THE ANISOTROPY PARAMETERS OF THE IMINOXYL RADICAL CONTAINING ^{15}N

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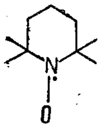
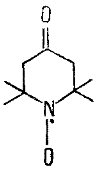
The study of the motion of stable iminoxyl radicals of the type  in macromolecular compounds by the ESR method [1-3] makes it possible to obtain new information on the supermolecular packing and dynamics of polymeric molecules, particularly in the theoretical analysis of the ESR spectra [4, 5]. The analysis makes it possible to select a correct model for the rotational movements of the radical, and from the form of the spectrum to determine the effective frequencies of these motions. The solution of this problem is also extremely important for the correct interpretation of a large number of experiments on the study of biomolecules in solution by the "spin label" method using the iminoxyl radical as label.

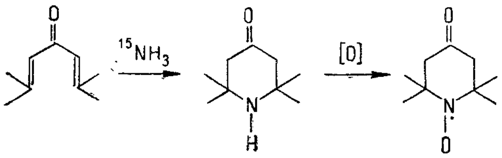
The corresponding calculations, however, encounter a number of methodological difficulties [4, 5], which can be decreased considerably if the radical containing the ^{15}N isotope (0.38%) is used in place of the radical with the most common isotope ^{14}N (99.62%). The spin of the ^{15}N nucleus is equal to 1/2, instead of 1 for ^{14}N. Thus the number of possible combinations of the HFS levels is smaller for ^{15}N than for ^{14}N (as a consequence, the number of equations is also smaller). Moreover, we would hope that the use of the iminoxyl radical containing ^{15}N would make it possible to explain the nature of the previously detected explicit breakdown of the simple isotropic model of the rotation of the radical in solid polymers [1-3].

In order to solve these problems, we prepared and isolated in the crystalline state the iminoxyl radical I containing the ^{15}N isotope



(I)

(in [6, 7], the iminoxyl radical containing ^{15}N was not isolated from solution). The preparation was carried out by the condensation of chromatographically pure phorone with subsequent catalytic oxidation of the resulting triacetoneamine to give 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxide [8-10]:



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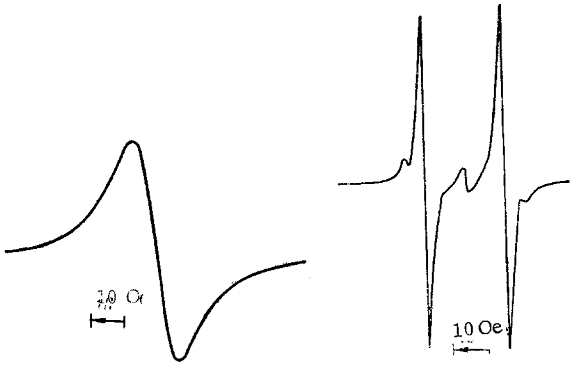

Fig. 1. ESR spectra of the crystalline radical I containing ^{15}N (a) and the radical dissolved in GKZh-94 oil (b), T = 296°K.

The radical isolated in crystalline form, like the radical containing ^{14}N, is obtained as a yellow powder with mp = 36°C, which practically coincides with the melting point of the radical containing ^{14}N. The ESR spectra of the crystalline radicals containing ^{15}N and ^{14}N, recorded on an RÉ-1301 spectrometer ($\lambda \simeq 3$ cm), coincide. The spectrum of the crystalline radical (Fig. 1) consists of a line narrowed by exchange, with width $\Delta H = 12.5$ Oe and $g = 2.0066 \pm 0.0004$. For a density $\rho \simeq 1.1$ g/cm^3 in the first roughest approximation of the isotropic arrangement of the radicals, the average distance between the spins in the crystal is equal to 6.4 Å; the second dipole moment is $\Delta H_p^2 \simeq 2000$ Oe^2, and the effective frequency of exchange, determined from the width of the ESR line by means of the Anderson–Weiss equation [11], in the crystalline radical is $\nu_e \simeq 5.5 \cdot 10^9$ sec^{-1} ($h\nu_e/k \simeq 0.2$°K). The spectrum of the radical containing ^{15}N in the state of a dilute solution with low viscosity consists of a doublet corresponding to the projections of the nuclear spin $I = \pm 1/2$ (Fig. 1b). The distance between the components is equal to the contact interaction constant $a = 21.4$ Oe. The ESR spectra of a radical which has migrated from the vapor into polyethylene at 296°K are given in Fig. 2. The isotropic constants a of the radicals in silicone oil (Fig. 1, b) and in polyethylene practically coincide.

The central regions of the spectra (Figs. 1b and 2b) show an HFS line with $m_I = 0$, corresponding to a small quantity of the radical containing the ^{14}N isotope. The fact that this line lies exactly in the middle of the doublet shows that the parameters, averaged by rapid rotation, of the tensor of the g factor for the unpaired electron $g_0 = 1/3\,(g_{xx} + g_{yy} + g_{zz})$ for the two radicals coincide; the experimental value is $g_0 = 2.0062 \pm 0.0004$. With decrease in temperature, the ESR spectrum becomes appreciably broader, because of the decrease in the frequency of the rotational movements of the radical, and at a sufficiently low temperature it acquires the form characteristic of completely retarded rotations (Fig. 3b). For comparison, Fig. 3a gives the spectrum of the completely retarded rotations for the radical containing ^{14}N.

For the interpretation of the ESR spectrum of a radical in viscous media, it is necessary to know the parameters of the tensor of the g factor and the tensor $\hat{T}$ of the hyperfine interaction of the unpaired electron. Their values can be obtained by comparison with the corresponding values of the parameters for the radical I containing ^{14}N, determined earlier [12]. The spin Hamiltonian for the interaction of the unpaired electron with an external field H and the nucleus is written in the form

$$\mathscr{H} = |\beta|\, s\hat{g}\mathbf{H} + h\,(As_zI_z + Bs_xI_x + Cs_yI_y), \tag{1}$$

where A, B, and C characterize the hyperfine interaction, and β is the Bohr magneton. As shown in [12], for the iminoxyl radicals the principal axes of the $\hat{g}$ and $\hat{T}$ tensors coincide. It is natural to assume that the density of the distribution of the unpaired electron is not affected by isotopic substitution. As will be seen below, this is confirmed indirectly by the experimental results. The components of the electronic tensor for the radicals containing ^{15}N and ^{14}N then coincide and are close to those measured in [12] (a discrepancy may arise as a consequence of the influence of the medium);

$$g_{xx} = 2.0089, \quad g_{yy} = 2.0061, \quad g_{zz} = 2.0027.$$

This is confirmed by the fact, indicated above, that the values of g_0 for the radicals coincide.

To determine A, B, and C we make use of the fact that

$$A = A_d + a; \quad B = B_d + a; \quad C = C_d + a, \tag{2}$$

$$a = 1/3\,(A + B + C), \tag{3}$$

where a is the constant of the isotropic Fermi interaction, and A_d, B_d, and C_d are the anisotropic dipole parts of the hyperfine interaction. By making use of the familiar expressions for the constants of the contact and dipole-dipole hyperfine interaction [13, 14], it can readily be shown that the ratio of the constants

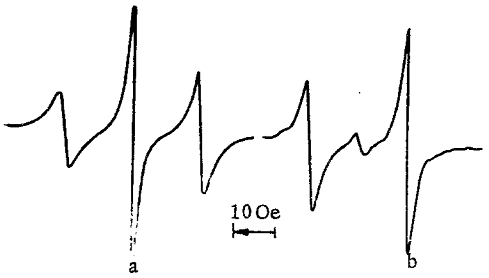

Fig. 2

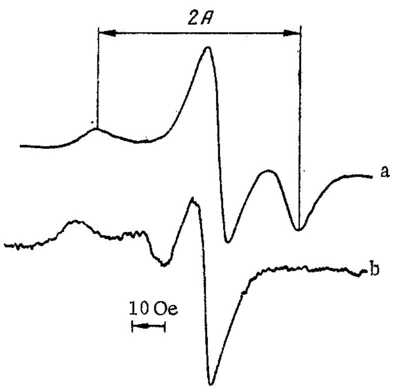

Fig. 3

Fig. 1. ESR spectrum of the rapid rotations of radical I in polyethylene, T = 296°K: a) radical containing ^{14}N; b) radical containing ^{15}N.

Fig. 2. ESR spectrum of completely retarded rotations of radical I in polyethylene, T = 77°K: a) radical containing ^{14}N; b) radical containing ^{15}N.

a and A_d, B_d, and C_d for the ^{14}N and ^{15}N isotopes is equal to the ratio of the nuclear g_N factors or the gyromagnetic ratios of the nuclei γ_N. For ^{14}N, $\gamma_N = 307.7$ sec^{-1} Oe^{-1}, and for ^{15}N, $\gamma_N = 431.6$ sec^{-1} Oe^{-1} [15], that is the ratio $\gamma_{^{15}N}/\gamma_{^{14}N} = 1.402$. Thus the ratio of the constants of the hyperfine interactions a, A_d, B_d, and C_d, and hence of A, B, and C for the radicals containing ^{15}N and ^{14}N is also equal to 1.4. This conclusion is confirmed experimentally. For the radical I containing ^{14}N, $a = 14.8$ Oe (see Fig. 2) and the ratio of the constants is $a_{^{15}N}/a_{^{14}N} = 1.4$. To determine A, B, and C for the radical containing ^{15}N from the experimental results, it is sufficient to make use of the qualitative conclusion [12] that B and C are equal, that is that the hyperfine interaction of the unpaired electron has axial symmetry. Exact calculation [5] shows that the distance between the extreme maxima in the spectra of the retarded rotations (see Fig. 3) is equal to 2A. From this we find A = 31.5 Oe, and, by making use of Eq. (3), a = 14.8 Oe and B = 6.5 Oe. Thus, for the radical containing ^{15}N, A = 44.0 Oe and B = 9.1 Oe. Comparison of the values of these parameters for ^{14}N with the parameters obtained from measurements for dilute single crystals of radical I [12] shows that the hyperfine interaction constants in the polymer are altered slightly.

To confirm these conclusions regarding the magnitude of the constants for the radical containing ^{15}N, in addition to the data on the quantities a and g_0, it is possible to use the ratio of the products of the electronic anisotropy parameters

$$\Delta\gamma b = \frac{\beta}{\hbar}\left(g_{zz} - \frac{1}{2}(g_{xx} + g_{yy})\right)\frac{4\pi}{3}(A - B)$$

of the radicals containing ^{15}N and ^{14}N, which appear in Kivelson's equation [16] for the relaxational width of the HFS lines for rotation of the radical in a viscous medium (in the range of rapid rotations). For this purpose we analyzed the ESR spectrum of the radicals containing ^{15}N and ^{14}N in glycerol at 296°C (Fig. 4). It may be noted that the constants for the radicals in the dipolar liquid glycerol are slightly higher than those in polyethylene and silicone oil $a^g_{^{14}N} = 16.2$ Oe, $a^g_{^{15}N} =$ 23 Oe; for the radical containing ^{14}N, the transformed Kivelson equation is written in the form [1-3]

$$\frac{\Delta\nu(M)}{\Delta\nu(0)} = 1 - \frac{4}{15}\frac{\tau_c b \Delta\gamma H_0}{\Delta\nu(0)\pi\sqrt{3}}M + \frac{b^2\tau_c}{8\pi\sqrt{3}\Delta\nu(0)}M^2, \tag{4}$$

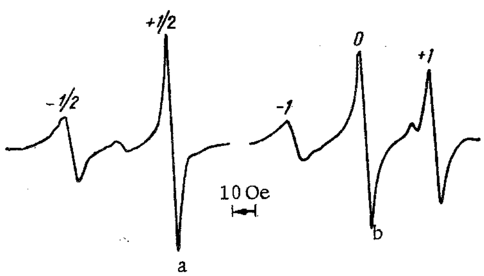

Fig. 4. ESR spectrum of radical I in glycerol, T = 293°K: a) radical containing ^{15}N: b) radical containing ^{14}N.

where M = ± 1.0 represents the spin projections of the ^{14}N nucleus, $\Delta\nu$ is the distance between the maxima of the derivative absorption line, τ_c is the correlation time of the rotational movements of the radical, and H_0 = 3300 Oe is the external magnetic field. The applicability of Eq. (4), that is the isotropic nature of the rotation of the radical, is confirmed by the fact that the times τ_c' and τ_c'', calculated from the values of the coefficients for M and M^2, coincide within the limits of experimental error. By making use of the numerical values of b and $\Delta\gamma$ for the radical containing ^{14}N in glycerol at 293°K, we obtain $\tau_c = 1.3 \times 10^{-9}$ sec. For the radical containing ^{15}N, the equation corresponding to Eq. (4) (high-field approximation) is written in the form [16]

$$\Delta\nu_{-1/2} - \Delta\nu_{+1/2} = \frac{4}{15}\frac{\tau_c}{\pi\sqrt{3}} b\Delta\gamma H_0, \tag{5}$$

where $\Delta\nu_{\pm 1/2}$ represents the widths of the components with M = ± 1/2. With the assumption that the correlation times τ_c for the two radicals coincide, it can readily be found from Eqs. (4) and (5) that the ratio $(\Delta\gamma b)_{^{15}N}/(\Delta\gamma b)_{^{14}N} = 1.4$, as expected.

In conclusion we thank A. V. Lazarev for drawing our attention to the use of the radical containing ^{15}N, A. K. Shilova for kindly providing a specimen containing ^{15}N, and I. V. Aleksandrov and I. F. Shchegolev for discussion.

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