STUDY OF ELECTRON PARAMAGNETIC RESONANCE IN BIRADICALS OF THE HYDRAZINE SERIES

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structural formulas

Figure 1: structural formulas

Abstract

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STUDY OF ELECTRON PARAMAGNETIC RESONANCE IN BIRADICALS OF THE HYDRAZINE SERIES

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One of the basic questions connected with the investigation of the magnetic properties of biradicals is the study of the nature of the interactions between the two unpaired electrons of the biradical molecule. The method of electron paramagnetic resonance (e.p.r.) has unique possibilities for such investigations.

The study of spin exchange in biradicals derived from Chichibabin's hydrocarbon ($^{1-4}$) showed that the intramolecular exchange interactions are so weak that they do not appear in the e.p.r. spectra. With the aid of various models, attempts were made to give a theoretical explanation of the experimental facts obtained ($^{5-7}$). Recently reports have appeared on e.p.r. in biradicals prepared on the basis of phenoxy radicals ($^{8-10}$) and metalloketyls (^{11}). For these biradicals it proved possible to detect exchange interactions leading to pairing of the electron spins and formation of a triplet paramagnetic state.

Finally, in (^{12}) results are presented on the study of the mono- and biradical of bihydrazine (see formula I), which were obtained independently of those described in the present work. Although in (^{12}) the biradical form I could not be detected by the e.p.r. method, its existence was established by other methods. There is complete agreement between the constants of the isotropic HFS of the bihydrazine monoradical I in (^{12}) and our data.

We have studied the e.p.r. spectra of solutions of biradicals whose molecules contain two hydrazyl groups. The corresponding initial hydrazines have structural formulas (^{13}):

(I) (II)

Fig. 1

Figure 2: Fig. 1

The e.p.r. spectrum of a biradical in liquid solution can be described by the Hamiltonian

$$\hat{\mathscr{H}} = g\beta\vec{H}(S_1 + S_2) + \sum A_{1\mathrm{I}}\vec{S}_1 \cdot \vec{I}_\mathrm{I} + \sum A_{2j}\vec{S}_2 \cdot \vec{I}_j + J\vec{S}_1 \cdot \vec{S}_2,$$

which includes the term $J\vec{S}_1 \cdot \vec{S}_2$, taking into account the interaction between electron spins, where J is the exchange integral, $A_{1\mathrm{I}}, A_{2j}$ are constants of isotrop-

hyperfine interactions between spin 1 and nucleus I and spin 2 and nucleus j; $\vec{S}$ and $\vec{I}$ are the spin operators, respectively, for the electron and the nucleus. The indices 1 and 2 refer to electrons on the corresponding halves of the molecule. Let us consider two limiting cases: 1) $A \gg J$, i.e., the frequency of exchange of electrons between the halves of the molecule is much less than the hyperfine frequency. The e.p.r. spectrum observed in this case is similar to the spectrum of a monoradical; 2) $A \ll J$, the case in which each electron interacts with the nuclei of both halves of the molecule as a whole. In this case the e.p.r. spectrum of the biradical corresponds to a triplet paramagnetic state with total spin $S = 1$.

To study the isotropic hyperfine structure (h.f.s.), evacuated solutions I and II in dioxane were prepared, the spectra of which were recorded on an RE-1301 spectrometer. The choice of solvent was dictated by the good solubility in it of the starting hydrazines. Oxidation was carried out in vacuum with lead dioxide. For the best resolution of the h.f.s., solutions diluted to 10^{-3} mole/liter were used. The form of the spectrum and the h.f.s. constants for I and II varied depending on the ratio of oxidizing agent to oxidized hydrazine. To exclude the possibility of destruction of the molecules during oxidation with an excess of PbO_2, for II an oxidation method was used that exploited the property of hydrogen-atom transfer from a hydrazine molecule forming the more stable radical to a hydrazine molecule forming the less stable radical. As the latter, a solution of α,α-diphenyl-β-di-(ortho-, para)-nitrophenylhydrazine was used, which was added to the solution of hydrazine II.

Fig. 1. *a* –Experimental e.p.r. spectrum corresponding to monoradicals I and II. *b* –Experimental, *c* –theoretical spectrum of biradical I.

By creating different oxidation conditions, one can observe the transition from the e.p.r. spectrum corresponding to a monoradical to the spectrum of a biradical.

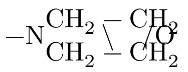
As was shown earlier in (^{14}), the h.f.s. of the spectra of DPPH derivatives with various substituents in the meta position of the picryl group is due to the interaction of the unpaired electron with two nitrogen atoms of the hydrazine and does not depend on the nature of the substituent. For all the radicals studied the ratio of the isotropic h.f.s. constants was found to be $A_{\mathrm{N1}}/A_{\mathrm{N2}} \sim 0.98$. Similar spectra were observed in liquid solutions of the free radicals I and II in all cases when only one half of the molecule was oxidized (Fig. 1*a*).

Carrying out further oxidation of I, i.e., removing the second hydrogen atom, we obtain the spectrum shown in Fig. 1*b*.

This spectrum is in good agreement with the spectrum constructed theoretically (Fig. 1*c*) under the condition that the unpaired electron interacts only with two nonequivalent nitrogen atoms: $A_{\mathrm{N1}}/A_{\mathrm{N2}} = 0.64$; $A_{\mathrm{N1}} + A_{\mathrm{N2}} = 17.13$ Oe; $\delta H = 4.05$ Oe. (δH is the width of an individual h.f.s. component.) This makes it possible to consider that in biradical I $J \ll A$. The changes in the e.p.r. spectrum of I observed in the transition from mono- to biradical are probably connected with a change in the possibility for the "picryl" group to take part in the delocalization of the two unpaired electrons.

Upon oxidation of II to the biradical, a spectrum is observed (Fig. 2*a*) consisting of nine h.f.s. components. Comparison of the areas under the integral

by the absorption curves for solutions with equal molar concentration of biradical II and of a radical derived from DPPH with the substituent

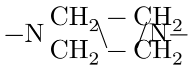


$$-\mathrm{N}\begin{matrix}\mathrm{CH_2}-\mathrm{CH_2}\\ \backslash\ /\mathrm{O}\\ \mathrm{CH_2}-\mathrm{CH_2}\end{matrix}$$

in the meta position of the picryl group [14] gave the ratio 2 : 1.

The addition of hydrazine II to a solution of the biradical converts the nine-component spectrum into the original five-component spectrum (see Fig. 1a). These facts show that the 9 EPR lines are due precisely to biradical II. Since the isotropic h.f.s. observed in solutions of free radicals is due to contact $\vec{I}\vec{S}$ interactions, the spectrum obtained indicates a distribution of spin density over four nitrogen atoms. A theoretical spectrum consisting of 9 components with an intensity ratio 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1 (Fig. 2b) shows that these nitrogen atoms are magnetically equivalent.

Taking into account the results of [14], in explaining the nine-component spectrum of II it is necessary to assume that the unpaired electrons are not each bound to its own hydrazyl group, but migrate from one half of the molecule to the other, i.e., the condition $J \gg A$ is fulfilled. Since in the present case bonding through the bridge



$$-\mathrm{N}\begin{matrix}\mathrm{CH_2}-\mathrm{CH_2}\\ \backslash\ /\mathrm{N}-\\ \mathrm{CH_2}-\mathrm{CH_2}\end{matrix}$$

is excluded, then for such exchange interactions to arise it is necessary for the $p\pi$-orbitals of the hydrazyl nitrogen atoms, on which the unpaired electrons are

Fig. 2. a —experimental, b —theoretical spectrum of biradical II

Figure 3: Fig. 2. a —experimental, b —theoretical spectrum of biradical II

delocalized, to overlap. Apparently, such overlap can occur only as a result of bending of the chain of molecule II, in which both halves are at a sufficiently short distance.

Fig. 2. *a* —experimental, *b* —theoretical spectrum of biradical II

Delocalization of each unpaired electron over the nitrogen atoms of the hydrazyl of the adjacent half of the biradical II molecule reduces the probability of finding the electron on "its own" pair of hydrazyl nitrogen atoms by approximately a factor of two. As a consequence, the isotropic coupling constant of the unpaired electron with the nitrogen nuclei should decrease by the same factor. Indeed, the value of the constant obtained by us for biradical II, $A_{\mathrm{N}} = 4.2$ Oe, is approximately one half of the value $A_{\mathrm{N\,av}} = (A_{\mathrm{N1}} + A_{\mathrm{N2}})/2$, found for the corresponding monoradical. It should be noted that the approach of the halves of molecule II to the distance necessary for the appearance of exchange interactions most likely corresponds to a strained state of the molecule. Therefore it is possible that the conditions for overlap of the orbitals of the unpaired electrons are created as a result of sufficiently rapid vibrations of the molecule with frequency $\nu \gg 10^7$ Hz (the magnitude of the hyperfine splittings in frequency units).

Transitions in the triplet paramagnetic state, expected for biradical II, should give, because of the presence of fine splittings, an anisotropic EPR spectrum. However, an isotropic spectrum with $g = 2.0035$ is observed. This shows that in a liquid solution the anisotropy is averaged to zero by sufficiently rapid molecular motion and the spectrum obtained is equivalent to transitions in a degenerate triplet state.

Reasonable estimates make it possible to consider that the fine-splitting parameter D does not exceed 0.01 cm^{-1}.

No temperature dependence of the intensity of the EPR spectrum of biradical II in liquid solution could be detected in the interval $+60^\circ$ to -50°. Further lowering of the temperature leads to broadening of the EPR lines and to the disappearance of the hyperfine structure. In the supercooled solution, one EPR line is observed, with a width of ~ 20 Oe and with the same value $g = 2.0035$. Other lines characteristic of $S = 1$, as well as transitions with $\Delta m = \pm 2$, were likewise not detected. This may be connected with the low intensity of the $\Delta m = \pm 2$ transitions in solution (for biradical II it is not possible to obtain a concentration > 0.07 mol/l) and with disruption of the exchange coupling between the halves of the molecule upon transition to the solid state. In this case the anisotropic h.f.s., characteristic of hydrazyls with $S = 1/2$, is not resolved because of dipolar broadening.

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Note: Figure translations are in progress. See original paper for figures.