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Strong intramolecular exchange interactions between nitronyl nitroxide radicals bridged by olefinic spacers

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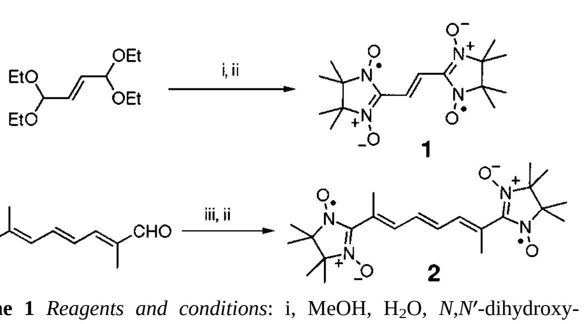
Nitronyl nitroxide radicals bridged by olefinic spacers display strong intramolecular and antiferromagnetic exchange interactions, the magnitude of which depends on the length of the spacer and on steric crowding around the radicaloid subunits.

An essential concern for the development of organic molecular magnetic materials involves minimizing undesired radical–radical interactions whilst promoting efficient exchange coupling along the molecular axis. Because of the inherent difficulty in coupling organic radicals through a bridging framework the use of bis-radicaloid systems has proved less popular than the alternative approach of using transition metals to separate monoradicals.[1] For example, nitronyl nitroxide (NIT) radicals interact only weakly through the π orbitals of an interspersed aromatic spacer because of stereoelectronic inhibition of cross-conjugation[2,3] while directly-linked NIT diradicals exhibit through-space antiferromagnetic coupling.[4] We now report that olefinic spacers promote strong through-bond (TB) interaction between terminal NIT radicals in such a way that complexation to paramagnetic cations might provide novel ferrimagnetic materials.

The deep green diradicals **1**[5] and **2** were synthesised as outlined in Scheme 1.† The all-*trans* conformation of the polyenic skeleton of each diradical was confirmed by X-ray crystallography (Fig. 1).‡ In **1**, the two radicals lie coplanar with the olefinic moiety while the crystal packing shows that the molecules are quasi-isolated with the shortest intermolecular NO···ON distances being > 5 Å. In contrast, the two radical centres in **2** are tilted from coplanarity by 24.9°, due to steric crowding with the neighbouring methyl groups. The crystal packing of **2** reveals relatively short contacts [NO···ON at 3.70 and 3.65 Å, respectively, for OO′ and ON′] between neighbouring molecules within a crystallographic chain [$x + 1, y, z + 1$]. Here, the head-to-tail arrangement of the NO subunits, and their relative orientation, are favourable for intermolecular antiferromagnetic interactions. This is indicated by an α angle of 82° for the ON···O′ and by a β angle of 90° formed between a vector normal to the π^* orbitals of the NIT radicals and the N_2O_2 plane.[6]



Scheme 1 *Reagents and conditions*: i, MeOH, H_2O, *N,N′*-dihydroxy-2,3-diamino-2,3-dimethylbutane sulfate salt, 20 h; ii, $NaIO_4$, H_2O, CH_2Cl_2, 1 h; iii, Benzene, *N,N′*-dihydroxy-2,3-diamino-2,3-dimethylbutane, azeotropic distillation, 0.5 h.

The magnetic properties of these two diradicals were studied with a SQUID susceptometer. At 300 K, the product of molar susceptibility and temperature (χT) for both **1** (0.373 emu K mol^{-1}) and **2** (0.613 emu K mol^{-1}) is lower than that expected for two independent spins [0.75 emu K mol^{-1}]. This indicates the predominance of antiferromagnetic interactions. With decreasing temperature, χT for **1** shows a monotonous decrease to zero while a maximum in the susceptibility curve is seen at 75 K for **2** (Fig. 2). The Curie tail observed at low temperature is due to a weak amount (*ca.* 0.1%) of paramagnetic impurities.

In order to avoid intermolecular interactions, compounds **1** and **2** were dispersed in a polystyrene matrix and studied over the 200–300 K temperature range. The χT *vs.* T and the χ *vs.* T plots, respectively, for **1** and **2** display features similar to those found for microcrystalline samples. For **2**, maximal susceptibility is again found around 75 K [inset in Fig. 2(*b*)]. No relevant intermolecular contacts are seen for **1**, such that a good fit of the experimental data was obtained using the Bleaney–Bowers law for an isolated two-spin 1/2 model[7] where the magnetic exchange coupling constant J corresponds to a Hamiltonian of the form $H = -2JS_1S_2$. Here, a large singlet–triplet splitting of $2J/k_B = -469$ K was found, indicating strong TB antiferromagnetic interaction.

In order to fit the susceptibility data for **2**, the Bleaney–Bowers expression for the magnetic susceptibility of a dimer had to be modified by including a mean-field approximation, estimated by a Weiss temperature θ. This describes the average intermolecular interactions throughout the crystal. With respect to **1**, a much weaker TB antiferromagnetic coupling ($2J/k_B = -90$ K) was found, after correction for a mean field temperature of $\theta = -32$ K.

EPR spectra of **1** and **2** were recorded at room temperature in deoxygenated CH_2Cl_2 solutions (*ca.* 5×10^{-5} mol dm^{-3}) and in polystyrene matrices (*ca.* 3.6% w/w). In solution, the EPR

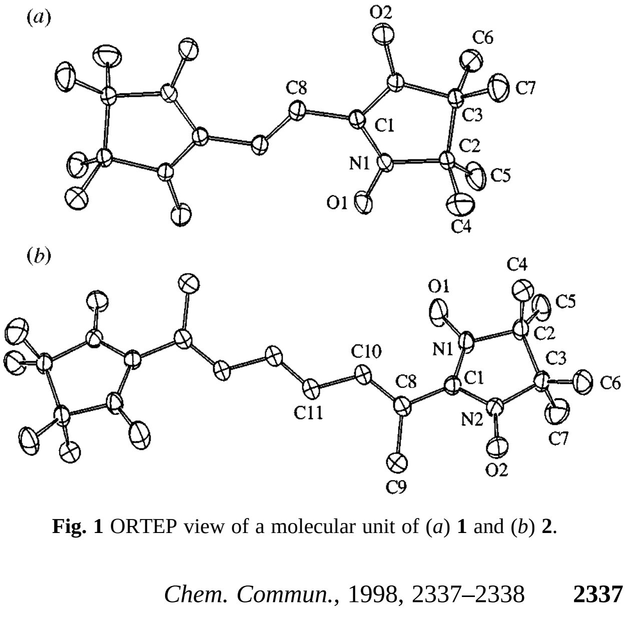


Fig. 1 ORTEP view of a molecular unit of (*a*) **1** and (*b*) **2**.

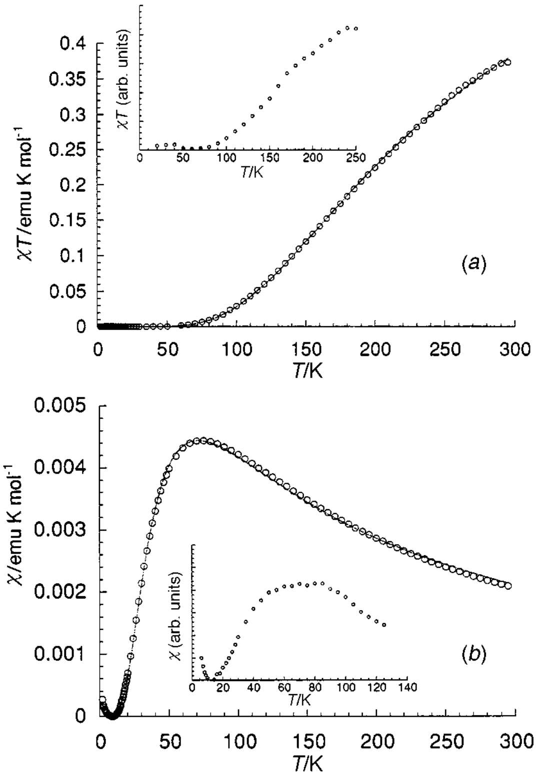


Fig. 2 Temperature dependence of the product of the magnetic susceptibility and temperature ($H = 0.5$ tesla): (*a*) χT *vs.* T for **1** and (*b*) χ *vs.* T for **2**. The solid line represents the best fit to the experimental data. Insets: χT *vs.* T for **1** and χ *vs.* T for **2** dispersed in a polystyrene matrix.

signal obtained from **2** consists of nine well-separated lines centred at $g_{\mathrm{iso}} = 2.0065$, corresponding to an isotropic hyperfine coupling constant $a_{\mathrm{N}} = 3.76$ G. This pattern is consistent with strong exchange interaction between a pair of NIT radicals. The solution EPR spectrum of **1** is distorted and centred at $g_{\mathrm{iso}} = 2.0067$, with the observable peaks being separated by *ca.* 3.75 G and lying within the strong exchange limit. In frozen solution, each compound exhibits fine structure (dipolar) lines and a half-field signal ($g =$ *ca.* 4) due to the so-called forbidden ($\Delta M_{\mathrm{S}} = 2$) transitions (Fig. 3).[8] The zero field splitting (ZFS) parameters are estimated as $D = 168$ G for **1** and $D =$ *ca.* 31 G for **2**, in rough agreement with the values calculated from the crystal structure on the basis of the point dipole approximation ($146 < D < 302$ G for **1**, and $34 < D < 41$ G for **2**).

The experimental data can be well explained by taking into account strong TB antiferromagnetic interaction between the NIT radicals. The geometry and availability of a conductive pathway combine to favour TB interaction rather than through-space exchange. Indeed, the bridging polyenic spacer shows a high propensity for exchange interactions between remote NIT radicals. This is presumably due to efficient orbital overlap between the radicals and the conjugated framework. In this respect, the olefinic spacer is much more effective than aromatic groups. However, a marked stereoelectronic effect is present in **2**, owing to the presence of methyl substituents at the α position relative to the radicals, which curtails exchange interaction.

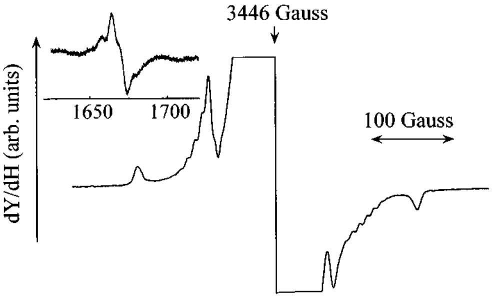


Fig. 3 Fine structured lines observed in the first derivative EPR absorption spectrum (X-band; $\nu = 9.73$ GHz) of **1** dispersed in a polymer matrix and recorded at room temperature. The inset shows the half-field signal.

In summary, in the absence of steric crowding an olefinic bridge favors a planar diradical in the solid state whose conformation is ideal for TB exchange interaction. This is in marked contrast to bis-NIT coupled directly[4] or *via* aryl spacers. Moreover, the magnetic and electronic properties observed in the crystals are conserved in a diluted polymeric matrix. The pronounced TB interaction inherent in these simple systems might provide access to ferrimagnetic scaffolds by judicious coordination to magnetic metal ions.

Notes and references

† On the basis of spectroscopic evidence, including EI-MS and elemental analysis, the structures of the new compounds were unequivocally authenticated. *Selected data* for **1**: *m/z* 338.2 (M); Found: C, 56.60; H, 7.55; N, 16.37%. For **2**: *m/z* 418.3 (M); Found: C, 62.86; H, 8.05; N, 13.15%.

‡ *Crystal data* for **1**: $C_{16}H_{26}N_4O_4$, monoclinic, space group $P12_1/c$, $a = 6.1877(5)$, $b = 11.095(2)$, $c = 13.130(1)$ Å, $\beta = 99.828(7)°$, $Z = 2$, 1199 independent reflections with $I > 3\sigma(I)$, $R = 0.053$, $R_w = 0.073$. For **2**: $C_{22}H_{34}N_4O_4$, monoclinic, space group $P12_1/n$, $a = 7.0087(4)$, $b = 16.270(1)$, $c = 10.3874(5)$ Å, $\beta = 99.244(4)°$, $Z = 2$, 1566 independent reflections with $I > 3\sigma(I)$, $R = 0.048$ and $R_w = 0.076$. Collection: MACH3 Nonius diffractometer, Mo-Kα, $\lambda = 0.71073$ Å, graphite monochromator, $T = 294$ K. CCDC 182/1034.

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