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Magnetic Properties of 2,2,6,6-Tetramethyl-4-Hydroxypiperidine-1-Oxyl-4-Derivatives

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The magnetic susceptibilities of TANOL and 4-substituted TANOL derivatives were observed in the temperature region from 1.8°K to 300°K. The Weiss constants are determined to be 0°K for methyl and ethyl, -1.5°K for isopropyl and tertbutyl, -1.0°K for phenyl, -2.5°K for cyclohexyl derivatives, and -6.0°K for TANOL. The temperature, T_m , which is proportional to the exchange interaction parameter, J , is roughly estimated to be 6.5°K for TANOL, 1.5°K for cyclohexyl, and 1°K for phenyl derivatives. Besides, the O-H vibration band in infrared absorption spectra was also observed in the radicals where the hydrogen bond is anticipated to be formed along a crystallographic *a*-axis. The effect of the substituents to the exchange interaction was discussed and it is concluded that the results are not contradictory to the assumption that TANOL may have a linear exchange interaction along *c*-axis.

INTRODUCTION

A number of studies on the magnetic properties of organic free radicals have been performed since the interesting discovery of the magnetic properties of Würster's blue perchlorate and attention is given to the magnetism of organic neutral radicals. Recently, it was confirmed from the susceptibility and specific heat measurements that Galvinoxyl radical exhibits a phase transition of first-order nature at 81.5°K.¹⁾ On the other hand, the magnetic properties of porphyrin show an alternating linear chain interaction of Ising type and no phase transition in the temperature range from 1.8°K to 300°K.²⁾ One of the present authors has discussed on the magnetic properties of the organic free radicals in detail and it is concluded that the neutral organic free radicals with one unpaired electron in a molecule have a one-dimensional antiferromagnetic spin array with a Heisenberg type isotropic exchange interaction.³⁾ 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (TANOL) is one of the typical model samples which show a linear antiferromagnetic Heisenberg interaction of an isotropic exchange.^{3,4)} The crystal structure, shown in Fig. 1, was determined to be monoclinic and $a=7.05\text{\AA}$, $b=14.08\text{\AA}$, $c=5.78\text{\AA}$, and $\beta=118^\circ40'$.⁵⁾ The molecules lie along *a*-axis through a hydrogen bond to form a linear chain. However, it is difficult to conclude whether the direction of linear exchange interaction is along the direction of hydrogen bonding or along *c*-axis, where the lattice constant is the shortest. To study the magnetic properties of

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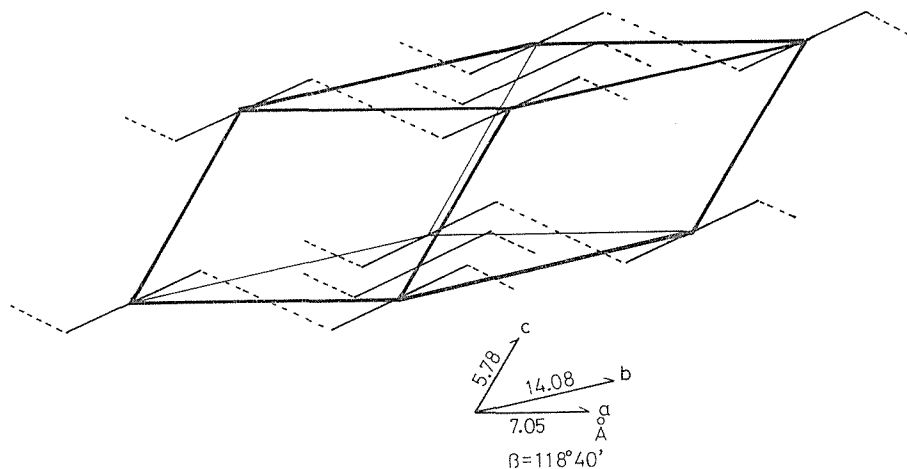
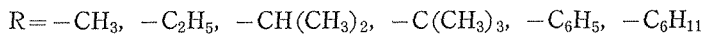
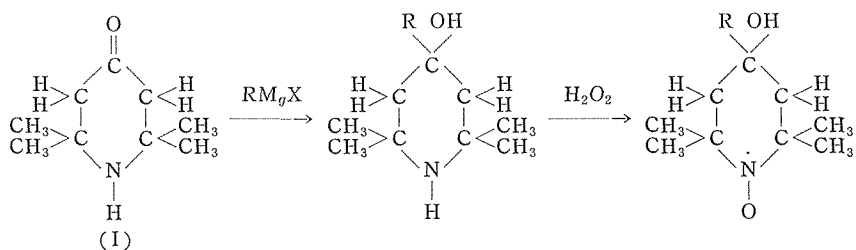


Fig. 1. Crystal structure of TANOL.....indicates hydrogen bond.

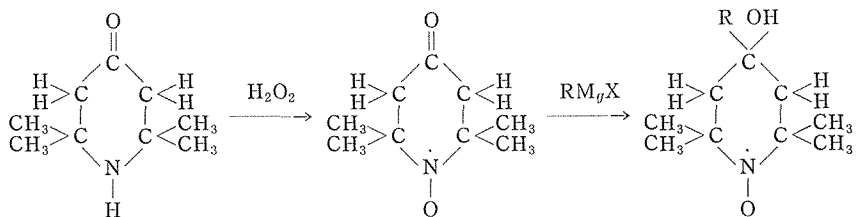
TANOL further and the effect of the substituents to the magnetic interaction, we measured the magnetic susceptibilities of TANOL 4-derivatives at low temperature region. The syntheses, ultraviolet and infrared absorption spectra, and electron spin resonance (ESR) spectra of TANOL derivatives have been already reported in this Bulletin.^{6,7)}

EXPERIMENTAL

TANOL and its derivatives were prepared through the oxidation of the corresponding amine of 4-substituted 2,2,6,6-tetramethyl-4-hydropiperidine following the process of Rozantsev.⁸⁾ Triacetoneamine (I) was reacted with Grignard reagent RM_gX and the product was oxidized by hydrogen peroxide as follows.



The other preparation is the procedure from 2,2,6,6-tetramethyl-4-piperidone-1-oxyl as



Magnetic Properties of TANOL Derivatives

The samples were purified by recrystallization and sublimation. The method of synthesis was described in detail in this Bulletin,⁶⁾ in which the ultraviolet and infrared absorption spectra were also reported. The susceptibility measurements were done, by means of a magnetic torsion balance,⁹⁾ on powder samples of about 100–50 mg in a field of 8.8 KOe. The detail of the experiment was also described elsewhere.³⁾

RESULTS AND DISCUSSION

The results of the susceptibility measurements of TANOL and its derivatives are shown in Fig. 2. The absolute molar susceptibility was corrected for diamagnetism using Pascal's constants.¹⁰⁾ TANOL shows a broad maximum in susceptibility at 6.5°K as is already reported.^{3,4)} On the other hand, the derivatives of TANOL exhibit no broad maximum above the temperature 1.8°K, but obey the Curie-Weiss law, $\chi_M = C / (T - \theta)$, where C and θ are the Curie and Weiss constants respectively. The Weiss constants are determined to be 0°K for methyl and ethyl, -1.5°K for isopropyl and tertbutyl, -1.0°K for phenyl, -2.5°K for cyclohexyl derivatives, and -6.0°K for TANOL. The susceptibility deviates from the Curie-Weiss law at low temperature region and seems to display a broad maximum at lower temperatures. In TANOL derivatives except methyl and ethyl ones the temperature, T_m , which shows broad maximum in susceptibility, is approximately estimated as in Table 1. Comparing the susceptibility results excepting that of TANOL, the temperature, T_m , which is proportional to an exchange interaction parameter, J , becomes large as the bulky substituent is attached to 4-position of TANOL. It can be presumed that the substituent in 4-position may cause a long distance between molecules along c -axis more than along a -axis, so the exchange interaction in TANOL is reduced by the substituent in 4-position of TANOL, for, according to the ESR spectra in solutions, the unpaired electron is almost localized on N-O bond and we can regard the electron spin as a localized

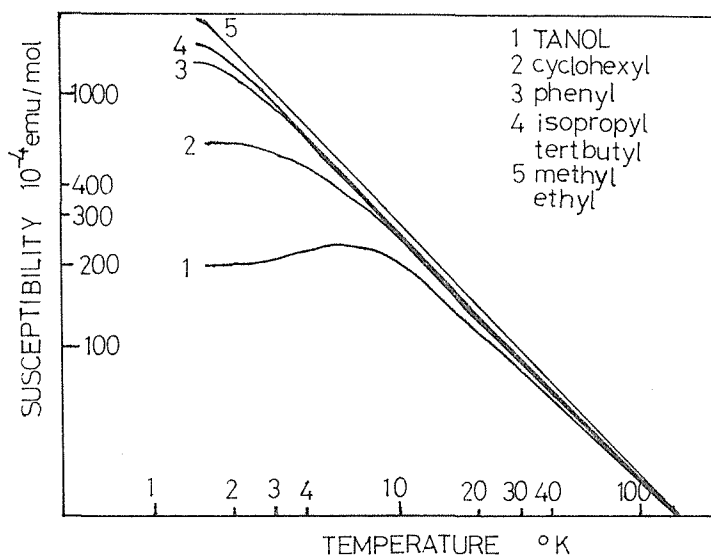


Fig. 2. Molar susceptibilities of TANOL and its derivatives.

Table 1

R	θ	T_m	OH [KBr]
H	-6.0°K	6.5°K	3410 cm ⁻¹
CH ₃	0	—	3500*
C ₂ H ₅	0	—	3445**
CH(CH ₃) ₂	-1.5	<1	3410
C(CH ₃) ₃	-1.5	<1	3470
C ₆ H ₅	-1.0	~1	3430
C ₆ H ₁₁	-2.5	1.5	3380

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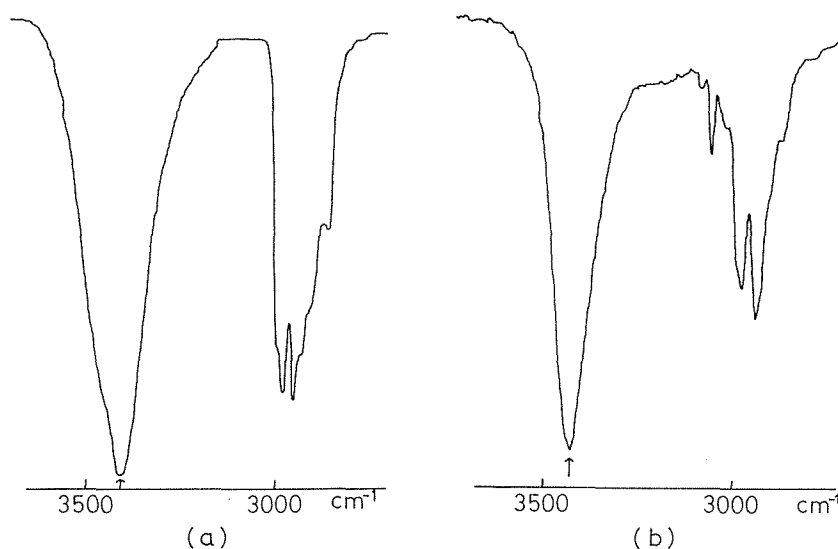


Fig. 3. OH vibration bands of infrared absorption spectra of TANOL (a) and phenyl derivative (b).

moment. However, the effect of a size of the substituents to the exchange interaction is not explainable, although it is very small. It may be due to the orientation of N-O bond in the crystal.

The strength of the hydrogen bond along *a*-axis remains almost same in TANOL and TANOL derivatives. It may be safely said from the broadening of the O-H vibration in infrared absorption spectra, as shown in Fig. 3, that the substituents have little effect to the crystal structure along *a*-axis, which is consistent with the presumption mentioned above. In conclusion our present results are not contradictory to the assumption that the TANOL radical may have a linear exchange interaction along *c*-axis, although the absence of the crystallographic data of TANOL derivatives does not reveal the situation clearly. We are now engaged in the experiment of the crystallographic analysis and the susceptibility measurement at lower temperatures.

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