DIASTEREOMERIC ANISOCHRONISM IN THE EPR SPECTRA OF PHOSPHORANYL RADICALS

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免费 radicals containing two asymmetric centers can be expected to show in the EPR spectra diastereomeric anisochronism, i.e., a small difference in the hyperfine coupling (hfc) constants of two stereoisomers; in certain cases this can be recorded experimentally [1, 2]. This effect should be most clearly shown when the constants of the hyperfine coupling with nuclei of the asymmetric centers are considerable. This condition is realized, in particular, in phosphoranyl radicals (PR), for which the hfc of an unpaired electron with phosphorus nucleus is 600-1300 Oe.

In the present work we studied PR obtained according to the following scheme:

\[
\begin{align*}
\text{Bu-t} & \quad \text{Bu-t} \\
\text{CH}_3 - N & \quad \text{NHR} \\
\text{CH}_3 - O & \quad \text{P} - \text{NHR} + \text{t-BuO}^- \quad \text{Bu-t} \\
(\text{IV}) & \quad (\text{VI}) \\
R & = \text{t-Bu} \quad (I), \quad (IV); \quad \text{sec-Bu} \quad (II), \quad (V); \quad \text{CH(Me)COOE} \quad (III), \quad (VI).
\end{align*}
\]

Radical (I) contains only one asymmetric phosphorus atom, while radicals (II) and (III) have a second asymmetric center on the carbon atom of the alkylamino group.

Usually a trigonal bipyramidal PR structure is assumed, in which the hfc constants of the atoms in the apical and equatorial positions differ sharply. In related PR, the following hfc constants are observed [3]:

\[
\begin{align*}
(I) \quad a_P &= 839, \quad a_N = 4.3 \,(2N), \quad a_H = 4.5 \,(1H); \\
(II) \quad a_P &= 723, \quad a_N = 23.2, \quad a_H = 5 \,(1H); \\
(III) \quad a_P &= 902, \quad a_N = a_Et = 4.2 \,Oe \,(1H, \,1N)
\end{align*}
\]

It follows from these data that hfc constants \(a_P\) as well as \(a_N\) depend on the ring orientation.

The EPR spectrum of radical (I) (Fig. 1) is characterized by hyperfine splitting due to P (\(a_P = 712.5\) Oe), N equatorial (\(a_N = 3.3\) Oe), and N apical (\(a_N = 13.9\) Oe) nuclei, and also on the quasiapical H of the five-membered ring (\(a_H = 9.5\) Oe).

From the comparison of the above data with the data in [3], we can assume that the radicals studied by us have the structure of type (2)
Radicals (2) and (3) exist at $-95^\circ$C in equilibrium at a ratio $(2)/(3) = 0.1$ [3]. In the present study, type (3) radical was not observed, probably because of strong steric interaction of the equatorial tert-butyl substituent of the five-membered ring with the equatorial RNH group.

Figure 1 shows that in the radical (I) spectrum, both low- and high-field components of the phosphorus doublet are symmetrical, while those of the radical (II) spectrum (Fig. 2) have a sharply expressed asymmetry. It must be assumed that the $a^N$ and $a^H$ constants change inappreciably as the result of changes in the type of the amino group [3, 4]. Then, in the spectrum of radical (II), the increase in the extent of the low-field component of the spectrum by 4 Oe and the high-field component by 2.6 Oe, compared with that of radical (I), indicate a superposition of spectra of the two diastereomers differing with respect to the $a^P$ constants by 6.6 Oe (see Fig. 2).

The difference in the extension of the low- and high-field multiplets (1.4 Oe) of radical (II) is due to the superposition of the spectra of the diastereomers, characterized by high $a^P$ constants. At high hfc constants, comparable with the value of the magnetic field intensity $H$, a marked nonlinearity is observed in the dependence of the position of the levels of the unpaired electron on the field intensity. This leads to asymmetry in the hyperfine structure lines in relation to the g factor of the radical.

Due to the above shown asymmetry in the disposition of the components of the phosphorus doublet, superposition of the spectra of two different stereoisomers (A) and (B), which differ in the value of $a^P$, leads to differences in the extension of the multiplets recorded in the low and high fields. In this case, in accordance with the Bright–Rabi formula [5], it is possible to find the position of the phosphorus doublet for the two stereoisomers and to evaluate the expected difference in the EPR spectra.

Assuming that the values of the constants in one form is $a^P_A = 710$ Oe, and in the other form $a^P_B = 716.6$ Oe, and the g factor is 2.003 for the two forms [3], we find the position of the lines of the phosphorus doublet for forms (A) and (B):

- $H_{AH} = 2901.78$ Oe; $H_{AB} = 3627.16$ Oe
- $H_{BH} = 2905.89$ Oe; $H_{BB} = 3624.50$ Oe.

From these values it is easy to determine the difference in the extension of the low- and high-field components for radical (II), compared with (I), 4.11 and 266 Oe, which agrees well with the experimental values.

A similar pattern was obtained in the study of radical (III). The decay kinetics of radicals (I–(III)) in temperature range from −40 to $-100^\circ$C is first order. The EPR spectrum at 0°C of the tert-butyl radical shows that phosphoranyl radical decay is due to $\beta$-splitting of the tert-butyl substituent on the O atom.