the only energy input, since each of the electrodes in such a cell will be at the reversible H^+/H_2 potential (Scheme III) when the electrodes are short circuited under illumination.

Considering all of the direct photochemical fuel-producing systems,[23] the WS_2-based cell for driving reaction 10 stands quite high: (1) the system is durable; (2) visible light efficiency is respectable; (3) starting reagents are abundant and inexpensive; (4) the rate of conversion can be quite high; (5) the products that are generated are useful. It is particularly noteworthy that the WS_2 photoanode operates at nearly optimum efficiency when short circuited to a reversible H_2 electrode. That is, the value of E_V at the so-called maximum power point of the photocurrent–voltage curve is nearly equal to $E_r(H^+/H_2)$, providing a near perfect match to the potential needed to effect the overall process represented by reaction 10 when the cathode has little overvoltage as is the case with Pt.

Acknowledgment. We thank the United States Department of Energy, Basic Energy Sciences, Chemical Sciences Division, and the Dow Chemical Company for support of this research.

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^1H and ^{13}C ENDOR Investigations of Sterically Hindered Galvinoxyl Radicals†

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Abstract: A variety of overcrowded novel galvinoxyl radicals have been synthesized. Steric requirements of bulky substituents have been studied by means of ESR, ENDOR, TRIPLE, and ENDOR-induced ESR spectroscopy. From ^1H and ^{13}C ENDOR measurements in nematic and smectic phases of liquid crystals anisotropic hyperfine contributions could be determined. The results suggest that steric interactions cause different geometrical arrangements within the galvinoxyl moiety. It is shown that one of the galvinoxyls exists in two stable conformations which can be discriminated by ENDOR-induced ESR. In case of significantly *differently* twisted aroxy rings (0–30°/80°) the galvinoxyl radical resembles a phenoxyl-type radical with equilibrating quinoid/benzoid rings rather than being a real delocalized system. This is accompanied by unusual relaxation properties of the central carbon atom.

ENDOR and TRIPLE resonance techniques have proved to be not only useful for the investigation of the static properties of organic radicals but also can be extended to the studies of temperature-dependent geometrical changes, e.g., in hybridization, or rapid structural interconversions.

Since dynamic intramolecular processes can affect widths and positions of spectral lines, detailed knowledge of the mechanisms involved in these dynamics is an essential prerequisite for an unambiguous analysis of complex ESR and ENDOR spectra. In recent papers we have shown that the spectra of galvinoxyl radicals are significantly altered when bulky substituents are introduced.[1-3] We have now prepared several novel galvinoxyls with different space-filling substituents. This enabled us to study steric effects of groups with different steric requirements. For the purpose of ^{13}C ENDOR investigations we have synthesized several ^{13}C labeled compounds. ^{13}C hyperfine coupling constants are known to be very sensitive to structural changes within the carbon skeleton.[4] Finally measurements in liquid-crystalline solutions have been performed, yielding information about the anisotropic hyperfine interactions, especially of the ^{13}C nucleus. For comparison with the galvinoxyls similarly structured phenoxyls have been investigated. In this context we want to demonstrate that steric interactions may cause a drastic change of the magnetic behavior of the galvinoxyl system; strictly speaking, the galvinoxyl may tend to behave like a phenoxyl-type radical.

Experimental Section

The mass spectra were recorded on a CH 5-DF Varian-MAT spectrometer. The ^1H NMR spectra were recorded on a Varian XL 100. The ^{13}C NMR spectra were taken on a Bruker WH-270 with a 10-mm diameter sample tube and $CDCl_3$ or $CDCl_3/Me_2SO\text{-}d_6$ solvent.

The spectrometer used for ESR, ENDOR, and TRIPLE basically consists of a Bruker ER 220 D ESR spectrometer equipped with a Bruker cavity (ER 200 ENB) and home-built NMR facilities described elsewhere.[5] ENDOR spectra were accumulated by using a Nicolet Signal Averager 1170 employing 1K data points; typically 32 sweeps were taken, 30 s per scan. The temperature was varied with a Bruker B-VT 1000 temperature control unit, constant to ±1 K and checked by means of a thermocouple.

Preparation of Compounds. Previously we have shown that a variety of the precursors of galvinoxyl radicals, viz., the galvinols, can be obtained via an organometallic synthetic pathway.[6] According to this procedure carboxylic esters are treated with (2,6-di-*tert*-butyl-4-lithiophenoxy)trimethylsilane to give the respective carbinols. Subsequently the protecting trimethylsilyl groups are eliminated, yielding the galvinols. To obtain the ^{13}C labeled galvinols, the respective ^{13}C labeled carboxylic esters have been used, which were synthesized by a Grignard reaction from the appropriate halide and $^{13}CO_2$ followed by esterification. The galvinol **1c** was prepared by a cleavage reaction from tris(3,5-di-*tert*-butyl-4-hydroxyphenyl)methane-^{13}C.[7] The syntheses of the ^{13}C labeled galvinol **6c**[2] and the ketone **6e**[8] were described previously. The ^{13}C labeled ketone **5e** was obtained by the reaction between the ^{13}C labeled carboxylic acid, trifluoroacetic acid anhydride, and 2,6-di-*tert*-butylphenol.[9] The galvinol **2a** was recently synthesized by a different pathway.[10]

(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methane-^{13}C (1c). Bis(3,5-di-*tert*-butyl-4-

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† Dedicated to Professor G. Manecke in honor of his 65th birthday.

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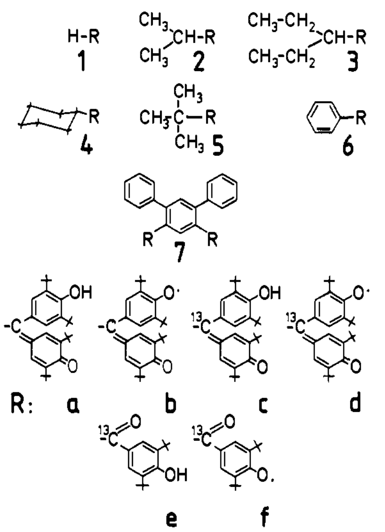

Figure 1. Numbering scheme of compounds.

hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-methane-^{13}C (0.1 g), 5 g of zinc dust, and 10 mL of concentrated acetic acid yielded 0.08 g of tris(3,5-di-*tert*-butyl-4-hydroxyphenyl)methane-^{13}C. This compound was treated with an excess of alkaline $K_3[Fe(CN)_6]$ solution, followed by reduction with NaI/acetic acid in benzene to give **1c** and byproducts. Purification by thick-layer chromatography (SiO_2/benzene) yielded 0.02 g of **1c**.

2-[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]propane (2a). 2-Methylpropanoic acid methyl ester (0.5 g), 7.14 g of (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane, 12 mL of *n*-butyllithium in *n*-hexane (20%), and 4 mL of (*N*,*N*,*N'*,*N'*-tetramethyldiamino)ethane, followed by elimination of the trimethylsilyl groups with KOH/methanol (5%, 1 h, 25 °C), careful acidification, and subsequent column chromatography (SiO_2/toluene) yielded 0.9 g of **2a**; mp 148 °C. Anal. Calcd: C, 82.70; H, 10.41. Found: C, 82.44; H, 10.26. Mass spectrum (70 eV), *m/e* 464 (M^+), Galvinol moiety: ^{1}H NMR (CCl_4). δ 7.52 (d, 1 H, $J = 3$ Hz, quinoid), 6.86 (s, 2 H, aryl), 6.60 (d, 1 H, $J = 3$ Hz, quinoid), 5.21 (s, 1 H, OH), 1.46 (s, 18 H, *t*-Bu), 1.34 (s, 9 H, *t*-Bu), 1.09 (s, 9 H, *t*-Bu). Alkyl group: ^{1}H NMR (CCl_4) 3.58 (septet, 1 H, $J = 7$ Hz, CH) and 1.15 (d, 6 H, $J = 7$ Hz, CH_3).

2-[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl-^{13}C]propane (2c). 2-Bromopropane (7.4 g), 1.45 g of Mg, and $^{13}CO_2$ from 10 g of $Ba^{13}CO_3$ yielded 3.52 g of 2-methylpropanoic acid-*carboxyl*-^{13}C; 0.6 g of this acid, 0.7 mL of trimethylsilyl chloride, and 0.85 mL of triethylamine gave the respective trimethylsilyl ester. Following the procedure of **2a** the yield of **2c** was 0.4 g.

3-[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]pentane (3a). 2-Ethylbutanoic acid (0.6 g), 0.7 mL of trimethylsilyl chloride, and 0.85 mL of triethylamine gave 2-ethylbutanoic acid trimethylsilyl ester; the obtained ester, 7.14 g of (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane, 12 mL of *n*-butyllithium in *n*-hexane, and 4 mL of (*N*,*N*,*N'*,*N'*-tetramethyldiamino)ethane, followed by elimination of the trimethylsilyl groups with dilute hydrochloric acid and column chromatography (SiO_2/toluene) yielded 0.8 g of **3a**; mp 176 °C. Anal. Calcd: C, 82.87; H, 10.64. Found: C, 82.64; H, 10.74. Mass spectrum (70 eV), *m/e* 492 (M^+). Galvinol moiety: ^{1}H NMR (CCl_4) δ 7.52, 6.90, 6.63, 5.22, 1.47, 1.34, 1.11 (cf. **2a**). Alkyl group: ^{1}H NMR (CCl_4) 3.04 (quintet, 1 H, $J = 7$ Hz, CH), 1.54 (quintet, 4 H, $J = 7$ Hz, CH_2), and 0.98 (t, 6 H, $J = 7$ Hz, CH_3).

[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]cyclohexane (4a). Cyclohexanecarboxylic acid methyl ester (0.7 g) was treated in a manner similar to the preparation of **3a**; yield 0.7 g of **4a**; mp 186 °C. Anal. Calcd: C, 83.28; H, 10.38. Found: C, 83.56; H, 10.48. Mass spectrum (70 eV), *m/e* 504 (M^+). Galvinol moiety: ^{1}H NMR (CCl_4), δ 7.47, 6.83, 6.52, 5.17, 1.46, 1.33, 1.07 (cf. **2a**). Cyclohexyl group: ^{1}H NMR (CCl_4) 3.1 (m, 1 H) and 1.5–1.9 (10H(?)).

2-[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl-^{13}C]-2-methylpropane (5c). 2-Methyl-2-bromopropane (6.9 g), 1.2 g of Mg, and $^{13}CO_2$ from 5 g of $Ba^{13}CO_3$ yielded 1.24 g of 2,2-dimethylpropanoic acid-*carboxyl*-^{13}C; 0.5 g of the ^{13}C labeled acid, 0.7 mL of trimethylsilyl chloride, and 0.8 mL of triethylamine gave the respective trimethylsilyl ester, which was treated as described for **3a**; yield 0.2 g of **5c**. **5a**, Galvinol moiety: ^{1}H NMR (CCl_4) δ 7.79, 6.65, 6.40, 5.16, 1.47, 1.34, 1.04 (cf. **2a**). Alkyl group: ^{1}H NMR (CCl_4) 1.38 (s, 9 H).

4',6'-Bis[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]-*m*-terphenyl (7aa). 4',6'-*m*-Terphenyl dicarboxylic acid dimethyl ester (1 g) was treated as described for the preparation of **3a**; yield 2.7 g of **7aa**; mp 255–257 °C. Anal. Calcd: C, 85.19; H, 8.84. Found: C, 85.46; H, 9.05. Mass spectrum (70 eV), *m/e* 1070 (M^+).

1-(2,6-Di-tert-butyl-4-hydroxyphenyl)-2,2-dimethylpropan-1-one-1-^{13}C (5e). 2,2-Dimethylpropanoic acid-*carboxyl*-^{13}C (2.06 g), 2.8 mL of trifluoroacetic acid anhydride, and 3.1 g of 2,6-di-*tert*-butylphenol gave, after purification by column chromatography (SiO_2/toluene), 2.3 g of **5e**; mp 131 °C.

The chemical properties of the ^{13}C labeled compounds are identical with those of the unlabeled compounds, cf. ref 11 for the unlabeled ketones. The ^{13}C contents of the labeled compounds (**1c**, **2c**, **5c**, and **5e**) were determined by mass spectroscopy at low voltages (<30 eV), where the ejection of hydrogen is no longer observed. The results were as follows: **1c**, (89 ± 3)%; **2c**, 97%; **5c**, 97%; **5e**, 98%. The lower ^{13}C contents of **1c** is due to the lower isotopic enrichment of the $Ba^{13}CO_3$ employed as starting material.

The galvinoxyl and phenoxyl radicals were prepared by oxidizing carefully degassed solutions of the galvinols or phenols with lead dioxide. To obtain **7ab** free from **7bb**, only part of the solution of the galvinol **7aa** was oxidized and then mixed with another excess part of that solution.

Results and Discussion

^{13}C NMR Measurements of Bis(galvinol) 7aa. The ^{13}C NMR investigation of the highly overcrowded bis(galvinol) **7aa** is particularly interesting. From the proton-noise-decoupled ^{13}C NMR spectrum (64,89 MHz, $CDCl_3$) 47 signals can be extracted. By taking a $^{13}C\{^{1}H\}$ off-resonance spectrum ("NORD")[12] 24 singlets can be assigned to quaternary carbons. Two signals at 186 and 186.3 ppm, respectively, unambiguously are caused by two different carbonyl carbon atoms. The intensity ratio of the latter of roughly 2:1 at 265 K indicates two different species to exist in a 2:1 concentration ratio in the sample under study. (The two carbons can be assumed to have the same relaxation behavior because the environments are quite similar.) By using NMR shift reagents[13] it can actually be shown that the carbonyl groups belong to different types of molecules. From the temperature dependence of the spectra is is obvious that these species are interconverting; hence they are different conformations of **7aa**.

The total number of signals demonstrates that the two species must be symmetric. Assuming either C_2 or C_s symmetry for the molecule, two different arrangements of the benzoid and quinoid rings in the galvinol moieties are conceivable. Provided the phenyl rings in the *m*-terphenyl fragment and the hydroxyphenyl rings are freely rotating, one expects 25 ^{13}C NMR signals for each of the two symmetric conformations, i.e., a total number of 50 signals. This is in fair agreement with the number of 47 signals found experimentally. When adding a trace of KOH in Me_2SO-d_6 to the solution, exchange phenomena cause broadening and thus disappearance of all the lines belonging to the galvinol moieties. With an excess of base the dianion of **7aa** is formed and 13 sharp singlets are obtained, whereas 15 signals are expected from symmetry arguments. On acidification the original NMR spectrum of the neutral compound is recovered, clearly indicating the reversibility of the dianion formation.

Summarizing the NMR results, the bis(galvinol) **7aa** exists in two symmetric conformations of different thermodynamic stability. These conformations can be interconverted by restricted rotation of the galvinol moieties or via a base-catalyzed proton-transfer process. Additional evidence for the strong steric hindrance within this molecule is found during the ENDOR studies of the first oxidation step, viz., the monoradical **7ab**, vide infra.

Measurements and Assignments of Isotropic Hyperfine Coupling Constants. The isotropic hyperfine coupling constants of the compounds under study have been measured by ENDOR spectroscopy in the solvents toluene and mineral oil (Table I). Relative

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(13) Roth, K. *Anal. Chem.* **1976**, *48*, 2277.

Table I. Hyperfine Coupling Constants (MHz)[a]

compd	T, K	solvent	galvinoxyl (phenoxyl) moiety ^{13}C	H_m	$H_{t\text{-Bu}}$	substituent
1d	190	toluene	−27.79[b]	+3.76 (4)	+0.14 (36)	
2d	195	toluene	−24.48	+4.02 (2), +2.65 (2)	(+0.17)[c]	−1.46 (1), (+0.17)[c]
	310	min. oil	−22.42	+3.32 (4)	(+0.16)[c]	−0.46 (1), (+0.16)[c]
3b	195	toluene		+3.43 (4)	+0.13	−1.27 (1), +0.38
	330	min. oil		+4.11 (2), +2.72 (2)		
4b	205	toluene		+4.16 (2), +2.38 (2)	+0.15	−1.31 (1), +0.61, +0.29
	310	min. oil		+4.51 (2), +2.00 (2)	+0.16	+0.49
5d	195	toluene	−16.95	+4.80 (2), +1.38 (1), +0.35 (1)	+0.15	+0.80 (9)
	280	toluene	−17.08	+2.91 (4)	+0.20	+0.76 (9)
6d	200	toluene	−27.73[b]	+3.57 (2), +3.71 (2)	+0.13	+0.56, −0.20, +0.62
7ab[d]	220	toluene		+4.31, +4.20, +2.98, +2.78	0.15	0.52
				+3.85, +3.75, +3.60, +3.34	0.12	0.38
5f	205	toluene	−16.23	+5.62 (2)	+0.19 (18)	+0.54 (9)
6f	205	toluene	−17.09	+5.64 (2)	+0.21	

[a] Measured by ENDOR, accurate within ±0.01 MHz. The number of equivalent protons is given in parentheses. [b] Measured at 230 K. [c] Not resolved, see text. [d] Two conformations, see text.

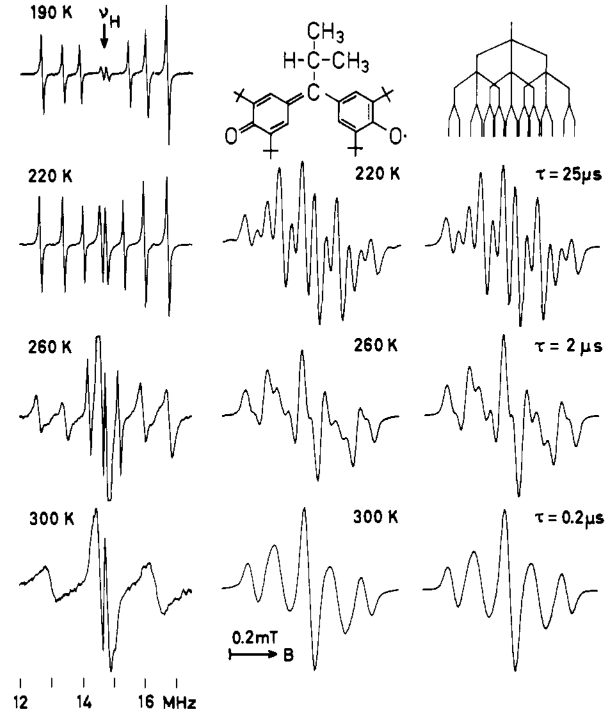

Figure 2. ENDOR spectra (left) and experimental (center) and computer-simulated (right) ESR spectra of **2b** for a series of different temperatures. The simulated spectra were obtained by using the coupling constants given in Table I, taking account of their temperature dependence (Table II) and adjusting the lifetime parameter τ to match the experimental spectra.

Table II. Temperature Coefficients of the Hyperfine Coupling Constants (kHz/K)[a]

compd	H_m[b]	H_β	^{13}C[c]
2d	+2.2, −2.8	+8.5	+16.7
3b	+5.4, −6.4	+6.4	
4b	+2.4, −3.0	+9.6	

[a] da/dT, measured by ENDOR, solvent toluene (180–250 K), accurate within ±0.1 kHz/K. [b] Same ordering as in Table I. [c] Toluene (200–300 K), ±0.2 kHz/K.

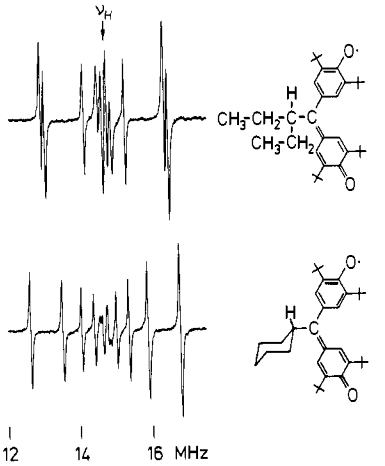

Figure 3. ENDOR spectra of **3b** (top; toluene, 220 K) and **4b** (bottom; toluene, 210 K); B_{NMR} = 0.4 mT (rotating frame).

sign determination was achieved by means of the general TRIPLE technique (vide infra),[14] and the absolute signs given are established by NMR[15] and liquid-crystal measurements.[7] The ESR and ENDOR spectra of **2b**–**5b** show a striking temperature dependence of coupling constants and line shapes. For example, the spectra of **2b** are depicted in Figure 2 for a series of temperatures. The low-temperature ESR spectrum of **2b** can be analyzed, favorably by using the ENDOR data, in terms of a triplet of triplets of doublets. Consequently, the four galvinoxyl ring protons cannot be equivalent (vide infra). The temperature dependence of the coupling constants becomes obvious when regarding the ENDOR spectra, being most pronounced for the third largest splitting (Table II). Moreover, the ENDOR lines belonging to the largest two splittings show a selective broadening and finally coalescence with increasing temperature. Low-temperature ENDOR spectra of **3b** and **4b** are reproduced in Figure 3.

The assignment of hyperfine coupling constants to the ring and *tert*-butyl protons within the galvinoxyl moiety is based on a comparison with Coppinger's radical (**1b**) and other galvinoxyl systems. At low temperatures, the galvinoxyl ring protons of **2b**–**6b** are inequivalent, whereas at high temperatures an average coupling constant is measured, except for **3b**. The assignment of the negative couplings to the (single) β protons of the alkyl substituents in **2b**–**4b** is based on computer simulations of the ESR spectra and is in accordance with an analogous assignment in cyclopropylgalvinoxyl.[3] The remaining coupling constant of **3b** was assigned to the methylene γ protons. The ENDOR lines of the methyl γ protons in the isopropyl group of **2b** coincide with those of the *tert*-butyl groups within the ENDOR line width, but resolution could be achieved by using liquid-crystalline solvents (vide infra; a_{CH} = +0.19 MHz, $a_{t\text{-Bu}}$ = +0.14 MHz, 8CB, 298 K). Except for the β-proton coupling, the ENDOR spectra of **4b** reveal

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[15] Kreilick, R. W. *Mol. Pys.* **1968**, *14*, 495.

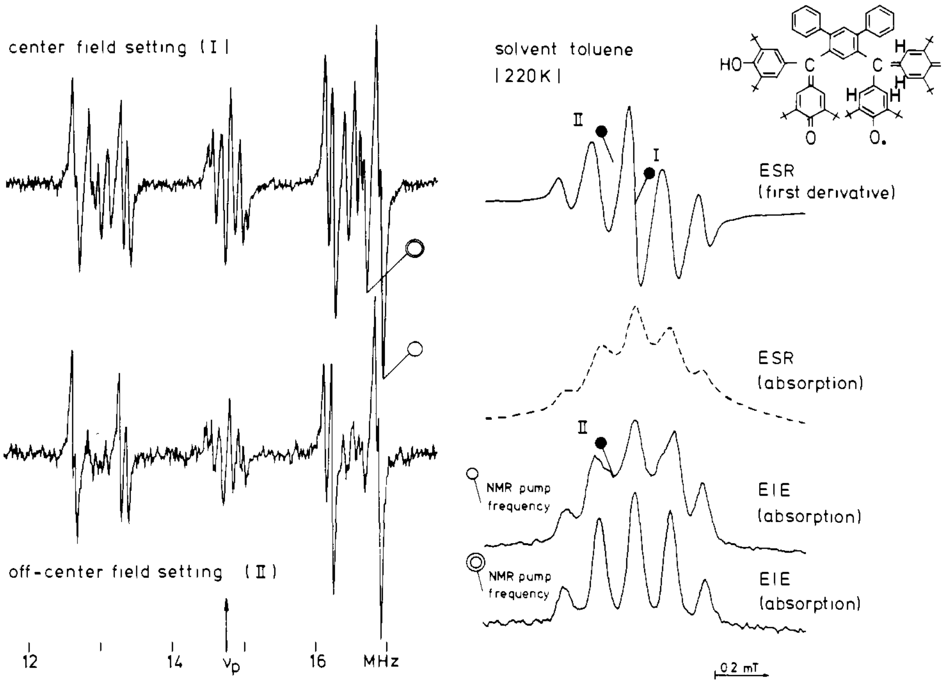

Figure 4. ENDOR (left), ESR, and ENDOR-induced ESR (EIE) spectra (right) of **7ab** (toluene, 220 K). Note that ENDOR lines from two different conformations show up at the center field setting (top), whereas those due to one of the conformations are selectively obtained at an off-center field setting (bottom), see text.

two further coupling constants arising from the cyclohexyl group. They might tentatively be assigned to axial and equatorial γ protons. The relatively large hyperfine coupling of the *tert*-butyl γ protons (substituent) in **5b** is responsible for the low resolution of the ESR spectrum;[1] the assignment was confirmed by computer simulations.

Regarding compound **7ab** one expects a more symmetric species when compared to the respective diamagnetic precursor **7aa** (vide supra) because of the delocalization of the unpaired spin over the entire galvinoxyl moiety resulting in two equivalent aroxy rings. The experimental results, however, clearly establish that two different monoradicals are present in the sample under study. While the ESR spectrum is relatively insignificant—actually one finds the typical five-line hyperfine pattern of a galvinoxyl-type radical but without the proper 1:4:6:4:1 intensity ratio—the ENDOR spectrum surprisingly exhibits eight ENDOR line pairs for only four aroxy ring protons (Figure 4). Even if one assumes all four protons to be inequivalent owing to steric hindrance, one would expect a maximum number of only four line pairs. Hence there are two different conformations. This interpretation is confirmed by general TRIPLE and ENDOR-induced ESR measurements, which are described in the next paragraph.

In a general TRIPLE experiment the sample is additionally irradiated with a strongly saturating NMR field at one of the resonance frequencies of one nucleus ("pumping field"), while the second rf field is swept through the resonance region ("scanning field"). This technique yields not only direct information about relative signs of hyperfine coupling constants but can also be used for discrimination between different species within one sample. In the present case pumping of one of the ENDOR lines affects only seven aroxy ring proton lines, i.e., only seven ENDOR amplitudes are decreased or increased by the pumping field. The same holds if one switches the pumping radio frequency to a suitable ENDOR line belonging to the other set of lines. It stands to reason that only those ENDOR lines are affected by an additional pumping radio frequency that belong to the species causing the absorption to which the pumping frequency is being adjusted. An even more convincing experiment is ENDOR-induced ESR.[16] In this type of experiment the radio frequency is adjusted to the peak of a suitable ENDOR line, and the variations in the amplitude of the ENDOR signal are recorded as the static external field is swept through the range of the entire ESR spectrum. Hence by setting the radio frequency on one particular ENDOR line of one species and running the external field, one obtains an ESR-type spectrum (in absorption) only of this species (Figure 4). Switching the pumping frequency to another suitable ENDOR line yields the ENDOR-induced ESR spectrum of the other species. Now it is possible to select an external field setting resulting in minimum ESR absorption of one species. Running the ENDOR spectrum again under these conditions, one actually finds essentially the ENDOR spectrum of the monoradical that still shows considerable ESR absorption at the external field position selected (Figure 4). It is noteworthy that line widths and positions in the ENDOR spectrum of **7ab** are essentially independent of temperature in a temperature range suitable for high-resolution ENDOR experiments (190–250 K, toluene).

As we have reported previously, diamagnetic precursors bearing more than one galvinoxyl fragment can be oxidized to give the respective biradicals and triradicals.[2,17] From the isotropic solution ESR/ENDOR measurements $|J| >> |a|$ and from the rigid matrix measurements of the bis(galvinoxyls), usually D values of about 30–100 MHz could be deduced. Complete oxidation of **7aa** yields the biradical **7bb**. Since the electron–electron dipolar interaction (D = 60 MHz) causes broadening of fluid solution ESR and ENDOR lines (increased W_e), detection of different conformations failed. The ESR spectrum of **7bb** taken in glassy solution (toluene, 150 K) is apparently due to one single species. Under these conditions the ENDOR resonance absorption at the free proton frequency could be observed. The occurrence of this line gives additional evidence of the existence of a biradical species to be present in the sample under study.[17b]

^{13}C ENDOR Measurements. In order to get a more detailed insight into the spin density distributions, several ^{13}C labeled compounds have been investigated (Table I and Figures 5 and 6). It should be noted that the ^{13}C coupling of **5d** shows a markedly different behavior from those of other galvinoxyls not

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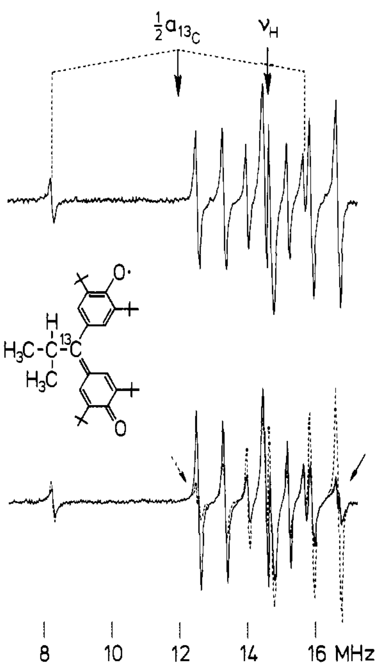

Figure 5. ENDOR and general TRIPLE spectra of **2d** (toluene, 230 K). The arrows in the TRIPLE spectra indicate the setting of the pump frequency in the two experiments (solid and dashed lines, respectively); B_{NMR} (scan) = 0.4 mT, B_{NMR} (pump) = 0.6 mT.

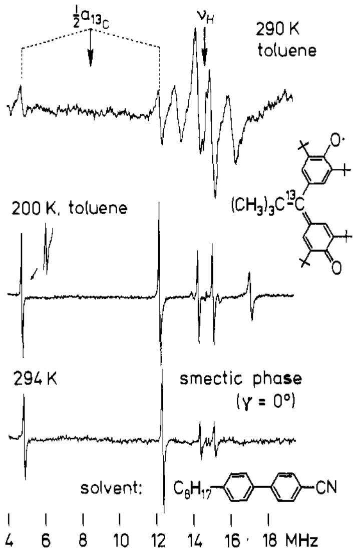

Figure 6. ENDOR spectra of **5d** in toluene and in the smectic phase of 4-cyano-4′-octylbiphenyl (bottom). Note that the high-frequency ^{13}C ENDOR line accidentally coincides with one of the ^{1}H ENDOR lines in the center spectrum. The inset in the center spectrum shows the low-frequency ^{13}C ENDOR line recorded in natural abundance (**5b**; 400 scans, time constant 40 ms).

only with respect to its magnitude but also with respect to the relaxation properties. Thus, it is normally found that higher radio frequency fields are needed to achieve saturation of ^{13}C ENDOR lines and that the optimum ENDOR response occurs at higher temperatures as compared to protons.[2,4] Moreover, the ^{13}C ENDOR lines are broader (width ~ 120 kHz) than the optimum ^{1}H ENDOR signals.[7] On the other hand, the maximum ^{13}C ENDOR response of **5d** occurs at a somewhat lower temperature (~190 K, toluene) than that of the protons (200–210 K), and an unsaturated line width of about 40 kHz was obtained. A similar behavior was previously observed for a phenoxyl radical (**6f**).[8] Since the ^{13}C ENDOR relaxation behavior as compared with ^{1}H ENDOR is mainly governed by the relative magnitudes of the hyperfine anisotropies, i.e., $\mathrm{Tr}(A'^2)$,[18] it can be concluded that the hyperfine anisotropy and therefore the π spin population at the central carbon atom of **5d** is exceptionally small (vide infra). For comparison, the coupling constants of the phenoxyls **5f** and **6f** are included in Table I.

Table III. Hyperfine Coupling Constant Shifts (MHz)[a]

compd	$\Delta a(^{13}\mathrm{C})$	$\Delta a(H_{\mathrm{m}})$	Δa-($H_{t\text{-Bu}}$)	Δa-(H_β)	Δa-(H_γ)
1d[b]	+4.40[c]	+0.38			
2d	+0.39		0.00	+0.11	+0.10
3b		0.00, −0.11	0.00	(+0.1)	
5d	+0.07		≤0.01		≤0.01
6d	+1.1[c]	+0.06	+0.03		*d*
5f	+0.24	+0.35	+0.06		+0.01
6f	+0.31	+0.43	+0.06		*e*

[a] Measured by ENDOR. Solvent: smectic phase of 4-cyano-4′-octylbiphenyl, 293 K. [b] Solvent: nematic phase IV, 298 K. [c] Measured by ESR. [d] Phenyl ring: ortho, +0.24 MHz; para, +0.01 MHz. [e] Phenyl ring: ≥0.30 MHz (presumably ortho positions).

Recently we succeeded in performing ^{13}C ENDOR spectroscopy on unlabeled benzoyl-di-*tert*-butylphenoxyl radical.[8] Since the ^{13}C ENDOR relaxation properties of **5d** are quite similar to those of **6f** we felt encouraged to look for natural abundance ^{13}C ENDOR signals of **5b**. By adjusting the external field off-center on a ^{13}C ESR satellite position we actually found the low-frequency ^{13}C ENDOR line of unlabeled *tert*-butylgalvinoxyl (**5b**), whereas the high frequency ^{13}C signal coincided with a proton ENDOR line (Figure 6). Moreover, by increasing the number of accumulated scans two additional ^{13}C ENDOR lines could be detected (a = 14.35 MHz). It stands to reason that these lines could not be assigned to molecular positions.

The ^{13}C coupling of **2d** shows behavior which is in between those of "normal" galvinoxyls (**1d**, **6d**) and **5d**. Its magnitude is substantially smaller than that of **1d** (Table I), and the relaxation properties of the respective ENDOR lines indicate a somewhat smaller hyperfine anisotropy (line width about 80 kHz, optimum temperature about 220 K, toluene). Moreover, in contrast to all other ^{13}C labeled galvinoxyls investigated so far,[2,7] the ^{13}C coupling constant of **2d** is strongly temperature dependent. Its temperature coefficient amounts to +17 kHz/K (Table II) compared to values ranging from −2 to −5 kHz/K which are normally found.

Liquid-Crystal Measurements of Anisotropic Hyperfine Shifts. The investigation of the galvinoxyls and phenoxyls has been extended to liquid-crystalline solutions. The ESR and ENDOR spectra of radicals dissolved in nematic or smectic phases show a shift of the observed hyperfine coupling constants owing to anisotropic hyperfine contributions.[19,20] The anisotropic shifts can be determined with reference to a measurement in the isotropic phase or more accurately by using a smectic A phase.

$$\Delta a = \tfrac{2}{3}[\bar{a}(0°) - \bar{a}(90°)] \qquad (1)$$

The interpretation of these shifts is rather straightforward in the case of ^{13}C nuclei, because their anisotropic hyperfine tensors are mainly determined by the π spin populations at these atoms, whereas contributions from atoms further removed cannot be neglected in the case of protons.[21] If axial symmetry of the hyperfine tensor is assumed, the anisotropic ^{13}C hyperfine shift is given by

$$\Delta a = O_{33}A'_{33} \qquad (2)$$

where

$$A'_{33} = 181.6\rho_\pi \qquad (3)$$

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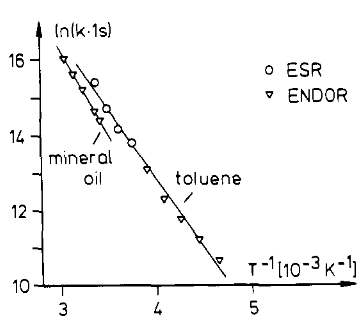

Figure 7. Arrhenius plots of ln k vs. T^{-1} for **2b**.

if contributions from neighboring atoms are neglected.[22]

Concerning the sterically hindered galvinoxyls, the spin population at the central carbon atom of the galvinoxyl moiety appears to be of special interest. The isotropic ^{13}C hyperfine couplings, however, do not give a direct measure of the spin population at this atom but rather depend on the spin populations at the neighboring centers, too.[23] Considering the results for **1d**, **6d**, **2d**, and **5d**, one finds a strong decrease of the anisotropic ^{13}C hyperfine shifts in this series (Table III). The lower value for **6d** as compared to **1d** is certainly due to a lower value of the ordering parameter ($O_{33} = -0.08$ instead of $O_{33} = -0.31$)[7] because of the phenyl substituent and higher twist angles of the phenoxy groups. Although the ordering parameter of **5d** might be still somewhat smaller, one can safely assume that the ansiotropic hyperfine interaction and therefore the π spin population at the central carbon atom is much smaller than in **1d** or **6d**. Similarly, the small shifts observed for the phenoxyls **5f** and **6f** indicate low π spin populations.

It is noteworthy that these results concerning the hyperfine shifts are in agreement with the different relaxation behavior of the ^{13}C nuclei discussed above. Remarkably strong ^{13}C ENDOR signals of **5f**, **6f**, **2d**, and **5d** were obtained in the smectic phase (Figure 6). This behavior is quite unusual, since normally even the viscosity of nematic phases is too high to allow for a strong ^{13}C ENDOR response.[7] However, it is in accordance with the observations made in isotropic solvents and supports the conclusions drawn with respect to the anisotropic hyperfine interaction, i.e., Tr(A'^2).

Line-Shape Analysis and Determination of Activation Parameters. A brief survey on the methods employed for extracting kinetic data of jump processes from ESR and ENDOR line shapes has been given in our recent paper.[3] In the present investigation, a fairly accurate determination of activation parameters was only possible in the case of isopropylgalvinoxyl. Regarding the other radicals, reliable ENDOR line-width analyses could not be carried out in a sufficiently wide temperature range, and their ESR spectra are only poorly resolved. The kinetic analysis of isopropylgalvinoxyl (**2b**) was performed by means of ENDOR line-width measurements in the slow-jump (solvent toluene) and fast-jump region (mineral oil) and additionally by computer simulations of the ESR spectra (Figure 2). A two-jump model was assumed, although a four-jump model might be more appropriate, since four protons (i.e., four sites) are involved.[3,24] The following results were obtained (Figure 7). Toluene: $E_A = 31 \pm 2$ kJ/mol, $k_0 = 1.1 \times 10^{12}$ s^{-1}, $\Delta H^{\ddagger} = 29 \pm 2$ kJ/mol, $\Delta S^{\ddagger} = -21 \pm 6$ J mol^{-1} K^{-1}. Mineral oil: $E_A = 37 \pm 2$ kJ/mol, $k_0 = 8.5 \times 10^{12}$ s^{-1}, $\Delta H^{\ddagger} = 35 \pm 2$ kJ/mol, $\Delta S^{\ddagger} = -6 \pm 6$ J mol^{-1} K^{-1}. These values are comparable in magnitude to those of cyclopropyl-substituted galvinoxyls reported previously.[3]

Coalescence of the ring proton lines was found in the ENDOR spectra of *tert*-butylgalvinoxyl (**5b**; ca. 240 K, toluene) and cyclohexylgalvinoxyl (**4b**; ca. 350 K, mineral oil), whereas the respective ENDOR lines of (1-ethylpropyl)galvinoxyl (**3b**) are still far from coalescence at 350 K (mineral oil). Thus, a comparison of some $\Delta G^{\ddagger}$ values of these radicals is possible: 240 K (toluene), 29 kJ/mol (**5b**); 33.9 kJ/mol (**2b**); 350 K (mineral oil), 36.8 kJ/mol (**2b**); 43 kJ/mol (**4b**); >48 kJ/mol (**3b**). These data show that there is no straightforward correlation of the bulkiness of the substituent with the free energy of activation. Apparently, the greater flexibility of the 1-ethylpropyl group as compared to the cyclohexyl group is responsible for the severe steric hindrance in (1-ethylpropyl)galvinoxyl. It should be noted that a stronger steric hindrance of open-chain substituents as compared to cyclic analogues was also found in studies of chemical reaction kinetics.[25]

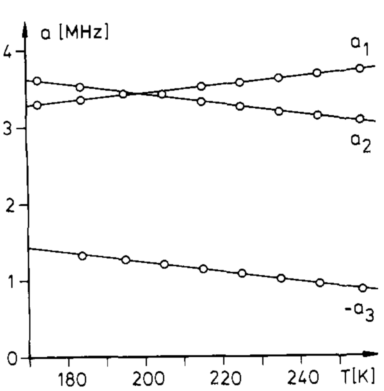

Figure 8. Temperature dependence of the hyperfine coupling constants of **3b**.

Temperature Dependence of Hyperfine Couplings. The temperature dependence of β-proton hyperfine couplings of alkyl groups undergoing restricted rotation is in general successfully described by assuming a $\cos^2 \theta$ dependence of the couplings[26] and performing a statistical procedure.[27] According to this model, the β-proton coupling should approach the value of a freely rotating methyl group at elevated temperatures.[28] Actually, the temperature dependence of the β-proton splitting in cyclopropylgalvinoxyls could be described in this way, although the agreement was not complete.[3] However, the absolute values of the β-proton coupling constants in **2b**–**4b** are much smaller than that of methylgalvinoxyl (6.44 MHz)[29] and are still decreasing when the temperature is increased.

The results obtained for the isotropic ^{13}C coupling constant of **2d** and the ^{13}C hyperfine shift (see Table III) indicate that the π spin population at the central carbon atom of **2d** is substantially smaller than **1d**. If a linear dependence of the isotropic ^{13}C coupling constant on the spin population at the central carbon atom (**1d**, −0.075; **5d**, ~0) is assumed, a rough estimate gives a reduction of the spin population ranging from about −0.05 (200 K) to −0.04 (300 K). This accounts in part for the anomalously low value of the β-proton coupling constant of the isopropyl group in **2d** and its temperature dependence. Moreover, since the temperature dependence of the ^{13}C and the ring proton couplings is evidently caused by a change in the equilibrium geometries (vide infra), the dihedral angle θ of the alkyl group (between the C–H bond and the carbon p_z orbital) is also affected. An explanation can then be given by assuming a locked conformation of the alkyl group with a dihedral angle θ larger than 60°, increasing with increasing temperature. This result for the secondary alkyl or cyclohexyl groups is in contrast to that for cyclopropyl galvinoxyl, where conformations with $\theta < 45°$ are preferred.[3]

A remarkable feature in Figure 8 showing the temperature dependence of the coupling constants of **3b** is the crossover of the lines for the galvinoxyl ring protons. There is no "coalescence" as in the case of line-shape effects due to dynamic processes, since

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Table IV. Calculated Spin Populations for Different Twist Angles in Galvinoxyls[a]

θ_A, deg	θ_B, deg	ζ_{center}	$\zeta_{m,A}$	$\zeta_{m,B}$
20	20	−0.07316	−0.04478	−0.04478
30	10	−0.07277	−0.05066	−0.03872
40	20	−0.07552	−0.05379	−0.03485
50	20	−0.07165	−0.06087	−0.02700
60	30	−0.06743	−0.06657	−0.02015
70	20	−0.03712	−0.07746	−0.00879
80	30	−0.01435	−0.08302	−0.00269
80	10	−0.01055	−0.08368	−0.00215
90	0	0.00000	−0.08567	0.00000

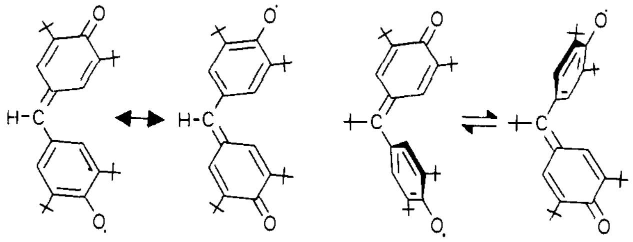
[a] HMO/McLachlan calculation with $\lambda = 1.2$, $h_O = 1.3$, $k_{CO} = 1.5$, and $k(\theta) = \cos\theta$.

the effect is not accompanied by line broadening. Probably the twist angles of the two aroxy rings are roughly equal at low temperatures and become increasingly different at higher temperatures.

Discussion of the Molecular Structure of Galvinoxyls. In Coppinger's radical (**1b**), the unpaired electron appears to be completely delocalized over the two aroxy rings. MO calculations predict an appreciable amount of (negative) π spin population at the central carbon atom ($\rho = -0.0748$).[30] This is in agreement with the ^{13}C hyperfine anisotropy observed for the labeled compound **1d**.[7] While the two aroxy rings are equivalent, this does not strictly hold for the four ring protons. Although in liquid solution ESR and ENDOR measurements a line splitting due to an inequivalence has never been found, such a splitting could recently be observed by using a smectic phase.[31] Consequently, interior and exterior ring protons are slightly inequivalent (~100 kHz), but usually this cannot be observed because it is averaged out on the ESR/ENDOR time scale by a rapid rotation of the aroxy rings.

The introduction of a bulky substituent at the central carbon of the galvinoxyl moiety can have the following effects: The twist angles of the aroxy rings might be altered, possibly by a different amount, thus lowering the symmetry, and the barrier to internal rotation might be increased. Looking at phenylgalvinoxyl (**6b**), the ENDOR spectra now reveal a slight inequivalence of the ring protons even in isotropic solvents at low temperatures.[2,32] Evidently the barrier to internal rotation is somewhat higher than in Coppinger's radical (**1b**), but the aroxy rings are still evenly twisted. In the case of 2-biphenylgalvinoxyl, all four ring protons are inequivalent at low temperatures.[2] The larger inequivalence is ascribed to different twist angles of the aroxy rings, probably induced by the unsymmetrical substituent. However, the investigation of ^{13}C labeled phenyl and biphenylgalvinoxyls has proved that electronically both have to be regarded as real galvinoxyl systems, since the isotropic and the anisotropic ^{13}C couplings are essentially the same as those of Coppinger's radical. Moreover, the UV spectra of these radicals are quite similar.[1] As a matter of fact even the two different conformations of **7ab**, each of them having differently twisted aroxy rings, behave like "real galvinoxyls". The geometrical arrangements of the galvinoxyl fragments in these conformations are found to be completely locked at least referred to the ESR/ENDOR time scale.

On the other hand, the situation is quite different with *tert*-butylgalvinoxyl (**5b**). It had been concluded from low-temperature ^1H ENDOR and UV results that this system should be described more adequately as a phenoxyl radical.[1] Our ^{13}C ENDOR studies now definitely prove this assumption. The isotropic ^{13}C coupling is considerably different from those of the above-mentioned galvinoxyls, but it is nearly the same as that of the pivaloylphenoxyl **5f**. Moreover, judging from the anisotropic hyperfine shifts measured in liquid crystals and from the relaxation behavior, the anisotropic ^{13}C coupling is as small as in the phenoxyl. Consequently, the π spin population at the central carbon atom must be approximately zero. Finally, the isotropic ^{13}C coupling is essentially temperature independent, ruling out any change in hybridization or a flattening of the molecule with increasing temperature. The apparent equivalence of the two aroxy rings at higher temperatures is merely due to the fact that the jump process is reaching the fast limit on the ESR/ENDOR time scale, but there is no true "delocalization" of the unpaired electron. While the valence-bond structures of Coppinger's radical (**1b**) showing a quinoid and a benzoid ring are merely a formal description, there is a real equilibrium in the case of *tert*-butylgalvinoxyl (**5b**).



In order to get a more quantitative verification of these models, we have performed HMO/McLachlan calculations for a series of different twist angles (Table IV). Within the scope of these calculations, identical spin densities are obtained for the two meta (and ortho) positions of each ring. However, in agreement with the above-mentioned arguments a higher spin population in the more highly twisted ring is predicted, and for $\theta = 90°$ the limiting case of a phenoxyl-type radical is obtained. There is also a strong decrease of the π spin population at the central carbon atom for twist angles greater than about 60°. Consequently, the experimental results for **5d** can be accounted for by assuming twist angles of about 80° for the "phenoxyl" ring and 0–30° for the "quinoid" ring. The employed model is insufficient to achieve agreement for the quinoid ring; in particular, the marked inequivalence of the ring protons cannot be explained. It is known that McLachlan calculations are not reliable in cases of high twist angles, and the effects of π–σ delocalization would have to be taken into account.[33]

Conclusions

Steric requirements of bulky substituents result in changes of equilibrium geometries and in increased barriers to internal rotation. Provided the aroxy rings of the galvinoxyl moiety are drastically differently twisted (e.g., 30°/80°), the properties of the galvinoxyl change from those of a delocalized system to a phenoxyl-type radical with really equilibrating quinoid/benzoid rings. The more twisted aroxy ring bears the higher π spin population which tends to be zero at the central carbon atom. This spin distribution accounts for the vanishingly small ^{13}C anisotropic hyperfine shift and the attendant unusual relaxation behavior of the central carbon nucleus.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (Normalverfahren) and the Fonds der Chemischen Industrie, which is gratefully acknowledged.

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