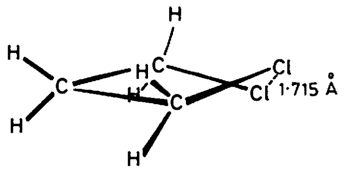
Electron Spin Resonance Spectra and Structure of the Radical Cations of Dibromoalkanes and Monobromoalkanes

Akinori Hasegawa *
Department of Chemistry, Kogakkan University, Ise-shi 516, Japan
Martyn C. R. Symons
Department of Chemistry, The University, Leicester LE1 7RH
Masaru Shiotani
Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724, Japan

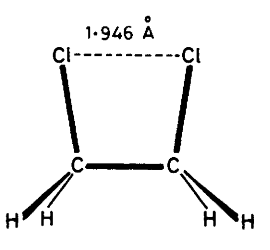
The radical cations of dibromoalkanes containing two bromines separated by an alkyl chain, have been generated by exposing dilute solutions of the dibromoalkanes in freon to *X*-rays at 77 K. Two types of e.s.r. spectra were observed for these cations. The spectra obtained for $Br(CH_2)_nBr$, $n = 1$–7, show septet features characteristic of two equivalent Br nuclei. The coupling constant of the septet increases and reaches a plateau, with increased n in these dibromoalkanes. This indicates that a positive hole in these cations is shared, not by the two Br nuclei connected through σ-delocalization over the chain, but by the two Br nuclei directly bonded to each other, in accordance with conclusions recently drawn from e.s.r. studies of dichloroalkane cations.

In contrast, the e.s.r. spectra obtained for $Br(CH_2)_nBr$, $n > 7$, are more complicated. When similar experiments were carried out with $H(CH_2)_nBr$, $n > 7$, analogous spectra were obtained, indicating that the spectra observed for these dibromoalkanes can be interpreted in terms of hyperfine interactions to only one of the two Br nuclei and to two nuclei with nuclear spins of 1/2. This result, considered together with the fact that similar cationic centres were detected for $H(CH_2)_nBr$, $n > 3$, and with the spectral change observed for $Br(CH_2)_nBr$ and $H(CH_2)_nBr$ cations in different matrices (CCl_2FCClF_2, CCl_3F, and CCl_4) indicates that cyclization also occurs for these cations, the positive hole being occupied in a three-centre bond comprising a Br nucleus, a C nucleus (four atoms away from the Br nucleus), and an H nucleus bonded to the C nucleus.

We recently reported e.s.r. spectra for the radical cations of dichloroalkanes containing two chlorines separated by an alkyl chain.[1] The cations were produced by irradiation of solid solutions containing the dichloroalkanes in freon which has been shown to stabilize radical cations.[2–4] The e.s.r. spectrum assigned to the $[Cl(CH_2)_3Cl]^{+\bullet}$ cation has lines attributable to hyperfine interactions to two equivalent Cl nuclei and to two equivalent protons. CNDO/2 calculations for the cation suggested a non-planar cyclic structure (**1**) having a Cl–Cl three electron bond ($\sigma_1{}^2\sigma_2{}^1$) and the coupled protons on terminal CH_2 groups.



(1)



(2)

In contrast, the $[Cl(CH_2)_2Cl]^{+\bullet}$ cation gave an e.s.r. spectrum attributable to two equivalent Cl nuclei alone and the result of geometrical optimization by CNDO/2 calculations, satisfactorily explaining the observed spectrum, suggested that the cation has the structure of the planar four-membered ring (**2**) formed by tilting the two CH_2Cl groups by 10° from the *cis* conformation so as to reduce the Cl–Cl distance, and stabilize the positive hole in the Cl–Cl bond.

Similar spectra, indicating a hole on two equivalent Cl nuclei, were also obtained for $Cl(CH_2)_nCl$, $n = 1$, 4, and 5, whereas different spectra were obtained for dichloroalkanes within $n = 8$ and 10. This may imply that matrix molecules prevent such cyclizations of long dichloroalkanes.

The radical cations of linear alkanes have been reported by Iwasaki *et al.*[5] The major splitting to a 1:2:1 triplet in the spectra was assigned to the two protons in either terminal CH_3 group and it was observed that the coupling constant of the splitting steadily decreased with increasing carbon number of the alkyl chain. Accordingly, they concluded that the two end protons are connected through σ-delocalization over the chain.[5] Therefore, there is clear difference in the holes between the dichloroalkane cations and the alkane cations: namely, a hole in the former case is located in the Cl–Cl bond formed as a result of cyclization, whilst it is shared by the two end-protons connected through σ-delocalization over the chain, in the latter case.

Nevertheless, e.s.r. spectra for these dichloroalkane cations have not been well enough defined to warrant reliable analyses and detailed discussion. Therefore, similar experiments were carried out with the dibromoalkanes which were expected to give cations showing clear and large splitting due to Br nuclei in their e.s.r. spectra.

There were four major aims in this study. The first was to investigate whether radical cations can be formed from dibromalkanes as well as dichloroalkanes. The second was to prove whether a hole in the cations is shared by the two Br atoms directly bonded with each other as a result of cyclization, or by the two atoms connected through σ-delocalization. If the cyclization mechanism is correct, matrix molecules would prevent the large movement required for such cyclizations in long-chain dibromoalkanes so that there may be a limit to the

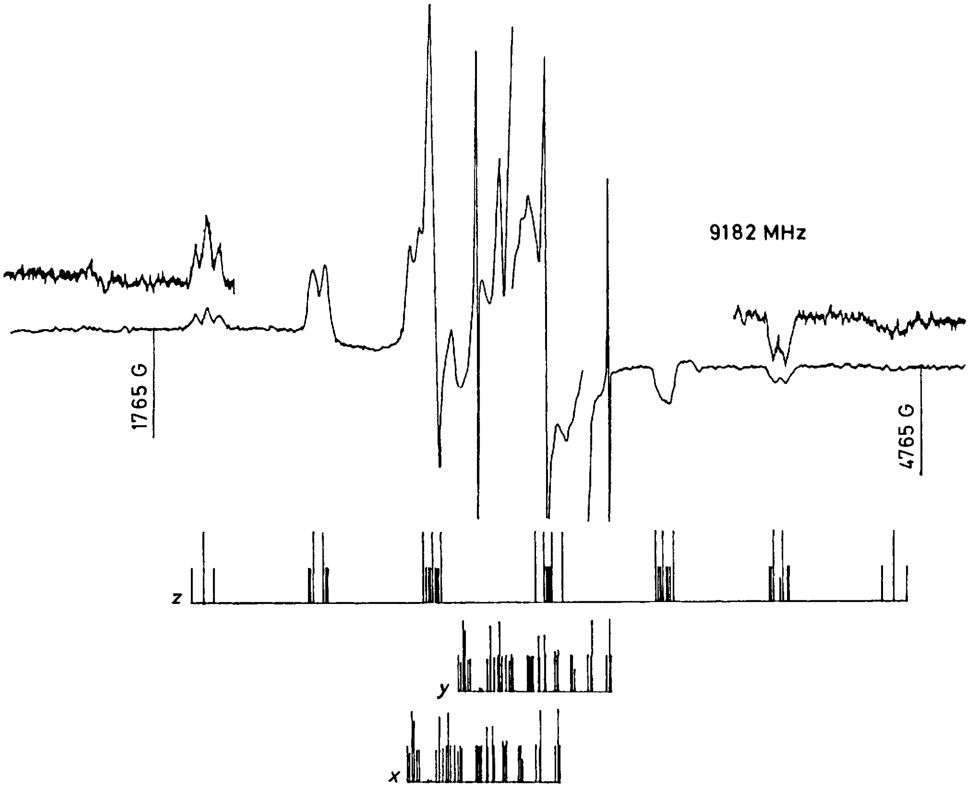


Figure 1. First-derivative X-band e.s.r. spectrum of a solution containing *ca.* 1 vol% $Br(CH_2)_3Br$ in CCl_2FCClF_2 after exposure to *X*-rays at 77 K, showing features assigned to $[Br(CH_2)_3Br]^{+\cdot}$, and stick diagrams for the cation calculated using the e.s.r. parameters listed in the Table.

length of the alkyl chain of the dibromoalkanes for which cyclization can occur. Therefore, the third aim was to examine the maximum number of carbon atoms in the cation for which e.s.r. spectra attributable to two equivalent Br nuclei were observed. The last was to identify the radical cations formed for the dibromoalkanes with long alkyl chains.

This study follows a series of studies of alkyl halide cations in CCl_3F matrices,[6,7] alkyl halide dimer cations,[6] cations of di-, tri-, and tetra-bromomethane,[8] and cations of dichloroalkanes,[1] as described in the introductory section of our recent paper.[1]

Experimental

A range of dibromoalkanes, $Br(CH_2)_nBr$, $n = 1$–10, and of monobromoalkanes, $H(CH_2)_nBr$, $n = 1$–10, and CCl_2FCClF_2, CCl_3F, and CCl_4 were purchased from Tokyo Kasei Co. Solutions of these dibromo- or monobromo-alkanes, in *ca.* 1 vol% concentrations, in either CCl_2FCClF_2, CCl_3F, or CCl_4 were degassed using standard vacuum techniques, frozen in Spectrosil e.s.r. tubes, and exposed to *X*-rays (Cu target, 40 kV, 20 mA) for 3 h at 77 K. After the samples had been irradiated, e.s.r. spectra were measured at 77 K on a JEOL JES-FE1XG spectrometer. Similar experiments were also carried out after exposure to γ-rays at 4 K followed by e.s.r. observations at 4 K and at various higher temperatures.

For comparison with the present results for bromoalkanes in CCl_2FCClF_2, solutions of chloroalkanes in this solvent were also studied.

Results and Discussion

The Cation Derived from $Br(CH_2)_3Br$.—Exposure of a dilute solution of $Br(CH_2)_3Br$ in CCl_2FCClF_2 to *X*-rays at 77 K gave an e.s.r. spectrum largely composed of parallel (*z*) features of a septet, as shown in Figure 1. The outermost components of the septet contain three lines with an intensity ratio of 1:2:1, which clearly indicates that two equivalent Br nuclei are involved in the spectrum since these three lines can be assigned to the characteristic pairs $^{81}Br,^{81}Br$, $^{81}Br,^{79}Br$, and $^{79}Br,^{79}Br$; bromine having two isotopes, ^{81}Br and ^{79}Br, in almost equal abundance. Thus, the spectrum implies the formation of the symmetrical $[Br(CH_2)_3Br]^{+\cdot}$ cation.

This interpretation of the spectrum was strongly supported by good accordance between the observed spectrum and the stick diagrams calculated by a strict matrix diagonalization method, using the e.s.r. parameters for the cation listed in the Table. For the assignments of the *x* and *y* components, different *g* values were used as for the cations $[C_2H_5Br\dot{-}ClCCl_2F]^+$,[6,7] $C_2H_5I^{+\cdot}$,[6] and $[Cl(CH_2)_3Cl]^{+\cdot}$.[1] However, the components were so poorly resolved that these assignments are somewhat arbitrary.

The values for the hyperfine tensor of each Br nucleus were used to estimate approximate spin densities of $\rho_s = 0.025$ in the 4s orbital and $\rho_p = 0.51$ in a 4p orbital on the nucleus, when the atomic values of hyperfine coupling constants for a Br nucleus were used.[9] Thus, it is reasonable to conclude that the positive hole is shared equally and is effectively confined to the 4p orbitals on the two Br nuclei which must be almost parallel to each other. It is common to find spin densities slightly greater than unity using this procedure for radical cations. This occurs for at least two reasons: (*a*) because atomic values are used, no correction being made for the positive charge, and (*b*) because of the frequent occurrence of negative spin densities on adjacent atoms.

In the case of $[Cl(CH_2)_3Cl]^{+\cdot}$ which has been reported to form in the same matrix, splittings due to two equivalent ^1H nuclei in the cation were observed in addition to a septet from two equivalent Cl nuclei.[1] Using these additional ^1H couplings as indicators, the conformation of the cation was investigated

Table. E.s.r. parameters for the radical derived from mono- and di-bromoalkanes in CCl_2FCClF_2 matrices.

		g tensor			No. of	^{81}Br h.f. tensor[a]			^1H h.f. couplings
Radical cations	n	g_x[c]	g_y[c]	g_z	Br	A_x[c]	A_y[c]	A_z/G[b]	a(isotropic)/G[b]
$[Br(CH_2)_nBr]^{+\bullet}$	3	2.100	2.059	1.978	2	86	86	465	
	4–7	2.10	2.06	1.978	2	80	80	486	
	8–10	2.026	2.010	1.983	1	95	95	380	111, 41.4
$[H(CH_2)_nBr]^{+\bullet}$	10–8	2.027	2.010	1.988	1	95	95	373	111, 41.4
	7	2.03	2.01	1.987	1	95	95	376	111, 41.6
	6	2.03	2.01	1.987	1	95	95	380	111, 42, 42
	5	2.03	2.01	1.986	1	90	90	390	111, 42, 42
	4	—	—	1.980	1	—	—	432	*ca.* 80, —, —
$[H(CH_2)_nBr \dot{-} ClCCl_2FCClF_2]^{+}$[d]	3, 2	*ca.* 2.39	*ca.* 2.08	*ca.* 1.90	1	*ca.* 180	*ca.* 180	*ca.* 500	

[a] Hyperfine tensor for ^{79}Br is omitted in this table, although it was used for calculation. [b] $G = 10^{-4}$ T. [c] These parameters may contain some errors due to poor spectral definition. [d] Parameters for these cations were estimated from those for $[C_2D_5Br \dot{-} ClCCl_2FCClF_2]^+$.[6]

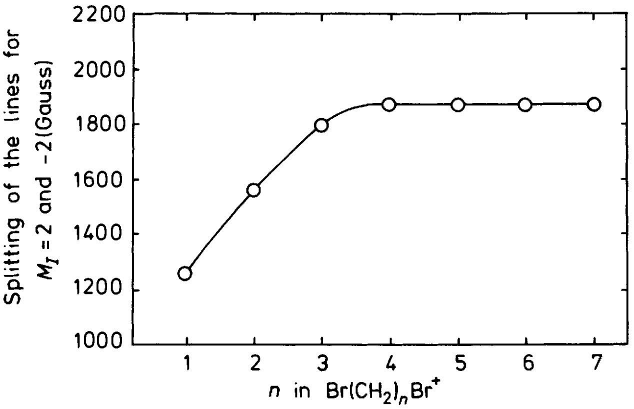


Figure 2. The change in separation between the centres of the two lines corresponding to $M_I = 2$ and to $M_I = -2$, where $M_I = m_{I_1} + m_{I_2}$ for two equivalent Br nuclei, associated with the number of carbon atoms, n, in $Br(CH_2)_nBr$.

using CNDO/2 calculations, and the non-planar structure of a five-membered ring (1) is proposed for the cation. In the present case, unfortunately, no additional ^1H couplings were observed, and our CNDO/2 program was not parametrized for bromine.

Cations Derived from $Br(CH_2)_nBr$, n = 1 *to* 7.—A series of alkanes $Br(CH_2)_nBr$ were similarly exposed to *X*-rays in CCl_2FCClF_2 matrices at 77 K. E.s.r. spectra similar to those assigned to $[Br(CH_2)_3Br]^{+\bullet}$ were observed for $Br(CH_2)_nBr$, n = 1, 2, and 4–7. In every case, clear doublet splittings, appeared for the components corresponding to $M_I = m_{I_1} + m_{I_2} = \pm 2$ for the two equivalent Br nuclei. The separation between the centres of the doublets in these two components increased with increased values of n, ($n \leqslant 3$), but reached a plateau, for n larger than 3, as shown in Figure 2.

It is of interest to compare this trend with that reported by Iwasaki *et al.* for the alkane cations $[H(CH_2)_nH]^{+\bullet}$ formed in CCl_2FCClF_2 matrices.[5] These e.s.r. spectra are characterized by three-line structures with large hyperfine couplings which were assigned to the two protons in either terminal CH_3 group (end protons). This coupling decreased steadily with increasing carbon number in the alkyl chain. Hence, they concluded that these two end-protons were connected through σ-delocalization over the chain.[5]

In clear contrast, no change in hyperfine coupling was observed for these dibromoalkane cations with alkyl chains for n = 4–7. Therefore, it may be reasonable to assume that a positive hole in these cations is shared not by the two Br nuclei connected through σ-delocalization over the chain, but by the two Br nuclei directly and weakly bonded to each other. Such hole-sharing by the two bonded halogens has been proposed for $[Cl(CH_2)_2Cl]^{+\bullet}$ and $[Cl(CH_2)_3Cl]^{+\bullet}$, and supported by CNDO/2 calculations.[1] Therefore, we propose that $[Br(CH_2)_3Br]^{+\bullet}$ has a non-planar five-membered ring structure containing the two Br atoms bonded to each other as in structure (**1**), and $[Br(CH_2)_2Br]^{+\bullet}$ has a planar four-membered ring as in structure (**2**), despite the fact that their neutral parent molecules have extended *gauche* conformers in the crystalline solid state.[10] The positive hole in these cations is in the σ* bond which is intramolecularly formed between the two Br nuclei. In other words, these cations have cyclic structures containing a Br–Br three-electron bond ($\sigma_1{}^2\sigma_2{}^1$). Similar cyclizations can also be proposed for the cations of the other dibromoalkanes having alkyl chains with n = 1–7 and giving features attributable to two equivalent Br nuclei.

The smaller splitting in the Br hyperfine structure for a smaller value of n, which is shown in Figure 2, probably arises because the p orbitals on the two Br nuclei sharing one positive hole are not parallel to each other because of the strain in the cyclic structure of the cation with the shorter alkyl chains. This is consistent with the 32° calculated for the angle between the two p orbitals in $[Cl(CH_2)_2Cl]^{+\bullet}$.[1]

Cations Derived from $Br(CH_2)_nBr$, n > 7.—It is somewhat surprising that such cyclizations occur for cations having alkyl chains of up to seven carbons, in CCl_2FCClF_2 solid matrices at 77 K. Presumably for dibromoalkanes with longer chains, the matrix molecules would prevent the large movement required for such cyclizations. In fact, spectra completely different from those observed already were obtained after irradiation of dibromoalkanes with longer alkyl chains ($n > 7$). The features of the spectra are independent of the length of the alkyl chain, for $n > 7$, a typical spectrum, obtained for $n = 9$, being shown in Figure 3. The spectrum comprises four sets of lines which are clearly assignable to the $M_I = \pm 3/2$ and $\pm 1/2$ features for a monobromo cation, with complex additional splitting on each feature. This extra splitting might arise from hyperfine coupling to chlorine as is the case for the ethyl bromide cation which forms a weak σ* complex, $[RBr \dot{-} ClX]^+$. However the spectra are very different, with $A_{max.}$(Br) and $g_{max.}$ greatly reduced for the new species compared with those for the ethyl derivative [Table 1 in ref. (6)]. Thus it seems unlikely that these are similar solvent complexes. Furthermore, the spectra were unchanged in the three solvents, CCl_3F, CCl_4, and CCl_2FCClF_2, which is not usually the case for these solvent adducts.

There remain at least two possibilities that the additional splitting stems from proton hyperfine coupling or from the second bromine nucleus. To probe the latter, we have studied $H(CH_2)_nBr$ cations with $n > 7$.

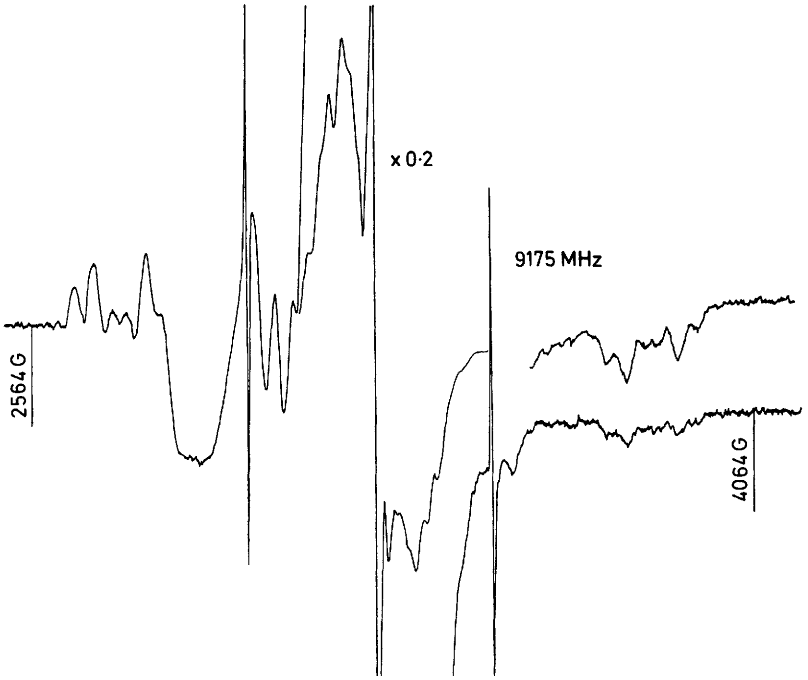


Figure 3. First-derivative X-band e.s.r. spectrum of a solution containing *ca.* 1 vol% $Br(CH_2)_9Br$ in CCl_2FCClF_2 after exposure to *X*-rays at 77 K, showing features assigned to the $[Br(CH_2)_9Br]^{+\bullet}$ radical cation.

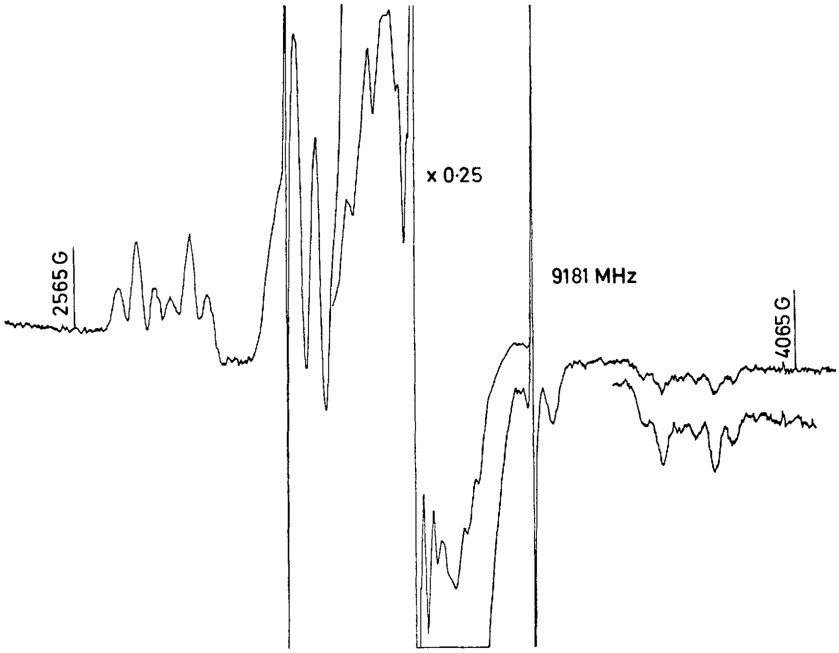


Figure 4. First-derivative X-band e.s.r. spectrum of a solution containing *ca.* 1 vol% $H(CH_2)_{10}Br$ in CCl_2FCClF_2 after exposure to *X*-rays at 77 K, showing features assigned to the $[H(CH_2)_{10}Br]^{+\bullet}$ radical cation.

Cations Derived from $H(CH_2)_nBr$, $n > 7$.—In order to ascertain the number of Br nuclei involved in the spectrum shown in Figure 3, similar experiments were carried out with monobromoalkanes having only one Br nucleus in a molecule. These monobromoalkanes having alkyl chains with carbon number larger than 7 gave analogous e.s.r. spectra, in fundamental agreement with the spectrum observed for $Br(CH_2)_9Br$, as revealed by the spectrum for $H(CH_2)_{10}Br$ shown in Figure 4. Accordingly, only one of the two Br nuclei in $[Br(CH_2)_nBr]^{+\bullet}$, $n > 7$, is involved in these e.s.r. spectra.

If the major quartet of parallel (*z*) features were due to a Br nucleus as expected, splitting originating from the presence of ^{81}Br and ^{79}Br isotopes would appear in the spectra. In fact, the splitting of 41.4 G found in both the wings is in reasonable agreement with that expected for the isotope splitting of the major Br quartet. In order to reproduce the six-line features, a second splitting of *ca.* 41.4 G and a larger splitting of 111 G were required. The simplest explanation of this result is that there are two coupled protons giving 41.4 and 111 G splittings, respectively, and in view of the arguments given above, this is the favoured interpretation. The possibility remains that this splitting is due to chlorine hyperfine coupling with a rather large

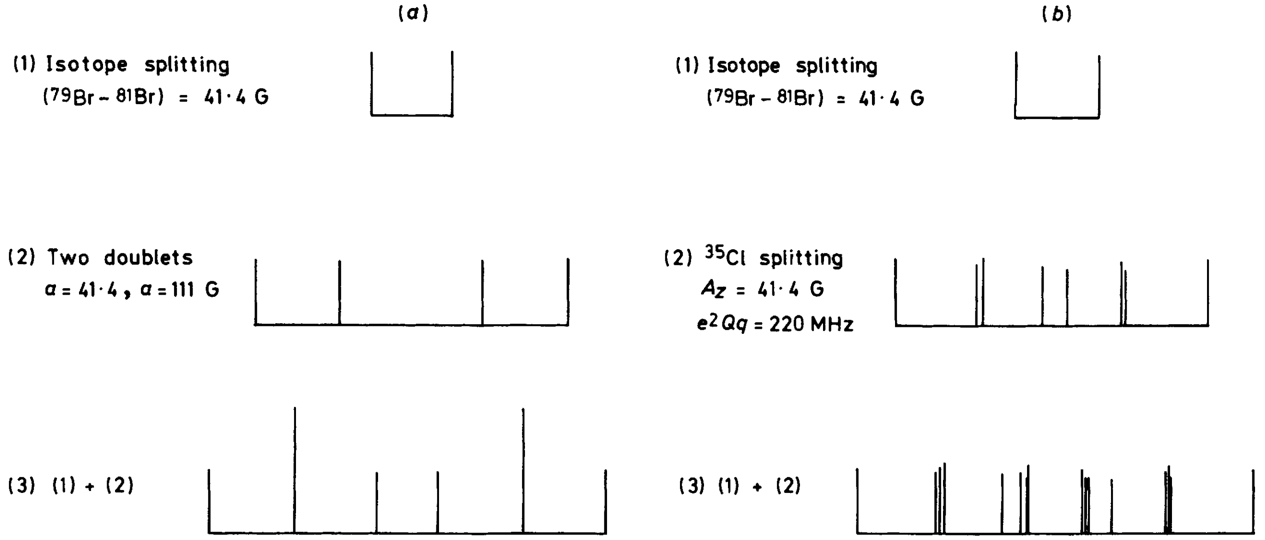


Figure 5. (1) The isotope splitting of 41.4 G due to a Br nucleus, detected in the wing components of the spectra for $[Br(CH_2)_nBr]^{+\bullet}$, $n > 7$, and $[H(CH_2)_nBr]^{+\bullet}$, $n > 7$. (2) Splittings from two doublets with coupling constants of 41.4 and 111 G (*a*) or a ^{35}Cl hyperfine splitting affected by a quadrupole interaction to the ^{35}Cl nucleus, $A_z = 41.4$ G and $e^2Qq = 220$ MHz (b). (3) The resultant wing features.

quadrupole effect destroying the even distribution of the lines. Such an unequally separated Cl hyperfine structure would be possible in the *z* components of the major Br quartet, if the major principal *z* axis of the hyperfine tensor for the Br quartet is perpendicular to the major axis of the quadrupole interaction to the Cl nucleus. A theory of quadrupole interaction in e.s.r. spectra was applied to these four unequally separated lines.[11,12] To fit the spectra, 41.4 G and 220 MHz were obtained for the hyperfine coupling constant, A_z, and the nuclear quadrupole coupling constant, e^2Qq, respectively, for the ^{35}Cl nucleus. For these parameters, however, a strict calculation with this theory yielded several forbidden lines as well as the allowed lines, with almost equal intensities, in the case of the magnetic field parallel to the *z* axis, as shown in Figure 5(*b*) (2). When the isotope splitting of 41.4 G is added to these splittings, there is a complicated distribution of lines in the wing regions, as shown in Figure 5(*b*) (3).

In order to determine which is the better model, the two-doublets model or the model of the Cl hyperfine structure affected by the quadrupole interaction, computer simulations were performed using a program written using a second-order perturbation method for a *g* tensor and a Br hyperfine tensor in orthorhombic symmetries.[13] Isotropic splittings were assumed for the two doublets. For the splittings due to the Cl nucleus, the major axis of quadrupole interaction to the Cl nucleus was assumed to be perpendicular to the *z* axis of the Br hyperfine tensor, as described earlier, and calculation by a strict matrix diagonalization was performed for every direction of the magnetic field applied. These splittings were added to those due to the Br nucleus, in the manner of a first-order approximation.

As a result, the spectrum simulated for the two-doublets model with the e.s.r. parameters listed for $[Br(CH_2)_9Br]^{+\bullet}$ in the Table, has the wing features of six lines with two weak lines separated narrowly in the central part, as shown in Figure 6(*a*). However, the spectrum obtained for the Cl hyperfine structure affected by the quadrupole interaction, had wing features with two intense lines in the central part, as shown in Figure 6(*b*). Comparison of these spectra with the observed spectra shown in Figures 3 and 4, strongly suggests that the two-doublets model is much preferable to the model of Cl hyperfine structure affected by the quadrupole interaction. The spectrum simulated for the two-doublets model would be improved if broad signals due to other radical species, in the central and the lower-field regions, were added and parameters for *x* and *y* components were chosen more carefully. Thus, it can be concluded that two nuclei of $I = 1/2$ having the coupling constants of 111 and 41.1 G are involved in the observed spectra.

The fact that similar spectra were observed in CCl_3F and, particularly, in CCl_4, leads us to the conclusion that the two nuclei of $I = 1/2$ can be assigned to ^1H nuclei in the alkyl chain of the cation. For the determination of the positions of these nuclei in the alkyl chain, selective deuteriation should be used. However, owing to practical restrictions, this method was abandoned and the observations of e.s.r. spectra of cations and their matrix effects were carried out instead with monobromoalkanes of variable alkyl chain lengths.

Cations Derived from $H(CH_2)_nBr$, n = 7.— Exposure of a solution containing $H(CH_2)_7Br$ in CCl_2FCClF_2 gave an e.s.r. spectrum very similar to those obtained for longer bromoalkanes but with a slightly larger A_z value for the Br quartet. However, in the e.s.r. spectra observed for $H(CH_2)_6Br$ the outermost components differ from those obtained for longer bromoalkanes. For the former seven lines are found, as shown in Figure 7(*c*), whilst six lines of intensity ratio 1:2:1:1:2:1 are observed for longer bromoalkanes, as shown in Figure 7(*a*) and (*b*). The seven lines seen to be composed of two groups, partly overlapping, each of four lines of intensity ratio of 1:3:3:1. These may be interpreted in terms of the isotope splitting for the major Br quartet, a doublet with a large coupling, and two doublets with couplings almost equal to the value of the isotope splitting. This also supports the two-doublets model proposed for the cations of $Br(CH_2)_nBr$, $n > 7$. The highest-field component of the e.s.r. spectrum for $H(CH_2)_5Br$ clearly exhibits seven lines, although the seven lines in the lowest-field component are partly masked by one of intense broad signals, as shown in Figure 7(*d*). The splitting of the major Br quartet gradually increases with decreased chain length.

In contrast, the spectrum for $H(CH_2)_4Br$ cations in CCl_2FCClF_2 shows four broad lines with poorly defined features. Only the lowest-field component of the four lines is shown in Figure 7(*e*). In spite of the clear difference in the features, however, the positions of the four lines are exactly those expected for the Br quartet of the cation of $H(CH_2)_4Br$, from the extrapolation of the splittings for the Br quartets in the series of the cationic species under consideration. Therefore, it

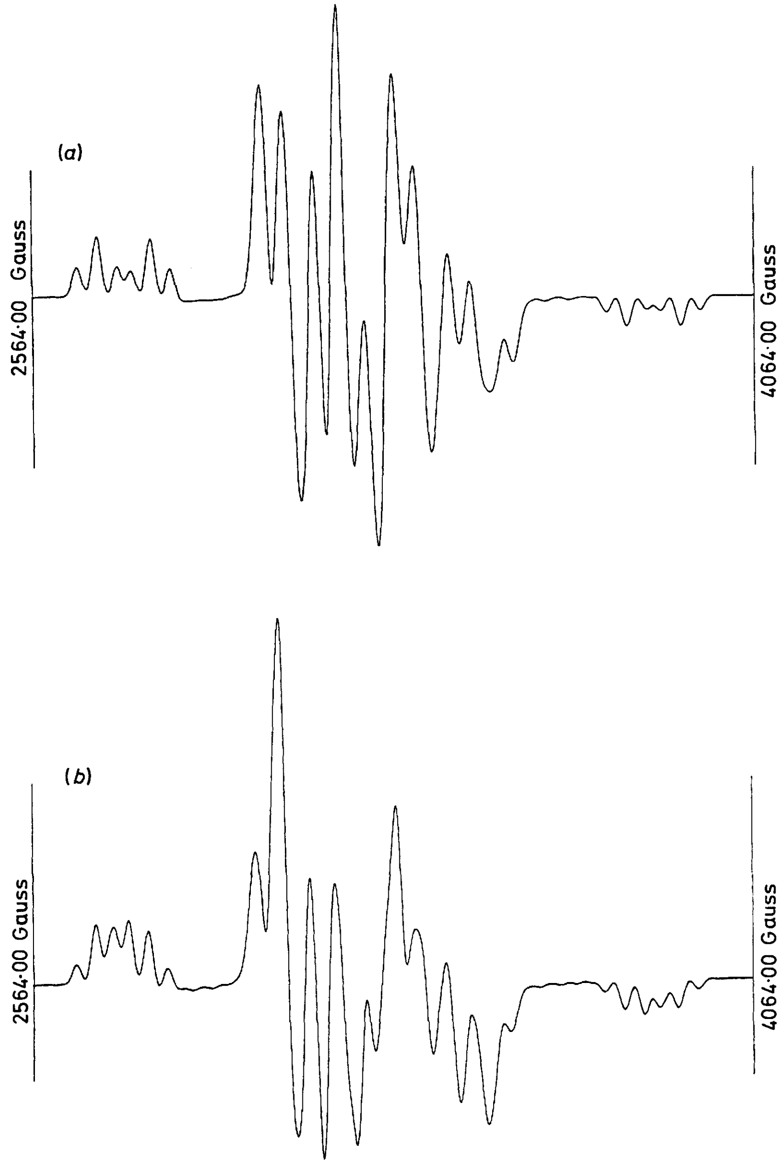


Figure 6. Simulated spectra for the $[Br(CH_2)_9Br]^{+\bullet}$ cation, calculated from (*a*) the two-doublet model and (*b*) the model of the Cl hyperfine splitting affected by a quadrupole interaction with the Cl nucleus.

may be concluded that the species of the radical cation for this bromoalkane is similar to that of the cations of other longer bromoalkanes and that the features of the lines for this cation are poorly resolved owing to the participation of other nuclei. In contrast with the increase in the coupling of the Br quartet, the coupling of the doublet giving a larger value decreases considerably in this case. E.s.r. parameters for these cations are listed in the Table.

The spectrum obtained for $H(CH_2)_3Br$, shown in Figure 8(*a*), is very similar to that for $H(CH_2)_2Br$ cations, having asymmetric broad features with a much greater coupling to bromine. These spectra are so different from those for longer bromoalkanes that it is obvious that different types of radical cations are involved. In order to identify the radical species and to investigate any matrix effects, similar experiments were carried out using the CCl_3F matrix.

Exposure of a dilute solution of $H(CH_2)_3Br$ in CCl_3F to *X*-rays at 77 K gave an e.s.r. spectrum which showed several lines in the low-field region, as shown in Figure 8(*b*). Almost the same spectra have already been observed for $H(CH_2)_2Br$ in the CCl_3F and assigned to the radical cation coupled to a Cl atom of the CCl_3F matrix molecule, $[H(CH_2)_2Br\dot{-}ClCCl_2F]^+$. Splittings due to a Cl nucleus were clearly observed in experiments with $D(CD_2)_2Br$ although they were smeared out in the case of $H(CH_2)_2Br$. Therefore, the spectra for $H(CH_2)_3Br$ in CCl_3F and CCl_2FCClF_2 are both thought to be due to $RBr^{+\bullet}$ cation complexed to one solvent chlorine atom, in spite of the difference in spectral features observed between these two matrices.

Except for line widths, the spectrum obtained for $H(CH_2)_4Br$ in CCl_3F is similar to that run in CCl_2FCClF_2 as shown in Figure 7(*f*) but is quite different from those obtained for shorter bromoalkanes. This suggests that the matrix effect in this case is much smaller than that for the radical species in which a matrix molecule directly participates and that the cationic centre formed from $H(CH_2)_4Br$ is different from that derived from shorter bromoalkanes. The spectrum obtained for $H(CH_2)_5Br$ in CCl_3F has wing features consisting of seven lines very similar to those obtained in CCl_2FCClF_2, whereas the spectrum for $H(CH_2)_6Br$ in CCl_3F has wing features consisting of six lines, in contrast with the corresponding spectrum recorded in CCl_2FCClF_2. For cations derived from longer bromoalkanes,

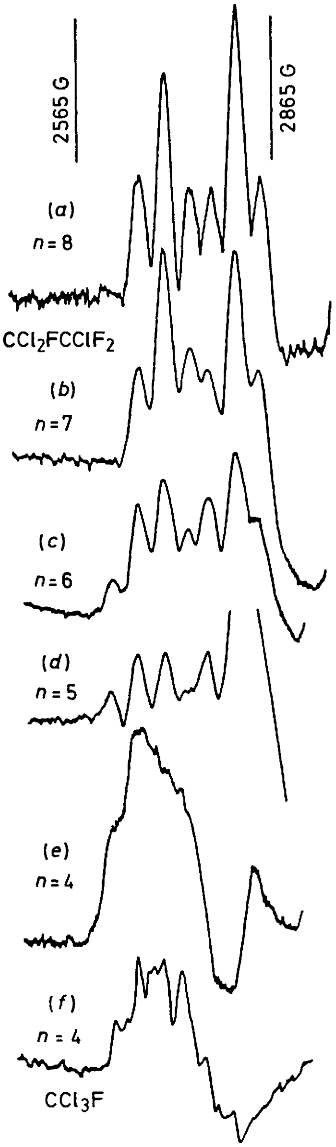


Figure 7. Features of the lowest-field components in the spectra of $[H(CH_2)_nBr]^{+\bullet}$, $n = 8$ to 4, in CCl_2FCClF_2 [(*a*)–(*e*) respectively] and bromoalkane with $n = 4$ in CCl_3F (*f*).

no significant difference was detected between the spectra run in CCl_3F and CCl_2FCClF_2.

In order to discover whether the third doublet appearing in the case of bromoalkanes with $n = 5$ and 6 in CCl_2FCClF_2, and $n = 5$ in CCl_3F, is due to an extra ^1H nucleus in the cations or possibly a ^{19}F nucleus in a matrix molecule, similar experiments were carried out with these bromoalkanes in CCl_4 matrices. Unfortunately, the only signals observed were those assigned to $CCl_4^{+\bullet}$ cations and $\dot{C}Cl_3$,[14,15] radicals. However, the equal splittings of these doublets in both CCl_2FCClF_2 and CCl_3F suggest that the doublet originates not from a matrix molecule but from the bromoalkane cation itself.

These experiments involving various bromoalkanes in different matrices, lead us to the following conclusions. Similar cationic centres are formed from $H(CH_2)_nBr$, $n > 3$ which are analogous to those formed in cations derived from $Br(CH_2)_nBr$, $n > 7$. In many of these cations, the e.s.r. spectra contain splittings due to a Br and two H nuclei. An extra H nucleus is involved in the spectra of $H(CH_2)_nBr$, $n = 5$ and 6 in CCl_2FCClF_2, and $n = 5$ in CCl_3F. Furthermore, other protons may be responsible for the poorly defined features for $H(CH_2)_4Br$ in both matrices. These cations are obviously distinct from the cation derived from $H(CH_2)_nBr$, $n < 4$ which is coupled to a Cl nucleus in one of the matrix molecules.

Identification of the Cations Derived from $Br(CH_2)_nBr$, $n > 7$ *and* $H(CH_2)_nBr$, $n > 3$.—Similar cationic centres were obtained for the radical cations of $Br(CH_2)_nBr$, $n > 7$, and $H(CH_2)_nBr$, $n > 3$. A large ^1H splitting of 111 G was observed in many cases. This value is close to those reported for the end-protons in the distorted cations of CH_4 (121.7 G),[16] C_2H_6 (152.5 G),[5] and C_3H_8 (105.5 G)[5] and for β-protons in the cations of cyclic ethers (97–135 G)[17,18] and aldehydes (135–138 G).[19–22] The simplest explanation for such a large coupling is that the nucleus is a β-proton bonded to the carbon atom adjacent to the Br atom. However, in contrast with oxygen atoms in the cations of ethers and aldehydes, the Br atoms in the present cations have small spin densities (*ca.* 0.40, see below), which may suggest much smaller β-proton couplings. Furthermore, the present results clearly suggest that it is imperative for these cationic centres that the protons on C(4) are involved. Note also that the ^1H coupling is almost independent of the length of the alkyl chain, when $n > 4$, and the change in the A_z of the Br quartet *vs.* the length of the alkyl chain is small compared with the change in the coupling of the end-protons of alkane cations.[5] Lastly, in the case of $n = 4$, the proton coupling decreased considerably but its decrease was compensated by an increase in the coupling of the Br quartet. This proton is therefore neither an end-proton nor a β-proton, and it may be in an unique position, probably bonded to the C(4) atom and sharing a positive hole with the Br nucleus.

A possible structure containing a six-membered ring was obtained using molecular models and is shown in Figure 9. The 4p orbital, having a calculated spin density of 0.38 on the Br nucleus, would lie toward the H(4) nucleus bonded to the C(4) nucleus, as shown in Figure 9. When this ring structure was examined, it was found that the direction of the 4p orbital on the Br nucleus is approximately parallel with that of the bond between C(1) and the hydrogen [H(1)] bonded to C(1). Since H(1) is a β-proton, it is plausible to expect a considerable spin density through the appropriate Heller–McConnell $\cos^2\theta$ and McConnell relations.[23] Thus, the doublet with a coupling constant of *ca.* 41 G may be assigned to H(1).

When usual atomic hyperfine coupling constants were used,[9] a spin density of *ca.* 0.3 remained unassigned for the cation derived from $Br(CH_2)_nBr$, $n > 7$; the spin densities $\rho_{4s} = 0.02$ and $\rho_{4p} = 0.38$ on the Br nucleus and $\rho_{1s} = 0.22$ from the ^1H coupling of 111 G and positive spin density of $\rho_{1s} = 0.08$ for the proton with the ^1H coupling of 41.4 G, having already been assigned. Let us consider a parent bromoalkane having two electrons in each of the non-bonding orbitals on the Br nucleus and a C(4)–H(4) bond. When one electron is released from the non-bonding orbital by irradiation and the orbital approaches the C(4)–H(4) bond, the remaining electron on the Br and the H nuclei and one electron on the C(4) nucleus may form a three-centre bond similar to that in diborane[24] and reported for several hypervalent radicals.[25,26] Therefore, we expect a considerable spin density on the C(4) atom, which can explain the 'missing' fraction of *ca.* 0.3. This is consistent with the fact that poorly defined features, which may be caused by the other two protons bonded to the C(4) nucleus, were observed for the cation derived from $H(CH_2)_4Br$.

There remains one more ^1H doublet to be assigned. Having a coupling constant almost equal to that for the smaller 1-H nucleus, this doublet was observed for the cation derived from $H(CH_2)_nBr$, $n = 5$ and 6 in CCl_2FCClF_2, and the bromoalkane with $n = 5$ in CCl_3F. It may be supposed that the doublet is due to the H nuclei in a C(5)–H bond lying in the plane containing the three-centre bond. The absence of the doublet for

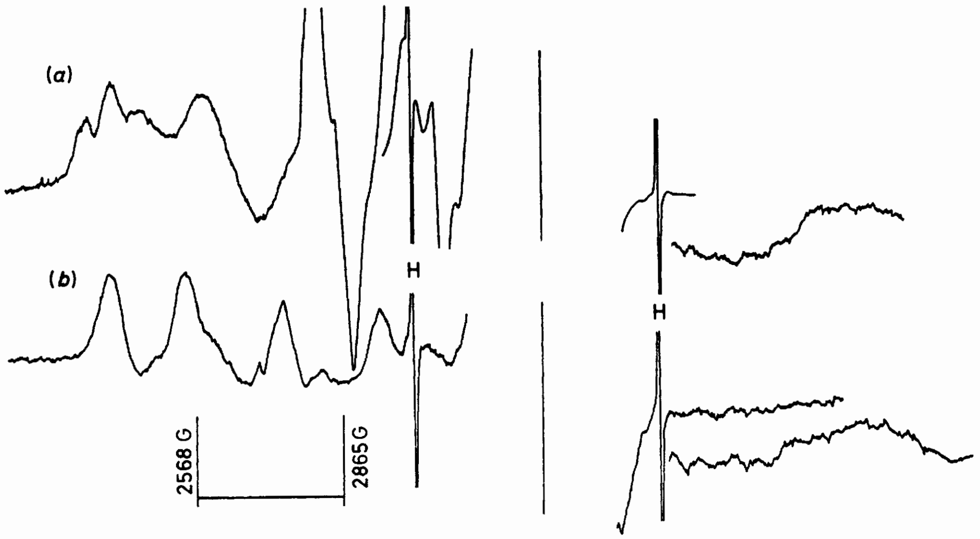


Figure 8. First-derivative X-band e.s.r. spectra of solutions containing *ca.* 1 vol% $H(CH_2)_3Br$ in (*a*) CCl_2FCClF_2 and (*b*) CCl_3F after exposure to *X*-rays at 77 K, with (*b*) showing features very similar to those assigned to the $[H(CH_2)_2Br\dot{-}ClCCl_2F]^+$ cation, and the region of the magnetic field where the lowest-field components shown in Figure 7 appear, being indicated by a solid line beneath the spectra.

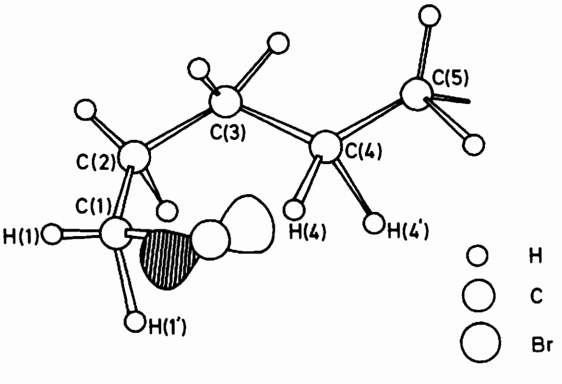


Figure 9. The structure proposed for the radical cations of $Br(CH_2)_nBr$, $n > 7$, and $H(CH_2)_nBr$, $n > 3$, comprising a six-membered ring resulting from partial cyclization. H(4) and H(1) nuclei are assigned to the doublets with the splittings of 111 and 41.4 G, respectively.

$H(CH_2)_6Br$ in CCl_3F may be interpreted as the conformational change of the terminal CH_3 group caused by a matrix effect. The spectra of cations derived from longer bromoalkanes and $Br(CH_2)_nBr$, $n > 7$ do not display this doublet, which indicates that these cations have conformations with no C(5)–H bond in the plane of the three-centre bond.

Comparison between the Two Types of Cations Formed from $Br(CH_2)_nBr$.—It is interesting to compare the two types of cations formed from a series of dibromoalkanes: one has a hole shared equally by the two Br nuclei and the other is supposed to contain a hole largely shared between one of the two Br atoms, the relevant C(4) atom, and the hydrogen atom bonded to C(4). The former is the result of cyclization of the radical, in which the two terminal Br nuclei are bonded to each other, whilst the latter has a six-membered ring containing four carbon, the H(4), and the Br nuclei. The two are competitive, the former being preferred for dibromoalkanes $Br(CH_2)_nBr$, $n < 8$, and the latter for longer dibromoalkanes. Note also that these cyclizations are somewhat similar to the cyclization of the 1,5-hexadiene cation to cyclohexane cation,[27] and opposite to the ring opening reported for the cations of cyclic oxiranes,[28–32] cyclopropanes,[33] cyclopropylamines,[34] and so on.

These cyclizations must be effected by some thermal motion of the cations in the matrices. Further studies to establish this, involving irradiations at 4 K followed by e.s.r. observations at 4 K and above, are under way. Preliminary results indicate that a different type of cation having a major spin density on one Br nucleus, is formed upon irradiation of $Br(CH_2)_6Br$ in CCl_2FCClF_2 at 4 K. On being annealed at 77 K, however, this cation was irreversibly converted into a cation containing two equivalent Br nuclei which gave e.s.r. spectra very similar to the foregoing spectra measured at 77 K after irradiation at 77 K. On the other hand, when $H(CH_2)_{10}Br$ was in CCl_2FCClF_2 was irradiated at 4 K, an intense broad line and a trace of lines characteristic of the cation with the partial cyclization to the six-membered ring were observed in the spectrum recorded at 4 K. Upon annealing at 77 K, the decrease in the intensity of the broad line was compensated by an increase in the intensity of the signals due to the cation with the six-membered ring. Accordingly, these preliminary experiments satisfactorily show that thermal motion is required for the accomplishment of either cyclization and that the motion needed for cyclization to the six-membered ring is smaller than that for the cyclization of the whole radical of long dibromoalkanes, as expected. Details and the identification of the precursors detected at 4 K will be published elsewhere.

We have described in our recent paper that e.s.r. spectra with the splittings due to two equivalent Cl nuclei were observed after irradiation of $Cl(CH_2)_nCl$, $n = 1$–5, in CCl_2FCClF_2, whilst a different type of spectrum was obtained for longer dichloroalkanes, for example, with $n = 8$ and 10.[1] Hence, in order to investigate whether spectra similar to the latter can be obtained by the irradiation of $H(CH_2)_nCl$, similar experiments were carried out with a series of chloroalkanes. As a result, similar spectra were obtained for $H(CH_2)_nCl$, $n > 6$, in accordance with the results of bromoalkanes. Unfortunately, however, these spectra are too complicated to allow detailed analysis.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 61470012) from the Japanese Ministry of Education, Science, and Culture.

References

1 A. Hasegawa, M. C. R. Symons, and M. Shiotani, *J. Chem. Soc., Perkin Trans. 2*, 1989, 147.

2 T. Shida, E. Haselbach, and T. Bally, *Acc. Chem. Res.*, 1984, **17**, 180.

3 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393.

4 M. Shiotani, *Magn. Reson. Rev.*, 1987, **12**, 333.

5 K. Toriyama, K. Nunome, and M. Iwasaki, *J. Chem. Phys.*, 1982, **77**, 5891.

6 G. W. Eastland, S. P. Maj, M. C. R. Symons, A. Hasegawa, C. Glidewell, M. Hayashi, and T. Wakabayashi, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1439.

7 M. C. R. Symons, H. Muto, K. Toriyama, K. Nunome, and M. Iwasaki, *J. Chem. Soc., Perkin Trans. 2*, 1986, 2011.

8 M. C. R. Symons, *J. Chem. Res. (S)*, 1985, 256.

9 M. C. R. Symons, 'Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy,' Van Nostrand Reinhold Co. Ltd., Wokingham, 1978.

10 J. K. Brown and N. Sheppard, *Proc. R. Soc. London, Ser. A*, 1955, **231**, 555.

11 N. M. Atherton, 'Electron Spin Resonance, Theory and Applications,' Ellis Horwood Ltd., Chichester, 1973, p. 227.

12 F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, 1972, **56**, 6251.

13 N. M. Atherton and C. J. Winscom, *Inorg. Chem.*, 1973, **12**, 383.

14 S. P. Mishra and M. C. R. Symons, *Radiat. Phys. Chem.*, 1975, **7**, 617.

15 M. C. R. Symons, E. Albano, T. F. Slater, and A. Tomasi, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 2205.

16 L. B. Knight, Jr., J. Steadman, D. Feller, and E. R. Davidson, *J. Am. Chem. Soc.*, 1984, **106**, 3700.

17 H. Kubodera, T. Shida, and K. Shimokoshi, *J. Phys. Chem.*, 1981, **85**, 2583.

18 L. D. Snow, J. T. Wang, and F. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 2062.

19 L. B. Knight, Jr., J. M. Bostick, R. W. Woodward, and J. Steadman, *J. Chem. Phys.*, 1983, **78**, 6415.

20 L. B. Knight, Jr., B. W. Gregory, S. T. Cobranchi, F. Williams, and X.-Z. Qin, *J. Am. Chem. Soc.*, 1988, **110**, 327.

21 L. D. Snow and F. Williams, *Chem. Phys. Lett.*, 1983, **100**, 198.

22 P. J. Boon, M. C. R. Symons, K. Ushida, and T. Shida, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1213.

23 See, *e.g.* W. Gordy, 'Theory and Applications of Electron Spin Resonance,' Wiley, New York, 1980, ch. VI, p. 198.

24 H. C. Longuet-Higgins, *J. Chim. Phys.*, 1949, **46**, 275.

25 T. Gillbro and F. Williams, *J. Am. Chem. Soc.*, 1974, **96**, 5032.

26 A. Hasegawa, K. Ohnishi, K. Sogabe, and M. Miura, *Mol. Phys.*, 1975, **30**, 1367.

27 Q.-Z. Guo, X.-Z. Qin, J. T. Wang, and F. Williams, *J. Am. Chem. Soc.*, 1988, **110**, 1974.

28 L. D. Snow, J. T. Wang, and F. Williams, *Chem. Phys. Lett.*, 1983, **100**, 193.

29 T. Bally, S. Nitsche, and E. Haselbach, *Helv. Chim. Acta*, 1984, **67**, 86.

30 X.-Z. Qin, L. D. Snow, and F. Williams, *J. Am. Chem. Soc.*, 1985, **107**, 3366.

31 X.-Z. Qin, L. D. Snow, and F. Williams, *J. Phys. Chem.*, 1985, **89**, 3602.

32 J. Rideout, M. C. R. Symons, and B. W. Wren, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 167.

33 X.-Z. Qin and F. Williams, *Tetrahedron*, 1986, **42**, 6301.

34 X.-Z. Qin and F. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 595.

Received 17*th June* 1988; *Paper* 8/02428F