Ferromagnetism in Organic Radical Crystal of 4-(*p*-Chlorobenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-oxyl

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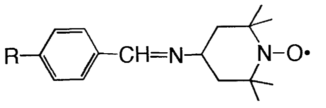
The magnetic measurements of the polycrystalline sample of the title radical exhibited a ferromagnetic phase transition at about 0.4 K. The relationship between the magnetic properties and crystal structures for derivatives possessing H, Br, or Ph in place of Cl is discussed. A possible mechanism of the ferromagnetic couplings was proposed.

The research on organic ferromagnets with well-defined crystal structures has greatly progressed in recent years.[1-6] In the course of our study on the magnetic properties of various derivatives from ferromagnets **1**[3] and **2**,[4] we have recently found a new organic ferromagnet, 4-(*p*-chlorobenzylideneamino)-TEMPO (**3**, TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl). We discuss here the comparison of the magnetisms and crystal structures of **2**, **3** and a *p*-bromo derivative (**4**).



R = H (**1**), Ph (**2**),
Cl (**3**), Br (**4**)

The polycrystalline samples of **3** (mp. 118-120 °C) and **4** (mp. 138-139 °C) were prepared according to the method reported.[3,4] The static magnetic susceptibility down to 1.8 K at 0.5 T was obtained on a SQUID magnetometer. With decreasing temperature their magnetic moments monotonously increased and reached 2.20 μ_B for **3** and 1.93 μ_B for **4** at 1.8 K. The plots of the reciprocal susceptibility against temperature gave positive Weiss temperatures of +0.69 K for **3** and +0.36 K for **4**.

The ac susceptibility, χ_{ac}, was measured at the ac magnetic field of about 3.5 μT (125 Hz)[7] down to about 50 mK by a ^{3}He-^{4}He dilution refrigerator. The result of **3** is plotted as a function of temperature in Figure 1, which shows that a sharp divergence starts at about 0.4 K and reaches a maximum at 0.3 K. We here define the transition temperature, T_c, where χ_{ac} starts to diverge.[4] Compound **4** exhibited no transition in the measurements of ac susceptibility above 40 mK.

In order to elucidate the nature of the magnetic phase transition of **3** at 0.4 K, we measured *M-H* curves below and above this temperature by an integration technique.[8] As the inset of Figure 1 shows, a typical ferromagnetic curve with a small hysteresis was obtained below T_c (50 mK). On the other hand, a linear paramagnetic feature was observed above T_c (740 mK). The coercive force is small (about 5 Oe at 50 mK), indicating that the specimen is a soft ferromagnet, as reported previously on the other organic ferromagnets.[1,2,4-6]

The crystal structures of **3** and **4** at room temperature were determined by X-ray crystallography.[9] Figure 2 shows the arrangements of the N-O sites of **3** and **4**. The nearest neighbor N-O sites of **3** are related by a translation along the *a* axis, and the second nearest sites are arranged along the *c* axis in a zigzag manner. They construct a two-dimensional network parallel to the *ac* plane. The intra-sheet O···O distances are 5.91 and 5.95 Å along the *a* and *c* axes respectively (O···O does not necessarily mean a direct interaction among the N-O sites because there are methyl groups intervening between them. For a detailed mechanism of the ferromagnetic coupling, see below). The nearest O···O distance between the sheets is 10.86 Å. This N-O network is almost the same as that of **2** except for the difference of the inter-sheet distances.[4]

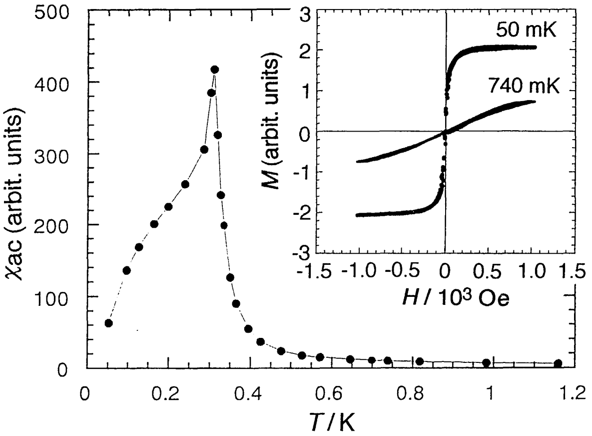


Figure 1. Temperature dependence of the ac magnetic susceptibility of **3** below 1.2 K, showing the ferromagnetic transition at *ca.* 0.4 K (T_C). Inset: the *M-H* curves of **3** measured at 50 mK (below T_C) and at 740 mK (above T_C).

The crystal of **4** similarly possesses a sheet structure of the N-O sites, but one of the intra-sheet O···O distances is 7.54 Å which is longer than those of **1**,[3] **2**,[4] and **3** (about 6 Å). On the other hand, the inter-sheet O···O distance of **4** is shorter than those of **1** - **3**. Several geometrical parameters together with Weiss and transition temperatures are summarized in Table 1.

Although the inter-sheet O···O distance of **3** is shorter than that of **2**, the transition temperatures are not influenced by the distances. Furthermore, compound **4** shows no transition in spite of the short inter-sheet O···O distance. The N-O sites of ferromagnets **1** - **3** locate in two-dimensional zigzag planes with their mutual distances of *ca.* 6 Å. The crystal of **4**, however, does not possess such a structure. The weak ferromagnetic interaction of **4** as indicated by the lack of ferromagnetic transition and the small Weiss temperature is probably due to the relatively long intra-sheet O···O distance. Therefore, the ferromagnetism arises mainly from two-dimensional ordering within the sheet.

Theoretical calculations suggested that direct through-space exchange interaction was negligible for longer distances than 5 Å.[10] We can propose a spin polarization mechanism through

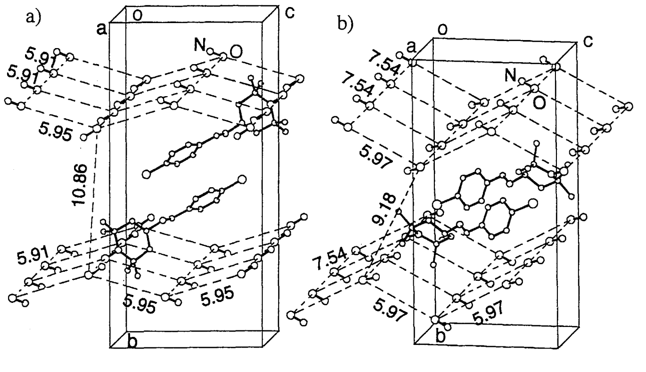


Figure 2. Arrangements of N-O sites of **3** (a) and **4** (b) viewed almost along the *a* axis. Selected O···O distances are shown (in Å) with broken lines. Two molecular structures are shown. Hydrogen atoms are omitted.

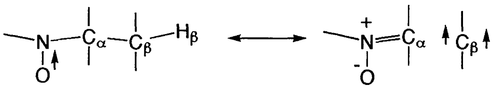
Table 1. Selected magnetic and structural parameters

Compound		**2**[a]	**3**	**4**
Weiss temperature (K)		0.63	0.69	0.36
Transition temperature (K)		0.4	0.4	(<0.04)[b]
Nearest O···O distances (Å)[c] and angles between N-O bonds (degree)	[a][d]	5.96; 0	5.91; 0	7.54; 0
	[c][d]	6.09; 48	5.95; 48	5.97; 33
Nearest O···H distances (Å)[c] and ∠N-O···H (degree)	[a][d]	2.82; 126	2.76; 122	3.88; 115
	[c][d]	2.69; 140	2.60; 140	2.48; 135
Inter-sheet nearest O···O distance (Å)		13.40	10.86	9.18

a) See ref. 4. b) No transition was observed above 0.04 K. c) Intermolecular distances within the sheet. d) [a]: Along the *a* axis. [c]: Along the *c* axis.

intervening aliphatic groups for the ferromagnetic interaction, since the oxygen atoms of the N-O sites were revealed to locate always near β-hydrogen atoms in the adjacent molecules; O···H (methyl or methylene) distances of **1** - **4** are 2.5 - 2.8 Å which are close to the sum of van der Waals radii (2.6 Å).

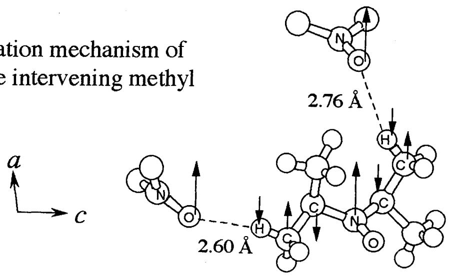
The spin distribution to the methyl and methylene groups was confirmed by UHF/MNDO-PM3 calculation[11] based on the geometry of **3**. The spin densities on the α-C, β-C and β-H atoms through the nearest pathway along the *a* axis are calculated to be -0.020, 0.024, and -0.002 respectively, and those along the *c* axis to be -0.022, 0.054, and -0.001 respectively. These results are consistent with the ENDOR and NMR studies on TEMPO and related compounds which revealed that the signs of the ^{1}H and ^{13}C hyperfine splitting constants alternated throughout the hydrocarbon framework and that negative spin was induced on the β-hydrogen atoms.[12] These facts can be interpreted in terms of hyperconjugation as: [13]



$$-\underset{\underset{\mathrm{O}}{|}}{\mathrm{N}}-\mathrm{C}_\alpha-\mathrm{C}_\beta-\mathrm{H}_\beta \longleftrightarrow -\underset{\underset{\mathrm{O}}{|}}{\overset{+}{\mathrm{N}}}=\mathrm{C}_\alpha \quad \mathrm{C}_\beta \quad \mathrm{H}_\beta$$

The crystal structure analysis indicated that the π*(N-O) orbital and the nearest 1s(H) orbital in the neighboring molecule were not geometrically orthogonal. The negative spin on the β-hydrogen can induce positive spin on the adjacent N-O site through the orbital overlap. Thus, the ferromagnetic coupling between the N-O sites which are *ca.* 6 Å apart each other can be explained as drawn in Scheme 1. However, more experimental instances and theoretical calculations are necessary for valuation of more distant interactions.

Scheme 1.
Spin polarization mechanism of **3** through the intervening methyl groups.



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7 The ac magnetic field in the χ_{ac} measurements in refs. 3 and 4 must be corrected to 4 μT and 5 μT respectively.

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9 Crystallographic data: **3**, monoclinic, $P2_1/c$, a=5.909(3), b=24.475(5), c=11.421(4) Å, β=103.84(3)°, V=1604(1) Å^3, Z=4, D_{calc}=1.217 g cm^{-3}, R=0.085 for 1734 observed reflections. **4**, monoclinic, $P2_1/c$, a=7.541(1), b=20.847(3), c=10.590(1) Å, β=91.56(2)°, V=1664.3(4) Å^3, Z=4, D_{calc}=1.350 g cm^{-3}, R=0.054 for 2041 observed reflections. The diffraction data were obtained on RIGAKU AFC-4 and -5R diffractometers for **3** and **4** respectively using Mo K_α radiation.

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