Selectively Weakened C–C σ-Bond in Cation Radicals of Linear and Branched Pentanes As Studied by Electron Spin Resonance

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Radical cations which have the fully extended structure (trans–trans conformation) but have lost the symmetry of the mother molecules were detected by electron spin resonance for *n*-pentane, 3-methylpentane, and 3,3-dimethylpentane in frozen matrices at 4 K. It was indicated, with the aid of an INDO calculation, that one of the two inner C–C bonds in the main chain is elongated and the unpaired electron tends to be confined in this bond. Selective bond elongation was also shown for the trans–gauche conformers of 3-methylpentane and 3,3-dimethylpentane cations. These facts suggest that selective elongation of a C–C bond is essential with alkane cations even if it is not Jahn–Teller active. This selective weakening of a skeletal bond should be related to the selectivity in the bond scission in alkane radiolysis. In addition, hole migration between the solute alkanes in the frozen matrices at 77 K was suggested from the radical conversion between the different conformers.

Introduction

From a series of electron spin resonance (ESR) studies on the structure and the reaction of alkane cation radicals, Iwasaki et al. deduced that the deprotonation reaction of the alkane cation radical takes place preferentially from the C–H bond with the highest unpaired electron density.[1,2] On the contrary, the relation between the C–C bond scission in the radiolysis of alkanes and the spin distributions in its cations has been little discussed. This may come from the fact that it is hard to get experimental evidence for the weakening of specific C–C bonds, such as hfc for the carbons, although elongation of the skeletal C–C bonds in the cation radical is expected from their electron-deficient nature and has been suggested from ab initio MO[3] as well as semiempirical MO calculations.[4]

Recently we found an asymmetric propane cation radical in the C_3F_8 matrix, where a large part of the unpaired electron is concentrated in one of the two C–C bonds.[5] Propane cations in other matrices, which had been thought to maintain the symmetry of mother molecule (C_{2v}),[1b] were also found to be distorted to some extent. From these facts elongation of one of the C–C bonds is indicated, because in the case of propane cation the observed asymmetry could not be explained by other deformations such as twisting. In addition, since the deformation is largest in C_3F_8 and this matrix may give a substitutional site for the solute propane cation with a similar shape and a little larger volume, we argued that the asymmetric bond elongation may be the intrinsic nature of the propane cation radical rather than a matrix effect. Similar distortion in cation radicals of alkyl substituted cycloalkanes was reported[6,7] but was ascribed to the stabilization of Jahn–Teller distortion.[6]

In the present work, we investigated the structure of the cation radical of *n*-pentane and its methyl-substituted compounds by low-temperature matrix ESR, in order to get further evidences for the selective bond elongation. We employed *n*-pentane, which is the simplest odd-*n*-alkane larger than propane, since in the case of odd-*n*-alkanes the selective bond elongation must accompany the lowering of molecular symmetry, which should be reflected to the ESR parameters. The unpaired electron density in an *n*-alkane cation radical is predicted to be highest at the center of the molecule,[8] so the selective bond elongation may take place in this region. In the case of even-*n*-alkane, elongation of the central C–C bond does not reduce the molecular symmetry, and the change may not be detected on the ESR spectrum.

n-Pentane and 3,3-dimethylpentane (3,3-DMP) have the following rotational isomers: trans–trans (TT), trans–gauche (TG), and gauche–gauche (GG). In the case of 3-methylpentane (3MP), we need additional conformational parameters: gauche or trans (g, t) with respect to the side methyl group. Thus there are two TG conformers for 3MP; i.e., TGgt and TGgg. Among these, only the TT or GG conformer have the mirror symmetry, which may be lost upon selective elongation of one of the two equivalent C–C bonds. In previous works, both the cation radicals of *n*-pentane with TT and TG form were already detected in freons and in SF_6,[1,4,9] but no distortion could be detected. While, in the case of 3MP and 3,3-DMP, only the TG conformers were reported.[10–13]

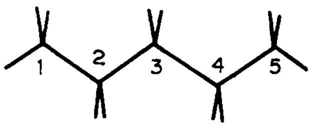
Experimental Section

The samples of *n*-pentane, 3-methylpentane (3MP), 3,3-dimethylpentane (3,3-DMP), and $CFCl_2CF_2Cl$ (F113) were obtained from Tokyo Kasei Kogyo (Tokyo), and perfluoropentane (n-C_5F_{12}), perfluorohexane (n-C_6F_{14}), and perfluorooctane (C_8F_{18}) were purchased from PCR (Florida). The content of *n*-isomers was about 85% for the perfluoropentane and was larger than 70% for the hexane. All of these materials were used after trap-to-trap distillation. The fluoroalkane solution containing 0.2–3.0 wt % of the alkane was degassed by the freeze–pump–thaw technique and sealed under ca. 100 Torr of He gas. The cation radicals were generated by irradiating the frozen sample solution with X-rays at 4 K or with γ-rays at 77 K. ESR measurements were made at 4, 77, and 90–140 K, with a Varian E-12 spectrometer equipped with an on-line personal computer system.[2]

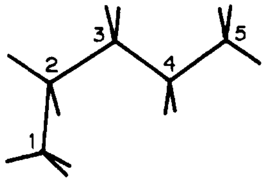
Results

***n*-Pentane.** Figure 1 shows the ESR spectra of *n*-pentane cation radical in various matrices. The spectrum of the cation radical in SF_6 at 4 K (a) is composed of four lines with equal intensities and the hfc's of two protons are 6.0 and 4.0 mT. When measurement is made at 77 K (b), it changes reversibly into a three-line one with the averaged separation of 5.0 mT. In C_6F_{14} (c) the three-line spectrum, which does not show a temperature change between 4 and 77 K, was observed. The hfc (5.5 mT) is a little larger than that in SF_6.

The cation radicals of *n*-pentane with two different conformations were identified previously in F113 at 77 K.[1b,4] As shown with trace e and the stick diagrams, they are the TT conformer, which gives the three-line spectrum (I) with the relative intensities of 1:2:1, and the TG conformer for the four-line spectrum (II) with equal intensities.[1b] The hyperfine couplings for the TT form were assigned to the two in-plane methyl protons at both ends of the molecule (a = 5.5 mT), while those of the TG conformer were assigned to one proton from the terminal methyl group (a = 5.8 mT) and another from the C_2-methylene group (a = 9.0



(I)



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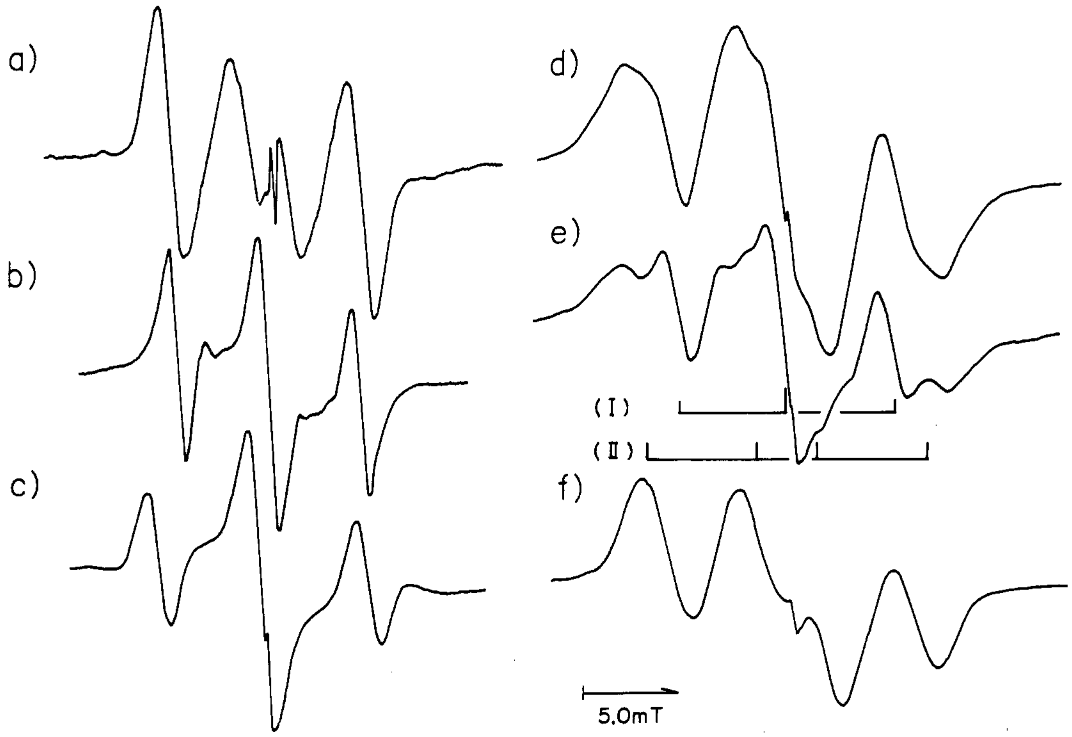


Figure 1. ESR spectra of *n*-pentane cation radical generated in SF_6 (a, b), *n*-C_6F_{14} (c), $CFCl_2CF_2Cl$ (d, e), and CF_3CCl_3 (f) by X-irradiation at 4 K. Observation was made at 4 K (a, c, d, f) and at 77 K (b, e). For a and b, the background signal is numerically subtracted. The spectrum in C_6F_{14} does not show any temperature dependencies from 4 to 77 K.

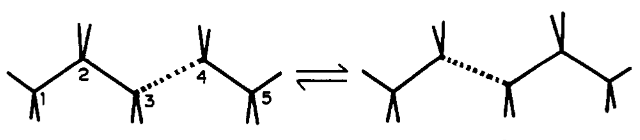
TABLE I: Observed and Calculated Hyperfine Coupling Constants for *n*-Pentane Cation Radical[a]

		hf coupling/mT						spin density on carbon				
		obsd			calcd							
matrix	geom (sym)	H_1	H_5	H_2	H_1	H_5	H_2	C_1	C_2	C_3	C_4	C_5
SF_6	TT (C_s)	4.0	6.0		3.89	5.76		0.126	0.156	0.261	0.249	0.066
C_6F_{14}	TT (C_{2v})	5.5	5.5		4.85	4.85		0.112	0.205	0.252	0.205	0.112
F113	TT (C_{2v})	5.7	5.7[b]									
	TG		5.8	9.0[b]	1.98	5.30	9.35	−0.005	0.160	0.230	0.194	0.096
CF_3CCl_3	TG		5.0	7.95								

[a] The parameters used in this calculation are $R(C–C) = 0.154$ nm, $R(C–H) = 0.1102$ nm, and θ = tetrahedral angle. In the case of distorted TT conformer (TT(C_S)), only the C_3–C_4 bond was elongated by 0.01 nm. [b] Reference 1b.

mT) which come in the molecular plane. When irradiation is made at 4 K (d), both of the two components are formed essentially in the same way, but the fraction of the four-line is much larger than that of the three-line.

From the comparison with those, the cation formed in C_6F_{14} (c) was assigned to the TT conformer (I) since the hfc (a = 5.5 mT) is equal to that of the three-line observed in F113. On the other hand, the four-line spectrum in SF_6 (a) could not be attributed to the TG conformer (II), since the hfc's are obviously different from those of II in F113 (see Table I). The averaged hfc (5.0 mT) is rather close to that of I. So, in the same way as in our previous study on the asymmetric propane cation in C_3F_8,[5] we tentatively assigned the four-line spectrum in SF_6 to the *n*-pentane cation with fully extended form but distorted to C_s symmetry by selective elongation of one of the two inner C–C bonds, C_3–C_4 for example (III).



(III) (III′)

In this geometry, the unpaired electron density in the C_3–C_4 bond is expected to be higher than that in the symmetric form, and thus the spin density on $H(C_1)$ is reduced. For the hfc of $H(C_5)$, however, the increase of hyperconjugation with the C_3–C_4 bond compensates the decrease in spin delocalization. The temperature dependence of the ESR spectrum (a, b) is interpreted as due to the interchange between two equivalent structures, III and its mirror image III′. An INDO calculation was made to confirm the above assignment, and the result is shown in Figure 2b. Hfc's close to the experimental result are obtained for asymmetric TT conformer by elongating one of the inner C–C bonds (C_3–C_4) by 0.01 nm. One may consider the end C_4–C_5 bond as another choice for the elongation. In this deformation, however, decrease of the hfc's for both of the in-plane end protons is expected, because the higher spin distribution in $2p(C_5)$ orbital causes a more negative spin on C_5–H by spin polarization. In fact this possibility was rejected by INDO calculation.

In CF_3CCl_3, a pure four-line spectrum with large hfc's was observed and assigned to the TG conformer (f). When observed at 77 K, this spectrum changes to a very complicate one[4,9] due to the internal rotation of the end methyl and ethyl group.[14] [The *n*-pentane cation radical trapped in CF_3CCl_3 was previously assigned to the TT conformer from the broadened spectrum at 77 K.[9] The authors suggested that this cation changes its conformation reversibly into GG form at around 130 K. From the present experiment at 4 K and at higher temperatures, we concluded that it has TG conformation throughout the temperature from 4 to 130 K. The details will be given elsewhere.]

3-Methylpentane. Figure 3 shows the ESR spectra of 3MP cation generated by X-ray irradiation at 4 K in C_8F_{18} (a–c). The spectrum observed at 4 K (a) was changed irreversibly to b after annealing at 77 K, but the decrease of the total radical concentration during this change was only 11 ± 5%. Spectra e, a

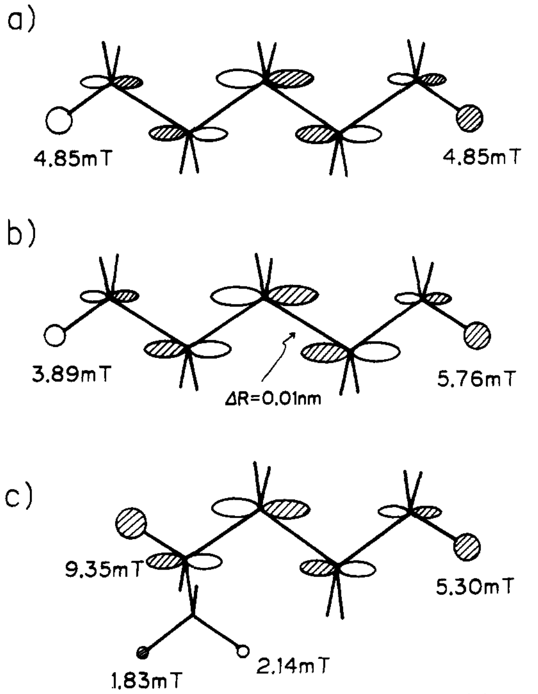
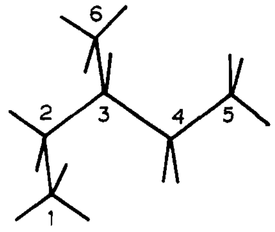


Figure 2. Hfc's obtained by INDO-MO calculation for *n*-pentane cation radicals with symmetric TT form (C_{2v}) (a), with asymmetric TT form (b), and with TG conformation (c). In the case of (b), the C_3–C_4 bond was elongated by 0.01 nm. The other parameters were fixed to the standard values.

three-line with the separation of 4.5 mT (intensity ratio 1:2:1) and f, a four-line with the hfc of about 4.6 mT (intensity ratio 1:3:3:1) were obtained by numerical subtraction of spectra a and b. Spectra a and b are reconstructed with the two components e and f at the ratio of 7:3 and 5:5, respectively (see the dotted lines and the broken line in a and b). This irreversible spectral change, a to b, is interpreted as the conversion of the three-line component into the four-line one. On the other hand, once the sample is annealed at 77 K, the temperature change of the spectrum between b and c is reversible. The spectral change between b and c may be caused by the broadening of the three-line component due to a dynamic process.

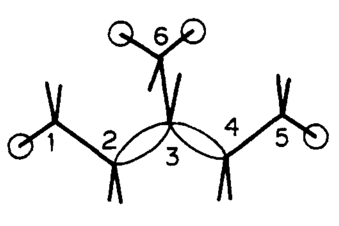
The four-line component f is almost the same with that observed in F113 previously and assigned to the 3MP cation radical with TG conformation (IV),[10,11] whose spectrum at 4 K is shown as



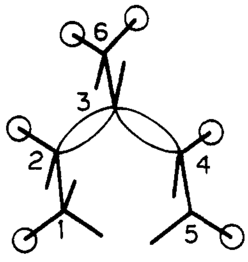
(IV)

trace d. In this cation most of the unpaired electron is confined in C_3–C_4 bond to allocate hfc's (ca. 4.6 mT) to the three trans-β-protons by the hyperconjugation effect.[15] The individual hfc's of these three protons, H(C_2), H(C_5), and H(C_6), have been determined by Ohta and Ichikawa using partially deuteriated 3MP's as 5.29, 4.99, and 3.93 mT, respectively.[11]

Without considering a distortion, the three-line spectrum cannot be expected from either of the rest two conformers TT nor GG. In the case of undistorted TT (V) or GG (VI), for example, four



(V)



(VI)

or six hydrogens with large hfc are expected since the unpaired electron should be distributed equally in C_2–C_3 and C_3–C_4.

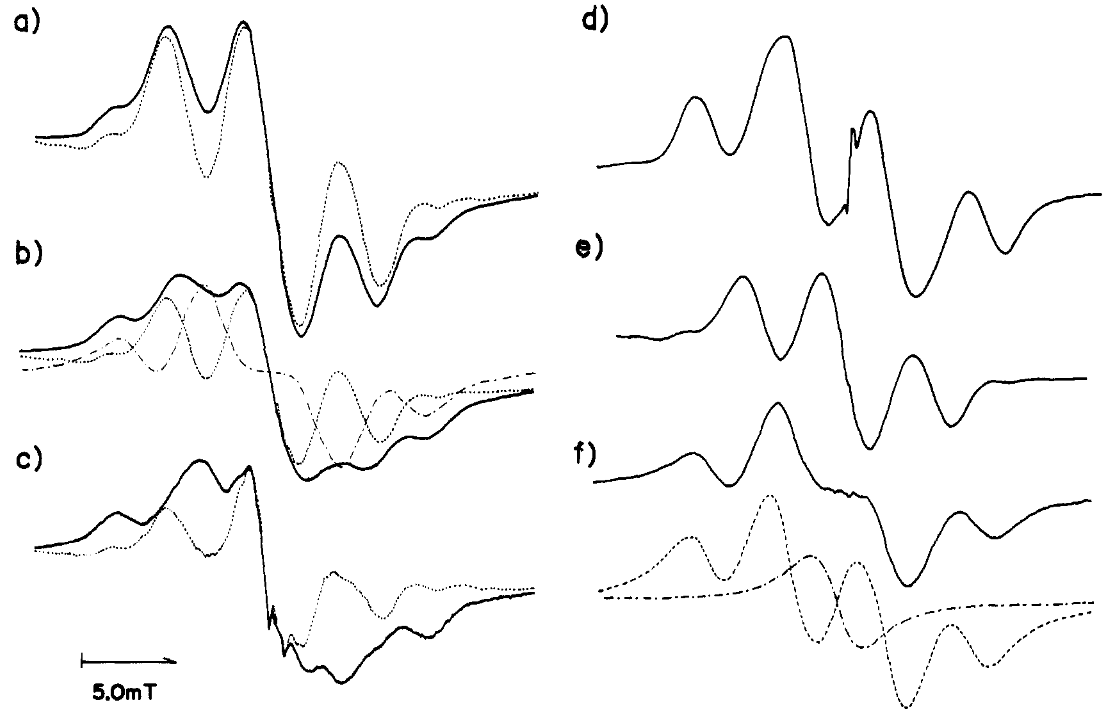


Figure 3. ESR spectra of 3MP cation radical formed by X-irradiation at 4 K in C_8F_{18} (a–c) and F113 (d). Observations were made at 4 K without raising sample temperature (a, d), after warming up once to 77 K (b), or at 77 K (c). Spectra (e) and (f) were obtained by numerical subtractions of the spectrum between (a) and (b). The spectrum drawn with dotted line and broken line in (f) are the simulations with the parameters of a = 4.2 mT (2H), a = 5.5 mT (1H) (ΔH_{pp} = 2.7 mT (Lorentzian) and single line with ΔH_{pp} = 2.7 mT. The relative intensity is 7:1.

TABLE II: Observed and Calculated Hyperfine Coupling Constants for 3-Methylpentane and 3,3-Dimethylpentane Cation Radicals[a]

		hf coupling/mT											
		obsd	calcd				spin density on carbon						
matrix	geom (sym)	H_2, H_5, H_6, H_7	H_2	H_5	H_6	H_7	C_1	C_2	C_3	C_4	C_5	C_6	C_7
3MP													
C_8F_{18}[b]	TT (C_s)	4.50 (2H)		4.88	5.52		0.105	0.081	0.233	0.298	0.018	0.016	
	TG	4.60 (3H)	6.58	4.80	5.52		0.027	0.010	0.225	0.281	−0.005	0.058	
F113	TG	4.50 (3H)											
		5.25, 4.99, 3.93[c]											
3,3-DMP													
C_8F_{18}[b]	TT (C_s)	3.55 (3H)		3.27	4.35	4.35	0.070	0.007	0.230	0.252	−0.018	0.073	0.073
	TG	3.65 (4H)	5.63	5.12	4.32	4.18	0.044	0.007	0.228	0.315	−0.006	0.009	0.025
F113		3.75 (4H)											

[a] In this calculation the standard geometrical parameters, R(C–C) = 0.154 nm, R(C–H) = 0.1102 nm, and θ = tetrahedral angle were assumed except for the following: $R(C_3–C_4)$ = 0.164 nm, $\langle C_2C_3C_4$ = 107.0°, and $\langle C_6C_3H$ (3MP) or $\langle C_6C_3C_7$ (3,3-DMP) = 112.0°. [b] Almost the same spectrum was also observed in C_5F_{12} and C_6F_{14}. [c] From reference 11.

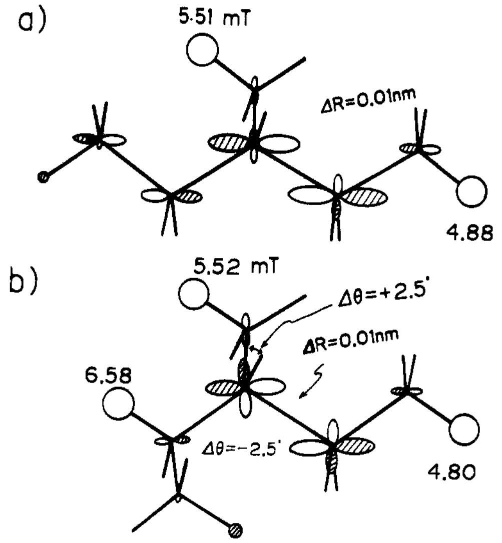
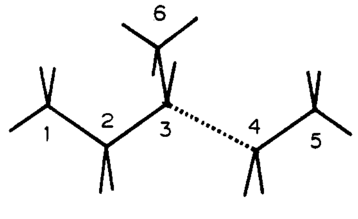


Figure 4. Hfc's and spin distributions obtained by INDO-MO calculation for 3MP cation radical with fully extended structure (TT form) (a) and for that with TG conformation (b). For both of them the $C_3–C_4$ bond was elongated by 0.01 nm. In the case of TG conformer, the angle $C_2C_3C_4$ was reduced by 2.5° and the $\angle HC(CH_3)$ at the central carbon was increased by 2.5° from the tetrahedral angle.

Therefore, we have to consider some deformations as have been introduced in the case of propane and *n*-pentane cations. In the case of GG conformer, a four-line spectrum is expected since three protons at trans-β-position from the elongated C–C bond may have large hfc's. In contrast, we can expect two protons with large hfc for the distorted TT conformer with only one inner C–C bond ($C_3–C_4$ bond for example) elongated (VII). Where the unpaired electron is expected to be mainly confined in this elongated bond and the two protons which cause the three-line hyperfine structure are assigned to the inplane $H(C_5)$ and $H(C_6)$ (substituted methyl group). These two C–H bonds can hyperconjugate efficiently with the unpaired electron in $C_3–C_4$ σ-bond. Shown in Figure 4a are the hfc's and spin distribution estimated by INDO-MO calculation for this asymmetric 3MP cation radical. With the elongation of $C_3–C_4$ by 0.01 nm, more than 40% of the unpaired electron is concentrated in this σ-bond, and the hfc's of 4.88 and 5.10 mT were obtained for C_5–H and C_6–H, respectively (Table II). The average of these two hfc's (4.99 mT) is close to the splitting of the three-line spectrum, 4.35 mT. The calculated hfc's for the molecule with elongated $C_4–C_5$ (or $C_1–C_2$) bond were not consistent with the experiment.



(VII)

In principle, it is possible to assign the three-line spectrum to the distorted TG conformer if $C_2–C_3$ is elongated. However, we think this is less probable because of the following reasons: (1) The calculated hfc's of $H(C_6)$ and $H(C_5)$ (6.92 and 4.40 mT, average = 5.66 mT) are too much larger than the observed values (4.5 mT). (2) The TG conformer with the four-line ESR spectrum is observed in many matrices, such as $CFCl_3$, CF_3CCl_3, CF_3-c-C_6F_{11}, and F113, as a stable form. Thus it is not natural to expect another stable TG conformer.

At the final stage of the present work, we found that Ohta et al. observed a three-line ESR spectrum of 3MP cation in CF_2BrCF_2Br,[16] which is almost identical with our spectrum in C_8F_{18}. They assigned it to a structure, with the ethyl group rotated around the $C_2–C_3$ bond by 40° from the gauche form, so that the C_2–H cannot hyperconjugate efficiently with the unpaired electron in $C_3–C_4$ bond. However, their assignment has a serious difficulty that their conformation is close to the eclipsed form around the $C_2–C_3$ bond, and thus it should be energetically unstable. On the other hand, their assignment of the hyperfine couplings using partially deuteriated 3MP is compatible with ours: one proton from the terminal methyl and another form the substituted methyl. [The authors of ref 16 misunderstand that the gauche conformation around the $C_2–C_3$ is obtained by rotating the ethyl group around this bond by ±60° from the trans conformation, rather than ±120°, which is the correct rotational angle. Therefore, the conformations described as GGtg (θ = 0, θ' = 0) and GGgg (θ = 0, θ' = 0) in the ref 16 are actually the eclipsed forms.]

It should be noted that, for the TG conformer of 3MP cation which gives the four-line spectrum, the elongation of one inner C–C bond was necessary to obtain the hfc's satisfactory for the experimental values. The calculated result with the $C_3–C_4$ bond elongated by 0.01 nm is shown in Figure 4b and in Table II. In this case, beside of the bond elongation, the angle $\angle C_2C_3C_4$ was decreased by 2.5° and $\angle HC(CH_3)$ at the central carbon was increased by the same amount. These structural modifications were made as suggested by ab initio MO calculations for the alkane cation.[3]

3,3-Dimethylpentane. Figure 5 shows the spectra of 3,3-DMP cation generated by X-ray irradiation at 4 K in C_8F_{18} and observed at 4 K before (a) and after the thermal treatment at 77 K (b). Spectrum b does not show any temperature dependencies from 4 to 77 K. The change from a to b is irreversible, and the decrease of the total radical concentration during this change was 8 ± 5%. Spectra a and b were decomposed into the component spectra of c and d by numerical subtraction. Spectra a and b could be reconstructed by superposing c and d with the relative weights of 6:4 and 3:7, respectively. This fact indicates that the five-line spectrum dominates the other initially and a part of them is converted into the four-line spectrum by thermal annealing at 77 K.

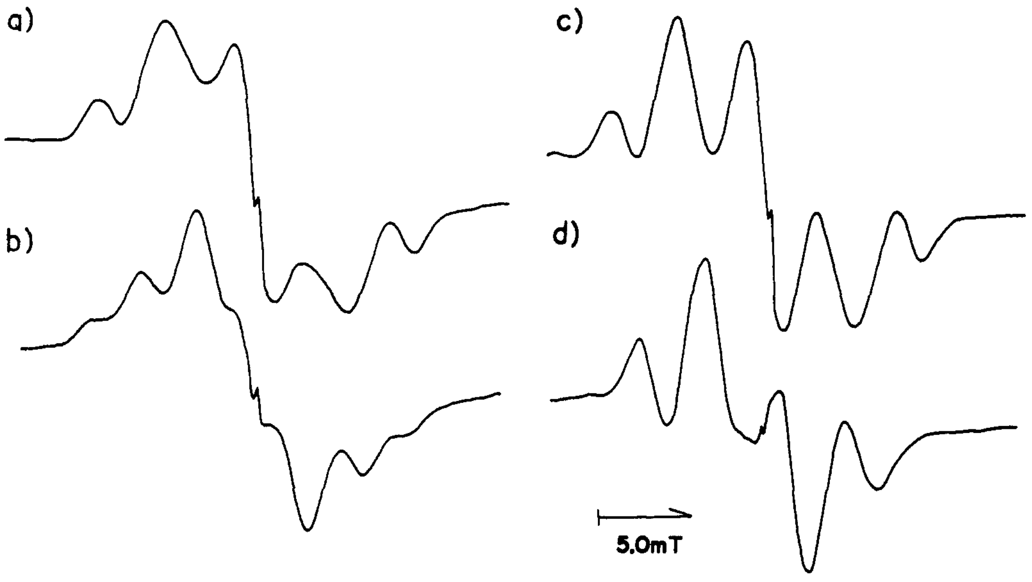
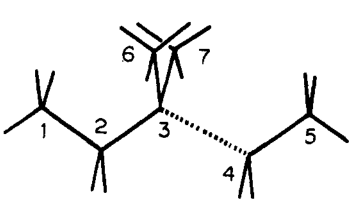
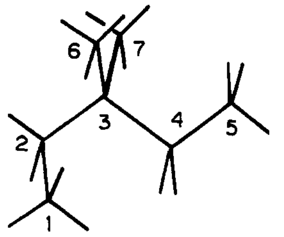


Figure 5. ESR spectra of 3,3-DMP cation produced by X-irradiation at 4 K in C_8F_{18}. Observation was made at 4 K before (a) and after (b) the thermal treatment at 77 K. The spectra (c) and (d) were obtained by the numerical subtractions, (a) − (b) × f and (b) − (a) × f', respectively.

When the tertiary proton of 3MP cation radical with asymmetric structure (IV or VII) is replaced with a methyl group, one additional proton on the methyl group would contribute to the hyperfine structure. On the other hand, two additional hyperfine couplings would appear for the cation with symmetric form (V or VI). Therefore, the four-line is attributed to the 3,3-DMP cation with the distorted TT from (VIII) and the five-line to the TG conformer (IX). The INDO MO calculation shown in Figure 6 and listed in Table II supports the above assignments. For the distorted TT conformer (VIII), elongation of one of the inner C–C bonds by 0.01 nm was assumed as in the same way for the 3MP cation with distorted TT form. The result of calculation for the TG conformer was also given in b. In this case, the bond angles at the central carbon were modified in addition to the lengthening of C_3–C_4 as in the case for the 3MP cation with TG form. Essentially the same results as those in C_8F_{18} were obtained using CF_3-c-C_6F_{11} matrix, while only the TG conformer was detected previously in F113 matrix.[12]



(VIII)



(IX)

Discussion

Selective Bond Elongation in Alkane Cation Radical. The selective bond elongation was indicated for the cations with TT conformation of n-pentane, 3-methylpentane, and 3,3-dimethylpentane, through analyzing the ESR spectra, which are explained only with the asymmetrically deformed structures due to one bond elongation. In addition, from INDO calculation, similar selective bond elongation was suggested for the TG conformers of 3MP and 3,3-DMP cations. Thus, it is suggested that the selective bond elongation may be a general nature of the σ-delocalized cations. Examples of such specific bond elongation has been accumulated since the finding of the asymmetric propane cation, although weakening of the skeletal bonds is naturally expected for the electron-deficient molecules, i.e., cations.[5,11] Recently, a similar bond elongation was reported for the methylsilacyclohexane cation by Shiotani et al.[17]

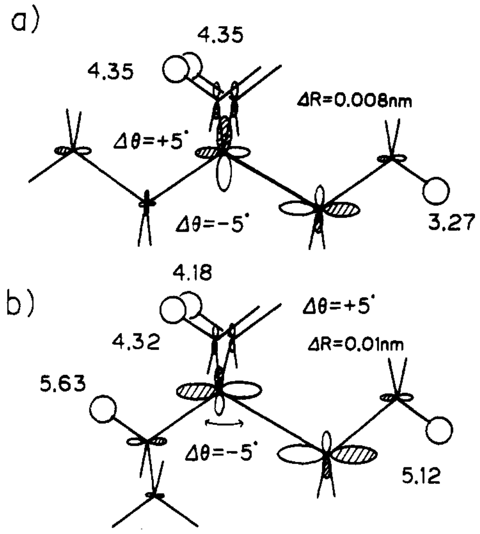


Figure 6. Hfc's estimated by the INDO-MO calculation for 3,3-DMP cation radical with fully extended structure (a) and for that with TG conformation (b). In this calculation, the C_3–C_4 bond was elongated by 0.01 nm. In addition, in the case of TG conformer the angle $C_2C_3C_4$ was reduced by 5.0° and the $\angle(CH_3)C(CH_3)$ at the central carbon was increased by 5.0° from the tetrahedral angle.

We believe this selective elongation in C–C skeleton in alkane cations is an intrinsic phenomenon, especially in branched alkane cations, since without this idea less realistic models must be introduced to account for the experimental result. For example, Shiotani et al.[12,16] claimed that the conformation of 3MP cation trapped in F113 (four-line spectrum) should be "GGgt" rather than TGgt or TGgg as was assigned in our previous work.[10] However, their conformation is hard to accept, since it is the eclipsed form around the C_3–C_4 bond (see Figure 3 in ref 16). It should be mentioned that they obtained this less realistic conformation from the INDO calculation with fixing *all* the geometrical parameters to the "standard values", except for the rotational angles around the C_2–C_3 and C_3–C_4. On the other hand, as shown in Figure 4b, the experimental result was well reproduced with the reasonable trans–gauche form by the INDO MO calculation when the C_3–C_4 bond is lengthened by 0.01 nm.

The selective elongation of the C_3–C_4 bond derived in this work for the cation radicals of n-pentane, 3MP, and 3,3-DMP suggests that this bond is the most weakened one in these cations and will be broken preferentially in the degradation reaction. According to the product analysis on the radiolysis of alkanes in the liquid phase, ethane and propane (by almost equal amount) are the major products in the degradation of *n*-pentane,[18] while ethane and *n*-butane are produced mainly in the case of 3MP.[19] These products are expected when the elongated bond (C_3–C_4) is broken. The present result suggests a close correlation between the structure of cation radical and the mode of C–C bond scission in alkane radiolysis.

Role of the Substituents. For the asymmetrically distorted cations, exchange between the two equivalent structures (related with each other by mirror reflection) is expected.[5] In the case of *n*-pentane, the potential barrier for this dynamics must be very low, since only the averaged structure is observed at 77 K (though it is static at 4 K). On the contrary, the exchange between the two forms of 3,3-DMP cation was not observed up to 100 K. In the case of 3MP cation, the broadening of the spectrum observed at 77 K is interpreted as due to the slow exchange. These facts indicate that the barrier for the internal exchange becomes higher with the number of methyl groups substituted to the central carbon. Therefore, the location of the bond elongation and thus the localized spin on this bond is fixed more firmly with the increase of substituted methyl groups, and in the linear alkane only the averaged structure is observed.

It is noted that the efficiency of the spin concentration to the elongated bond, estimated from the hfc's as well as INDO calculation, is higher in the 3MP and 3,3-DMP cations than that in the *n*-pentane cation even if distortion by the same magnitude is assumed. These must be the role of substituents on the σ-delocalization in the cation radical of alkanes,[15] which has been shown in the explicit form for the first time.

Positive Hole Migration among the Solute Alkanes. The conversion from the TT form to the TG form was detected for 3MP cation and that from the TG form to the TT form in the case of 3,3-DMP and *n*-pentane cation radicals. These conversions in the conformation of cation radical can be interpreted as due to hole hopping between the solute alkanes with two conformations:

$$3\mathrm{MP(TT)}^+ + 3\mathrm{MP(TG)} \rightarrow 3\mathrm{MP(TT)} + 3\mathrm{MP(TG)}^+ \quad (1)$$

Accumulation of the TG form by thermal annealing at 77 K indicates that the 3MP cation with TG form ($3\mathrm{MP(TG)}^+$) is more stable than that of TT form ($3\mathrm{MP(TT)}^+$). In the frozen fluorocarbon matrix below 77 K, hole hopping may proceed by thermally activated tunneling, since the solute are dispersed in the rigid matrix whose ionization potential is much higher than that of the solute. The radical conversion of 3,3-DMP and *n*-pentane cation can be interpreted with the same mechanism, although in these cases, the TT conformers are more stable in fluoroalkane and F113 matrices.

One may consider that the conformational change of the cation radical through the internal rotation of the ethyl group is an alternative interpretation of the above phenomenon. However, this is less probable below 77 K because the barrier for the internal rotation of ethyl group is higher than 3–4 kcal/mol or more even in the gas phase.[20,14] In a rigid frozen matrix, the conformational change must be much more difficult because some matrix molecules should be translationally moved upon this process. On the other hand, hole migration among the alkane molecules has been reported even in the solid phase as low as 4 K.[21] In addition, we observed previously that benzene cation (Bz^+) formed in the frozen F113 matrix was converted into the dimer cation (Bz_2^+) upon raising the sample temperature from 77 to 100 K, and attributed it to hole transfer from the isolated benzene to the site where two benzene molecules are trapped closely to be easily converted to the dimer cation.[22]

Conclusion

The selective bond elongation which reduces the molecular symmetry of the cation radical was found for *n*-pentane, 3-methylpentane, and 3,3-dimethylpentane. In other words, the unpaired electron cannot be distributed evenly in the two equivalent inner C–C σ-bonds, so that the cation is distorted to lose the mirror symmetry of the mother molecule. The uneven bond elongation found previously in propane cation has been shown in the other alkane cations even if it is not Jahn–Teller active. The role of methyl substitution on the localization of the unpaired electron, which otherwise tends to spread overall the molecular frame, is shown in the simplest system, i.e., pentane. Positive hole hopping between the solute alkanes was suggested from the apparent conformational change of the cation radicals in the frozen matrices below 77 K.

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Registry No. Pentane, 109-66-0; 3-methylpentane, 96-14-0; 3,3-dimethylpentane, 562-49-2; pentane radical cation, 34479-74-8; 3-methylpentane radical cation, 79003-92-2; 3,3-dimethylpentane radical cation, 124846-40-8.

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