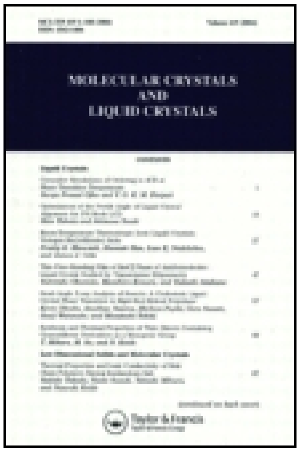

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Ferromagnetism of Organic Radical Crystals of Perdeuterated Tempo Derivatives

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FERROMAGNETISM OF ORGANIC RADICAL CRYSTALS OF PERDEUTERATED TEMPO DERIVATIVES

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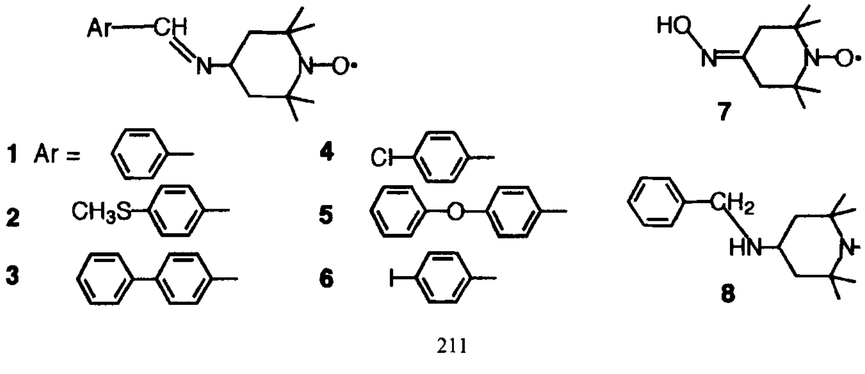
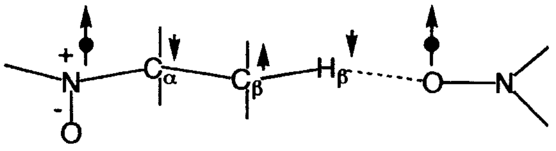
Abstract Perdeuterated compounds, 4-benzylideneamino-TEMPO-d_{23}, 4-(*p*-chlorobenzylideneamino)-TEMPO-d_{22}, and 4-hydroxyimino-TEMPO-d_{17} (TEMPO = 2,2,6,6-tetramethylpiperidin-1-yloxyl) were synthesized and their magnetic properties were studied. The magnetic measurements down to 1.8 K did not show significant difference by the replacement of hydrogens with deuteriums. The temperature of the ferromagnetic phase transition of 4-hydroxyimino-TEMPO did not change by deuterium substitution.

INTRODUCTION

We have recently reported organic ferromagnets possessing a 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) group, **1** - **8** (T_c = 0.2 - 0.4 K).[1,2] A possible mechanism of ferromagnetic coupling of a series of organic radical ferromagnets was presented,[1,3,4] based on their crystal structures and molecular-orbital calculations. These radical crystals have characteristic features that oxygen atoms of N-O radical sites of TEMPO moieties always locate near methyl- and/or methylene-hydrogens at β-positions of N-O in the TEMPO moieties of adjacent molecules. A positive spin on the N-O site induces negative spin densities on the β-hydrogen atoms due to an intramolecular spin-polarization, ON(↑)-C(↓)-C(↑)-H(↓). β-Hydrogen atoms having negative spin densities induce a positive spin on the N-O sites of the adjacent molecules (Scheme 1).



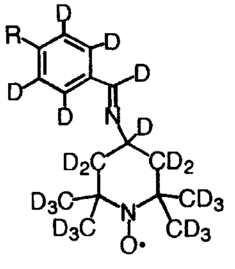
SCHEME 1 Spin alternation mechanism for intermolecular ferromagnetic interaction.



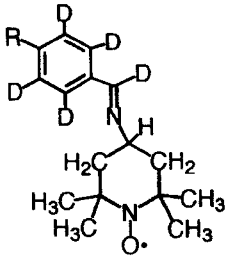
The isotope effects on the magnetism caused by the substitution of hydrogen atoms with deuterium atoms is of great interest from the viewpoint of the proposed spin alternation mechanism. The C-D bonds are generally shorter than the C-H ones by 0.009 Å,[5] so that the spin densities on the β-hydrogen atoms may be perturbed by deuterium substitution. The X-ray crystal structure analysis revealed that the crystal of **2** and **3** possessed structures similar to **1** and **4** respectively.[1] We chose radicals **1**, **4**, and **7** on behalf of the TEMPO-based organic ferromagnets. We have synthesized perdeuterated radicals **1**-d_{23}, **4**-d_{22}, and **7**-d_{17}, and report here their magnetic properties.

EXPERIMENTAL

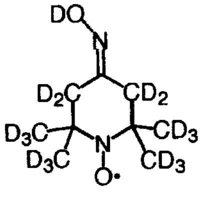
The deuterated spin-label reagents, 4-(H_2N)TEMPO-d_{17} (98.1 atom% D) and 4-oxo-TEMPO-d_{16} (98.6 atom% D) were purchased from CDN Isotopes and ISOTEC, respectively. Materials **1**-d_{23} and **4**-d_{22} were synthesized by condensation of C_6D_5CDO and *p*-ClC_6D_4CDO, respectively, with 4-(H_2N)TEMPO-d_{17} in refluxing EtOH. The perdeuterated aldehydes C_6D_5CDO and *p*-ClC_6D_4CDO were prepared by lithiation of C_6D_5Br (99.5 atom% D, Aldrich) and *p*-ClC_6D_4Br (99 atom% D, CDN isotopes), respectively, with BuLi followed by formylation with $DCON(CD_3)_2$ (99.5 atm% D, Aldrich). Material **7**-d_{17} was synthesized by condensation of 4-oxo-TEMPO-d_{16} and ND_2OD•DCl (98 atom% D, Aldrich) in D_2O (99.75 atom% D, Merck). The deuterium contents of **1**-d_{23}, **4**-d_{22}, and **7**-d_{17} were estimated to be ≥ 95% by means of the positive EI mass spectral analysis (JEOL JMS-600H and Shimadzu GCMS QP-1000 mass spectrometers). Materials **1**-d_6, **4**-d_5, and **7**-d_1 possessing deuterated substituents at 4-position of TEMPO were also synthesized and characterized.



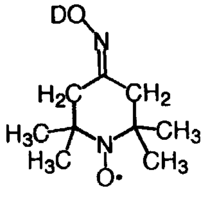
1-d_{23} (R = D)
4-d_{22} (R = Cl)



1-d_6 (R = D)
4-d_5 (R = Cl)



7-d_{17}



7-d_1

The paramagnetic susceptibility was measured on an MPMS-7 SQUID magnetometer (Quantum Design) down to 1.8 K at 0.5 T. The magnetization curves were measured up to 7 T. The diamagnetic contributions were estimated from the Pascal atomic constants. The ac magnetic susceptibility was measured down to about 0.04 K at an ac magnetic field of about 35 mOe (127 Hz). The experimental details on the measurements of ac magnetic susceptibility and magnetization curves in a temperature region of a ^{3}He-^{4}He dilution refrigerator were described elsewhere.[6]

RESULTS AND DISCUSSION

Although the ferromagnetic phase transitions of nondeuterated **1**, **4**, and **7** were previously reported,[1] we re-examined the presence of ferromagnetic interactions in their crystals. The magnetic properties of the corresponding deuterated materials **1**-d_{23}, **4**-d_{22}, and **7**-d_{17} were measured under the same conditions. The results of the SQUID measurements are summarized in Table 1. The Weiss constants with statistics errors were calculated by the linear fit to the Curie-Weiss law by using the data in a temperature range 1.8 - 100 K. Those of partially deuterated materials **1**-d_6, **4**-d_5, and **7**-d_1 are also shown in Table 1. We could not find any significant differences of the Weiss constants between nondeuterated and deuterated compounds, taking account of the accidental errors due to possible crystal defects and deviations of the crystal-size distribution.

We measured the magnetization curves at 1.8 and 2.5 K. They exceeded the theoretical S = 1/2 Brillouin function, and the saturation was more evident at lower temperatures for all cases. Figure 1 shows the magnetization curves of **4** and **4**-d_{22} and Figure 2 shows those of **7** and **7**-d_{17}. The best fit values of spin quantum numbers (S) at 1.8 and 2.5 K are shown in Table 1. These values are averages reflected in statistic distribution of the spin quantum numbers which are given as n•1/2. The apparent S values were close to each other within $\Delta S = \pm 0.1$ among non- and perdeuterated materials. We can conclude here that no significant difference was found between them in the magnetic properties down to 1.8 K.

In order to investigate whether or not deuterium isotope effects on the ferromagnetic transition can be observed, we measured the ac magnetic susceptibilities (χ_{ac}) of **7** and **7**-d_{17} in a temperature region of a ^{3}He-^{4}He dilution refrigerator. Figure 2 shows that a sharp divergence starts at about 0.25 K for both **7** and **7**-d_{17}. The difference of the χ_{ac} intensities is probably due to a demagnetization effect caused by different crystal sizes. We could not find any appreciable change of transition temperatures between **7** and **7**-d_{17}.

TABLE 1 The Weiss constants and apparent spin quantum numbers of nondeuterated **1**, **4**, and **7** and their deuterated derivatives.

compounds	θ / K	S (1.8 K)	S (2.5 K)
1	+0.539 ± 0.009	1.3_6	1.1_5
1-d_{22}	+0.568 ± 0.010	1.4_3	1.2_2
1-d_6	+0.529 ± 0.010		
4	+0.606 ± 0.010	1.4_9	1.2_2
4-d_{22}	+0.617 ± 0.008	1.4_8	1.2_0
4-d_5	+0.627 ± 0.009		
7	+0.431 ± 0.006	1.0_4	0.8_9
7-d_{17}	+0.416 ± 0.006	0.9_8	0.8_7
7-d_1[a)]	+0.442 ± 0.007		

a) See ref. 1.

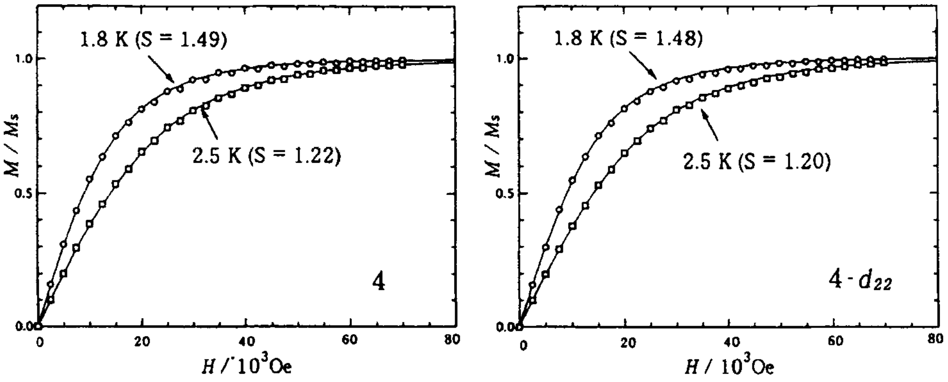


FIGURE 1 Magnetization curves of **4** and **4**-d_{22} measured at 1.8 and 2.5 K.

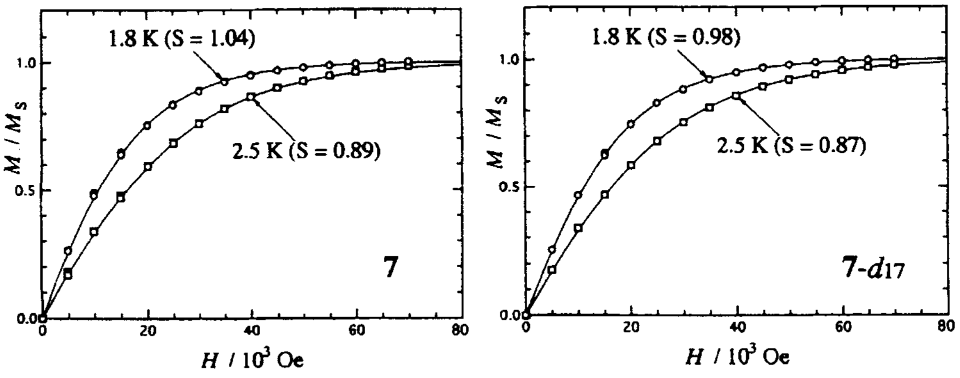


FIGURE 2 Magnetization curves of **7** and **7**-d_{17} measured at 1.8 and 2.5 K.

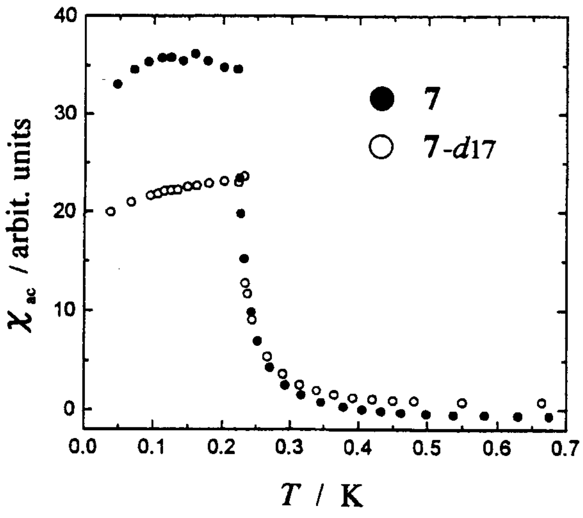
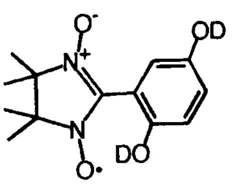


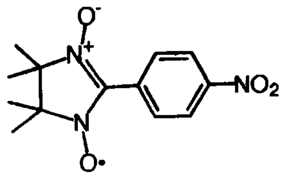
FIGURE 3 Temperature dependence of the ac susceptibilities of **7** and **7**-d_{17}.

We have very recently reported that the Weiss constant of **7**-d_1 (OD) was the same as that of **7**.[1] The magnetic measurements on materials **1**-d_6 and **4**-d_5 indicated that no change of the Weiss temperatures was observed by deuterium substitution. These results are compatible with the proposed exchange mechanism for intermolecular ferromagnetic couplings because the hydroxy and benzylideneamino groups do not participate in the intermolecular ferromagnetic interaction. However, perdeuterated materials **1**-d_{23}, **4**-d_{22}, and **7**-d_{17} have deuteriums at β-positions and they are located on the interactive pathways (Scheme 1).

Very recently, Sugawara et al. reported that the Weiss constant of HQNN-(OD)$_2$ was smaller than that of nondeuterated HQNN.[7] They pointed out that hydroxy groups controlled the orientation of the molecules and also afforded a channel for ferromagnetic couplings. Veciana et al. developed the potential utility of hydroxy groups for molecule-assembled organic ferromagnets.[8] However, generally weak CH···ON hydrogen bonds have less effect on the magnetic interaction and on the crystal-control than strong OH···ON hydrogen bonds have. The finding that almost no deuterium isotope effect was



HQNN-(OD)$_2$



p-NPNN

observed for **1**-d_{23}, **4**-d_{22}, and **7**-d_{17} can be understood because the ferromagnetic couplings are transmitted through weak CH···ON hydrogen bonds.

Takeda et al. reported that the ferromagnetic interaction of *p*-NPNN decreased under pressure.[9] The deuterium substitution studied here may correspond to a pressure effect in view of shortening of intra- and intermolecular atomic distances. It is possible that the ferromagnetic interactions of deuterated materials are smaller than those of nondeuterated materials, although we could not observed any difference of magnetic interactions in TEMPO-based materials, **1**, **4**, and **7**. The crystal-structure analysis of **1**-d_{23}, **4**-d_{22},[10] and **7**-d_{17} is necessary for further discussion.

ACKNOWLEDGEMENT

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