Mobility and e.s.r. spectra of alkyl free radicals trapped in irradiated mats of solution-grown polyethylene

Shigetaka Shimada and Hisatsugu Kashiwabara
Nagoya Institute of Technology, Showa-ku, Nagoya 466, *Japan*
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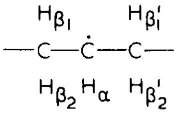
E.s.r. studies of alkyl free radicals,  $-\underset{H_{\beta_2}}{\overset{H_{\beta_1}}{C}}-\underset{H_{\alpha}}{\dot{C}}-\underset{H_{\beta'_2}}{\overset{H_{\beta'_1}}{C}}-$, trapped in irradiated mats of solution-grown polyethylene crystals have been studied. The crystal mat was aligned so that the crystallites *c*-axes were perpendicular to its surface. When the angle between the direction of applied magnetic field and the *c*-axis of the crystallite was varied, the observed e.s.r. spectra showed apparent anisotropy due to α-proton hyperfine splitting. The principal values and directions of the $\tilde{A}$ tensor due to the α-proton at 77 and 254K were determined using the line shapes of uniaxially-oriented samples. The principal axis directions, A_1 were assigned along the polymer chain axis and A_2 and A_3 were perpendicular to the chain axis. The maximum principal value A_1 did not change with temperature, but the lower principal values, A_2 and A_3 averaged out at high temperatures. Hence, it was concluded that the temperature dependence of the $\tilde{A}$ tensor reflects hindered oscillation around the main chain axis at high temperature. A twisted configuration for the methylene group with 4.5° deviation from the *trans–trans* configuration was also evident for the rigid state configuration of the alkyl radicals at 77K. Temperature dependences of the hyperfine splitting widths due to β-protons were observed and analysed in terms of hindered oscillations of the β-methylene group.

INTRODUCTION

Structures and mobilities of alkyl radicals trapped in the powdered polyethylene samples in urea–polyethylene complexes has been discussed[1]. A twisted methylene group configuration combined with hindered oscillation of the β-methylene group were found by analysis of the hyperfine splitting widths due to β-protons. However, temperature dependence of the hyperfine splitting width due to the α-proton and its mobility are the subject of further study. Before discussing anisotropic α-proton motion, the temperature and orientation dependences of spectral line shapes using uniaxially-oriented samples must be studied. Anisotropic e.s.r. spectra are observed[2,3] from mats of solution-grown polyethylene crystals, where the *c*-axes of the molecular chain are aligned perpendicular to the plane of the mat. This anisotropy has been interpreted by anisotropic hyperfine splitting due to the α-proton located in the crystalline region. Detailed interpretation has already been presented on the locations of alkyl free radicals (on the crystal surface or in inner crystalline regions) and separation of superposed spectrum was reasonably achieved[4]. To observe trapped radical spectra in the crystalline region, the specimen were stored at room temperature for a long time. Here, we first estimate the hyperfine splitting widths due to the β-protons and the principal values and directions of the $\tilde{A}$ tensor due to the α-proton are estimated from the anisotropic spectra of alkyl radicals trapped in the mat by computer simulation; secondly, the structure of alkyl radicals and the mobilities of α- and β-protons are discussed by comparison with results obtained from powdered samples.

EXPERIMENTAL

Sample preparation

High density polyethylene, Sholex 6050 (Showa Electric Industry Co.) was purified by the method used in the previous paper[4]. The specimen was recrystallized from dilute xylene solution (~0.025 wt%) for more than 48 h at 71°C in a vessel fitted with a glass filter. Good alignment of the crystal *c*-axis was achieved by slow filtration of xylene using a water jet-pump. The resulting plate-shaped materials were dried thoroughly in a vacuum oven before being inserted in e.s.r sample tubes; the sample tube was set parallel to the plane of the mat.

Irradiation technique

The sample was subjected to Co^{60} γ-irradiation at liquid nitrogen temperature under 10^{-4} torr. Total dose was 3.4. Mrad with a dose rate of 0.22 Mrad h^{-1}.

E.s.r.

Spectra were recorded with a JEOL ME-2 spectrometer (X-band) with a field modulation of 100 kHz. Online spectrum computer JEOL EC-6 was

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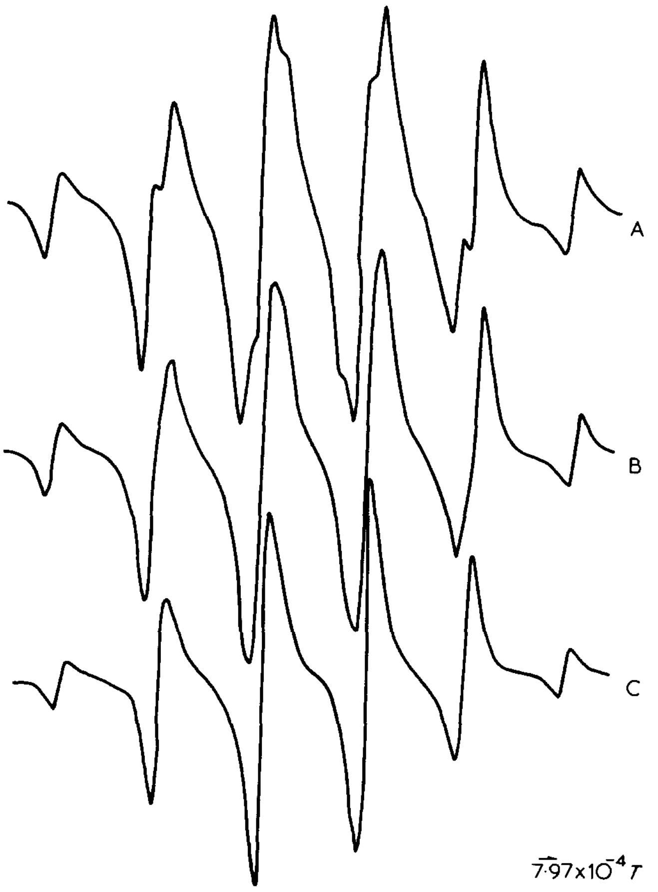
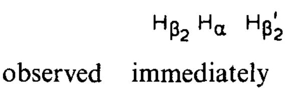


Figure 1 Variation of e.s.r. spectra of alkyl radicals trapped in an irradiated mat of solution-grown crystals with temperature of observation. $\delta = 90°$. A, 77K; B, 143K; C, 294K

connected to the spectrometer and 8 data were punched out on the paper tape by an A–D converter. Analyses were conducted by electronic computer HITAC 8400 in the Computer Center of Nagoya Institute of Technology.

RESULTS AND DISCUSSION

Variation in e.s.r. spectra with temperature

Figures 1 and *2* show the changes in e.s.r. spectra with temperature. *Figure 1* shows the spectra observed when the angle between the crystal *c*-axis and the direction of the applied magnetic field, δ, was 0° and *Figure 2* shows the spectra observed for $\delta = 90°$. These spectra are for alkyl-type free radicals,  $\sim\underset{H_{\beta_2}}{\overset{H_{\beta_1}}{C}}-\underset{H_\alpha}{\dot{C}}-\underset{H_{\beta_2}'}{\overset{H_{\beta_1}'}{C}}\sim$. Where an e.s.r. spectrum was observed immediately after γ-irradiation, a superposed spectrum composed of broad and narrow sextets was observed. However, the broad sextet, which was attributed to alkyl radicals located at the crystal surface, disappeared after the heat treatment at room temperature. The spectra in *Figures 1* and *2* were observed after heat treatment at room temperature for 30 min, which caused trapping of only the alkyl radicals located in the inner crystalline region. Six-line and ten-line patterns were observed for $\delta = 90°$ and $\delta = 0°$, respectively. This anisotropic e.s.r. spectrum could be interpreted in terms of anisotropic dipole–dipole interaction due to the α-proton (see below). As indicated in *Figures 1* and *2*, both six-line and the ten-line patterns change significantly with temperature; the variations of the whole spreads, the relative intensities of each component and the line subsplittings are recorded. These temperature dependences may be caused by the decrease of line width, the averaging of anisotropy of the coupling constant due to the α-proton and the variation of coupling constant due to the β-protons.

Line shapes for uniaxially-oriented samples

Rotational or oscillational motion around the molecular chain axis affects e.s.r. line shape, and provides evidence for the interpretation of the variation in $\tilde{A}$ tensor of hyperfine splittings due to α-proton. Iwasaki *et al.*[5] derived the line shapes of peroxy radicals in a uniaxially-oriented sample and discussed the averaging of the *g* tensor by rotational motion. We applied this method to the $\tilde{A}$ tensor for alkyl radicals. In perfectly-oriented polymer chains, the main chains are parallel to the crystallites *c*-axes. When the magnetic field is perpendicular to the molecular chain axis, $\delta = 0°$, the C_α–H_α bonds are randomly distributed ranging from parallel to perpendicular orientation with respect to the magnetic field, because of the uniaxially orientation of the chains. The spectral line is then due to two dimensional random orientation (*Figure 3*). The shape function for such an orientation is calculated in a manner similar to three dimensional random orientation[6]. The principal values, A_1, A_2, A_3 and the directions of the $\tilde{A}$ tensor were assumed

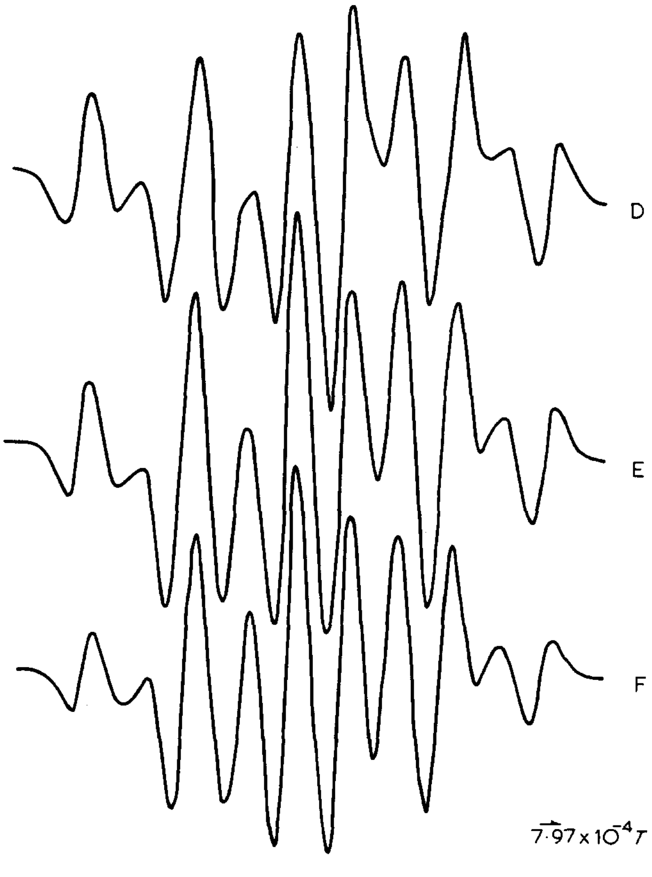


Figure 2 Variation of e.s.r. spectra of alkyl radicals trapped in an irradiated mat of solution-grown crystals with temperature of observation. $\delta = 0°$. D, 77K; E, 141K; F, 294K

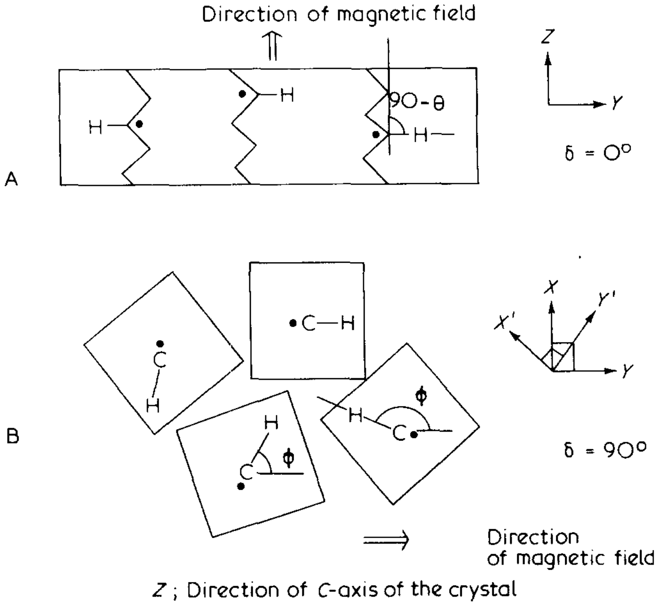


Figure 3 Schematic representations of angles between the C_α–H_α bonds direction and the applied magnetic field in solution grown crystals. (a) Single crystal of polyethylene is projected on a plane containing a polymer chain of *trans–trans* conformation. *Z*-axis indicates the direction of the polymer chain axis. (b) Solution grown crystals of polyethylene are projected on a plane perpendicular to the polymer chain axis. *Y, Y'* indicates the direction of the C_α–H_α bonds. ϕ indicates the angle between the direction of C_α–H_α bonds and the applied magnetic field

to be those in *Figure 3*. The resonant shift, H–H_0, due to α protons is expressed by:

$$H\text{–}H_0 = M_I(A_1{}^2\cos^2\theta + A_2{}^2\sin^2\theta\sin^2\varphi + A_3{}^2\sin^2\theta\cos^2\varphi)^{1/2} \tag{1}$$

where φ and θ are the angles (polar coordinates) by which the field direction is rotated with respect to the principal coordinates of the $\tilde{A}$ tensor; M_I is nuclear spin quantum number. For $\delta = 0°$ ($\theta = 0°$):

$$H\text{–}H_0 = M_I A_1 \tag{2}$$

Here, there is no distribution of hyperfine splitting widths. However, for $\delta = 0°$ ($\theta = 0°$):

$$H\text{–}H_0 = M_I(A_2{}^2\cos^2\varphi + A_3{}^2\sin^2\varphi)^{1/2} \tag{3}$$

The azimuthal angle φ should range from 0° to 360°. If the normalized shape function is denoted by $S(H)$, $S(H)\mathrm{d}H$ is the probability of finding the C_α–H_α bond angle in the range φ to $\varphi + \mathrm{d}\varphi$. As a result:

$$S(H)\mathrm{d}H = \mathrm{d}\varphi/\frac{\pi}{2} \tag{4}$$

and

$$S(H) = \frac{2}{\pi}\left(\frac{\mathrm{d}H}{\mathrm{d}\varphi}\right)^{-1} \tag{5}$$

Substitution of equation (3) into equation (5) gives:

$$S(H) = \frac{1}{\pi}\cdot\frac{H\text{–}H_0}{\{(H\text{–}H_0)^2 - M_I{}^2A_3{}^2\}\{-(H\text{–}H_0)^2 + M_I{}^2A_2{}^2\}^{1/2}} \tag{6}$$

Using spectral values for A_2, A_3 and $M_I = 1/2$, we can calculate the spectral intensities, $S(H)$, to obtain the theoretical doublet spectra due to the α-proton assuming that each component has Gaussian line shape. Several theoretical spectra were calculated, changing the values of spectral parameters gradually. These spectra were recorded on an X–Y plotter and compared with the observed spectra to find the best fit.

Averaging of the $\tilde{A}$ tensor: molecular motion around the main chain axis

The outermost line shapes at low magnetic field have been expanded in *Figure 5* for both $\delta = 0°$ and 90°. These line shapes represent doublet spectrum due to the alkyl radical α-proton. By computer simulation principal values could be determined. When the direction of the applied magnetic field was perpendicular to the *c*-axis of the crystal, a maximum hyperfine splitting width due to α-proton was obtained. Consequently, the direction of principal axis 1 was determined as that of the polymer chain axis. For $\delta = 0°$ (equation 2), only one value of hyperfine splitting width due to α-proton is taken into account and the theoretical spectrum obtained assumes the two lines (separation A_1) are Gaussian (....., *Figure 6*). Comparing this calculated curve with experiment (——, *Figure 6*) A_1 at 77K was determined to be 33×10^{-4}T (1 gauss $= 10^{-4}$T). A_1 does not change with temperature (*Table 1*).

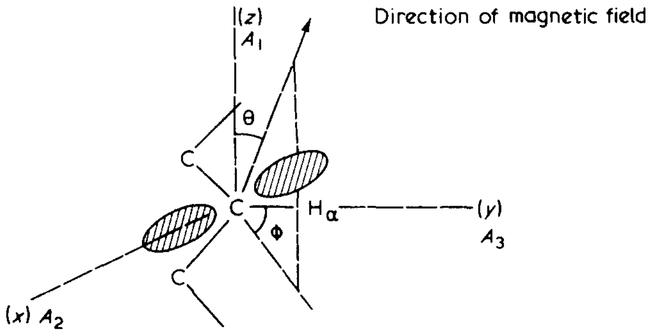


Figure 4 Molecular axis of the crystal

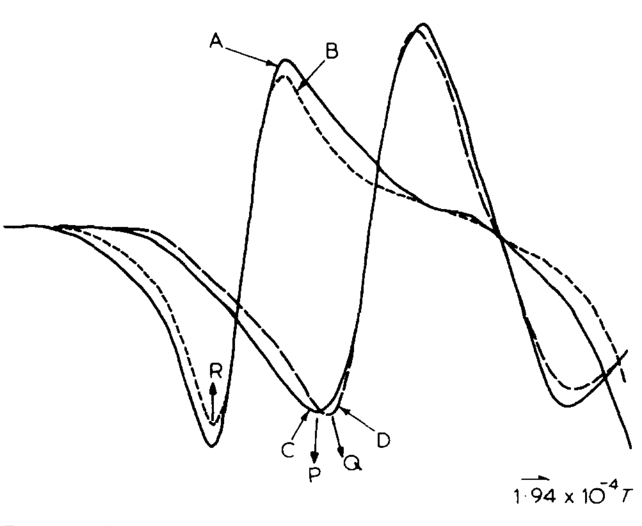


Figure 5 Outermost line shapes at low magnetic field. Various temperatures of observation. A, $\delta = 0°$ (77K); B, $\delta = 0°$ (294K); C, $\delta = 90°$ (77K); D, $\delta = 90°$ (294K)

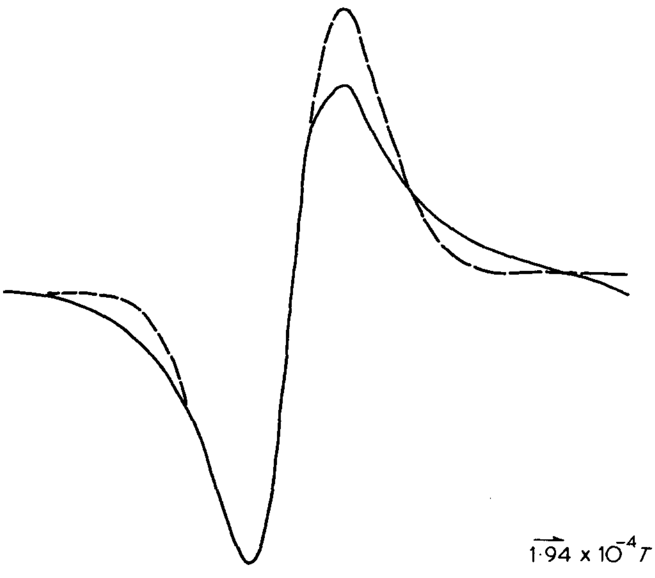


Figure 6 Comparison of the experimental outermost line shape with the calculated curve. $\delta = 90°$; ——, experimental; – – – –, calculated

Table 1 Principal values for alkyl radicals trapped in solution grown crystals

Temperature (K)	A_1 (T)	A_2 (T)	A_3 (T)
77	33.0×10^{-4}	22.0×10^{-4}T	9.0×10^{-4}
254	33.0×10^{-4}	20.3×10^{-4}T	10.0×10^{-4}

The e.s.r. spectrum observed for $\theta = 0°$ was analysed using equation (6). *Figure 7* indicates a remarkable change in the calculated patterns; the position of the intensity maximum (shown by arrow S) shifts, with a slight change in A_3. Hence, A_2 is defined to be larger than A_3. *Figure 8* shows one of the experimental spectra together with the best-fit calculated spectrum. Principal values A_2 and A_3 can be determined by this computer simulation. In contrast to $\delta = 0°$, A_2 and A_3 tended to average out at high temperatures (*Table 1*). The variations in experimental spectra (*Figure 5*) reflect these phenomena, i.e. positions P and Q for $\delta = 90°$ change with temperature whereas R when $\delta = 0°$ does not. The directions of the principal axes 2 and 3 cannot be determined directly from our experiments in the uniaxially oriented sample. However, according to McConnell and Strathdee[7], the directions of the principal axes, 2 and 3, are the directions of the *p*-orbital and the C_α–H_α bond, respectively. Consequently, the assignment of the directions of A_2 and A_3 in *Figure 4* is reasonable. It is concluded that the temperature dependence of the $\tilde{A}$ tensor is caused by hindered oscillation around the polymer chain axis at high temperature.

Structure of alkyl radicals and hindered oscillation determined by hyperfine splitting due to β-protons

A twisted configuration and hindered oscillation of alkyl radicals was found by analysis of e.s.r. data in powdered samples[1] and the same should be true for mats of solution-grown crystals. A computer simulation method similar to that used for powdered samples was used for the mat of solution-grown crystals. Using the values of the $\tilde{A}$ tensor due to the α-proton obtained above, we calculated the whole spectra by using various values of the hyperfine splitting width due to β-protons, $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$. *Figure 9* shows a few examples of calculated spectra with different values of $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ for $\delta = 0°$; spectra observed at 77K (broken lines) are also shown for comparison. The configuration of the free radical site can be clarified by exact estimation of the hyperfine splitting due to β-protons. Heller and McConnell[8] found that the hyperfine splitting due to β-protons of the neighbouring methylene group, $\Delta H_{\beta i}$, could be determined by:

$$\Delta H_{\beta i} = K\rho \cos^2\theta_i = B\cos^2\theta_i \qquad (7)$$

where K is a constant, ρ is the spin density, and θ_i is the projected angle between the $C_{\beta i}$–$H_{\beta i}$ bond and the π electron axis in the plane perpendicular to the direction of the C_α–C_β bond. When $\theta_1 = \theta_2 = 30°$, i.e. alkyl radicals take a regular *trans–trans* configuration, $\Delta H_{\beta 1} = \Delta H_{\beta 2}$ is derived from equation (7). As shown in *Figure 9*, the

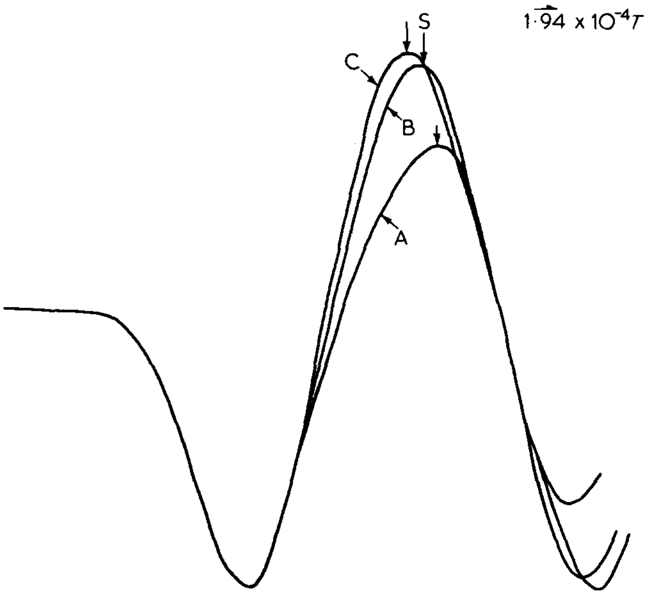


Figure 7 Calculated outermost line shapes for various values of A_3 and constant A_2. $\delta = 90°$.

$A_2 = 22.0 \times 10^{-4}$T $A_3 = 5.0 \times 10^{-4}$T (curve A)
$A_2 = 22.0 \times 10^{-4}$T $A_3 = 7.0 \times 10^{-4}$T (curve B)
$A_2 = 22.0 \times 10^{-4}$T $A_3 = 9.0 \times 10^{-4}$T (curve C)

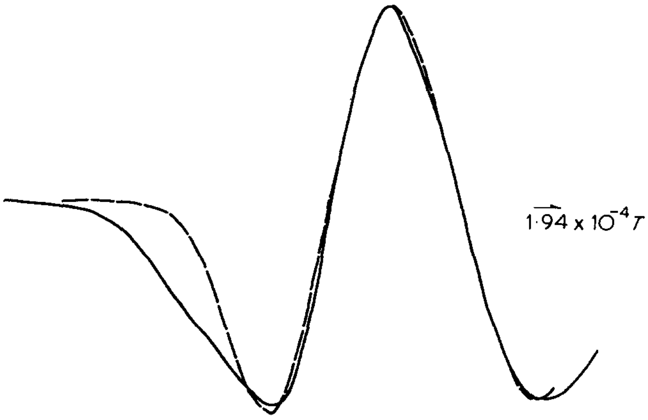


Figure 8 Comparison of the experimental outermost line shape with the calculated curve. $\delta = 90°$; ——, experimental (77K); – – – –, calculated (A_2 = 22.0G; A_3 = 9.0G)

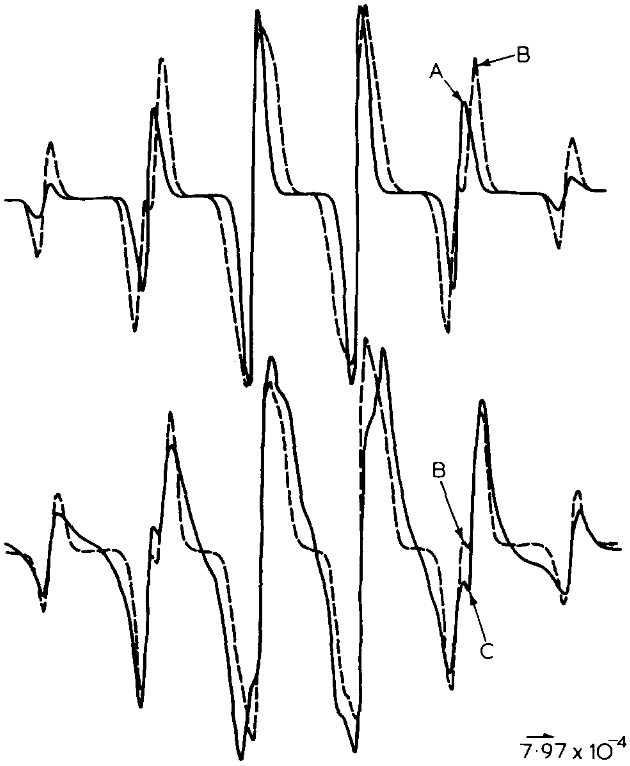


Figure 9 Comparison of the experimental e.s.r. spectrum of alkyl radicals observed at 77K with calculated spectra. $\delta = 0°$. — — — —, Experimental (B); ———, calculated, $\Delta H_{\beta_1} = 32.8 \times 10^{-4}$T; $\Delta H_{\beta_2} = 32.8 \times 10^{-4}$T (A). $\Delta H_{\beta_1} = 29.8 \times 10^{-4}$T; $\Delta H_{\beta_2} = 35.8 \times 10^{-4}$T (C)

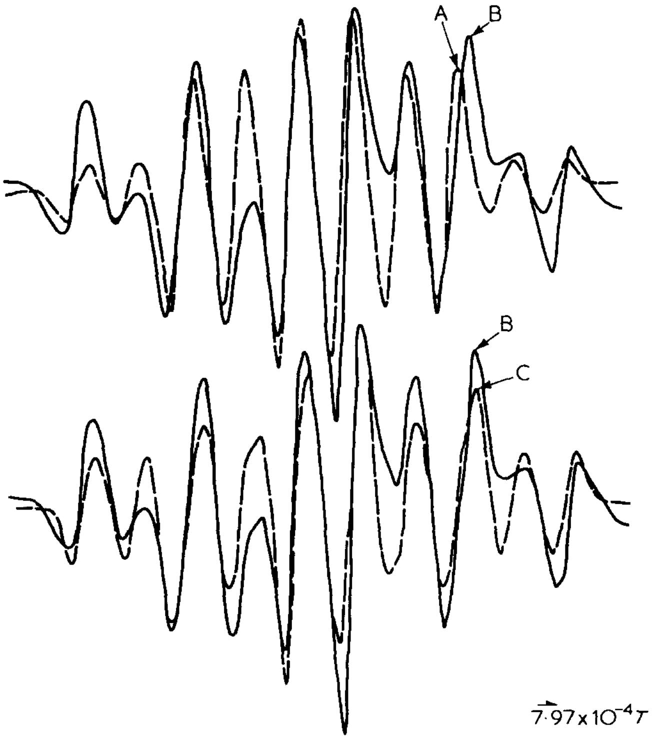


Figure 10 Comparison of the experimental e.s.r. spectrum of alkyl radicals observed at 77K with calculated spectra. $\delta = 90°$, — — — —, Experimental (B); ———, calculated, $\Delta H_{\beta_1} = 32.8 \times 10^{-4}$T; $\Delta H_{\beta_2} = 32.8 \times 10^{-4}$T (A). $\Delta H_{\beta_1} = 29.9 \times 10^{-4}$T; $\Delta H_{\beta_1} = 35.7 \times 10^{-4}$T (C)

Figure 11 Comparison of the experimental e.s.r. spectrum of alkyl radicals observed at 254K with calculated spectra. $\delta = 0°$. ———, Experimental; — — — —, calculated, $\Delta H_{\beta_1} = 30.2 \times 10^{-4}$T, $\Delta H_{\beta_2} = 33.8 \times 10^{-4}$T

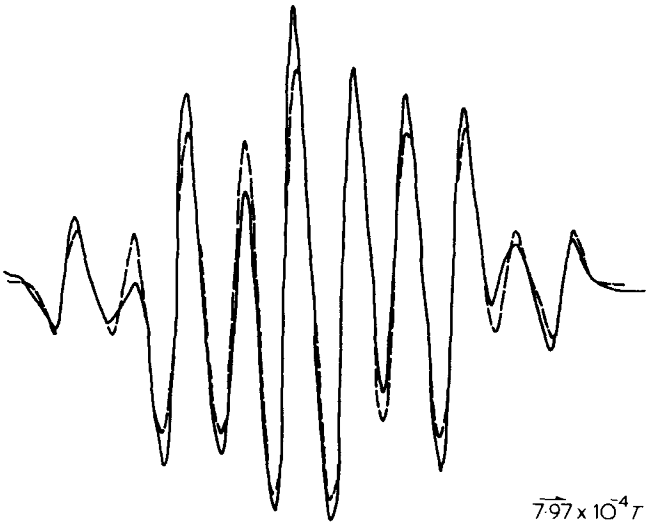


Figure 12 Comparison of the experimental e.s.r. spectrum of alkyl radicals observed at 254K with calculated spectra. $\delta = 90°$. ———, Experimental; — — — —, calculated, $\Delta H_{\beta_1} = 30.5 \times 10^{-4}$T, $\Delta H_{\beta_2} = 34.2 \times 10^{-4}$T

calculated spectrum in the case of $\Delta H_{\beta 1} = \Delta H_{\beta 2}$ is extremely different from experiment with respect to the relative intensity of each component, sub-splittings and the peak positions (upper pattern A). However, when the value of $\Delta H_{\beta 1}$ is different from that of $\Delta H_{\beta 2}$, the calculated spectrum has small sub-splittings and its relative intensity deviated the binominal. This is closer to experiment than for $\Delta H_{\beta 1} = \Delta H_{\beta 2}$. The calculated spectrum in *Figure 9c* seems to be the best fit with respect to the whole line shape and peak positions. By this computer simulation, the following values of $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ at 77K were determined (the same values of $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ were also obtained for $\delta = 90°$ as shown in *Figure 10*)

$$\Delta H_{\beta 1} = 29.8 \times 10^{-4}\mathrm{T}, \quad \Delta H_{\beta 2} = 35.8 \times 10^{-4}\mathrm{T} \tag{8}$$

Equation (8) is substituted into equation (7) and then:

$$\theta_1 = 34.5°, \qquad \theta_2 = 25.5° \tag{9}$$

is obtained. This result suggests that the alkyl radical takes up a twisted configuration in which the methylene group rotated 4.5° from the regular *trans–trans* configuration. This structure was in good agreement with results obtained in our previous study on powdered samples[1]. Similar simulations as for 77K were carried out for 294K and $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ were determined to be 30.2×10^{-4}T and 33.8×10^{-4}T when the *c*-axis of its crystallites was parallel to the external magnetic field ($\delta = 0°$) as shown in *Figure 11*. Theoretical 10-line spectra in the case of $\theta = 0°$ (*Figure 11*) were calculated using A_2 and A_3 as determined in the previous section and changing $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ slightly. Almost the same values of $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ as for $\delta = 0°$ were obtained by computer simulation as shown in *Figure 12*. $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ approach the same value with increasing temperature. This temperature dependence of the hyperfine splitting widths due to the β-protons is interpreted in terms of hindered oscillation of the β-methylene group around the C_α–C_β bond as discussed previously for radicals trapped in powdered urea–polyethylene complex and solution-grown crystals[1].

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