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ESR study of structural characteristics and intramolecular motions of tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine free radical in toluene

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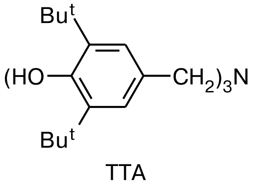
The magnetic and dynamic properties of tris(2,6-di-*tert*-butyl-4-hydroxybenzyl)amine free radical was studied by ESR spectroscopy in the temperature range from 170 to 350 K in toluene. Symmetrical conformers in the rigid toluene matrix with characteristic angles $\theta_1 = 26°$ and $\theta_2 = 60°$ between the symmetry axis of the $2p_z$-orbital on the C_α atom of the phenoxyl ring and the direction of the C_α—C_β bond of the CH_2 fragment were determined. The activation energy of transition between the conformers was determined to be 8.2 kcal mol^{-1}. The correlation time of transition between the conformers was established as $8.2 \cdot 10^{-1}$ s.

Key words: phenoxyl, free radical, ESR spectroscopy, conformers, conformational angles, correlation time of conformational transitions.

Phenols represent a class of chemical compounds in which chemists and industrial workers are especially interested. The most frequent use of substituted phenols in industry is their application as antioxidants.[1—3] The antioxidation properties of these phenols are due, to a great extent, to the easy detachment of the phenolic hydrogen atom and the efficient interaction of the phenoxyls formed with peroxyl and alkoxyl radicals, being the main reactants in self-oxidation.[4] In some cases, intermediate phenoxyl radicals can undergo further oxidation leading to the formation of quinoid products.[5] As shown earlier,[6] the oxidation of the methoxy-substituted phenoxyl radical is the main mechanism of photoinduced yellowing of paper. It is known[7,8] that the efficiency of antioxidation effect of a series of phenol stabilizers is determined by their spatial structure. At the same time, literature data on the spatial structure of similar compounds in solutions and on conformations of products of their oxidation, which play an important role in the inhibited oxidation process, are insufficient.

Tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (TTA) is a polynuclear phenol, *i.e.*, such phenols contain more than one phenol group per molecule. When phenol fragments are separated from each other by an aliphatic chain of at least three atoms, chemical changes in one phenol fragment exert almost no effect on the reactivity and other properties of the rest unreacted phenol fragments.[9,10]



TTA

Phenoxyl radicals formed from polynuclear phenols were studied to a considerably less extent than free radicals of mononuclear phenols. A comparison of radicals of alkylated bis, tris-, and tetraphenols with their mononuclear analogs[9] shows that they exhibit, as a rule, no substantial difference in HFC constants and, hence, in spin density distribution and predominant conformation. In such radicals an unpaired electron is localized on only one aromatic ring.

In this work, the free radical of tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (TTA$^•$) was studied by the ESR method, its isotropic HFC constants were obtained, the preferential conformations of the phenoxyl fragment relative to rotation about the C_α—C_β bond were determined, and the activation energy of transition between these conformations was found.

Experimental

Commercially available initial amine (Chem Service, USA) was used. Free radical was obtained by the oxidation with lead dioxide of the initial compound dissolved in toluene in a concentration of $1 \cdot 10^{-3}$ mol L^{-1}. The procedure on oxygen removal from the samples by freezing—evacuation—thawing out was carried out three times.

ESR spectra were recorded on an Elexsys E500 3-cm range radiospectrometer (Bruker, Germany). A TE_{102} rectangular resonator was used in measurements. The choice of detection modes was determined by requirements of undisturbed recording of the first derivative of the ESR signal. The measurement error of

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magnetic parameters mainly depends on errors of the frequency meter and magnetometer, stability of resonance conditions, and ESR line width, being $\pm 3 \cdot 10^{-2}$ G for HFC constants and $\pm 1 \cdot 10^{-4}$ for g-factors.

The temperature variator from the package of the spectrometer was used to detect the temperature dependence of the spectra.

Magnetic resonance parameters and relative intensities of the spectral components were determined by computer simulation of the experimental ESR spectra using the WinSim simulation program, which makes it possible to find the main parameters of the isotropic spectrum by automatic fitting.

Results and Discussion

The experimental ESR spectra of the free radical TTA$^{\bullet}$ in the temperature range from 170 to 350 K in toluene are shown in Fig. 1, *a*. In the rigid matrix below the freezing point of neat toluene (178 K) there are (Fig. 1, *b*) four broad lines, and two medium lines of them gradually broaden with temperature (170—250 K) and, hence, decrease in intensity and are brought together (see Fig. 1, *a*). One averaged broad line appears instead of them at 250 K.

Such a character of the spectra is explained by the existence of energetically equivalent conformers **1** and **2** between which conformational transitions occur. In this case, angle θ is the angle between the symmetry axis of the $2p_z$-orbital on the C_α atoms and the direction of the C_α—H_β bond. When β-protons are in nonequivalent positions, then $A_1 \neq A_2$ and the HFC constants (*a*) are not equal. Four lines of equal intensity are seen. If $A_1 = A_2$, *i.e.*, the both β-protons are equivalent, three lines with the intensity ratio 1 : 2 : 1 are observed. The *a* values for predominant conformers can be estimated from the ESR spectra using the equation

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

where parameter $b = 23.3$ G for the β-protons in the *para*-position with respect to the phenoxyl group.[9]

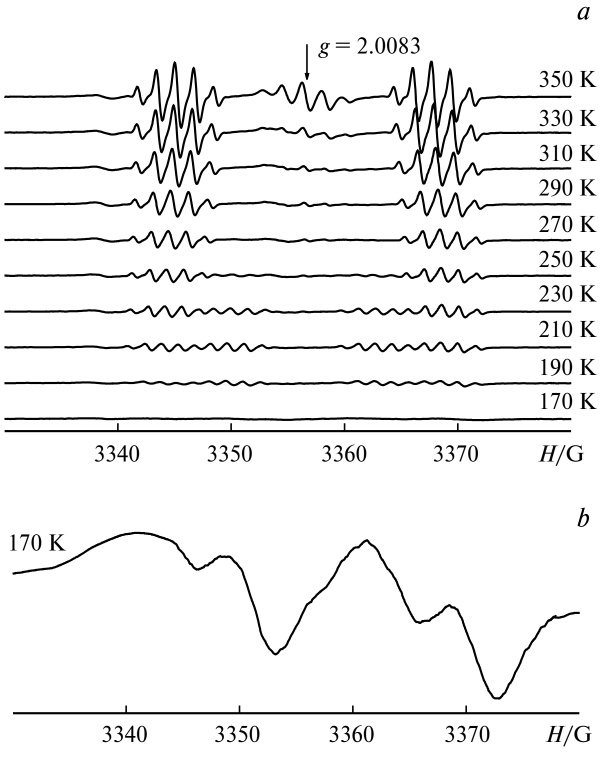

Fig. 1. Temperature dependence of the ESR spectra of the TTA$^{\bullet}$ radical (*a*) and its ESR spectrum at 170 K (*b*).

Let us particularly consider the spectrum at 210 K (Fig. 2). It is a doublet of doublets of quintets caused by the interaction of an unpaired electron with two nonequivalent β-protons with the HFC constants $a_{\mathrm{H}(\beta_1)} = 18.9$ G and $a_{\mathrm{H}(\beta_2)} = 5.8$ G, two protons of the phenoxyl ring in the *meta*-position to the phenoxyl group, and the ^{14}N nitrogen nucleus near the C_β atom with the constants $a_{\mathrm{H}(m)} =$ $= 1.5$ G and $a_\mathrm{N} = 1.4$ G, respectively.

Further we will be interested in the interaction with the β-protons. This is the difference in HFC constants with β-protons which is due to the existence of various conformers and transitions between them.

Transitions between two conformers result in the situation when the β-protons transfer from one position to another and thus cause modulation in the counterphase of hyperfine splitting, due to which ESR line widths alternate. These transitions become intense with temperature and their frequency becomes comparable with the difference in the HFC constants of the β-protons. Two central quintets (marked by dotted brackets in Fig. 2) broaden, decrease in intensity, and are brought together until join into one averaged line at 250 K, which increases in intensity with temperature, *i.e.*, with an increase in the frequency of the transition between the conformers, and is resolved to a quintet at 360 K.

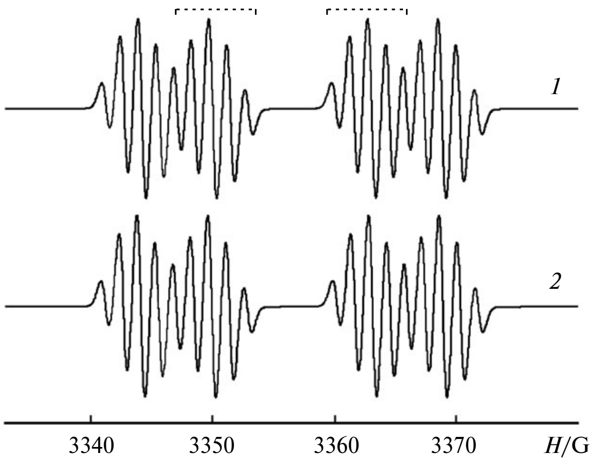

Fig. 2. ESR spectrum of the TTA$^{\bullet}$ radical at 210 K (*1*) and simulation of this spectrum (*2*). Internal quintets of the spectrum are marked by dotted brackets.

Let us consider the ESR spectrum of the free radical TTA$^{\cdot}$ at 350 K (see Fig. 1). The acceleration of rotation about the C_{α}—C_{β} axis results in averaging of the splitting constants: $a_{H(\beta_1)} = 12.2$ G and $a_{H(\beta_2)} = 10.5$ G. The aforementioned central quintets are brought together still more and join with the further temperature increase to form a triplet of quintets.

The shift can be determined from the ESR lines that are not overlapped in the initial spectrum. The shift is related to the lifetime τ (or the correlation time of the process) between the conformational transitions by the equation[11]

$$(\Delta H_0{}^2 - \Delta H_e{}^2)^{1/2} = 2^{1/2}/(\gamma_e\tau), \qquad (2)$$

where ΔH_0 is the distance between the lines in the absence of mutual transformations *a* and *b*, and ΔH_e is the distance between the lines in the case of mutual transformations. To fulfill Eq. (2), it is necessary that the individual line width of ESR lines δH would be much shorter than the distance between the lines. Presenting the temperature dependence of τ in the form

$$\tau = A\exp[E_a/(RT)], \qquad (3)$$

one can construct the plot of lnτ *vs* $1/T$. This plot is a straight line with the slope E_a/R, *i.e.*, the Arrhenius line (Fig. 3), whose slope makes it possible to determine the activation energy of transitions between conformers **1** and **2** for the free radical TTA$^{\cdot}$. The activation energy is equal to 8.2 kcal mol^{-1}.

The correlation time of rotation for the case where the atoms H_{β} transfer from one position to another and thus cause the alternation effect of the ESR line width can be presented as follows[11]:

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

where $I_{\pm 1}$ and I_0 are the intensities of ultimate non-overlapped lines of multiplets corresponding to the projections of the nuclear magnetic moment $m_I(CH_2) = \pm 1.0$; $T_{2,0}{}^{-1}$ is the contribution to the line widths from other relaxation mechanisms independent of $m_I(CH_2)$; and γ_e is the gyromagnetic ratio of an electron.

The correlation time τ can be calculated for radical TTA$^{\cdot}$, since the constants $a_1(H_{\beta})$ and $a_2(H_{\beta})$ are discernible at low temperatures. For temperature 210 K we obtain by formula (4) that $\tau \approx 8.2 \cdot 10^{-10}$ s ($2I_{\pm 1} = 111.4$, $I_0 = 97.1$, $T_{2,0}{}^{-1} = 1.91 \cdot 10^6$ Hz).

The values of conformational angles for the radical under study can be calculated by formula (1): $\theta_1 = 26°$ and $\theta_2 = 60°$, when $b = 23.3$ G,[9] $a_{H(\beta_1)} = 18.9$ G, and $a_{H(\beta_1)} = 5.8$ G.

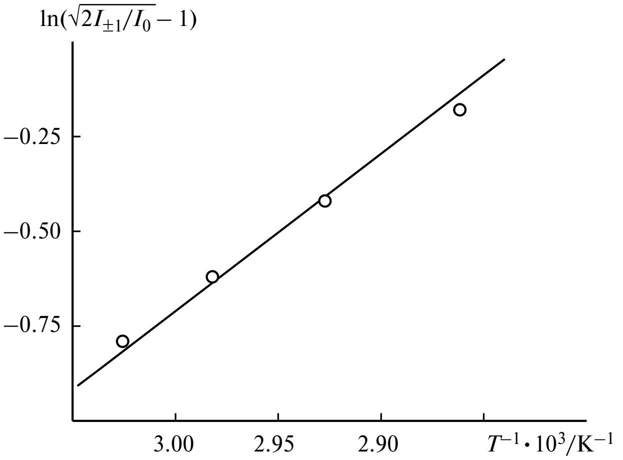

Fig. 3. Arrhenius curve for the TTA$^{\cdot}$ radical.

Thus, particular conformers were detected by the ESR spectra of the free radical tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine at low temperatures. The temperature dependence of the ESR spectra made it possible to calculate the correlation time of transition between these conformers and to estimate the activation energy of this process.

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