

Figure 1. E.s.r. spectra of a series of polycrystalline n-alkanes subject to γ -irradiation and measured at 77 K. (a) n-C₈H₁₈, (b) n-C₉H₂₀, (c) n-C₈H₁₈, (d) n-C₉H₂₀, (e) n-C₁₀H₂₂, (f) n-C₁₁H₂₄, (g) n-C₁₂H₂₆, (h) n-C₁₃H₂₈, (i) n-C₁₄H₃₀, (j) n-C₁₅H₃₂, (k) n-C₁₆H₃₄, (l) n-C₁₇H₃₆, (m) n-C₁₈H₃₈, (n) n-C₁₉H₄₀, (o) n-C₂₀H₄₂, (p) n-C₂₁H₄₄, (q) n-C₂₂H₄₆, (r) n-C₂₃H₄₈, (s) n-C₂₄H₅₀, (t) n-C₂₅H₅₂. The arrows indicate the position of the DPPH marker.

tion of the spectra has been confirmed up to n-C₂₅.[†] Although alternation of the spectra from n-C₁₁ to n-C₁₆ has been previously pointed out in an earlier paper by Cherniak *et al.*,⁶ they do not give a reason for this spectral difference. As shown in Figure 2, the spectral characteristic of the odd homologues is due to the prominent contribution from radicals of type (I), which is about 30–50% of the total yield, the rest being from types (II) and (III). This is in marked contrast to the even homologues, in which types (II) and (III) are mainly formed.

The e.s.r. profile for the chain end alkyl radicals markedly depends upon the conformation of the β -CH₂ group with respect to the unpaired electron orbital as well as the intramolecular motion of the end CH₂ group. The observed spectrum of (I) can be simulated from the following α -proton coupling tensor: $A_1 = -29.0$ G along the C(1)–C(2) bond, $A_2 = -17.6$ G perpendicular to the C(1)–C(2) bond in the radical plane, and $A_3 = -19.6$ G along the C_{2p} orbital, together with nearly isotropic couplings with the two β -protons, 21 and 36 G. The α -proton coupling tensor used assumes a rapid proton exchange with a fixed $2p_\pi$ orbital in space,⁷ giving a fixed conformation of the β -CH₂ group. If one assumes the

$\rho B_2 \cos^2 \theta$ rule for the β -proton coupling, the above mentioned values give $\rho B_2 = 40.5$ G, $\theta_1 = 17$ and $\theta_2 = 43^\circ$. Although the reason for the relatively small ρB_2 value as compared with the usual values (46–50 G) is not clear, the chain end alkyl radicals produced in 1,8-dichloro-octane by dissociative electron attachment exhibit similar β -proton couplings, *i.e.*, 25.5 and 36.7 G, giving $\rho B_2 = 42.1$ G, $\theta_1 = 21$ and $\theta_2 = 39^\circ$ (Figure 3).[‡]

On the other hand, the spectra of the even homologues can be simulated from types (II) and (III) using the coupling constants reported in ref. 1 (see caption to Figure 2). Although a minor contribution from type (I) may not be excluded from the spectra of polycrystalline samples, the single crystal analyses reported by Gillbro and Lund¹ show that type (I) is not detectable at 77 K in a number of even n-alkanes.

The crystal structures of n-alkanes starting from C₁₁ show regular alternation between triclinic and orthorhombic unit cells for even and odd alkanes, respectively.⁹ It is well known that the melting points and other properties of linear alkanes, which are related to the crystal structures, exhibit a marked even–odd alternation. Our observation with the e.s.r. spectra is probably related to the alternation of the crystal structures.

[†] The samples used are those of a standard kit for gas chromatography. Among the 20 n-alkanes 15 samples had purities higher than 99.8% and the rest ranged from 99.0 to 99.7%.

[‡] These values were obtained from our polycrystalline spectrum, although values of 24 and 38 G have been obtained from single crystals.⁸

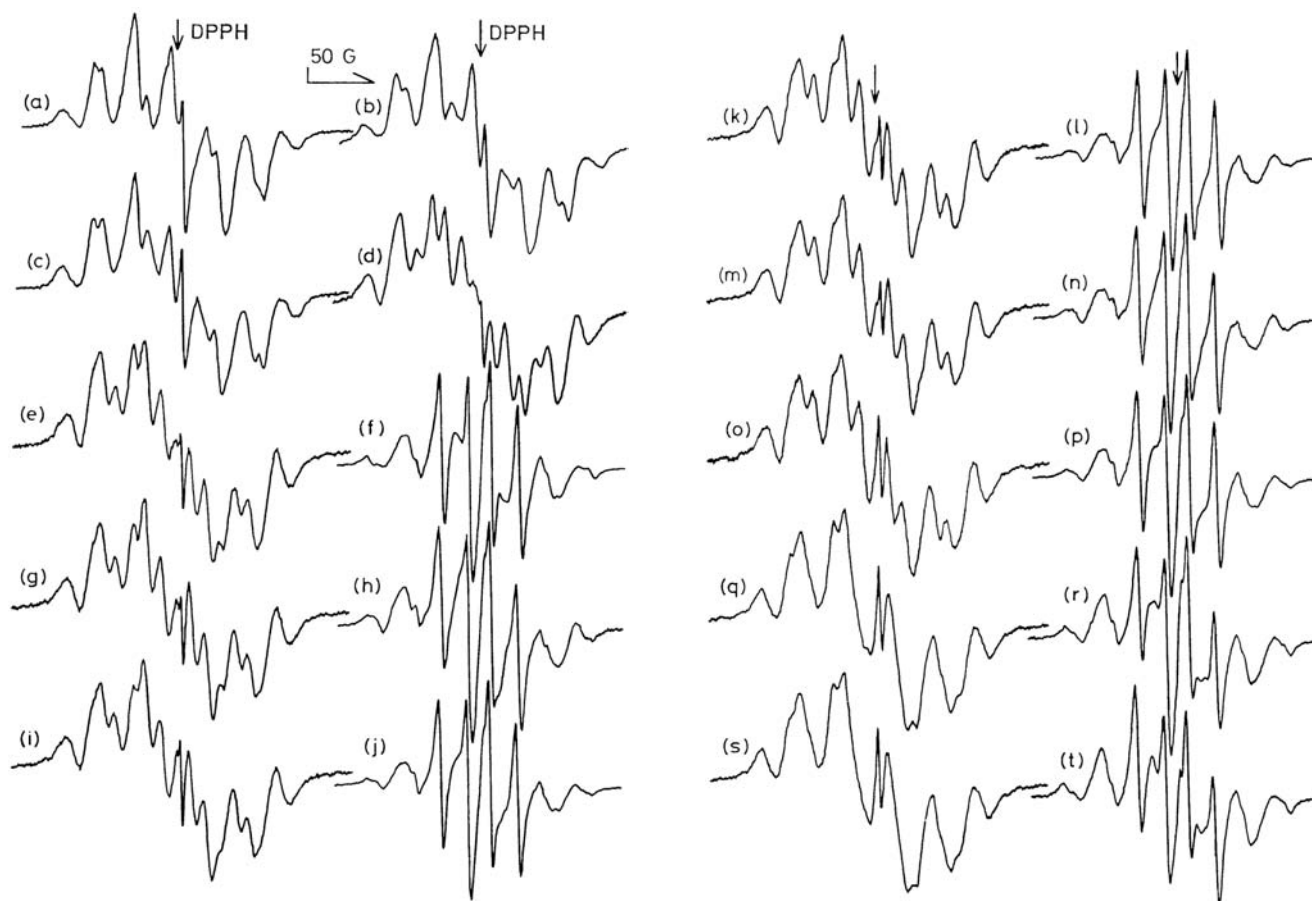


Figure 1. E.s.r. spectra of a series of polycrystalline n-alkanes subject to γ -irradiation and measured at 77 K. (a) n-C₈H₁₈, (b) n-C₉H₂₀, (c) n-C₈H₁₈, (d) n-C₉H₂₀, (e) n-C₁₀H₂₂, (f) n-C₁₁H₂₄, (g) n-C₁₂H₂₆, (h) n-C₁₃H₂₈, (i) n-C₁₄H₃₀, (j) n-C₁₅H₃₂, (k) n-C₁₆H₃₄, (l) n-C₁₇H₃₆, (m) n-C₁₈H₃₈, (n) n-C₁₉H₄₀, (o) n-C₂₀H₄₂, (p) n-C₂₁H₄₄, (q) n-C₂₂H₄₆, (r) n-C₂₃H₄₈, (s) n-C₂₄H₅₀, (t) n-C₂₅H₅₂. The arrows indicate the position of the DPPH marker.

tion of the spectra has been confirmed up to n-C₂₅.[†] Although alternation of the spectra from n-C₁₁ to n-C₁₆ has been previously pointed out in an earlier paper by Cherniak *et al.*,⁶ they do not give a reason for this spectral difference. As shown in Figure 2, the spectral characteristic of the odd homologues is due to the prominent contribution from radicals of type (I), which is about 30–50% of the total yield, the rest being from types (II) and (III). This is in marked contrast to the even homologues, in which types (II) and (III) are mainly formed.

The e.s.r. profile for the chain end alkyl radicals markedly depends upon the conformation of the β -CH₂ group with respect to the unpaired electron orbital as well as the intramolecular motion of the end CH₂ group. The observed spectrum of (I) can be simulated from the following α -proton coupling tensor: $A_1 = -29.0$ G along the C(1)–C(2) bond, $A_2 = -17.6$ G perpendicular to the C(1)–C(2) bond in the radical plane, and $A_3 = -19.6$ G along the C_{2p} orbital, together with nearly isotropic couplings with the two β -protons, 21 and 36 G. The α -proton coupling tensor used assumes a rapid proton exchange with a fixed $2p_\pi$ orbital in space,⁷ giving a fixed conformation of the β -CH₂ group. If one assumes the

$\rho B_2 \cos^2 \theta$ rule for the β -proton coupling, the above mentioned values give $\rho B_2 = 40.5$ G, $\theta_1 = 17$ and $\theta_2 = 43^\circ$. Although the reason for the relatively small ρB_2 value as compared with the usual values (46–50 G) is not clear, the chain end alkyl radicals produced in 1,8-dichloro-octane by dissociative electron attachment exhibit similar β -proton couplings, *i.e.*, 25.5 and 36.7 G, giving $\rho B_2 = 42.1$ G, $\theta_1 = 21$ and $\theta_2 = 39^\circ$ (Figure 3).[‡]

On the other hand, the spectra of the even homologues can be simulated from types (II) and (III) using the coupling constants reported in ref. 1 (see caption to Figure 2). Although a minor contribution from type (I) may not be excluded from the spectra of polycrystalline samples, the single crystal analyses reported by Gillbro and Lund¹ show that type (I) is not detectable at 77 K in a number of even n-alkanes.

The crystal structures of n-alkanes starting from C₁₁ show regular alternation between triclinic and orthorhombic unit cells for even and odd alkanes, respectively.⁹ It is well known that the melting points and other properties of linear alkanes, which are related to the crystal structures, exhibit a marked even–odd alternation. Our observation with the e.s.r. spectra is probably related to the alternation of the crystal structures.

[†] The samples used are those of a standard kit for gas chromatography. Among the 20 n-alkanes 15 samples had purities higher than 99.8% and the rest ranged from 99.0 to 99.7%.

[‡] These values were obtained from our polycrystalline spectrum, although values of 24 and 38 G have been obtained from single crystals.⁸

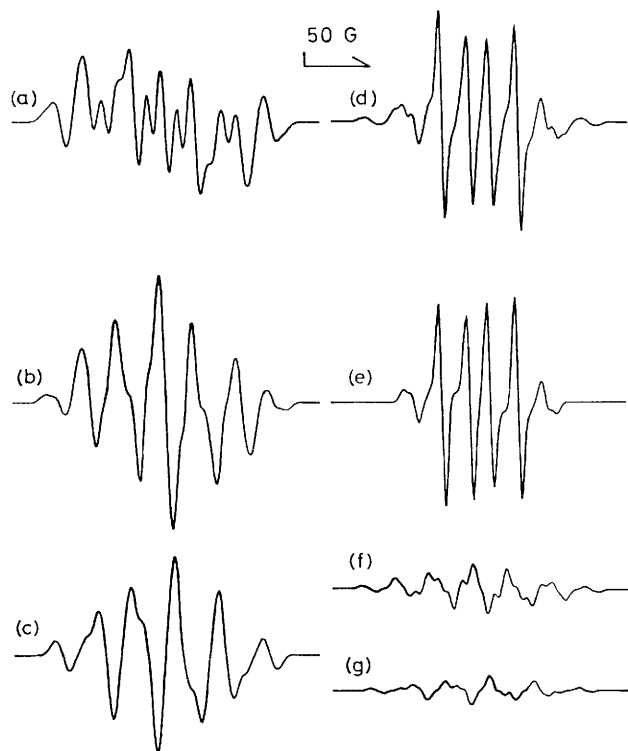


Figure 2. Typical examples of the simulated e.s.r. spectra for even and odd n-alkanes. (a) The spectrum simulated from (II) and (III) with the abundance ratio of (II):(III) = 0.65:0.35, individually shown in (b) and (c), respectively; (d) the spectrum simulated from (I), (II), and (III) with the abundance ratio of (I):(II):(III) = 0.50:0.37:0.13, individually shown in (e), (f), and (g), respectively. The following hyperfine coupling values are assumed: (b) $A_1 = -11.7$, $A_2 = -19.6$, $A_3 = -35.2$ G for α -H, $A_{\parallel} = 26.6$, $A_{\perp} = 23.0$ G for β -CH₃ protons, and 33.8 G for β -CH₂ protons, $\Delta H_{msl} = 7$ G; (c) the same values as for (b) for α -H and 33.0 G for β -CH₂, $\Delta H_{msl} = 7$ G; (e) $A_1 = -17.6$, $A_2 = -19.6$, $A_3 = -29.0$ G for α -H, 21 and 36 G for β -H, $\Delta H_{msl} = 5$ G; (f) the same values as for (b) for α -H, 25 G for β -CH₃ and 33 G for β -CH₂, $\Delta H_{msl} = 5$ G; (g) the same values as for (b) for α -H and 33 G for β -CH₂, $\Delta H_{msl} = 5$ G. All the spectra are simulated using the Gaussian type lineshape function.

A similarity in the e.s.r. spectral features of the odd homologues from C₁₁ to C₂₅ suggests that the yield of radicals of type (I) is not much affected by chain length. This may imply that the phenomenon is related to differences in molecular packing and alignment of the chain ends. The possibility of main chain scission forming (I) may be low.

§ Salovey and Falconer reported that product analysis studies of irradiated n-hexadecane and n-heptadecane in the crystalline phases show notable difference in the yield of linear dimers.^{4b}

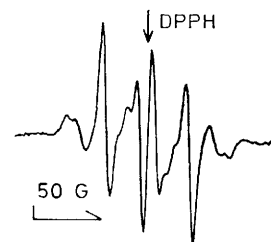


Figure 3. E.s.r. spectra of polycrystalline 1,8-dichloro-octane subject to γ -irradiation and measured at 77 K.

Preliminary experiments show that the spectrum obtained from n-C₁₃H₂₈ irradiated at 4.2 K is different not only from that obtained at 77 K but also from those of the even homologues irradiated at 4.2 K. We have further found that the total yield of alkyl radicals at 77 K also exhibits marked even-odd alternation from C₁₁ to C₂₅.⁹ These results suggest that both the initial formation of radicals and the following secondary processes in irradiated crystalline alkanes are controlled by crystal structure, as was often observed in our previous studies on irradiated single crystals of a number of organic compounds.^{11,12}

Received, 5th August 1982; Com. 926

References

- 1 T. Gillbro and A. Lund, *Int. J. Radiat. Phys. Chem.*, 1976, **8**, 625, and references cited therein.
- 2 S. J. Chappas and J. Silverman, *Radiat. Phys. Chem.*, 1980, **16**, 431, 437.
- 3 M. Iwasaki, K. Toriyama, H. Muto, and K. Nunome, *J. Chem. Phys.*, 1976, **65**, 596.
- 4 (a) L. Kevan and W. F. Libby, *J. Chem. Phys.*, 1963, **39**, 1288; (b) R. Salovey and W. E. Falconer, *J. Phys. Chem.*, 1966, **70**, 3203, and references cited therein; (c) B. Tilquin, P. Tilman, and P. Claes, *Radiat. Phys. Chem.*, 1980, **16**, 321.
- 5 M. Iwasaki, K. Toriyama, and K. Nunome, *J. Am. Chem. Soc.*, 1981, **103**, 3591; K. Toriyama, K. Nunome, and M. Iwasaki, *J. Phys. Chem.*, 1981, **75**, 1633.
- 6 N. Ia. Cherniak, N. N. Bubnov, L. S. Poliak, Iu. D. Tsvetkov, and V. V. Voevodski, *Opt. Spectrosc. (USSR)* (English trans.), 1959, **6**, 360.
- 7 M. Fujimoto and J. Janecka, *J. Chem. Phys.*, 1971, **55**, 5.
- 8 O. Claesson and A. Lund, *Chem. Phys.*, 1978, **35**, 63.
- 9 M. Fukaya, K. Toriyama, M. Iwasaki, T. Ichikawa, and N. Ohta, *Radiat. Phys. Chem.*, 1982, in the press.
- 10 N. Norman and H. Mathisen, *Acta Chem. Scan.*, 1972, **26**, 3913; E. F. Westrum, Jr., 'Physics and Chemistry of the Organic Solid State,' ed. D. Fox, M. M. Labes, and A. Weissberger, Interscience, New York, 1963, Vol. 1, p. 1.
- 11 M. Iwasaki, 'Magnetic Resonance,' ed. C. A. McDowell, MTP International Review of Science: Physical Chemistry Series 1, Butterworths, London, 1972, Vol. 4, p. 317.
- 12 M. Iwasaki and K. Toriyama, *Chem. Phys. Lett.*, 1976, **41**, 59, and references cited therein.