Electron Spin Resonance Spectra of Aliphatic Nitrile Radicals

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Nitrile radicals have been generated in solution by photolysis of azo-compounds at 20 °C, and their electron spin resonance spectra have been studied. The radicals have the formula $CH_3\dot{C}(CN)R$ where $R = -CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$ or $-CH_2CO_2CH_3$.

A method which has been widely used to study the electron spin resonance (ESR) spectra of transient free radicals in solution is the continuous flow technique, which was first used in investigating peroxidase-substrate oxidations[1]. The technique was developed by DIXON and NORMAN[2], who allowed aqueous acidic solutions of titanous chloride and hydrogen peroxide to mix immediately before passing through the resonance cavity of an ESR spectrometer. A number of substrates were added to the solutions in order to study the radicals formed when the radicals generated in the redox reaction reacted with the substrates. Other redox systems have been used, but they have not been as generally useful as the titanous chloride-hydrogen peroxide system. It was used, for instance, by FISCHER[3] in his studies of the ESR spectra of radicals derived from acrylic and methacrylic monomers and related compounds. Fischer found that the widths of the individual lines in his spectra were 0.7 – 1.4 gauss, and he considered that oxygen which was generated in the redox reaction caused a broadening of the lines in his spectra. Both DIXON et al.[2, 4] and FISCHER[3] failed to detect coupling to protons of $-OH$ and $-COOH$ groups, and they attributed this to rapid exchange of these labile protons with the protons of the aqueous solutions employed. Fischer considered that this exchange also resulted in a broadening of the lines in the spectra of radicals with $-COOH$ substituents.

Some of the difficulties associated with the use of flow systems may be avoided if radicals are generated by irradiation of a suitable liquid sample within the resonance cavity. PIETTE and LANDGRAF[5] identified the radical products of the photolysis of n-butyl, sec-butyl and t-butyl hydroperoxides in this way, and measured their recombination rate constants. FESSENDEN and SCHULER[6] described the ESR spectra of a large number of alkyl radicals formed in liquid hydrocarbons during irradiation by 2.8 MeV electrons. Linewidths were in the range 0.13 – 0.4 gauss and in some cases second order structure and coupling to γ-protons was resolved. Using a similar technique the spectra of the radicals $CF_3^{\cdot}$ and $CHF_2^{\cdot}$[7] and $FO_2^{\cdot}$[8] were studied. LIVINGSTON and ZELDES used a technique in which solutions were irradiated, using a mercury vapour lamp, while flowing through the resonance cavity. In one group of experiments solutions of hydrogen peroxide in alcohols were used; photolysis of the hydrogen peroxide gave $OH^{\cdot}$ radicals which reacted with the alcohol[9, 10]. In other experiments solutions of acetone[10, 11], acetaldehyde, diacetyl and acetoin[12] were photolysed. ADAMS[13] irradiated solutions of

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[1] I. YAMAZAKI, H. S. MASON, and L. PIETTE, J. Biol. Chem. **235**, 2444 [1960].

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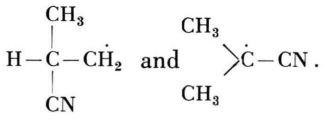
di-t-butyl peroxide and various alcohols in isooctane as they flowed through the cavity of an ESR spectrometer. Photolysis of the di-t-butyl peroxide was presumed to give t-butoxy radicals, which reacted with the alcohols by removal of hydrogen atoms. Independently, KRUSIC and KOCHI[14] described a versatile technique for studying organic free radicals which also used di-t-butyl peroxide as a source of free radicals. By photolysing static solutions of di-t-butyl peroxide in hydrocarbons they were able to study the ESR spectra of a number of alkyl radicals formed when t-butoxy radicals abstracted protons from the hydrocarbons. Some excellent spectra were obtained by this technique[14, 15]. VANDERKOOI and FOX[16] studied the photolysis products of CF_3OF and CF_3OOCF_3 between -196 °C and -170 °C. They used a mixed CF_4-CF_3Cl solvent which remained liquid well below -196 °C.

Of the free radicals we have studied, it appears that only ESR spectra of the radical $(CH_3)_2\dot{C}-CN$ are reported in the literature. BICHUTINSKII et al.[17] generated this radical by thermal decomposition of solutions of 2,2′-azo-bis-isobutyronitrile, and the hyperfine coupling constants reported (128 °C) were $\alpha_H = 19.5$ gauss and $\alpha_N = 3.1$ gauss. WEINER and HAMMOND[18] decomposed solutions of 2,2′-azo-bis-isobutyronitrile by photochemical means, and found $\alpha_H = 20.4$ gauss and $\alpha_N = 3.3$ gauss. PEARSON, SMITH and SMITH[19], using a titanous chloride-hydrogen peroxide flow system, found that when isobutyronitrile was present as a substrate an ESR spectrum was observed which was attributed to a mixture of the radicals,



$$H-\overset{CH_3}{\underset{CN}{C}}-\dot{C}H_2 \quad \text{and} \quad {}^{CH_3}_{CH_3}\!\!>\dot{C}-CN\,.$$

The hyperfine coupling constants reported for the radical $(CH_3)_2\dot{C}-CN$ were

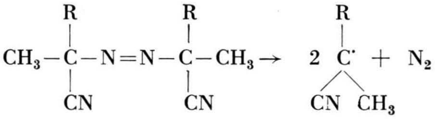
$$\alpha_H = (21.5 \pm 0.5) \text{ gauss}$$

and

$$\alpha_N = (\ \ 3.6 \pm 0.4) \text{ gauss}.$$

CHACHATY and SCHMIDT[20] studied the ESR spectrum of the same radical, which was formed when hydrogen atoms reacted with methacrylonitrile. The radicals were trapped in a solid matrix at 77 °K, and as a consequence of anisotropic interactions the ESR spectra were incompletely resolved. However, the isotropic coupling constants appeared to be in approximate agreement with the values of Pearson, Smith and Smith. HIRANO, MIKI and TSURUTA[21] found that a solution of 2,2′-azo-bis-isobutyronitrile and aluminium triethyl in benzene at 54 °C gave an ESR spectrum which they attributed to a mixture of ethyl radicals and $(CH_3)_2\dot{C}-CN$ radicals. The coupling constants reported for the latter radical were $\alpha_H = 10.1$ gauss and $\alpha_N = 3.4$ gauss. This value of α_H was about half the values previously reported.

In our experiments radicals were generated by a method similar to that used by WEINER and HAMMOND[18, 22]. Solutions of azo-compounds in benzene or chloroform were photolysed at 20 °C in the cavity of the ESR spectrometer. Under the experimental conditions the azo-compounds decomposed according to the equation:



$$CH_3-\overset{R}{\underset{CN}{C}}-N=N-\overset{R}{\underset{CN}{C}}-CH_3 \rightarrow 2\ \overset{R}{\underset{CN\ \ CH_3}{C^{\cdot}}} + N_2$$

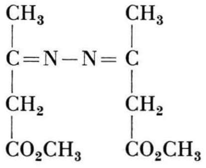
1. Experimental

2,2′-azo-bis-isobutyronitrile, supplied by Koch Light Laboratories Ltd., was recrystallized from methanol and from chloroform.

2,2′-azo-bis-2-methylbutyronitrile was prepared by the method of DOX[23].

2,2′-azo-bis-2-methylvaleronitrile was prepared by the method of OVERBERGER et al.[24].

Methyl acetoacetate azine



$$\begin{matrix} CH_3 & & CH_3 \\ | & & | \\ C & =N-N= & C \\ | & & | \\ CH_2 & & CH_2 \\ | & & | \\ CO_2CH_3 & & CO_2CH_3 \end{matrix}$$

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[14] P. J. KRUSIC and J. K. KOCHI, J. Am. Chem. Soc. **90**, 7155 [1968].

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[21] T. HIRANO, T. MIKI, and T. TSURUTA, Makromolecul. Chem. **104**, 230 [1967].

[22] S. A. WEINER and G. S. HAMMOND, J. Am. Chem. Soc. **91**, 986 [1969].

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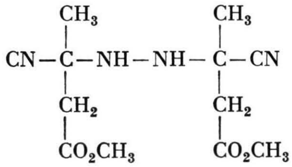
This was prepared by a modification of the method used by Wolff[25] to prepare ethyl acetoacetate azine. 232 g methyl acetoacetate were added to a solution of 130 g hydrazine sulphate and 106 g anhydrous sodium carbonate in 1 l water, and the mixture was stirred at room temperature for 1½ hours. The azine was separated from the reaction medium by ether extraction, and purified by recrystallization from ethanol. Colourless needles, m. pt. 50 – 51°.

Analysis:	theory	found
%C	52.6	52.55
%H	7.02	7.00
%N	12.3	12.06

3,3′-hydrazo-bis-methyl-3-cyanobutyrate

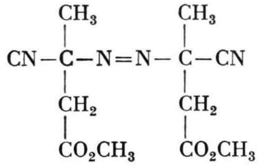


$$\begin{array}{ccccc} & \mathrm{CH_3} & & \mathrm{CH_3} & \\ & | & & | & \\ \mathrm{CN-} & \mathrm{C} & \mathrm{-NH-NH-} & \mathrm{C} & \mathrm{-CN} \\ & | & & | & \\ & \mathrm{CH_2} & & \mathrm{CH_2} & \\ & | & & | & \\ & \mathrm{CO_2CH_3} & & \mathrm{CO_2CH_3} & \end{array}$$

104 g liquid hydrogen cyanide was added to 39 g methyl acetoacetate azine and the mixture was allowed to stand for two weeks at about 15 °C. After allowing excess hydrogen cyanide to evaporate off, a portion of the solid residue was purified by recrystallization, first from a water-methanol mixture and secondly from methanol. Colourless crystals, m. pt. 105 – 106°.

Analysis:	theory	found
%C	51.05	51.02
%H	6.38	6.30
%N	19.9	19.6

3,3′-azo-bis-methyl-3-cyanobutyrate



$$\begin{array}{ccccc} & \mathrm{CH_3} & & \mathrm{CH_3} & \\ & | & & | & \\ \mathrm{CN-} & \mathrm{C} & \mathrm{-N{=}N-} & \mathrm{C} & \mathrm{-CN} \\ & | & & | & \\ & \mathrm{CH_2} & & \mathrm{CH_2} & \\ & | & & | & \\ & \mathrm{CO_2CH_3} & & \mathrm{CO_2CH_3} & \end{array}$$

10 g of the unpurified portion of 3,3′-hydrazo-bis-methyl-3-cyanobutyrate were dissolved in 15 g hot methanol, cooled to 0 °C in a cardice-methanol bath (a super-saturated solution was obtained), and a solution of bromine in methanol was added dropwise, while stirring and maintaining the temperature at 0 °C, until the colour of bromine persisted. Excess bromine was removed by adding a few drops of an aqueous solution of potassium metabisulphite. The reaction mixture (total weight 54 g) was poured into 100 g water at 0 °C. The precipitate which separated was filtered off and recrystallized twice from methanol. Colourless crystals, melting at 115 – 116° with effervescence.

Analysis:	theory	found
%C	51.45	51.52
%H	5.72	5.65
%N	20.0	20.3

In preparing the samples for irradiation in the spectrometer cavity the concentrations of the azo-compounds, and the solvents used, are shown in Table 1. Analytical reagent grades of benzene and chloroform, supplied by BDH Ltd., were used. (The latter contained about 1% w/w ethanol.) The samples were thoroughly de-gassed, and the spectrometer cells sealed under high vacuum.

Azo-compound	Concentration mole/l	Solvent
2,2′-azo-bis-isobutyronitrile	0.305	Benzene
2,2′-azo-bis-2-methylbutyronitrile	0.521	Benzene
2,2′-azo-bis-2-methylvaleronitrile	0.455	Benzene
3,3′-azo-bis-methyl-3-cyanobutyrate	0.357	Chloroform

Table 1. Compositions of samples photolysed in the spectrometer cavity.

One of the spectrometer cells was constructed with a Radiospares TH-B12 bead thermistor sealed into a constriction in the silica end of the cell with Araldite. The thermistor formed one arm of an unbalanced Wheatstone bridge; the other components of the Wheatstone bridge were a Mallory mercury cell (RM-3R), a Scalamp spot galvanometer, and three carbon resistors of 1800 Ω. After calibration, the deflection of the galvanometer was used to ascertain the temperature of the sample in the cell.

A Varian E-3 spectrometer was used. The TE_{102} cavity had a grid front with 50% transmittance to light. The radiation from a 250 watt ME/D mercury vapour lamp was focussed on this grid by the use of silica lenses.

2. Results

In Table 2 the free radicals we have studied are listed, together with their parent azo-compounds, the hyperfine coupling constants assigned to the radicals, and the linewidths. The spectra of the radicals are shown in Figures 1 and 2.

The spectra shown in Figure 1 were continuous sweeps recorded with a single sample under conditions of over-modulation. Radical concentrations decreased noticeably during the scan from left to right (about three hours). The absorption peaks to high field of the centres of the spectra, causing assymmetry in the spectra, are due to impurities in the silica of the spectrometer cells. (Similar peaks were observed when the empty tubes were irradiated.)

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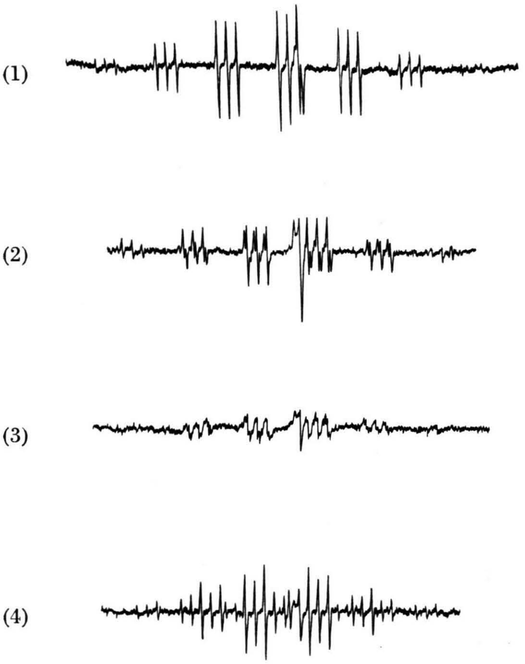
[25] L. Wolff, Chem. Ber. **37**, 28 [1904].

Azo-compound	Radical	Hyperfine coupling constants (gauss)				Line-width (gauss)
		$\alpha_{\mathrm{H}(\beta)}^{-\mathrm{CH}_3}$	$\alpha_{\mathrm{H}(\beta)}^{-\mathrm{CH}_2-}$	$\alpha_{\mathrm{H}(\gamma)}$	α_{N}	
2,2′-azo-bis-isobutyronitrile	$(CH_3)_2\dot{C}-CN$	20.4	—	—	3.3	0.15
2,2′-azo-bis-2-methylbutyronitrile	$CH_3\dot{C}(CN)C_2H_5$	20.4	21.2	0.19	3.3	0.15
2,2′-azo-bis-2-methylvaleronitrile	$CH_3\dot{C}(CN)CH_2C_2H_5$	20.5	19.5	0.63	3.3	0.29
3,3′-azo-bis-methyl-3-cyanobutyrate	$CH_3\dot{C}(CN)CH_2CO_2CH_3$	21.2	14.65	—	3.3	0.37

Table 2. Summary of data derived from ESR spectra recorded at 20 °C.



(1) $(CH_3)_2\dot{C}-CN$ (2) $CH_3\dot{C}(CN)CH_2CH_3$
(3) $CH_3\dot{C}(CN)CH_2CH_2CH_3$ (4) $CH_3\dot{C}(CN)CH_2CO_2CH_3$

Fig. 1. ESR spectra. Field increases left to right.

The spectra shown in Figure 2 were recorded under reduced modulation amplitude and are expanded to show the additional hyperfine structure resolved. The spectrum of the radical $CH_3\dot{C}(CN)CH_2CO_2CH_3$ is not included in this Figure because additional hyperfine structure was not resolved under these conditions. For the purposes of presentation portions of the spectra showing no fine structure are ommitted. Because of the greater time needed to record these spectra, two samples were generally used for each complete spectrum.

The coupling constants reported in Table 2 were derived from the spectra shown in Figure 2. To do this, it was assumed that second order splittings were adequately described by the treatment of FESSENDEN[26], and that the absorption peaks were of Lorentzian shape. Coupling constants and linewidths were then adjusted to give the best agreement between experimental and theoretical spectra. Theoretical spectra, calculated in this way, are shown beside the experimental spectra in Figure 2, and it is seen that the agreement is satisfactory. The term "linewidth" is used to denote the separation of the maximum and minimum of the first derivative of the (Lorentzian) absorption curve of a single hyperfine component, in the absence of second order splittings. Linewidths quoted in Table 2 have the same significance.

The errors in the coupling constants and linewidths reported in Table 2 are estimated to be not greater than ± 0.05 gauss. Sample temperatures were within $\pm 1^\circ$ of 20 °C.

Careful examination of the spectrum of the radical $CH_3\dot{C}(CN)CH_2CO_2CH_3$ (Figure 1) shows that it consists of only 30 hyperfine components, not 36 as expected. This arose because, to a close approximation, $\alpha_{\mathrm{H}(\beta)}^{-\mathrm{CH}_3} - \alpha_{\mathrm{H}(\beta)}^{-\mathrm{CH}_2} = 2\,\alpha_{\mathrm{N}}$. Consequently lines 6, 11, 13, 18, 20 and 25 consist of pairs of lines superimposed. Even under conditions of maximum resolution, however, these lines were not detectably broader than the others.

3. Discussion

FESSENDEN and SCHULER[6], following CHESNUT[27], considered that the hyperfine coupling constant of a β-proton of a methyl group, $\alpha_{\mathrm{H}(\beta)}^{-\mathrm{CH}_3}$, was proportional to the spin density in the $2p_z$ orbital of the trigonal carbon atom to which the methyl group was bonded, ϱ. Thus,

$$\alpha_{\mathrm{H}(\beta)}^{-\mathrm{CH}_3} = Q_{\mathrm{H}(\beta)}^{-\mathrm{CH}_3} \cdot \varrho \,. \qquad (1)$$

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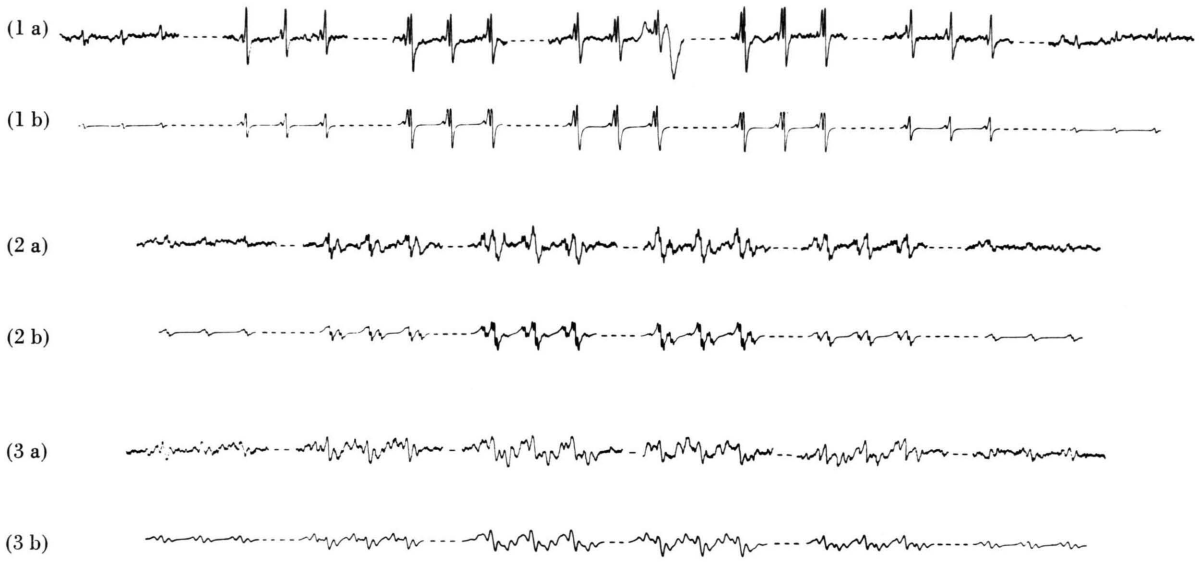
[26] R. W. FESSENDEN, J. Chem. Phys. **37**, 747 [1962].

[27] D. B. CHESNUT, J. Chem. Phys. **29**, 43 [1958].



(1) $(CH_3)_2\dot{C}-CN$; (2) $CH_3\dot{C}(CN)CH_2CH_3$; (3) $CH_3\dot{C}(CN)CH_2CH_2CH_3$.
Fig. 2. ESR spectra; (a) experimental; (b) calculated. Field increases left to right.

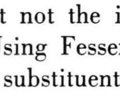
The constant of proportionality was given by,

$$Q_{H(\beta)}^{-CH_3} = (29.30 \pm 0.05) \text{ gauss} \qquad (2)$$

and for ethyl, isopropyl and t-butyl radicals ϱ was given by,

$$\varrho = (1 - 0.081)^n \qquad (3)$$

where n was the number of methyl groups attached to the trigonal carbon atom. Equations (1) and (2) were arrived at by considering radicals derived from hydrocarbons, but FISCHER[3, 28] suggested that they might also be applied to radicals with polar substituents. Moreover, Fischer proposed that for radicals with polar substituents, represented by,



$$X_1X_3\dot{C}-X_2$$

ϱ would be given by Eq. (4),

$$\varrho = \prod_{i=1}^{3} [1 - \Delta(X_i)]. \qquad (4)$$

$\Delta(X_i)$ was an empirical parameter related to the mesomeric effect (but not the inductive effect) of the substituent X_i. Using Fessenden and Schuler's values of $\Delta(X_i)$ for substituents $-H$ and $-CH_3$ (zero and 0.081 respectively[6]) Fischer used Eqs. (1), (2) and (4) to calculate $\Delta(X_i)$ for a variety of substituents[28]. By the same procedure $\Delta(X_i)$ for the substituents $-CN$, $-CH_2CH_3$, $-CH_2CH_2CH_3$ and $-CH_2CO_2CH_3$ may be calculated from the data of Table 2, and the values obtained in this way are shown in Table 3. Our value of $\Delta(CN)$ (0.176), relating to the radical $(CH_3)_2\dot{C}-CN$, may be compared with Fischer's value of 0.148, which related to the radical $CH_3\dot{C}(CN)CH_2OH$. Fischer considered that Eq. (4) might break down for "strong" substituents such as $-CN$, but he supposed that for most substituents $\Delta(X_i)$ was approximately independent of temperature and of the nature of the other substituents of the radical. When the substituent contains β-protons it is doubtful whether these assumptions are justified. In these cases the main mechanism for delocalization of the unpaired electron seems to be hyperconjugation, which is dependent on the orientation of the radical. Thus the value of $\Delta(X_i)$ would be expected to depend on factors which influence rotation about the $C-X_i$ bond. Evidence that this is so is provided by Fessenden and Schuler's spectral data for the radicals $(CH_3)_2\dot{C}-C_2H_5$ (-125 °C) and $CH_3\dot{C}HC_2H_5$ (-80 °C)[6]. The values of $\Delta(C_2H_5)$ calculated from their data are 0.080 and 0.090 respectively. The former value is in agreement with the value shown in Table 3 for $CH_3\dot{C}(CN)C_2H_5$, but when the ethyl group is more free to rotate, as in $CH_3\dot{C}HC_2H_5$, $\Delta(C_2H_5)$ increases. It seems possible that the decreasing values of $\Delta(X_i)$ in the series $X_i = -CH_2CH_3$,

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[28] H. FISCHER, Z. Naturforsch. **20 a**, 428 [1965].

$-CH_2CH_2CH_3$ and $-CH_2CO_2CH_3$ (Table 3) are attributable to the increasing size of these substituents. If steric effects on hyperconjugation were ignored, similar values of $\Delta(X_i)$ in this series would be expected.

Radical	ϱ	X_i	$\Delta(X_i)$
$(CH_3)_2\dot{C}-CN$	0.696	$-CN$	0.176
$CH_3\dot{C}(CN)C_2H_5$	0.696	$-CH_2CH_3$	0.080
$CH_3\dot{C}(CN)CH_2C_2H_5$	0.700	$-CH_2CH_2CH_3$	0.075
$CH_3\dot{C}(CN)CH_2CO_2CH_3$	0.724	$-CH_2CO_2CH_3$	0.043

Table 3. Calculated spin densities and $\Delta(X_i)$ functions.

So far only β-proton hyperfine coupling constants of methyl groups have been considered. A more general description of β-proton coupling constants must take account of the orientation-dependence of the coupling, which has already been referred to. Heller and McConnell [29] considered that in the equation,

$$\alpha_{H(\beta)} = Q_{H(\beta)}\,\varrho\,, \tag{5}$$

$Q_{H(\beta)}$ depended on the angle θ between the α carbon $2p_z$ orbital and the plane containing the β-proton $C-H$ bond, according to Eq. (6).

$$Q_{H(\beta)} = A + B\cos^2\theta\,. \tag{6}$$

The term A was expected to be small compared with $B\cos^2\theta$, which represented the coupling by a hyperconjugative mechanism. The evidence suggests that methyl groups normally rotate sufficiently freely for all values of θ to be equally probable, so that $\cos^2\theta$ in Eq. (6) may be replaced by an average value of $\frac{1}{2}$. Fessenden and Schuler [6], considering the methyl groups of ethyl, isopropyl and t-butyl radicals, concluded that in Eq. (6), if $A=0$, $B=(58.6 \pm 0.1)$ gauss. For substituents other than methyl in general not all values of θ are equally probable, so that $(\cos^2\theta)_{\text{av.}}$ may differ from $\frac{1}{2}$. Stone and Maki [30] considered the effect of hindered internal rotation on β-proton hyperfine splittings and derived an expression for the dependence of $(\cos^2\theta)_{\text{av.}}$ on the potential energy barriers to internal rotation. Fessenden and Schuler [6] adopted a similar approach when discussing alkyl radicals. The approach of Fischer [3] was rather different. Of the radicals with β-CH_2-groups studied by Fischer, all but two (polymethacrylic acid and polymethylmethacrylate radicals) had β-protons which appeared equivalent in the ESR spectra. In these cases Fischer argued that rapid transitions occurred between two favoured configurations. In one of these configurations the orientations of the β-hydrogen atoms, H_1 and H_2, were θ_1 and θ_2 respectively. The rotationally-averaged β-proton coupling constant was given by,

$$\alpha_{H(\beta)} = B\,\varrho\,\tfrac{1}{2}\,(\cos^2\theta_1 + \cos^2\theta_2)\,. \tag{7}$$

Since θ_1 and θ_2 were related $(\theta_1+\theta_2=120°)$, Fischer was able to calculate the precise orientations of the favoured configurations from observed coupling constants. The weakness of this approach is that it takes no account of contributions to $\alpha_{H(\beta)}$ arising from configurations intermediate between the two favoured configurations. That such configurations do make an important contribution to $\alpha_{H(\beta)}$ in hindered radicals is shown by the fact that β-proton coupling constants are often markedly temperature-dependent.

In the light of these comments the values of $\alpha_{H(\beta)}^{-CH_2-}$ reported in Table 2 may be discussed. For the radicals with ethyl and n-propyl substituents these values do not differ greatly from the values of $\alpha_{H(\beta)}^{-CH_3}$. In the former radical the β-proton coupling constant for the ethyl group is actually larger than for the methyl group. This suggests that configurations in which the γ-CH_3 group lies approximately in the plane of the trigonal carbon atom are favoured. A similar situation was observed by Fischer [4] for the radical $CH_3\dot{C}(CN)CH_2OH$ and by Fessenden and Schuler [6] for the radical $CH_3\dot{C}HC_2H_5$. For the radical $CH_3\dot{C}(CN)CH_2CH_2CH_3$ the β-proton coupling constant of the n-propyl group is smaller than for the methyl group. This is the situation that is found in the majority of sterically hindered radicals of this type. It can be explained by supposing that configurations in which the group attached to the β-CH_2-group lies approximately perpendicular to the plane of the trigonal carbon atom are sterically favoured. The effect is particularly noticeable in the $CH_3\dot{C}(CN)CH_2CO_2CH_3$ radical, and it seems possible that rotation of the $-CH_2CO_2CH_3$ substituent is severely restricted.

To date no satisfactory theoretical description of hyperfine coupling to γ-protons has been given. Fessenden and Schuler's studies of the temperature-

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dependence of γ-proton coupling in the propyl radical led to the opinion that the coupling was very sensitive to the precise orientation of the radical[6]. Our studies of $CH_3\dot{C}(CN)CH_2CH_3$ and $CH_3\dot{C}(CN)CH_2CH_2CH_3$ radicals lead to the same conclusion. Although these radicals are structurally rather similar, their γ-proton coupling constants differ by a factor of about three. The steric requirements for maximum γ-proton coupling are still not clear.

The hyperfine coupling constants of nitrogen atoms in our radicals are of similar magnitude to those found by other workers for similar radicals. The observation that all nitrogen hyperfine coupling constants in the radicals studied by us are the same, within experimental error, is not surprising since for the nitrile group a significant orientation-dependence is not expected. A dependence of the nitrogen hyperfine coupling constant on ϱ (Table 3) might be expected[31], but the effect is too small to be detected in our experiments.

It is noticeable (Table 2) that the linewidths, although small in all cases, increased with increasing radical size. This may be understood in a general way, since correlation times are proportional to the effective volumes of radicals, if variations in viscosity may be neglected[32].

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Barrier to Internal Rotation, Centrifugal Distortion Analysis and Structural Considerations of Methanesulfenylchloride

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An investigation of the microwave spectrum of CH_3SCl^{35} in the excited torsional state has been carried out. The barrier to internal rotation and other connected parameters are thus obtained. A centrifugal distortion analysis of the microwave spectrum of CH_3SCl^{35} in the ground state is also performed to predict high *J* transitions. A r_0-structure and bond axis quadrupole coupling constants are also considered.

In a preceeding paper the microwave spectrum of methanesulfenylchloride has been investigated[1]. The rotational constants and the quadrupole coupling constants have been given for both isotopic species CH_3SCl^{35} and CH_3SCl^{37} in the ground state. The dipole moment of the CH_3SCl^{35} species has also been determined.

Since a splitting due to internal rotation motion of the CH_3-group could not be observed, the present work was undertaken to investigate high *J* transitions in the ground state and transitions in the first excited torsional state. Considerations concerning structure and quadrupole coupling constants are also given.

The microwave spectrometer is a conventional 100 kHz Stark effect spectrometer operating in the range 6 – 37 GHz described elsewhere[2, 3].

Frequency measurements are believed to be accurate within ±0.03 MHz. The sample of methanesulfenylchloride was prepared by J. ROSENBAUM, Freiburg, and used without further purification.

Centrifugal Distortion Analysis

The centrifugal distortion analysis has been made essentially to predict the high *J* transition frequencies of CH_3SCl^{35} in the ground state. Thereby it was possible to find such lines and check for a possible splitting due to internal rotation.

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