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Anomalous Magnetic Properties of Crystalline Galvinoxyl Radical. IV. Effect of the Deuterium Substituent

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The stable organic galvinoxyl radical is known to undergo a first-order phase transition induced magnetically at 82 K, accompanied by pairing of magnetic spins, as is recognized from the results of magnetic susceptibility[1,2] and heat capacity[3] measurements. The Galvinoxyl radical is paramagnetic above the magnetic transition point, 82 K, where the susceptibility drops very sharply on cooling, and shows a weak paramagnetism below this point, with positive Weiss constants in both regions above and below the transition temperature. The entropy change at the transition point, which corresponds to Rln 9.45, cannot be explained by taking only the magnetic contribution. On the other hand, the phenol derivative, the corresponding diamagnetic substance, has no thermal anomaly in the temperature region 12—300 K.

It has been reported[4-7] that deuterium substitution causes two effects on the ESR spectrum of native undeuterated radicals. First, the proton splittings at the undeuterated positions are altered, and second, the ratio of the deuteron to the proton splitting differs from the ratio $(a^D/a^H)=0.1535$ calculated on the basis of the magnetic moments and spins of the two nuclei. Both isotope effects should result from the difference in mass of the proton and deuteron, and this difference can be manifested only through the molecular vibrations. The above results were successfully analyzed[6,8] in terms of a model for the effect of the difference in the CH and CD out-of-plane bending motion. This vibration can affect the sigma-pi coupling, the pi-electron spin-density distribution, or both.

Galvinoxyl D-Galvinoxyl

Fig. 1. Structures of galvinoxyl and D-galvinoxyl radicals.

We have synthesized the deuterium derivative (D-galvinoxyl, see Fig. 1) of the galvinoxyl radical, and studied its magnetic properties in order to see the effect of deuterium substitution on the anomalous magnetic property of galvinoxyl by ESR and magnetic susceptibility measurements.

Experimental

Materials. D-Galvinoxyl was synthesized following the method of Kharasch and Joshi[9] or Coppinger.[10] After condensation of 2,6-di-*t*-butylphenol with dideuteroformaldehyde (Merck, deuterierungsgrad 99%), the deuterized bisphenol, 3,3′,5,5′-tetra-*t*-butyl-4,4′-dihydroxydiphenyldideuteromethane, was synthesized, and it was recrystallized from ethanol. Mp 157.0—157.7 °C. The ultraviolet absorption spectrum in ethanol with $\lambda_{\max}=278\ \mathrm{m}\mu$ (ε 3990) and proton NMR spectrum with $\tau_{C(CH_3)_3}=1.42$ ppm, $\tau_{OH}=4.87$ ppm, and $\tau_{m\text{-}H}=6.85$ ppm are in good agreement with those of the corresponding bisphenol, except for the disappearance of the proton NMR absorption due to center methylene

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protons of the undeuterized bisphenol ($\tau_{CH_2}=3.75$ ppm). The D-galvinoxyl radical was prepared by the oxidation of the bisphenol with lead peroxide in ether under nitrogen atmosphere. Mp 154—159 °C. The absorption spectrum in ethanol with $\lambda_{max}=424$ mμ (ε 175000) of the D-galvinoxyl is also in good agreement with that of the galvinoxyl.

Apparatus. Magnetic susceptibility measurements were carried out in the continuous temperature range 59—290 K, using a Shimadzu MB-2 type magnetic torsion balance field up to 10 kOe. The ESR measurements were carried out using a JES-ME-3X spectrometer equipped with Takeda-Riken microwave frequency counter. ESR hyperfine splittings and g values were measured relative to those of $(KSO_3)_2NO$ ($a^N=13.05\pm0.03$ G; $g=2.0054$[11]).

Results and Discussion

The ESR spectra of galvinoxyl and D-galvinoxyl in THF at room temperature are shown in Figs. 2-(a) and -(b), respectively. The observed hyperfine splitting constants and g values of galvinoxyl[12] and D-galvinoxyl are listed in Table 1. The g value of D-galvinoxyl, $2.0052_1\pm0.0000_2$, is in agreement with that of Galvinoxyl, $2.0051_8\pm0.0000_2$. The hyperfine splitting ($a_m{}^H$) due to the *meta* ring hydrogen atoms of D-galvinoxyl is also the same as that of galvinoxyl, within experimental error. In contrast, the ratio 0.149 ± 0.002 of the deuteron to the proton splittings at center methylene position differs from the theoretical ratio $(a^D/a^H)=0.1535$ expected on the basis of the magnetic moments and spins of the two nuclei. The result can be explained as due to the difference in the CH and CD out-of-plane bending motion in these radicals.[6]

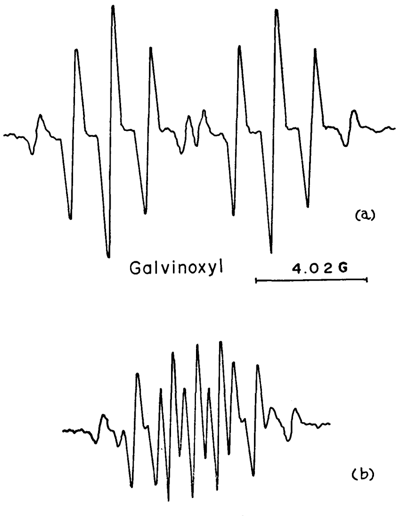

Fig. 2. ESR spectra of (a) galvinoxyl and (b) D-galvinoxyl radicals in THF at room temperature.

Table 1. Hyperfine splittings and g values of galvinoxyl and D-galvinoxyl radicals

	$a_m{}^H$	$a^{H(D)}_{CH(CD)}$	g value
Galvinoxyl	1.38 ± 0.02G	5.94 ± 0.02G	$2.0051_8\pm0.0000_2$
D-Galvinoxyl	1.38 ± 0.02G	0.89 ± 0.02G	$2.0052_1\pm0.0000_2$

The measured molar paramagnetic susceptibility, χ_P, as shown in Fig. 3 as a function of the temperature, has been corrected for the diamagnetic contribution of $\chi_{dia}=-0.276\times10^{-3}$ emu/mol calculated by Pascal's method. Between 84 and 290 K, χ_P follows the Curie-Weiss law, with a Weiss constant of $\theta=+6\pm3$ K and a spin concentration of $102\pm3\%$. At 84 K χ_P rapidly decreases by about 70 percent of its maximum value within about ten degrees, and afterward falls gradually to 68 K and again increases to 59 K.

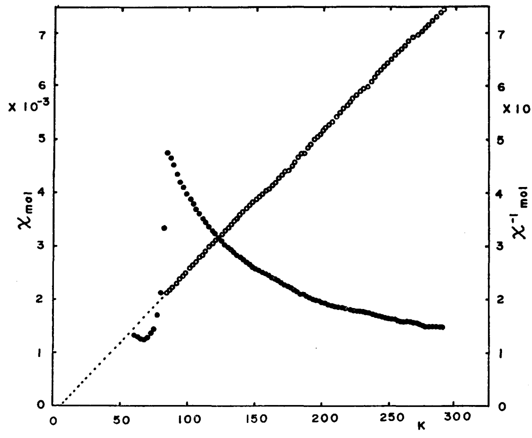

Fig. 3. (●) Molar and (○) inverse molar susceptibilities of the D-galvinoxyl radical *versus* temperature (59—290 K).

Since the anomaly in galvinoxyl is known to result from a transition accompanied by a pairing of the magnetic spins at around the position of the –CH= group as reported before, we can expect that the difference in the CH and CD out-of-plane bending motion in galvinoxyl and D-galvinoxyl, as observed in ESR measurement of the ratio (a^D/a^H), may induce some change in the anomaly in the magnetic susceptibility of galvinoxyl. However, the magnetic behavior is the same as that of galvinoxyl within experimental error, in contrast to our expectation. The result, together with the agreement of position and intensity of absorption maxima in optical spectra and of hyperfine splitting at undeuterated positions, indicates that the perturbation on the structure of galvinoxyl radical by deuterium substitution is too small to induce a change in the anomaly in magnetic susceptibility.

Paramagnetic susceptibility measurements of most crystalline aromatic free radicals usually give negative Weiss constants, showing that the spins on adjacent free radicals in the crystal lattice antiferromagnetically couple with each other. As far as we are aware, the positive Weiss constant observed with both galvinoxyl and D-galvinoxyl radicals is the first example of a positive Weiss constant in solid organic free radicals. McConnell[13] pointed out the possibility of a ferromagnetic exchange interaction favoring parallel (total) spin angular momentum on neighboring molecules in

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certain aromatic and olefinic free radicals (especially odd-alternant radicals) in which there are large positive and negative atomic π-spin densities. The unpaired electron distribution on galvinoxyl really corresponds to this case as calculated[14] by the conventional valence-bond method. In addition, the result of X-ray analysis[15] of galvinoxyl shows that galvinoxyl may stack in the crystal lattice so that the atoms of positive spin density are exchange-coupled most strongly to the atoms of negative spin-density in neighboring molecules. This gives a ferromagnetic exchange interaction, that is, positive Weiss constant in both radicals.

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