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Antiferromagnetic interactions arising from a close contact between nitroxyl oxygen and β-methyl carbon atoms carrying an α-spin in the solid state

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Antiferromagnetic interactions ($|J|/k_B > 4.0$), which were observed by the magnetization measurement of the powder samples of the racemic nitroxyl radicals *trans*-2,5-bis(4-methylphenyl)-2,5-dimethylpyrrolidine-1-oxy [(±)-**1a**] and *trans*-2,5-bis(4-bromophenyl)-2,5-dimethylpyrrolidine-1-oxy [(±)-**2a**] at low temperatures, were rationalised in terms of the intermolecular spin polarization exchange coupling or the SOMO–SOMO overlapping owing to a short contact between the nitroxyl oxygen atom and the β-carbon atom of a neighbouring molecule by X-ray crystallographic analysis and DFT calculations.

The appearance of ferromagnetic interactions for localised and delocalised nitroxyl (NO) radicals in the solid state is usually due to the favoured intra- and intermolecular spin polarization exchange coupling and an avoidance of intermolecular contact between the SOMOs,[1] whereas that of antiferromagnetic interactions for them is mostly owing to the SOMO–SOMO overlapping by the direct close contact between the NO groups or the π–π stacking.[1,2]

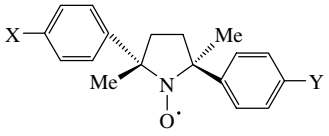
During our studies on the preparation and magnetic properties of all-organic paramagnetic liquid crystals using (±)-*trans*- and (2*S*,5*S*)-2,5-dimethyl-2,5-diphenylpyrrolidine-1-oxy derivatives,[3–6] we noticed that C_2-symmetric (±)-**1a** and (±)-**2a** showed weak but distinct antiferromagnetic interactions at low temperatures by the magnetization measurements at 0.5 T over a temperature range of 2–300 K, while C_1-symmetric racemic *trans*-2-(4-methylphenyl)-2,5-dimethyl-5-phenylpyrrolidine-1-oxy [(±)-**1b**] and *trans*-2-(4-bromophenyl)-2,5-dimethyl-5-phenylpyrrolidine-1-oxy [(±)-**2b**] remained paramagnetic over the same temperature

Table 1 Magnetic properties of (±)-**1** and (±)-**2**.

Compound	C^a/emu K mol^{-1}	θ^b/K	$J\,k_B^{-1}$ ^{c}/K
(±)-**1a**	0.381	–1.95	–4.53
(±)-**1b**	0.371	0.007	—
(±)-**2a**	0.375	–2.48	–4.58
(±)-**2b**	0.383	0.110	—

[a]Curie constant. [b]Weiss temperature. [c]Following equation was used: $\chi_m T = [(Ng^2\mu_B^2/k_B)(A + Bx + Cx^2)/(1 + Dx + Ex^2 + Fx^3)]\alpha$, where x is $|J|/k_BT$ and α denotes the radical purity of the sample.

range (Figure 1, Table 1). To clarify this difference, we performed X-ray crystallographic analysis of their single crystals and found that there exists no close contact between the NO moieties in these cases. Here, we describe that the observed antiferromagnetic interactions are attributed to the intermolecular spin polarization exchange coupling or the SOMO–SOMO overlapping owing to a short contact between the NO oxygen atom and the β-Me carbon atom of the neighbouring molecule, which also brings about the intermolecular SOMO–LUMO interaction.



1a X = Y = Me **2a** X = Y = Br
1b X = Me, Y = H **2b** X = Br, Y = H

The single crystals of (±)-**1a**, (±)-**1b**, (±)-**2a** and (±)-**2b** were obtained by crystallization from CH_2Cl_2/hexane. The crystal structures of (±)-**1a** and (±)-**1b** were isomorphous with those of (±)-**2a** and (±)-**2b**, respectively.[†,7] The crystal structure of (±)-**1a** was characterised by two kinds of CH/π interactions and a CH···O interaction on the *ac* plane resulting in the two-dimensional (2D) sheet structure [Figure 2(*a*)]. More important is the intermolecular interaction that is responsible for the observed antiferromagnetic property. Since there is no close contact between the NO moieties, we searched alternative interactions. Consequently, we found that the NO group approaches a β-Me group of the neighbouring molecule to give a 1D chain along the *c* axis [Figure 2(*a*),(*b*)]. A similar 1D chain structure formed by the interaction between an NO group and a β-Me group of the neighbouring molecule is observed for (±)-**1b** [Figure 2(*c*)], but the O(1)···C(13) distance (3.600 Å) is longer than that (3.294 Å) of (±)-**1a**. A similar tendency is seen in (±)-**2a** [O(1)···C(13) distance of 3.272 Å] and (±)-**2b** (3.517 Å) [Figure 2(*d*),(*e*)]. Furthermore, the N(1)–O(1)–C(13) angles of (±)-**1a** (144.38°) and (±)-**2a** (146.74°) are larger than those of (±)-**1b** (132.68°) and (±)-**2b** (128.54°), while the O(1)–H(17) distances of (±)-**1a** (2.727 Å) and (±)-**2a** (2.739 Å) are longer than those of (±)-**1b** (2.679 Å) and (±)-**2b** (2.623 Å), respectively. Therefore, the intermolecularly closer contact between the O(1) with an α spin and the C(13) with a β spin is most likely responsible for the distinct antiferromagnetic interactions observed for (±)-**1a** and (±)-**2a**.

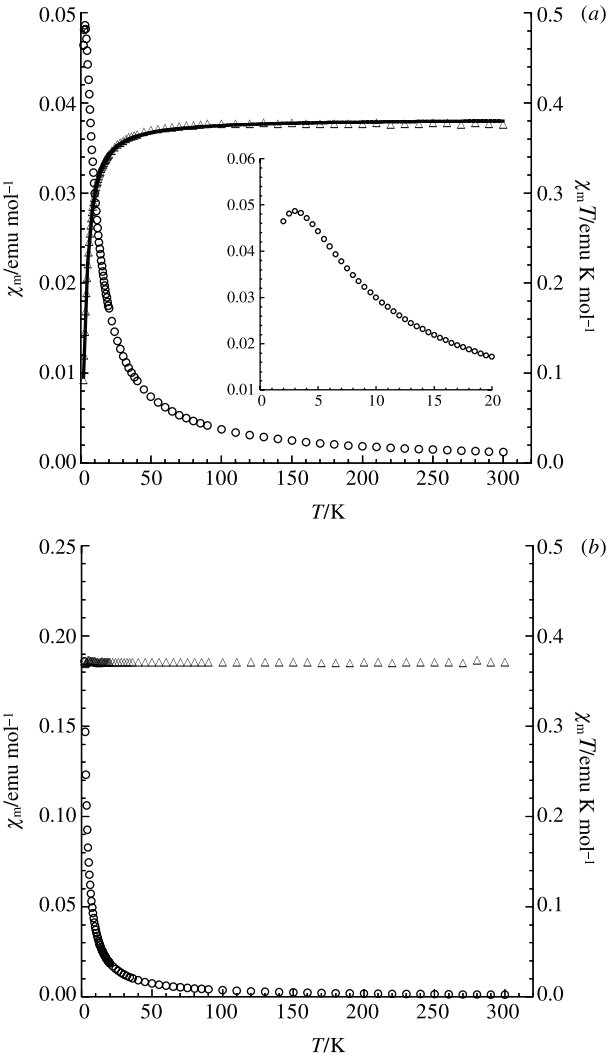


Figure 1 Temperature dependence of χ_m (circle) and $\chi_m T$ (triangle) for (*a*) (±)-**1a** and (*b*) (±)-**1b**. The solid line indicates a theoretical curve. The inset in panel (*a*) shows the magnification of the χ_m *vs.* *T* plots over a temperature range of 2–20 K.

To confirm this assumption, the SOMO, LUMO and spin density distribution were calculated for (±)-**1a** at UB3LYP/6-31G** and UBLYP/6-31G* levels, with and without an admixture of the Hartree–Fock exchange, respectively, using the Spartan'02 software on the coordinates obtained by the X-ray analysis. As expected, at UB3LYP/6-31G** or UBLYP/6-31G* levels, the C(13) shows an appreciable α spin density of +0.016 or +0.017, compared with that of +0.505 or +0.484 for O(1), respectively [Figure 3(*c*)]. Furthermore, Figures 3(*a*) and 3(*b*) indicate the high possibility of both intermolecular SOMO–LUMO and SOMO–SOMO interactions between the O(1) and C(13) atoms.

In accordance with the crystal structures of (±)-**1a** and (±)-**2a**, their magnetic behaviours can be best fitted to a 1D regular Heisenberg-linear model of $S = 1/2$ with J/k_B of –4.53 and –4.58 K, respectively, and 100% radical purity [Table 1 and Figure 1(*a*)]. To gain a theoretical insight into the observed antiferromagnetic interactions, the same DFT calculations for the energy difference between the singlet and triplet states ($\Delta E = E_{singlet} - E_{triplet} = J$ for a dimer model) were performed on the dimeric coordinates of (±)-**1a** and (±)-**2a** extracted from their 1D chain structure, giving J/k_B values of –1.8 and –2.7 K for UB3LYP/6-31G** level, and –3.8 and –5.6 K for UBLYP/6-31G* level,[2(a),8] respectively, which are consistent with the above experimental values. For (±)-**1b** and (±)-**2b**, however, the energy in the singlet state did not converge at the two calculation levels, indicating no intermolecular magnetic interaction.

[†] The crystal structure was solved by the direct methods and refined using the full-matrix least squares method against *F* in the anisotropic–isotropic approximation. All non-hydrogen atoms were refined anisotropically. All calculations were performed using the CrystalStructure crystallographic software package.

Crystallographic data for (±)-**1a**: $C_{20}H_{24}ON$, $M_r = 294.42$, monoclinic, space group $P2_1/c$ (#14), $a = 8.881(6)$, $b = 19.95(1)$, $c = 10.215(4)$ Å, $\beta = 112.93(4)°$, $V = 1666(1)$ Å^3, $T = 173$ K, $Z = 4$, $d_{calc} = 1.173$ g cm^{-3}, $2\theta = 55.0°$, MoKα ($\lambda = 0.71075$ Å), $\mu = 0.71$ cm^{-1}, $R = 0.051$, $R_w = 0.066$ [$I > 3\sigma(I)$] for 7669 observed reflections.

Crystallographic data for (±)-**1b**: $C_{19}H_{22}ON$, $M_r = 280.39$, monoclinic, space group $P2_1/c$ (#14), $a = 8.671(2)$, $b = 11.769(3)$, $c = 16.304(2)$ Å, $\beta = 105.30(2)°$, $V = 1604.8(5)$ Å^3, $T = 296$ K, $Z = 4$, $d_{calc} = 1.160$ g cm^{-3}, $2\theta = 55.0°$, MoKα ($\lambda = 0.71075$Å), $\mu = 0.71$ cm^{-1}, $R = 0.043$, $R_w = 0.061$ [$I > 3\sigma(I)$] for 1543 observed reflections.

Crystallographic data for (±)-**2a**: $C_{18}H_{18}ONBr_2$, $M_r = 424.15$, monoclinic, space group $P2_1/c$ (#14), $a = 9.004(1)$, $b = 19.859(3)$, $c = 10.070(2)$ Å, $\beta = 112.19(1)°$, $V = 1667.3(5)$ Å^3, $T = 173$ K, $Z = 4$, $d_{calc} = 1.690$ g cm^{-3}, $2\theta = 55.0°$, MoKα ($\lambda = 0.71075$ Å), $\mu = 48.77$ cm^{-1}, $R = 0.059$, $R_w = 0.079$ [$I > 3\sigma(I)$] for 2477 observed reflections.

Crystallographic data for (±)-**2b**: $C_{18}H_{19}ONPBr$, $M_r = 345.26$, monoclinic, space group $P2_1/n$ (#14), $a = 8.7277(1)$, $b = 11.8131(2)$, $c = 15.8949(4)$ Å, $\beta = 106.379(1)°$, $V = 1572.28(5)$ Å^3, $T = 173$ K, $Z = 4$, $d_{calc} = 1.458$ g cm^{-3}, $2\theta = 54.9°$, MoKα ($\lambda = 0.71075$ Å), $\mu = 26.21$ cm^{-1}, $R = 0.037$, $R_w = 0.041$ [$I > 3\sigma(I)$] for 2355 observed reflections.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 299036–299039. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

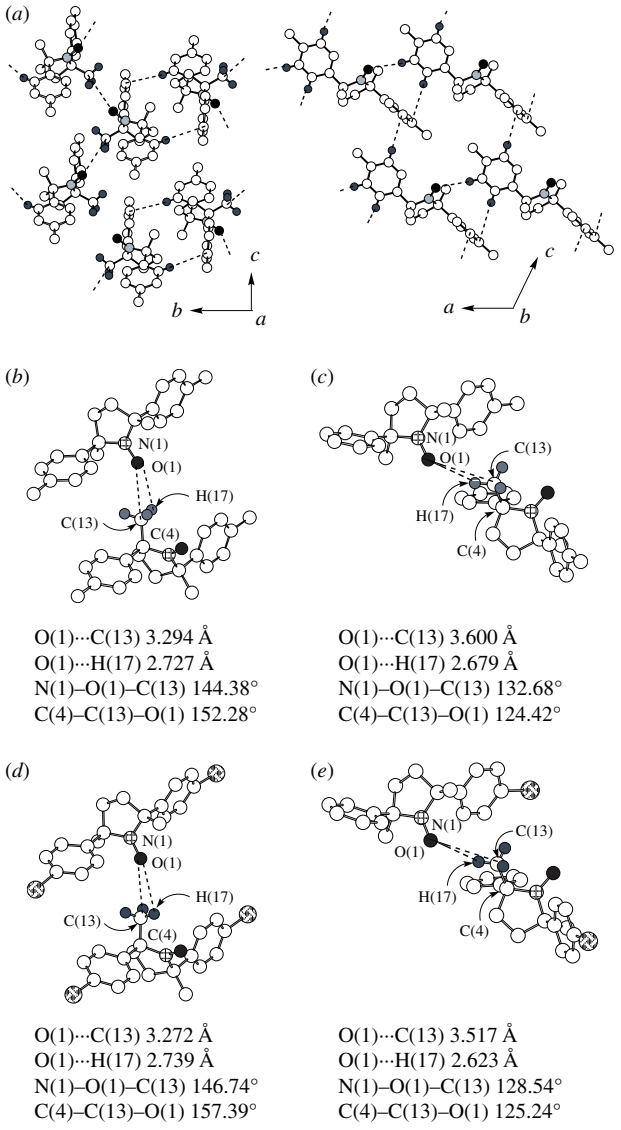


Figure 2 (*a*) Crystal structure of (±)-**1a** viewed down the *a* and *b* axes, and intermolecular interactions between the NO radical group and the β-methyl carbon or hydrogen atom for (*b*) (±)-**1a**, (*c*) (±)-**1b**, (*d*) (±)-**2a** and (*e*) (±)-**2b**.

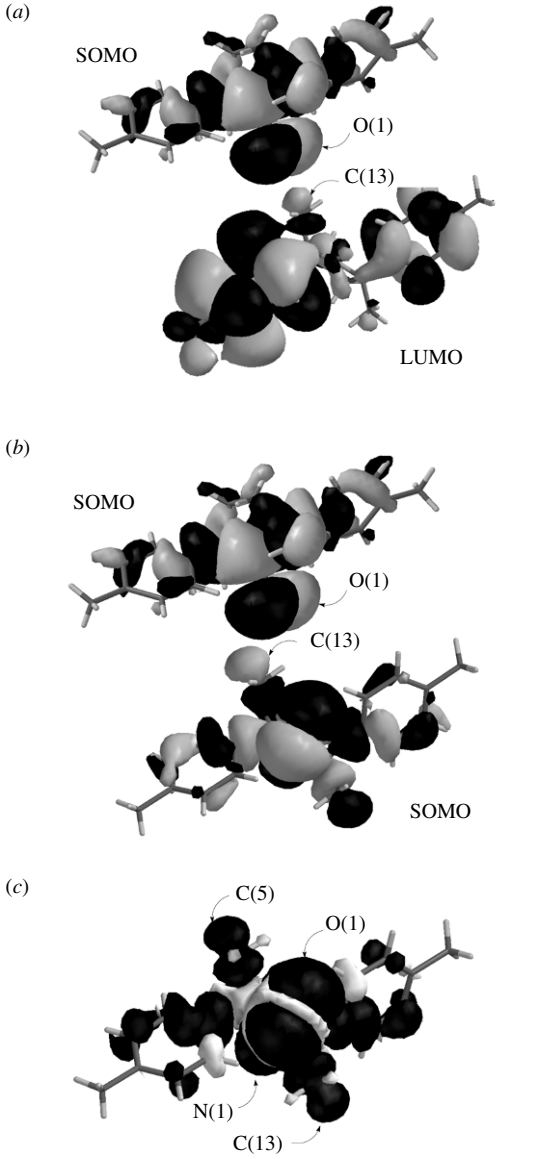


Figure 3 Possible intermolecular (*a*) SOMO–LUMO and (*b*) SOMO–SOMO interactions, and (*c*) the spin density distribution for (±)-**1a**, obtained by the DFT calculations at UBLYP/6-31G* level. In panels (*a*) and (*b*), two molecules are arranged arbitrarily for clarity.

In summary, we found a distinct example that the molecular packing mode in a crystal can allow an intermolecular direct contact between the NO oxygen atom and the neighbouring β-Me carbon atom with an α spin, causing macroscopic antiferromagnetic interactions by a spin polarization mechanism or a SOMO–SOMO overlapping.

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