ESR, Structure and Reactions of Specifically Deuterated C₆—C₈ n-alkane Cations in Halogenated Matrices

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Dilute frozen solutions (1–2%) of specifically labelled n-hexane, n-heptane and n-octane in three halogenated matrices (CFC₁₃, CF₃CC₁₃ and CF₂CICFC₁₂) 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 CFC₁₃ with one exception. INDO MO calculations show that tilting of the CH₃ group towards the –CH₂– chain lowers the energy and gives better agreement with experimental values for the hyperfine coupling constants. CF₂CC₁₃ seemed to induce the largest distortions in the geometry of the ions. The nature of a distorted conformer of hexane⁺ in CF₂CC₁₃ has been determined with the aid of observed couplings and INDO MO calculations.

Photobleaching causes disappearance of the cations in the CFC₁₃ and CF₂CICFC₁₂ matrices and fragmentation to produce 2-butene cations in CF₂CC₁₃. 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 C₂–C₃ 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 CFC₁₃, CF₂CC₁₃ and CF₂CICFC₁₂ to elucidate how the geometry of the ions is affected by the matrix.

In CF₂CC₁₃ 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 accepted. 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: C₄F₁₄ (Fluka, purum), C₆H₁₄ (Merck, p.a. 99%), C₇H₁₈ (Kebo, puriss. > 99%), C₈H₁₈ (Kebo, puriss. > 99%).
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The specifically labelled n-alkanes were synthesized according to the following procedures. The hexane-1,6-d₆ was prepared by reaction between the Grignard of 1,4-dibromobutane and CdI₂ in presence of Li₂CuCl₄. The hexane-3,4-d₄ was obtained by the reaction of 3-hexyne in toluene solution with D₂ in presence of fresh tris(triphenylphosphin) rhodium chloride. The hexane-2,5-d₄ was synthesized in three steps, starting from the 2,5-hexanediene which was converted by LiAlD₄ into 2,5-hexanediol, deuterated in positions 2 and 5 and on the two hydroxyl groups. Then, by reaction with PBr₃, the 2,5-dibromohexane-2,5-d₄ was obtained which gave the hexane-2,5-d₄ by reduction by LiD/LiAlD₄.

The heptane-1,7-d₆ and the octane-1,8-d₆ were obtained by a reaction scheme identical to the one described for the hexane-1,6-d₆, 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-d₆ contained 3.3% d₁, hexane-2,5-d₄ 6.3% of d₃ and 4.2% of d₁, and hexane-3,4-d₄ 2.7% of d₃ and 7.6% of d₁. No analysis is available for heptane-1,7-d₆ and octane-1,8-d₆.

CF₃CCl₃ (Aldrich, 98%), CF₂ClCCl₂ (Fluka > 99% or Merck > 99.7%) and CFCl₃ (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 thermo-couple.

First and second derivative spectra were recorded with modulation amplitudes of 2 G. The reported linewidths (Δν) 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-d₆

The esr spectra of hexane-d₁⁺ were measured in the three halogenated matrices and perfect agreement was obtained with the published data [1—5]. In C₆F₁₄, the esr spectrum of C₆H₁₄⁺ is a triplet with a = 40 G and a Δν of 18 G. The yield was about one tenth of that in CF₃CCl₃.

In CF₂ClCCl₂, 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 CF₂ClCCl₂, the esr spectrum of C₆H₁₄⁺ vanishes at about 102 K and is not restored when the temperature is lowered to 77 K. The residual spectrum at 102 K is broad and of low intensity.

Bleaching experiments were made in CFCl₃ and in CF₃CCl₃. In CFCl₃ illumination for three minutes with red light (λ > 630 nm) is enough to bleach ca. 80% of the hexane⁺. No new paramagnetic product is formed in contrast with the results obtained in CF₃CCl₃. In the latter case illumination for 10 min with red light (λ > 630 nm) affects only one of the center lines which is presumably due to the matrix. In CF₃CCl₃ quantitative (≥ 50%) conversion to 2-butene⁺⁺ (5) was observed with lights of various wavelengths < 630 nm.

B) Hexane-3,4-d₄ and-2,5-d₄

a) CF₃CCl₃

The 77 K first derivative esr spectra of these two internally labelled hexanes in CF₃CCl₃ are shown in Fig. 2a (2,5-d₄) and b (3,4-d₄). They consist of a triplet with a = 41 G and a Δν of 12 G. A substructure with a = 4 G is more apparent for the 2,5-d₄ than for the 3,4-d₄. No weak side lines are appearing in the 2,5-d₄ spectrum, but such lines are indeed observed for the 3,4-d₄, at different field values than for hexane-d₁. When the temperature is raised the intensity of the esr spectrum decreases for both
compounds. Some lines due to hexane-d₄⁺ ions are still present, more clearly for 2,5-d₄ as it gives better resolution (Figure 3 a).

Bleaching experiments were done with white light or with various filters. In all cases the same weak second derivative spectrum was obtained (Fig. 3 b), 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-d₀.

b) CF₂CICFCI₂

In this matrix the 77 K spectra of the hexane-2,5-d₄⁺ (Fig. 4 a) and 3,4-d₄⁺ (Fig. 4 b) molecular ions are different. The 2,5-d₄ spectrum consists only of a triplet. The 3,4-d₄ molecular ions has broad outer lines and the triplet lines are narrower.

c) CFCl₃ and C₆F₁₄

The spectra obtained with the CFCl₃ matrix are similar to those recorded in CF₃CCl₃ but with a far better resolution. They consist of a triplet of quintets (ₐ₁ = 41.5 G, ₐ₂ = 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
Fig. 6. ESR spectra of hexane-1,6-d$_5^+$ in CF$_3$CCl$_3$ taken a) at 77 K, b) at 110 K. * shows a background signal.

Fig. 4. a) First derivative spectrum of a) hexane-2,5-d$_4^+$, b) hexane-3,4-d$_4^+$ in CF$_2$ClCFCl$_2$ at 77 K.

Fig. 6. ESR spectra of hexane-1,6-d$_5^+$ in CF$_3$ClFCl$_2$ at 77 K: a) first derivative, b) second derivative of central part, c) simulation of a) with 17% of extended form with $\alpha = 6.5$ G (2D, 4H), $\hbar\nu = 5$ G; 63% of conformer with $\alpha = 78$ G (1H), $\hbar\nu = 15$ G and 20% of conformer with $\alpha = 85$ G (2H), $\hbar\nu = 25$ G.

Fig. 5. First derivative ESR spectra of hexane-1,6-d$_5^+$ in CF$_3$ClCl$_3$ 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$_6$ and 1,7-d$_6$**

a) Heptane-d$_0$

The spectrum of heptane-d$_0$ in CF$_3$CCl$_3$ was re-measured 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$_3$CICFCl$_2$ 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 $\sim 113$ K.

In both CFCl$_3$ and C$_6$F$_{14}$, only a triplet was observed with $a = 30$ G. The yield in C$_6$F$_{14}$ was low.

b) Heptane-1,7-d$_6$

In CF$_3$CCl$_3$ 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$_6^+$, 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. 3b) 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 $\mu$W - 40 mW).
Fig. 8. Second derivative esr spectrum of a solution of heptane-1,7-d₆⁺ in CF₃CCl₃, at 134 K after 10 min of bleaching with λ > 475 nm.

In CF₂CICFCI₂ a single broad line (hv = 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 CFCl₃ the first derivative spectrum of heptane-1,7-d₆⁺ is the same as in CF₂CICFCI₂, with a hv 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 C₆F₁₄ a weak single broad line (hv = 24 G) was measured.

E) Octane-d₀ and -1,8-d₆

a) Octane-d₀

At 77 K in CF₃CCl₃ a triplet with a = 24 G and hv = 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 (λ > 540 nm) left the normal residual spectrum observed for the labelled hexanes (Figure 3 b).

At 77 K in CF₂CICFCI₂ the results were the same as in CF₃CCl₃, though there was nearly no interference from matrix lines. At 102 K the spectrum becomes irreversibly weak and broad.

In CFCl₃ 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 hv = 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 (λ > 630 nm) does not bleach the octane⁺⁺⁺, in sharp contrast with hexane⁺⁺⁺.

b) Octane-1,8-d₆

In CF₂CCl₃ the 77 K spectrum is a single line of hv = 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 (λ > 540 nm) did not affect this spectrum. The original spectrum is restored by cooling back to 77 K. In CF₂CICFCI₂ there is only a broad line with a hv of 20 G at 77 K. No detailed substructure is apparent. At 105 K the observed spectrum is weak and broad.
In CFCI₃ (Fig. 10b) at 77 K there is only a doublet with \( a = 45 \) G and a \( h_\nu \) of 20 G. No change occurred when the sample was heated to 135 K, and some octane-d₆⁺ 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-d₀

The only new result reported here and which needs to be interpreted is the identity of the conformer giving the side bands in CF₃CCl₃ at \( T < 110 \) K. The 77 K spectrum of Fig. 1a could be fitted (Fig. 1b) by taking in account two conformers, the extended conformer with \( a₁ = 41 \) G (2H), \( a₂ = 4 \) G (8H) and a conformer having \( a₁ = 100 \) G (2H), \( a₂ = 22 \) G (4H). 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 C₂–C₃ and C₄–C₅, 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. 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
Table 1. Hyperfine couplings and relative abundance of isotopic labelled conformer ions in CF₃CCl₃, CF₂CIFClF₂ and CFCl₃ 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.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>CF₃CCl₃</th>
<th>CF₂CIFClF₂</th>
<th>CFCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>coupling (G)</td>
<td>hfs (G)</td>
<td></td>
</tr>
<tr>
<td>hexane 70</td>
<td>extended</td>
<td>4 (2H: 1, 6)</td>
<td>6.5 (2H: 1, 6)</td>
</tr>
<tr>
<td>hexane-3,4-d₄</td>
<td>70-80</td>
<td>100 (2H: 2, 5)</td>
<td>22 (4H: 1, 6)</td>
</tr>
<tr>
<td>hexane-2,5-d₄</td>
<td>80</td>
<td>4 (2H: 1, 6)</td>
<td>6.5 (2H: 1, 6)</td>
</tr>
<tr>
<td>hexane-1,6-d₄</td>
<td>40</td>
<td>6.5 (4H: 2-5)</td>
<td>6.5 (4H: 2-5)</td>
</tr>
<tr>
<td>heptane 100</td>
<td>extended</td>
<td>4 (2H: 1, 7)</td>
<td>4 (10H: 2-6)</td>
</tr>
<tr>
<td>octane 100</td>
<td>extended</td>
<td>24 (2H: 1, 8)</td>
<td>4 (10H: 2-6)</td>
</tr>
<tr>
<td>octane-1,8-d₄</td>
<td>70</td>
<td>unresolved</td>
<td>4 (2D: 1, 7)</td>
</tr>
<tr>
<td>hexane 70</td>
<td>extended</td>
<td>41 (2H: 1, 6)</td>
<td>74 (1H: 2)</td>
</tr>
<tr>
<td>hexane-3,4-d₄</td>
<td>80</td>
<td>41 (2H: 1, 6)</td>
<td>74 (1H: 2)</td>
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<tr>
<td>hexane-2,5-d₄</td>
<td>80</td>
<td>41 (2H: 1, 6)</td>
<td>74 (1H: 2)</td>
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<tr>
<td>hexane-1,6-d₄</td>
<td>20</td>
<td>53 (1H: 6)</td>
<td>74 (1H: 2)</td>
</tr>
<tr>
<td>heptane 100</td>
<td>extended</td>
<td>29 (2H: 1, 7)</td>
<td>4 (10H: 2-6)</td>
</tr>
<tr>
<td>octane 100</td>
<td>extended</td>
<td>24 (2H: 1, 8)</td>
<td>4 (10H: 2-6)</td>
</tr>
<tr>
<td>octane-1,8-d₄</td>
<td>100</td>
<td>unresolved</td>
<td>4 (2D: 1, 7)</td>
</tr>
</tbody>
</table>

Table 2. Coupling constants given by INDO calculations for hexane cation conformers obtained by 120° rotations around Cᵢ₋Cᵢ₋₁ and Cᵢ₋₁₋Cᵢ bonds of extended geometry A) both clockwise (see Fig. 11), B) One clockwise the other anti-clockwise. One half of the number of couplings are given, the remaining are obtained by symmetry.

<table>
<thead>
<tr>
<th>Conformer A</th>
<th>Coupling (G)</th>
<th>Conformer B</th>
<th>Coupling (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>open</td>
<td>closed</td>
<td>open</td>
<td>closed</td>
</tr>
<tr>
<td>H₁,₁</td>
<td>13.7</td>
<td>14.0</td>
<td>18.2</td>
</tr>
<tr>
<td>H₂,₂</td>
<td>8.2</td>
<td>11.3</td>
<td>13.9</td>
</tr>
<tr>
<td>H₃,₃</td>
<td>-0.5</td>
<td>-0.4</td>
<td>-0.4</td>
</tr>
<tr>
<td>H₄,₁</td>
<td>80.7</td>
<td>76.7</td>
<td>61.0</td>
</tr>
<tr>
<td>H₅,₂</td>
<td>-2.5</td>
<td>-0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>H₆,₁</td>
<td>-3.2</td>
<td>-4.6</td>
<td>-1.4</td>
</tr>
<tr>
<td>H₇,₂</td>
<td>4.9</td>
<td>-4.0</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

CH₃; for A one CH₃ 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 H₂,₁ and H₃,₁ give rise to large splittings as in the case of the n-butane cation. The SOMO (singly occupied molecular orbital) in fact resembles the 7ₐ₀ orbital of the butane molecule (C₂ᵥ symmetry). The remaining four hydrogens with a resolved hyperfine structure are located on the CH₃ groups.

B) Hexane-2,5-d₄ and 3,4-d₄

The hexane-2,5-d₄ and the hexane-3,4-d₄ 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 CFCl₃ and CF₂CIFClF₂ (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-d₄ ion at 77 K in the CF₃CCl₃ matrix could not be fitted conclusively by either the parameters used for the d₀ gauche conformation 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-d₀.

In CF₃CICFCl₂, the same situation is encountered: the two hexane-d₄ 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-d₄ ion. It accounts for the two outmost lines in Fig. 5 b and about 30% of the yield of molecular ions.

The outmost lines can be nicely fitted with the couplings \( a_1 = 74 \, \text{G}, \ a_2 = 53 \, \text{G} \) obtained by Toriyama et al. [2] using unlabelled hexane. Their assignment of the spectrum as due to a gauche conformation obtained by a 120° rotation around the C₂–C₃ 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 C₂, and to C₆. Since a doublet splitting of \( a_1 = 78 \, \text{G} \) is observed in the gauche conformer of the hexane-1,6-d₆ ion (see below) we assign this coupling to an H on C₂ and \( a_2 = 53 \, \text{G} \) to an H on C₆.

According to this interpretation a gauche conformer of the 2,5-d₄ molecular ion would be a doublet with \( a = 53 \, \text{G} \), with some structure due to a D on C₂ with \( a_0 = 74/6.5 = 11 \, \text{G} \). This spectrum could very well be hidden under the spectrum of the extended conformer in Figure 4 a.

C) Hexane-1,6-d₆

In all the matrices studied, included C₆F₁₄, 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 2D and 4H atoms with a unique coupling constant of 6.5 G (Figure 7 c). We have tried to fit this nine-line spectrum with 8H and the fit is clearly not as good. As there are only 4H giving a resolvable substructure, the extended form is probably somewhat distorted, since both the experimental results in CFCl₃ [1, 2] and the INDO calculations give 8H 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 C₃–C₄. In this structure there are 4H atoms with a calculated hyperfine coupling constant of 3.2 G and four others with \( a \leq 0.8 \, \text{G} \). 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 C₂–C₃ and C₄–C₅, 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-d₆ cation can also take other configurations. In CF₃CICFCl₂ only 20% of the hexane-d₄⁺ are present as “extended”, the other 80% being a species having a doublet with \( a = 78 \, \text{G} \) (Fig. 6 c), 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 C₂ of the carbon chain. The SOMO is qualitatively similar to the 7b₁ orbital of the pentane molecule with C₃ᵥ symmetry [3]. The hyperfine coupling \( a_0 = 53/6.5 = 8 \, \text{G} \) due to the D atom at C₂ is unresolved.

In CF₃CCl₃ a quite different conformer is present accounting for 50–60% of the spectrum (Figure 5 a). It can be fitted by having the following sets of coupling constants; \( a_1 = 85 \, \text{G} \) (2H), \( a_2 = 55 \, \text{G} \) (1H), \( a_3 = 18 \, \text{G} \) (1H) for a single species or \( a_1 = 110 \, \text{G} \) (2H), \( a_2 = 18 \, \text{G} \) (1H) and \( a_1' = 60 \, \text{G} \) (2H), \( a_2' = 18 \, \text{G} \) (1H) 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-d₀⁺, 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 C₂–C₃ and C₄–C₅. 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-d₀ and 1,7-d₆

In all the matrices at 77 K the molecular ions of both the heptane-d₀ and 1,7-d₆ have only the extended form. The spectrum of the heptane-d₆ ion in CF₂CICFCI₂ (Fig. 9) can be fitted very well by having 2D with $a_1 = 4.6$ G and 10H with $a = 4$ G. The 77 K spectra in both CFCI₃ and CF₂CCLI₃ are perturbed by spurious lines, but are clearly to be assigned to the same structure.

When the temperature is raised above 100 K, heptane-d₀ and d₆ cations survive up to 158 K. In CF₂CCLI₃ the spectrum of the heptane-d₆ ion is not affected up to 137 K, but the spectrum of the heptane-d₀ ion is broadened.

In CF₂CICFCI₂ the spectrum obtained for heptane-d₀ 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-d₀- and octane-1,8-d₆

In CFCI₃ and CF₂CICFCI₂ the octane-d₀ molecular ion is present only in its extended form. The major component of the 77 K spectrum of octane-d₀ ion in CFCI₃ (Fig. 10a) is assigned to the gauche conformer with couplings of $a_1 = 41$ G (1H), $a_2 = 22$ G (1H) as identified by Toriyama et al. [3]. The assignment is supported by comparison with the spectrum of the octane-1,8-d₆ ion (Fig. 10b) which contains a doublet with $a_3 = 41$ 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 C₂ at the folding position of the carbon chain. We estimate that 80% of the octane-d₀ and more than 90% of the octane-1,8-d₆ ions are in this configuration in the CFCI₃ matrix. This species is present also in the CF₂CCLI₃ 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 C₂–C₃, a rotation around C₃–C₄, two rotations around C₂–C₃ and C₃–C₄ (for the case where both are clockwise and for the case when one is clockwise and the other counterclockwise), and two rotations around C₂–C₃ and C₄–C₅ (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 CH₃ groups (θ is the CH₃–CH₂–CH₃ bond angle) on the energy (+) and coupling constant (○) in the extended form of the n-hexane cation.](image-url)
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$_3$–C$_4$ 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$_3$CCl$_3$ is altered by this substitution. Thus, in CF$_3$CCl$_3$, 30% of hexane-d$_0^+$ is gauche conformer, compared to 50% for hexane-d$_0^+$. The same situation is encountered in CF$_3$CIFCF$_3$ where the change in the gauche conformer proportion is even greater: 30% for d$_0$ versus 80% for hexane-d$_0$. In CFC$_3$ there is only the extended conformer. For octane$^+$ this phenomenon of increase in conformer proportion is seen in CF$_3$CCl$_3$: no gauche conformer for -d$_0$ versus 30% for -d$_6$, and in CFC$_3$, 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$_3$ than in H$_1$, 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$_3$CCl$_3$ 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 CFC$_3$ the experimental value is 44 G for the two in plane hydrogens, compared to 41 G in CF$_3$CCl$_3$. 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 CFC$_3$ 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$_3$CCl$_3$ matrix (97°). It seems that the extended ion is more distorted from the equilibrium geometry in the CF$_3$CCl$_3$ than in the CFC$_3$ matrix. With a shorter alkane chain like n-pentane cation in CFC$_3$ 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<sub>6</sub> ions in CFC<sub>3</sub>Cl 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<sub>3</sub>CCl<sub>3</sub> 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<sub>1</sub>—C<sub>2</sub> and C<sub>5</sub>—C<sub>6</sub> 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<sub>3</sub>CCl<sub>3</sub> is not yet understood.

B) Deprotonation in CF<sub>3</sub>ClCFC<sub>1</sub><sub>3</sub>

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<sub>6</sub>, 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<sub>6</sub><sup>+</sup> in CF<sub>3</sub>CCl<sub>3</sub> 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<sub>6</sub>H<sub>14</sub><sup>+</sup> in gas phase giving C<sub>3</sub>H<sub>7</sub> and C<sub>2</sub>H<sub>5</sub><sup>+</sup>. Photofragmentation of C<sub>4</sub>H<sub>7</sub><sup>+</sup> in CF<sub>3</sub>CCl gives the 2-butene cations. We have confirmed that this photoinduced fragmentation does not occur in CF<sub>2</sub>ClCFC<sub>1</sub><sub>3</sub> and in CFC<sub>3</sub>. 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<sub>3</sub>Cl<sub>3</sub> and mainly for protiated C<sub>6</sub>—C<sub>8</sub> 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<sub>2</sub>ClCFC<sub>1</sub><sub>3</sub> [5]. Possibly, the original product of the cleavage is 1-butene<sup>+</sup>, which subsequently photoisomerizes to 2-butene<sup>+</sup> as this was proved possible in [11].

There seem to be at least two different mechanisms for the elimination of the trapped alkane radical cations by illumination. In the first case, which occurs in CFC<sub>3</sub>Cl and CFC<sub>2</sub>ClCFC<sub>1</sub><sub>3</sub> matrices it is assumed that the optically excited cation (A<sup>+</sup>)<sup>*</sup> 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<sup>-</sup>. 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 \( I_\text{M} - I_\Lambda \) (\( I = \) ionization potential).

Experimentally we found that red light is energetic enough to bleach hexane<sup>+</sup> but not octane<sup>+</sup> in CFC<sub>3</sub>. The optical excitation energies decrease with increasing chain length [13] implying that if the first step proceeds at a certain wavelength with hexane<sup>+</sup> it should also proceed with octane<sup>+</sup>. 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 CFC<sub>3</sub>Cl and CF<sub>2</sub>ClCFC<sub>1</sub><sub>3</sub> matrices. In the second case, which occurs in CF<sub>3</sub>CCl<sub>3</sub> 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$_3$CCl$_3$ 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.

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