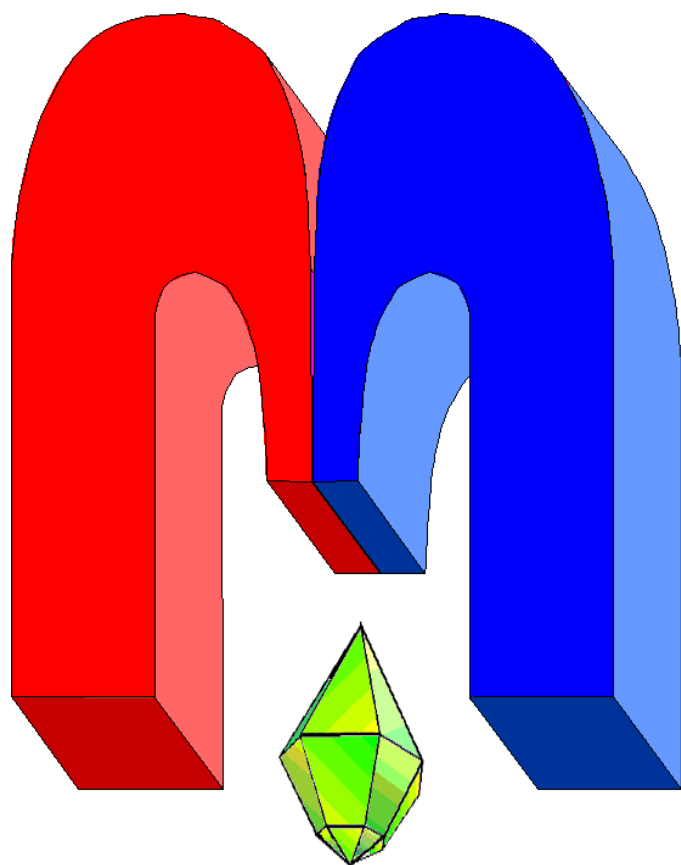


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In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

# EPR, structural characteristics and intramolecular movements of some phenoxy radicals in toluene

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The method of electron paramagnetic resonance (EPR) spectroscopy was used for studying magnetic and dynamic properties of phenoxy radicals in toluene at 170-370 K. Characteristics of intramolecular motion and structure of phenoxy radicals were determined from the temperature dependence of EPR spectra. For all the given compounds the activation energies of transitions between the conformers were calculated.

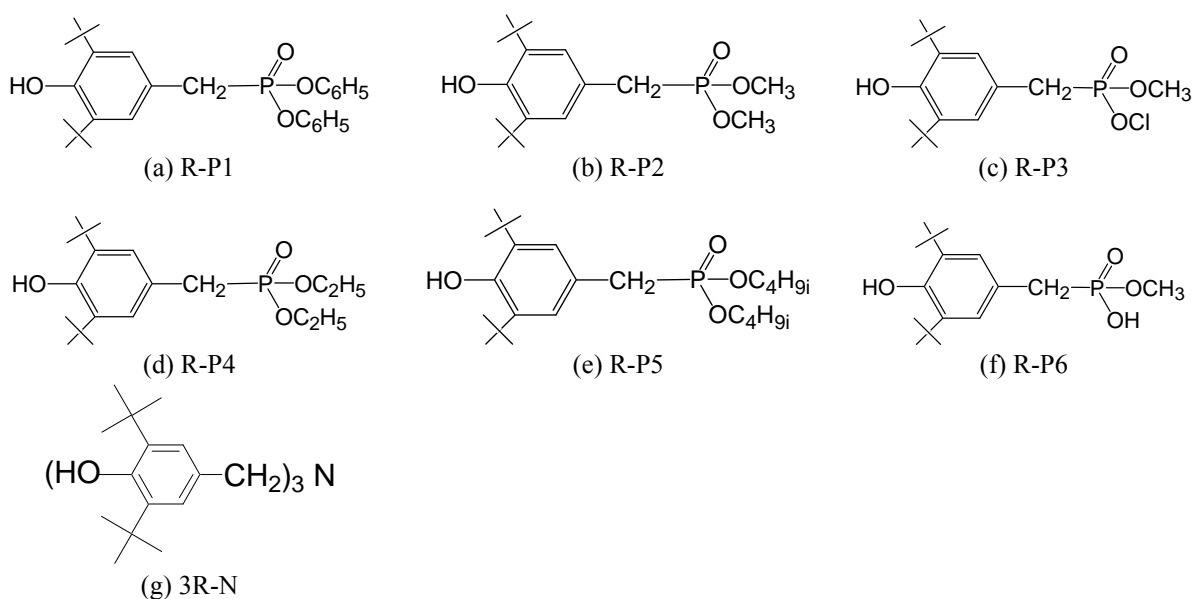
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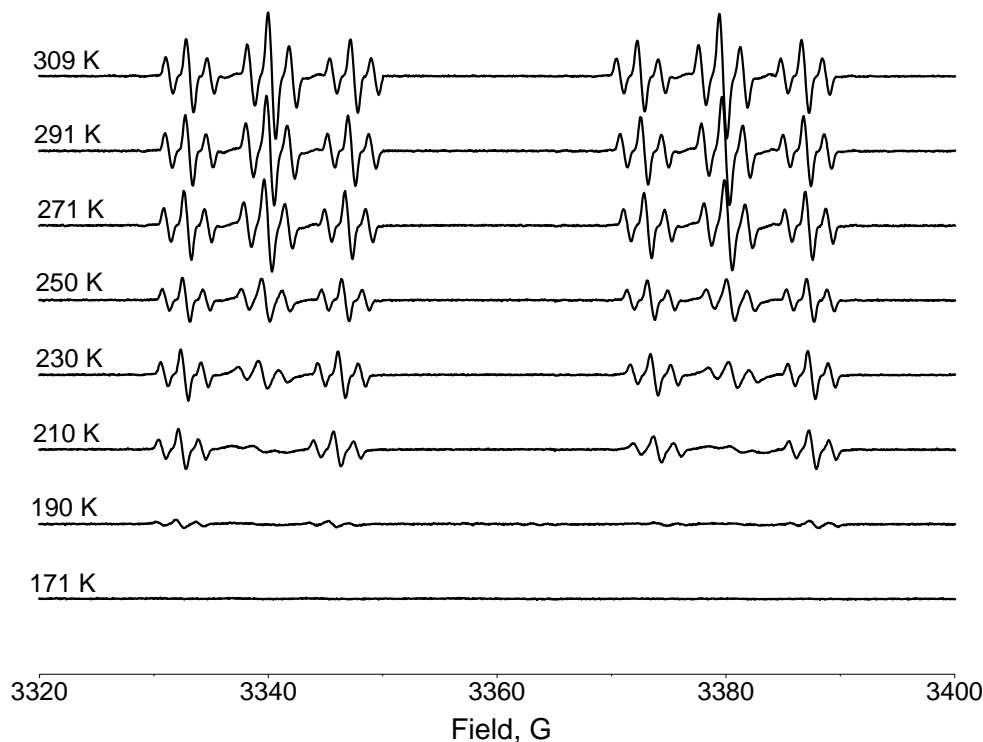
Phenols are a class of chemical compounds that have long been the subject of high interest of chemists and industrialists. The most common application of substituted phenols in the industry is their using as antioxidants [1-3]. The antioxidant properties of these phenols are caused by easy separation of the phenolic hydrogen and efficient purification of peroxy and alkoxy radicals which are key reagents in the autooxidation [4]. It is well known [5-6] that the efficiency of the antioxidant action of some phenolic stabilizers is determined by their spatial structure. At the same time the information about the spatial structure of these compounds in solutions and the conformations of their oxidation products is not enough.

Chemical changes in a phenolic moiety do almost not affect the reactivity and other properties of the unreacted phenolic fragments if the last separated by an aliphatic chain containing three atoms at least [7-8].

In this paper we considered some mono- and polynuclear phenols (Figure 1).



**Figure 1 (a-g).** Considered phenols with a short notations



**Figure 2.** Temperature dependence of EPR spectra for **R•-P1**

Free radicals were obtained by oxidation of source compounds dissolved in  $\text{PbO}_2$  toluene solution ( $1 \cdot 10^{-3}$  M). The oxidation of phenol represents a detaching hydroxyl hydrogen and forming the phenoxyl radical. Freezing-pumping-defrosting technique was used to remove oxygen from the samples.

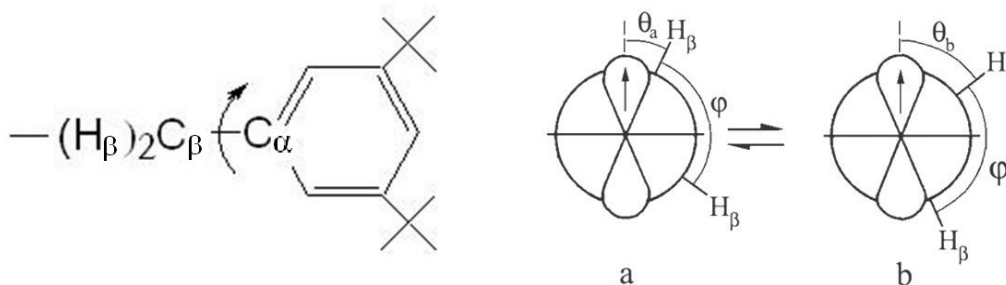
EPR spectra were recorded on Elexsys E500 (Bruker, Germany). Rectangular TE102 cavity was used in all measurements. Temperature dependences of the spectra were investigated using temperature control system ER 4131VT (Bruker, Germany).

Magnetic resonance parameters and relative intensities of the spectral components were determined by computer simulations of experimental EPR spectra using the simulation program WinSim.

Figure 2 shows EPR spectra of the free radical **R•-P1** obtained from phenol **R-P1** in the temperature range 170-309 K in toluene.

One may notice that the rise in temperature leads to increasing an intensity of the triplets central lines. The ratio of the lines intensities is 1:2:1 at a temperature 309 K.

This phenomenon is explained by the existence of energetically equivalent conformers 1 and 2 (Figure 3). There are conformational transitions between these conformers. If we consider only



**Figure 3.** Equivalent conformers of the phenoxyl radical

$\beta$ -protons the EPR spectrum should have four lines. If the  $\beta$ -protons are in nonequivalent positions, then  $A_1 \neq A_2$ , hyperfine structure (HFS) constants are not equal. So we can see 4 lines of equal intensity. If  $A_1 = A_2$ , i.e. both  $\beta$ -protons are equivalent, we observe 3 lines with intensity ratio 1:2:1.

Transitions between two conformers lead to transfer of  $\beta$ -protons from one position to another. It causes a modulation of hyperfine splitting in opposite phase. As a result an alternation of the EPR line widths is observed. When temperature is increasing these transitions become intensive, their frequency become comparable with a difference between the HFS constants of  $\beta$ -protons.

These preferred conformers can be estimated from the EPR spectra using the relation

$$a_{H\beta} = b \cos^2 \theta, \quad (1)$$

where parameter  $b$  is equal to 23.3 G for  $\beta$ -protons at the para-position to phenoxyl group [7].

For the EPR lines which in the initial spectrum are not overlapped the displacement is associated with a lifetime  $\tau$  (correlation time) of conformational transitions by an equation [9]

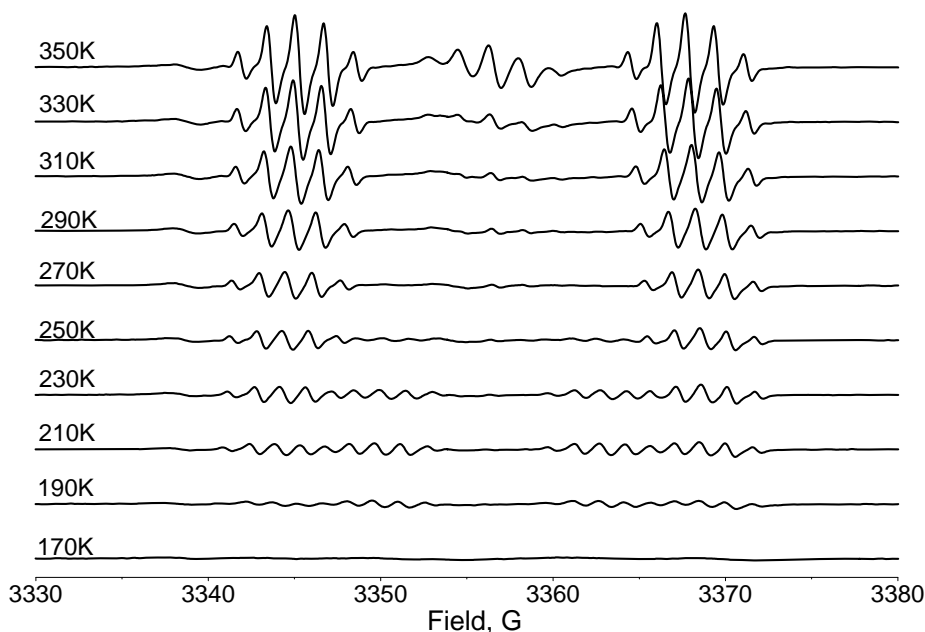
$$\sqrt{\Delta H_0^2 - \Delta H_e^2} = \frac{\sqrt{2}}{\gamma_e} \tau, \quad (2)$$

where  $\Delta H_0$  is a distance between the lines in the absence of mutual transformations of 1 and 2,  $\Delta H_e$  is that in the presence of mutual transformation. The temperature dependence of  $\tau$  can be represented as

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right). \quad (3)$$

The graph of dependence of  $\ln(\tau)$  on the  $1/T$  is a straight line (straight line of Arrhenius). Tilt of this line is equal to  $E_a/R$ . It is easy to verify that  $E_a = 4.5$  kcal/mol.

A similar temperature dependence of the EPR spectra were observed for the other phosphorus phenols: **R-P2**, **R-P3**, **R-P4**, **R-P5**, **R-P6** (difference is only in the constants of the HFS). The activation energies for these compounds are equal to 4.7, 3.1, 3.5, 5.4, 4.8 kcal/mol respectively.



**Figure 4.** Temperature dependence of EPR spectra for **3R-N**

So, for this group of phenoxyl radicals freezing of conformers does not occur in 170-310 K temperature range. The explanation of this effect is less hindered rotation due to the smaller steric influence of substituents.

Figure 4 shows the EPR spectra of free radical **3R·-N** in the temperature range 170-350 K in toluene. In a rigid matrix below the freezing point of pure toluene (178 K) one can see four broad lines; the middle two of them are becoming gradually broader when temperature increases (170-250 K). Consequently, these lines are reduced in intensity and come closer to each other.

Correlation time of rotation for the case when  $\beta$ -atoms of hydrogen transit from one position to another and thereby cause the effect of EPR linewidth alternation can be written as [9]

$$\tau = \left( \sqrt{\frac{2I_{\pm 1}}{I_0}} - 1 \right) \frac{8T_{2,0}^{-1}}{\gamma_e^2 (a_1 - a_2)^2}, \quad (4)$$

$I_{\pm 1}, I_0$  are intensities of flank non-overlapping lines of multiplets corresponding to the projections of the nuclear magnetic moment  $m_I(\text{CH}_2) = \pm 1, 0$ ;  $T_{2,0}^{-1}$  is contribution to the line width of the other relaxation mechanisms,  $\gamma_e$  is gyromagnetic ratio of electron.

Since for **3R·-N** radical  $a_1(\text{H}_\beta)$  and  $a_2(\text{H}_\beta)$  are different at low temperature from each other we can calculate the correlation time. In our case  $\tau \approx 8.2 \cdot 10^{-10}$  s ( $T = 210$  K). Using (1) one can verify that  $\theta_1 = 26^\circ$  and  $\theta_2 = 60^\circ$ .

So for the tris (2,6-di-tert-butyl-4-methyl-phenol) amine (**3R·-N**) individual conformers can be detected at low temperature. Therefore the correlation time of transition between these conformers can be calculated.

Thus the linewidths alternation of the EPR spectra of considered phenoxyl radicals is due to the intramolecular motions.

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