SIGNS OF THE HYPERFINE INTERACTION CONSTANTS AND THE SPIN DENSITIES IN PHENOXYL RADICALS

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On the basis of an analysis of the dipole moments of phenols and phenoxyls and also the EPR spectrum of an unsubstituted phenoxyl, some considerations on the distribution of the unpaired electron in the radical are expressed. The signs of the spin density in the nuclei containing a π-electron spin density are analyzed.

This work is devoted to the question of the distribution of the unpaired electron in phenoxyl radicals and the mechanism of the appearance of isotropic splitting in the C₁³, N₁⁴, and other nuclei in these radicals.

The EPR spectrum of an unsubstituted phenoxyl radical is characterized by the isotropic hyperfine interaction (HFI) constants for the protons: \( a₀ = 10.4 \), \( a₀ = 6.65 \), \( aₘ = 1.9 \text{ Oe} \) [1]. If the spin density is calculated from the σ-π-configuration interaction constant \( Q = 23.7 \text{ Oe} \) [2], it is shown that the greater part of the spin density is concentrated in the ring, on the basis of which, the phenoxyl radicals sometimes are considered as derivatives of the benzene cation [3].

The dipole moments (D.M.) of the stable phenoxyl radical

\[
\begin{aligned}
\text{t-C}_4\text{H}_9 & \quad \text{t-C}_4\text{H}_9 \\
\text{t-C}_4\text{H}_9 & \quad \text{t-C}_4\text{H}_9
\end{aligned}
\]

and the corresponding phenol II are equal to 2.84 and 4.36 D, respectively [4].

As the EPR spectrum of radical I shows, both of its phenoxyl fragments are equivalent, i.e., the frequency of the delocalization of the unpaired electron, which corresponds to the frequency of the mutual transitions of the resonance structures, is large. Therefore, the axis of symmetry, \( C₂v \), is the direction of the D.M. of the radical and it can be represented as the superposition of the D.M. of two types of structure — with an unpaired electron on the oxygen (A) and the structure with an unpaired electron in the ring, i.e., the quinolide structure (B). Then the overall D.M. of the radical is equal to

\[
\muₜ = 2 \cos \frac{\theta}{2} [Aρ₀ + B(1 - ρ₀)],
\]

where \( \muₜ = 2.84 \text{ D} \), the D.M. of radical I; \( θ = 120° \) (the angle C₂C₄C₆ at the central carbon atom in the radical), \( A = 0.8 \text{ D} \) (D.M. of structure \( \text{C}_4\text{H}_9 \)), \( B = 3.7 \text{ D} \) (D.M. of the quinolide structures determined from the D.M. of phenol II according to a vector diagram with an estimate of the internal rotation); \( ρ₀ \) is the spin density on one of the oxygen atoms. Hence, it follows that \( ρ₀ = 0.3 \), i.e., the spin density on the oxygen atoms in radical I amounts to 0.6 and in the rings 0.4. In this way, the analysis of the D.M. shows that the unpaired electron in the phenoxyl fragment is distributed approximately equally between the ring and the oxygen atom. Note that the analysis carried out is valid only if the D.M. of the \( σ \)-bonds remain unchanged in the phenol and the radical.

An analysis of the protonic HFI constants of the EPR spectrum of an unsubstituted phenoxyl with an estimate of the dependence of the McConnell constant on the size of the charge also leads to the notion that a considerable portion of the unpaired electron is localized on the oxygen atom. The appearance of the HFI in the protons of the...
Fig. 1. The EPR spectrum of 2,4,6-tri-tert-butyphenoxyl in n-decane at room temperature: a) at low intensity; b) at high intensity.

ring is connected with migration of the \( \pi \)-electron of the ring to the \( >C = O \) group, i.e., with the appearance of a positive charge in the ring. In this case, the McConnell constants are considered equal to 28-35 Oe \[5-8\]. For the average values for \( Q \approx 30-32 \) Oe, we find from the HFI constants of an unsubstituted phenoxyl that the spin densities of the ring orbitals and of the \( >C = O \) groups are approximately equal. In this way, approximations of the distribution of the unpaired electron, both by the EPR spectra and by dipole moments, show an approximately equal probability of the electron being found in the ring and in the \( >C = O \) group of the phenoxyl.

Let us now discuss the signs of the HFI constants in phenoxyls with nuclei containing a \( \pi \)-electron spin density. The theory of line widths, developed by Freed and Fraenkel, allows us to determine the signs of the HFI constants from the EPR spectra, recorded under such conditions that the modulation of the intramolecular anisotropic electron-nuclear dipole interaction and g-tensor perturbation caused by the anisotropy of the g-factor causes broadening of the HFS components depending on the magnetic quantum number of these components \[9\].

The spectrum of 2,4,6-tri-tert-butyphenoxyl is presented in Fig. 1. It is evident that the HFS of the wings does not reproduce the HFS of the main signal; the distance between the components in the satellites exceeds the distance between the components of the main signal by 30%, and the ratio of intensities in the satellites amounts to 1:4:8 (and not 1:2:1 as in the main signal). The HFS of the satellites can be interpreted as the overlapping of HFS components from \( C_{13} \) in various positions in the phenyl ring. The components of the satellites in the high fields are wider than the ones in the low fields, i.e., the sign of the spin density, at least in some of the \( C_{13} \) atoms which contribute to the intensity of the satellites, coincides with the sign of the isotropic constant. It is impossible to resolve the problem of the behavior of the HFS components unequivocally. It is most probable that the HFS of the satellites originates in the \( C_{13} \) nuclei in the para position (\( a_{C_{13}} \approx 12.6 \) Oe) and also in the \( C_{13} \) in the ortho and meta position of \( C_{11} \) adjacent to the oxygen atom. The HFS constants of \( C_{13} \) in the latter two positions, apparently, are close and smaller than \( a_{C_{13}} \); this explains the observed ratios of the intensities in the satellites. The widths in the high fields are attributable, apparently, only to the components from the \( C_{13} \) in the ortho and para positions, where \( \rho_{C_{13}} > 0 \), and where \( \rho_{C_{13}} \) is sufficiently large here to contribute to the dipole-dipole and g-tensor width.

In the Coppinger radical

\[
\begin{align*}
\text{H}_{2} & \quad 2 \text{ Oe} \\
\text{H}_{2} & \quad 15.6 \text{ Oe}
\end{align*}
\]

the unpaired electron, just as in I, is delocalized along both phenoxy fragments. From Fig. 2 it is evident that the nitrogen HFS components are more strongly broadened in the low fields, i.e., the sign of \( a_{N} \) is opposite to the sign of \( a_{C_{13}} \); if it is assumed that \( a_{N} < 0 \) (as in the central C atom in the allyl group), then \( a_{N} < 0 \).