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Magnetic Properties of Organic Stable Radicals. III. Diphenyl Nitric Oxide

Osamu TAKIZAWA,* Jun YAMAUCHI,** Hiroaki OHYA-NISHIGUCHI,* and Yasuo DEGUCHI*

*Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto

**The Institute for Chemical Research, Kyoto University, Uji, Kyoto

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We have already reported on the magnetic property of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (TANOL), which can be explained fairly well by theoretical calculations based on the one-dimensional Heisenberg model.[1] On the other hand, from the findings on the temperature dependence of the susceptibility of the porphyrexide radical, it has been proposed that this radical forms an Ising-type antiferromagnetic chain.[2] The difference between the magnetic properties of TANOL and porphyrexide is considered to be due to their different molecular structures; the former has a nonplanar molecular framework and a localized spin distribution, while the latter is somewhat planar and has a small delocalized spin distribution over the whole molecular frame. In order to examine the effect of the delocalization of spin on the magnetic exchange interaction, another organic stable radical with a more delocalized spin in the π-orbital has been chosen as the next sample. In the present paper we shall report the results of our susceptibility measurements of the diphenyl nitric oxide (DPNO) radical. In this radical the unpaired spin is delocalized in the conjugated π-electron system spreading over the whole molecule,[3] and the molecule is presumed to have a planar framework similar to those of benzophenone and di-*p*-anisyl-nitric-oxide.[4] Cambi has reported the magnetic susceptibility data of DPNO at room temperature only.[5] In the present paper, the magnetic measurements were extended to the temperature range between 1.5°K and 293°K.

A DPNO radical prepared by the method of Wieland and Roth[6] was recrystallized from ether, the melting point being 59.5—60.5°C. Its radical concentration was determined to be 96% by comparing it with the calculated value, using the Curie-Weiss law and the Weiss constant of $\theta = -3.5$°K at 77°K. The measurements were carried out by means of a magnetic torsion balance[7] in the magnetic field about 8 kOe. The diamagnetic correction was made employing -1.21×10^{-4} emu/mol. The results, shown in Fig. 1, obeyed the Curie-Weiss law in the temperature range above 30°K. After deviating from the Curie-Weiss law when the temperature was lowered, the magnetic susceptibility reached a broad maximum at 6.2°K. Thereafter, it decreased successively toward a finite value of 140×10^{-4} emu/mol. The broad maximum in the susceptibility can be attributed to the short-range magnetic ordering, for no intrinsic anisotropy of magnetic susceptibility could be found from the measurement of a single crystal of DPNO. In order to clarify the magnetic property of DPNO, it was compared with the theoretical results of the one-dimensional Heisenberg model (T_m=6.2°K) calculated by Bonner and Fisher,[8] which are also shown in Fig. 1. The theoretical results agree quite well with the present experimental results in the available temperature region.

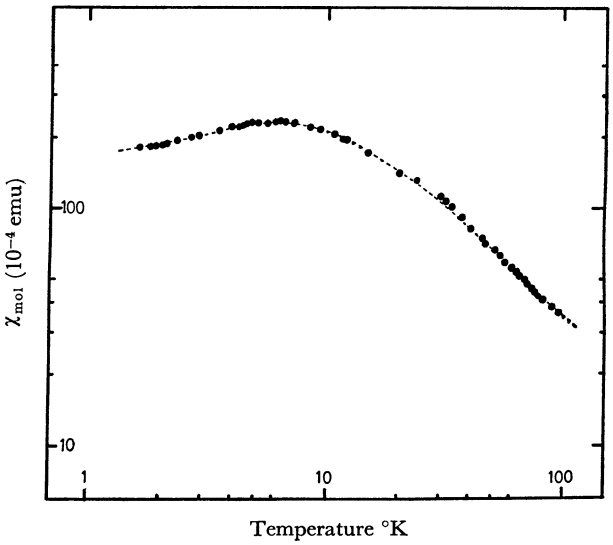

Fig. 1. Magnetic susceptibility of DPNO radical.
●: observed values, ------: calculated values of one-dimensional Heisenberg model

Recently, the magnetic properties of di-*p*-anisyl nitric oxide (DANO) have been shown to be consistent with the nearest-neighbor antiferromagnetic Heisenberg model of a quadratic layer lattice proposed by Duffy, Strandburg and Deck.[9] However, one of the present authors has discussed in detail the magnetic properties of some organic free radicals.[10] In his paper, it was 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 interaction, and was suggested that the DANO radical is a one-dimensional Heisenberg-type antiferromagnet. The present results on the DPNO radical are also consistent with the aforementioned conclusion regarding the neutral organic free radicals.

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