ENDOR Studies of the Hyperfine Interaction of Phenylgalvinoxyl Radicals in Solution

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The ENDOR spectra of ten kinds of phenylgalvinoxyl derivatives in solution have been observed, and the hyperfine splitting constants have been determined. The formally equivalent four meta ring protons of the galvinoxyl skeleton in the phenylgalvinoxyl radical become magnetically nonequivalent in two groups of two. This behavior may be explained by assuming that splittings arising through pure spin polarization, or through mixed hyperconjugation and spin polarization, are different for *syn* and *anti* meta ring protons of the phenylgalvinoxyl radical. A similar effect has been observed in the ENDOR spectra of other phenylgalvinoxyl derivatives. In radicals with a large substitution group at the meta or para position of the phenyl ring, the galvinoxyl skeleton twists unsymmetrically on either side; thus, all or three among the four meta ring protons become magnetically nonequivalent. The solvent dependence of the ENDOR spectra of the phenylgalvinoxyl radicals constituted strong evidence for the importance of the solvent in fixing the conformation and symmetric property of the radical molecules. The proposed analyses of the ENDOR spectra were also supported by the McLachlan Molecular Orbital calculations.

The galvinoxyl radical (I) (see Fig. 1) is well known as a very stable neutral radical.[1,2] The magnetic properties of galvinoxyl in solution and in the solid state have been extensively studied using several physical methods, such as ESR,[3] NMR,[4] ENDOR,[5] magnetic susceptibility,[6] and specific heat.[7] The quinone methide radicals obtained by the replacement of *t*-butyl groups by methoxyl or methyl groups have also been studied by means of ESR and ENDOR, showing some interesting aspects of the electronic structures of these radicals.[8]

The phenylgalvinoxyl radical (II) (see Fig. 1) has an electronic structure similar to galvinoxyl, and exhibits a stability approaching that of galvinoxyl.[9] Recent studies of the magnetic susceptibility of phenylgalvinoxyl (II) and some of its derivatives (IV)—(VIII) have clarified some interesting magnetic properties in the solid state, suggesting intermolecular ferromagnetic exchange interaction in some of these radicals.[10] The magnetic property is very sensitive to both the packing of the radical molecules in the crystal and the distribution of the unpaired electron on the radical. ESR is a frequently used method for determining the distribution of the unpaired electron on radical molecules. However, the ESR spectra of the above phenylgalvinoxyl radicals are usually resolved, showing only five line-splittings (a_m^H=1.32—1.35 G) due to the four meta ring protons in the galvinoxyl skeleton of the phenylgalvinoxyl radicals.[10-12] Therefore, it is not clear whether an unpaired electron spreads all over the molecular frame, since detailed analyses of the hyperfine splitting constants have never been attempted for these radicals.

Electron nuclear double resonance (ENDOR) spectroscopy is a valuable method for the determination of the proton isotropic hyperfine couplings of organic radicals in solution, since the effective resolution is much higher than for ESR. In the preliminary ENDOR experiment on phenylgalvinoxyl (II), the ENDOR line from the four meta ring protons was observed to be split, suggesting that there are two pairs of equivalent ring protons.[13] In the work, this splitting was tentatively ascribed to a restricted rotation with molecular asymmetry. On the other hand, all four meta ring protons of galvinoxyl are equivalent within the resolution of the ENDOR experiments.[5]

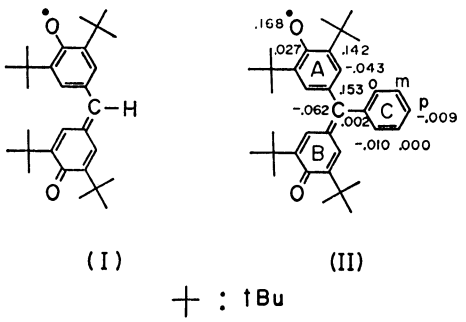

Fig. 1. Chemical structures of galvinoxyl (I) and phenylgalvinoxyl (II), showing numbering system and McLachlan unpaired spin densities.

In the present paper, proton hyperfine splitting constants measured from the solution ENDOR spectra of ten kinds of phenylgalvinoxyl radicals in toluene and, in some cases, in 2-methyltetrahydrofuran (2-MTHF) will be reported, in order to present fundamental data which are essential for a more detailed understanding of the magnetic properties of these radicals in the solid state. Even though these radicals show simple quintet ESR absorption spectra, the ENDOR experiments have yielded several notable results which, we think, could not have been obtained from the ESR spectra. Based on the ENDOR data, interesting conformational changes due to steric interactions and solvent effects for these radicals will be discussed.

Experimental

The galvinoxyl radical (I) was synthesized following the method of Kharash and Joshi[1] or Coppinger.[2] The syntheses and physical properties of the phenol precursors (P-II)—(P-X), except for the phenol (P-III), of the phenylgalvinoxyl radicals (II)—(X) (see Figs. 1 and 2) were reported previously.[10,12] The phenol (P-III) was prepared according to the method of Coffield *et al.*[14] After the condensation of 2,6-di-*t*-butylphenol with benzaldehyde-d_5 (E. Merck AG. 99%), the deuterated bisphenol (P-III) was synthesized; thereafter

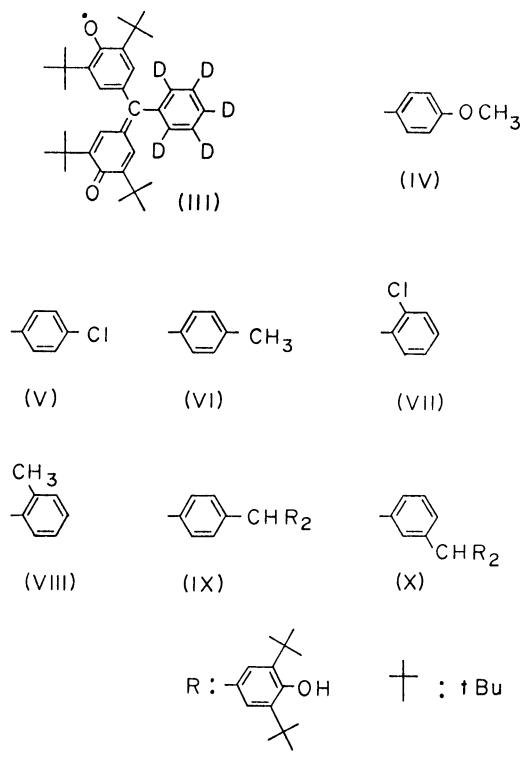

Fig. 2. Chemical structures of phenylgalvinoxyl derivatives (III)—(X).

it was recrystallized twice from ethanol. Mp 162.5—163.5 °C. Found: C, 83.44; H and D, 10.15%. Calcd for $C_{35}H_{43}D_5O_2$; C, 83.11; H and D, 10.56%. The ultraviolet absorption spectrum in ethanol with λ_{max}=279 nm ($\log \varepsilon$=3.65) and the proton NMR spectrum in CCl_4 with $\delta_{t\text{-Bu}}$=1.38, δ_{OH}=4.92, δ_{CH}=5.28, and $\delta_{m\ H}$=6.82 ppm (TMS as the standard) are in good agreement with those of the corresponding bisphenol, except for the disappearance of the proton NMR absorption due to five phenyl protons of the undeuterated bisphenol.

The phenylgalvinoxyl radicals (II)—(X) were prepared by the oxidation of the phenols with PbO_2 in toluene or 2-MTHF under a vacuum. The initial ESR spectra resulting from the slight oxidation of the phenols with PbO_2 were a doublet of triplets.[12] After further oxidation, the phenylgalvinoxyl radical, which has the structure shown in Fig. 1, and its derivatives were formed. The ESR spectra of these phenylgalvinoxyls show five line splitting with intensities of 1 : 4 : 6 : 4 : 1.

The ENDOR spectra were recorded by means of a JEOL-type ES-EDX-1 spectrometer, operated with 80 Hz magnetic field modulation.[15] About 150 watts of the continuous radio wave frequency modulated at 6.5 kHz were running inside of the cavity for NMR excitation. The ESR measurements were carried out using a JES-ME-3X spectrometer.

Results and Discussion

The ESR spectra of the phenylgalvinoxyl (II) and some of its derivatives (III)—(X) (see Figs. 1 and 2) show only five line splittings due to four meta ring protons of the quinone methide skeleton; we were unable to resolve the splittings from the other protons. The meta ring proton hyperfine splittings, a_m^H, observed in toluene at room temperature are listed in the first column of Table 1. Figures 3 and 4 show several typical ENDOR spectra of the phenylgalvinoxyl and some of its derivatives in toluene. The ENDOR spectra of these radicals were also measured in the 2-MTHF solvent. The results of the analyses of these spectra are also tabulated in Table 1, together with the data of the galvinoxyl radical used as reference. The temperatures (T) at which the best resolved ENDOR spectra were obtained are listed in Table 1.

ENDOR Spectra of Galvinoxyl (I), Phenylgalvinoxyl (II), and Phenyl-d_5-galvinoxyl (III). The ENDOR spectrum of galvinoxyl (I) in toluene (see Fig. 3(a)) shows three different proton hyperfine splittings (5.77_4, 1.36_6, and 0.05_5 G), which are attributable, respectively, to a methide proton, four ring protons, and the 36 tertiary butyl protons. On the other hand, the ENDOR spectrum of phenylgalvinoxyl (II) in toluene (see Fig. 3(b)) clearly exhibits four different proton hyperfine splittings (1.34_7, 1.27_2, 0.20_7, and 0.05_8 G). The larger two hyperfine splittings (1.34_7 and 1.27_2 G) are easily assigned to the four meta ring protons of phenoxyl groups, taking their ESR hyperfine coupling constants (a_m^H=1.32 G) into account. This assignment

Table 1. Hyperfine splitting constants of phenoxyl radicals (in Gauss)

Radical	In toluene						In 2-MTHF					
	ESR	ENDOR					ESR	ENDOR				
	a_m^H	a_m^H		$a_{ring\ C}^{o\text{-},p\text{-}H}$	a_{tBu}^H	T(°C)	a_m^H	a_m^H		$a_{ring\ C}^{o\text{-},p\text{-}H}$	a_{tBu}^H	T(°C)
(I)	1.42	1.36_6		—	0.05_5	−75						
(II)	1.32	1.34_7,	1.27_2	0.20_7	0.05_8	−60	1.33	1.32_8,	1.25_8	0.20_7	0.06_1	−63
(III)	1.32	1.34_1,	1.27_6	—	0.04_9	−68						
(IV)	1.34	1.30_8,	1.25_6	0.21_4	0.04_9	−80						
(V)	1.33	1.34_8,	1.28_1	0.20_2	0.05_5	−75						
(VI)	1.35	1.33_0,	1.27_8	0.13_5	0.04_9	−80						
(VII)	1.33	1.35_8,	1.29_1	0.11_6	0.05_1	−61	1.33	1.35_4,	1.28_7	0.11_7	0.04_7	−66
(VIII)	1.34	1.31_5,	1.24_9	0.12_6	0.04_9	−70	1.33	1.33_0,	1.26_8	0.12_7	0.05_8	−80
(IX)	1.30	1.40_7,	1.35_7	0.28_9	0.05_9	−45	1.34	1.37_0,	1.30_5	0.20_2	0.06_3	−65
		1.26_0,	1.20_7	0.18_3				1.26_0				
(X)	1.33	1.37_1,	1.32_1	0.18_1	0.05_7	−73	1.33	1.34_7,	1.27_4	0.18_9	0.06_1	−54
		1.26_8										

is also consistent with the known assignments for galvinoxyl (I).[3] Since, at the temperatures at which we measured the ENDOR signal, the intensities of the ENDOR transitions corresponding to the hyperfine couplings, 1.34_7 and 1.27_2 G, are equal, the four protons must be equivalent in two groups of two protons. Here, the splitting of the meta ring proton ENDOR signal at a low temperature is independent of both the microwave and radio frequency power,[5] and we are confident that it reflects a real difference in hyperfine coupling. Similar splittings are also observed in all the other radicals investigated, except for the (IX) and (X) radicals, as is shown in Figs. 3 and 4. Comparing the ENDOR spectrum of phenylgalvinoxyl with that of galvinoxyl, the hyperfine splitting of 0.20_7 G of the former, which has never been observed in the latter, can clearly be identified as the proton hyperfine splitting in the substituted phenyl ring. We confirmed that the splitting of 0.20_7 G can be assigned to the ring protons in the substituted phenyl, because it is lost in phenyl-d_5-galvinoxyl (see Fig. 3(c)). Thus, the smallest splitting of 0.05_8 G is attributable to that of tertiary butyl protons. This fact indicates that the unpaired electron spreads over the substituted phenyl ring, C, although the magnitude of the electron density is very small. Anticipating the results of the McLachlan Molecular Orbital calculations to be described later (see Fig. 1), the 0.20_7 G splitting will be assigned to the ortho and para ring protons of the substituted phenyl ring, C, in which the unpaired spin densities on meta ring carbon atoms are too small to explain the 0.20_7 G splitting or even the 0.05_8 G splitting.

As has been discussed above, the ENDOR results indicate that the four meta ring protons must be equivalent magnetically in two groups of two protons. In support of the present assumptions, one may refer to the accurate ESR and/or ENDOR data on the allyl radical[16] and 2-methylgalvinoxyl[8] (see the structure in Ref. 8), because both radicals have electronic structures (allyl skeletons) similar to that of phenylgalvinoxyl.

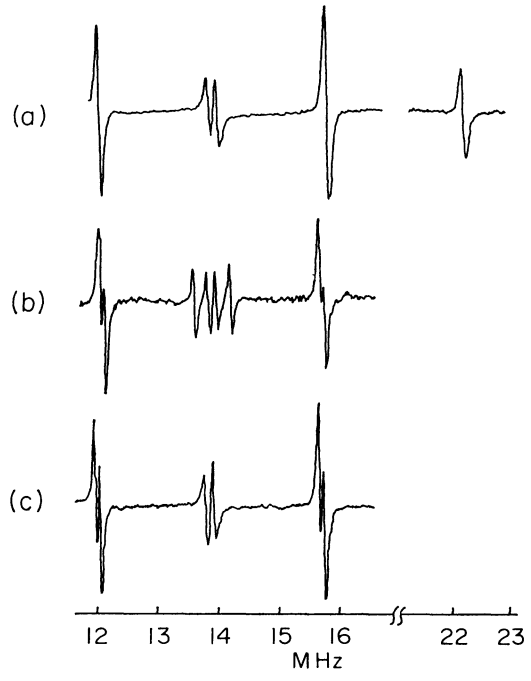

Fig. 3. ENDOR spectra of (a) galvinoxyl (I) (at −75 °C), (b) phenylgalvinoxyl (II) (at −60 °C), and (c) phenyl-d_5-galvinoxyl (III) (at −68 °C) in toluene.

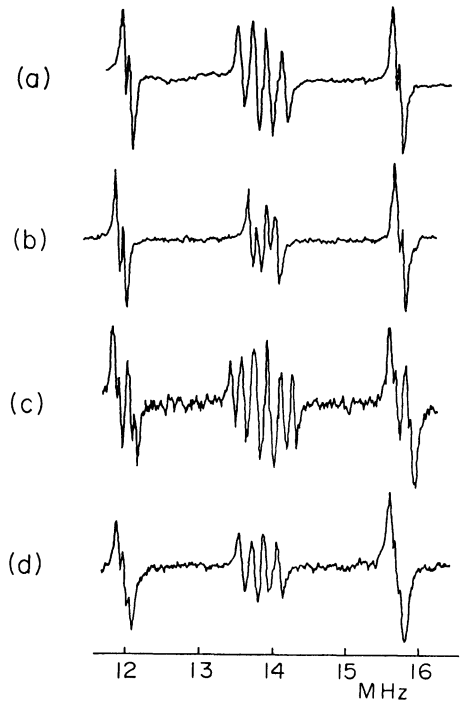

Fig. 4. ENDOR spectra of (a) radical (IV) (at −80 °C), (b) radical (VII) (at −61 °C), (c) radical (IX) (at −45 °C), and (d) radical (X) (at −73 °C) in toluene.

The low-temperature ESR spectrum of the allyl radical reveals two pairs of magnetically inequivalent *syn* and *anti* terminal protons (13.90 and 14.81 G), which give rise to a triplet-of-triplets hyperfine structure further split into doublets by the proton in the 2 position (4.06 G). The different splittings which are observed for formally equivalent methylene protons in allyl could be understood because the splitting arising through pure spin polarization, or through mixed hyperconjugation and spin polarization, is expected to be different for *syn* and *anti* terminal protons. A similar situation may be expected to explain the observed inequivalence of meta ring protons of phenylgalvinoxyl.

The non-equivalence of the methyl proton splitting has been observed in the ENDOR spectra at low temperatures of the 2-methyl-derivative of galvinoxyl by Steelink *et al.*[8] When the two *t*-butyl groups on one of the two phenyl rings of galvinoxyl are replaced by methyl groups, the two methyl groups are inequivalent, showing a splitting of the methyl proton ENDOR line. However, in this case, all four ring protons of 2-methylgalvinoxyl are equivalent within the resolution of the ENDOR experiments. The molecular structure and packing in crystalline galvinoxyl have been determined by X-ray diffraction.[17] The observed bond angle at methine carbon is 134 degrees, and the phenyl

groups are twisted by 12 degrees. On the other hand, the phenylgalvinoxyl radical may be considered rather as triphenylmethyl derivatives. The Stuart molecular model indicates that the main steric interaction in phenylgalvinoxyl works between the ring protons, although weak interactions can be seen between the substituted *t*-butyl groups. Thus, the radical most probably adopts a propeller configuration, with a bond angle of about 120° at the centered carbon and a twist angle of about 30°.[18] Therefore, the decrease in the bond angle at the centered carbon and the increase in the twist angle in phenylgalvinoxyl compared to those of galvinoxyl will induce the difference in the hyperfine splitting constants of two meta ring protons in each of two phenyl rings, A and B.

ENDOR Spectra of IV, V, and VI Radicals. The para-derivatives, (IV), (V), and (VI) (see Fig. 2), of phenylgalvinoxyl show spectra similar to that of phenylgalvinoxyl. For example, the spectrum of the IV radical clearly exhibits four different proton hyperfine splittings, as is shown in Fig. 4(a). The value of each hyperfine splitting is very close to the corresponding value of phenylgalvinoxyl. This indicates that the effects of the para-substitution of the phenyl ring C by CH_3O-, Cl-, and CH_3- groups are too small to induce any change in the unpaired spin distribution or molecular structure. The hyperfine splittings for the IV, V, and VI radicals are listed in Table 1.

ENDOR Spectra of VII and VIII Radicals. The effect of the ortho-substitution of the phenyl ring, C, by Cl- and CH_3- groups has been studied (see Fig. 2, (P-VII) and (P-VIII)). The ENDOR spectrum of the VII radical (ortho-Cl-derivative) in toluene is shown in Fig. 4(b), indicating again four different proton hyperfine splittings (1.35_8, 1.29_1, 0.11_6, and 0.05_1 G). The obvious assignments of the 1.35_8 and 1.29_1 G to two pairs of ring protons, the 0.11_6 G to the ortho and para protons of the phenyl ring, C, and the 0.05_1 G to the tertiary butyl protons, are consistent with the results for the II—VI radicals. A similar spectrum is obtained for the VIII radical (ortho-CH_3-derivative), and the hyperfine splittings observed are listed in Table 1.

As has been reported for the tris(*p*-nitrophenyl)-methyl radical from the results of X-ray analysis, three phenyl rings, A, B, and C, of the phenylgalvinoxyl are considered to be twisted with an equivalent angle, 30°. Ortho-substitution induces a strong interaction between the pendent group and the ring adjacent to the pendent group. Therefore, we can expect that the two rings, A and B, of the quinone methide skeleton will be distorted by different angles, θ_A and θ_B, respectively. If this effect is large, we can expect four kinds of ring-proton hyperfine splittings for these radicals. However, the VII and VIII radicals show two kinds of hyperfine splittings due to four meta ring protons, with values similar to that of phenylgalvinoxyl. On the other hand, the hyperfine splittings of the phenyl ring, C, are reduced to almost half of that of phenylgalvinoxyl.

Since the ring protons in the rings A and B are believed to be inequivalent, even if the steric effect by ortho-substitution is small, this perturbation might make some contribution to the width and shape of the meta ring proton absorption lines. In addition, since the steric effect of the ortho-CH_3-derivative (VIII) must, in principle, be different from that of the ortho-Cl-derivative (VII), this would also induce a difference in the width and shape of the absorption lines of these two ortho-derivatives. The surprising thing is that all of these effects are so small. These results can be understood, however, by assuming that the ring C, to which the pendent groups are attached, is twisted more than the other rings, A and B, and that the twisting angles, θ_A and θ_B, are nearly equal to each other, that is, $\theta_C > \theta_A \approx \theta_B$.

ENDOR Spectra of IX and X Radicals. The ENDOR spectrum of the IX and X radicals (see Fig. 2) in toluene at −45 and −73 °C are shown in Fig. 4(c) and (d) respectively. The spectrum of the IX radical consists of 14 lines symmetrically disposed on both sides of the free proton NMR frequency. This spectrum is very different from those of other phenylgalvinoxyls. A comparison of the present ENDOR results on IX with those of an earlier work on II suggests that one group of splittings (1.40_7, 1.35_7, 1.26_0, 1.20_7 G) should be assigned to the four meta ring protons, and the (0.05_0 G) splitting, to the *t*-butyl protons. Similarly, the (0.18_3 G) splitting is assigned to the two ortho protons, and that of 0.28_9 G, to the one remaining para-methylene proton of the phenyl ring, C. This result indicates that the galvinoxyl skeleton twists unsymmetrically on either side; thus, all four meta ring protons are magnetically inequivalent. The differences (0.05_0 and 0.05_3 G) between the two larger splittings (1.40_7, 1.35_7 G) and the two smaller splittings (1.26_0, 1.20_7 G) are similar to each other and are comparable with those of other phenylgalvinoxyls. Therefore, assuming the twist angles ($\theta_A < \theta_B$), the two larger splittings and the two smaller splittings are attributable to the two meta ring protons of the ring A and the ring B respectively of the galvinoxyl skeleton.

Figure 4(d) shows the ENDOR spectrum of the X radical in toluene at −73 °C, indicating five different hyperfine splittings. Similarly, the splitting of 0.18_1 G may be assigned to ortho and para protons of the phenyl ring C, and that of 0.05_8 G, to the *t*-butyl protons. Clearly the splittings of 1.37_1, 1.32_1, and 1.26_8 G are to be assigned to the four magnetically inequivalent meta ring protons. Again, the data may be explained tentatively by keeping in mind the fact that the galvinoxyl skeleton twists unsymmetrically on either side, but the difference in the twist angles is smaller than that in the IX radical, and thus the intermediate two splittings coincide with each other. The cause of such molecular asymmetry is steric interaction between the galvinoxyl skeleton ring and the large group substituted to the ring C. The Stuart molecular model supports the idea that such steric interaction is possible for these radicals, (IX) and (X).

Solvent Effect. The solvent dependences of the ENDOR spectra of the II, VII, VIII, IX, and X radicals were also examined. In the II, VII, and VIII radicals, the ENDOR spectra in toluene and in 2-MTHF are similar to each other, and the observed values of the hyperfine splittings show a good accordance, within

the limits of experimental error, as is shown in Table 1. On the other hand, notable solvent dependences were observed in the ENDOR spectra of the IX and X radicals. The ENDOR spectrum of the IX radical in toluene at −40°——60 °C (see Fig. 4(c)) consists of 14 lines symmetrically disposed on both sides of the free proton NMR frequency. On the other hand, the ENDOR spectrum in 2-MTHF of the same radical (IX) at −50°——70 °C consists of 10 lines. This spectrum is quite similar to that of the X radical in toluene, shown in Fig. 4(d). Clearly, in 2-MTHF, the meta ring protons show three kinds of hyperfine splittings. This result may be explained by assuming that the degree of molecular asymmetry, that is, the difference in the twist angles, θ_A and θ_B, observed for the IX radical in toluene, was decreased in 2-MTHF. The splitting of 0.28_9 G due to the para methylene proton of the phenyl ring C, also disappeared in 2-MTHF. This must be due to the change in the dihedral angle of the CH bond to the $2p_z$ orbital of the ring C. Similar solvent effects were observed for the X radical. The ENDOR spectrum of the X radical in 2-MTHF at −54 °C shows four kinds of splittings, 1.34_7 and 1.27_4 G due to meta ring protons, 0.18_9 G due to phenyl ring C protons, and 0.06_1 G due to *t*-butyl protons. This result differs from the five kinds of splittings of the same radical seen in toluene at −40°——75 °C; it implies that the molecular asymmetry of the X radical observed in toluene is eliminated in 2-MTHF.

Many investigations of the solvent effect of free radicals, including phenoxyl radicals, have been reported.[19] The effect has been explained as a redistribution of the π-electron spin density in a radical molecule induced by the electrostatic interaction and/or the hydrogen bond formation between the radical and the solvent molecules. However, in all the phenoxyl radicals studied in the present work, the variation in the hyperfine splitting constants, and thus the π-electron spin density induced by these effects, are both thought to be small because of the steric effect of tertiary butyl groups in these molecules. In fact, the observed change in the hyperfine splittings of the II, VI, and VIII radicals in toluene and 2-MTHF is negligible, as is shown in Table 1. On the other hand, the notable solvent effect in the hyperfine splitting of the IX and X radicals observed here may be explained by assuming a change in the steric structure of the radical molecules due to the solvents. Therefore, in other words, the present solvent dependences observed for the phenylgalvinoxyls serve as evidence that solvent molecules play an important role in fixing the conformations and symmetric properties of the radical molecules.

MO Calculations. Using the same parameters for the oxygen atom as those used for the galvinoxyl radical by Luckhurst,[20] the McLachlan spin density of the phenylgalvinoxyl radical was calculated. In this calculation all three phenyl groups were assumed to be twisted by 30° about the methyl carbon bonds. The choice of 30° was made on the basis of the results of the X-ray analysis of the tris(*p*-nitrophenyl)methyl radical,[18] because steric hindrance between substituted *t*-butyl groups in the phenylgalvinoxyl radical is considered to be small from the Stuart molecular model; thus, the structure of the phenylgalvinoxyl mainly depends on that of the triphenylmethyl skeleton. Spin densities are not very sensitive to the choice of this angle as long as it is small, since the resonance integral between the methyl carbon and the attached phenyl carbon varies as $\beta=\beta_0\cos\theta$. The results are given in Fig. 1. They can explain the qualitative ENDOR spectrum of phenylgalvinoxyl, assuming the Q values of 23 G for ring protons and 0.28 G[19] for tertiary butyl protons. The orbitals containing an unpaired electron of the phenylgalvinoxyls have, at least in the Hückel approximation, a node in the centered phenyl ring, C, and a carbon atom connected to the phenyl ring, giving a zero spin density on the phenyl ring. In the McLachlan approximation, the orbitals are spin-polarized so as to yield nonvanishing spin densities in the phenyl ring C of the radical. These spin densities are $\rho_{ortho}=-0.010$ and $\rho_{para}=-0.009$, and the hyperfine splitting constant ($a^H=0.20_7$ G) may be assigned to the ortho and para ring protons of the phenyl ring C. The unpaired spin densities ($\rho_{meta}=0.000$) on the meta carbon atoms are negligibly small.

Recent studies of the magnetic susceptibilities of phenylgalvinoxyl (II) and some of its derivatives (IV)—(VIII) have clarified some interesting magnetic properties in the solid states, suggesting intermolecular ferromagnetic exchange interaction in some of these radicals.[10] The sign and magnitude of the exchange interaction between the π-electron spins may depend on both the spin densities and the molecular packing.[21,22] The results of ENDOR measurements and McLachlan Molecular Orbital calculation show that there are large positive and negative atomic π-spin densities in these radicals, and it is quite possible that, in special cases, these radicals may pancake on top of one another in the crystal lattice so that atoms of a positive spin density are exchange-coupled most strongly to atoms of a negative spin density in neighboring molecules. In such a case, the apparent exchange interaction is ferromagnetic, corresponding to the results verified experimentally by magnetic susceptibility measurements.[6,10,22]

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