Crystal Structure of Organic Metamagnet: 4-Methacryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (MOTMP)

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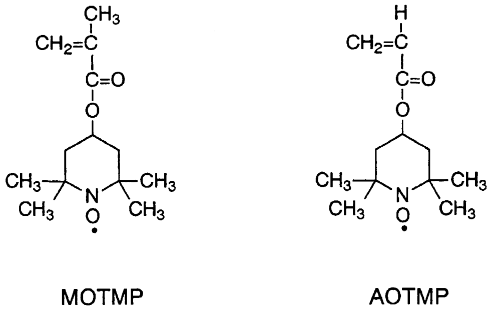
Structures of 4-methacryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (MOTMP) and 4-acryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (AOTMP) which have one-dimensional ferromagnetic coupling and antiferromagnetic interactions, respectively, have been determined by X-ray crystallographic analysis. The crystals of both compounds are monoclinic and have space group $P2_1$ (No. 4) with $Z=2$. The one-dimensional ordering of spins of NO radicals is explained by intermolecular superexchange interactions of NO radicals due to NO radical ···C=C–C=O···NO radical contacts shorter than the van der Waals radii sum (ca. 3.6 Å). The difference in magnetic behavior between MOTMP and AOTMP might be due to the difference in the torsion angle of the C=C–C=O moiety, as in the three-dimensional molecular arrangement in the crystals.

Recently, much attention has been paid to organic ferromagnets.[1,2] More than ten years ago, we studied the magnetic behavior of polymers of 4-methacryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (MOTMP) and 4-acryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (AOTMP), and found that antiferromagnetic interaction took place between the pendant radicals below 20 K.[3,4] In the course of the study on the magnetic behavior of the corresponding monomers, a ferromagnetic ordering was suggested below 4 K in the measurement of magnetic susceptibility in MOTMP. However, we did not pay attention to the ferromagnetic behavior of MOTMP, because the magnetic interaction seemed to be much weaker than that of poly MOTMP.

Recently, the existence of ferromagnetic organic free radicals has been found by several groups.[5,6] Studies on correlations between crystal structures and the magnetism of these compounds are essential for an understanding of the origin of the ferromagnetism of organic radicals. To our knowledge, the ferromagnetism of 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-yloxyl 3-oxide (*p*-NPNN),[7] 1,3,5,7-tetramethyl-2,6-diazaadamantane-2,6-diyl *N,N'*-dioxide,[8] 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-yloxyl 3-oxide,[9] and 4-benzylideneamino-2,2,6,6-tetramethyl-1-piperidinyloxyl[10] have been reported. The relation between the crystal structures and the magnetism is still unsolved. Accordingly, we investigated again the magnetic behavior of MOTMP and AOTMP by measurements of magnetic susceptibility and molar heat capacity (Scheme 1); results indicate that MOTMP form a one-dimensional ferromagnetic chain below 0.45 K and AOTMP form an antiferromagnetic chain.[11—13] These findings show that intermolecular magnetic interaction of these radicals changed from antiferromagnetic to ferromagnetic by substituting hydrogen at α-position with a methyl group. The reason why MOTMP is different in magnetic behavior from AOTMP is not clear.

In this paper, crystal structures of MOTMP and AOTMP are determined by X-ray diffraction for an understanding of the different magnetic behaviors.



Scheme 1.

Experimental

4-Methacryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (MOTMP) and 4-acryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (AOTMP) were prepared by the method previously reported.[14] Pale orange crystals obtained were recrystallized subsequently from hexane. X-Ray diffraction data were recorded on a Rigaku AFC 5R diffractometer with graphite monochromated Mo $K\alpha$ radiation and 12 kW rotating anode generator. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Crystallographic data and other pertinent information are given in Table 1. The crystal structures were solved by direct methods (MITHRIL and DIRDIF)[15] and the positions of the hydrogen atoms were determined from difference syntheses. A block-diagonal least-squares technique, with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms, was employed for the structure refinement. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.[16]

Results and Discussion

The crystals of MOTMP and AOTMP, which showed ferromagnetic and antiferromagnetic ordering of electron spins, respectively,[11,12] are both monoclinic and have $P2_1$ symmetry with similar cell constants (Table 1). The molecular structures are shown in Fig. 1, with atom numbering. Structural parameters of MOTMP and AOTMP are summarized in Tables 2

Table 1. Crystallographic Data for MOTMP and AOTMP

	MOTMP	AOTMP
Empirical formula	$C_{13}H_{22}O_3N$	$C_{12}H_{20}O_3N$
Formula weight	240.32	226.29
Crystal color	Pale orange	Pale orange
Crystal dimensions/mm	0.2×0.1×0.5	0.2×0.2×0.3
Crystal system	Monoclinic	Monoclinic
a/Å	6.071(2)	5.965(2)
b/Å	9.770(2)	11.254(2)
c/Å	11.828(1)	9.677(2)
β/deg	101.82(1)	98.93(2)
V/Å^3	686.7(2)	641.8(3)
Space group	$P2_1$	$P2_1$
Z	2	2
D_{calcd}/g cm^{-3}	1.162	1.171
$F(000)$	262	246
μ(Mo $K\alpha$)/cm^{-1}	0.76	0.78
Radiation	Mo $K\alpha$ (λ=0.71069 Å)	Mo $K\alpha$
Temperature/°C	23±1	23±1
Scan type	ω–2θ	ω–2θ
Scan rate/deg min^{-1}, in ω	8.0	8.0
Scan width/deg	1.21+0.35 tan θ	1.78+0.35 tan θ
$2\theta_{\max}$/deg	60.1	60.1
Measured data	2313	2146
Unique data	2134	1979
Data>$3\sigma(F)$	903	1029
No. variables	254	144
R	0.056	0.072
R_w	0.058	0.094

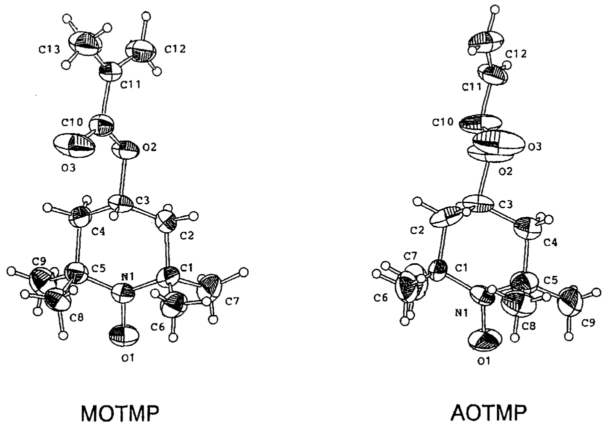


Fig. 1. Molecular structures of MOTMP (a) and AOTMP (b) and their atomic numbering schemes (Thermal ellipsoids are drawn at the 50% probability. The hydrogen atoms are given an arbitrary thermal parameter).

and 3, respectively.[17)] The most remarkable difference in the molecular structure is the relative orientation of the C=C and C=O bonds: The bond axis in methacryloyl group of MOTMP is *s-trans*, while that in acryloyloxyl group of AOTMP is *s-cis*. In the measurement of their molar heat capacities in the range of 0.1 to 300 K, no structural transition was observed, except for the magnetic transition and a hump due to one-dimensional magnetic ordering of electron spins of nitroxyl radicals at 0.16 and 0.4 K for MOTMP[11)] and 0.65 and 1 K for AOTMP,[18)] respectively. We will discuss the origin of magnetic interactions at very low temperature on the basis of the crystal structures at room temperature.

The distance between the nearest nitroxyl radicals is about 6 Å, which is too far for the magnetic ordering of spins to take place by a direct exchange interaction. Accordingly, we have to consider superexchange interaction of the radicals through some intermolecular-interacting groups.

In the crystal of MOTMP, there are five kinds of intermolecular contacts shorter than 3.6 Å, which is the possible distance for interacting through van der Waals forces. The vinyl group of a neighbor molecule and the carbonyl group of another neighbor molecule are located within 3.6 Å from the NO radical, suggesting that a superexchange magnetic interaction of the nitroxyl radicals is possible through a conjugated π-orbital of the C=C and C=O double bonds. The one-dimensional chain is parallel to the b-axis (Fig. 2), in agreement with the study of magnetic susceptibilities of the single crystal.[13)]

In the case of AOTMP, there are three kinds of intermolecular contacts which are shorter than 3.6 Å (Table 3). A superexchange interaction between nitroxyl radicals may be also possible in a crystal of AOTMP, as in MOTMP. The one-dimensional magnetic chain is approximately parallel to the c-axis, as shown in Fig. 3; this is consistent with the fact that the one-dimensional

Table 2. Structural Parameters of MOTMP

Positional and thermal parameters with esds in parentheses

Atom	x/a	y/b	z/c	B_{eq}
O1	−0.2087(7)	0.2500	0.2614(4)	5.5(2)
O2	0.3405(6)	−0.1938(4)	0.2708(3)	3.8(2)
O3	0.6061(7)	−0.1465(5)	0.1751(5)	7.3(3)
N1	−0.0695(7)	0.1497(5)	0.2619(4)	3.5(2)
C1	0.060(1)	0.1071(6)	0.3786(5)	3.7(3)
C2	0.159(1)	−0.0346(6)	0.3682(4)	3.5(2)
C3	0.2719(9)	−0.0501(6)	0.2666(4)	3.2(2)
C4	0.1087(9)	−0.0223(6)	0.1554(5)	3.3(2)
C5	0.0055(9)	0.1223(6)	0.1512(5)	3.5(2)
C6	0.244(1)	0.2137(7)	0.4206(5)	4.9(3)
C7	−0.103(1)	0.0994(8)	0.4607(5)	5.0(3)
C8	0.176(1)	0.2333(7)	0.1338(5)	4.4(3)
C9	−0.201(1)	0.1286(7)	0.0529(5)	4.8(3)
C10	0.5147(9)	−0.2272(6)	0.2248(5)	3.6(2)
C11	0.5774(9)	−0.3728(6)	0.2374(4)	3.4(2)
C12	0.463(1)	−0.4603(7)	0.2923(6)	5.0(3)
C13	0.770(1)	−0.4131(8)	0.1903(7)	6.4(4)

Selected bond lengths and angles

	Length/Å		Angle/deg
O1–N1	1.293(5)	C3–O2–C10	117.9(4)
O2–C3	1.462(7)	O1–N1–C1	115.7(4)
O2–C10	1.326(7)	O1–N1–C5	116.6(4)
O3–C10	1.187(8)	C1–N1–C5	124.0(4)
N1–C1	1.500(7)	N1–C1–C2	108.6(4)
N1–C5	1.497(8)	C1–C2–C3	114.0(5)
C1–C2	1.524(9)	O2–C3–C2	104.1(4)
C1–C6	1.533(9)	O2–C3–C4	109.6(4)
C1–C7	1.521(9)	C2–C3–C4	110.7(4)
C2–C3	1.510(8)	C3–C4–C5	112.6(4)
C3–C4	1.500(7)	N1–C5–C4	109.3(4)
C4–C5	1.542(8)	O2–C10–C3	122.2(5)
C5–C8	1.544(9)	O2–C10–C11	114.1(5)
C5–C9	1.527(7)	O3–C10–C11	123.7(6)
C10–C11	1.471(8)	C10–C11–C12	120.9(6)
C11–C12	1.350(9)	C10–C11–C13	115.8(5)
C11–C13	1.45(1)	C12–C11–C13	123.3(6)

Intermolecular interatomic distance (Å)

O1–C′13	3.393(8)	O3–C″9	3.372(9)
O1–C′12	3.524(8)	O3–N″1	3.533(7)
O3–C″4	3.336(7)		

′ and ″ at symbol of element refer to the following equivalent positions relative to the x,y,z set: $'=(x-1,y+1,z)$, $''=(x-1,y,z)$.

Table 3. Structural Parameters of AOTMP

Positional and thermal parameters with esds in parentheses

Atom	x/a	y/b	z/c	B_{eq}
O1	0.6073(8)	0.2500	0.5981(5)	7.2(2)
O2	0.1967(6)	0.253(1)	1.0606(3)	7.8(3)
O3	−0.1233(9)	0.177(5)	1.0280(5)	9.1(4)
N1	0.5019(7)	0.259(5)	0.7041(4)	4.1(2)
C1	0.409(1)	0.372(1)	0.7421(8)	3.2(3)
C2	0.350(1)	0.364(1)	0.8889(9)	4.4(4)
C3	0.2211(9)	0.265(1)	0.9136(5)	4.1(2)
C4	0.356(2)	0.147(1)	0.889(1)	5.2(5)
C5	0.416(2)	0.140(1)	0.740(1)	5.1(5)
C6	0.207(2)	0.406(1)	0.639(1)	5.9(6)
C7	0.596(2)	0.459(1)	0.737(1)	6.4(6)
C8	0.204(2)	0.106(1)	0.633(1)	5.9(6)
C9	0.600(2)	0.044(1)	0.740(1)	6.5(6)
C10	0.011(1)	0.260(2)	1.1021(6)	5.8(3)
C11	0.004(1)	0.251(2)	1.2497(5)	5.1(3)
C12	−0.182(1)	0.251(1)	1.3030(6)	5.8(3)

Selected bond lengths and angles

	Length/Å		Angle/deg
O1–N1	1.288(5)	C3–O2–C10	122.7(5)
O2–C3	1.458(6)	O1–N1–C1	121.3(8)
O2–C10	1.239(6)	O1–N1–C5	110.1(9)
O3–C10	1.36(1)	C1–N1–C5	124.5(4)
N1–C1	1.46(1)	N1–C1–C2	109.7(7)
N1–C5	1.50(1)	C1–C2–C3	114.9(7)
C1–C2	1.52(1)	O2–C3–C2	112.4(8)
C1–C6	1.49(1)	O2–C3–C4	101.4(8)
C1–C7	1.49(1)	C2–C3–C4	110.0(4)
C2–C3	1.40(1)	C3–C4–C5	112.3(7)
C3–C4	1.59(2)	N1–C5–C4	108.3(8)
C4–C5	1.54(1)	O2–C10–C3	105.4(9)
C5–C8	1.56(1)	O2–C10–C11	118.8(6)
C5–C9	1.54(1)	O3–C10–C11	114.4(8)
C10–C11	1.439(7)	C10–C11–C12	123.7(6)
C11–C12	1.291(7)		

Intermolecular interatomic distance (Å)

O1–C′12	3.295(6)	O3–C″9	3.37(2)
O3–C″4	3.21(1)		

′ and ″ at symbol of element refer to the following equivalent positions relative to the x,y,z set: $'=(x-1,y,z+1)$, $''=(x-1,y,z)$.

chain was observed at ca. 1 K in the measurements of molar heat capacity.[18)]

The one-dimensional magnetic chain in MOTMP is considered to be similar to that in AOTMP except for a little difference in the location of their intermolecular contacts. In the two-dimensional plane which is constructed by one-dimensional magnetic chains, the distance between one-dimensional chains is similar in both compounds. The difference is found in the relative orientation of NO bonds in the two-dimensional neighboring plane. In the crystal of MOTMP, the direction of NO bond is nearly orthogonal to that of neighboring layers parallel to the *ab*-plane, as shown in Fig. 4. In the case of AOTMP, the direction of the NO bond is antiparallel to that of neighboring planes parallel to the *ac*-plane, as shown in Fig. 5. The difference in the relative orientation of the NO bonds between MOTMP and AOTMP might be one origin of the difference in magnetic properties between these organic radicals. However, the distance of NO radical in the neighboring layers is too far to cause the difference in the magnetic behavior between MOTMP and AOTMP. Accordingly, we again paid attention to the one-dimensional magnetic chain. The difference which was found in the intramolecular conformation of conjugated π-orbital of the C=C and C=O bonds of both compounds is considered the origin of superexchange interaction of NO radicals: the conformation is *s-trans* for MOTMP, while it is *s-cis* for AOTMP. The differences in bond distances

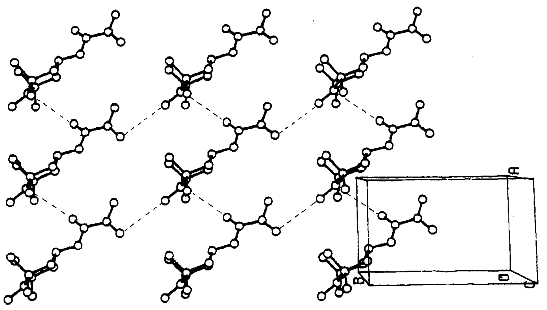


Fig. 2. Two-dimensional periodic array of MOTMP parallel to the *ab*-plane.

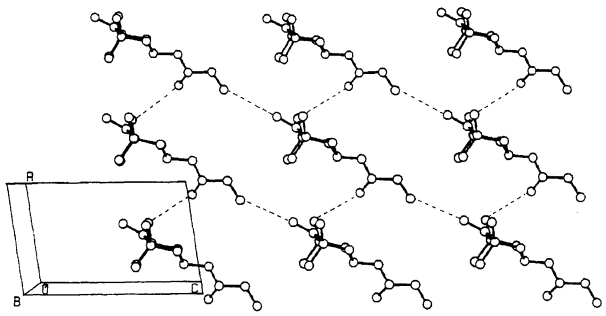


Fig. 3. Two-dimensional periodic array of AOTMP parallel to the *ac*-plane.

of C=C and C=O bonds in MOTMP and AOTMP may influence the strength of spin exchange interaction (J).

In conclusion, the magnetic behaviors of MOTMP and AOTMP might be due to the difference in the conformation of π-conjugated system and in the location of the intermolecular contacts.

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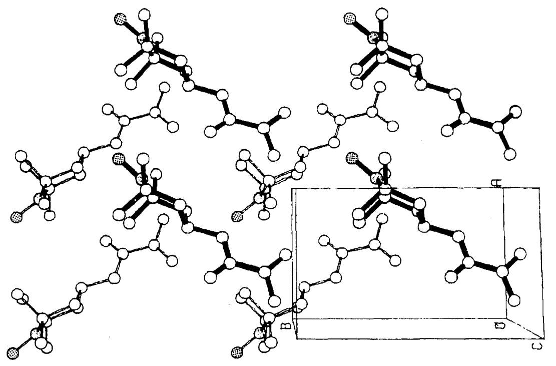

Fig. 4. Crystal structure of MOTMP projected to the *ab*-plane: (●) O atom and (○) N atom of NO-radicals.

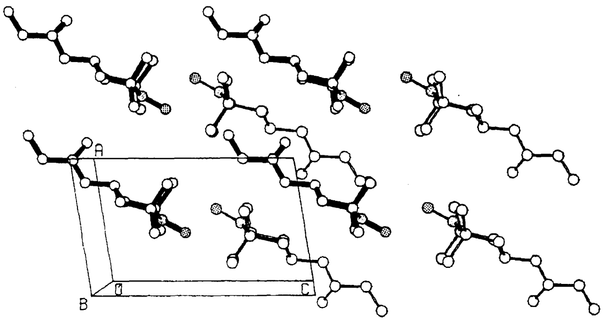

Fig. 5. Crystal structure of AOTMP projected to the *ac*-plane: (●) O atom and (○) N atom of NO-radicals.

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