices. However, much synthetic and theoretical work is needed in order to truly design a lattice showing a predetermined magnetic interaction between spins belonging to neighboring molecules.

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