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Magnetic Properties of Organic Stable Radicals. II. Porphyrexide

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The magnetic properties of triacetonamine-oxyl and its derivatives have been studied by many investigators.[1] In these radicals having penta-, hexa- or haptacyclic structures, the N–O group is masked by four methyl groups. Recently it has been found that one of these radicals, 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (TANOL), exhibits a temperature depedence of its magnetic susceptibility which can be understood by the one-dimensional Heisenberg model.[2–4] The molecular structure of porphyrexide is different from that of the TANOL radical, that is, porphyrexide is pentacyclic with a somewhat planar molecular structure, and it has a π-orbital in its cyclic ring. It has only two methyl groups, so the N–O group is not completely shielded. Therefore, it is presumed to show different magnetic properties from the TANOL radical. Müller and Müller-Rodloff have reported[5] that the paramagnetic susceptibility of porphyrexide obeys the Curie-Weiss law in the temperature range from 300°K to 90°K, with the Weiss constant $\theta=-6\pm5$°K and $\chi_{\text{mol}}=40.1\times10^{-4}$ emu at 90°K. We have measured the magnetic susceptibility of this radical at lower temperatures, the results are shown in Fig. 1.

The sample was obtained commercially and was used with no further purification. Its radical concentration was determined to be 91% by comparing the measured susceptibility with that calculated at 77°K. Magnetic susceptibility measurements were carried out using a magnetic torsion balance developed in our laboratory.[6] Diamagnetic correction was made employing the experimental value reported by Müller and Müller-Rodloff:[5] $\chi_{\text{dia}}=0.85\times10^{-4}$ emu/mol. The magnetic susceptibility of this radical follows the Curie-Weiss law (Weiss constant $\theta=-8$°K) in the temperature range from 300°K to 20K°, as Müller and Müller-Rodoff. At lower temperatures, however, it deviates from this law and reaches a broad maximum at 7.2°K, where $\chi_{\text{max}}=207.2\times10^{-4}$ emu/mol, and they gradually decrease below 7.2°K. In order to make clear the magnetism of the radical, it would be appropriate to compare this result with several typical theoretical models: the pair model, the linear Ising model, and the one-dimensional Heisenberg model (Fig. 1). χ_p is given as follows:

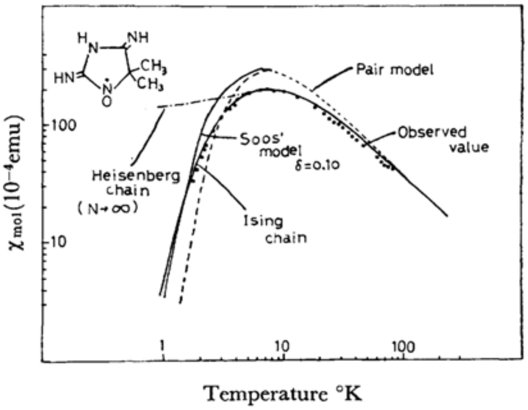

Fig. 1. Magnetic susceptibility of porpflyrexide.
Solid Curve : theoretcical susceptibility of the linear Ising model with $J/k=-7.2$°K and Soos's model with $\delta=0.10$
Dashed Curve: that of pair model with $\Delta/k=11.6$°K
Chain Curve : that of one–dimensional Heisenberg model $J/k=5.76$°K
● : observed values

$$\text{pair model: } \chi_p=\frac{Ng^2\beta^2S(S+1)}{kT}\cdot\frac{1}{3+e^{\Delta/kT}}$$

$$\text{linear Ising model: } \chi_p=\frac{Ng^2\beta^2}{4kT}e^{J/kT}$$

where Δ is the energy splitting between the ground singlet and the excited triplet states, where J is the spin-spin exchange interaction energy, and where the other letters have the usual meanings. The parameters, Δ/k and J/k, are determined to be 11.6°K and −7.2°K respectively from the temperature of the susceptibility maximum, Tm.

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The theoretical calculation of the one-dimensional Heisenberg model has been performed by Bonner and Fisher for the case of $\gamma=1$ and $N \rightarrow \infty$.[2,7] In our case $J/k=5.76$°K is obtained by fitting Tm to the theoretical value. It can be seen from Fig. 1 that the observed value fits the linear Ising model better than the others. Thus, porphyrexide has different magnetic properties from TANOL, which has a character like that of the one-dimensional Heisenberg model, as has already been reported.[2-4] The difference in the magnetic behavior of these two radicals may be attributed to the difference in their molecular frameworks. The TANOL radical has a non-planar molecular framework and forms intermolecular hydrogen bonds parallel to the a-axis,[8] and it makes one-dimensional antiferromagnetic chains by means of isotropic exchange interaction. On the other hand, porphyrexide has a somewhat planar molecular structure, like BDPA,[9] and it makes one-dimensional antiferromagnetic chains of anisotropic exchange interaction through π-orbital, probably arranged in such a way that one molecular plane is stacked upon another. Another fit is obtained when the alternating linear Heisenberg antiferromagnet model proposed by Soos[10] is used with the alternating parameter, δ, being 0.1. We can not conclude which is the better model, the Ising or Soos's model, in this case. We are now, however, performing a study of the single crystals of this radical by using the magnetic torsion balance, an ESR spectrometer and an X-ray diffractometer in order to reach definite conclusions.

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