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EPR and ENDOR Investigations of Dynamic Processes in Sterically Overcrowded Phenoxyl-Type Galvinoxyl Radicals

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The syntheses of *tert*-butylgalvinol with perdeuteriated *tert*-butyl groups and of 1,4-bicyclo[2.2.2]octanebisgalvinol are described. The EPR and ENDOR spectra of the corresponding galvinoxyl monoradicals reveal selective line broadening due to dynamic processes associated with hindered internal rotation of the phenoxy rings. Deuteriation of the central *tert*-butyl group in *tert*-butylgalvinoxyl gives rise to a substantial decrease of EPR line widths, allowing the determination of the kinetic parameters by means of line-shape analyses ($\Delta H^{+} = 21.8$ kJ mol^{-1}, $\Delta S^{+} = -32$ J mol^{-1} K^{-1}). The biradical 1,4-bicyclo[2.2.2]octanebisgalvinoxyl exhibits strong scalar and dipolar electron interactions ($D = 97$ MHz).

KEY WORDS EPR ENDOR Galvinoxyls Deuteriation Dynamic processes Biradicals

INTRODUCTION

Galvinoxyl, which is also known as Coppinger's radical,[1] has been widely used as a suitable organic doublet radical in magnetic resonance studies.[2,3] Its properties are significantly altered when bulky substituents are introduced at the central position.[4,5] The consequences of steric hindrance are particularly pronounced for *tert*-butyl or 1-adamantyl substituents, distorting the galvinoxyl moiety to an extent that at low temperatures the unpaired electron is essentially confined to one phenoxy ring. In other words, these species resemble phenoxyl-type radicals. With increasing temperature a dynamic process takes place, giving rise to an equilibration of the quinoid and the benzoid (phenoxyl) ring. This behaviour can be studied in detail by EPR and more advantageously by ENDOR (electron nuclear double resonance[6,7]) spectroscopy. These techniques also allow quantitative kinetic analyses of intramolecular dynamic processes.[7] The kinetic parameters (activation enthalpies and entropies) of a variety of substituted galvinoxyl radicals have, in fact, been determined from studies of the temperature dependence of EPR and ENDOR line shapes.[5,8]

However, quantitative kinetic data for *tert*-butylgalvinoxyl (**7a**) (apart from ΔG^{+} at the coalescence temperature) have not so far been accessible for the following reasons. In ENDOR spectroscopy strong line broadening and poor signal-to-noise ratios prevent reliable line-width analyses over a wider range of temperatures. Meaningful line-shape analyses cannot be performed for the EPR spectra, either, because the dynamic line-width effects are obscured by inhomogeneous line broadening caused by the central *tert*-butyl group. This problem might be overcome by deuteriation of the central *tert*-butyl group; a drastically higher resolution of the EPR spectrum of Coppinger's radical with perdeuteriated *tert*-butyl groups (*within* the galvinoxyl moiety) relative to the unlabelled compound has been demonstrated recently.[9]

In this paper we report the syntheses of *tert*-butylgalvinol with (a) a perdeuteriated *tert*-butyl group at the central position (**7b**) and (b) with all *tert*-butyl groups perdeuteriated (**7c**) and (c) of 1,4-bicyclo[2.2.2]octanebisgalvinol (**12**). A detailed EPR and ENDOR study of the intramolecular dynamic effects exhibited by the doublet radicals derived from these galvinols is described. Since the bisgalvinol can be oxidized further to generate a bisgalvinoxyl biradical, we wanted to study the steric influence on the scalar and dipolar electron interactions of this species, focusing on a comparison with a structurally related but sterically less demanding biradical.

EXPERIMENTAL

Compounds

Since the well established organometallic synthesis of galvinols involves the reaction of an appropriate ester with (2,6-di-*tert*-butyl-4-lithiophenoxy)trimethylsilane,[10] the key compound for the syntheses of the deuteriated *tert*-butylgalvinols **6b** and **6c** is [$^2H_9$]-2,2-dimethylpropanoic acid ethyl ester (**3**) (see Scheme 1). Compound **3** was prepared from *tert*-[$^2H_9$]butylmagnesium bromide and ethyl chloroformate. For the synthesis of the [$^2H_{45}$]galvinol **6c**, the deuteriated compound **5** is also required. A synthesis of **5** via Friedel–Crafts alkylation

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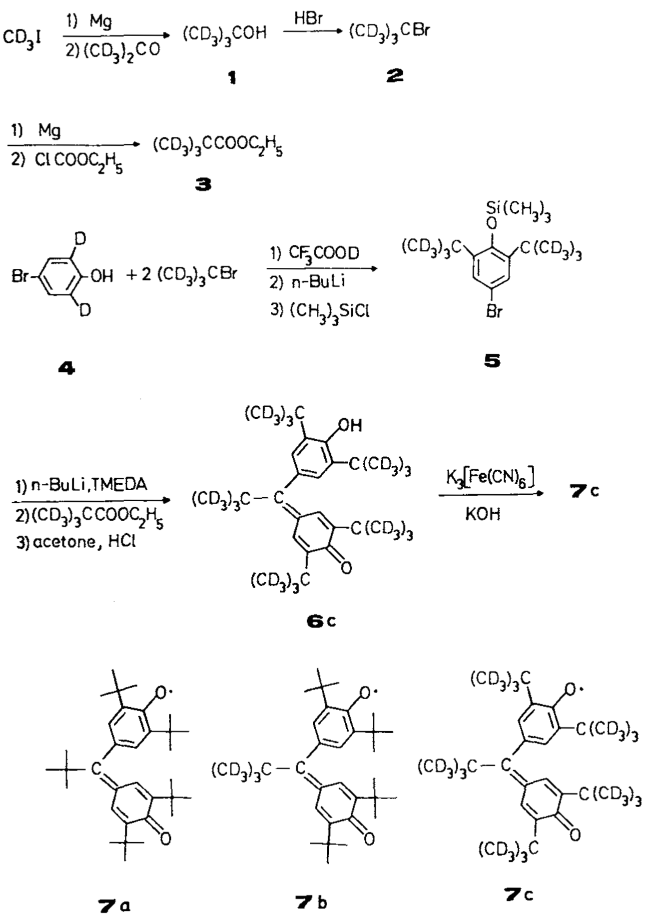


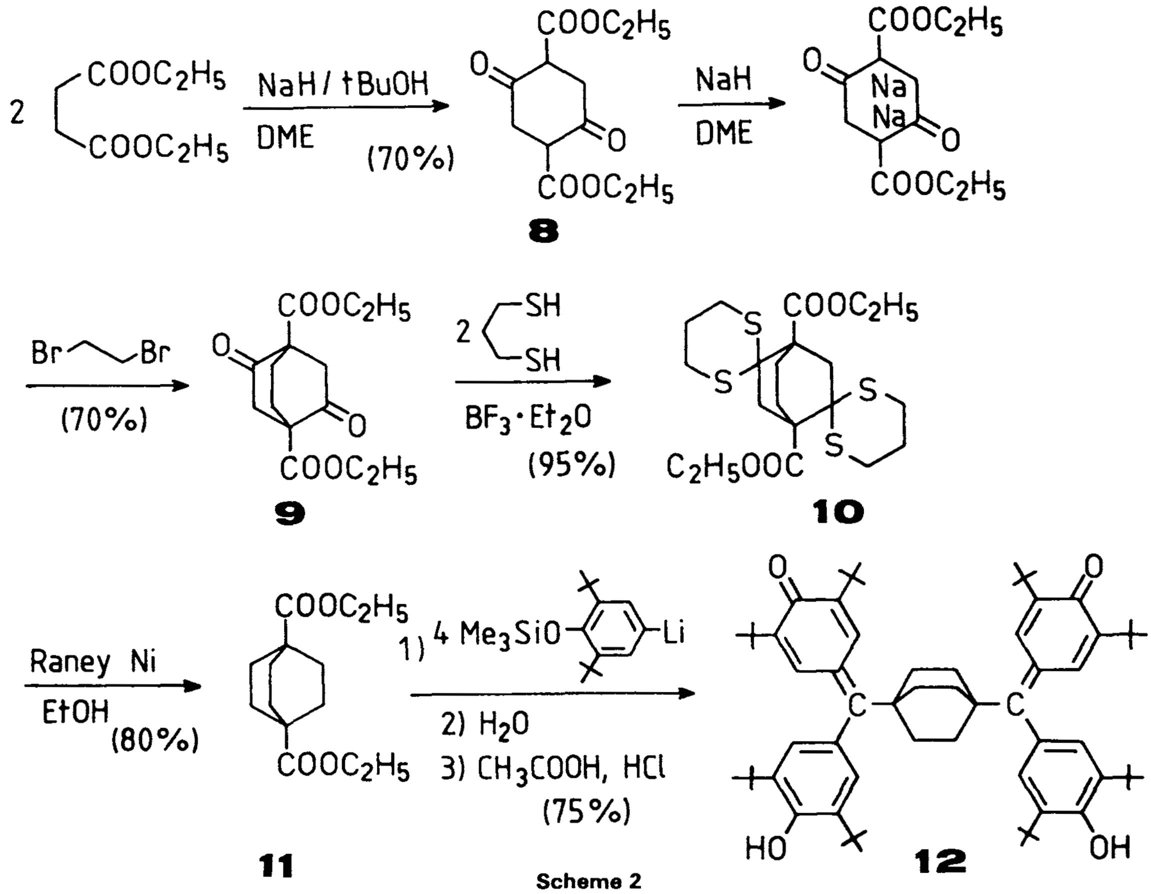
Scheme 1

of 4-bromo-[2,6-$^2H_2$]- phenol (**4**) with [$^2H_8$]isobutene has been described recently.[9] We have found that **5** can be obtained in a better yield with *tert*-[$^2H_9$]butyl bromide (**2**) as an alkylating agent in the presence of [^{2}H]trifluoroacetic acid.

The key compound for the preparation of the bisgalvinol **12** is 1,4-bicyclo[2.2.2]octanedicarboxylic acid diethyl ester (**11**), which was obtained by an improved synthesis as follows (Scheme 2). The dianion of **8**, prepared by self-condensation of diethyl succinate,[11] was reacted with 1,2-dibromoethane to introduce the ethano bridge.[12] Reduction of the two keto groups in **9** was achieved by the Wolfrom–Karabinos method via the dithiane **10** and subsequent desulphurization with Raney nickel.[13]

1. A 23.3 ml volume [$^2H_6$]acetone (0.32 mol) was added dropwise to [$^2H_3$]methylmagnesium iodide prepared from 20 ml of [$^2H_3$]methyl iodide (0.32 mol) and 11.7 g of Mg in diethyl ether (200 ml). Hydrolysis (with a saturated solution of NH_4Cl), removal of the ether and distillation yielded 17.3 g (65%) of **1**. B.p., 81–82 °C; $n_D^{20} = 1.3945$).

2. A 16.6 g amount of **1** (0.2 mol) was added to 59 g of concentrated H_2SO_4 and 103 g of 47% HBr (0.6 mol) with ice cooling. After stirring for 15 min, the product was isolated by distillation and dried over Na_2SO_4 and K_2CO_3. Yield: 20.4 g (70%). Degree of deuteriation: 95% (^{1}H NMR, from signal intensities of an equimolar mixture with *tert*-butanol).



Scheme 2

3. A 2.43 ml volume of **2** (0.02 mol) was reacted with 0.97 g of Mg in diethyl ether (40 ml). After refluxing for 30 min, the solution was transferred with Ar pressure to the dropping funnel of a second apparatus and added dropwise to 1.92 ml of ethyl chloroformate (0.02 mol) in diethyl ether (20 ml). After refluxing for 5 h, the reaction mixture was extracted with 100 ml of 5% NaOH. The organic layer was dried over Na_2SO_4 and distilled after removal of the solvent. Yield: 1.5 g (54%); b.p., 116 °C; $n_D^{20} = 1.3908$. Degree of deuteriation: 95% ($C_7H_5D_9O_2$, *m/z* 139; MS, EI at 80 eV).

5. A mixture of 3.6 g of **4** (20.4 mmol),[9,14] 7 g of [^{2}H]trifluoroacetic acid and 8.94 g of **2** (61.2 mmol) was stirred for 1 h at 110 °C under reflux. After cooling, 200 ml of pentane were added and the solution was washed with 100 ml of 10% NaOH. The organic layer was filtered through silica gel and the solvent was removed under vacuum. The crude product (2.6 g, yellowish oil) was dissolved in tetrahydrofuran (40 ml) and treated with butyllithium (6.4 ml, 15% in hexane) at −10 °C and then with chlorotrimethylsilane until a hydrolysed sample proved to be acidic. The solvent was removed under vacuum and the residue was dissolved in pentane, washed with water and dried over Na_2SO_4. Crystallization from the concentrated solution gave 0.68 g of **5** (8.8% with respect to **4**); m.p., 141 °C. Degree of deuteriation: 94.6% (MS, EI at 22 eV).

6b. (*tert*-[$^2H_9$]butylgalvinol). A 0.1 g amount of powdered (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane (0.28 mmol) was treated with butyllithium (0.35 ml, 15% in hexane) and *N,N,N′,N′*-tetramethylethylenediamine (0.08 ml) at −10 °C, and 0.02 g of **3** (0.14 mmol) was added after 45 s. After 30 min, 5 ml of pentane were added and the reaction mixture was washed with water. Removal of the protective trimethylsilyl groups was achieved by heating in acetone (10 ml) with a drop of concentrated HCl. Purification was by thin-layer chromatography (silica gel, toluene). Yield: 20 mg (30%); m.p., 166 °C. Degree of deuteriation: 94.4% ($C_{33}H_{41}D_9O_2$, *m/z* 487; MS, EI at 80 eV).

6c. This was prepared by analogy with **6b** by using the deuteriated silane **5**. Degree of deuteriation: 81% ($C_{33}H_5D_{45}O_2$, calculated *m/z* 523; MS, EI at 80 eV).

7a–7c. Radicals were generated by oxidation of a solution of the respective galvinol (**6a–6c**) in toluene with an aqueous alkaline solution of potassium hexacyanoferrate(III). The organic layer was separated, transferred to the sample tube and carefully deoxygenated prior to EPR/ENDOR measurements by flushing with purified nitrogen.

8. To a vigorously stirred suspension of 1 mol of NaH (40 g of a 60% dispersion in mineral oil) in 1,2-dimethoxyethane (400 ml) 2.5 g of *tert*-butanol were added and the mixture was heated at 60 °C. After the end of gas evolution, 174 g of diethyl succinate (1 mol) were added dropwise over 30 min. After stirring for 12 h at 60 °C, the solution was acidified with cold 6 N H_2SO_4. The precipitate was collected by suction filtration, washed with hexane and water and recrystallized from ethanol. Yield: 90 g of yellowish crystals (70%); m.p., 126–127 °C.

9. A 64 g amount of **8** (0.25 mol) and 0.5 mol of NaH (20 g of a 60% dispersion in mineral oil) were added alternately in small portions to 500 ml of 1,2-dimethoxyethane. After refluxing for 3 h most of the solvent was removed and 700 ml of 1,2-dibromoethane (8 mol) were added. After stirring for 40 h at 100–110 °C, excess of 1,2-dibromoethane was removed by steam distillation. The solid residue was collected by suction filtration, washed with 1% NaOH, water, ethanol and hexane and recrystallized from ethanol. Yield: 49 g (70%); m.p., 111–112 °C.

10. A solution of 50 g of **9** (0.177 mol) in chloroform and 71 ml of 1,3-dimercaptopropane (0.71 mol) were added slowly to a solution of 75 ml of boron trifluoride etherate in chloroform (250 ml) with ice cooling. After stirring for 1 h at room temperature, excess of 1,3-dimercaptopropane and precipitated boric acid were extracted with 2 N NaOH, then the organic layer was washed with water. After removal of the solvent the residue was crystallized from hexane. Yield: 77.3 g (95%); m.p., 118–119 °C.

11. A 77 g amount of **10** (0.167 mol) and 500 g of neutral Raney nickel were refluxed in ethanol for 48 h. The nickel was removed by filtration through diatomite. The solution was reacted with a further 250 g of Raney nickel for 48 h, then the nickel was filtered and the ethanol was removed. Yield: 33.5 g of colourless oil (79%); $n_D^{25} = 1.4665$. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.10 (4H, q, $J = 7.1$ Hz), 1.81 (12H, s) and 1.23 (6H, t, $J = 7.1$ Hz).

12. A 7.0 g amount of powdered (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane (0.02 mol) was treated with butyllithium (12.5 ml, 15% in hexane, 0.02 mol) and *N,N,N′,N′*-tetramethylethylenediamine (3 ml) with cooling in an ice–salt mixture, then 0.85 g of **11** (3.3 mmol) was added after 45 s and after a few minutes the reaction mixture was hydrolysed with water. Removal of the trimethylsilyl groups was achieved by heating in acetic acid with a few drops of concentrated HCl. The product precipitated from the boiling solution and was collected by suction filtration. Recystallization from benzene–acetic acid and from acetone gave 2.35 g (75%) of yellow crystals; m.p., 283 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.96 (2H, d, $J = 2.2$ Hz), 6.69 (4H, s), 6.47 (2H, d, $J = 2.2$ Hz), 5.20 (2H, s, *OH*), 2.01 (12H, s), 1.42 (36H, s), 1.39 (18H, s) and 1.05 (18H, s).

13, 14. The bisgalvinoxyl **14** was generated by careful oxidation of **12** as described above for **7a–7c**. A solution of the monoradical **13** was obtained by adding an excess of **12** to a solution of **14**.

Instrumentation

EPR and ENDOR spectra were recorded on a Bruker ER 220D EPR spectrometer equipped with a Bruker cavity (ER 200ENB) and laboratory-built NMR facilities described elsewhere.[6,7] The spectrometer was interfaced to a minicomputer (HP 1000/A600), used for controlling the scan oscillator and the RF power (which was kept constant over the frequency range) in addition to data acquisition and handling and storage of the spectra. NMR spectra were recorded with a Bruker AC 250 spectrometer. Mass spectra were obtained on Varian-MAT CH5DF and Varian-MAT 711 double-focusing instruments.

RESULTS AND DISCUSSION

The low-temperature EPR and ENDOR spectra of unlabelled and selectively deuteriated *tert*-butylgalvinoxyls **7a**–**7c** are compared in Fig. 1. The EPR spectrum of **7a** shows a triplet pattern ($a_H = 4.78$ MHz) which is typical for phenoxyl-type radicals, i.e. the electron spin density is localized on one phenoxy ring. In the EPR spectrum of **7b**, the resolution is substantially enhanced because of the reduced inhomogeneous line broadening. Moreover, an additional doublet splitting ($a_H \approx 1.4$ MHz) is now clearly visible. The spectral resolution is not improved much further in the case of **7c**, i.e. when the *tert*-butyl groups at the ring positions are also deuteriated. (Admittedly, the degree of deuteriation at these positions was only approximately 78% in the sample under study.) Deuteriation of the central *tert*-butyl group also proved to be advantageous with respect to the interpretation of the ENDOR spectra (Fig. 1, right). In the ENDOR spectrum of **7a**, the intense pair of signals due to these *tert*-butyl protons prevents an accurate determination of the other hyperfine coupling constants (except for the largest splitting). On the other hand, five coupling constants can be extracted from the ENDOR spectrum of **7b** (in MHz; toluene, 200 K): 4.78 (2H), 1.38 (1H), 0.80 (9H), 0.35 (1H) and 0.17 (18–36H). Thus, previous

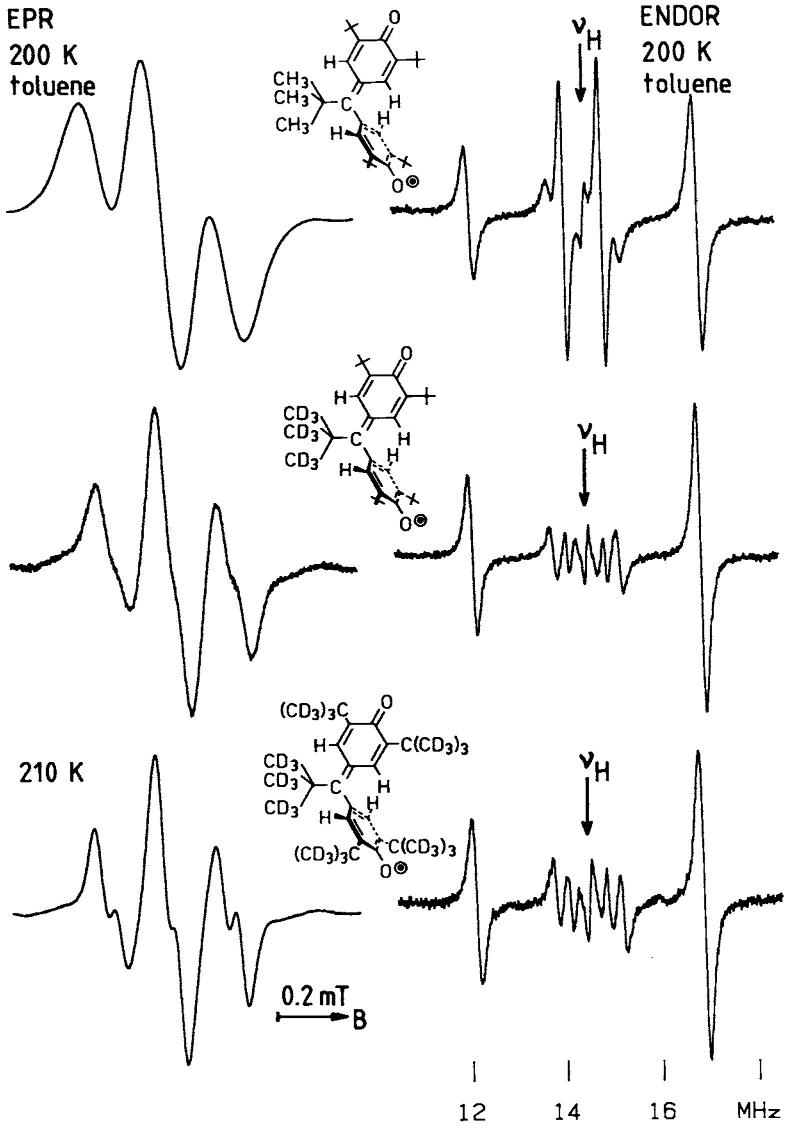


Figure 1. EPR (left) and ENDOR spectra (right) of unlabelled *tert*-butylgalvinoxyl **7a** (top) and of the selectively deuteriated radicals **7b** (centre) and **7c** (bottom) recorded in toluene at 200 K. Experimental parameters for ENDOR: MW power 20 mW, RF power 60 W, corresponding to $B_{rot} = 0.3$ mT, FM modulation amplitude ±40 kHz, time constant 12.5 ms, sweep time 30 s, 1000 data points; 90 scans were accumulated.

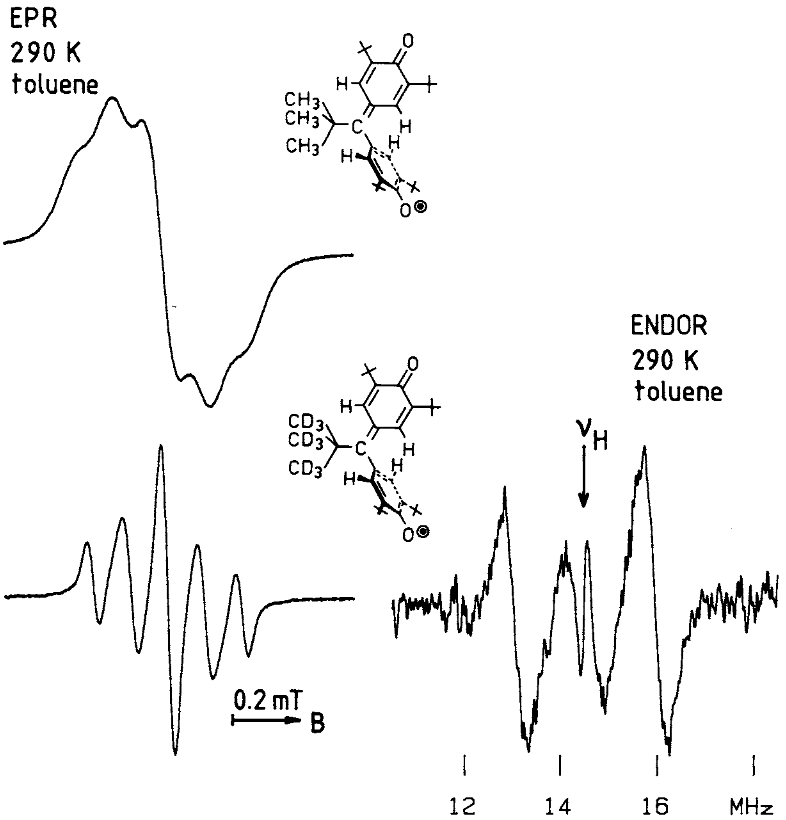


Figure 2. EPR spectra of **7a** (top left) and of **7b** (bottom left) and ENDOR spectrum of **7b** (right) recorded in toluene at 290 K.

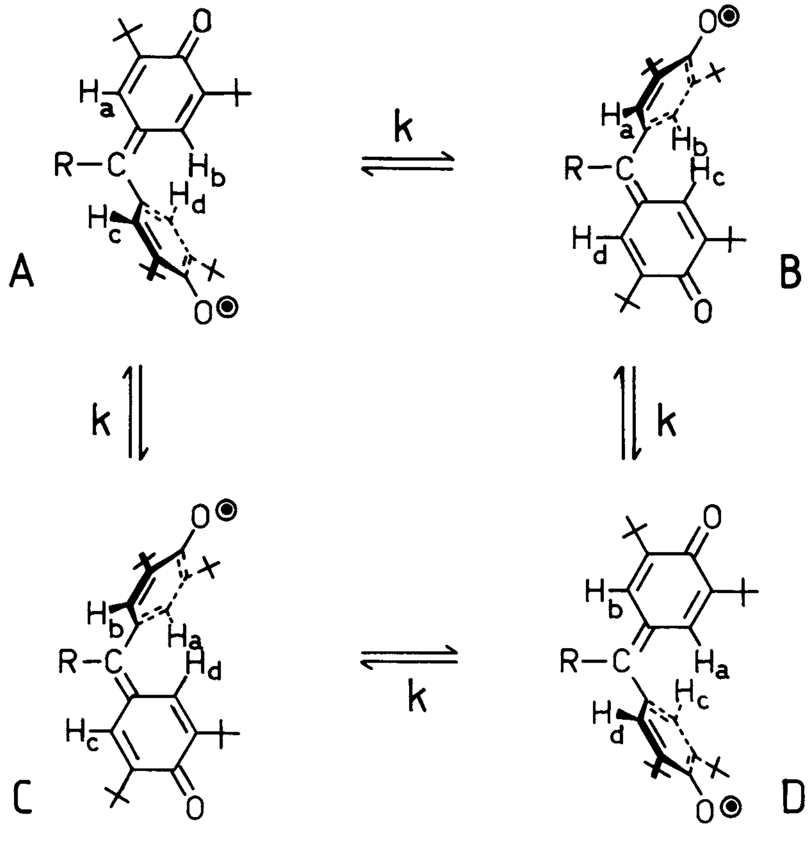


Figure 3. Representation of the four-jump process giving rise to equilibrating benzoid and quinoid rings in sterically overcrowded galvinoxyl radicals.

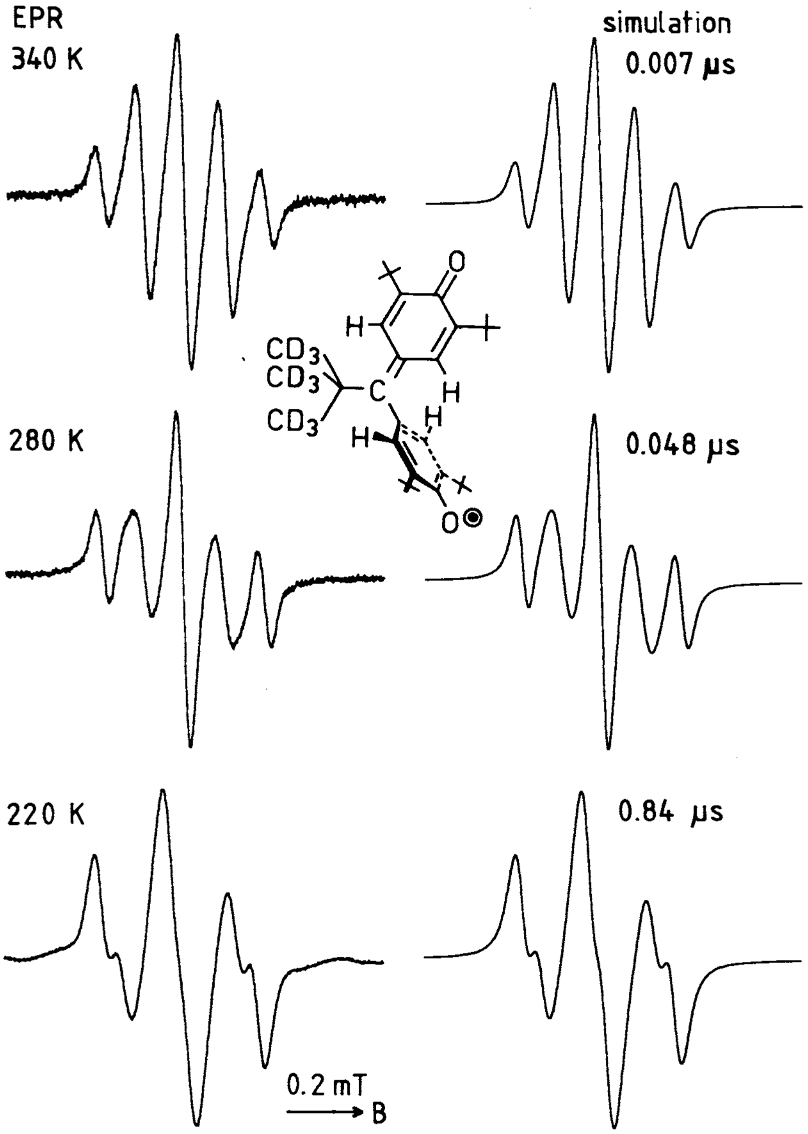


Figure 4. Experimental (left; solvent toluene) and computer-fitted EPR spectra (right) of **7b**. The temperatures and the mean lifetimes of the species involved in the intramolecular dynamic process are given.

assignments are confirmed.[5] Obviously the electron spin density in the quinoid ring is much smaller than in the phenoxyl ring, and the two quinoid protons are strongly inequivalent (1.38 and 0.35 MHz).

With increasing temperature the EPR and ENDOR spectra of **7b** show selective line broadening (alternating line-width effect[15,16]). As is evident from Fig. 2, the EPR spectrum of **7b** at 290 K exhibits a quintet pattern with a coupling constant of 2.91 MHz (4H; ENDOR data). Comparison with the EPR spectrum of **7a** demonstrates that the gain in resolution achieved by deuteriation is even more pronounced than in the case of the low-temperature spectra (cf. Fig. 1). However, the intensity pattern of the quintet still does not correspond to the binomial ratio (1:4:6:4:1) up to 360 K, because of dynamic line broadening. It should be mentioned that, in contrast to **7b**, a satisfactory ENDOR spectrum of **7a** could not be recorded in toluene at 290 K, whereas a more viscous solvent such as mineral oil proved to be successful.[4]

The signal-to-noise ratio of the ENDOR spectra was not sufficient for a reliable line-width analysis over a wide range of temperatures, especially as an extrapolation to vanishingly small RF power is required.[7,8] Therefore, a determination of the kinetic data (mean lifetime τ of individual conformers or rate constant k) was performed by means of a line-shape analysis of the EPR spectra. Because of remaining inhomogeneous line broadening and overlapping signals, a simple line-width analysis does not produce reliable results. For this reason, recourse was made to computer simulations of the line shape based on an appropriate model; specifically, a four-jump model was assumed[16] (see Fig. 3).

The low-temperature proton coupling constants of **7b** are accurately known from ENDOR measurements. Since ^2H ENDOR signals could not be observed, the *tert*-butyl deuteron coupling constant was calculated from the respective proton value ($a_D = 0.12$ MHz). The mean lifetime τ of the conformers was determined by means of an iterative least-squares fitting procedure

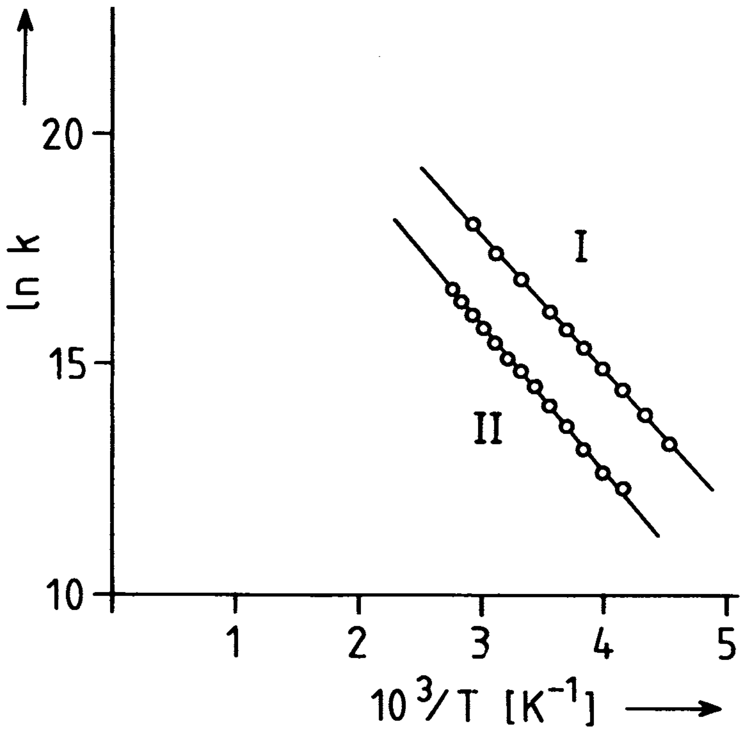


Figure 5. Arrhenius plots of ln k vs $1/T$ for **7b** (I) and **13** (II). **7b**: $E_a = 24.2 \pm 0.2$ kJ mol^{-1} and $k_0 = 3.5 \times 10^{11}$ s^{-1}. **13**: $E_a = 26.3 \pm 0.3$ kJ mol^{-1} and $k_0 = 1.1 \times 10^{11}$ s^{-1}.

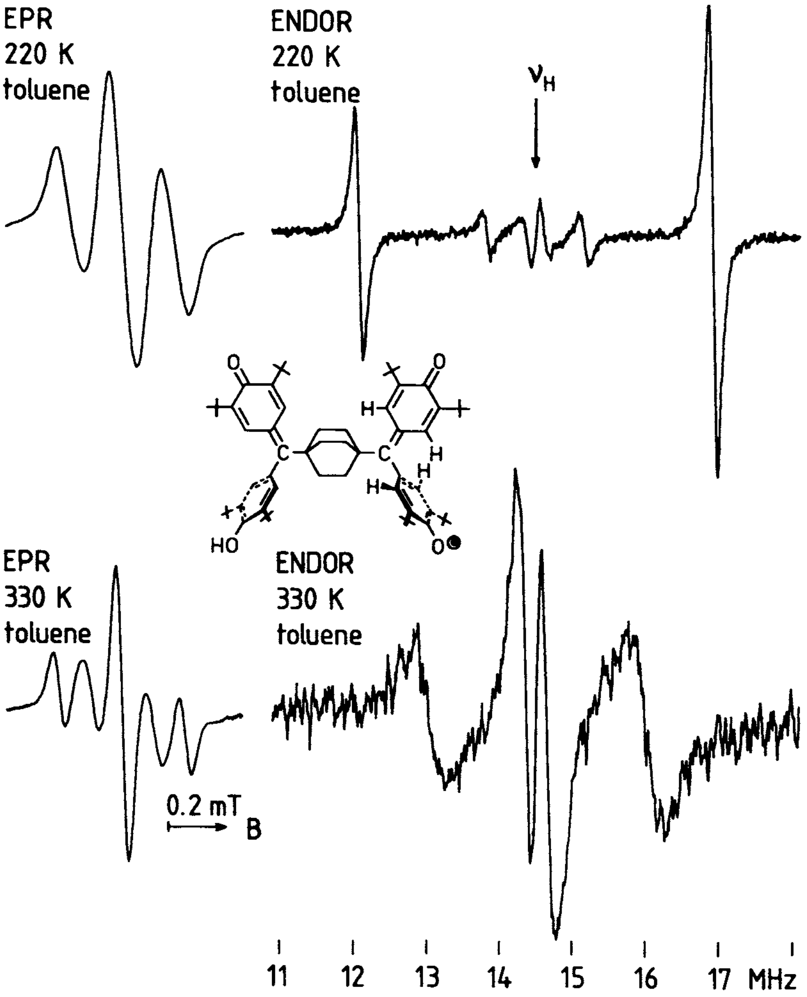


Figure 6. EPR (left) and ENDOR spectra (right) of **13** recorded in toluene at two temperatures.

described recently (program DYNFT).[17] Since the total width of the EPR spectra and also the room temperature ENDOR spectrum reveal a temperature dependence of the averaged ring proton coupling constant, this value had to be adjusted in simulations dealing with elevated temperatures. Actually, only the largest coupling was allowed to vary (4.80 MHz at 210 K, 4.96 MHz at 290 K and 5.05 MHz at 360 K). The EPR line shape proved to be reasonably sensitive to the dynamic effect in the temperature range 230–340 K, allowing the determination of the rate constant $k = 1/(2\tau)$ as a function of temperature. A series of EPR spectra are depicted in Fig. 4 together with the respective computer simulations, and an Arrhenius plot is shown in Fig. 5. The kinetic activation parameters were determined according to the Eyring equation from a plot of $\ln(k/T)$ versus $1/T$ (correlation coefficient -0.99987), yielding $\Delta H^{\ddagger} = 21.8 \pm 0.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -32.1 \pm 0.5$ J mol^{-1} K^{-1}.

EPR and ENDOR spectra of the monoradical **13** recorded at two temperatures are compared in Fig. 6. The hyperfine coupling constants of **13** [ENDOR data, toluene, 220 K: 4.86 MHz (2H), 1.33 MHz (1H), approximately 0.22 MHz; 330 K: 2.98 MHz (4H), approximately 0.29 MHz] and the dynamic behaviour are similar to those of **7b**. Well resolved ENDOR signals of the protons within the bridge could not be observed, however, probably because of line broadening caused by hindered rotation. The determination of the kinetic activation parameters of **13** has been reported previously[17]: $\Delta H^{\ddagger} = 23.8 \pm 0.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -42 \pm 1$ J mol^{-1} K^{-1}; an Arrhenius plot for **13** is included in Fig. 5. Although the kinetic data are not very different from those of **7b**, it is clear that the effective steric hindrance in **13** is larger, i.e. the activation enthalpy is larger and the rate constants at the same temperatures are smaller.

Investigation of the electron exchange interaction and the electron–electron dipolar interaction in the biradical **14**, generated from the bisgalvinol **12**, lends support to the interpretation that these radical systems are better described by equilibrating phenoxyls than by (delocalized) galvinoxyls. The determination of the dipolar interaction, expressed quantitatively by the zero-field splitting parameters D' and E, from an EPR spectrum taken in glassy solution is straightforward.[18] The EPR spectrum of **14** in rigid solution and a computer simulation (program POLFT[17]) are depicted in Fig. 7; the zero-field splitting parameters are $D = 97$ MHz and $E = 2.6$ MHz. It is noteworthy that the D parameter of **14** is almost twice as large as that of *p*-phenylenebisgalvinoxyl (53 MHz),[19] although the separation between the two galvinoxyl moieties is essentially the same. However, as has been pointed out above, the radicals **7b**, **13** and **14** should be considered as phenoxyl radicals, whereas derivatives of phenylgalvinoxyl exhibit a truly delocalized galvinoxyl system. Actually, an average separation of 930 pm between the two unpaired electrons in **14** can be estimated from the D parameter on the basis of a simple point-dipole

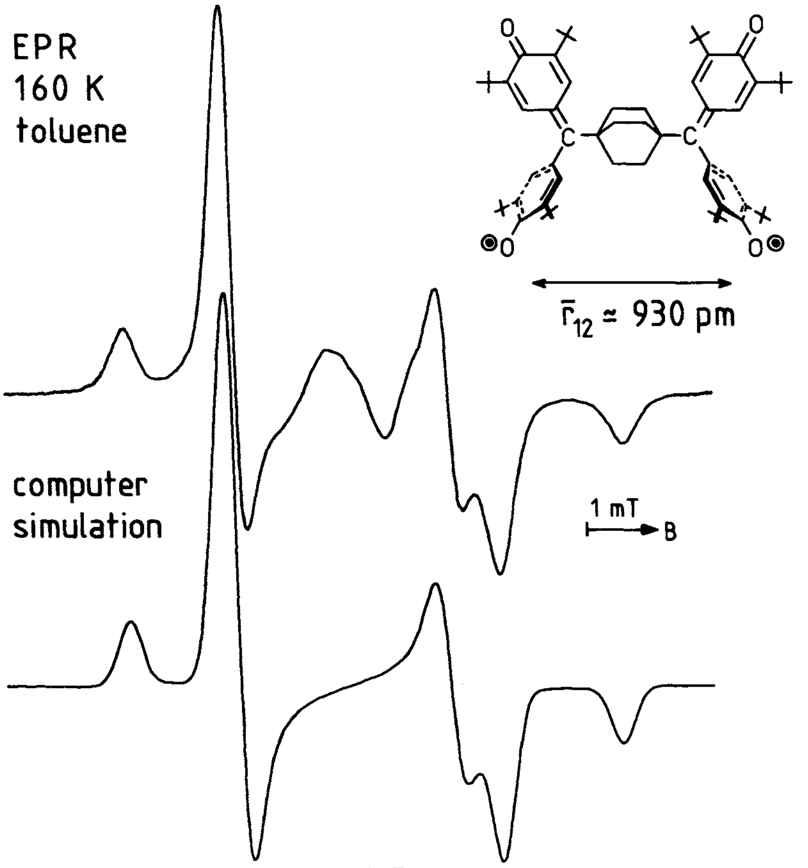


Figure 7. EPR spectrum of **14** recorded in glassy toluene (top) and computer-fitted spectrum (bottom). Parameters: $D = 97$ MHz, $E = 2.6$ MHz, $g_{xx} = 2.0064$, $g_{yy} = 2.0038$ and $g_{zz} = 2.0033$; Gaussian line shape with line width of 0.40 mT (full width at half-maximum).

model.[20] Model considerations show that a conformation with the two phenoxyl rings in *cis* (eclipsed) positions must be preferred in order to account for this short distance. It can be assumed that in this conformation a widening of one angle in the trigonal hydrocarbon bridge allows the accommodation of the two intruding quinoid rings.

In principle, the exchange interaction in biradicals can be estimated from the appearance of fluid-solution EPR spectra.[21,22] Previous investigations of bisgalvinoxyls, even with long and insulating spacers, have demonstrated that the exchange interaction is generally much larger than the hyperfine interaction ($|J| \gg |a|$).[23,24] In a recent study of a bisgalvinoxyl with a diphenyloctane bridge, it was concluded that the flexible spacer allows the approach of the two galvinoxyl moieties and hence through-space exchange in isotropic fluid solution, whereas in liquid-crystalline solution straight conformations are preferred and hence the electron exchange is suppressed.[25] Since in **14** the two galvinoxyl moieties are separated by a rigid insulating spacer, it seemed to be a likely candidate for a weak exchange interaction. Unfortunately, the strong electron–electron dipolar interaction in **14** causes severe line broadening in fluid-solution EPR spectra, particularly at ambient temperature and below. For **14**, only an unresolved broad signal is observed; the residual structure is due to monoradical impurities. It should be noted that one must be careful not to mistake monoradical impurities (possibly decomposition products) for biradicals with weak exchange interaction.[26] We conclude that the exchange interaction in **14** is still larger than the hyperfine interaction, but for a quantitative evaluation ^{13}C labelling would be required;[27] corresponding work is in progress.

CONCLUSIONS

We have shown that selective deuteriation of *tert*-butylgalvinoxyl improves the resolution of the EPR spectra to such an extent that a quantitative analysis of an alternating line-width effect exhibited by this radical is possible. Although the bulky *tert*-butyl group distorts the galvinoxyl moiety to such an extent that it must be regarded as a phenoxyl radical, the activation enthalpy (21.8 kJ mol^{-1}) of the dynamic process giving rise to an equilibration of the phenoxy ring and the quinoid ring is, in fact, no larger than that of galvinoxyl radicals with sterically less demanding substituents (16–35 kJ mol^{-1}).[5,8] Not surprisingly, the dynamic behaviour of the monoradical from 1,4-bicyclo[2.2.2]octanebisgalvinol is similar. The respective biradical exhibits strong scalar and dipolar interactions, which also reflect the steric influence of the bulky bridge linking the two radical moieties.

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