Control of the Structural Dimensionality in Hydrogen-bonded Self-assemblies of Open-shell Molecules. Extension of Intermolecular Ferromagnetic Interactions in α-Phenyl Nitronyl Nitroxide Radicals into Three Dimensions

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The variation of the number and position of OH substituents at the phenyl ring of α-phenyl nitronyl nitroxide radicals yields different hydrogen-bonded molecular self-assemblies with distinct dimensionalities; the mono-*ortho*-substituted isomer is most remarkable since it shows a three-dimensional network of weak hydrogen bonds exhibiting a bulk ferromagnetic transition at 0.45 K.

The macroscopic physical properties of molecular crystals are defined by the intermolecular electronic interactions present in the solid state. Consequently, there is a need for the development and study of crystalline design elements producing strong and highly directional intermolecular interactions which are able to generate predetermined molecular arrangements.

The high directionality of strong (O–H···O–N) and weak (C–H···O–N) hydrogen bonds makes them useful crystalline design elements for the preparation of molecular materials with controlled physical properties.[1,2] Very recently some of us have found evidence that both types of hydrogen bonds are able not only to control the crystal packing of open-shell molecules, but also to generate and propagate ferromagnetic interactions through them.[3–5] Thus, radical **1** shows ferromagnetic intermolecular interactions along two dimensions,[3] whilst coexistence of anti- and ferromagnetic intermolecular interactions is observed for radical **2**.[4] Meanwhile, Sugawara *et al.* have also obtained another dihydroxylated radical of this type which exclusively shows ferromagnetic intermolecular interactions.[6]

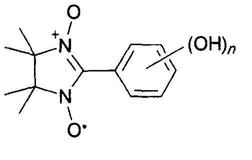
Herein we present three new examples of this family of free radicals:† the monohydroxylated derivatives at the *ortho* **3** and *meta* **4** positions of the phenyl ring as well as the dihydroxylated derivative **5**, with the OH groups in *meta* positions.

In **3**, the location of the OH group at the *ortho* position favours the formation of a strong intramolecular O–H···O–N bond ($d_{O\cdots H}$ 1.519(1) Å, O–H–O 163.5°) which gives rise to a seven-membered ring forcing a large twist angle of *ca.* 40° between the two rings of the molecule, inducing a large molecular asymmetry. The resulting crystal packing is therefore governed only by weak intermolecular hydrogen bonds (Fig. 1) established between the two NO groups and the H atoms of methyl groups and aromatic rings giving rise to a molecular self-assembly through a three-dimensional network of weak hydrogen bonds.

The formation of an intramolecular hydrogen bond is not favoured for radical **4**. By contrast, the presence of two self-complementary strong hydrogen-bonding groups on the same side of this radical promotes a dimerization in a side-by-side and head-to-tail fashion through two identical strong intermolecular O–H···O–N bonds ($d_{O\cdots H}$ 1.653(2) Å, O–H–O 173°) (Fig. 2, insert). The resulting dimers are then self-assembled by means of weak hydrogen bonds, forming two-dimensional layers of dimers along the (100) plane.

In **5** each molecular unit has an equal number of self-complementary strong hydrogen bonding groups which promote an increase of the dimensionality, from zero-(dimers) to one-dimensional (chains), of the molecular self-assembly built by the strong H-bonds. As in **4**, the molecules of **5** are arranged in a head-to-tail manner, through two very similar strong bonds of the O–H···O–N type ($d_{O\cdots H}$ 1.74(3), 1.87(3) Å; O–H–O 170, 173°), forming infinite molecular linear ribbons. These ribbons are linked together through two simultaneous weak C–H···O–C bonds. In this way, single corrugated planes parallel to the (10 − 1) plane of molecules, linked by a two-dimensional network of strong and weak hydrogen bonds, are formed.

In conclusion, the number and relative positions of the OH groups in this family of free radicals have a notable influence on their crystal packing and structural dimensionalities, since they control the molecular entities—dimeric clusters, infinite molecular ribbons or sheets—produced by strong O–H···O–N bonds. The self-assembling of such molecular entities also takes place through additional weak hydrogen bonds as well as other, even weaker, intermolecular forces that determine the final crystal packing. Consequently, the macroscopic magnetic properties of these molecular solids are notably affected by the number and relative positions of the NO and OH groups.



1 n = 1, *para*
2 n = 2, *meta, para*
3 n = 1, *ortho*
4 n = 1, *meta*
5 n = 2, *meta, meta*

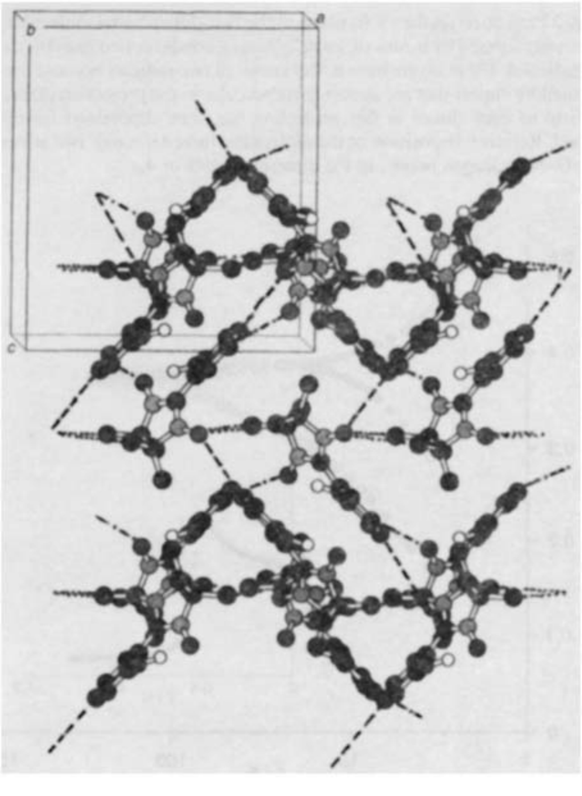


Fig. 1 Projection on the (010) plane of the crystal packing in **3**, in which the radicals are linked through a three-dimensional network of weak hydrogen bonds of the C–H···O–N type

Results of static magnetic susceptibility measurements with radicals **3**–**5** are shown in Fig. 3.‡ The data, plotted as $\chi \cdot T$ *vs.* T, are a clear indication of the existence of only one type of intermolecular magnetic interaction in **3** and **4**, which have ferro- (FM) and antiferro-magnetic (AFM) natures, respectively. By contrast, the presence in **5** of a broad maximum in the product $\chi \cdot T$ at *ca.* 35 K, similar to that recently reported for **2**,[4] indicates the simultaneous presence of both FM and AFM intermolecular interactions in this molecular solid.[7] The ac susceptibility of **3** shows a sharp rise at *ca.* 0.45 K, indicating that a ferromagnetic long-range order is achieved below this T_c. The above-mentioned divergence of the ac susceptibility, the saturation value of the magnetization (1 μ_B mol^{-1}) and the hysteresis curves of magnetization observed below T_c are in agreement with a bulk ferromagnetic transition, making radical **3** one of the rare examples of purely organic bulk ferromagnets yet known.[6,8]

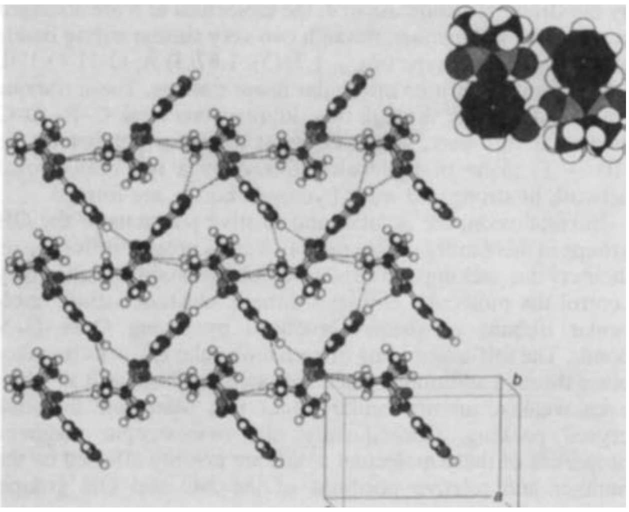


Fig. 2 Projection on the (100) plane of the two-dimensional molecular self-assembly formed by means of weak hydrogen bonds (dotted lines) of dimers of radical **4**. These layers have a 'thickness' of two radicals because they are formed by dimers that are almost perpendicular to the projection plane. One radical of each dimer in this projection has been suppressed for clarity. *Insert*: Relative disposition of the molecules, linked through two strong O–H···O–N hydrogen bonds, in the dimeric entities of **4**.

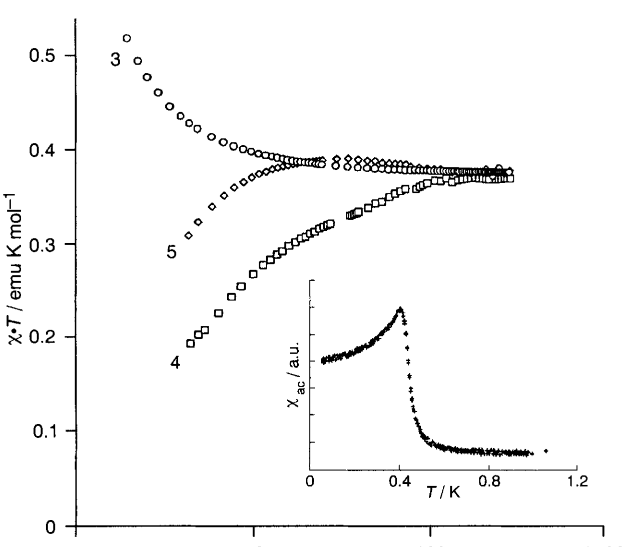


Fig. 3 Temperature dependences of products of molar paramagnetic susceptibility χ_M and temperature T of radicals **3**–**5** and (*insert*) of the ac susceptibility χ_{ac} of radical **3**

The distinct magnetic behaviour of the radicals studied can be explained by their different structural patterns, following the most widely accepted mechanisms for rationalizing the intermolecular magnetic interactions in organic open-shell molecules.[9] So, for this family of free radicals, those crystal engineering elements that favour 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 promote other kinds of contacts will induce ferromagnetic intermolecular interactions, which under favourable circumstances can be extended to yield a three-dimensional ferromagnetic ordering.

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Footnotes

† Radicals **3**, **4** and **5** were prepared following the usual procedure described by Ullman *et al.*[10] Analytical (elemental analyses) and spectroscopic (EI-MS, IR, EPR, and UV–VIS) characterization of these free radicals are in accordance with their molecular structures. Atomic coordinates, bond length and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Magnetic susceptibility measurements of radicals **3**–**5** were performed on a SQUID susceptometer from 300 to 4 K. For radical **3** such measurements were also performed from 1 K to 40 mK on an ac susceptometer under a zero-static magnetic field, perpendicular to the ac field of 100 mOe (500 Hz).

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