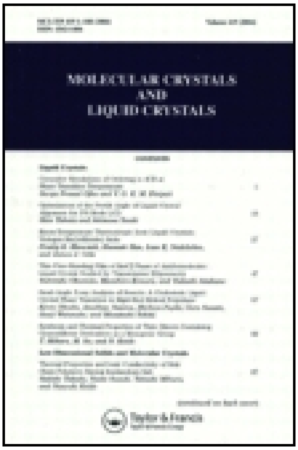

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From Ferromagnetic to Antiferromagnetic Order in Nitronyl Nitroxide Substituted Triazole Derivatives

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From Ferromagnetic to Antiferromagnetic Order in Nitronyl Nitroxide Substituted Triazole Derivatives

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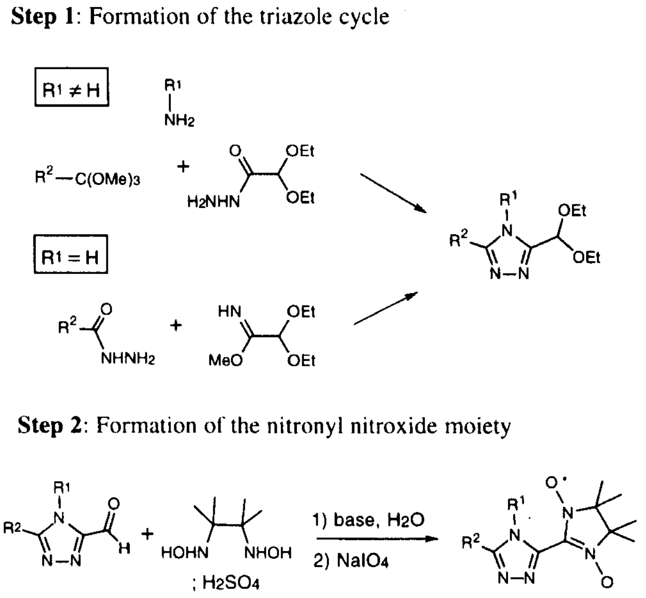
The chemical tuning of the bulk magnetic properties of an organic radical has been envisaged in a series of nitronyl nitroxide and imino nitroxide substituted triazole derivatives.

Keywords: molecular magnetism; nitronyl nitroxide; H-bonding; triazole

In the field of molecule-based magnetic materials nitroxyl radical derivatives play an important role. These rather robust spin carriers have been used to prepare purely organic ferromagnets and, associated with open-shell transition metal ions, ferri- and ferromagnetic coordination polymers.[1] The solid state properties of such compounds are not only governed by the radical moiety but they are also dramatically dependent on the core of the molecule to which the nitroxyl unit is attached. Indeed, this core will have an effect on the molecular packing in the solid state and may also take part in the intramolecular spin delocalization. Moreover, if judiciously chosen, the core can lead to chemical contacts such as H-bonding between neighboring molecules or improve the coordination ability of the radical to metal ions by incorporating a strong ligand.

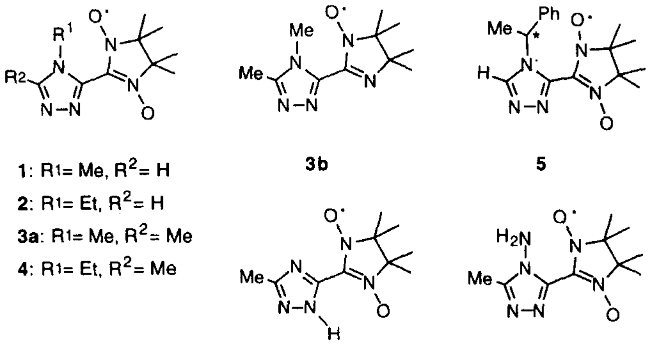
Recently, we considered the possibility of tuning the bulk magnetic properties of such an organic radical derivative through small chemical modifications of its core. The core we have chosen for this study is the triazole heterocycle substituted by a nitronyl nitroxide group. Our interest in this five membered ring arises from its synthetic pathways which allow us to introduce easily substituents in the 4- and/or 5-positions, the 3-position being substituted by the radical unit as depicted in Scheme 1.



SCHEME 1: Synthesis of nitronyl nitroxide substituted triazole derivatives.

Moreover, the conjugated π-electrons of the triazole might be involved in spin delocalization, as for benzene derivatives. Finally, the presence of N-atoms makes the triazole a good ligand for metal coordination.[2] The present results concern the potential of nitronyl nitroxide subtituted triazole derivatives as building blocks for organic magnetic materials.

A series of nitronyl nitroxide subtituted triazole derivatives have been synthesized according to the pathways described in scheme 1. The first step concerns the formation of the triazole unit. Two different routes are used depending on whether or not a substituent R^1, in the 4-position of the heterocycle is introduced. Both routes lead to a triazole bearing a protected aldehyde function in the 3-position. The deprotection of the latter in an acidic medium followed by the classical condensation reaction[3] with the 2,3-dimethyl-2,3-dihydroxylaminobutane yields after oxidation the expected nitronyl nitroxide subtituted triazole derivative (Chart 1).



1: R^1= Me, R^2= H
2: R^1= Et, R^2= H
3a: R^1= Me, R^2= Me
4: R^1= Et, R^2= Me

3b

5

6

7

CHART 1.

A first family of compounds, **1-5**, displays a substituent on the N-atom in the 4-position of the core and either a H, Me or a benzyl group in the 5-position. Two derivatives, **1** and **3a**, were already reported to exhibit intermolecular ferromagnetic interactions in the solid state.[4,5] The investigation of the magnetic properties of both **1** and **3a** have revealed the coexistence of dominant intermolecular ferromagnetic and weaker antiferromagnetic interactions. Their $\chi_M T$ versus T curves (χ_M = molar magnetic susceptibility, T = temperature) present a maximum at 1.60 K ($\chi_M T = 0.54$ cm^3 K mol^{-1}) and 1 K ($\chi_M T = 0.58$ cm^3 K mol^{-1}) for **1** and **3a**, respectively. Compound **3a** exhibits a long-range antiferromagnetic ordering at $T_N = 0.33$ K, and below T_N behaves as a metamagnet with a critical field of 700 Oe.

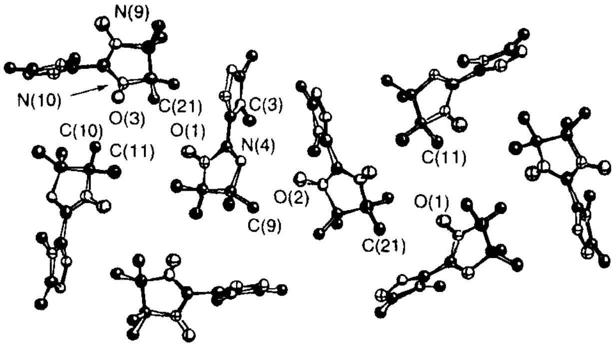


FIGURE 1. View of the crystal packing of **3b** (space group: P2$_1$/n). Selected intermolecular distances in Å: O(3)-C(10): 3.14, O(2)-C(3): 3.64, O(1)-C(21): 3.67, O(1)-C(11): 3.81 O(2)-C(9): 3.84, O(1)-O(3): 4.30, O(2)-N(4): 4.76.

The effect of small chemical differences on the magnetic behavior of these two compounds has been investigated first on the radical unit itself. The reduction of the nitronyl nitroxide unit of **3a** to the imino nitroxide radical led to compound **3b**. A view of the molecular packing of this compound is shown in Figure 1. The imino nitroxide group of one of the two molecules forming the asymmetric unit is partly disordered such that the nitroxide O atom has been found localized either on N(9) or N(10) with 2/3 and 1/3 probabilities. The shortest intermolecular distances involving the O atom of the nitroxyl are found with CH$_3$ groups of neighboring radical moieties and the Me-substituent in 4-position on the triazole (See Figure 1). The methyl groups of the nitronyl nitroxide unit are known to bear some spin density and thus may take part in intermolecular magnetic interactions. The shortest intermolecular distances between atoms bearing the unpaired electrons are 4.30 Å and 4.76 Å for O(1)-O(3) and O(2)-N(4), respectively. These separations can be considered as too large for significant magnetic interactions. The temperature dependence of the magnetic susceptibility of **3b** in the solid state is characteristic of intermolecular antiferromagnetic interactions. From 300 to *ca.* 30 K $\chi_M T$ is equal to 0.38 cm^3 K mol^{-1} and below this temperature decreases to reach 0.21 cm^3 K mol^{-1} at 2 K. This dramatic change in the bulk magnetic properties when going from a nitronyl nitroxide derivative to its imino nitroxide analogue is well documented.[6]

In compounds **2** and **4** the chemical changes concern the core. An ethyl-substituent has been introduced in the 4-position of the triazole. The X-ray structure analysis of **4** revealed a rather complex molecular packing as compared to those obtained before in this series of compounds (Figure 2a,b).

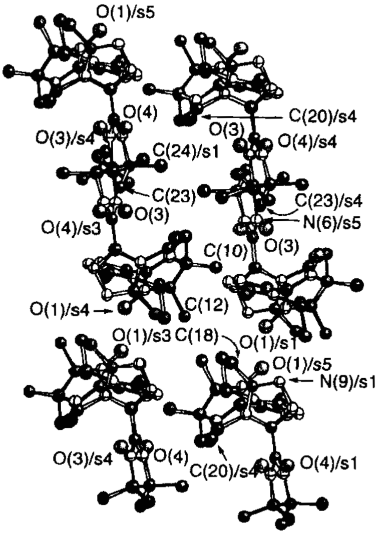


FIGURE 2a. View of the crystal packing of **4**, (space group: $P2_1/a$), Projection into the *ac* plane.

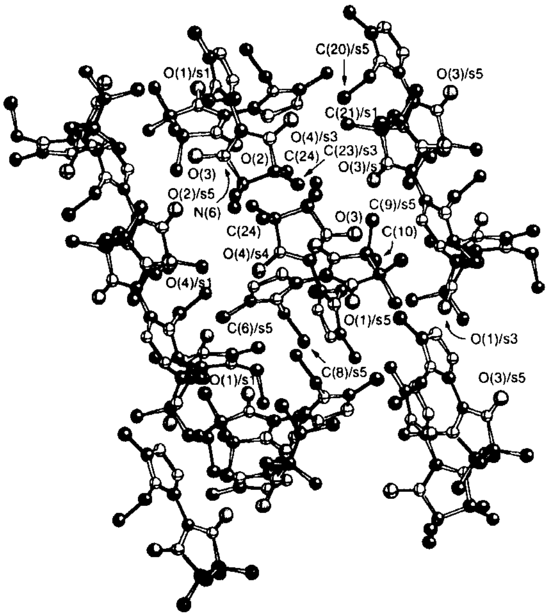
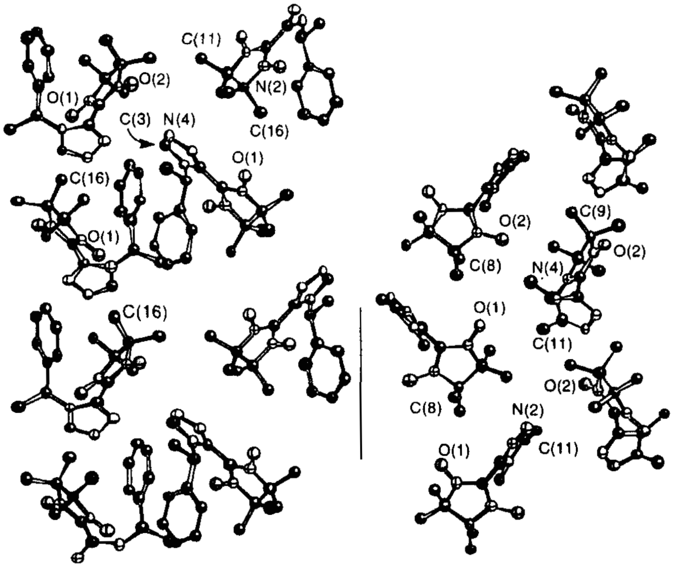


FIGURE 2b. View of the crystal packing of **4** projection into the *bc* plane. Selected intermolecular distances in Å: O(1)/s1: C(8)/s5, 3.56; C(18)/s5, 3.56; C(6)/s5, 3.57. O(2)/s1 and O(2)/s5-C(24)/s3, 3.47 and 3.43, respectively. O(3)/s4: C(10)/s5, 3.36; C(23)/s5, 3.64. O(4)/s3: C(20)/s5, 3.37; C(6)/s4, 3.41, C(21)/s1, 3.70. O(2)/s5-N(6)/s3, 3.93.

As for compound **3b** the shortest intermolecular distances involving the O atoms of the nitroxyl groups are found mainly with the Me groups of the nitronyl nitroxide units. The Me and Et substituents of the triazole are involved too. It is noticeable that each NO moiety is in close proximity (< 4 Å) to several neighboring molecules leading thus to a pseudo-3D network. The smallest intermolecular separations of two NO moieties are 3.93 and 4.84 Å for O(2)-N(6) and O(3)-O(4), respectively. The temperature dependence of the magnetic susceptibility in the solid state shows that compound **2** behaves as a paramagnetic species down to *ca.* 10 K, weak intermolecular antiferromagnetic interactions being evident at lower temperature. For compound **4** the magnetic interactions within the lattice are much stronger as evidenced by the maximum of χ_M observed at 4 K. Taking into account the possible pathways for the magnetic interactions *via* the Me-groups of the nitronyl nitroxide units as suggested by the molecular packing, the maximum in χ_M versus T might result from an antiferromagnetic ordering of the magnetic moments at low temperature.



5 **3a**

FIGURE 3. a) Crystal packing of **5** (space group: $P2_12_12_1$). b) Crystal packing of **3a** (space group: $P2_12_12_1$). Selected intermolecular distances in Å: for **5**: O(1)-C(16): 3.38, O(2)-C(3): 3.54, O(2)-C(11), 3.79, O(2)-N(4), 3.89, O(1)-N(2), 5.76. For **3a**: O(1)-C(18), 3.44, O(1)-C(11), 3.60, O(2)-C(11), 3.36, O(2)-N(4), 3.91, O(2)-C(9), 3.69, O(2)-N(2), 4.11.

The introduction of a larger substituent in the 4-position such as the benzyl group in the optically active derivative **5**[7] leads to an helical arrangement of the molecules along the crystallographic c-axis as previously observed for compounds **1** and **3a** (Figure 3). As a consequence of the bulkier core the separation of the spin carriers is more pronounced. The shortest distance involving two NO units is 5.76 Å found between O(2) and N(2). However, distances below 4 Å still exist between nitroxyl O-atoms and methyl groups of neighboring nitronyl nitroxides units as depicted in Figure 3a. The magnetic behavior of compound **5** in the solid state is characterized by weak antiferromagnetic interactions visible below 30 K.

The information gathered with compounds **1** to **5** already confirm that small differences in the chemical structure of nitronyl nitroxide substituted triazole derivatives may have a dramatic effect on their bulk magnetic properties. Indeed, the solid state molecular arrangement appears to be especially influenced by the substituent in the 4-position, R^1. Interestingly, the substituent in the 5-position, R^2, seems to have less importance in this respect as shown for compounds **1** and **3a**. This trend is confirmed by preliminary results obtained for a derivative with R^1= Me, R^2= Ph which exhibits a magnetic behavior very similar to that of **1** and **3a**.

Solely on the basis of the crystal structures it is hazardous to draw any conclusions about pathways for the magnetic interactions. However, the comparison of **3a** and **5**, which crystallize in the same space group with a very similar molecular packing, leads to the following observations. In both compounds the shortest intermolecular distances involving an O-atom of the nitroxyl and the nitronyl nitroxide Me groups of the neighboring molecule within the helical arrangement along the crystallographic c-axis are very much the same: O(1)-C(8) : 3.44 Å for **3a** and O(1)-C(16): 3.38 Å for **5**. The same is true for the separations between these pseudo-chains: O(2)-C(9): 3.69 Å for **3a** and O(2)-C(11): 3.79 Å for **5**. Even the rather close proximity to the N-atom in the 1-position of the triazole which has been shown to display negative spin density in compound **1**[4] is retained: O(2)-N(2): 4.11 Å for **3a** and O(2)-N(4): 3.89 Å for **5**. The difference is found for the distances between two NO moieties, O(2)-N(4) = 3.91 Å in **3a** *versus* 5.76 Å in **5** (see Figure 3). It is worth noting that the dihedral angle between the ONCNO mean planes of the adjacent molecules for both compounds are close to 90°. This strongly suggests that the dominant ferromagnetic interaction observed with **3a** arises at least partly from smaller distances between nitroxide NO groups as compared to **5**.

In compounds **1-5** described above the magnetic interactions between the molecules occur through space and are consequently rather weak. It is well known that the transmission of magnetic information through chemical bonds may strengthen the magnetic interaction.[8] An efficient way to introduce chemical contacts between molecules is offered by the hydrogen bond. Moreover, introduction of hydrogen bonding sites can be an efficient way of controlling the molecular arrangement in the crystal. This well-used concept in supramolecular chemistry has been applied recently to the preparation of molecule-based magnetic materials.[9] The triazole derivatives are suitable starting materials for such a self-assembling approach. Two compounds, **6** and **7**, have been prepared for this purpose.

In compound **6** an hydrogen atom is localized on the more basic N-atom in the 2-position of the triazole. Thus one amine proton is available for H-bonding. The X-ray structure of **6** confirmed the molecular assembling by H-bonding between the NH hydrogen of one molecule and a nitroxyl O-atom of the neighboring molecule, giving rise to a chain. The temperature dependence of the magnetic susceptibility of **6** clearly shows dominant ferromagnetic interactions with a maximum of $\chi_M T$ at 4.5 K. The intrachain interaction parameter has been found to be $J = 14.8\ \mathrm{cm}^{-1}$ ($H = -J S_i . S_{i+1}$).[10]

Substituting an NH_2 group on the triazole core in compound **7** results in the presence of two NH protons likely to be involved in H-bonds. The preliminary data of the X-ray crystal structure of **7** reveals a molecular assembling in an helical chain resulting from the linkages of the NH_2 group of one molecule, N(6), and the N-atom in the 2-position of the triazole, N(4), of a neighboring molecule as depicted in Figure 4. Moreover, the rather small dihedral angle between the triazole and nitronyl nitroxide mean planes (*ca.* 40° versus 80° in **3a**) strongly suggests an intramolecular H-bond involving the second hydrogen of the NH_2 group and an oxygen of the radical moiety.

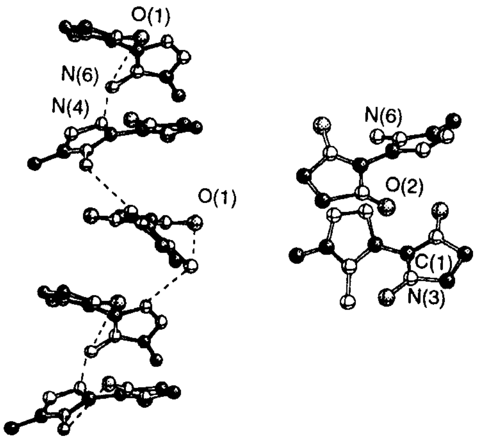


FIGURE 4. View of the molecular assembling of **7** (space group: $P3_1$) (H atoms and Me grouping of the radical are omitted for clarity). Detail of the O(2)-C(1) proximity. Selected distances in Å: N(4)-N(6), 1.30; O(1)-N(6), 1.29; O(2)-C(1), 3.78; O(2)-N(3), 3.88.

It can be noticed that within the chains the separation of the nitroxyl O-atom, O(2), and C(1) of the neighboring radical unit is 3.78 Å. The shortest interchain distances involving the nitroxyl oxygen are found with the nitronyl nitroxide Me groups. Despite the rather close proximity of the spin carriers compound **7** exhibits a paramagnetic behavior down to 10 K and below this temperature weak antiferromagnetic interactions become visible. This behavior is rather puzzling compared to related compounds showing a noticeable enhancement of the magnetic interactions within the supramolecular structure.[10,11]

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