The Effect of the Deuterium Substituent on the Anomalous Phase Transition of the Crystalline Galvinoxyl Radical

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Two kinds of deuterium substituents of the galvinoxyl radical have been synthesized, and the effect of the deuterium substitution on the anomalous phase transition of the crystalline galvinoxyl radical at 82 K has been studied. The results, investigated by means of ESR and magnetic susceptibility measurements, indicate that the effect was not strong enough to induce any observable change in the transition.

In the previous papers,[1–3] we have reported that the galvinoxyl radical shows a first-order phase transition accompanying the pairing of magnetic spins at 82 K; the magnetic susceptibility is paramagnetic above the magnetic transition point, 82 K, where the susceptibility drops very sharply on cooling, while it is diamagnetic (weak paramagnetic) below this point. The anomaly at 82 K in the galvinoxyl has disappeared in the bisindophenoxyl radical, in which the centered methylidyne group (–CH=) of galvinoxyl is replaced by a nitrogen atom (–N=).[2] The magnetic susceptibility of the bisindophenoxyl radical exhibits a broad maximum at 54±2 K. This susceptibility can be explained approximately using a model which consists of a singlet ground state and a triplet state lying slightly above the ground state. On the other hand, the deuterated galvinoxyl radical, in which a centered methylidyne proton of galvinoxyl is replaced by a deuteron, showed a quite similar anomaly at 82 K.[4]

It has been reported that the deuterium substitution causes changes in the proton hyperfine splittings at the undeuterated positions of deuterated radicals.[5–9] Karplus *et al.*[10] have successfully analyzed the above results in terms of a model for the effect of the difference in the CH and CD out-of-plane bending motions. This vibration can affect the sigma-pi coupling, the pi-electron spin-density distribution, or both.

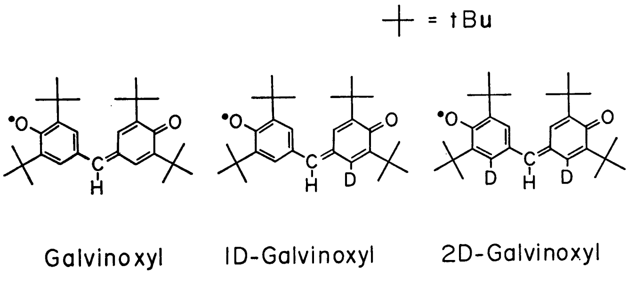

Fig. 1. Molecular structures of the galvinoxyl, 1D-galvinoxyl, and 2D-galvinoxyl radicals.

In the present paper, we have synthesized two mono- and di-deuterium derivatives, in which one and two of four *meta*-ring protons of the galvinoxyl radical are deuterated respectively (hereafter, they will be denoted as 1D- and 2D-galvinoxyl; see Fig. 1) and studied the magnetic properties of these radicals by means of ESR and magnetic susceptibility measurements.

Experimental

Materials. 2,6-Di-*t*-butylphenol and 2,6-di-*t*-butyl-4-methoxymethylphenol are commercially available. The synthesis of 2,6-di-*t*-butyl-3-deuteriophenol (bp 128—132°C/13 Torr) was reported previously.[11] The degree of deuterium substitution was determined as at least 95% from the NMR data of 2,6-di-*t*-butyl-3-deuteriophenol. 3,3′,5,5′-Tetra-*t*-butyl-diphenylmethane-4,4′-diol, phenol (I) (mp 157.0—157.5 °C (lit, 154 °C)) was prepared according to the method of Kharash and Joshi.[12] 3,3′,5,5′-Tetra-*t*-butyl-2,2′-dideuteriodiphenylmethane-4,4′-diol, phenol (III), was also similarly prepared from 2,6-di-*t*-butyl-3-deuteriophenol by condensation with formaldehyde in a KOH–ethanol solution. Mp 157.5—158.0 °C. (Found: C, 81.57; H, 10.82%. Calcd for $C_{29}H_{42}D_2O_2$: C, 81.63; H, 10.87%). UV spectrum (λ_{max}=279 nm, $\log\varepsilon$=3.53 in ethanol). NMR spectrum ($\delta_{C(CH_3)_3}$=1.40 ppm (36), δ_{CH_2}=3.74 (2), δ_{OH}=4.86 (2). $\delta_{m\text{-}H}$=6.85 (2); δ in CCl_4, with TMS as the internal standard). 3,3′,5,5′-Tetra-*t*-butyl-2-deuterio-diphenylmethane-4,4′-diol, phenol (II), was prepared by the reaction of 2,6-di-*t*-butyl-3-deuteriophenol and 2,6-di-*t*-butyl-4-methoxymethylphenol in a KOH–methanol solution, according to the procedure used by Steelink *et al.*[13] to prepare 3,5-di-*t*-butyl-3′,5′-dimethyl-4,4′-dihydroxydiphenylmethane. Mp 156.0—157.0 °C. (Found: C, 82.22; H, 10.72%. Calcd for $C_{29}H_{43}D_1O_2$: C, 81.83; H, 10.66%). UV spectrum (λ_{max}=279 nm, $\log\varepsilon$=3.51 in ethanol). NMR spectrum ($\delta_{C(CH_3)_3}$=1.41 ppm (36), δ_{CH_2}=3.76 (2), δ_{OH}=4.88 (2), $\delta_{m\text{-}H}$=6.89 (3); δ in CCl_4, with TMS as the internal standard.

The galvinoxyl (I), 1D-galvinoxyl (II), and 2D-galvinoxyl (III) radicals (see Fig. 1) were prepared according to the methods of Coppinger[14] and of Bartlett and Funahashi.[15] The diphenylmethane precursors, phenols (I)—(III), were oxidized

Table 1. Chemical and physical properties of galvinoxyl, 1D-, and 2D-galvinoxyls

	Mp (°C)	UV		Visible		Calcd (%)		Found (%)	
		λ_{max}	$\log\varepsilon$	λ_{max}	$\log\varepsilon$	C	H	C	H
Galvinoxyl	151.0—152.5	289nm	4.06	430nm	5.23	82.61	9.80	82.55	9.88
1D-Galvinoxyl	150.5—151.5	289	4.03	430	5.21	82.41	10.02	82.33	9.90
2D-Galvinoxyl	149.0—150.5	289	4.03	429	5.21	82.22	10.23	81.75	10.06

with PbO_2 in diethyl ether, with the temperature kept between 0 and 5°C under nitrogen gas throughout. The PbO_2 was then filtered off carefully, and the diethyl ether solvent was slowly evaporated under nitrogen gas. Very dark blue crystalline compounds of the galvinoxyl (I)—(III) remained in the round-bottomed flask. This flask was connected to a vacuum line (5×10^{-3} Torr) for two hours to remove the diethyl ether solvent completely. The chemical and physical properties of these radicals are summarized in Table 1. All these values show good accordance with each other within the limits of experimental error.

Apparatus. The susceptibility measurements were carried out with a Shimadzu-type MB-2 magnetic torsion balance, equipped with a low-temperature cryostat. The temperatures were measured using an AuCo-Cu thermocouple. Manganese Tutton salt was used for the calibration of the themometers and the field gradient. The ESR measurements were carried out using a JES-ME-3X spectrometer equipped with a Takeda-Riken microwave frequency counter. The ESR hyperfine splittings and *g*-values were measured relative to those of $(KSO_3)_2NO$ ($a^{\text{N}}=13.05\pm0.03$ G; $g=2.0054$[16]). The NMR spectra were taken on a JEOLCO 4H-100 100 MHz NMR spectrometer.

Results and Discussion

Initial slight oxidations of 3,3′,5,5′-tetra-*t*-butyldiphenylmethane-4,4′-diol and 3,3′,5,5′-tetra-*t*-butyl-2,2′-dideuteriodiphenylmethane-4,4′-diol, (I) and (III) phenols, with PbO_2 in toluene in a sealed, degassed system give ESR spectra consisting of triplet-triplet or triplet-doublet splittings respectively. We assign the spectra to the primary phenoxyl radicals (I-P) and (III-P) formed from the parent phenols by the abstraction of a phenolic hydrogen atom. The large triplet splittings ($a^{\text{H}}=9.58$ G for (I-P) and $a^{\text{H}}=9.57$ G for (III-P) at 15 °C) in the primary radicals are clearly due to the para methylene group, and the triplet or doublet splittings ($a^{\text{H}}=1.65$ G for (I-P) and 1.68 G for (III-P)) can be explained by the meta hydrogens. One group of large triplet splittings of (I-P) and (III-P) is shown in Figs. 2(a) and (b). The spectrum shown in Fig. 2(b) includes also a weak triplet signal arising from undeuterized phenol. The theoretical ratio ($a^{\text{D}}/a^{\text{H}}$) of the deuteron to the proton splittings expected on the basis of the magnetic moments and spins of the two nuclei is 0.1535; thus, we can expect 0.25 G as the deuteron hyperfine splitting for the (III-P) radical. However, the deuteron hyperfine splitting (a^{D}_{m}) due to the *meta*-ring deuteron of the (III-P) primary radical was not resolved, as is shown in Fig. 2(b). On the basis of the relative intensities and line widths of the ESR spectrum consisting of doublet and triplet splittings, it is estimated that the samples contain approximately 8% undeuterized protons. This value shows a good agreement with that of 5% estimated from the NMR spectrum. The spectrum of the primary radical (II-P) obtained by the PbO_2 oxidation of phenol (II) may be explained as resulting from the addition of the spectra from (I-P) and (III-P).

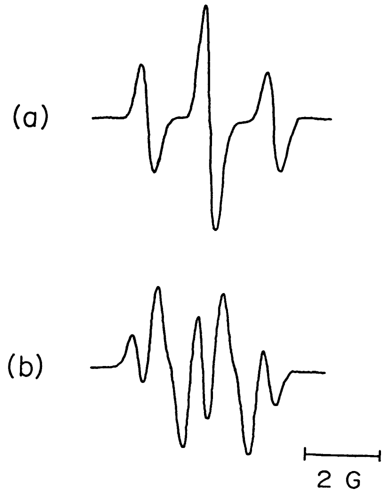

Fig. 2. ESR spectra of the primary radicals, (a) (I-P) and (b) (III-P), obtained by the PbO_2 oxidation of the phenols, (I) and (III), in toluene at 15 °C. One group of the three identical absorption groups is shown in Fig. 2(a) and (b), respectively.

As the oxidation of the phenol (I) solution proceeds, a further absorption due to a secondary radical, galvinoxyl, appeared, and finally the spectrum was completely altered to a doublet-quintet spectrum with hyperfine splittings, $a^{\text{H}}_{\text{CH}}=5.77$ G and $a^{\text{H}}_{\text{m}}=1.41$ G.[17] The (II) and (III) phenols also show similar behavior; they give doublet-quartet and doublet-triplet spectra due to 1D- and 2D-galvinoxyl radicals. The deuteron hyperfine splittings were not resolved, as is to be expected from the results obtained for the primary radicals. Recordings of the 1D-galvinoxyl spectrum also include

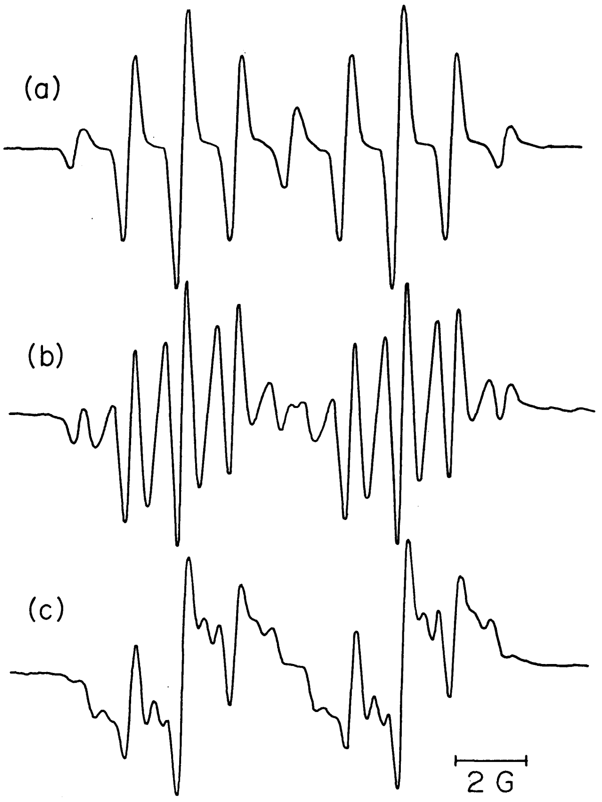

Fig. 3. ESR spectra of (a) galvinoxyl, (b) 1D-galvinoxyl, and (c) 2D-galvinoxyl radicals obtained by the PbO_2 oxidation of the phenols, (I), (II), and (III), in toluene at 20 °C.

Table 2. Hyperfine splittings and G-values of galvinoxyl, 1D-, and 2D-galvinoxyls

	$A^{\mathrm{H}}_{\text{-CH=}}$ (G)	$A^{\mathrm{H}}_{\mathrm{m}}$ (G)	G-value
Galvinoxyl	5.77±0.04	1.41±0.04	2.00434±0.00003
1D-Galvinoxyl	5.82±0.04	1.36±0.04	2.00433±0.00003
2D-Galvinoxyl	5.86±0.04	1.35±0.04	2.00431±0.00003

the doublet-quintet spectrum of undeuterated galvinoxyl, because the sample of the monodeuterated diphenylmethane precursor (phenol (II)) contains the diphenylmethane (phenol (I)) as an impurity. Similarly, the spectrum of the 2D-galvinoxyl radical sample also includes signals due to both 1D-galvinoxyl and galvinoxyl radical impurities. These spectra are shown in Fig. 3. The g-values of these radicals in toluene were also measured. All these values are listed in Table 2. Both the hyperfine splittings and the g-values of these radicals remain constant, within the limits of experimental error, indicating that deuterium substitution to the *meta*-ring proton of the phenyl rings does not significantly affect the unpaired electron distribution.

The molar susceptibilities obtained for the galvinoxyl radical are shown in Fig. 4 as a function of the temperature. The data have been corrected for a calculated diamagnetism of -0.276×10^{-3} emu/mol. The susceptibility of galvinoxyl follows the Curie-Weiss law with a Curie constant of 0.358 K emu/mol and a Weiss constant of 13.0±2.0 K in the temperature region between 86 and 300 K. At 85.1±2.0 K, χ_{P} rapidly decreases by 93% of its maximum value within about three degrees, and afterward falls off gradually until 55 K. The residual paramagnetic radical concentration, calculated from the susceptibility at 55 K assuming Curie law, is only 1.1%. As has been reported before, the anomaly in the galvinoxyl is thought to be a first-order phase transition, accompanied by a pairing of the magnetic spins.[2] It has also been reported before that the magnetic susceptibilities in the low-temperature region (5—50 K) obey the Curie-Weiss law, with different spin concentrations from about 10 to 30 mol % for the three independently-prepared samples; thus, the low-temperature susceptibilities are probably due to the residual unpaired galvinoxyl radicals with a spin of 1/2, the radicals being randomly located in the lattice. In the present work, poly crystals of the galvinoxyl radical were prepared by careful, slow evaporation from a saturated etherial solution under nitrogen throughout in order to decrease the quantity of residual unpaired spins. In fact, the residual radical concentration (1.1%) obtained is much smaller than the values (from about 10 to 30 mol %) reported before for the galvinoxyl.

The 1D- and 2D-galvinoxyl radical samples were similarly prepared. The magnetic susceptibilities of these radicals between 55 and 300 K are shown in Fig. 4, together with those of the galvinoxyl radical. As is clear from the results shown in Fig. 4, the temperature dependences of the magnetic susceptibilities of the 1D- and 2D-galvinoxyl radicals are very similar to that of the galvinoxyl. The values of the Curie constants (C), the Weiss constants (θ), the radical concentrations, the transition temperatures ($T_{\max}$), and the residual radical concentrations obtained in this work are summarized in Table 3. The small differences observed between these radicals for the radical concentrations above the transition temperature and the residual radical concentrations below it must be due to differences in the sample preparation. On the other hand, the expected change in the phase-transition temperature and the Weiss constant upon the deuterium substitution to the *meta*-ring protons of the galvinoxyl was not observed. It has been reported by ESR studies that the deuterium substitution to aromatic radicals can produce significant modifications in the proton hyperfine splittings (a^{H}) for ring positions other than that of substitution. The most notable effect is observed in the benzenide anion;[5,6] the equal hyperfine splittings ($a^{\mathrm{H}}=3.75$ G) obtained at all positions in $C_6H_6^-$ are replaced in the benzenide-1-d anion by $a^{\mathrm{H}}_2=a^{\mathrm{H}}_3=3.95$ G, $a^{\mathrm{H}}_4=3.49$ G and in the benzenide-2,6-d_2 anion by

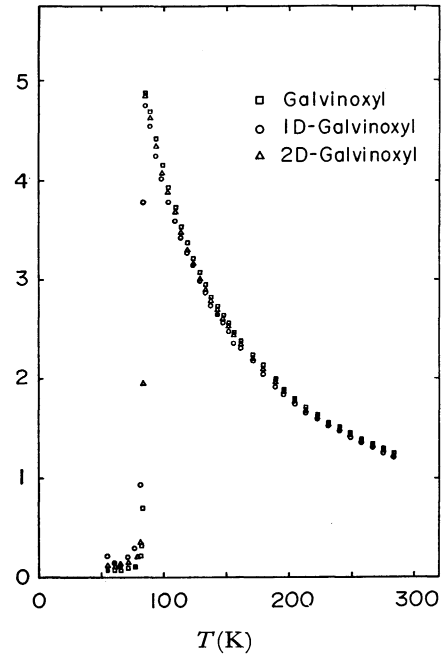

Fig. 4. Molar susceptibilities of the galvinoxyl (open square, □), 1D-galvinoxyl (open circle, ○), and 2D-galvinoxyl (open triangle, △) radicals versus temperature (55—300 K).

Table 3. Results from susceptibility measurements of galvinoxyl, 1D-, and 2D-galvinoxyls

	C (emu K/mol)	θ (K)	Radical concentration (%)	$T_{\max}$ (K)	Residual para (%)
Galvinoxyl	0.358	13.0±2.0	95.0±2.0	85.1±2.0	1.1±0.5
1D-Galvinoxyl	0.343	13.2±2.0	90.9±2.0	84.3±2.0	3.2±0.5
2D-Galvinoxyl	0.347	13.6±2.0	92.1±2.0	84.9±2.0	1.7±0.5

$a_1^H=a_4^H=4.16$ G, $a_3^H=3.61$ G. Smaller changes are observed in deuterated naphthalenide anions[7] and in the *N*-deuterated dihydropyrazine cation and its methyl derivatives.[8] However, all the results obtained for the galvinoxyl, 1D-, and 2D-galvinoxyl radicals in the solid state and in solution indicate that the perturbations in electronic and magnetic properties resulting from the deuterium substitution are quite small in these radicals.

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