

^{19}F , ^{13}C single- and two-bond 2D NMR correlations in perfluoroheptanoic acid

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Abstract

The first ^{19}F , ^{13}C single- and multi-bond 2D NMR correlations using fluorine detection methods are reported for a perfluorinated alkyl chain. These heteronuclear correlations are observed in perfluoroheptanoic acid and combined with ^{19}F -decoupled ^{13}C data and homonuclear ^{19}F , ^{19}F COSY to derive a full set of unequivocal ^{19}F and ^{13}C assignments. © Elsevier Science S.A.

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1. Introduction

Perfluorinated alkyl compounds are currently in use as blood substitutes [1], breathing media in lungs and as monitors of oxygen tension in tissues [2,3] and tumors [4]. Despite their wide application, there is currently a paucity of ^{13}C data on these compounds, as their ^{13}C NMR spectra in the absence of fluorine decoupling are very complex, i.e. the ^{13}C resonances are split by multi-bond ^{19}F - ^{13}C couplings, and the spectra are further complicated by the fact that the chemical shifts of the fluorinated carbon nuclei are very near to one another. ^{13}C NMR spectral simplification through complete ^{19}F decoupling and two dimensional (2D) ^{19}F , ^{13}C NMR correlation spectroscopy would be ideal and highly attractive approaches to the analyses of these compounds, if certain technical and experimental difficulties can be surmounted.

^{19}F decoupling is currently not in general use as most NMR spectrometers are not equipped with this capability. ^{19}F decoupling of fluoroalkyl chains also presents a special challenge with a need to simultaneously excite ^{19}F resonances over a wide spectral range. Ideally, ^{19}F decoupling would also be accomplished at low decoupler power levels so that heating of the sample does not occur. Our laboratory [5], Berger [6], and Bourdonneau and Brevard [7] have recently reported the first ^{19}F , ^{13}C 2D NMR correlations for simple fluorinated molecules. Its application to fluoroalkyl chains [8] requires correlation of a large ^{19}F window against a large ^{13}C window. We [5,8] have faced and overcome many of

the experimental difficulties and can now routinely implement ^{19}F decoupling and ^{19}F , ^{13}C correlation strategies in our laboratory. In this paper we report for the first time the complete NMR analysis of a perfluorinated alkyl chain. We have applied homonuclear ^{19}F , ^{19}F 2D NMR, ^{19}F -decoupled ^{13}C 1D NMR and heteronuclear ^{19}F , ^{13}C 2D NMR correlation methods to derive a full set of unequivocal ^{19}F and ^{13}C assignments for perfluoroheptanoic acid.

2. Experimental details

Perfluorinated heptanoic acid [7,7,7 6,6 5,5 4,4 3,3 2,2 trideca-fluoro-1-heptanoic acid; $\text{CF}_3-(\text{CF}_2)_5-\text{COOH}$] was purchased from Aldrich Chemical Co., Milwaukee, WI and was used without further purification. NMR data were recorded on a 30% v/v sample in $\text{DMSO}-d_6$ in a 5 mm NMR tube at 28 °C using a Varian Unity 500 spectrometer. NMR spectra were obtained using a 5 mm Varian inverse probe with the high band coil tuned for ^{19}F resonance at 470.38 MHz and the low band coil tuned for ^{13}C resonance at 125.72 MHz. The ^{19}F 90° pulse was 8 μs . The recording of ^{19}F 1D NMR spectra between -80 and -135 ppm required the use of a 25 873 kHz spectral window which was highly digitized with 100 032 points. This same, relatively wide, spectral window was used with 4K points for 2D COSY [9,10].

COSY spectra [9,10] were recorded in the absolute value mode. To ensure reasonable digital resolution in the t_1 dimen-

sion at the 25.9 kHz ^{19}F window, 2048 time increments were collected. The data were zero-filled to 4096 points and apodized with sine–bell weighting along both dimensions. Sixteen scans were collected per increment and the relaxation delay was 1 s.

The ^{13}C 90° pulse was 10 μs . 1D ^{13}C NMR spectra were recorded between 30 and 170 ppm using a 17.598 kHz spectral window digitized into 128 000 points. The ^{19}F decoupler was calibrated directly on the ^{19}F -coupled C7 CF_3 resonance which is a clear quadruplet of triplets with $^1J_{\text{CF}}$ of ≈ 287 Hz centered about 116.9 ppm (Fig. 3). Off-resonance decoupling gave reduced values of $^1J_{\text{CF}}$ which were used to obtain $\gamma\text{H}2/2\Pi$ at various decoupler power values. At < 2 W power GARP1 decoupling [11] gave $\gamma\text{H}2/2\Pi$ fields of > 32 kHz which sufficed to decouple the CF_3 and CF_2 ^{19}F regions simultaneously.

Single-bond ^1H , ^{13}C correlations based on the ^1H -detected HMQC method [12,13] have been used extensively to study hydrocarbon molecules. The HMQC experiment was adapted to record single-bond ^{19}F , ^{13}C heteronuclear chemical shift correlation spectra with ^{19}F detection and full ^{13}C decoupling using GARP1 [11]. Two separate HMQC experiments were carried out. The first correlated a 25.873 kHz ^{19}F window against a 17.598 kHz ^{13}C window to detect cross peaks from CF_3 as well as CF_2 groups. The second correlated a 5.191 kHz ^{19}F window with a 8.172 kHz ^{13}C window optimized over the CF_2 region. The HMQC experiments used a BIRD [14] filter to obtain better suppression of unwanted signals. In each 2D run, two sets of 300 time increments were obtained in phase sensitive mode, processed using Gaussian functions, and zero-filled to a final size of $2\text{K} \times 2\text{K}$. The relaxation delay was 1.2 s with 32 transients per increment. The HMQC experiment was optimized for an average $^1J_{\text{CF}}$ coupling of ≈ 275 Hz which corresponds to a delay of 1.8 ms.

The ^1H -detected multiple bond correlation (HMBC) experiment [13,15] was similarly adapted for ^{19}F , ^{13}C correlations. Two separate, fluorine-detected HMBC experiments were carried out at the same spectral widths as the fluorine-detected HMQC experiments. The HMBC spectra were recorded in the phase sensitive mode without ^{13}C decoupling during acquisition [13,15]. They are plotted in mixed mode [absolute value in f_2 (^{19}F) and phase sensitive in f_1 (^{13}C)]. A shifted Gaussian weighting function was used along f_2 and a cosine weighting function was used along f_1 . Two sets of 300 time increments were zero-filled to a final size of $2\text{K} \times 2\text{K}$. The relaxation delay was 1.2 s, the filter delay corresponded to an average $^1J_{\text{CF}}$ of 275 Hz, and 64 transients were obtained per increment. The HMBC experiments were optimized for an average two-bond ^{19}F – ^{13}C coupling of ≈ 33 Hz which corresponds to a delay of ≈ 15 ms.

3. Results and discussion

The 470 MHz ^{19}F NMR spectrum of perfluoroheptanoic acid reveals the single perfluoromethyl (CF_3) and five per-

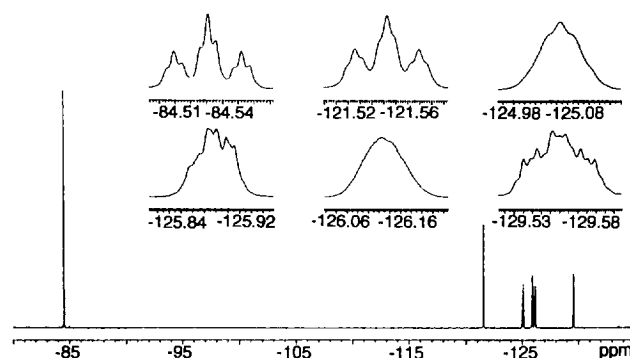


Fig. 1. 470 MHz ^{19}F NMR spectrum of perfluoroheptanoic acid in DMSO-d_6 showing the CF_3 signal at -84.5 ppm and the CF_2 resonances at -121 to -130 ppm. On expansion, the -84.5 ppm CF_3 and the -121.5 ppm CF_2 are seen to be triplets of triplets; the -125.8 and -129.6 ppm CF_2 multiplets show transitions with fine structure but the -125.0 and -126.1 ppm CF_2 resonances are featureless multiplets with unresolvable couplings.

fluoromethylene (CF_2) groups to resonate as six distinct ^{19}F signals between -80 and -130 ppm (Fig. 1). The -84.5 ppm signal is assigned to C7 (CF_3) based on intensity and chemical shift/structural considerations. The expansion reveals the CF_3 signal to be a triplet of triplets with resolved ^{19}F , ^{19}F scalar couplings of 10 and 2.4 Hz. These are taken as $^4J_{\text{FF}}$ and $^5J_{\text{FF}}$ couplings as linear perfluoro compounds are known to have small $^3J_{\text{FF}}$ vicinal couplings [16], and Battais et al. [17] have performed careful decoupling experiments which located $^4J_{\text{FF}}$ and $^5J_{\text{FF}}$ couplings of ≈ 10.7 and ≈ 2.5 Hz at the CF_3 of a perfluorobutyl chain. The assignment of the CF_2 groups is not obvious from the 1D spectrum. The CF_2 group adjacent to the CF_3 of fluoroalkyl chains is usually found at the most upfield CF_2 position [16–20]. On this basis, the -129.6 ppm signal can be assigned to C6 CF_2 group. Because of extensive scalar coupling, particularly from the long range couplings, the CF_2 signals are complex multiplets with many NMR transitions that contribute to varying line-shapes. For example, on expansion, the -121.6 ppm CF_2 resonance is seen as a triplet of triplets with couplings of 12.6 and ≈ 3 Hz. The -125.9 and -129.6 ppm resonances are complicated multiplets with fine structure splittings in the range of 4–15 Hz. The NMR transitions in the -125.1 and -126.1 ppm signals are closely spaced, and these signals appear broad and poorly resolved. The effective linewidths of most of the CF_2 signals are about 45 Hz, while the center line of the CF_3 multiplet has an effective linewidth of about 6 Hz.

A very useful feature of COSY is its ability to detect spin–spin couplings between nuclei even when the signals are broad and the coupling is not resolved. This arises because the amplitude of cross peaks in COSY is known to depend on the T_2 relaxation of the coupled nuclei, and not on T_2^* which governs the effective linewidth of a resonance [10]. ^{19}F , ^{19}F 2D COSY previously has been used to explore couplings in fluorinated alkyl chains [6,21,22]. Fig. 2(A) and (B) show the full and expanded ^{19}F , ^{19}F 2D COSY maps for perfluoroheptanoic acid. The CF_3 resonance at -84.5 ppm shows a strong cross peak to the -126.1 ppm CF_2 and a

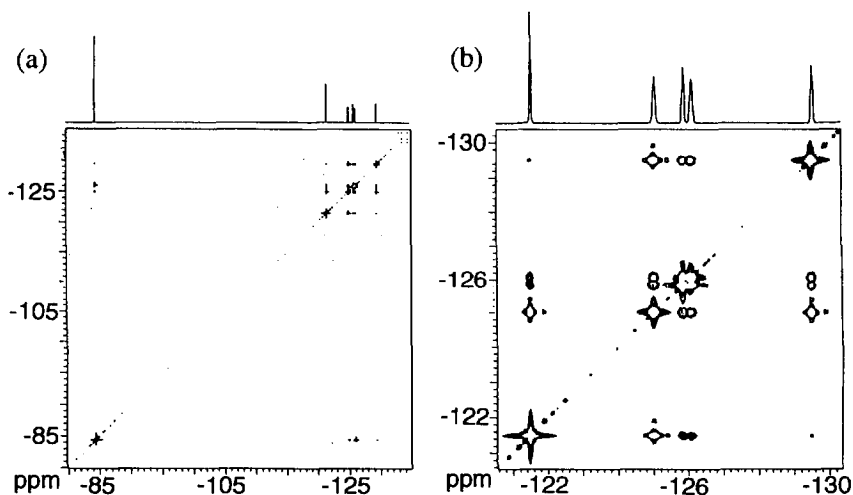


Fig. 2. (A) 470 MHz 2D COSY map showing the ^{19}F - ^{19}F spin connectivities between CF_3 and CF_2 regions of perfluoroheptanoic acid in DMSO-d_6 . (B) Expanded 2D map showing connectivities within the CF_2 region. Note the presence of dominant and weak cross peaks reflecting unusual multiple connectivities from the presence of three-, four-, and five-bond ^{19}F - ^{19}F couplings. For example, the -125.1 ppm CF_2 group (assigned to C4) shows strong cross peaks to the -121.6 and -129.6 ppm resonances and weaker correlations to the -125.9 CF_2 , the -126.1 ppm CF_2 and the -84.5 ppm CF_3 signals.

weak cross peak to the -125.1 ppm CF_2 line. Each CF_2 peak shows multiple off-diagonal connectivities. For example, the -125.1 ppm CF_3 resonance shows strong cross peaks to the -121.6 and -129.6 ppm CF_2 signals and weak cross peaks to the -125.9 and -126.1 ppm signals and the -84.5 ppm CF_3 signal. Since $^4J_{\text{FF}}$ is usually larger than $^3J_{\text{FF}}$ and $^5J_{\text{FF}}$ in heterofluoropolymers [21] and perfluorinated chains [16,17,21,22], the dominant COSY connectivities are properly interpreted as due to $n, n+2$ couplings, i.e. between next nearest neighbor groups. The dominant COSY connectivity from the CF_3 (C7) assigns the -126.1 ppm CF_2 peak to C5. The COSY map has sufficient digital resolution so that the COSY cross peak from C5 at -126.1 ppm to the neighboring -125.9 ppm CF_2 signal is clearly resolved, thus assigning C3. Similarly, the dominant COSY connectivity from the -129.6 ppm CF_2 (C6) allows the assignment of the -125.1 ppm CF_3 signal to C4. The subsequent dominant COSY cross peak from C4 then assigns the -121.6 ppm CF_2 signal to C2. The weak COSY connectivities arise from $^3J_{\text{FF}}$ and $^5J_{\text{FF}}$ couplings. The results provide further evidence that the ^{19}F - ^{19}F couplings in perfluorinated alkyl chains persist across 3, 4 or 5 bonds [8,21,22]. The $^3J_{\text{FF}}$, $^4J_{\text{FF}}$ and $^5J_{\text{FF}}$ couplings are detected by COSY despite being small relative to the apparent linewidths of the ^{19}F resonances.

To obtain ^{13}C data, we first considered the instrumental requirements for ^{19}F decoupling. One-bond ^{19}F - ^{13}C couplings are about two times larger than one bond ^1H - ^{13}C couplings, and ^{19}F shifts occur over a wider spectral range than ^1H shifts. The separation between CF_3 and CF_2 resonances on a 500 MHz NMR spectrometer, is some 30 kHz, or about six times larger than the 5 kHz needed to span a 10 ppm ^1H window. Thus, in essence for routine work with perfluorinated alkyl chains, complete ^{19}F decoupling is about a factor of 12 more difficult to achieve than complete ^1H decoupling. In early work on fluoroalkanes using noise decoupling methods [23–25], two separate ^{13}C spectra were recorded, first with the ^{19}F decoupler set at the CF_3 resonance and then at

the midpoint of the CF_2 resonances. Complete wide-band ^{19}F decoupling which allowed the recording of a single ^{13}C spectrum was only achieved by using high power (50 W) decoupler units [23,25]. At 50 W decoupler power, a rapid stream of nitrogen gas was used to cool the decoupling coil [25]. In the present study, we achieve the complete ^{19}F decoupling of CF_3 and CF_2 resonances using <2 W of power with the implementation of the GARP1 broadband decoupling scheme [11]. This low power decoupling strategy avoids the sample heating which could arise when using high power decoupling.

Fig. 3(A) shows the fully coupled 125 MHz ^{13}C NMR spectrum of perfluoroheptanoic acid processed with a 4 Hz

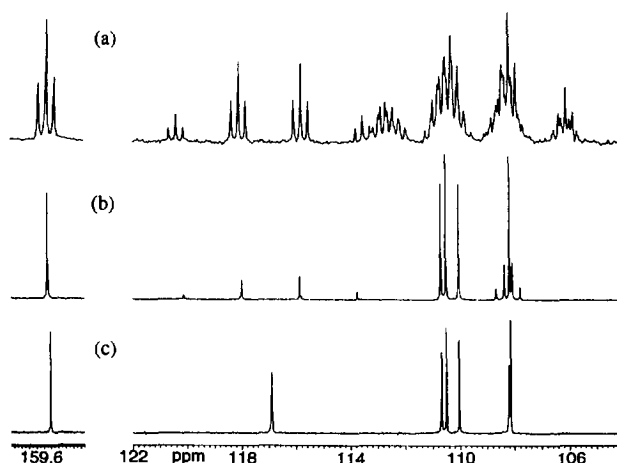


Fig. 3. Expansions of 125 MHz ^{13}C NMR spectra of perfluoroheptanoic acid in DMSO-d_6 . (A) Fluorine-coupled spectrum, 2048 scans. The six fluorinated carbon nuclei (C2–C7) give rise to >47 lines in the 15 ppm window between 121 and 106 ppm. The C1 (carboxyl) resonance appears as a triplet at 159.4 ppm with $^2J_{\text{FC}}$ of ≈ 27 Hz. (B) ^{13}C NMR spectrum with ^{19}F -decoupling of the CF_2 signals, 400 scans. The C2–C5 resonances are decoupled singlets. The quartet at 116.9 ppm with $^1J_{\text{FC}}$ arises from the C7 CF_3 . The quartet at 108.82 ppm with $^2J_{\text{FC}}$ splitting of 37 Hz is identified as C6. (C) With simultaneous ^{19}F decoupling of the CF_2 and CF_3 resonances, the fluorinated ^{13}C resonances simplify to singlets.

line broadening. The six fluorinated carbons (C2–C7) give rise to >47 resolved lines in a narrow region between 106 and 121 ppm due to one-, two- and possibly three-bond fluorine–carbon couplings. The CF₃ signal is easily recognized as the ¹³C quadruplet of triplets centered at ≈ 116.9 ppm with a one-bond ¹⁹F–¹³C coupling of 287.6 Hz and a two-bond ¹⁹F–¹³C coupling of 33 Hz. The triplet at 159.4 ppm with a two-bond ¹⁹F–¹³C coupling of ≈ 27 Hz clearly arises from the carboxyl signal. When the spectrum is processed with 0.25 Hz line broadening, these resolved multiplets hint at an upper limit of about 1 Hz for a possible three-bond fluorine–carbon coupling constant. The overlapped multiplets in the 114–106 ppm region arise from the five CF₂ groups. These multiplets yield estimates of about 267 Hz and 27–30 Hz for one- and two-bond ¹⁹F–¹³C couplings in the CF₂ groups. When low power GARP1 fluorine decoupling is applied to simultaneously decouple the CF₃ and CF₂ resonances, the ¹⁹F–¹³C couplings collapse and the fluorinated carbon signals simplify to singlets (Fig. 3(C)), allowing the location of their chemical shift values. When the decoupler is set to decouple only the CF₂ resonances, the CF₃ quadruplet of triplets centered at ≈ 116.9 ppm (C7) collapses to a simple quartet with a one-bond ¹⁹F–¹³C coupling (Fig. 3(B)). A second ¹³C quartet appears at 108.2 ppm with a two-bond ¹⁹F–¹³C coupling of ≈ 36.8 Hz. This quartet clearly arises from the perfluoromethylene next to the CF₃ group, i.e. the C6 CF₂. The remaining CF₂ resonances and the carboxyl signal are simplified to singlets.

¹⁹F, ¹³C heteronuclear 2D NMR spectroscopy on fluoro-hydrocarbons is at present essentially unexplored [5–8]. In the ¹H-detected HMQC experiment for single-bond ¹H–¹³C correlations in aliphatic hydrocarbons, the multiple quantum coherence delay is usually set to optimize for an average one-bond ¹H–¹³C coupling of ≈ 140 Hz. In perfluoroheptanoic acid, where ¹J_{CF} is ≈ 287 Hz for the CF₃ group and ≈ 266 Hz for the CF₂ groups, we used an average ¹J_{CF} coupling constant of ≈ 275 Hz for the ¹⁹F-detected HMQC experiment. Fig. 4(A) and (C) respectively show the resultant ¹⁹F, ¹³C single-bond (HMQC) shift correlation maps for perfluoroheptanoic acid obtained at a 25.873 kHz ¹⁹F spectral window to include the CF₃ group and at a 5.194 kHz ¹⁹F window to optimize for the correlations in the CF₂ region. The corresponding 1D ¹⁹F and ¹⁹F-decoupled ¹³C spectra are plotted on the top and side of the 2D maps. We have implemented ¹³C decoupling in the *f*₁ dimension to collapse the ¹³C multiplets to their chemical shift positions. Under these conditions, the HMQC experiment is expected to show single cross peaks between the A spin (¹⁹F) and the X spin (¹³C). Five single, AX-type cross peaks are clearly seen for the CF₂ groups in the wide (Fig. 4(A)) and narrow (Fig. 4(C)) window HMQC maps. Three “apparent” cross peaks are seen for the CF₃ group in the wide window map (Fig. 4(A)). The two outer cross peaks are “sinc wiggles” artifacts from the weighting function used in data processing as a “compromise” choice due to the large variation in the ¹⁹F NMR

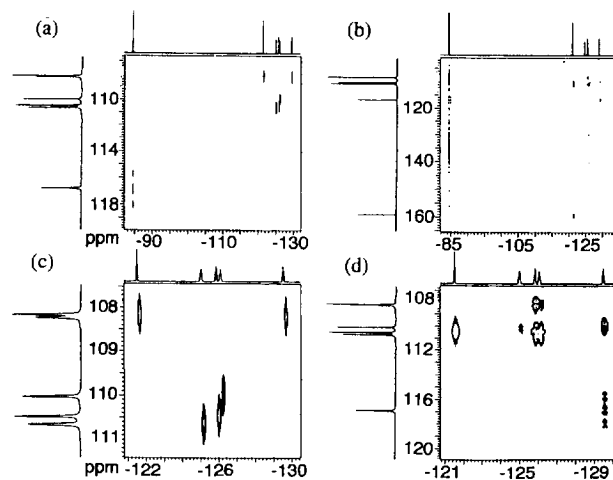


Fig. 4. (A), (C) ¹⁹F-detected 2D ¹⁹F–¹³C single bond correlation (HMQC) maps of perfluoroheptanoic acid in DMSO-*d*₆; (B), (D) ¹⁹F-detected 2D ¹⁹F–¹³C multi-bond correlation (HMBC) maps of perfluoroheptanoic acid optimized for ²J_{FC} couplings of ≈ 33 Hz. The responses from the CF₃ at 116.9 ppm show “sinc wiggles” due to the weighting function in the data processing.

lineshapes. Only the central cross peak is the “true” AX correlation for the CF₃ group.

The HMQC cross peaks connect the fluorine atoms of the single CF₃ and five CF₂ groups to their respective carbons. With COSY data available, the HMQC results could be directly interpreted to yield the ¹³C assignments. However, we choose to first independently consider the heteronuclear evidence. The 116.9 and 108.2 ppm ¹³C resonances were unequivocally identified as C7 and C6 by fluorine decoupling (above). The direct correlations from these ¹³C signals to the –84.5 ppm and –129.6 ppm ¹⁹F resonances further validates their assignment to the C7 CF₃ and C6 CF₂ groups obtained by COSY. This leaves the four central CF₂ groups (C2–C5) to be considered.

Fig. 4(B) and (D) show the corresponding multi-bond (HMBC) ¹⁹F, ¹³C shift correlation maps for perfluoroheptanoic acid. Similar to HMQC, these are the results of two separate experiments—one at a 25.873 kHz ¹⁹F window to include multi-bond correlations from the CF₃ group and one at a 5.174 kHz ¹⁹F window to optimize for the multi-bond correlations in the CF₂ region. In the ¹H-detected HMBC experiment, the long range multiple quantum coherence is typically tuned for delays ranging from 50 to 90 ms, corresponding to two- and three-bond ¹H, ¹³C couplings of 10–6 Hz [13,15]. Unlike the case for hydrocarbon molecules where the ²J_{HC} and ³J_{HC} couplings are in the same range, ²J_{FC} is usually larger than ³J_{FC} in fluorinated molecules. Indeed, the fluorine-coupled carbon spectrum of perfluoroheptanoic acid (Fig. 3(A)) suggests an upper limit of 1 Hz for ³J_{FC}, while ²J_{FC} is an order of magnitude larger and in the vicinity of ≈ 30 Hz. This implies that the long range multiple quantum coherence in fluorinated alkyl chains can be simply optimized for two-bond ¹⁹F, ¹³C couplings ranging from 27 to 36 Hz, corresponding to delays of 18.5–13.9 ms. Experimentally, we found a 15 ms delay time in HMBC to be very

Table 1
 ^{19}F and ^{13}C NMR assignments of $\text{CF}_3(\text{CF}_2)_5\text{COOH}^a$

	^{19}F (ppm) ^b	^{13}C (ppm) ^c
C1 (COOH)		159.410
C2 (CF ₂)	– 121.553	108.164
C3 (CF ₂)	– 125.902	110.513
C4 (CF ₂)	– 125.068	110.690
C5 (CF ₂)	– 126.126	110.052
C6 (CF ₂)	– 129.561	108.234
C7 (CF ₃)	– 84.531	116.910

^a Data at 28 °C.

^b ^{19}F chemical shifts expressed relative to CFCl_3 scale by setting a 3% trifluoroacetic acid in D_2O solution to –76.0 ppm. The negative values indicate resonances towards higher field.

^c ^{13}C chemical shifts expressed on TMS scale by setting $\text{DMSO}-d_6$ to 39.5 ppm.

effective for the observation of two-bond ^{19}F , ^{13}C correlations in perfluoroheptanoic acid. For example, in the wide window HMBC (Fig. 4(B)), the C7 CF₃ signal at –84.5 ppm elicits a strong $^2J_{\text{FC}}$ response at 108.2 ppm (C6) with an additional ^{19}F -coupled direct response at 116.9 ppm (C7). The –121.6 ppm CF₂ resonance evokes a strong $^2J_{\text{FC}}$ correlation at the 159.4 ppm carboxyl resonance, and can thus be assigned to the C2 CF₂ group, in agreement with the COSY data. It also elicits a strong $^2J_{\text{FC}}$ connectivity to the 110.5 ppm signal, which can now be assigned to C3. In the narrow window HMBC (Fig. 4(D)), the C6 CF₂ (–129.6 ppm) shows two strong two-bond cross peaks. The first is the $^2J_{\text{FC}}$ correlation to C7 at 116.9 ppm, which again appears as three “apparent” cross peaks due to “sinc wiggle” artifacts. Again, only the central cross peak is the “true” two-bond correlation from the C6 CF₂ to the C7 CF₃. The second $^2J_{\text{FC}}$ correlation from the C6 CF₂ is to the 110.1 ppm CF₂ carbon signal, which is now assigned as C5. These six separate two-bond responses suffice for a full assignment from the heteronuclear data. Only the ^{13}C signal at 110.7 ppm and the ^{19}F signal at –125.1 ppm remain to be assigned to the C4 CF₂. Further expansions and analysis of the remaining multi-bond responses from the C4, C3 and C5 CF₂ signals in the narrow window HMBC showed that we observed a full complement of two-bond correlations in perfluoroheptanoic acid. The remaining data served as a check for consistency of the ^{19}F and ^{13}C NMR assignments summarized in Table 1. The ^{19}F assignments derived from the ^{19}F -decoupled ^{13}C spectra and the ^{19}F , ^{13}C correlation strategies agree completely with the results from the COSY.

Our ^{19}F NMR assignments for the C2–C5 CF₂ groups of perfluoroheptanoic acid in Table 1 differ from those reported by Battais et al. [26]. The most disturbing contrast is their assignment of the –121.5 ppm signal to an interior CF₂ group (C5) instead of the CF₂ group adjacent to the carboxylic acid, i.e. C2. We believe their CF₂ assignments for perfluoroheptanoic acid to be in error as they reported their findings from a one-dimensional ^{19}F NMR spectrum of a complex mixture of perfluorinated acids (ranging from two

to seven carbon chains) obtained by the potassium permanganate oxidation of a mixture of perfluoroolefins. Our observations from the COSY connectivities and the two-bond HMBC correlation to the carboxyl resonance give clear evidence that the –121.5 ppm signal arises from the C2 CF₂ group. This agrees with recent 2D COSY data for perfluoroheptanoic acid [24,25]. The literature assignments have been used by the French group [26–28] to derive paramagnetic ^{19}F shift increments for the carboxylic acid group and to develop models for the a priori calculation of the ^{19}F chemical shifts of linear fluoroalkyl carboxylic acids. The quality of the calculational models ultimately depends on correct experimental assignments and shifts.

4. Conclusion

In this paper we have combined efficient fluorine decoupling with the successful implementation of ^{19}F -detected HMQC and HMBC NMR experiments to obtain single- and two-bond ^{19}F , ^{13}C 2D NMR correlations in perfluoroheptanoic acid. This represents a new approach with potential for a fuller structural characterization of the carbon backbones of fluorocarbon molecules. A complete set of unequivocal ^{19}F and ^{13}C NMR assignments for perfluoroheptanoic acid has been derived.

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