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The Magnetic Susceptibility of the 1,3-Bis-(4-methylphenyl)-5-phenyl-verdazyl Radical from 1.55 to 300°K

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Recently, the magnetic properties of several species of stable crystalline neutral radicals, including hydrazyl,[1] nitroxide,[2] and phenoxyl[3] radicals, were reported. On the other hand, the verdazyls, a series of very stable neutral radicals containing four nitrogen nuclei, were previously studied by Kuhn, Neugebauer, and Trischmann.[4,5] However, the magnetic properties of the verdazyls have never been studied except for the preliminary susceptibility measurements, which showed the presence of one unpaired electron per molecule. We wish to describe here the magnetic susceptibility of a verdazyl radical in the temperature range from 1.55 to 300°K; this radical has the structure shown in Fig. 1.

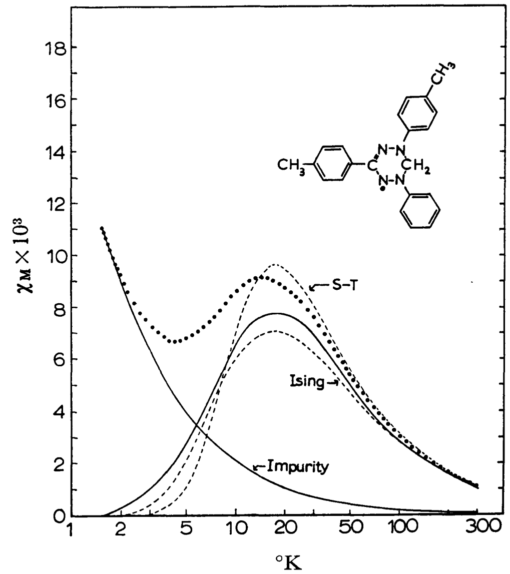

Fig. 1. Paramagnetic molar susceptibility of 1,3-Bis(4-methylphenyl)-5-phenyl-verdazyl radical. The "full circle" curve is the experimental curve. The "impurity" curve is an extrapolation of the low-temperature Curie-Weiss data. The solid line curve is the difference between experimental and impurity curves. The dashed curves are theoretical fits as explained in the text.

Experimental

1,3-Bis-(4-methylphenyl)-5-phenyl-verdazyl was prepared from the corresponding formazan by ring formation with formaldehyde, following the same process as that of Kuhn *et al.* After recrystallizing two times from methanol, a deep green crystalline compound, mp 116.0—116.3°C, was obtained.

The susceptibility measurements were carried out in the continuous temperature range between 1.55°K and 300°K, using a magnetic torsion balance on powder samples of about 100 mg in a heterogeneous magnetic field up to about 10 koe.[6]

Results and Discussion

The measured molar paramagnetic susceptibility, χ_p, shown in Fig. 1 as a function of the temperature, has been corrected for the diamagnetic contribution of $\chi_{dia} = -0.200 \times 10^{-3}$ emu/mol calculated by Pascal's method. Between 30°K and room temperature χ_p follows the Curie-Weiss law, with a Weiss constant of $\theta = -14.6 \pm 0.4$°K and a spin concentration of 93.9%. When the temperature is lowered from 30°K, the $\chi_p - T$ curve gradually deviates from the Curie-Weiss law and reaches a broad maximum at 14.2±0.5°K. After passing through the maximum, χ_p falls off slowly till 4°K. However, below 4°K the susceptibility increases again as the temperature is lowered. In the region from 1.55°—1.8°K, the Curie-Weiss law was observed, corresponding to a spin concentration of 5.8% and a Weiss constant of −0.4±0.1°K. When this low-temperature paramagnetic impurity curve

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is extrapolated to higher temperatures and substracted from the experimental curve observed there, the corrected curve shown in Fig. 1 is obtained. The experimental curve has a general appearance very similar to that found in many organic free radical and radical salts; thus, the unpaired electrons on the verdazyl molecules also appear to be paired up by an negative exchange interaction.

In order to account for the experimental data on the verdazyl radical, we shall examine two typical models, that is, the singlet-triplet model[7] and the linear Ising model.[8]

In the singlet-triplet model (Case I), the susceptibility is given by:

$$\chi_p = \frac{N_0 g^2 \beta^2}{kT} \cdot \frac{1}{3+e^{\delta/kT}}$$

where δ is the singlet-triplet energy separation and equals to $2|J|$, and where N_0 is Avogadro's number. The other subscripts have the usual meanings.

In the linear Ising model (Case II), the susceptibility is expressed by:

$$\chi_p = \frac{N_0 g^2 \beta^2}{4kT} e^{J/kT}$$

The values of the exchange energy, J, in both models are determined from the temperature, $T_{\max}$, at which the corrected susceptibility shows a maximum, by using the relations $J=-0.81kT_{\max}$ for case I and $J=-kT_{\max}$ for case II. Taking this temperature as 17.0°K, the values of J are estimated to be 9.5 cm^{-1} (Case I) and 11.8 cm^{-1} (Case II) respectively. The theoretical curves require multiplication by a constant p if they are to be compared with the experimental data. Thus, with $p=0.881$, the two theoretical curves can be fitted to the experimental data.

Figure 1 indicates that the linear Ising model gives rather a better fit with the observed susceptibility of the verdazyl. A good agreement may be obtained if Soos's alternating parameter is taken into account.[9]

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