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Abstract

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ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF INDIVIDUAL POLYRADICALS

(Presented by Academician V. N. Kondrat̕ ev on 21 January 1965)

In the preceding work (^{1}) the e.p.r. spectra of nitroxyl biradicals with weak exchange interaction were considered. The present article is devoted to an analysis of the e.p.r. spectra of tri- and tetraradicals of the nitroxyl series (^{2}-^{4}).

The spectra of the following individual polyradicals were studied:

[chemical structures I-IV]

where $\dot{R} =$

[nitroxyl radical fragment]

Experimental details and particulars of the investigation, as well as an analysis of the spin distribution in the fragment $\dot{R}$, were given by us in the study of biradicals (^{1}). As in the case of biradicals, the absorption spectra of tri- and tetraradicals in the visible and ultraviolet regions differ hardly at all from the corresponding spectra of monoradicals; however, their e.p.r. spectra reveal more interesting features.

[EPR spectra]

Fig. 1. E.p.r. spectra of triradical I in hexane:
a –20, *b* –130, *c* –150°

Figure 1 shows the e.p.r. spectra of triradical I in hexane. At 20° all three spins behave independently (a triplet e.p.r. spectrum due to the nucleus N^{14}); however, with increasing temperature, when the intensity of intramolecular motions increases, all the spins begin to participate in exchange, which leads to the appearance in the e.p.r. spectra of an additional four lines with steadily increasing intensity.

In triradical II the intensity of the interactions of the paramagnetic fragments of the radical is sufficiently high that it leads to strong exchange of all three spins already at 20° (in ethanol, hexane, and chloroform); the EPR spectrum accordingly contains seven lines (Fig. 2). However, in acetic acid the spin

Fig. 2

Figure 1: Fig. 2

Fig. 3

Figure 2: Fig. 3

exchange is greatly slowed, and in the EPR spectrum only spin exchange through pairwise interactions is manifested (Fig. 2, *c*). This dependence of the form of the spectrum on the solvent confirms the regularities that were found in work (1).

The EPR spectrum of tetraradical III at 20° in benzene (Fig. 3, *a*) is similar to the EPR spectrum of the corresponding biradical. This means that only pairwise spins, with their nearest neighbors, take part in the spin exchange. With intense intramolecular motions (138°, in benzene), all 4 spins participate in the electron exchange, and 9 lines appear in the EPR spectrum; their intensity ratio is close to that which should occur when the electron is delocalized over four equivalent N^{14} nuclei (Fig. 3, *b*).

Fig. 2. EPR spectra of triradical II at 20°:
a –chloroform, *b* –ethanol, *c* –acetic acid

In tetraradical IV, already at 20° the intensity of intramolecular motions is sufficient for all 4 spins to take part in the exchange (Fig. 4).

Fig. 3. EPR spectra of tetraradical III in benzene: *a* –20, *b* –138°

Fig. 4. EPR spectrum of tetraradical IV in benzene at 20°

For all polyradicals, the splittings in the triplet spectra were 15.6 Oe, in the five-line spectrum 7.8 Oe, and in the nine-line spectrum 4.0 Oe. The g-factors of the tri- and tetraradicals studied do not differ from the g-factors of the corresponding monoradicals. In none of the polyradicals was it possible to detect electronic transitions with $\Delta m > 1$.

Thus, the data presented here confirm the possibility of exchange interaction not only of two but also of many spins, which makes it possible to investigate much more broadly questions associated with such exchange.

It should be noted that earlier, both in work (1) and in the cited ⋯

In (1), only the exchange of two electrons was considered. In the present work, such cases have been discovered for the first time in which the number of unpaired electrons participating in the exchange exceeds two. In this connection

Fig. 4

Figure 3: Fig. 4

the question arises of the mechanism of the exchange interactions. Analysis of the data presented earlier (1) and here shows that the possibility of exchange through triple, quadruple, etc., collisions must be rejected at once. One should consider only the possibility of successive transfer of the perturbation from spin to spin through pair collisions, i.e., a kind of "memory" of the electron, capable of transmitting information about the perturbation at a definite rate.

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