THE ROYAL SOCIETY

Crystal architectures of organic molecular-based magnets

By David B. Amabilino, Joan Cirujeda and Jaume Veciana

*Institut de Ciència de Materials de Barcelona (CSIC),
Campus Universitari, 08193-Bellaterra, Spain*

The crystal architectures of molecular materials play deciding roles when it comes to the determination of magnetic properties. In turn, the build-up of these arrangements is shown to depend on the molecular features present in the compounds employed. An analysis of the molecular and supramolecular aspects of the α-nitronyl aminoxyl radicals is presented, and a critical appraisal of the state of the art in interpretation of magnetic interactions and ability to crystallize predetermined relative orientations between radicals is presented.

Keywords: organic magnets; magnetic interactions; McConnell I; hydrogen bonds; supramolecular chemsitry; structure–magnetism correlation

1. Introduction

An organic ferromagnet—this elusive target has spurred the efforts of many research groups over the last decade, and few have attained it (Takahashi *et al.* 1991; Stephens *et al.* 1992; Chiarelli *et al.* 1993; Cirujeda *et al.* 1995*a*; Nogami *et al.* 1995*a*; Banister *et al.* 1996; Matsushita *et al.* 1997). The group of free radicals which have attracted most attention in this regard are the α-nitronyl aminoxyl family (figure 1). Their appeal derives from their relative stability, and (normally) relatively easy synthesis which allows the introduction of a wide variety of functional groups. While the weak magnetic interactions between the unpaired electrons occasion transition temperatures which are extremely low (always below 2 K), these molecules are ideal for studies on magnetism, owing to the well-defined location of the unpaired electron.

Experiment (Zheludev *et al.* 1994; Bonnet *et al.* 1995) and *ab initio* calculations (Novoa *et al.* 1995; Yamanaka *et al.* 1995) agree that in the α-nitronyl aminoxyl unit the spin density in the singly occupied molecular orbital (SOMO) is distributed mainly over the two oxygen and two nitrogen atoms of the ONCNO conjugated system. The central carbon atom of this moiety is a node in the SOMO. However, extrapolating the knowledge of the electronic nature of the molecules to understanding and predicting magnetic behaviours in these organic compounds is an abstruse quandary.

In an effort to rationalize and understand the magnetic properties of these compounds, we seek to exploit the intimate relationship between the structural and electronic characteristics of the molecules. In particular, analysis of the bank of structural data concerning the α-nitronyl aminoxyl radicals in the solid state permits access to a gamut of information which in principle could provide insight into the driving forces that decide the magnetic interactions between the molecules. For this reason, a

Phil. Trans. R. Soc. Lond. A (1999) **357**, 2873–2891

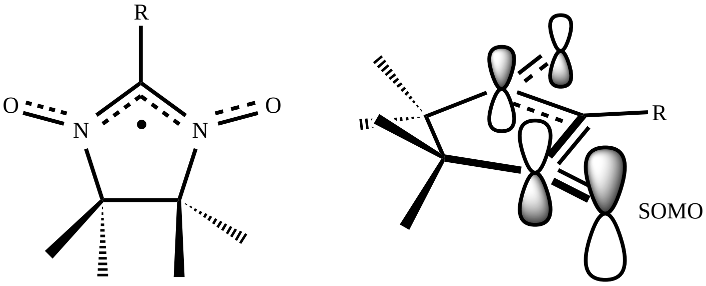


Figure 1. General chemical structure of the family of α-nitronyl aminoxyl radicals and a representation of their singly occupied molecular orbital (SOMO).

data base has been constructed (Cirujeda 1997; Deumal *et al.* 1998*a*) which contains the X-ray structures of the majority of the α-nitronyl aminoxyl radicals whose magnetic properties have been measured. With this tool in hand it is possible to attempt correlation between molecular or supramolecular structures and the bulk properties. Before looking at the crystal architecture, it is instructive to scrutinize the bricks of which it is made. The discussion here will start from the bottom—the molecule—and work up to considering the way in which the units aggregate and interact.

2. Statistical analysis of the geometry of the radicals in the solid state

A data base used for the statistical analysis of the radicals was constructed (Cirujeda 1997) from crystal structures in the Cambridge Crystallographic Structure Data Base as well as from personal communications. It comprised (after removal of structures with disorder or of poor resolution, and of structures whose distances within the imidazolyl ring were greater by three times the standard deviation of the mean) 110 crystal structures incorporating 135 crystallographically independent α-nitronyl aminoxyl units of purely organic radicals and their related coordination compounds.

Firstly, we will only consider the molecular aspects of the imidazolyl ring of the radicals, with the covalently attached oxygen atoms, which carry mainly the unpaired electron, and the pendant methyl groups at the 4 and 5-positions, which protect the radical centre sterically, but may also prove important in the propagation of magnetic interactions. This common unit to all the α-nitronyl aminoxyl radicals in the data base is shown in figure 2 together with the atom numbering which has been employed in the subsequent discussion. The structural correlation was carried out according to the method described by Bürgi & Dunitz (1994). All the interatomic distances have been analysed, along with the angles formed by the covalent bonds between any three of the atoms, as well as the torsion angles present. The results are presented in table 1, and the mean values are presented in figure 3.

In the case of the distances and angles—which show unimodal distributions (figure 4)—the statistical treatment of the unweighted sample mean is trivial, and most of the values are as might be expected based on the known averages for each type of bond (Bürgi & Dunitz 1994). For example, the C4—C5 bond length is 1.545 Å, compared with 1.543 Å for the C_{sp^3}—C_{sp^3} bond in the structure correlation analysis of cyclopentane. The distances between C4 and C5 and their neighbouring nitrogen atoms are 1.499 and 1.500 Å, identical (within the standard deviation) to the overall mean of all C_{sp^3}—N^+ distances.

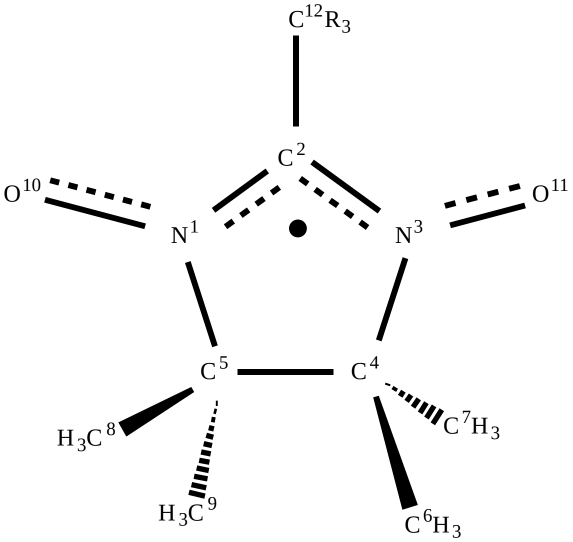


Figure 2. Atom numbering used in the discussion of the statistical analysis of the geometries of the α-nitronyl aminoxyl radicals.

Interestingly, the values of the C—N distances between the two nitrogen atoms in the ring and the carbon atom between them are not statistically different, and have a mean value of approximately 1.344 Å, in accord with the conjugated nature of the system. The distances in imidazole for the C_{sp^2}—N bond (N1—C2) and the C_{sp^2}=N bond (C2=N3) are 1.349 and 1.313 Å, respectively. This observation implies that little of the π-electron density is located in the C—N bond in the α-nitronyl aminoxyl radicals. The N—O distances are statistically identical, being approximately 1.281 Å long, slightly more than the N—O distance in pyridine N-oxides (1.304 Å).

The distances, angles and torsion angles on either 'side' of the α-nitronyl aminoxyl unit are the same within the error involved in the measurement, supporting the notion that the ONCNO group is fully conjugated. Indeed, the torsion angles associated with the conjugated unit are extremely small.

In the case of the few bond angles and the torsion angles which exhibit bimodal distributions, the standard deviation is, as would be expected intuitively, large. It is noteworthy that the smallest standard deviations pertain to the conjugated parts of the molecules, described by four of the torsion angles to be encountered in table 1. The bimodal nature of the torsion angle N1—C5—C4—N3, which describes the puckering of the imidazolyl moiety, is displayed in figure 5 (Minguet *et al.* 1999*a*). Analysis of the puckering angle using a principal component analysis reveals that the conformation of the imidazole moiety can be described to a level of significance of 97% by only *one* of *any* of the torsion angles, for example N1—C5—C4—N3, and all the other angles are defined by this one. This result is caused by the conjugation of three of the five atoms in the ring. Therefore, there are two predominant conformations, the $^5T_4$ and $^4T_5$, which are depicted in figure 5. The statistically most probable angles for the torsion, referred to from now on as T_{IM}, are $+24°$ and $-24°$, as determined by statistical analysis. The most favoured torsion angles are found between 16 and 32°, and angles greater than the latter are highly unlikely, marking a significant increase

Table 1. *Mean distances and angles, along with their standard deviations, in the α-nitronyl aminoxyl radicals in their crystals*

variable	distance (Å) and standard deviation (Å)	variable	angle (deg) and standard deviation (Å)	variable[b]	torsion angle (deg) and standard deviation (Å)
N1–C2	1.340 (0.016)	N1–C2–N3	108.3 (1.2)	N1–C2–N3–C4	−0.5 (8.0)
C2–N3	1.347 (0.015)	C2–N3–C4	112.3 (1.2)	C2–N3–C4–C5	1.5 (18.7)
N3–C4	1.500 (0.013)	N3–C4–C5	101.1 (1.2)	N3–C4–C5–N1	−1.7 (20.4)
C4–C5	1.545 (0.019)	C4–C5–N1	100.8 (1.0)	C4–C5–N1–C2	1.7 (18.6)
C5–N1	1.499 (0.014)	C5–N1–C2	112.7 (1.3)	C5–N1–C2–N3	−0.8 (7.8)
N1–O10	1.285 (0.014)	O10–N1–C2	125.7 (1.2)	O10–N1–C2–N3	0.7 (3.7)
N3–O11	1.278 (0.014)	C2–N3–O11	125.7 (1.2)	N1–C2–N3–O11	0.3 (3.4)
C4–C6	1.521 (0.030)	O11–N3–C4	121.7 (1.2)	O11–N3–C4–C5	−1.3 (13.3)
C4–C7	1.518 (0.033)	C5–N1–O10	121.1 (1.4)	O11–N3–C4–C6	61.0 (15.6)
C5–C8	1.514 (0.034)	N1–C5–C8	107.8 (2.5)[a]	O11–N3–C4–C7	−57.7 (15.9)
C5–C9	1.522 (0.028)	N1–C5–C9	107.5 (2.6)[a]	N3–C4–C5–C8	−117.6 (23.5)
		N3–C4–C6	107.7 (2.5)[a]	N3–C4–C5–C9	113.5 (23.7)
		N3–C4–C7	107.8 (2.5)[a]	C4–C5–N1–O10	−1.64 (12.8)
		C4–C5–C8	114.9 (2.3)[a]	C6–C4–N3–C2	−118.9 (21.1)
		C4–C5–C9	114.5 (2.6)[a]	C6–C4–C5–N1	113.7 (23.4)
		C5–C4–C6	114.4 (2.5)[a]	C6–C4–C5–C8	−2.1 (26.7)
		C5–C4–C7	114.8 (2.6)[a]	C6–C4–C5–C9	−131.1 (26.8)
		C6–C4–C7	110.1 (2.0)	C6–C4–N3–C2	122.4 (21.3)
		C8–C5–C9	110.1 (2.1)	C7–C4–C5–N1	−117.6 (23.6)
				C7–C4–C5–C8	126.6 (26.9)
				C7–C4–C5–C9	−2.4 (26.9)
				C8–C5–N1–C2	122.6 (20.9)
				C8–C5–N1–O10	−57.5 (15.1)
				C9–C5–N1–C2	−118.7 (21.1)
				C9–C5–N1–O10	61.2 (15.3)
				O10–N1–C2–C12	−0.6 (4.6)
				O11–N3–C2–C12	−0.3 (4.4)

[a] These values have bimodal distributions.

[b] All the torsion angles present bimodal distributions.

in the potential energy curve at this point. In contrast, the slope of the curve towards a planar arrangement is much shallower.

The vast majority of the α-nitronyl aminoxyl radicals which have been prepared and studied to date are of the phenyl variety, with a melange of substituents scattered around the positions of the aromatic ring, whose nature has been determined by commercial or synthetic accessibility to the aldehyde precursors. The introduction of this group brings with it an additional stereochemical aspect to the conformation of the molecules. When the angle between the plane formed by the ONCNO unit and the phenyl substituent, A_{PNN}, is non-zero, and considering that there are two possible enantiomeric conformations for the imidazolyl ring, four diastereomeric conformations exist, comprising two enantiomeric pairs (figure 6). The twist angles

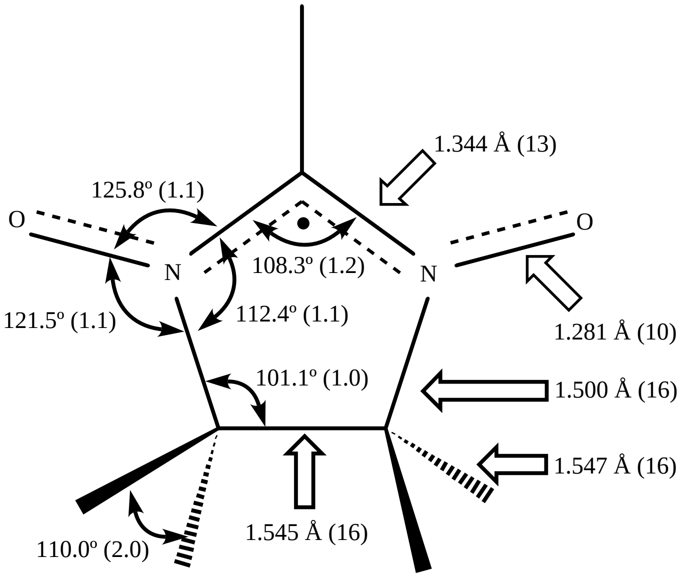


Figure 3. Average bond distances and angles from the statistical analysis of crystals containing α-nitronyl aminoxyl radicals.

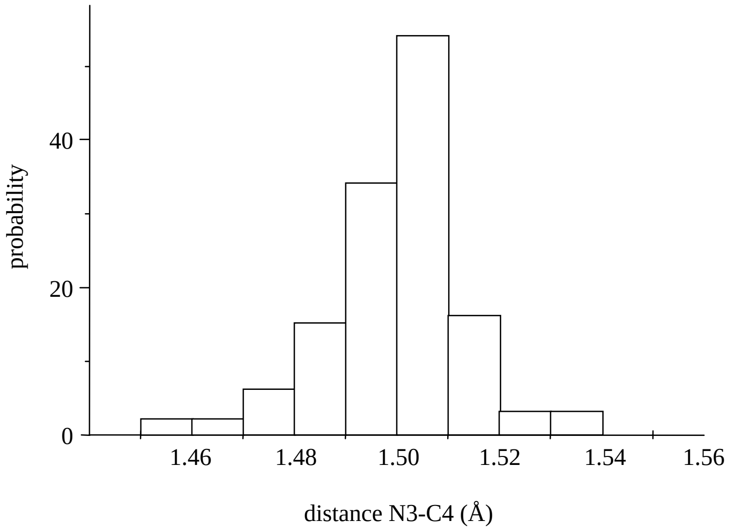


Figure 4. An example of the unimodal distributions obtained for the bond distances, in this case for the N3—C4 bond.

can be named using the helical denominators for left- and right-handed helices, M and P, respectively. Therefore, the two enantiomeric pairs are MP and PM and MM and PP. In the former enantiomers, the twists of the imidazolyl unit and the angle between the two rings are opposite, and the global conformation is more or less flat, with the atoms C4 and C5 eclipsed approximately with the plane of the phenyl group. Therefore the MP and PM enantiomeric conformations are referred

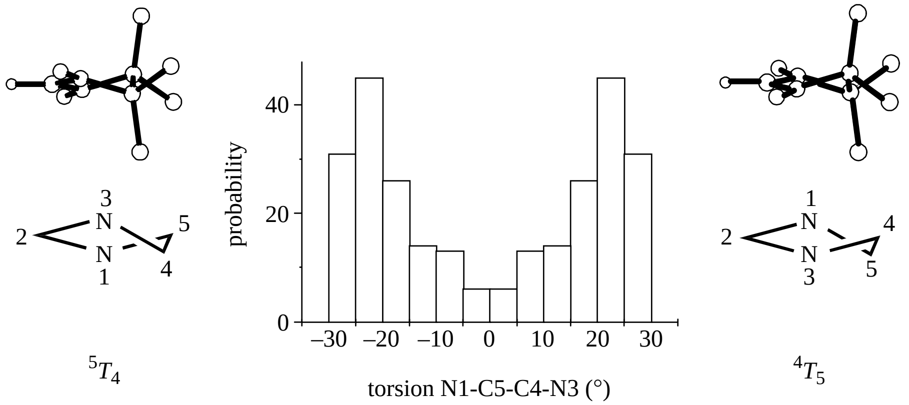


Figure 5. The bimodal distribution obtained from the statistical study for the torsion angle formed by the atoms N1—C5—C4—N3, corresponding to the puckering of the imidazolyl moiety in the radicals, which gives rise to the two enanatiomers depicted.

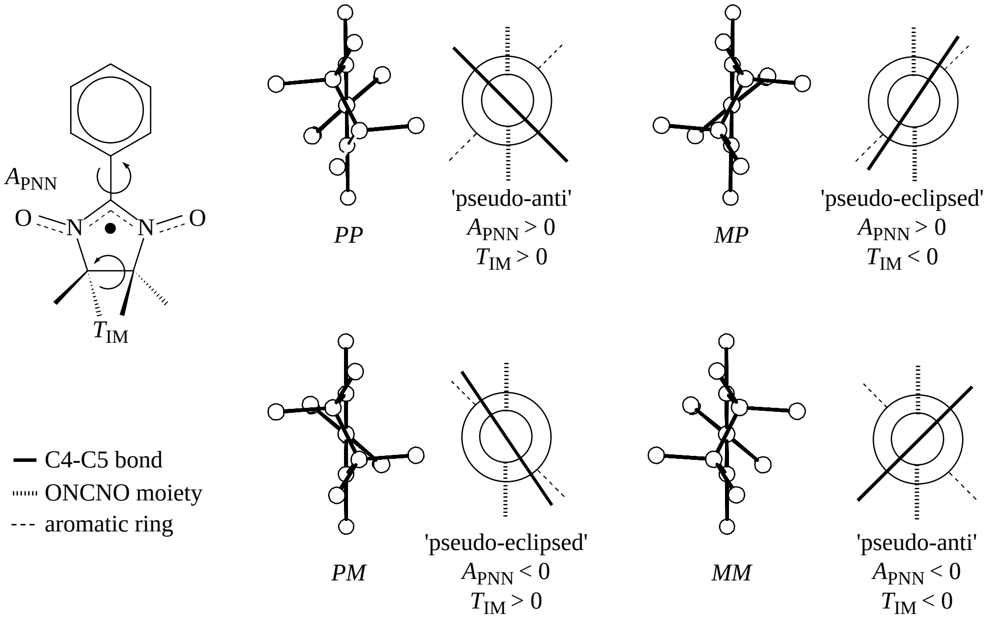


Figure 6. Definition of the angles $A_{\rm PNN}$ and $T_{\rm IM}$ and their signs in the four diastereomeric conformations that phenyl α-nitronyl aminoxyl radicals can adopt.

to as *pseudo-eclipsed*. The remaining diastereomeric conformers have a single-handed twist down the length of the molecule, and are referred to as *pseudo-anti*.

Let as first deal with the angles $T_{\rm IM}$ and $A_{\rm PNN}$ independently. As we have seen, the analysis of the crystal structures shows that the torsion angle formed by the atoms N1, C5, C4 and N3 present in the imidazolyl ring must always be present. Indeed, AM1 semiempirical calculations (Cirujeda 1997) reveal that the planar conformation is a local energy maximum, the minima being located at +25° and −25°. It is likely that the interconversion between the two enantiomers is an extremely rapid equilibrium at room temperature in solution, since the barrier to the process is a mere 0.6 kcal mol^{-1}. As for the angle between the imidazolyl and aromatic rings, A_{PNN}, in the crystal structures in the data base the average of its absolute value is 27.5°, with a standard deviation of 8.5°. The angles are located principally between 10 and 45°. The value is surely determined by various factors, among them: (i) the tendency to form a planar conformation to encourage π-electron conjugation; (ii) the presence of a hydrogen bond between the *ortho* hydrogen atoms of the phenyl group and the oxygen atoms of the radical; (iii) the presence of a bulky group in the *ortho* position of the phenyl ring which induces a high angle; (iv) non-covalent interactions between the molecules, i.e. hydrogen bonds; and (v) other crystal packing forces. We shall return to the latter aspect subsequently.

In an effort to detect a relation between T_{IM} and A_{PNN} in the crystals of the phenyl α-nitronyl aminoxyl radicals, we have plotted the calculated probability of the global conformation of the molecules in terms of the two angles, the result of which is shown in figure 7. Clearly, the most favoured conformers are the pseudo-eclipsed ones, MP and PM, which point to an overall flat conformation. The preference for this latter conformation is statistically significant, since it was ratified in all the statistical tests tried. There is no excess of either of the two enantiomers, since none of the sample contained chiral molecules. Therefore, although some of the molecules crystallize in chiral space groups, there are, in principle at least, an equal number of dextro- and levo-rotatory crystals. It should be pointed out that the introduction of a chiral substituent to the phenyl nitronyl nitroxide induces the preferential formation of only one of the enantiomers of one of the diastereomers (Minguet *et al*. 1999*b*).

One of the important questions related to our analysis of the crystal structures of these radicals is: are the conformations observed in the solid a result of intrinsic preference for one conformation, or are they bound by crystal packing forces? The answer to this question will have an influence on how the crystals of new radicals are forged. In this regard, it is interesting to remark that in our statistical analysis, the conformation with $A_{\mathrm{PNN}} = 0$ is clearly disfavoured. However, in the radical 2-phenylbenzimidazol-1-yl N, N′-dioxide (figure 8), in which the $-\mathrm{CMe_2CMe_2}-$ group is replaced by an *ortho*-substituted benzene ring, this angle is only 10.3°, and the molecule, whose crystals have dominantly antiferromagnetic interactions present, has a practically planar shape (Kusaba *et al*. 1997). The absence of a twisting force in the imidazolyl unit in this structure would seem to favour a low A_{PNN} angle, and indicates that the reason for the favoured pseudo-eclipsed geometry is the presence of a molecule with a flat shape in the crystal, in line with the ideas put forward by Kitaigorodskii (1961).

3. Crystal architecture and magnetism–structure correlations

Naturally, the structural study tells us little about the electronic distribution of the molecules in the crystals, for which neutron diffraction studies are necessary (Zheludev *et al*. 1994), which in turn relies on the formation of relatively large single crystals, a requisite that cannot always be fulfilled. An alternative procedure for studying the spin distribution of molecules in crystals is the analysis of solid state ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (Heisse *et al*. 1999), combined with *ab initio* calculations and with other spectroscopic methods such as UV–visible and electron paramagnetic resonance (EPR) spectroscopies. The latter technique

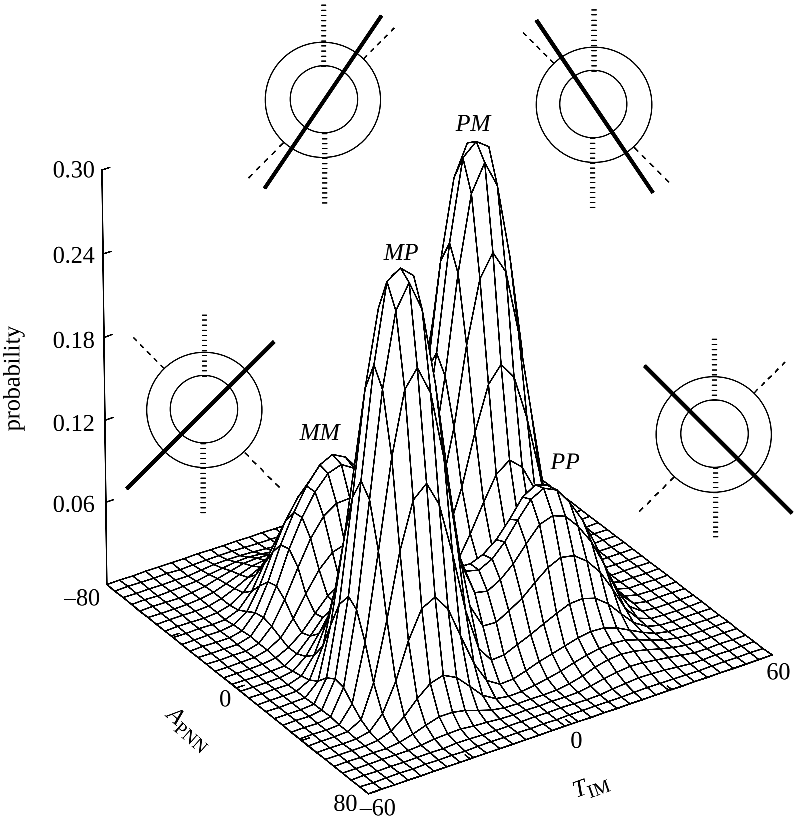


Figure 7. Distribution of the conformations of phenyl α-nitronyl aminoxyl radicals in their crystals, as defined by the angles A_{PNN} and T_{IM}.

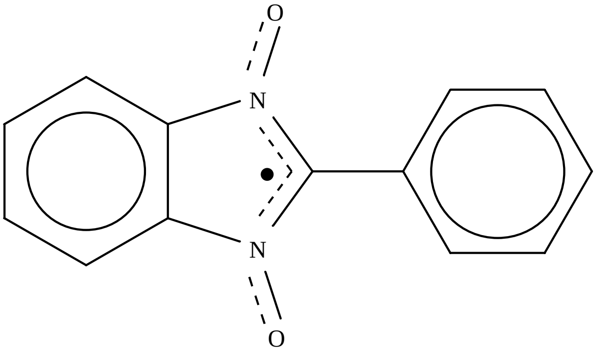


Figure 8. The radical 2-phenylbenzimidazol-1-yl N, N′-dioxide.

provides the interesting opportunity of studying the spin distribution in the isolated molecules in solution. For example, studies of the conformations of phenyl α-nitronyl aminoxyl radicals in solution using UV–vis spectroscopy—aided by applying a linear solvation energy relationship multiparametric analysis—shows that the angle A_{PNN} varies dramatically with the polarity of the solvent (Cirujeda *et al.* 1997). Generally, as the polarity of the solvent increases so does the angle A_{PNN}, an effect which has also been followed by EPR spectroscopy (Cirujeda *et al.* 1999). The spin density of the free electron on the aromatic moiety decreases dramatically as the torsion angle increases. A similar situation might be expected in the solid state, which in turn will influence the interactions between the delocalized free electrons and therefore sway dramatically the bulk properties.

So far, we have seen that it is possible to establish the conformational and electronic structure of α-nitronyl aminoxyl compounds based on a combination of solid-state structural data and solution-state spectroscopic data. However, the identification of the magnetic interaction pathways is elusive. Indeed, perhaps one of the most important unanswered questions remaining in the area of molecular magnetism of systems incorporating organic molecules is: what are the molecular arrangements—what one might call *magnetic synthons* (not necessarily the same as the supramolecular synthons)—which favour ferromagnetic interactions?

Currently, the analyses of interactions based on structural data use mainly the first model described by McConnell (1963), which is based on a Heisenberg spin Hamiltonian and is proposed to explain through space magnetic interactions and the dependence of distance and relative disposition of the orbitals in which the unpaired electron(s) move. Ferromagnetic interactions are predicted only when 'touching' molecules have spin populations of opposite sign close to one another. Therefore, one would predict that if the single occupied molecular orbitals of the oxygen atoms come into close proximity (figure 9), an antiferromagnetic interaction will result, while if the oxygen atom of one molecule approaches one or more of the four methyl groups located above the carbon atom between the two nitrogen atoms of the imidazolyl moiety of another molecule, the interaction will generally be ferromagnetic.

If the scenario painted by the McConnell (1963) I model is correct, one might expect that there would be spatial segregation of ferromagnetic and antiferromagnetic relative dispositions of radical moieties. We employed in collaboration with J. J. Novoa (Universitat de Barcelona) our structural database to test this hypothesis (Deumal *et al.* 1998*a*, 1999). A group of 47 purely organic α-nitronyl aminoxyl radicals was chosen which showed either dominant ferromagnetic (FM, 23 of them) or dominant antiferromagnetic (AFM, 24 of them) interactions. In order to describe the relative orientations of the ONCNO units in the radicals, six parameters are necessary (figure 10): the closest oxygen–oxygen distance, two N—O···O angles, two C—N—O···O torsion angles and one N—O···O—N torsion angle.

Only considering the closest O···O distances (below 10 Å, of which there were 1312), the shortest distances in the FM and AFM subsets were 3.158 and 3.159 Å, respectively, and is a general state of affairs across the sample. In fact the distribution of subsets is independent of the distance cut-off, be it $3, 4, 5, 6, 7, 8$ or 9 Å. Therefore, short N—O···O—N distances *per se* do not rule out ferromagnetic interactions. At all these distances, the angular distributions are averaged. In principle, one should expect clustering at certain angles for FM or AFM subsets. This situation was not observed. Therefore, given that looking at one distance and one torsion angle does not show division of subsets, the common application of these parameters to describe magnetic interactions must be questioned. Even allowance for hydrogen bonding did not separate the subsets. The situation is even more disparaging when one considers that a factor analysis of all six parameters showed interpenetration of the FM and AFM subsets. So how should the magnetic interactions be evalu-

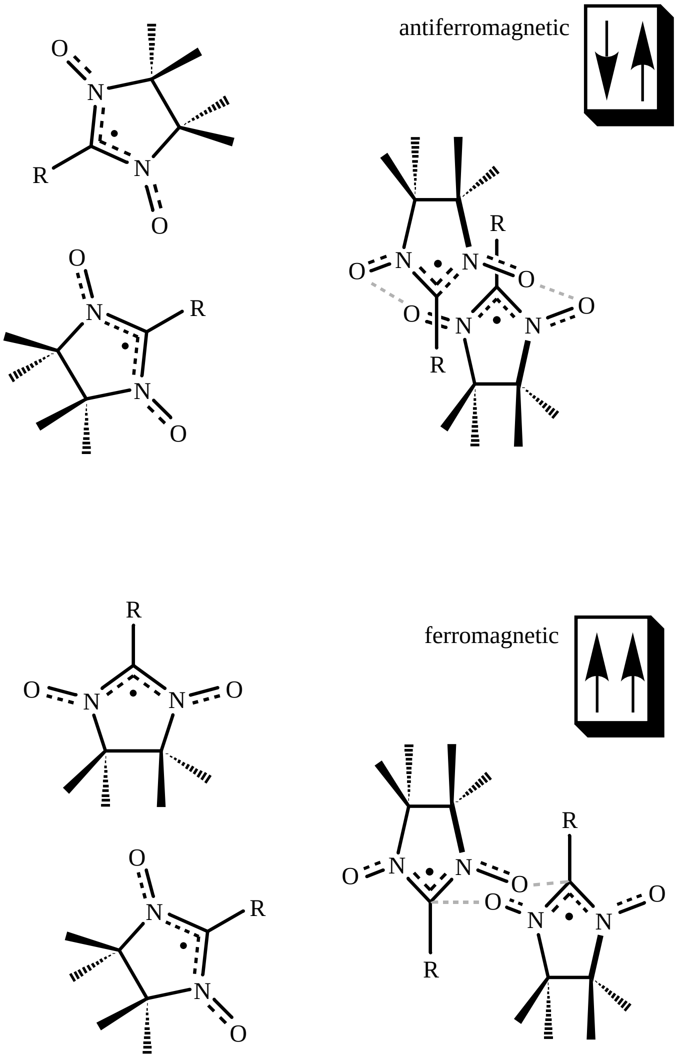


Figure 9. Schematic representation of relative dispositions of radical fragments and the interactions that they would be expected to show according to the McConnell (1963) I theory.

ated? As only the ONCNO unit was considered in this statistical analysis, it seems likely that consideration of the whole molecule is necessary to describe the magnetic interaction. A small spin density could be combined with a large exchange coupling between the free electrons to produce a significant magnetic interaction. The testing of this hypothesis is being realized presently. Another important issue in this field is the scope and limitations of the McConnell (1963) I model, whose validity has been analysed recently (Deumal *et al.* 1998*b*)

4. Crystal architectures engineered

In the face of the uncertain significance of certain packing arrangements for the propagation of ferromagnetic interactions, a necessity still exists to 'engineer' crystals such

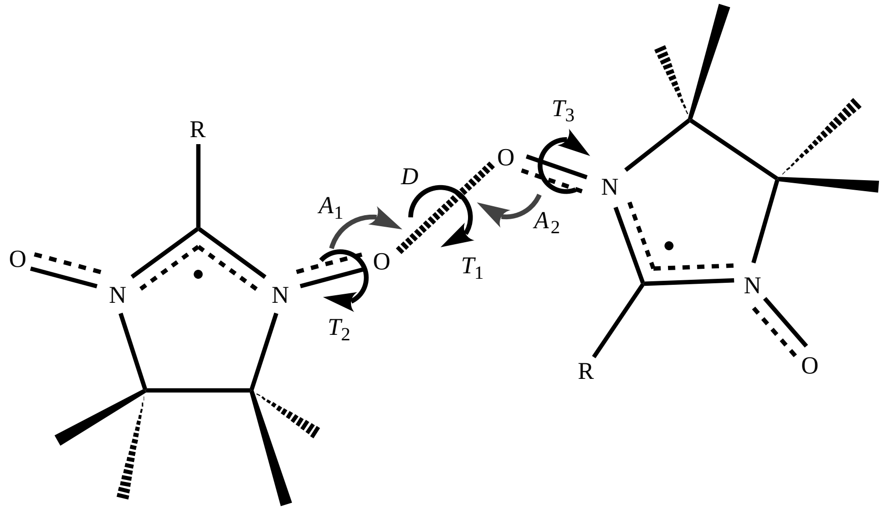
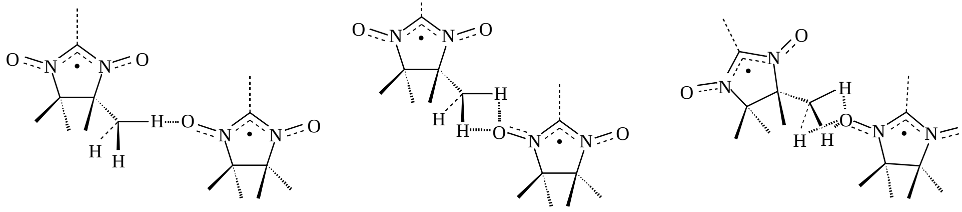
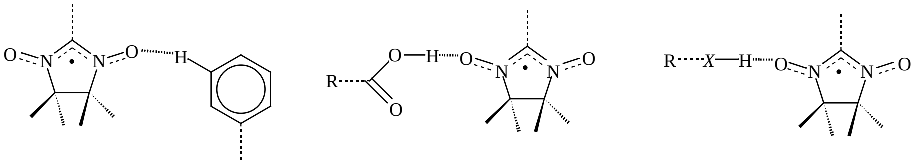


Figure 10. The distances and angles used to define the relative orientations of radical fragments in the crystals of purely organic α-nitronyl aminoxyl radicals.



C_{sp3}–H···O-N



C_{sp2}–H···O-N

RCOOH···O-N

RXH···O-N
X = O, N, S

Figure 11. Supramolecular synthons relevant to the crystal design of α-nitronyl aminoxyl radicals.

that the relative dispositions of the radicals and the dimensionality of the interactions between them is controlled. In order to control relative dispositions, dominion over non-covalent interactions is necessary, and the concept of ‘supramolecular synthons’ (Desiraju 1995) is a useful one. The α-nitronyl aminoxyl radicals have recurring patterns in their crystal structures which can be regarded as ‘supramolecular synthons’. These synthons include (figure 11): C_{sp^3}—H···O hydrogen bonds (Desiraju

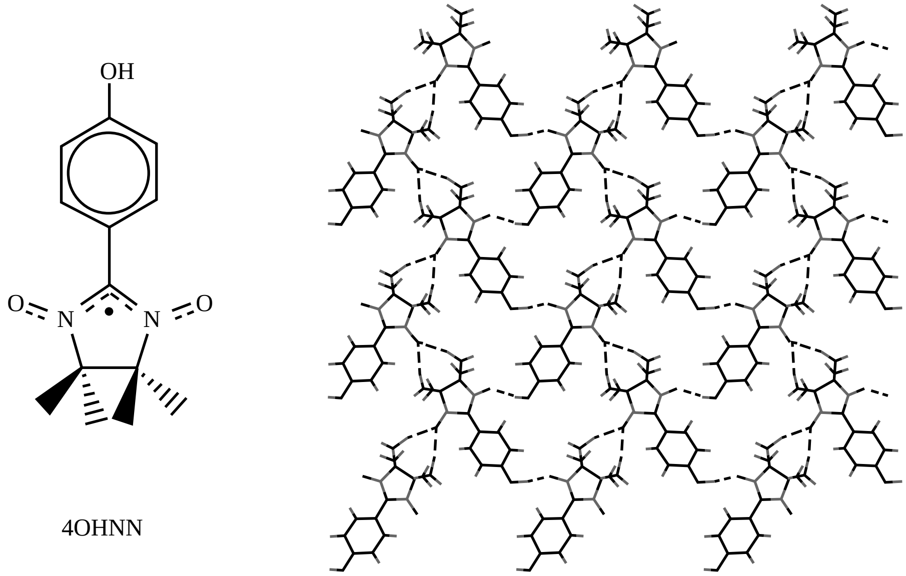
1996; Steiner 1997, 1999) from the methyl groups attached to the radical ring to the oxygen atoms bearing the unpaired electron; C_{sp^2}—H···O hydrogen bonds from the aromatic ring to the same oxygen atoms; and X—H···O hydrogen bonds, where X is an electronegative atom.

The weak C_{sp^3}—H···O hydrogen bonds are a frequently encountered cement between the α-nitronyl aminoxyl radicals (Novoa *et al*. 1997; Novoa & Deumal 1997), and may be involved in the propagation of magnetic interactions within them, as has been implied in the case of TEMPO-derived magnets (Nogami *et al*. 1994, 1995*b*; Maruta *et al*. 1999), most notably in 2OHNN (Cirujeda *et al*. 1995*a*) in which a three-dimensional network of hydrogen bonds results in crystals which show ferromagnetic ordering. Additional types of weak forces which have been used recently (Jürgens *et al*. 1997) in an attempt to influence crystal packing are C—H···Cl (Taylor & Kennard 1982) and Cl···Cl interactions. In this case, while the crystal packing was modified, the magnetic interactions were antiferromagnetic in all the examples studied. Stronger intermolecular hydrogen bonds have proven a particularly versatile tool for the preparation of organic molecular magnets, and have also been invoked to explain transmission of spin–spin magnetic interactions (Pontillon *et al*. 1997).

A particularly interesting clan of radicals which are substituted with hydrogen-bond donors are those in which the aromatic moiety has a pendant hydroxyl group. The phenolic hydrogen atom is an extremely good hydrogen-bond donor. For example, the radical 4OHNN (Hernàndez *et al*. 1993; Cirujeda *et al*. 1995*b*), in which the molecules form chains in which hydrogen bonds are given by the hydroxyl group at the 4-position of the phenyl ring and received by one of the oxygen atoms of the radical moiety (figure 12). In turn, these chains are bonded by two C_{sp^3}—H···O hydrogen bonds from diametrically opposite methyl groups in one radical moiety and the remaining NO group of a molecule in the adjacent chain. The resulting two-dimensional sheet is virtually flat. Indeed, the ferromagnetic interactions are quasi-two-dimensional, as revealed by EPR studies on oriented single crystals.

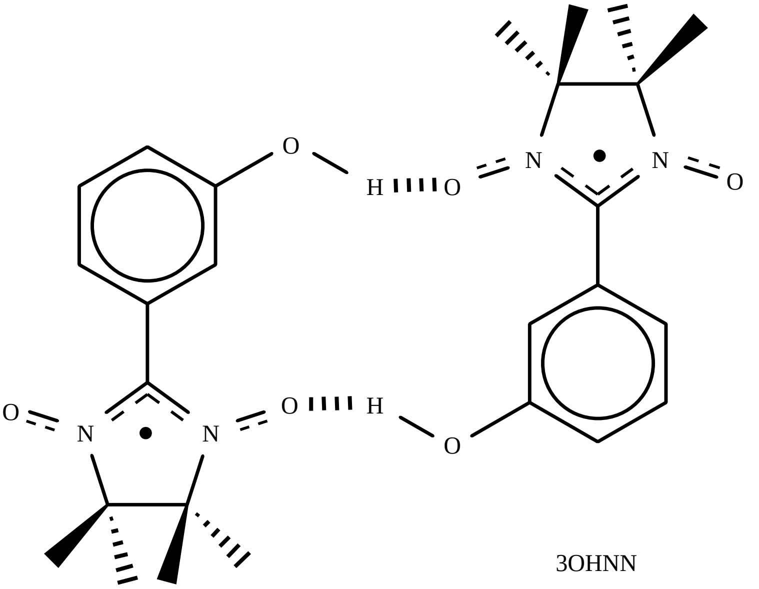
In contrast to its *para*-substituted cousin, the radical 3OHNN forms dimers with itself in the solid state, as depicted schematically in figure 13. These dimers pack together in the crystals in manners which are determined by weaker C—H···O hydrogen bonds, forming a herringbone-type pattern two molecules thick (Cirujeda *et al*. 1995*a*) to give a solid which has dominantly antiferromagnetic interactions between the spins.

It is possible to use the 3OHNN synthon for the preparation of solids with higher structural dimensionality as far as the strong interactions are concerned, as in the case of the dihydroxyphenyl radicals 34OHNN and 35OHNN shown in figure 14. The dimers of the type shown in 3OHNN are also present in the crystals formed by both these radicals. In the case of 34OHNN (Cirujeda *et al*. 1995*c*) the second OH group forms a hydrogen bond to the NO group not involved in formation of the head-to-tail dimer, so as to generate a chain. In these crystals there are very apparent competing ferro- and antiferromagnetic interactions. Meanwhile, 35OHNN (Cirujeda *et al*. 1996; Matsushita *et al*. 1997) forms one-dimensional chains containing the 3OHNN synthon in polymeric tapes. In these crystals, which show dominant antiferromagnetic interactions, the tapes come together thanks to C—H···O hydrogen bonds from the methyl groups in one tape to the phenolic oxygen atoms in another. Remarkably, one of the phases of the related 25OHNN, which also has structures which are replete with hydrogen bonds, is a bulk ferromagnet (Matsushita *et al*. 1997).



4OHNN

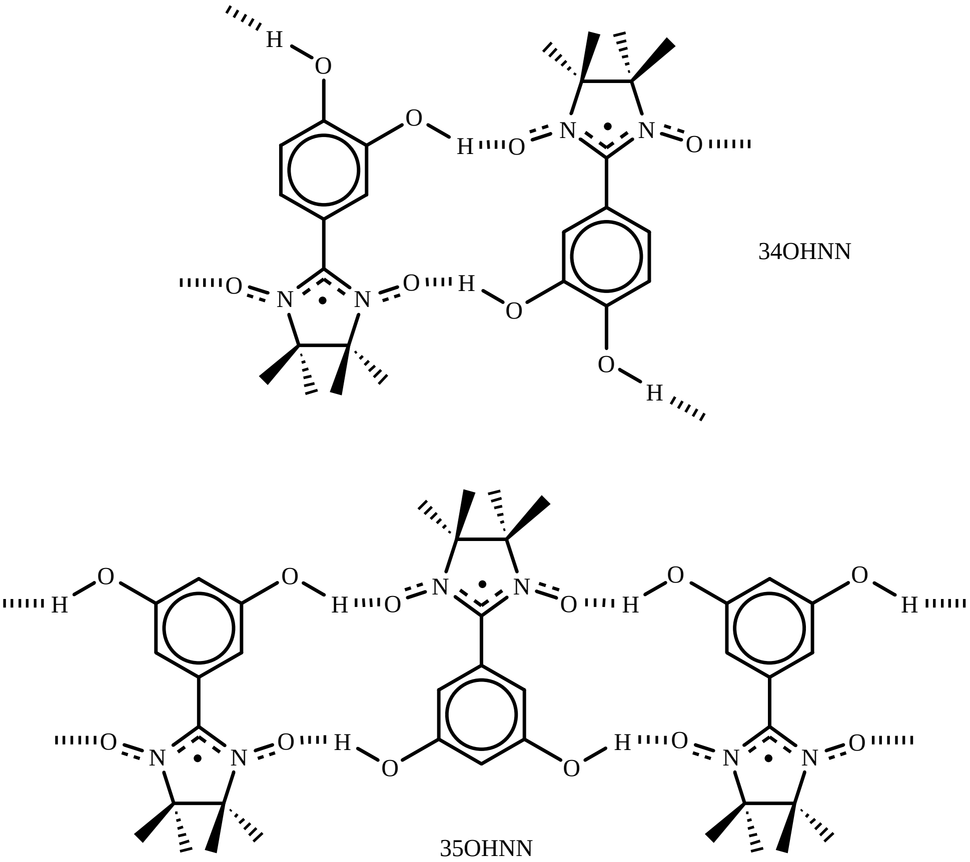
Figure 12. The radical 4OHNN and the two-dimensional sheet which it forms in its crystals.



3OHNN

Figure 13. The hydrogen-bonded dimer formed by 3OHNN.

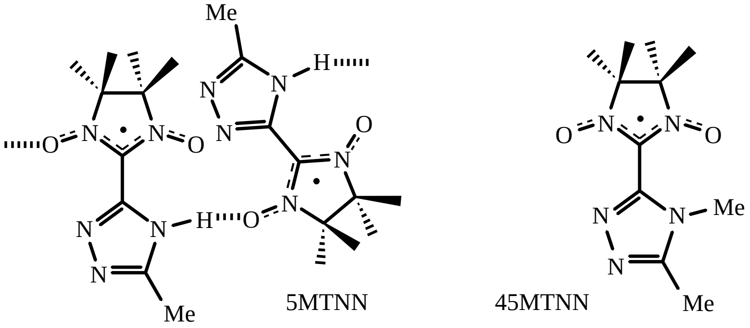
A quite intriguing example of an α-nitronyl aminoxyl radical which is hydrogen bonded in the solid state is that derived from 5-methyl-1,2,4-triazole (5MTNN, Lang *et al.* 1996). The molecules form chains which are sustained by N—H···O hydrogen bonds (shown schematically in figure 15) from N3 of the triazole ring to the nitroxide oxygen atom. The ferromagnetic interactions in the crystals are extremely strong



34OHNN

35OHNN

Figure 14. Schematic representation of the packing patterns of the radicals 34OHNN and 35OHNN which contain the supramolecular synthon discovered in 3OHNN.



5MTNN

45MTNN

Figure 15. The radical 5MTNN whose crystals contain chains of molecules linked through strong hydrogen bonds and the radical 45MTNN whose packing is determined by weaker intermolecular forces.

for an organic molecule, with $J = 14.8\,\mathrm{cm}^{-1}$. The 4,5-dimethyl triazole derivative (45MTNN), which does not have the strong hydrogen bonds between the radicals, shows metamagnetic behaviour (Sutter *et al.* 1997).

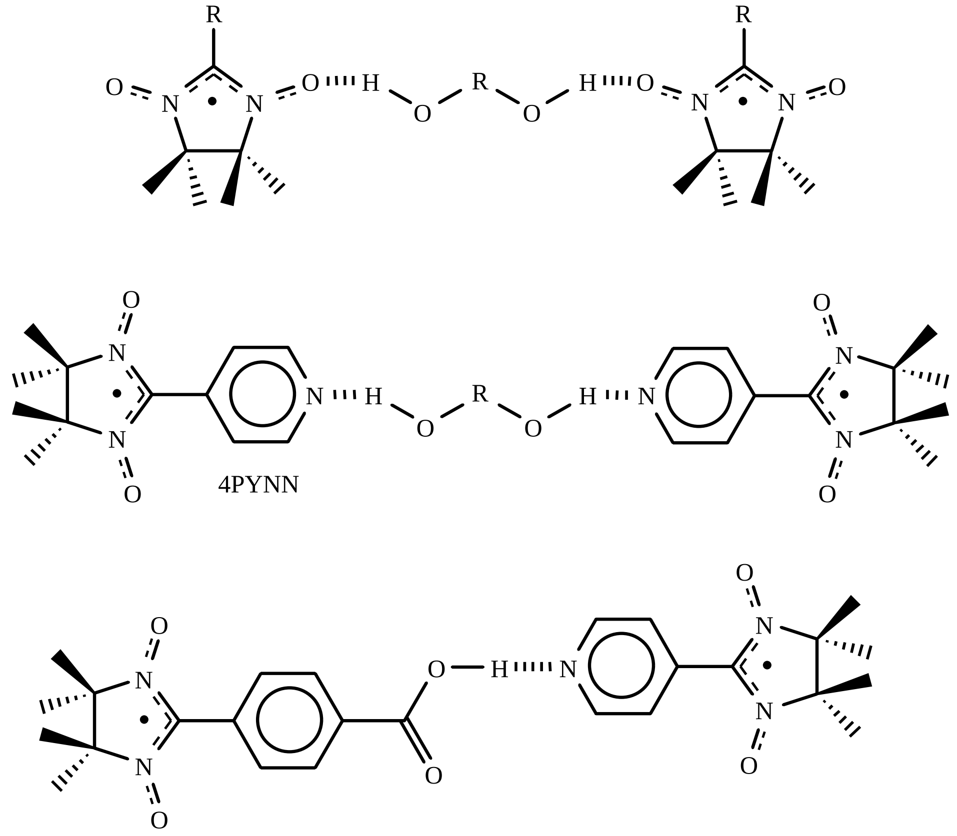


Figure 16. Examples of zero-dimensional trimeric and dimeric aggregates incorporating α-nitronyl aminoxyl radicals.

The discussion has centred so far on radicals which crystallize in a way which is dominated by non-covalent interactions. An attractive possibility which is available to chemists, and which appeals more to the idea of crystal engineering, is to cocrystallize radicals, either with neutral molecules or with other radicals. For example, cocrystallization of 4PYNN with three diacids has produced zero-dimensional 2:1 radical:acid hydrogen-bonded complexes (Otsuka *et al*. 1998). Similar heteroradical complexes have been prepared by crystallizing 4PYNN or 3PYNN with 4COOHNN (Otsuka *et al*. 1997). All these crystalline complexes show antiferromagnetic coupling between the radical units. Attempts have also been made to cocrystallize di- or tri-α-nitronyl aminoxyl radicals—which have intramolecular ferromagnetic interactions between free electrons—into stacks with diamagnetic or radical species in order to try and extend the magnetic interactions beyond the molecule (Izuoka *et al*. 1995). However, the sought after ferro- or ferrimagnetic were not forthcoming, perhaps because of antiferromagnetic interactions between stacks.

One complex which does show ferromagnetic interactions is the one formed between the phenyl α-nitronyl aminoxyl radical and phenylboronic acid, which consists of helical chains comprising alternating components, linked by strong hydrogen bonds between the acid groups of the diamagnetic species and the oxygen atoms of the radical (Akita *et al.* 1995). At this stage, it is unclear whether the magnetic interaction results from coupling through the boronic acid or by close approaches of radicals between helical chains.

In all these examples, although control has been demonstrated in the formation of the zero- or one-dimensional complexes, the next dimension of crystal does not possess controlling elements, and this situation reflects a general obstacle that exists in the field of crystal engineering. While crystal engineers have achieved interesting results with zero-dimensional dimers, one-dimensional, and a few two-dimensional packing patterns that can be more or less designed, it is at present impossible to contrive *a priori* even simple molecules that will come together in a predetermined way in three dimensions, let alone molecules with a function. In particular, the 'grammar of crystal packing' (Pratt Brock & Dunitz 1994) for the group of compounds discussed here has yet to be deciphered, although, as demonstrated, there are many letters and words! In the realm of molecular magnets, interlayer packing often rules, and holds sway over the nature of the bulk properties.

Perhaps a way forward in unravelling the supramolecular synthons which are appropriate for the propagation of ferromagnetic interactions is to generate small discrete zero- or one-dimensional aggregates in solution and to study their magnetic properties. The radical 3OHNN and some derivatives related to it are presently being studied in collaboration with J. J. Novoa using various techniques to test the viability of this approach.

5. Conclusions and outlook

The analysis of the molecular and supramolecular aspects of α-nitronyl aminoxyl radicals in their crystals using structure correlation methods gives the mean molecular geometries of the molecules, and has allowed a structure–magnetism relationship which does not show any clear-cut regions of ferromagnetic or antiferromagnetic interactions. While the analysis presented in this paper is applied to the family of α-nitronyl aminoxyl radicals, it is also useful in the analysis of other organic radicals. It seems likely that appreciation of interactions between molecules as a whole, and not only the parts which bear mainly the spin, is necessary to account for the magnetic behaviour of the materials. This assertion implies that even small spin densities in certain regions of the molecules can have profound effects on their properties. For instance, hydrogen bonds between the oxygen atoms bearing the majority of the spin density in the radicals to hydrogen atoms with very small spin densities have proven to be very significant in the transmittance of magnetic interactions. The analysis of spin densities in the solution and solid states, and their correlation with structure and properties, will help to confirm or repeal this hypothesis.

We thank all our collaborators whose names are cited in the references and who have contributed to this work over the years, especially Ms Maria Minguet for her recent contribution to the study of conformations in the phenyl α-nitronyl aminoxyl radical derivatives, and also to Professor Juan J. Novoa and Dr Mercè Deumal (Universitat de Barcelona) for their continuous eagerness to perform calculations and valuable comments. We also thank the Fundación Ramón Areces for generous financial support of a project, and to DGES (proyecto PB96-0862-C02-C01), CIRIT (1998 SGR-96-00106) and to the 3MD Network of the EU TMR programme (contract ERBFMRXCT980181).

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Discussion

P. Day (*The Royal Institution, London, UK*). What are the implications of the task of correlation between mean neighbour intermolecular spacing and the magnetic exchange for the mechanism of the exchange?

J. Veciana. The magneto-structural correlation performed with this family of free radicals has important implications relative to the mechanism of magnetic exchange between neighbouring molecules. The fact that no direct relationship exists between the sign of dominant magnetic interactions and the intermolecular distances and disposition of the groups carrying the vast majority of the free electron spin density could be due to two different reasons. Firstly, the McConnell I model might not be valid and could be just an oversimplification of the actual operative mechanism. Secondly, dominant magnetic interactions could originate from the relative disposition of all the magnetically active sites with little or large spin density instead of local contacts between ‘touching’ molecules. So far, there is no experimental evidence that rules out either of the two options. It is therefore necessary to perform further experimental and theoretical work in order to clarify this issue. This is a crucial point in molecular magnetism since most molecular solids and open-shell molecules are designed under considerations based on the McConnell I model.