ESR, Structure and Reactions of Specifically Deuterated $C_6 - C_8$ n-alkane Cations in Halogenated Matrices

G. Dolivo

Institute of Physical Chemistry, Federal Institute of Technology, EPFL-Ecublens, CH-1015 Lausanne, Switzerland

A. Lund

The Studsvik Science Research Laboratory, Nyköping, Sweden

Dilute frozen solutions (1−2%) of specifically labelled n-hexane, n-heptane and n-octane in three halogenated matrices ($CFCl_3$, CF_3CCl_3 and $CF_2ClCFCl_2$) have been X-irradiated at 77 K in order to produce the molecular cations. ESR spectra were recorded to temperatures up to the glass transition or melting points of the matrices. Several conformers differing in the geometric structure were observed. The 120° gauche conformers of the n-alkane molecular ions are stabilized by end D-labelling. Revised assignments of their coupling constants were obtained. The extended geometry was predominant in $CFCl_3$ with one exception. INDO MO calculations show that tilting of the CH_3 group towards the $-CH_2-$ chain lowers the energy and gives better agreement with experimental values for the hyperfine coupling constants. CF_3CCl_3 seemed to induce the largest distortions in the geometry of the ions. The nature of a distorted conformer of hexane$^+$ in CF_3CCl_3 has been determined with the aid of observed couplings and INDO MO calculations.

Photobleaching causes disappearance of the cations in the $CFCl_3$ and $CF_2ClCFCl_2$ matrices and fragmentation to produce 2-butene cations in CF_3CCl_3. This product was not identified when labelled compounds were employed. The mechanism is discussed.

Introduction

Isolated molecular ions of n-alkanes can be generated and stabilized in various halogenated matrices [1−5]. As they are formed by charge transfer from the matrix cations, their internal energy is low and there are no fragmentation products present under such conditions. Their esr spectra are characterized by a triplet structure, attributed to the two in-plane H attached to the end C atoms in the extended chain configuration. Recently it was reported [3] that, under certain conditions, n-alkane molecular ions of pentane, hexane and octane have also the structure of a gauche conformer obtained by a 120° rotation around the C_2-C_3 bond. Use of specifically D-labelled compounds allows us to clarify the assignment of the hyperfine coupling constants in the gauche conformer. In the present study we have employed three different halogenated matrices, namely $CFCl_3$, CF_3CCl_3 and $CF_2ClCFCl_2$ to elucidate how the geometry of the ions is affected by the matrix.

In CF_3CCl_3 the hexane and heptane molecular ions undergo a photoinduced cleavage to yield 2-butene cations [5]. The use of specifically labelled compounds was an obvious way of gaining insight on the mechanism of this reaction, as it is widely and successfully employed in the gas phase to elucidate cracking patterns of ions by mass spectrometry [6].

INDO calculations give consistently too low values for the inplane H coupling constants for n-alkanes$^+$ in the extended configuration [2]. This could be a deficiency of the theoretical method, but it could also be due to a change of geometry upon ionization. It was thus decided to do calculations using a modified INDO program [7] to find out the reason of this discrepancy, as well as to check the assignment of hyperfine coupling constants made by Toriyama et al. [2].

I. Experimental

The following chemicals were used without further purification: C_6F_{14} (Fluka, purum), C_6H_{14} (Merck, p.a. 99%), C_7H_{16} (Kebo, puriss. > 99%), C_8H_{18}

(Fluka, puriss. p.a. > 99.5%). The specifically labelled n-alkanes were synthetized according to the following procedures. The hexane-1,6-d_6 was prepared by reaction between the Grignard of 1,4-dibromobutane and CD_3I, in presence of Li_2CuCl_4. The hexane-3,4-d_4 was obtained by the reaction of 3-hexyne in toluene solution with D_2 in presence of fresh tristriphenylphosphin rhodium chloride. The hexane-2,5-d_4 was synthetized in three steps, starting from the 2,5-hexanedione which was converted by $LiAlD_4$ into 2,5-hexanediol, deuterated in positions 2 and 5 and on the two hydroxyl groups. Then, by reaction with PBr_3, the 2,5-dibromohexane-2,5-d_2 was obtained which gave the hexane-2,5-d_4 by reduction by $LiD/LiAlD_4$.

The heptane-1,7-d_6 and the octane-1,8-d_6 were obtained by a reaction scheme identical to the one described for the hexane-1,6-d_6, starting from the 1,5-dibromopentane and from the 1,6-dibromohexane, respectively. The chemical purity of these substances was better than 99.95% and they contained the following isotopic impurities as determined by GC/MS: hexane-1,6-d_6 contained 3.3% d_5, hexane-2,5-d_4 6.3% of d_5 and 4.2% of d_3, and hexane-3,4-d_4 2.7% of d_5 and 7.6% of d_3. No analysis is available for heptane-1,7-d_6 and octane-1,8-d_6.

CF_3CCl_3 (Aldrich, 98%), $CF_2ClCFCl_2$ (Fluka > 99% or Merck > 99.7%) and $CFCl_3$ (Alfax) were degassed and then distilled to a reservoir attached to a vacuum line. The quantity used to make the samples was determined by allowing the solvent to expand to a known pressure in a calibrated volume. A measured volume of alkane was injected with a microsyringe through a septum directly into the evaporated esr quartz tube. The alkane condensed in the tip of the tube kept at 77 K. The concentration of the solute could thus be varied very easily and be adjusted with good reproducibility.

X-irradiations were made with an X-ray tube with a Au anode operated at 70 kV and 20 mA.

Esr spectra were recorded on a Varian E-9 spectrometer with 100 kHz field modulation, fitted with a double cavity and a temperature control device. The temperature was measured with a thermocouple.

First and second derivative spectra were recorded with modulation amplitudes of 2 G. The reported linewidths (lw) are the peak-peak widths of the first derivative lines.

Bleaching experiments were done at 77 K with the 150 W lamp of a slide projector fitted with Oriel glass coloured filters. INDO calculations were performed with a program due to Oloff [7].

ESR and bleaching results

A) Hexane-d_0

The esr spectra of hexane-$d_0^{+\cdot}$ were measured in the three halogenated matrices and perfect agreement was obtained with the published data [1−5]. In C_6F_{14}, the esr spectrum of $C_6H_{14}^+$ is a triplet with $a = 40$ G and a lw of 18 G. The yield was about one tenth of that in CF_3CCl_3.

In CF_3CCl_3, small bands were observed on each side of the main spectrum (Fig. 1a) at 77 K. They decrease by 50% at 107 K and disappeared completely at 137 K. When the sample was cooled back to 107 and 97 K, these bands reappeared with their original intensities.

In $CF_2ClCFCl_2$, the esr spectrum of $C_6H_{14}^{+\cdot}$ vanishes at about 102 K and is not restored when the temperaure is lowered to 77 K. The residual spectrum at 102 K is broad and of low intensity.

Bleaching experiments were made in $CFCl_3$ and in CF_3CCl_3. In $CFCl_3$ illumination for three minutes with red light ($\lambda > 630$ nm) is enough to bleach ca. 80% of the hexane$^+$: No new paramagnetic product is formed in contrast with the results obtained in CF_3CCl_3. In the latter case illumination for 10 min with red light ($\lambda > 630$ nm) affects only one of the center lines which is presumably due to the matrix. In CF_3CCl_3 quantitative ($\geqq 50\%$) conversion to 2-butene$^{+\cdot}$ (5) was observed with lights of various wavelengths < 630 nm.

B) Hexane-3,4-d_4 and -2,5-d_4

a) CF_3CCl_3

The 77 K first derivative esr spectra of these two internally labelled hexanes in CF_3CCl_3 are shown in Fig. 2a (2,5-d_4) and b (3,4-d_4). They consist of a triplet with $a = 41$ G and a lw of 12 G. A substructure with $a = 4$ G is more apparent for the 2,5-d_4 than for the 3,4-d_4. No weak side lines are appearing in the 2,5-d_4 spectrum, but such lines are indeed observed for the 3,4-d_4, at different field values than for hexane-d_0. When the temperature is raised the intensity of the esr spectrum decreases for both
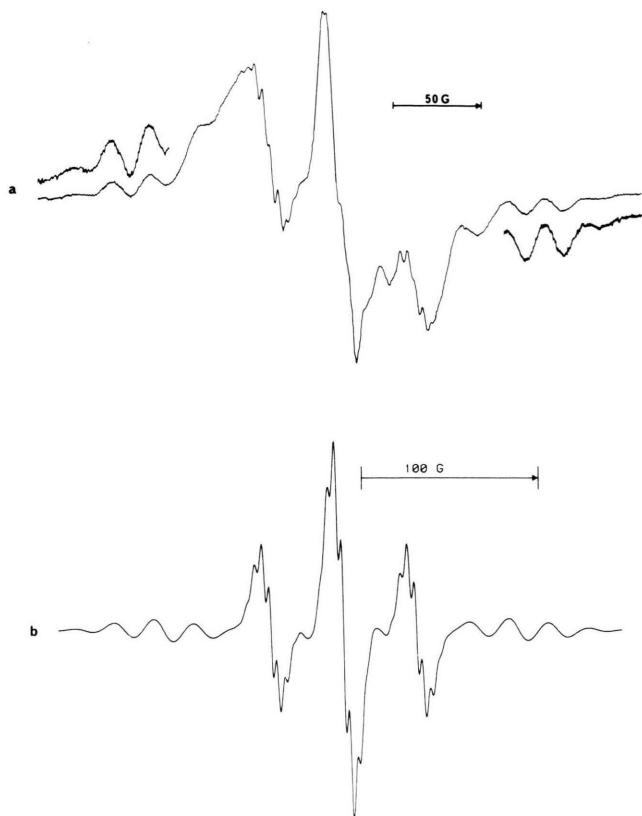
Fig. 1. a) First derivative esr spectrum of hexane$^{·+}$ in CF_3CCl_3 at 77 K. b) Simulation of 1a), taking 70% of extended form with $a_1 = 41$ G (2 H), $a_2 = 4$ G (8 H), $lw = 4$ G (peak-peak width of derivative line) and 30% of gauche conformer with $a'_1 = 100$ G (2 H), $a'_2 = 22$ G (4 H), $lw = 12$ G.
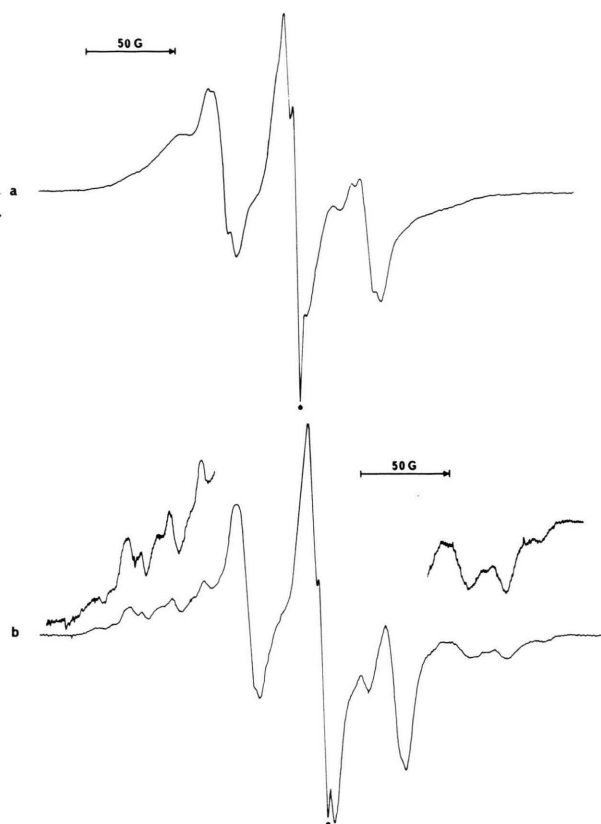
Fig. 2. First derivative esr spectrum of a) hexane-2,5-$d_4^{·+}$. b) hexane-3,4-$d_4^{·+}$ in CF_3CCl_3 at 77 K. ● shows a background signal.

compounds. Some lines due to hexane-d_4^+ ions are still present, more clearly for 2,5-d_4 as it gives better resolution (Figure 3a).

Bleaching experiments were done with white light or with various filters. In all cases the same weak second derivative spectrum was obtained (Fig. 3b), with an intensity of about 5% of the original hexane$^{+·}$ spectrum. Most of the lines of the residual spectrum were already present before bleaching and are attributed to the matrix. The final spectrum after bleaching was identical in all cases independent of the wavelength used. There is no evidence of the spectrum due to 2-butene cations found under the same experimental conditions with samples containing hexane-d_0.

b) $CF_2ClCFCl_2$

In this matrix the 77 K spectra of the hexane-2,5-d_4 (Fig. 4a) and 3,4-d_4 (Fig. 4b) molecular ions are different. The 2,5-d_4 spectrum consists only of a triplet. The 3,4-d_4 molecular ions has broad outer lines and the triplet lines are narrower.

c) $CFCl_3$ and C_6F_{14}

The spectra obtained with the $CFCl_3$ matrix are similar to those recorded in CF_3CCl_3 but with a far better resolution. They consist of a triplet of quintets ($a_1 = 41.5$ G, $a_2 = 4.5$ G). When the temperature is raised to 135 K, the intensity decreases by a factor 5. On cooling back to 77 K, neither the

intensity nor the good resolution are fully restored, but the original spectrum is clearly recognizable. Bleaching with light of $\lambda > 630$ nm for 3 min decreases the original 77 spectrum by more than 90% without giving rise to any new paramagnetic species. In C_6F_{14}, as for hexane-d_0, poor yields and bad resolution were observed in spectra consisting only of a triplet with $a = 40.5$ G ($lw = 18$ G). Bleaching with white light left a broad first derivative spectrum.

C) Hexane-1,6-d_6

a) In CF_3CCl_3

At 77 K (Fig. 5a) the spectrum of the hexane-1,6-d_6 ion consists of a well resolved multiplet ($a = 6.5$ G) and some weaker broad bands. The spectrum is unfortunately distorted by matrix lines and this problem is so bad in second derivative spectra that they are impossible to examine. When the temperature is raised to 110 K (Fig. 5b), the central multiplet is less resolved and its intensity decreases, whereas the broad side bands are still clearly present. Bleaching, either at 77 K or at 137 K, causes the spectrum to disappear without the appearance of any new spectrum.

b) In $CF_2ClCFCl_2$

At 77 K (Fig. 6a) there is a central part, with nine lines ($a = 6.5$ G) a broad doublet ($a = 78$ G, $lw = 19$ G) and a third component which gives the shoulders on each wing. In Fig. 6b is shown a second derivative spectrum of the central multiplet, showing more clearly its multiplicity. As for all other hexanes the spectrum of the molecular ion disappears irreversibly upon heating to 100 K, leaving the matrix spectrum growing.

c) In $CFCl_3$ and in C_6F_{14}

In $CFCl_3$ the spectrum of hexane-1,6-$d_6^{\cdot+}$ consists only of the well resolved multiplet already observed in $CF_2ClCFCl_2$, and CF_3CCl_3. There are no broad side lines of any kind in this matrix. On a second derivative spectrum taken at 77 K, 2 sets of lines ($lw = 2.5$ G, $a = 6.5$ G) appear quite clearly (Fig. 7a), the strongest set being composed of 9 lines. They are both centered at $g = 2.0030$. When a spectrum is taken with a microwave power of 10 mW, the minor component is slightly enhanced in comparison to

the other. After annealing to 135 K (Fig. 7b) one gets only a nine lines spectrum about half as intense, similar to the nine lines observed after X-irradiation, but with a larger line width of 5 G. When the temperature is raised above 100 K, the spectrum narrows progressively and at 135 K, it consists of one broad line ($lw = 22$ G) with some substructure visible. There is no large decrease in the intensity upon heating to 135 K. In C_6F_{14} the spectrum at 77 K is like the one detected in $CFCl_3$ after anneal-
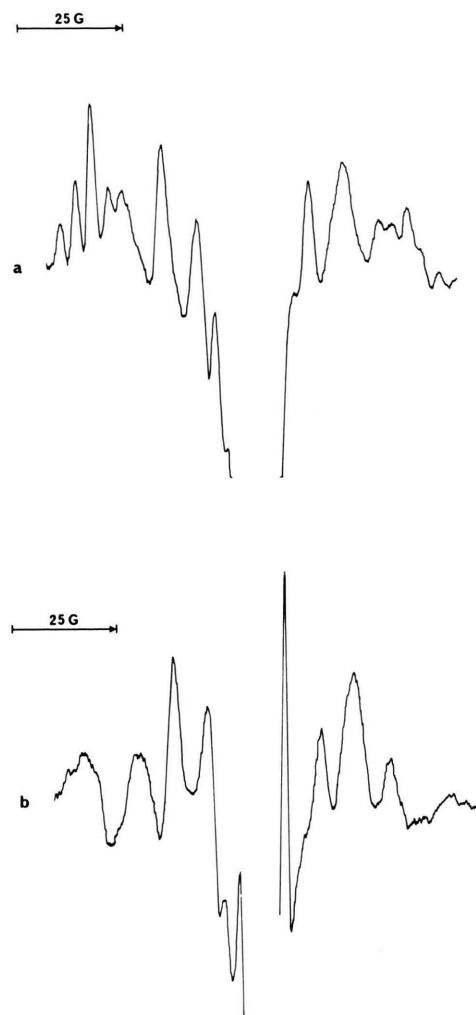

Fig. 3. a) Second derivative esr spectrum of hexane-2,5-$d_4^{\cdot+}$ in CF_3CCl_3 at 139 K, taken with a high gain. b) Second derivative esr spectrum of the same sample after 75 s of bleaching with white light.
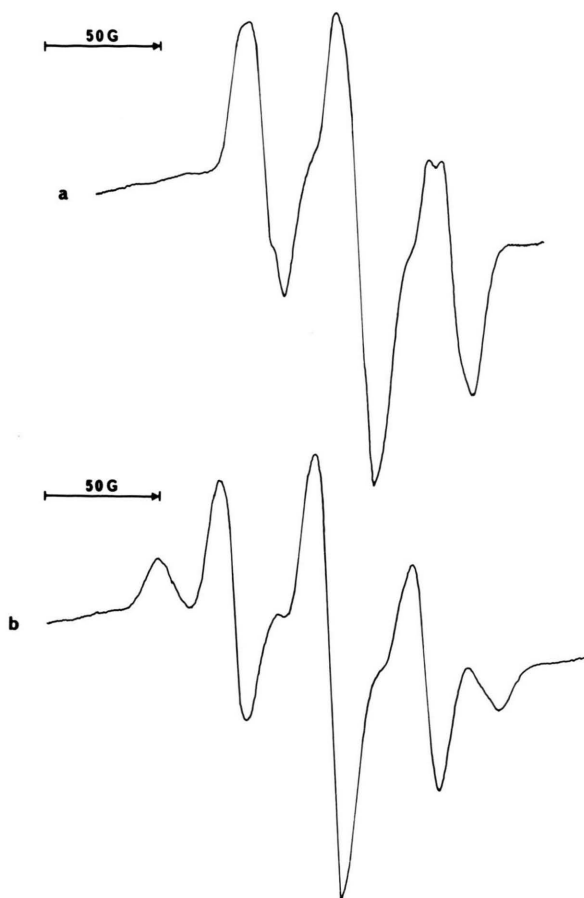
Fig. 4. a) First derivative spectrum of a) hexane-2,5-$d_4^{+\cdot}$, b) hexane-3,4-d_4^+ in $CF_2ClCFCl_2$ at 77 K.

Fig. 6. esr spectra of hexane-1,6-$d_6^{\cdot+}$ in $CF_2ClCFCl_2$ at 77 K: a) first derivative, b) second derivative of central part, c) simulation of a) with 17% of extended form with $a_1 = 6.5$ G (2 D, 4 H), $lw = 5$ G; 63% of conformer with $a_1' = 78$ G (1 H), $lw = 15$ G and 20% of conformer with $a_1'' = 85$ G (2 H), $lw = 25$ G.

Fig. 5. First derivative esr spectra of hexane-1,6-$d_6^{\cdot+}$ in CF_3CCl_3 taken a) at 77 K, b) at 110 K. ● shows a background signal.

ing, i.e. a strong multiplet (9 lines, $a = 6.5$ G) somewhat less resolved and with no broad side bands at all.

D) Heptane-d_0 and 1,7-d_6

a) Heptane-d_0

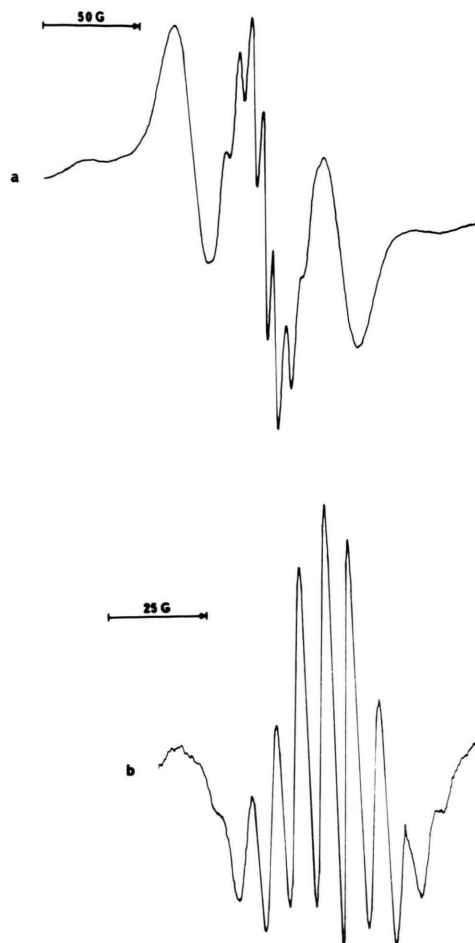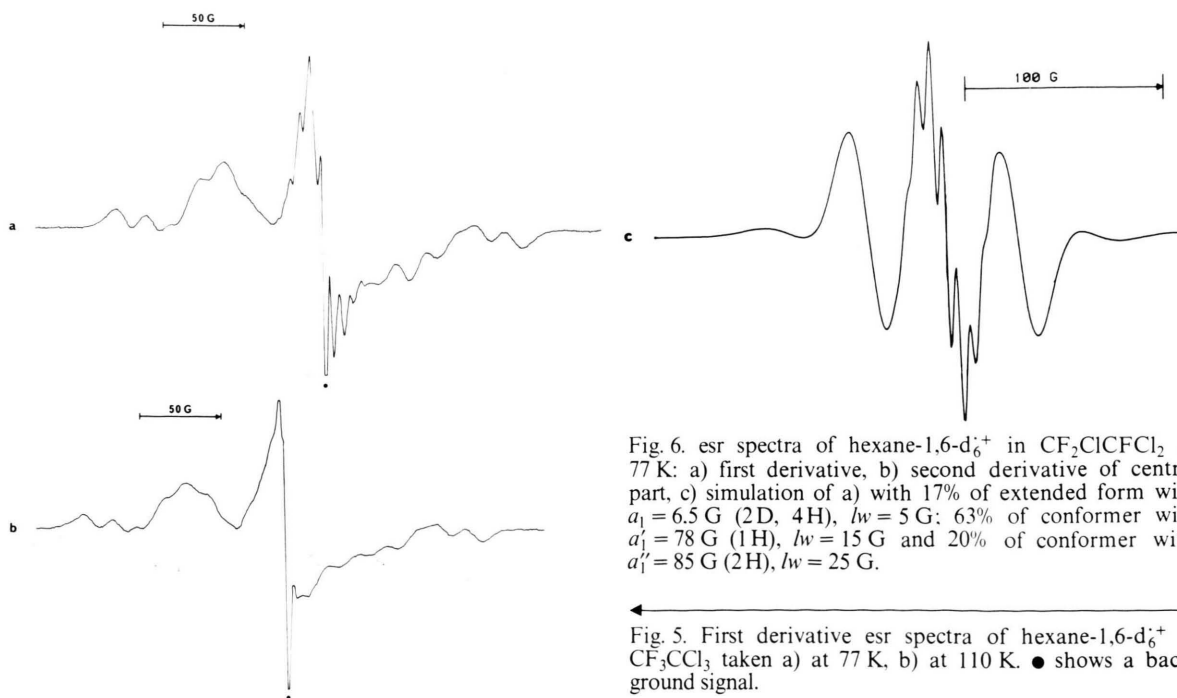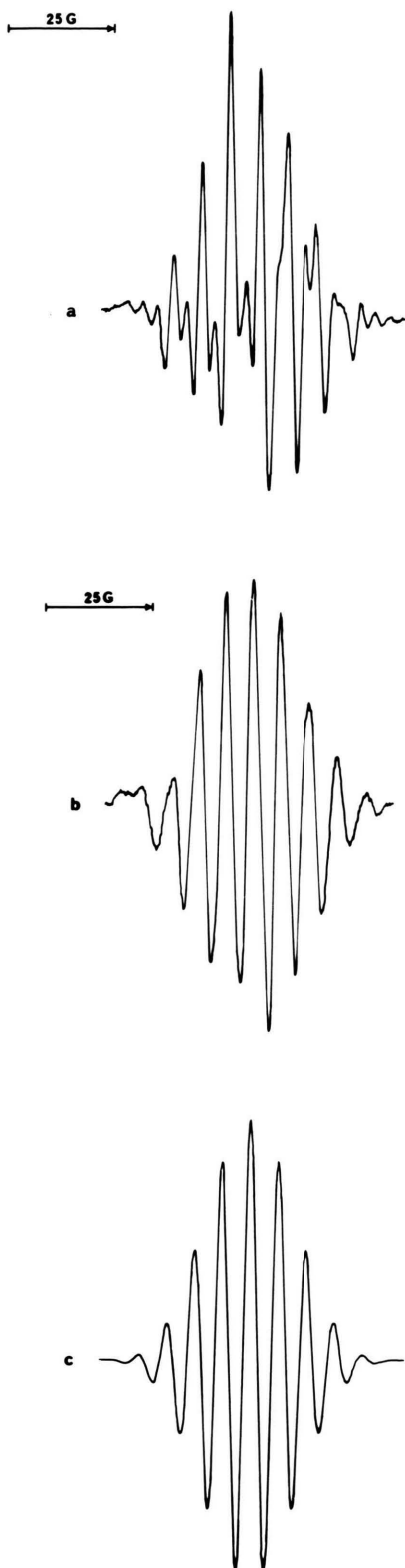The spectrum of heptane-$d_0^{\dot{+}}$ in CF_3CCl_3 was remeasured and found as reported in [5]: a triplet with $a_1 = 29.5$ G, $lw = 18$ G and some substructure with $a_2 = 4$ G appearing in a second derivative spectrum. Upon heating the triplet disappears reversibly. Bleaching for 10 min with yellow light ($\lambda > 540$ nm) was enough to obtain the spectrum of the 2-butene ion. In $CF_2ClCFCl_2$ the 77 K spectrum was found again as reported in the literature [2], a triplet with $a = 29$ G and $lw = 12$ G. When heated to 105 K a broad ($lw = 13$ G) and weak sextet begins to appear with $a = 22-23$ G. Its intensity is about one tenth of the intensity of the spectrum of the heptane molecular ion. The spectrum disappears at ~ 113 K.

In both $CFCl_3$ and C_6F_{14}, only a triplet was observed with $a = 30$ G. The yield in C_6F_{14} was low.

b) Heptane-1,7-d_6

In CF_3CCl_3 a broad single band was observed at 77 K, with a lw of 18 G and some substructure (13 lines) with $a = 4$ G was clearly seen on a second derivative spectrum. This spectrum was, as for the hexane-1,6-$d_6^{\dot{+}}$, severely disturbed by the matrix lines. Upon heating to 137 K, the spectrum narrows to a lw of 13 G and the substructure disappears. Its intensity is unaffected.

Upon bleaching with yellow light ($\lambda > 475$ nm) a weak spectrum (about 10% of the original intensity) is obtained (Figure 8). Red light ($\lambda > 630$ nm) was less efficient but seemed to give the same spectrum as yellow light. When compared to the spectra obtained after bleaching of specifically labelled hexanes (Fig. 3 b) it is clear that several more lines are present. They are bleached away by light of shorter wavelength ($\lambda < 475$ nm). They could not be more clearly resolved when the microwave power was changed (50 μW – 40 mW).

Fig. 7. Second derivative esr spectrum of hexane-1,6-d_6^+ in $CFCl_3$ at 77 K: a) immediately after x-irradiation, b) after annealing at 135 K, c) simulation of b) using $a = 6.4$ G (2 D, 4 H), $lw = 4$ G.
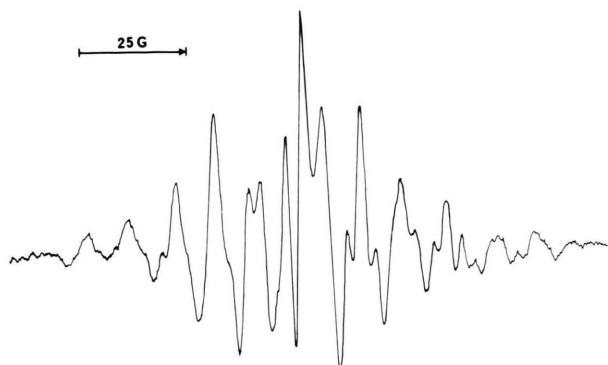
Fig. 8. Second derivative esr spectrum of a solution of heptane-1,7-d_6^+ in CF_3CCl_3, at 134 K after 10 min of bleaching with $\lambda > 475$ nm.
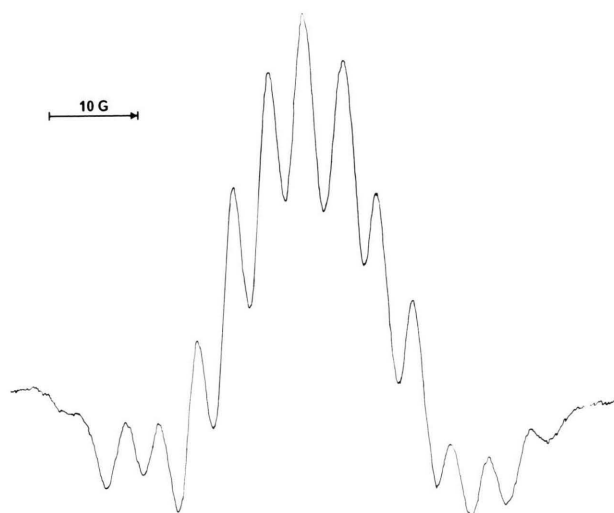

Fig. 9. Second derivative esr spectrum of heptane-1,7-d_6^+ in $CF_2ClCFCl_2$, recorded at 77 K.

In $CF_2ClCFCl_2$ a single broad line ($lw = 21$ G) with a substructure is observed at 77 K. A second derivative spectrum shown in Fig. 9 is composed of $13 - 15$ lines with $a = 4.2$ G. When the sample is heated to 102 K, the signal disappears irreversibly.

In $CFCl_3$ the first derivative spectrum of heptane-1,7-d_6^+ is the same as in $CF_2ClCFCl_2$, with a lw of 20 G and a substructure with $a = 4$ G. When heated, the spectrum does not disappear as for the hexanes, but changes progressively to a single line without any substructure at 135 K. At 155 K the spectrum was still quite intense. In C_6F_{14} a weak single broad line ($lw = 24$ G) was measured.

E) Octane-d_0 and $-1,8$-d_6

a) Octane-d_0

At 77 K in CF_3CCl_3 a triplet with $a = 24$ G and $lw = 14$ G was observed. No side bands were detected. At 136 K, the triplet disappears, leaving a spectrum looking much like the one of the pure matrix. Illumination for 5 min with yellow light ($\lambda > 540$ nm) left the normal residual spectrum observed for the labelled hexanes (Figure 3 b).

At 77 K in $CF_2ClCFCl_2$ the results were the same as in CF_3CCl_3, though there was nearly no interference from matrix lines. At 102 K the spectrum becomes irreversibly weak and broad.

In $CFCl_3$ at 77 K the spectrum is clearly different from the ones reported in the two other matrices (Fig. 10 a): a broad doublet with $a = 65$ G and $lw = 25$ G. There seems to be some contributions in the central part from the extended form of octane, but even after bleaching with red light, there were still some spurious lines complicating the interpretation. When the sample is heated above 100 K, the intensity of the spectrum decreases, but is restored when the sample is cooled back to 77 K. At 158 K the spectrum due to octane$^+$ was barely detectable among matrix lines. It should be mentioned that illumination for 5 min with red light ($\lambda > 630$ nm) does not bleach the octane$^+$, in sharp contrast with hexane$^+$.

b) Octane-1,8-d_6

In CF_3CCl_3 the 77 K spectrum is a single line of $lw = 12$ G, on which is superposed a sharp background signal. On each side of this single line lies a weaker, broad line. Some substructure ($a = 3.5$ G) of the central line is detectable in a second derivative spectrum but the presence of an intense spurious line prevents a determination of the multiplicity. Upon heating to 136 K, a substructure is appearing ($a = 10$ G), both in the broad side lines and in the central component of the 77 K spectrum. The spectrum is about half as intense as at 77 K and, is similar to the weak residual spectrum obtained after bleaching of most specifically labelled *n*-alkanes. Bleaching with yellow light ($\lambda > 540$ nm) did not affect this spectrum. The original spectrum is restored by cooling back to 77 K. In $CF_2ClCFCl_2$ there is only a broad line with a lw of 20 G at 77 K. No detailed substructure is apparent. At 105 K the observed spectrum is weak and broad.
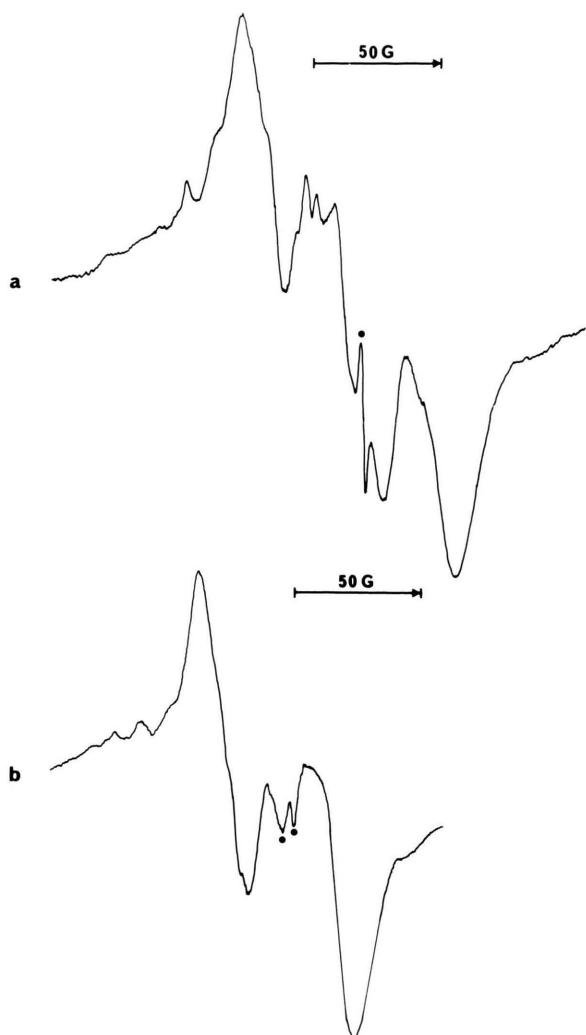
a

b

Fig. 10. First derivative spectra at 77 K of a) octane$^{\cdot+}$ in CFCl$_3$, b) octane-1,8-d$_6^{\cdot+}$ in CFCl$_3$. ● indicates spurious lines.

In CFCl$_3$ (Fig. 10 b) at 77 K there is only a doublet with $a = 45$ G and a lw of 20 G. No change occurred when the sample was heated to 135 K, and some octane-d$_6^{\cdot+}$ was still clearly detectable among the matrix lines at 156 K.

III. Interpretation of ESR Results

All interpretations were made after having made computer simulations of the esr spectra reported in Section II. The data were summarized in Table 1. Details are given below.

A) Hexane-d$_0$

The only new result reported here and which needs to be interpreted is the identity of the conformer giving the side bands in CF$_3$CCl$_3$ at $T < 110$ K. The 77 K spectrum of Fig. 1 a could be fitted (Fig. 1 b) by taking in account two conformers, the extended conformer with $a_1 = 41$ G (2 H), $a_2 = 4$ G (8 H) and a conformer having $a_1 = 100$ G (2 H), $a_2 = 22$ G (4 H). The intensity ratio is about 2 : 1. On the basis of INDO calculations, we attribute the latter structure to one of the two following conformers obtained by two 120° rotations around C_2-C_3 and C_4-C_5, A) both clockwise (Fig. 11) and B) one clockwise and the other counterclockwise.

The total energy of these conformers is quite high: -51.5582 (A) and -51.5586 a. u. (B) compared to -51.5826 a. u. for the extended conformer. The coupling constants from the INDO calculations are given in Table 2. These conformers have the structure of extended n-butane with one equatorial H on each end C atom being substituted by a
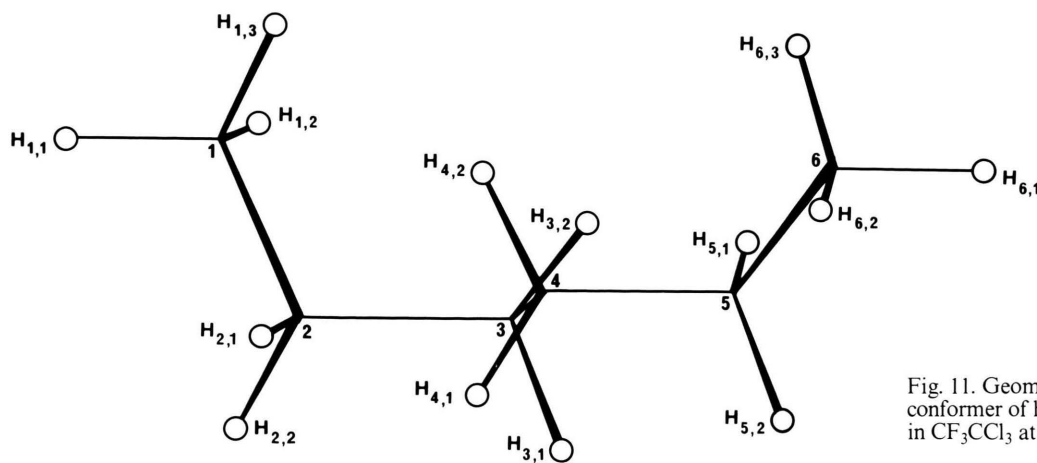

Fig. 11. Geometry of the gauche conformer of hexane$^{\cdot+}$ in CF$_3$CCl$_3$ at 77 K.

Table 1. Hyperfine couplings and relative abundance of isotopic labelled conformer ions in CF_3CCl_3, $CF_2ClCFCl_2$ and $CFCl_3$ matrices after x-irradiation at 77 K. The last column gives the coupling, and within parenthesis the number and the position (C-atom) of the H or D atoms.

Molecule		CF_3CCl_3	
	%	conformer	hfs (G)
hexane	70	extended	41 (2 H: 1, 6)
			4 (8 H: 2−5)
	30	120° C_2−C_3	100 (2 H: 2, 5)
		120° C_4−C_5	22 (4 H: 1, 6)
hexane-3,4-d_4	70−80	extended	41 (2 H: 1, 6)
			3 (4 H: 2, 5)
	20−30	not determined	−
hexane-2,5-d_4	80	extended	41 (2 H: 1, 6)
			4 (4 H: 3, 4)
hexane-1,6-d_6	40	extended	6.5 (2 H: 1, 6)
			6.5 (4 H: 2−5)
	60	two conformers	see text
heptane	100	extended	30 (2 H: 1, 7)
			4 (multiplet: 2−6)
heptane-1,7-d_6	100	extended	4 (2 D: 1, 7)
			4 (10 H: 2−6)
octane	100	extended	24 (2 H: 1, 8)
octane-1,8-d_6	70	extended	unresolved
	30	120° C_2−C_3	41 (1 H: 2)
		$CF_2ClCFCl_2$	
hexane	70	extended	41 (2 H: 1, 6)
			4 (8 H: 2−5)
	30	120° C_2−C_3	74 (1 H: 2)
			53 (1 H: 6)
hexane-3,4-d_4	80	extended	41 (2 H: 1, 6)
	20	120° C_2−C_3	74 (1 H: 2)
			53 (1 H: 6)
hexane-2,5-d_4	80	extended	41 (2 H: 1, 6)
	20	120° C_2−C_3	53 (1 H: 2)
hexane-1,6-d_6	20	extended	6.5 (2 D: 1, 6)
			6.5 (4 H: 2−5)
	80	120° C_2−C_3	78 G (1 H: 2)
heptane	100	extended	29 (2 H: 1, 7)
heptane-1,7-d_6	100	extended	4.6 (2 D: 1, 7)
			4 (10 H: 2−6)
octane	100	extended	24 (2 H: 1, 8)
octane-1,8-d_6	100	extended	unresolved
		$CFCl_3$	
hexane	100	extended	44 (2 H: 1, 6)
			4 (8 H: 2−5)
hexane-3,4-d_4	100	extended	41 (2 H: 1, 6)
			4 (4 H: 2, 5)
hexane-2,5-d_4	80	extended	41 (2 H: 1, 6)
			4 (4 H: 3, 4)
hexane-1,6-d_6	100	extended ·	6.5 (2 D: 1, 6)
			6.5 (4 H: 2−5)

Table 1. (continued)

Molecule		$CFCl_3$	
	%	conformer	hfs (G)
heptane	100	extended	30 (2 H: 1, 7)
heptane-1,7-d_6	100	extended	4 (2 D: 1, 7)
			4 (multiplet: 2−6)
octane	20	extended	22 (2 H: 1, 8)
	80	120° C_2−C_3	41 (1 H: 2)
			22 (1 H: 8)
octane-1,8-d_6	≦ 10	extended	unresolved
	≧ 90	120° C_2−C_3	41 (1 H: 2)

Table 2. Coupling constants given by INDO calculations for hexane cation conformers obtained by 120° rotations around C_2−C_3 and C_4−C_5 bonds of extended geometry A) both clockwise (see Fig. 11), B) One clockwise the other anticlockwise. One half of the number of couplings are given, the remaining are obtained by symmetry.

	Conformer A coupling (G)		Conformer B coupling (G)	
	open	closed	open	closed
$H_{1,1}$	13.7	16.7	14.0	18.2
$H_{1,2}$	8.2	10.2	11.3	13.9
$H_{1,3}$	−0.5	−0.2	−0.4	−0.4
$H_{2,1}$	80.7	65.3	76.7	61.0
$H_{2,2}$	−2.5	−1.4	−0.5	0.9
$H_{3,1}$	−3.2	0.9	−4.6	−1.4
$H_{3,2}$	4.9	6.8	−4.0	−0.8

CH_3; for A one CH_3 points upwards and the other downwards, for B both are pointing to the same side of the plane formed by the butane skeleton. The axial hydrogens $H_{2,1}$ and $H_{5,1}$ give rise to large splittings as in the case of the n-butane cation. The SOMO (singly occupied molecular orbital) in fact resembles the $7\,a_g$ orbital of the butane molecule (C_{2h} symmetry). The remaining four hydrogens with a resolved hyperfine structure are located on the CH_3 groups.

B) Hexane-2,5-d_4 and 3,4-d_4

The hexane-2,5-d_4 and the hexane-3,4-d_4 ions are clearly present mainly as their extended conformer at 77 K in all three matrices. The structure of the outer components of the triplet, seen in $CFCl_3$ and CF_3CCl_3 (Fig. 2a), is attributed to couplings to the 4 equatorial H atoms left by the specific D-labelling.

The weak side lines detected in the esr spectrum of the hexane-3,4-d_4 ion at 77 K in the CF_3CCl_3 matrix could not be fitted conclusively by either the parameters used for the d_0 gauche conformer or by including two conformers with slightly different coupling constants. In any case this or these conformers do not account for more than 20−30% of the molecular ions and it is reasonable to assume that they are not too different from the conformers of hexane-d_0.

In $CF_2ClCFCl_2$, the same situation is encountered: the two hexane-d_4 molecular ions (2, 5) and (3, 4) are mainly present as their extended conformer. A gauche conformer is clearly present in the spectrum of the hexane-3,4-d_4 ion. It accounts for the two outmost lines in Fig. 5b and about 30% of the yield of molecular ions.

The outmost lines can be nicely fitted with the couplings $a_1 = 74$ G, $a_2 = 53$ G obtained by Toriyama et al. [2] using unlabelled hexane. Their assignment of the spectrum as due to a gauche conformer obtained by a 120° rotation around the C_2-C_3 bond of the extended geometry is supported by our data. According to the interpretation the splittings are due to in plane hydrogens attached to the folding position C_2, and to C_6. Since a doublet splitting of $a_1 = 78$ G is observed in the gauche conformer of the hexane-1,6-d_6 ion (see below) we assign this coupling to an H on C_2 and $a_2 = 53$ G to an H on C_6.

According to this interpretation a gauche conformer of the 2,5-d_4 molecular ion would be a doublet with $a = 53$ G, with some structure due to a D on C_2 with $a_D = 74/6.5 = 11$ G. This spectrum could very well be hidden under the spectrum of the extended conformer in Figure 4a.

C) Hexane-1,6-d_6

In all the matrices studied, included C_6F_{14}, the central part of the spectrum is assigned to the extended form of the molecular ion. In every case it can be fitted very well by a simulation using 2 D and 4 H atoms with a unique coupling constant of 6.5 G (Figure 7c). We have tried to fit this nine-line spectrum with 8 H and the fit is clearly not as good. As there are only 4 H giving a resolvable substructure, the extended form is probably somewhat distorted, since both the experimental results in $CFCl_3$ [1, 2] and the INDO calculations give 8 H with resolvable couplings in the extended conformer of the unlabelled n-hexane cation. Extensive INDO calculations were made to find out the identity of this "extended" conformer. Two structures were found to fit these parameters.

a) A structure obtained by a 45° rotation around the bond C_3-C_4. In this structure there are 4 H atoms with a calculated hyperfine coupling constant of 3.2 G and four others with $a \leq 0.8$ G. It was found that tilting of both methyl groups towards the neighbouring methylene group (see Sect. IV) by more than 6° results in more than four resolvable coupling constants.

b) A structure obtained by two rotations of 30° around bonds C_2-C_3 and C_4-C_5, one being clockwise and the other counterclockwise (see Fig. 11 for help in understanding). It gave four couplings of 4−5 G each, the other couplings being smaller than 3 G when no tilting of methyl groups was admitted and smaller than 1 G as soon as tilting of 6°−12° was admitted.

Besides this "extended" form the hexane-1,6-d_6 cation can also take other configurations. In $CF_2ClCFCl_2$ only 20% of the hexane-d_6^+ are present as "extended", the other 80% being a species having a doublet with $a = 78$ G (Fig. 6c), and which corresponds to the 120° conformer described by Toriyama et al. [3]. The coupling is due to the in plane hydrogen attached to the folding position C_2 of the carbon chain. The SOMO is qualitatively similar to the $7b_1$ orbital of the pentane molecule with C_{2v} symmetry [3]. The hyperfine coupling $a_D = 53/6.5 = 8$ G due to the D atom at C_2 is unresolved.

In CF_3CCl_3 a quite different conformer is present accounting for 50−60% of the spectrum (Figure 5a). It can be fitted by having the following sets of coupling constants; $a_1 = 85$ G (2 H), $a_2 = 55$ G (1 H), $a_3 = 18$ G (1 H) for a single species or $a_1 = 110$ G (2 H), $a_2 = 18$ G (1 H) and $a_1' = 60$ G (2 H), $a_2' = 18$ G (1 H) for two species.

On the basis of the INDO calculations, we have no structure corresponding to the first set of coupling constants. As for the second set, a_1 and eventually a_2 could be accomodated by a conformer similar to the one described (Fig. 11) for the hexane-d_0^+, and a_1' and eventually a_2' can be explained by the conformer obtained by two rotations of 90° (either both clockwise or one clockwise, the

other counterclockwise) around bonds C_2-C_3 and C_4-C_5. This conformer is similar to the high temperature form of some pentane molecular ions [8]. In the case of hexane, the interpretation is tentative, however.

D) Heptane-d_0 and 1,7-d_6

In all the matrices at 77 K the molecular ions of both the heptane-d_0 and 1,7-d_6 have only the extended form. The spectrum of the heptane-d_6 ion in $CF_2ClCFCl_2$ (Fig. 9) can be fitted very well by having 2 D with $a_1 = 4.6$ G and 10 H with $a = 4$ G. The 77 K spectra in both $CFCl_3$ and CF_3CCl_3 are perturbed by spurious lines, but are clearly to be assigned to the same structure.

When the temperature is raised above 100 K, heptane-d_0 and d_6 cations survive up to 158 K. In CF_3CCl_3 the spectrum of the heptane-d_6 ion is not affected up to 137 K, but the spectrum of the heptane-d_0 ion is broadened.

In $CF_2ClCFCl_2$ the spectrum obtained for heptane-d_0 after warming to $100-105$ K is tentatively assigned to the 2-heptyl radical, by comparison with the results obtained for pentane in the same matrix [8].

E) Octane-d_0- and octane-1,8-d_6

In CF_3CCl_3 and $CF_2ClCFCl_2$ the octane-d_0 molecular ion is present only in its extended form. The major component of the 77 K spectrum of octane-d_0 ion in $CFCl_3$ (Fig. 10 a) is assigned to the gauche conformer with couplings of $a_1 = 41$ G (1 H), $a_2 = 22$ G (1 H) as identified by Toriyama et al. [3]. The assignment is supported by comparison with the spectrum of the octane-1,8-d_6 ion (Fig. 10 b) which contains a doublet with $a_1 = 41$ G. On the basis of our INDO calculations and our results for hexane (see above) the coupling can be assigned to the in plane hydrogen atom attached to C_2 at the folding position of the carbon chain. We estimate that 80% of the octane-d_0 and more than 90% of the octane-1,8-d_6 ions are in this configuration in the $CFCl_3$ matrix. This species is present also in the CF_3CCl_3 matrix. There, the high temperature spectrum is assigned mainly to the matrix meaning that the spectrum of octane$^+$ is severely broadened.

IV. INDO Calculations

We have used the INDO program developed by Oloff [7] to find out the structure of the conformers of the hexane cations described in Section III. This program has an option based on a restricted Hartree-Fock formalism (referred to as closed option in Table 1 and below) as well as the original unrestricted version (referred to as open option). We have made calculations for geometries obtained by a rotation around C_2-C_3, a rotation around C_3-C_4, two rotations around C_2-C_3 and C_3-C_4 (for the case where both are clockwise and for the case when one is clockwise and the other counterclockwise), and two rotations around C_2-C_3 and C_4-C_5 (also for the two cases just mentioned above), using the closed and the open versions of the program. They gave the same ground states and similar values for the coupling constants with the exception of very twisted configurations. We found
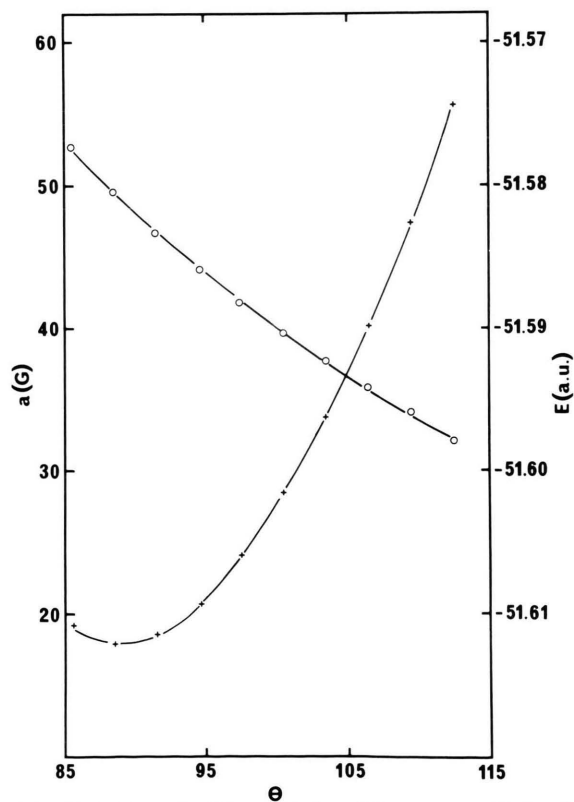

Fig. 12. Effect of tilting of the CH_3 groups (θ is the $CH_2-CH_2-CH_3$ bond angle) on the energy (+) and coupling constant (○) in the extended form of the *n*-hexane cation.

that the open option gives equatorial H coupling constants in better agreement with the experiment than the closed one (3.5–5 G vs 1.5–2 G).

We will only report here the results obtained by in plane tilting of both methyl groups towards the neighbouring $-CH_2$-group. From Fig. 12 it is seen that for the extended geometry the total energy is significantly lowered when the angle $C_1-C_2-C_3$ is decreased. There is a minimum for an angle of ca. 90°, as in pentane^{+} [8]. Simultaneously the calculated coupling constant increases. The best agreement with the experimental value of 41 G is obtained when the angle $C_1-C_2-C_3$ is about 98°.

We have checked that these two phenomena – lowering of total energy and increase of the coupling constants of the in-plane hydrogens – also occur for the conformers obtained by rotations of 30° around C_2-C_3 and C_4-C_5 (either two clockwise rotations or one clockwise the other counter clockwise), or by a rotation of 30°–45° around C_3-C_4.

V. Discussion

A) Structural aspects

The ESR data show that the identity and the relative importance of the conformers are affected by the D labelling as well as by the nature of the matrix. Thus, the end labelling by D increases considerably the proportion of the gauche conformers of hexane and octane molecular ions in all the freon matrices. Furthermore, the identities of the gauche conformer of hexane^{+} in CF_3CCl_3 is altered by this substitution. Thus, in CF_3CCl_3, 30% of hexane-d_0^{+} exists as gauche conformer, compared to 50% for hexane-d_6^{+}. The same situation is encountered in $CF_2ClCFCl_2$ where the change in the gauche conformer proportion is even greater: 30% for d_0 versus 80% for hexane-d_6. In $CFCl_3$ there is only the extended conformer. For octane^{+} this phenomenon of increase in conformer proportion is seen in CF_3CCl_3: no gauche conformer for -d_0 versus 30% for -d_6, and in $CFCl_3$, 80% for -d_0 and more than 90% for -d_6. We can only conjecture that this increased stability of the gauche conformers is related to the smaller amplitudes of the $C-CD_3$ bending and stretching motions because of the $-.CD_3$ substitution. It should be mentioned that these conformers do not lie in a minimum of energy: the molecular ion is thus "forced" by the matrix to take this configuration.

As has already been remarked the internal labelling of n-hexane at positions 3, 4 and 2, 5 allows us to confirm the identity of the gauche conformer of the cation proposed by Toriyama et al. [3] and to refine the assignment of coupling constants. The line broadening caused by unresolved hyperfine structure at positions 3, 4 and 2, 5 is decreased as the couplings are decreased by the factor 0.15 in comparison with the unlabelled ion. The fact that the 2,5-d_4 cation gives a better resolution than the 3,4-d_4 ion for the outer components of the triplet indicates that the spin density is slightly smaller on H_2, H_5 than in H_3, H_4, in good agreement with INDO calculations of [2]. There appears to be a misleading labeling of the published coupling constants (see Table III of [3]). Our assignment of the hydrogen atoms responsible for the splittings are well supported by the effect of D-labelling obtained here.

It seems that there are three different conformers of hexane^{+}-1,6-d_6 in CF_3CCl_3 as could also be the case for pentane-1,5-d_6^{+} in the same matrix [8]. The alternative mentioned in Sect. III (with only 2 conformers) is to be discarded, as we cannot find a structure for one of them. One is the extended form, the two others are very distorted and energetic conformers. The fact that they cannot be converted, even at high temperature (Fig. 6) to a structure of lower energy, suggests that the conformer geometry is imposed by the matrix.

The extended form of hexane-1,6-d_6^{+} in all the matrices is also distorted. As this conformer does not lie either in a minimum of energy, it is also "imposed" by the matrix.

Matrix effects seem to affect the value of the coupling constants of the extended conformer. Thus, in $CFCl_3$ the experimental value is 44 G for the two in plane hydrogens, compared to 41 G in CF_3CCl_3. According to the INDO results a tilting of the CH_3 groups towards the $-CH_2$-chain increases the hyperfine coupling constant and lowers the energy (Figure 12). In $CFCl_3$ the experimental and theoretical couplings agree at an angle of 95°. This is closer to the angle 90° obtained for the minimum in energy than in the CF_3CCl_3 matrix (97°). It seems that the extended ion is more distorted from the equilibrium geometry in the CF_3CCl_3 than in the $CFCl_3$ matrix. With a shorter alkane chain like n-pentane cation in $CFCl_3$ the experimental and theoretical couplings agree at the equilibrium angle,

possibly because a smaller molecule is less easily distorted by the matrix than a longer more flexible chain [8].

Matrix effects are also responsible for the appearance of the two cation species which are visible in the spectrum of hexane-1,-6-d_6 ions in $CFCl_3$ and the irreversible disappearance of one of the species after annealing at 135 K (Figure 7). The matrix probably undergoes a phase transition at about 140 K [4] allowing reorganization of the matrix molecules around the solute cation. This phenomenon, resulting in an increased line width, is general for all hexanes.

In a previous study of unlabelled hexane in CF_3CCl_3 it was found that the spectrum of the extended ion changed reversibly from a broad triplet at 77 K (Fig. 1) to a 9 line spectrum with $a = 6.7$ G at 141 K [5]. This change was attributed to the onset of free rotation of the methyl groups about the $C_1 - C_2$ and $C_5 - C_6$ bonds. None of the specifically labelled hexanes gave a high temperature spectrum consistent with this interpretation, however. In both internally labelled hexanes we could in fact detect weak outer lines of the triplet due to the extended form of the ion even at 135 K indicating that the methyl groups are not freely rotating. Therefore the high temperature spectrum of the unlabelled hexane cation in CF_3CCl_3 is not yet understood.

B) Deprotonation in $CF_2ClCFCl_2$

In line with results obtained for propane [3], butane [1, 2] and pentane [8] molecular ions, the yield of deprotonation at $(100 - 105)$ K decreases markedly for hexane, heptane and octane molecular ions. It was even difficult to decide whether or not there are some octyl radicals present. There is definitely an isotope effect for heptane-d_6, which gives practically no heptyl radicals. This is in agreement with published data on D-labelled propane [3]. This lower yield of deprotonation is preferentially occurring for the hydrogen atom with the higher spin density.

C) Photoinduced fragmentation of molecular ions

In agreement with some gas phase measurements [9, 10], there is a threshold for the photoinduced fragmentation of hexane-d_0^+ in CF_3CCl_3 at 630 nm.

But unlike the results reported in [9], there is no wavelength dependence of the identity of the product, and the product is clearly not the same, $C_6H_{14}^+$ in gas phase giving $C_3H_7^+$ and $C_4H_9^+$. Photofragmentation of $C_6H_{14}^+$ in CF_3CCl_3 gives the 2-butene cations. We have confirmed that this photoinduced fragmentation does not occur in $CF_2ClCFCl_2$ and in $CFCl_3$. In this latter matrix red light has enough energy to bleach away the molecular ion of hexane, without giving a paramagnetic species. It appears that this photoinduced fragmentation is uniquely possible in CF_3CCl_3 and mainly for protiated $C_4 - C_7$ molecular ions. It does not seem that this reaction is due to a specific conformer, as heptane does exist only under its extended form and yet undergoes cleavage in CF_3CCl_3 [5]. Possibly, the original product of the cleavage is 1-butene$^+$; which subsequently photoisomerizes to 2-butene$^+$ as this was proved possible in [11].

There seem to be at least two different mechanisms for the elimination of the trapped alcane radical cations by illumination. In the first case, which occurs in $CFCl_3$ and $CFCl_2CF_2Cl$ matrices it is assumed that the optically excited cation $(A^+)^*$ can extract an electron from a matrix molecule (M):

$$A^+ \xrightarrow{h\nu} (A^+)^* \rightarrow A + M^+.$$
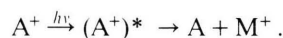
The radical cation disappears without giving rise to a secondary product. The matrix ion might be mobile and eventually recombine with the negatively charged ions, e.g. Cl^-. This is the process proposed by Shida and Takemura to account for the disappearance of the optical absorptions of the cations by photobleaching [12]. In a first approximation the photon energy should be sufficient to cause the excitation and the excitation energy should exceed $I_M - I_A$ (I = ionization potential).

Experimentally we found that red light is energetic enough to bleach hexane$^+$ but not octane$^+$ in $CFCl_3$. The optical excitation energies decrease with increasing chain length [13] implying that if the first step proceeds at a certain wavelength with hexane$^+$ it should also proceed with octane$^+$. On the other hand the ionization potentials of n-alkanes decrease with increasing chain length [14]. Therefore more energy has to be supplied for the second step of the process with octane than with hexane. It seems that the simple model can account for the observations in the $CFCl_3$ and $CF_2ClCFCl_2$ matrices. In the second case, which occurs in CF_3CCl_3 with

unlabelled hexane, heptane and octane the second bimolecular step does not take place. The simple model which neglects matrix-cation interactions cannot account for this difference in mechanism. Very probably the alkane cations are located in traps whose depths depend on the matrix, similar to the case of solvated electrons [15]. In this model the matrix molecules reorient to allow polar groups to point with their negative ends towards the ion. It is evident that a more detailed knowledge of the solvation structure is required in order to understand the different behaviour depending on the matrix. Unfortunately the photobleaching experiments with specifically labelled hexanes in CF_3CCl_3 aiming at elucidation of the mechanism were inconclusive as no paramagnetic secondary products could be identified. We are now setting up experiments for a GC/MS analysis of the end products with the hope to get information about possible isotope effects.

[1] J. T. Wang and Ff. Williams, Chem. Phys. Lett. **82**, 177 (1981).
[2] K. Toriyama, K. Nunome, and M. Iwasaki, J. Phys. Chem. **85**, 2149 (1981).
[3] K. Toriyama, K. Nunome, and M. Iwasaki, J. Chem. Phys. **77**, 5891 (1982).
[4] M. Iwasaki, K. Toriyama, and K. Nunome, Radiat. Phys. Chem. **21**, 147 (1983).
[5] M. Tabata and A. Lund, Radiat. Phys. Chem. **23**, 545 (1984).
[6] a) A. Lavanchy, R. Houriet, and T. Gäumann, Org. Mass. Spec. **13**, 410 (1978); b) J. L. Holmes, P. C. Burgers, M. Y. A. Mollah, and P. Wolkoff, J. Amer. Chem. Soc. **104**, 2879 (1982).
[7] H. Oloff, Thesis Regensburg 1981.
[8] G. Dolivo and A. Lund, unpublished results.
[9] a) R. C. Benz and R. C. Dunbar, J. Amer. Chem. Soc. **101**, 6363 (1979). b) R. C. Dunbar, Anal. Chem. **48**, 723 (1976).
[10] E. W. van Dishoeck, P. N. T. van Velzen, and W. J. van der Hart, Chem. Phys. Lett. **62**, 135 (1979).
[11] T. Shida, Y. Egawa, H. Kubodera, and T. Kato, J. Chem. Phys. **73**, 5963 (1980).
[12] T. Shida and Y. Takemura, Radiat. Phys. Chem. **21**, 157 (1983).
[13] R. Mehnert, J. Bös, and O. Brede, Radiochem. Radioanal. Lett. **38**, 47 (1979).
[14] R. P. Blaunstein and L. G. Christophorou, Radition Res. Rev. **3**, 69 (1971).
[15] For a review, see Electron-solvent and Anion-solvent interactions, ed. by L. Kevan and B. Webster, Elsevier, Amsterdam 1976.