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On the structure of the perfluorinated F-4-ethyl-3,4-dimethyl-hexan-3-yl carbanion: a structural dynamic ^{19}F-DNMR study

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Abstract

The perfluoro-4-ethyl-3,4-dimethylhexan-3-yl carbanion was prepared by reaction of tetramethylammonium fluoride with the parent C_2F_4-pentamer olefin in acetonitrile as a stable but moisture sensitive white salt. ^{13}C- and ^{19}F-NMR spectra of the carbanion were recorded, whereby the latter is first order with exception of the AB-type spectrum of the prochiral CF_2(5)-groups.

Low-temperature NMR spectra down to −90 °C show dynamic behavior, and a step-wise freezing out of molecular rotations occurs. Activation energies of such barriers of interconversion and rate constants were determined from spectral data. Likewise, the carbanion site structure is described. In addition, the molecular structure and its rotational isomers are calculated by the quantum chemical AM 1 method. As the major structural result, the carbanion site is flat and sp^2 hybridized in contrast to an inverting pyramidal carbon atom. This planar arrangement is confirmed by the occurrence of diastereotopic fluorines of the CF_2(2) group in the molecule, where the equatorial fluorine of that group is locked in the plane of the perpendicular p_z-orbital.

Fluorine containing groups in the neighborhood of the lone electron pair of the anion suffer strong electron deshielding and a remarkable ^{19}F-NMR downfield shift takes place as a consequence of a chemical shift anisotropy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Perfluorinated carbanion; Dynamic NMR; Freezing out of rotations; Activation barriers; Molecular structure; AM 1 calculations; Chemical shift anisotropy

1. Introduction

In the chemistry of unsaturated fluorocarbon compounds, the fluorinated carbanion is of an importance analogous to that of carbocations in unsaturated hydrocarbon chemistry. Fluorocarbanions are usually reactive intermediates which are formed, e.g. by the reaction of a fluoroolefin with a nucleophile. The reaction pathway follows generally an addition–elimination sequence, where the stability of the intermediate carbanion depends on structure. Fluorination in α-position to the charged site destabilizes the carbanion, while β-fluorination is essentially opposite.

Tertiary carbanions have been isolated in some cases as temperature stable but hydrolyzable salts [1], while primary and secondary carbanion structures do not exhibit sufficient kinetic stability to be monitored spectroscopically. The lifetime of the former is highly dependent on structure, counter ion and solvent.

The other way to fluorinated carbanions is deprotonation of hydrofluorocarbons. The considerably acidic hydrogen atom in these compounds may be abstracted by a base, whereby the formed carbanions in most cases immediately react to a more stable specie. Generally, fluorines present in a β-position to a single hydrogen influence the outcome of elimination reactions according to an E1c b mechanism, where carbanion intermediates are involved.

The stability of the fluorinated carbanions is controlled by a rather sensitive balance of steric and electronic factors and has been discussed in terms of the so-called fluorine-no bond resonance (negative anionic hyperconjugation) in diverse and controversial ways. The stereochemistry of such carbanions is of considerable interest. To minimize the steric requirements, a planar instead of a tetrahedral or a rapidly inverting tetrahedral system at the carbanionic center should be expected [1].

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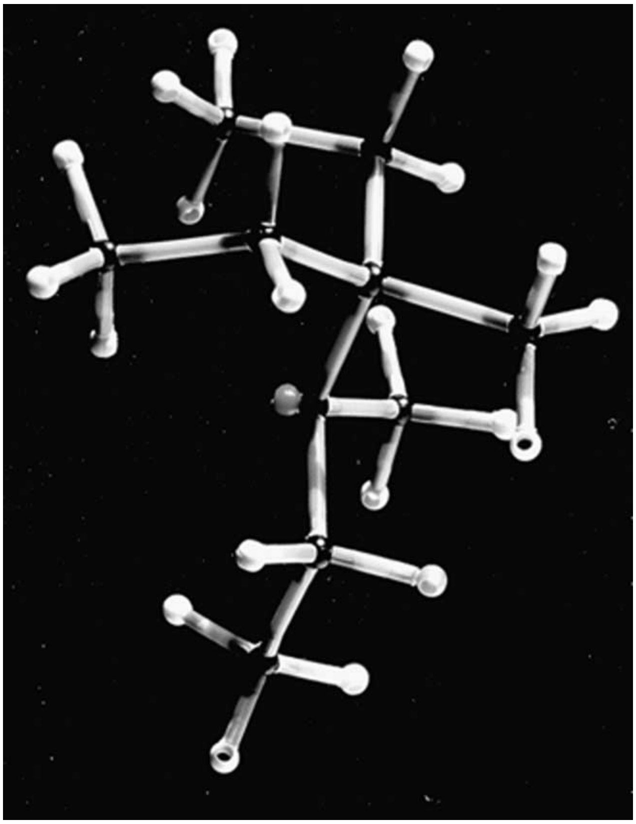


The above picture presents a model of a sterically demanding tetrahedral carbanion with the lone pair in the center, giving an impression of the crowded spatial arrangement.

Actually, there are a few examples where single crystals have been studied by X-ray investigations: F-1,3-dimethylcyclobutanide ion and 1,1,3,3-tetrakis-(trifluoromethyl)allyl anion are examples for a planar configuration [2]. Unfortunately, both structures exhibit geometric particularities which make generalizations doubtful: the first suffers from ring strain of the small four-membered ring, the latter is electronically stabilized by an acceptor molecule.

Unlike a single crystal structure of the solid state, the present study describes structure, dynamic conformers, their kinetics and energetic barriers of a dissolved molecule in solution.

The species under discussion was also the subject of investigations reported in [1], but the wanted anion could not be isolated in pure form. Caesium fluoride as the used fluoride ion source is only poorly soluble and therefore nearly unreactive under these conditions. According to the published spectra, the compound seems to be a 1:1 mixture with the starting olefin.

2. Experimental

The title F-carbanion is prepared by the reaction of the TFE-pentamer olefin with tetramethylammonium fluoride (TMAF) in CH_3CN as solvent. Because of the good solubility of TMAF in the solvent, the reaction is fast and quantitative forming a stable but moisture sensitive white salt. In the case of an incomplete reaction the NMR spectra show F-exchange with unreacted olefin and an upfield shift of signals close to the carbanion site. Therefore, excess of the fluoride ion is recommended for the reaction.

Due to its sensitivity to moisture, the salt and the dried solvents (CH_3CN, THF, C_2H_5CN especially for low temperature measurements) were handled in a dry box and with a vacuum line system. Elemental analysis was carried out by the Mikroanalytisches Labor Beller, Göttingen (Germany) confirming the analytical composition of the salt $C_{14}H_{12}F_{21}N$.

The NMR spectral data are as follows (for numbering the carbon atoms see Fig. 1):

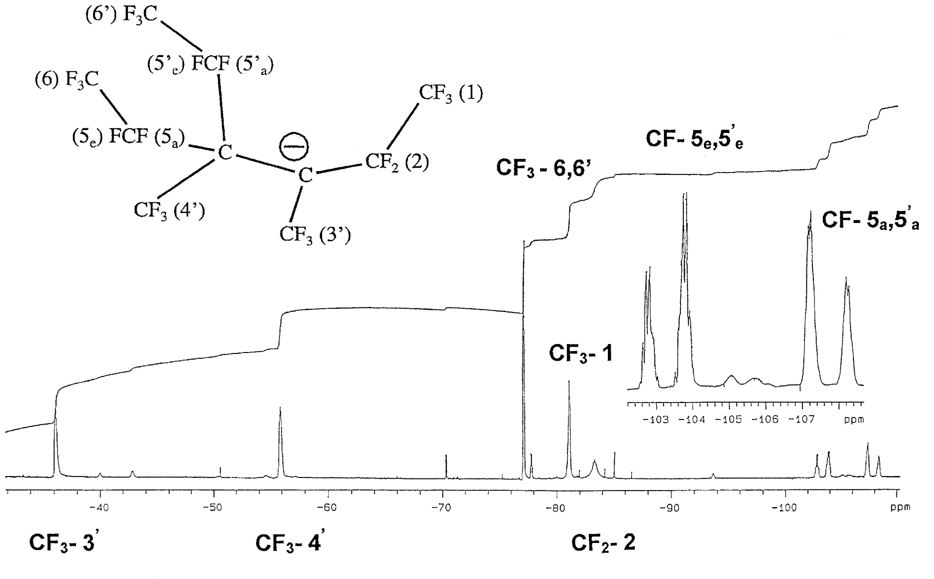


Fig. 1. ^{19}F-NMR spectrum of the F-4-ethyl-3,4-dimethylhexan-3-yl carbanion at 25 °C.

Table 1
Calculated Mulliken charges at selected carbon atoms of the perfluorinated alkene, radical, carbanion and alkane

	C_1	C_2	C_3	C'_3	C_4	C'_4
Alkene	0.454	0.115	−0.232	0.477	−0.106	0.426
Radical	0.398	0.278	−0.200	0.466	−0.128	0.424
Anion	0.334	0.409	−0.711	0.524	0.087	0.411
Alkane	0.401	0.216	0.037	0.411	−0.195	0.423

^{19}F: 1 (CF_3) −81.2 ppm, 2 (CF_2) −83.3, 3′ (CF_3) −36.3, 4′ (CF_3) −55.9, 5 (CF_2) AB −103.2/−107.4 (m), J_{AB} 296 Hz, 6 (CF_3) −77.2 (q) 12 Hz.

Peak integration is in full agreement with the compounds' composition.

^{13}C: 1 124.12 ppm (q 289 Hz; t 9.6 Hz), 2 117.14 (t 280; q 31.6), 3 (carbanion) 29.6 (m), 3′ 132.95 (q 261.7), 4 68.7 (m), 4′ 130.0 (266.5), 5 121.2 (t broad, 280), 6 120.11 (q 289.5; t 35.6).

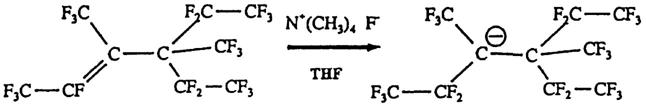
$(CH_3)_4N^+$-cation 56.1 ppm (q).

NMR spectra were recorded with a Bruker MSL 400 spectrometer, that at low temperatures with a JEOL JNM-LA 400 in propionitrile as solvent, and with Freon 11 (CCl_3F) as external standard. The structure of the carbanion and its rotational conformer including charge distribution, bond length and bond angles were computed with the Hyperchem program, using AM 1 and UHV for geometry optimization.

Comparing the charges at carbon of the different species in Table 1, remarkable deviations occur in the carbanion moiety. The strongest negative charge is located as expected at the carbanion site, while the neighboring carbon atoms are partially positive due to electron withdrawal. The alkene is electrophilic at carbon 2 of the double bond and differs basically from the corresponding alkane only at carbon 3.

3. Results and discussion

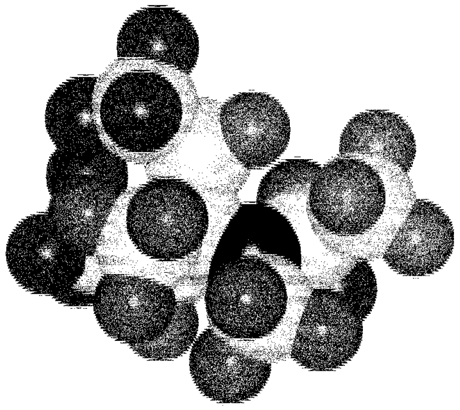
The title carbanion is straightforwardly prepared from the branched F-olefin by adding a highly active fluoride ion under strictly anhydrous conditions to the acetonitrile solution.



Because we were unable to grow suitable single crystals for X-ray analysis, a dynamic NMR study was undertaken to get structural information for the carbanion site. At room temperature, the ^{19}F-NMR shows a first order spectrum, which is easily assigned to the fluorine groups of the anion. The $CF_2(5)$ exhibits prochirality and splits into a AB-type subspectrum with a coupling constant of J_{AB} 296 Hz. Fluorine atoms close to the carbanion center are extremely deshielded and resonate at a lowered magnetic field. The downfield shift is discussed in the following in terms of a chemical shift anisotropy.

3.1. Semiempirical quantum chemical AM 1 calculations

The perfluorinated carbanion was studied by a semiempirical AM 1 calculation. These converge to a minimum of energy representing a flat molecular structure that implies a sp^2 hybridized carbanion site This so called *cis*-isomer ($CF_3(4')$ eclipsed to $CF_3(3')$) is somewhat more stable as compared to the *trans*-isomer. The following scheme shows the paramagnetic shielding effects of the carbanion negative charge onto planar and axial fluorine sites, where the calculated molecular arrangement of the *cis*-isomer is presented below.



Paramagnetic shielding effects of carbanion negative charge onto planar and axial fluorine sites

Segment	Δδ (^{19}F), approximate values (ppm)	Angle of segment versus plane (°)[a]
$CF_3(1)$	−4	68.0
$CF_3(3')$	+41	0
$CF_3(4')$	+21	17.6
$CF_3(6,6')$	0	Flexible
$CF_2(2)$	+21	0
$CF_2(5)$ F	−48, axial	49
F	0, nonaxial	
$CF_2(5')$F	−4.8, axial	80.4
F	0, nonaxial	

[a] Computed by HYPERCHEM/AM1, UHF, geometry optimization; from this result the plane (C2, C3′, C4) includes the anion site C3.

On the basis of a planar carbanion, bonding parameters are calculated. A comparison of C–C bond length at the carbanion site with that of the parent F-olefin F-3-methyl-4-methyl, ethyl-2-hexene, the saturated F-alkane $C_{10}F_{22}$ and the analogous perfluorinated radical [3] (which differs electronically only by one electron from the carbanion) is given.

3.2. Geometrical properties (from calculation)

Compound	Binding energy (kcal/mol)	Deviation angle (°) from planarity along C–C bonds			Bond length (Å)			Torsion angle of group versus plane (C2, C3′, C4) (°)			
		C2–C3	C3′–C3	C4–C3	C2–C3	C3′–C3	C4–C3	C1	C4′	C5	C5′
Olefin	−3015.9	1.78	1.79	1.85	1.364	1.5443	1.517	1.69	10.3	72.7	47.0
Anion	−3176.5	7.20	7.14	7.79	1.482	1.496	1.454	68.0	17.6	38.7	80.4
Radical[a]	−3078.1	7.98	7.92	8.67	1.525	1.497	1.541	67.9	18.2	39.6	80.8
F-alkane	−3155.5	53.47	52.80	57.49	1.613	1.626	1.588	–	–	–	–

[a] Computed by HYPERCHEM/AM1, RHF/UHF, geometry optimization.

Although these calculations are not at the highest level of theory, the trends of the different bonds are quite obvious. The C–C bond near to the negative charge is shortened to 148.2 pm, whereas the C–F bond in the neighboring $CF_2(5)$ is only slightly lengthened to 138.2 pm. This may be a result of the negative anionic hyperconjugation interaction of an antiparallel arrangement of the carbanion lone pair and C–F bond [4].

The same tendency is reflected in discussing the electronic properties as the calculated Mulliken charges q at carbon and fluorine: q carbanion, $C_3\ -0.724$; $C_2\ +0.41$ $C_4\ +0.09$. The atomic charges at the fluorines are not that strongly affected: they vary in a range from $q = -0.155$ to -0.188. This indicates that not much of the negative charge is delocalized to fluorine. On the contrary, the charge density at the carbanion has strongly increased (compare with the corresponding fluorinated radical $q\ -0.200$ [3]. The concentrated charge at the carbon with the lone pair localized in a perpendicular p_z-orbital decisively determines the chemical reactivity and the physical properties of the species.

In this regard the NMR chemical shifts as an expression of electronic shielding at a nucleus are affected in an unusual way.

3.3. Carbanion chemical shift anisotropy

Conventionally, it has been common to relate higher nuclear magnetic shielding, i.e. increased electron density, with higher field resonance. This is also the case with the ^{13}C-NMR chemical shift of carbon C_3 in the carbanion under study. The sp^2 carbon resonates at 29.6 ppm as a result of increased shielding due to the lone pair. In contrast to that, some of the observed ^{19}F-NMR chemical shifts are unexpected: instead of nuclear shielding fluorine-deshielding takes place.

One of the reasons for this type of NMR downfield shift is a chemical shift anisotropy, which is well known to occur in multiple bond and aromatic systems. In such centers of high electron density, the outer magnetic field induces a local electron circulation and, subsequently, a secondary anisotropic field with an oriented charge effect to adjacent bonds [5]. As in the above mentioned cases, a charge cone may also be created around the p_z-lone pair orbital. Fluorine nuclei of the carbanion within this sphere of charge are deshielded and, consequently shifted downfield. One obvious advantage of this effect is the helpful assignment of a magnetic nucleus in its conformational position for solving stereochemical questions (compare the diastereotopic fluorines in $CF_2(2)$ of next section).

The remarkable downfield shifts of fluorine in perfluorinated carbanions were first observed by Chambers et al. [6]. A convincing explanation was not given, because it is in contradiction to the charge model of shielding.

Considering the carbanion of this study, the $CF_3(3)$ group adjacent to the charge is strongest downfield shifted by about 41 ppm, whereas the neighbors in β-positions $CF_3(1)$ and $CF_3(4')$ are less but differently deshielded. Obviously, the position of $CF_3(1)$ out of the p_z-plane makes the difference.

3.4. Nuclear magnetic resonance spectral and kinetic data of structural relevance

3.4.1. Dynamic ^{19}F-NMR low temperature investigation

The room temperature spectrum in Fig. 1 shows the typical features of the carbanion: anisotropic chemical shifts and prochirality of the $CF_2(5)$ groups, while all molecular rotations are fast as compared to the NMR time scale.

The low temperature measurements revealed dynamic phenomena traced back to the freezing out of rotational motions. The steric background of this study was to distinguish a tetrahedrally inverted from a planar carbanion site from the occurrence of diastereotopic fluorines in $CF_2(5)$. In fact, by freezing out rotations, these geminal fluorines became magnetically non-equivalent and were, in addition, well separated from each other by about 13150 Hz.

To follow easily the arguments of discussion of the spectra and the thereby derived structural arrangements, the already given essential results reveal that

- the carbanion site is flat and thus the central carbon is sp^2 hybridized; that means the lone pair is localized but stereochemically inactive;

- the first rotation that stops on cooling is that of the central C3–C4 bond forming two isomers with a ratio of 65 and 35%; and
- the frozen-out geminal fluorines of $CF_2(2)$ of the minor isomer are diastereotopic, where the equatorial one is locked in the p_z-plane, as the consequence of which a strong anisotropic downfield shift is observed.

The dynamic NMR spectra were measured in dry propionitrile as solvent, because of its low melting point. Single spectra were recorded and integrated in temperature steps of 10 °C. Fig. 3 presents the observed spectral changes with temperature. For clarity, the spectra at −30 and −40 °C are not presented in the figure.

At a temperature of −40 °C, the $CF_3(1)$ peak at −81.2 ppm starts to split into a doublet with a 2:1 intensity ratio. This doublet indicates the freezing out of the C3–C4 bond to form two isomers. The exchange rate between them is slow and amounts to about 1000 cycles per second. The bulky groups at the bond give a relatively high activation energy of about 43.2 kJ/mole. The energy difference between the conformers is only 1.2 kJ/mole, indicating no predominant conformation of the two.

As to the structure itself, the major isomer of 65% has the $CF_3(3)$ eclipsing $CF_3(4)$ and the minor has the $CF_2(2)$ eclipsing $CF_3(4)$. This eclipsing also explains a 1.5 'through space' interaction that develops a peak splitting of $CF_2(5)$ with ongoing cooling. The preferred conformation at sp^2 carbon is the eclipsed position. According to Newmann projections, there are only two conformational positions possible: *cis-* and *trans*-arrangements with an energetic preference for the *cis*-isomer.

Next, the $CF_3(4)$, bond at the quarternary carbon, stops rotating in both the major and the minor isomers. At a coalescence temperature of −50 °C, the peak at −55.9 ppm is broadening and finally splits into two seperate signals in a 1:2 ratio; one belongs to the major the other one to the minor isomer. Both signals develop well resolved fine structure at −90 °C (Fig. 4).

The $CF_3(3)$ at −36.3 ppm is stopping with the major isomer at −55 °C, but this is not complete at −90 °C with the minor isomer, this $CF_3(3)$ is still rotating freely at −90 °C.

At −75 °C, the 'probe of the molecule', the $CF_2(2)$-group bonded to the carbanion site shows coalescence both in the *cis-* and *trans*-isomer. The initial thought is that the further development of the geminal difluoride implies a pyramidal geometry at the carbanion center and that one is seeing the freezing out of inversion at this center. It is, of course, possible to make models of conformers that are planar at this center and have the $CF_2(2)$ fluorines diastereotopic.

While in the major isomer the $CF_2(2)$ appears at −90 °C as a doublet at −72.2 ppm with J_{FF} 294 Hz (Fig. 4), flanking the $CF_3(6)$-peak; in the minor isomer it undergoes an extreme chemical shift separation of the two resonating fluorines by 13,150 Hz. The subspectrum is of an AX-type: F_A 63.7 ppm, F_X 98.1 ppm, J_{FF} 274 Hz.

A probable and convincing explanation is if one of the fluorines froze out in the same plane as the negative charge and the other at nearly 109° to it. This explanation holds only for a planar sp^2 carbanion site. Actually, the freezing out of

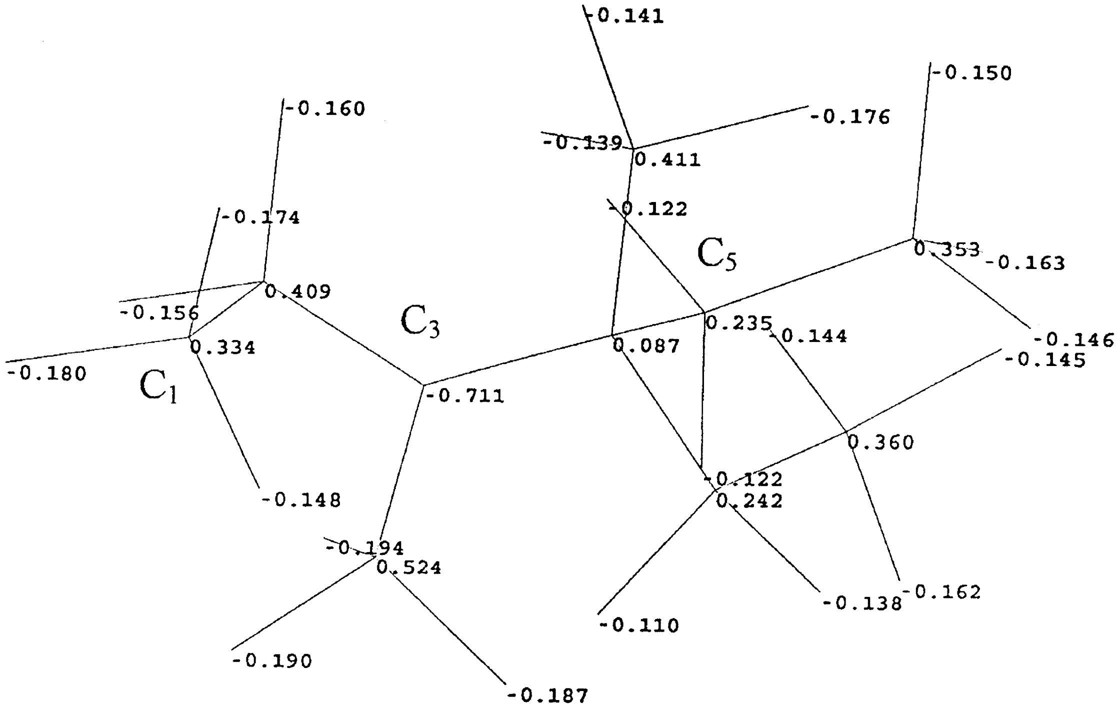


Fig. 2. Mulliken charges at carbon and fluorine of the perfluoro-carbanion.

Fig. 3. ^{19}F-NMR low temperature spectra of the carbanion in the temperature range up to −90 °C.

inversion would show a quite different spectrum. The geminal fluorines at the C(2)-carbon would generate an AB-type splitting as well with an expected coupling constant of about 300 Hz. Only a locked F-atom of CF_2(2) is able to interact in a way with the lone pair to become strongly deshielded as we actually found in our experiments.

The kinetic data in Table 2, e.g. the activation energy also underline the stopping of a rotation rather than the freezing out of a carbon inversion.

From the temperature dependent fluorine spectra, kinetic data concerning the different rotating groups of the frozen-out conformers were calculated from equations given by [7].

$$k_c = \frac{\pi\sqrt{\Delta\nu^2 + 6J^2}}{\sqrt{2}}$$

$$\Delta G^* = 8.3 \times T_c\left(\ln\frac{k_c}{T_c} - 27.7\right)$$

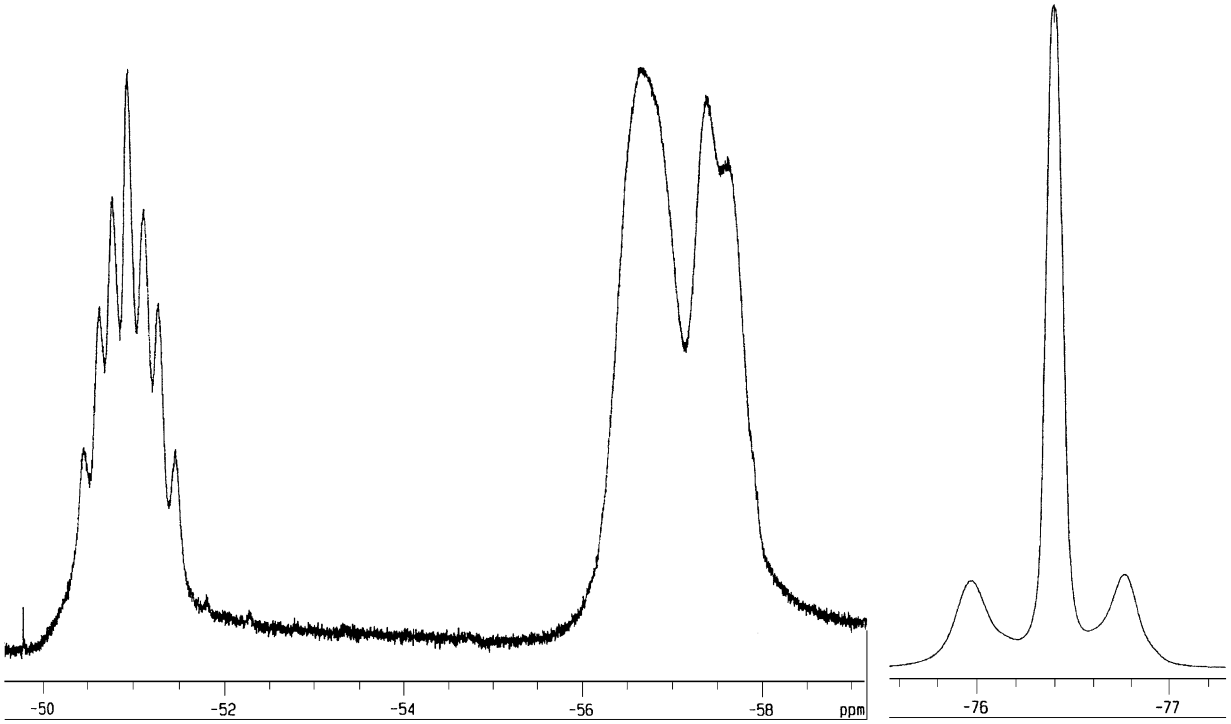


Fig. 4. Expanded part of the ^{19}F-NMR spectrum at −90 °C: (a) resolved $CF_3(4)$; (b) the frozen-out $CF_2(2)$ of the *cis*-isomer with diastereotopic fluorines.

For first order kinetics the relationship between the rate constant k_c and the coupling constant J, together with the chemical shift difference $\Delta\nu$ of an AB quartet at the coalescence temperature T_c obey the above formulae. Energy differences between conformers are calculated from

$$\Delta G = -RT \ln K$$

were K represents the equilibrium constant of the conformer mixture. From a known conformer ratio at a definite temperature, the ratio can be calculated for other temperatures.

Coalescence temperature, rate constants of rotations at T_c, free energies of activation for the interconversion of the conformers as well as calculated conformer ratios and energy differences between the corresponding conformers are presented in Table 2. From the free energies, it is to be seen that the carbanion is not a conformationally rigid molecule. Conformational energy differences are only about 1 kJ/mol and the rotational energy barriers are relatively low. This is also known from calculations of the rotational barriers involving a carbanion site [8].

3.4.2. ^{13}C-NMR spectroscopic investigations

The ^{13}C-NMR spectrum is recorded undecoupled at ambient temperature with a sequence of about 10.000 scans and is given in Fig. 5. All quartets and triplets of fluorine coupled carbons are fully assigned and in agreement with the proposed structure.

As expected, the carbon C_3 bearing the negative charge is extremely upfield shifted to 29.6 ppm, though sp^2 carbon commonly resonates at above 120 ppm. The observed ^{13}C chemical shifts of the deshielded carbon atoms adjacent to the negative charge $CF_3(3)$, $CF_3(4)$ and $CF_2(2)$ agree well with the trend of the calculated Mulliken charges in Fig. 2.

Table 2
Kinetic data of different molecular states after freezing out of molecular rotations

Bond/site	Coalescence temperature T_c (K)	Rate constant at T_c	Free energy of activation (kJ/mol)	Ratio of major to minor conformer at T_c	Energy difference between conformers (kJ/mol)
C3–C4	233	9.95×10^2	43.2	65:35	1.2
$CF_3(4)$	223	5.52×10^2	42.3		
$CF_3(3)$	218	5.11×10^3	37.3		
	198	6.66×10^2	37.0	65	1.0
$CF_2(2)$	198	2.94×10^4	30.8	35	

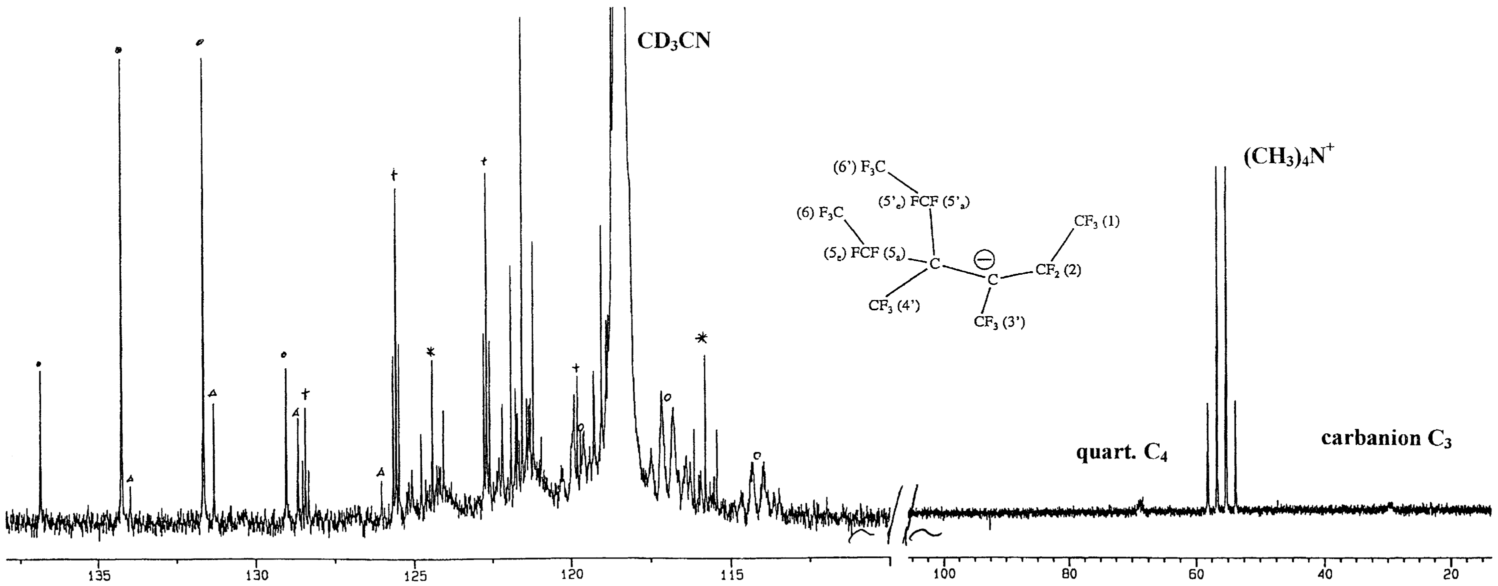
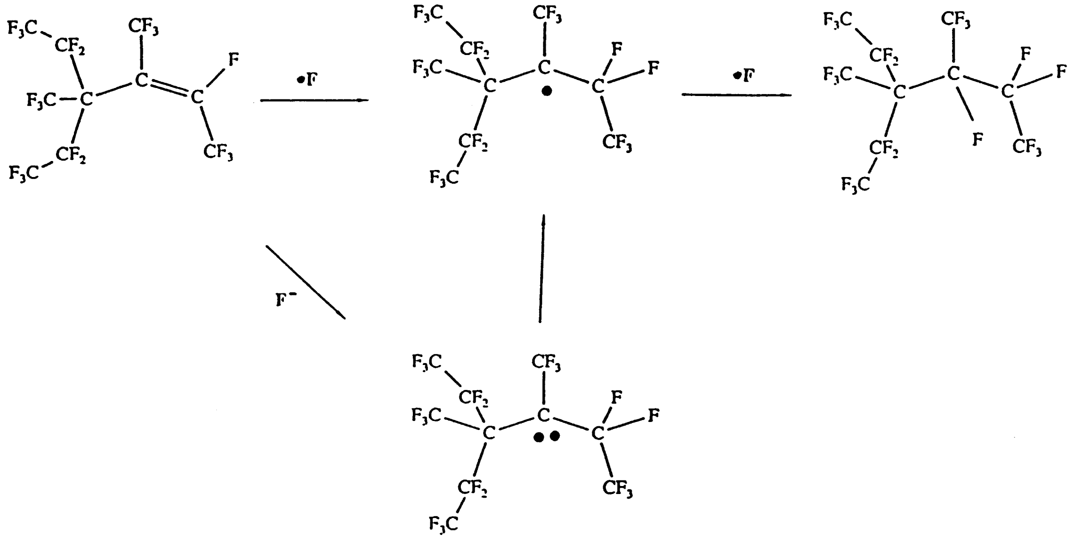


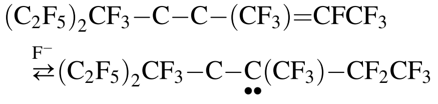
Fig. 5. ^{13}C-NMR spectrum of the perfluorinated carbanion dissolved in CD_3CN at 25 °C.

3.4.3. Exchange phenomena and chemical reactivity

To get a reliable F-NMR spectrum of the carbanion it is essential to prevent exchange phenomena in the measuring solution. Acceptable spectra are not obtained in the presence of the fluoroalkene because of a dynamic equilibrium. Depending on alkene concentration, some of the signals in the spectrum vary in their chemical shift between the position of the carbanion and that of the alkene. This effect is strongest with the most deshielded resonance $CF_3(3)$. In all the cases that suffer from exchange processes, the well resolved AB-type subspectrum of the prochiral $CF_2(2)$ groups of the carbanion collapses to a singlet.



At least two routes can be imagined that generate intermolecular exchange. Both are concentration dependent. The first is due to excess of F^- ion, whereas the second to excess of alkene. Basically, a fluoride ion is exchanging between different states of bonding and structures, respectively. As a result, signals are broadened, especially that of the exchangeable geminal difluoride $CF_2(2)$. In our room temperature spectra, this signal has a peak width at half height of about 170 Hz. In the case of excess of alkene, the carbanion as such becomes invisible spectroscopically.



$$(C_2F_5)_2CF_3{-}C{-}C{-}(CF_3){=}CFCF_3$$
$$\overset{F^-}{\rightleftarrows}(C_2F_5)_2CF_3{-}C{-}\underset{\bullet\bullet}{C}(CF_3){-}CF_2CF_3$$

From the chemical point of view the carbanion is a strong base and nucleophile. That is why it may undergo reactions with electrophiles, e.g. with alkyl halides to give semifluorinated R_F–R_H compounds. The reaction with acids, such as CF_3COOH or HCl yields the H-substituted compound in the 3-position. The carbanion salt is water sensitive and its hydrolysis is not straightforward. Obviously, after proton addition HF is split off to give the parent olefin. Then hydroxide is added to the double bond. In subsequent reactions with further loss of HF, a ketone is formed.

As shown in the reaction scheme, there exists an interesting series of reduction and oxidation reactions involving fluorine between the starting perfluoroalkene and the saturated alkane and the carbanion, respectively.

This sequence could be useful preparatively as well as for measuring oxidation potentials. The availability of these stable intermediates provides the opportunity to carry out physical organic investigations that were impossible to undertake. Some of these oxidations were shown to take place, for example the elemental fluorination of the alkene to the corresponding alkane via the stable radical [3]. The oxidation of the carbanion to the radical should be possible electrochemically at an anode. The reverse electron transfer from the radical to the fluorinated olefin was shown to take place under reductive conditions with electron donating reagents, but without trapping the intermediate carbanion [9].

4. Conclusion

Without having single crystal structural data, geometrical particulars are obtained for the highly branched stable perfluorocarbanion moiety formula by dynamic NMR investigations in solution. Below the coalescence temperature of 233 K, the carbanion exists as two flexible *cis*- and *trans*-isomers in a 2:1 ratio.

The lone pair at the carbanion site is not stereochemically active, but localized in the p_z-orbital its charge confers chemical shift anisotropy to the neighbors.

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