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Concomitant ferro- and antiferromagnetic interactions in an H-bonded molecular ribbon duplex

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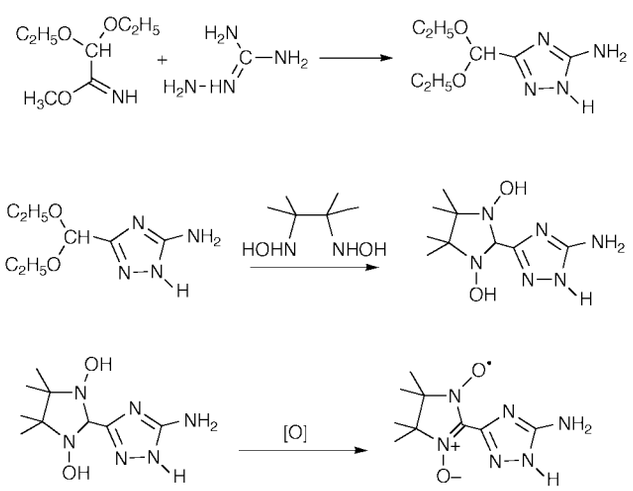
The title architecture is formed by self-association of a nitronyl aminoxyl substituted triazole derivative designed for multi-center H-bonding; moreover close π–π stacking of the resulting network produces duplex structures, as found by X-ray analysis, in which both ferro- and antiferromagnetic interactions take place.

A contemporary aspect of supramolecular chemistry concerns purely organic magnetic materials. Since the discovery of the first organic ferromagnet by Kinoshita *et al.*,[1] an extensive research effort has been devoted to the synthesis of such materials.[2] Very soon, it became obvious that to reach this goal control of the construction of the molecular network and the increase of the strength of the magnetic interactions between the spin carriers is essential. The basic tools of organic supramolecular chemistry provide solutions for a directed material design by means of the H-bonding strategy.[3,4] Interestingly, it has been suggested both from experimental and theoretical results that hydrogen bonds might mediate the intermolecular magnetic interaction as well.[5–17] Our contribution to this field concerns molecules involving NH moieties as H-donor sites.[18] A very promising result has been obtained for a nitronyl aminoxyl substituted triazole, which forms chains of ferromagnetically coupled molecules linked *via* hydrogen bonds.[19] Moreover, the highest interaction parameters, *J*, of H-bonded organic networks reported so far concern spin carriers linked by means of amino-group hydrogen atoms.[10,19]

A way of increasing the intermolecular interactions, from a chemical and magnetic point of view, would be to introduce multiple hydrogen bonding between the molecules. In this report, we describe a nitronyl aminoxyl substituted triazole derivative forming an extremely robust seven-center H-bonded molecular ribbon. Interestingly, in the resulting array of spin-carriers, both ferro and antiferromagnetic interactions are superimposed.

The 3-(4,4,5,5-tetramethyl-3-ylooxy-1-oxidoimidazolin-1-ium-2-yl)-5-aminotriazole, **1**, was synthesized in three steps according to Scheme 1.† The triazole heterocycle was formed by the reaction of 2,2-diethoxymethyl acetimidate with aminoguanidine. The nitronyl aminoxyl unit was then introduced by a classical Ullman condensation of the aldehyde moiety with 2,3-bis(hydroxyamino)-2,3-dimethylbutane. The subsequent oxidation with $NaIO_4$ afforded compound **1**. Small, well-shaped dark blue crystals were grown by slow evaporation of an aqueous solution of **1**.

The X-ray structure analysis‡ of compound **1** revealed that the asymmetric unit consists of two independent molecules which are related by a pseudo symmetry but differ in the bending of the nitronyl aminoxyl ring (Fig. 1). In both molecules, the aminoxyl radical moiety and the triazole are almost coplanar (3° and 8°). In related molecules, a dihedral angle of 30 to 50° is usually found.[18,20,21] The two independent molecules adopt a head-to-tail arrangement and are linked *via* hydrogen bonds in a one-dimensional molecular ribbon. Each



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Scheme 1

molecule is linked *via* H-interactions to two neighbouring molecules involving seven of its atoms. Two interacting molecules share three H-atoms belonging to their NH groups. The Lewis-base atoms involved as acceptor in the H-bonds are the O-atoms of the nitronyl aminoxyl unit and the sp^2-N atoms of the triazole heterocycle. Stabilisation of the network *via* bifurcated H-bonding seems to prevent disorder in the position of the hydrogen atoms of the triazole ring. The hydrogen bond lengths, ranging from 1.93 to 2.54 Å, are all significant (caption to Fig. 1). Within the ribbon, the distances between the O-atoms of the nitronyl aminoxyls are 5.247(3) Å (O(1)···O(2)) and 5.214(3) Å (O(3)···O(4)).

The general packing reveals that two ribbons stack in parallel giving rise to double ribbon bands. Such ribbon dimers are most probably the result of π–π stacking due to the aromatic nature of the triazole and the π-system of the imidazole moiety. The shortest distances between the two ribbons involve H atoms of the CH_3 groups and the O atoms of the radical moieties (C(9)H···O(4): 2.51(3) Å, C(16)H···O(4): 2.65(3) Å). In the duplex, the molecules are not superimposed but staggered. As a consequence each nitronyl aminoxyl unit overlaps two radical units of the second ribbon. The distances between the corresponding NO groups are 3.75(3) and 4.17(3) Å respectively for O(2)···O(3) ($-x$, $1-y$, $1-z$) and O(1)···O(4) ($1-x$, $1-y$, $1-z$). These NO–NO close contacts generate on each side of the duplex a 1D-array of spin carriers. In the crystal, the duplex architectures are arranged perpendicular to each other and run along the *a* axis (Fig. 2). Here too, short distances exist between the NO moieties and hydrogen atoms of the CH_3 groups of the adjacent duplex (O(1)···H(b)C(15), 2.72(3) Å; O(2)···H(b)C(18), 2.87(3) Å).

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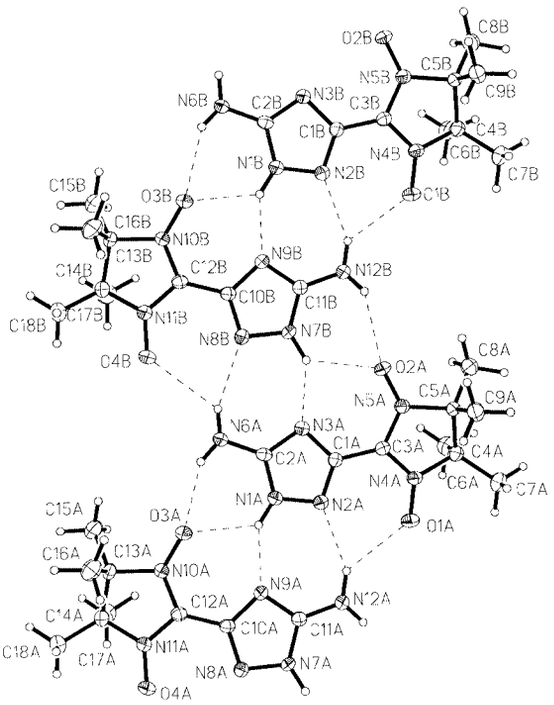

Fig. 1 View of the crystal structure highlighting the intermolecular H-bonds setting up the molecular ribbon. Selected bond lengths (Å) (and angles (°)): N(1)H···O(3), 2.19(3) (126(2)); N(1)H···N(9), 1.93(3) (146(3)); N(6)H···O(3), 2.21(3) (140(3)); N(6)H···O(4), 2.54(3) (128(2)); N(6)H···N(8), 2.15(4) (155(3)); N(7)H···O(2), 2.22(3) (129(3)); N(7)H···N(3), 1.97(3) (143(3)); N(12)H···O(1), 2.49(3) (133(2)); N(12)H···N(2), 2.15(3) (154(3)).

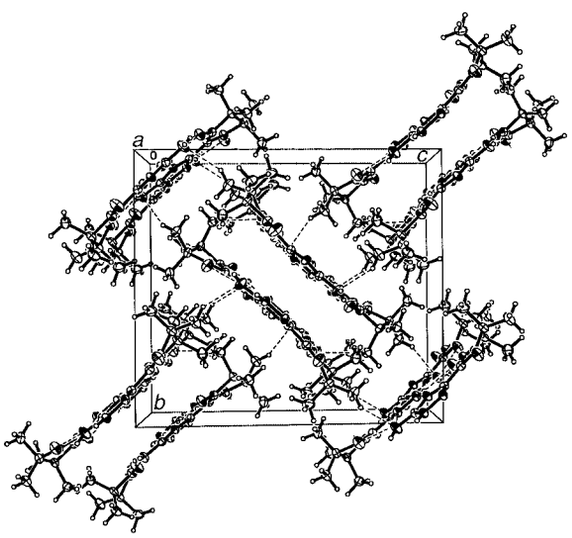

Fig. 2 View of the packing showing the duplex structures running along the *a* axis.

The temperature dependence of the magnetic susceptibility for compound **1** was investigated with a SQUID susceptometer in the temperature range 2–300 K, with an applied field of 1000 Oe. Fig. 3 shows the $\chi_M T$ *versus* T plot where χ_M is the molecular susceptibility and T, the temperature. At room temperature $\chi_M T$ is equal to 0.38 cm^3 K mol^{-1}, the expected value for non-correlated $S = \frac{1}{2}$ spins, and remains constant as the temperature is lowered to 40 K. At lower temperatures the $\chi_M T$ value decreases, which is characteristic of antiferromagnetic interactions. This overall behaviour is confirmed by the maximum at 6 K exhibited by the χ_M *versus* T curve.

In a first approach, the short distances found between the nitronyl aminoxyl groups within a duplex architecture could account for the observed behaviour. Indeed, antiferromagnetic interactions between the spin carriers within a 1D-array would tend to a decrease of the value of $\chi_M T$ as the temperature is

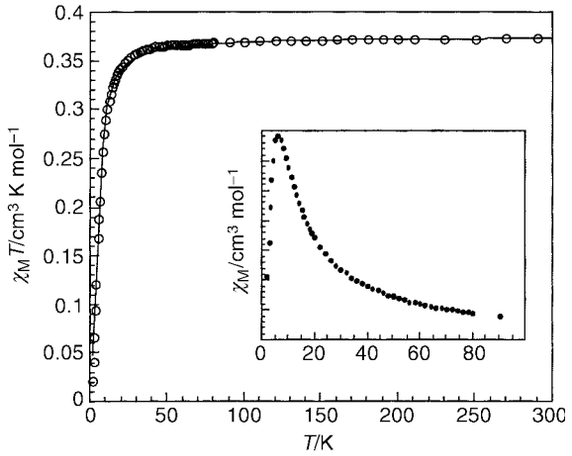

Fig. 3 Experimental (○) and calculated (—) $\chi_M T$ *versus* T curve for compound **1**. The inset is an expanded view of the χ_M *versus* T curve showing the maximum of χ_M at 6 K.

lowered. Considering the non-equivalent NO–NO separations, the magnetic behaviour of compound **1** has been analysed with an alternating chain model ($H = -J\sum_{i=1}^{n/2}[S_{A_{2i}} S_{A_{2i-1}} + \alpha S_{A_{2i}} S_{A_{2i+1}}]$).[22] The experimental $\chi_M T$ *versus* T curve could be perfectly reproduced leading to $J = -5.2$ cm^{-1} and $\alpha = -0.3$ ($\alpha J = +1.7$ cm^{-1}) showing that both ferro- and antiferromagnetic interactions take place concomitantly. Recently, a systematic analysis of the structural characteristics occurring in nitronyl aminoxyl derivatives resulted in the conclusion that the usually admitted magneto–structural correlations might be misleading.[23] Nevertheless, it is unlikely that both the ferro- and antiferromagnetic interactions found in **1** take place directly between the aminoxyl units. Obviously, other pathways exist for the magnetic interactions in the superstructure. The coplanarity of the nitronyl aminoxyl and triazole units should favour spin delocalisation over the whole molecule and consequently, provides several options for the intermolecular magnetic interactions to occur. It is very likely that the H-bonds mediate the magnetic information between the molecules.

The present example illustrates the possibility of close packing organic spin carriers by means of multi-bond interactions. It points also to the difficulty of anticipating the pathways for the intermolecular magnetic interactions and, consequently, of controlling the bulk properties. Further investigations are needed in order to understand the interactions occurring within this rather unusual supramolecular architecture.

Acknowledgements

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Notes and references

† *3-(Diethoxymethyl)-5-amino-1,2,4-triazole*: NaOMe (0.135 g, 2.5 mmol) was added to a solution of diethoxyacetonitrile (3.29 g, 25 mmol) in MeOH (10 mL) and the mixture was stirred for 2 h. A solution of aminoguanidinium nitrate (3.43 g, 25 mmol) in MeOH (50 mL) was neutralised with NaOMe (1.35 g, 25 mmol) and added to the former solution. The reaction mixture was refluxed overnight. The solvent was removed *in vacuo*, the residue extracted with acetone and $NaNO_3$ filtered off. The filtrate was concentrated to give a reddish oil from which the triazole derivative crystallised as a white solid by addition of CH_2Cl_2 (30 mL). The same crystallisation process was repeated on the residue of the CH_2Cl_2 solution (2.4 g, 51%). δ_H (200 MHz, 298 K, $CDCl_3$) = 5.54 (1 H, s, CH), 5.23 (2 H, br s, NH_2), 3.70

(4 H, m, CH_2), 1.24 (6 H, t, CH_3, $J = 7$ Hz). *3-(4,4,5,5-tetramethyl-3-ylooxy-1-oxidoimidazolin-1-ium-2-yl)-5-aminotriazole* **1**: The above triazole derivative (930 mg, 5 mmol) was dissolved in a 1 M sulfuric acid solution, heated at 70 °C during 15 h. After the solution cooled down to room temperature, the monosulfate salt of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (1.35 g, 5.5 mmol) was added and the pH was adjusted to 8 with KOH. The white precipitate was filtered off after 2 h, washed with water and dried *in vacuo* to yield the radical precursor (1.1 g, 90%). δ_H (200 MHz, 298 K, d_6-DMSO) 7.75 (2 H, br s, OH), 5.76 (2 H, br s, NH_2), 4.49 (1 H, s, CH), 1.06 and 1.02 (12 H, 2s, CH_3). The oxidation was performed by adding a solution of $NaIO_4$ (1.5 equivalents) in H_2O to a suspension of the precursor in H_2O at 0 °C to yield a blue solution. After removing the solvent *in vacuo*, the radical was extracted with a CH_2Cl_2–CH_3OH (90 : 10) mixture. Slow evaporation of an aqueous solution yielded **1** as a crystalline blue solid (70%). Found: C, 45.0; H, 6.5; N, 34.9%. Calc. for $C_9H_{15}N_6O_2$: C, 45.2; H, 6.3; N, 35.1%.

‡ X-Ray data collection and refinement: A dark blue needle ($0.40 \times 0.10 \times 0.05$ mm^3) was measured on a SMART CCD diffractometer (Siemens) at 173(2) K. Final cell constants were calculated from the *xyz* centroids of 8087 strong reflections from the actual data collection after integration (SAINTPLUS).[24] The intensity data were corrected for absorption (SADABS).[25] The structure was solved and refined using SHELXS-86 and SHELXL-97:[26] $C_9H_{15}N_6O_2$, formula weight 239.27, monoclinic, $P2_1/c$, $a = 9.6167(4)$ Å, $b = 14.6927(6)$ Å, $c = 16.5683(7)$ Å, $\beta = 94.110(1)°$, $V = 2335.0(2)$ Å^3, $Z = 8$, $\mu = 0.101$ mm^{-1}, 16655 reflections collected, 4097 independent ($R_{int} = 0.075$). All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were refined with individual isotropic displacement parameters. The final full matrix least squares refinement converged to $R_1 = 0.063$, $wR_2 = 0.133$ (F^2, all data), and *GooF* 1.065 for 429 parameters. CCDC reference number 188/242. See http://www.rsc.org/suppdata/p2/b0/b001684p/ for crystallographic files in .cif format.

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