

## Proton and Carbon-13 Splittings in the ESR Spectra of two Phenoxy Radicals

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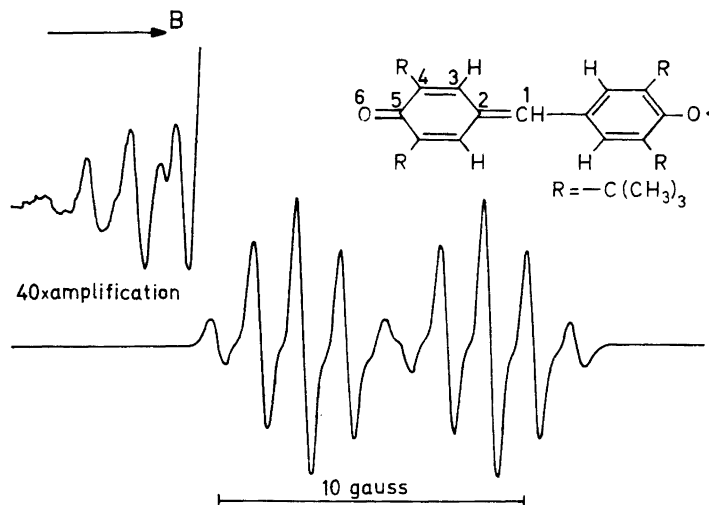
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The proton and  $^{13}\text{C}$  splittings in the ESR spectrum of the free radical galvinoxyl have been obtained. The radical resulting when one *tert*-butyl in each ring of galvinoxyl is replaced by methyl has been prepared, and the ESR spectrum has been interpreted. Attempts have been made to correlate proton and  $^{13}\text{C}$  splittings to spin densities calculated from conventional VB methods.

The proton hyperfine structure in the ESR spectrum of the stable free radical 2,6-di-*tert*-butyl- $\alpha$ -(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-*p*-tolyl-oxo (see Fig. 1), hereafter referred to as galvinoxyl, has already been described.<sup>1,2</sup> We find from dilute benzene solutions 1.44 and 6.1 gauss splittings from protons 1 and 3 in good agreement with Ref.<sup>2</sup> (the numbering of the carbon and oxygen atoms for the discussion of the ESR data is given in Fig. 1). The splitting from the *tert*-butyl protons is less than 0.05 gauss. In addition, with higher gain,  $^{13}\text{C}$  splittings are detected (Fig. 1). The largest  $^{13}\text{C}$  splitting is 11.0 gauss with an intensity of about 1 % compared to the corresponding proton hyperfine lines. This shows, that the 11.0 gauss  $^{13}\text{C}$  splitting is due to a group of two carbon atoms.

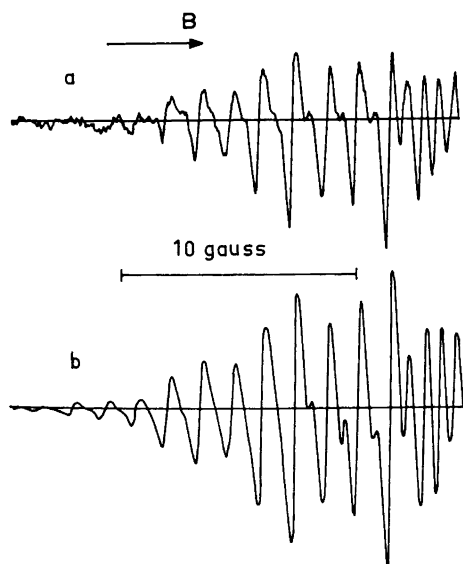
When one of the *tert*-butyl groups in each ring is replaced by a methyl group the spectrum in Fig. 2 is obtained. This can unambiguously be interpreted in terms of proton splittings 5.95, 1.37, and 3.95 gauss from protons 1, 3 and the methyl groups, respectively, as shown in Fig. 2, by comparing with a calculated spectrum. In less resolved spectra with higher modulation field, weak lines are observed in the wings of the spectrum in complete agreement with the calculated spectrum.

The spin densities were calculated from the relation  $a_{\text{H}} = Q \rho_{\text{C}}$  (Refs.<sup>3,4</sup>). Taking  $|Q| = 28$  gauss for both aromatic and methyl protons we get  $|\rho_{\text{C}}^1| = 0.22$ ,  $|\rho_{\text{C}}^3| = 0.05$  and  $|\rho_{\text{C}}^4| = 0.14$ . We have tried to correlate these values with densities calculated by standard techniques. The simple Hückel molecular



*Fig. 1.* ESR spectrum of a dilute benzene solution of the galvinoxyl free radical at low modulation field and low microwave power. The numbering in the figure refers only to the discussion of the ESR data in the text.

orbital method<sup>5</sup> does not work since, for example, it predicts zero spin density at  $C_1$ . We have used the conventional valence-bond method,<sup>6</sup> which also has been applied by Becconsall *et al.*<sup>2</sup> to phenoxy radicals with one aromatic ring. Following their procedure we neglect ionic structures and structures with long bonds. The total wave function is then a sum of ten structures but, for



*Fig. 2.* a) ESR spectrum of a dilute benzene solution of the radical obtained when one *tert*-butyl group in each ring of galvinoxyl is replaced by methyl. Only one half of the spectrum is shown.  
b) Calculated spectrum obtained by superpositioning Lorentzian lines (width 0.25 gauss) with proton splittings  $a_{H^1} = 5.95$ ,  $a_{CH_3} = 3.95$  and  $a_{H^3} = 1.37$  gauss.

symmetry reasons, with only two independent constants. The wavefunction can be written as

$$\Psi = a \Psi_2 + b \Psi_4 + c \Psi_6$$

where  $\Psi_i$  stands for structures with the unpaired electron in position  $i$  and equivalent positions. The spin density can be obtained from the wavefunction by McConnell's rules.<sup>7</sup> For example, with the oxygen atoms replaced by  $\text{CH}_2$  we obtained the constants in the wave function by diagonalisation of the energy matrix, and the calculated densities are  $\rho_c^1 = -0.181$ ,  $\rho_c^3 = -0.138$  and  $\rho_c^4 = 0.211$ . For the phenoxy radicals, we have the difficulty of estimating all the integrals involved. Therefore we have not solved the secular equation but have only tried to fit the wave function to the experimental data (*cf.* Ref.<sup>2</sup>). However, this does not seem to be possible. If we adjust the wave function to  $\rho_c^1$  and  $\rho_c^4$  (with the very reasonable assumption that  $\rho_c^4 > 0 > \rho_c^1$ ), we get  $a = 0.127$ ,  $b = 0.082$  and  $c = 0.250$ . This wave function gives  $\rho_c^3 = 0.114$ , which differs more than a factor two from the experimental value. Furthermore,  $\rho_c^2$  becomes 0.396. Using the formula by Karplus and Fraenkel,<sup>8</sup> we get from this value together with the experimental  $\rho_c^1$  and  $\rho_c^3$  the  $^{13}\text{C}$  splittings  $a_c^1 = -18.8$  and  $a_c^2 = 16.5$  gauss. These are much larger than the experimental values and only by reducing  $\rho_c^2$  by a factor of two, we get  $^{13}\text{C}$  splittings of correct magnitude.

Thus, our valence-bond wave function does not seem to give correct spin densities. Therefore we cannot decide which of  $\text{C}_2$  and  $\text{C}_5$  is responsible for the largest  $^{13}\text{C}$  splitting. One serious approximation common to our calculations and to those in Ref.<sup>2</sup>, is that the effect of the *tert*-butyl and methyl groups on the  $\pi$ -electron distribution has been neglected. That such an effect exists is evidenced by investigations of semiquinones (see Ref.<sup>5</sup>, p. 156). To account for our experimental results a modified molecular orbital treatment might be more fruitful, as this more easily permits inclusion of effects from substituents.

## EXPERIMENTAL

*Materials.* Galvinoxyl, m.p. 153–4°, was prepared according to Ref.<sup>9</sup> from 2,6-di-*tert*-butylphenol. After condensation with formaldehyde, the product was oxidized with lead dioxide in ether.

2-Methyl-6-*tert*-butylphenol (I), b.p. 108–112°/12 mm Hg, was prepared according to Hart and Haglund<sup>10</sup> from *o*-cresol, which, after bromination in the 4-position, was alkylated with isobutylene in the 6-position. The bromine atom was then removed by reduction with Raney-nickel alloy. Hart and Haglund showed that Tchitchibabine's method<sup>11</sup> of direct alkylation of *o*-cresol with *tert*-butylalcohol and phosphoric acid gave the 2,4-isomer, and they also showed that (I) rearranged to 2-methyl-4-*tert*-butylphenol in the presence of sulfuric acid or phosphoric acid.

3,3'-Dimethyl-4,4'-dihydroxy-5,5'-di-*tert*-butyl-diphenylmethane (II), m.p. 96.5–98.5°, has been reported earlier in a patent by Filberg and Coffield,<sup>12</sup> who condensed dialkyl phenols with formaldehyde in a monohydric alcohol as the solvent, and in the presence of catalytic amounts of alkali metal hydroxides. (I) is stated as starting material. We have found that the reaction between (I) and formaldehyde under the same conditions as for 2,6-di-*tert*-butylphenol above<sup>9</sup> gave a syrup, from which (II), m.p. 102–104°, was isolated. Its structure was evident from its NMR-spectrum, the ESR-spectrum of the oxidation product and from the methods of preparation. Attempts were made to oxidize 3,3',5,5'-tetramethyl-4,4'-dihydroxy-diphenylmethane<sup>13</sup> in the same manner as described below.

Only a faint green colour was observed, and the presence of free radicals could not be detected.

*3,3'-Dimethyl-4,4'-dihydroxy-5,5'-di-tert-butyl-diphenyl-methane.* A solution of 2-methyl-6-*tert*-butylphenol<sup>10</sup> (16.4 g, 0.1 mole), 36 % formaldehyde (15 ml), sodium hydroxide (8 g), water (15 ml), and ethanol (50 ml) under an atmosphere of nitrogen was heated to 65° for 90 min while it was stirred. After cooling, it was acidified with hydrochloric acid. The separated yellow oil was taken up in ether, washed with water, and dried. After evaporating of the solvent *in vacuo*, there remained a syrup weighing 17.5 g, in which crystals appeared after a few hours. Two days later 7.5 g (44 %) of almost colourless crystals were isolated by adding 5 ml of ligroin and filtering. After one recrystallization from ligroin (Norit), the substance melted 102–104°. Probably, if a higher, branched alcohol is used as a solvent instead of ethanol, a better yield will be obtained.<sup>14</sup> NMR-spectrum (13 % in CS<sub>2</sub>) (numbering as in formula above):  $\tau_{\text{C}(\text{CH}_3)}$  = 1.32 ppm;  $\tau_{\text{CH}_3}$  = 2.08 ppm;  $\tau_{\text{CH}_2}$  = 3.64 ppm;  $\tau_{\text{OH}}$  = 4.35 ppm;  $\tau_{\text{C}^2}$  = 6.66 ppm;  $\tau_{\text{C}^6}$  = 6.87 ppm;  $J_{26}$  = 2.2c/s. The doublet at  $\tau$  = 6.66 ppm was further split owing to coupling to the methyl group. (Found: C 81.37; H 9.46. Calc. for C<sub>23</sub>H<sub>32</sub>O<sub>2</sub> (340.5): C 81.13; H 9.47.)

*2-Methyl-6-tert-butyl-a-(3-methyl-5-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-p-tolyl-oxo.* A solution of (II) (1.1 g) in benzene (15 ml) was drop-wise added to a well stirred mixture of K<sub>3</sub>Fe(CN)<sub>6</sub> (4 g), KOH (0.5 g), water (15 ml), and benzene (100 ml) in an atmosphere of nitrogen. After an intense dark green colour had appeared, indicating the presence of the free radical, the two layers were allowed to separate for a few minutes, and some of the benzene solution was pipetted up and transferred to tubes for recording the ESR-spectra. The one represented in Fig. 2 was obtained when half the amount of solution was added. Signals from the free radical could then be detected in the ESR-apparatus for two hours, after which period it disappeared. When the last milliliters were added, the colour rapidly changed to intense yellow. This solution contained no radicals. The IR-spectrum of the free radical (0.1 mm cells) shows a strong peak at 6.13  $\mu$ . Absorption in this region is considered characteristic of compounds of this type having a quinonoid structure.<sup>15</sup>

The samples prepared as described above were deoxygenated by bubbling argon through the solution immediately before the ESR investigation. The spectra were obtained with a Varian V-4500 spectrometer utilizing 100 kc/s modulation.

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