# Analysis of the <sup>19</sup>F and <sup>1</sup>H NMR Spectra of a Number of Polyfluoroindenes

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<sup>19</sup>F and <sup>1</sup>H NMR spectra of the products of nucleophilic attack on octafluoroindene are analysed and structures assigned. The major product in the reaction of butyllithium with octafluoroindene is 3-methylheptafluoroindene, with sodium borohydride it is 2-hydroheptafluoroindene and with sodium methoxide it is 3-methoxyheptafluoroindene. Vacuum pyrolysis of undecafluorotricyclo[5.2.2.0<sup>2,6</sup>]undeca-2,5,8-triene, with elimination of  $C_2F_4$ , gives 6-hydroheptafluoroindene as the major product. The NMR assignments are based on the unambiguous synthesis via vacuum pyrolysis of 5,6-dihydrohexafluoroindene, 3-hydro- and 3-methyl-heptafluoroindene and the large long-range coupling of 15 Hz assigned to the F-2, F-6 interaction.

# INTRODUCTION

The syntheses of octafluoroindene (1) and several substituted polyfluoroindenes have been reported.<sup>1-3</sup> Octafluoroindene can be obtained quantitatively by the pyrolysis *in vacuo* of polycyclic precursors. Substituted polyfluoroindenes can be prepared by an analogous route or by nucleophilic substitution in octafluoroindene.<sup>2.4</sup>

This paper reports the analysis of the <sup>19</sup>F and <sup>1</sup>H NMR spectra of some polyfluoroindenes, prepared by nucleophilic substitution in octafluoroindene, and outlines their structural assignments by NMR spectroscopy.

<sup>19</sup>F NMR studies of tetrafluorobenzo[b]furans<sup>5-7</sup> and tetrafluorobenzo[b]thiophens<sup>8,9</sup> have been reported. In these systems and in perfluoro-1,2dihydronaphthalene<sup>10</sup> substitution of fluorine by nucleophiles occurs in the aromatic ring, unlike octafluoroindene where substitution takes place in the 5-membered ring, or octafluorostyrene<sup>11</sup> where substitution occurs in both the ring and sidechain. Russian workers<sup>12</sup> have reported the chemical shifts of some substituted fluorinated indenes but have not carried out complete <sup>19</sup>F NMR analysis. There are also reports on partially or completely fluorinated molecules containing condensed 5- and 6-membered rings which provide some analogous <sup>19</sup>F shift information.<sup>13,14</sup>

The diagnostic importance of through-space *peri* F,F coupling constants (30–82 Hz) has been indicated in <sup>19</sup>F NMR studies of polyfluoronaphthalenes<sup>15</sup> and perfluoroazanaphthalenes,<sup>16</sup> and it is also well known that *ortho* and *para* F,F coupling constants are useful in structural elucidation, although the ranges of J(FF) ortho (19–21 Hz) and J(FF) para (10–20 Hz) overlap; the values of J(FF) meta are much smaller. There is, however, no information on long-range interring F,F coupling constants in indene systems.

In the case of octafluoroindene (1) the *peri* internuclear distances F-1, F-7 and F-3, F-4 are much larger than in polyfluoronaphthalenes. The *peri* F,F coupling constants are thus expected to be quite small and may be in the *para*- or even the *meta*-F,F coupling constant range. This was one of the main problems encountered in making unambiguous assignments in the indene system. The other complication was the appearance of surprisingly large inter-ring F,F coupling constants.

## EXPERIMENTAL

<sup>19</sup>F and <sup>1</sup>H NMR spectra were measured on a Brüker HX90E at 84.670 MHz and 90.000 MHz at 22 °C with internal deuterium lock at 13,810 MHz; *d*-chloroform was the standard solvent and CFCl<sub>3</sub> and TMS, respectively, were the internal references. Measurements were made on calibrated paper at expansions up to 1 Hz/cm and sweep rates down to 0.1 Hz/s. Sweeps were linear within the accuracy of the frequency counter ( $\pm$ 0.1 Hz) and, consequently, the accuracy of the measurements was estimated as  $\pm$ 0.2 Hz providing high resolution was available, e.g. **1**. One typical limitation was the broadening of multiplets by a number of unresolvable small couplings.

During the preparative work measurements were carried out under varying conditions, depending mainly on the stability and the quantity of the sample (see Table 2).

<sup>19</sup>F and <sup>1</sup>H spectra were also measured on a Varian A56/60D at 56.46 MHz and 60.00 MHz at 40 °C. The sweepwidths were calibrated by audio modulation of the magnetic field. Chemical shifts (downfield positive) are reported in ppm from the reference.

## **RESULTS AND ANALYSIS**

Assignment of the <sup>19</sup>F spectrum of 1 was supported by a partial analysis<sup>13</sup> of the <sup>19</sup>F spectrum (Fig. 1) of the

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Figure 1. The <sup>19</sup>F NMR spectrum of perfluoro-1,2dihydronapthalene (12) at 84.670 MHz.

related compound perfluoro-1,2-dihydronaphthalene (12) (Table 1). Two large through-space  ${}^{4}J(FF)peri$  couplings identified the F-1, F-8 and F-4/F-5 resonances, the shift of the F-2 absorptions being ascertained by elimination. A high-field resonance at -158 ppm, distinct from the rest of the spectrum, was assigned to a vinylic fluorine by analogy with F-3 in 1. J(45)peri was characteristic of the naphthalenic pericoupling whilst J(18)peri was consistent with the equivalent couplings in the related compounds 13.<sup>17,18</sup> An alternative assignment of 12 with the 32 Hz coupling reassigned to J(23) was discounted as the equivalent coupling in perfluorocyclopentene is 15 Hz, and in perfluorocyclohexadiene is 13 Hz.<sup>19</sup>



The most novel feature in the analysis of 1 is the magnitude of the inter-ring coupling constants, which are much larger than analogous F,F coupling constants in fluorinated styrenes.<sup>20,21</sup> The validity of these large inter-ring couplings and the remainder of this assignment of 1 is evident after examining the <sup>19</sup>F NMR spectra of a number of specifically substituted polyfluoroindenes (**2–11**). The coupling constants and chemical shifts are presented in Tables 2 and 3.

Table 1. <sup>19</sup>F Chemical shifts and coupling constants of 12<sup>a</sup>

$\begin{array}{c} 5 \\ 7 \\ \hline F \\ 8 \\ 1 \end{array}$						
Chemical shift (ppm)	Assignment	(F)				
-117.12 [2]	Methylene—F	(1)				
-125.49 [2]	Methylene—F	(2)				
-135.71 [1]	Aromatic-F	(8)				
-138.53 [1]	Vinylic/aromatic—F	(4/5)				
-140.56 [1]	Vinylic/aromaticF	(4/5)				
-146.20 [1]	Aromatic—F	(6/7)				
-148.33 [1]	Aromatic—F	(6/7)				
-158.58 [1]	Vinylic—F	(3)				
$J(45) = 62 \pm 2 Hz$	J(18) = 32.2	$J(18) = 32.2 \pm 0.2$ Hz				

<sup>a</sup> Brackets include relative integrations. Measured in CDCl<sub>a</sub>, internal CFCl<sub>3</sub>.

In the hexafluoroindenes (6 and 9) and the tetrafluoroindene (10) replacement of F-2 or F-6 resulted



in the absence of the long-range J(26) coupling, as expected. The structure of **6**, obtained by nucleophilic substitution of **1** with borohydride, was confirmed by other spectroscopic and analytical data whilst **9** and **10** have been unambiguously synthesized and fully characterized.<sup>2,17</sup>

1,1,4,5,6,7-Hexafluoroindene(6) exhibited four <sup>19</sup>F triplets and an AB type proton spectrum. The strong CF=CF stretching vibration at  $1754 \text{ cm}^{-1}$  in the IR spectrum of 1 corresponded only to a weak absorption at  $1592 \text{ cm}^{-1}$  for 6, as anticipated for a vinylic CH=CH stretching vibration.

Pyrolysis of undecafluorotricyclo $[5.2.2.0^{2.6}]$ undeca-2,5,8-triene (14), *in vacuo*, yields an unequal mixture of the two heptafluoroindenes 7 and 8. The <sup>19</sup>F NMR spectrum can be used to identify the major and minor isomers from the data in this paper, and it seems unlikely that any other technique could offer a solution to this analytical problem which is of great mechanistic interest.



The <sup>19</sup>F NMR spectrum of a mixture of 7 (20%) and 8 (80%) was analysed using SCS ( $F \rightarrow H$ ) predictions from analogous fluorinated benzothiophenes<sup>5</sup> and benzofurans,<sup>8</sup> i.e. SCS ( $F \rightarrow H$ ) ortho = +20±2 ppm and SCS ( $F \rightarrow H$ ) meta = -4±1 ppm [SCS( $F \rightarrow H$ ) is the substituent chemical shift induced in a fluorine resonance by the hypothetical replacement of a neighbouring fluorine atom by a hydrogen atom]. The following scheme gives the experimental SCS and the predicted values are in parentheses. The sequence of the assignments of F-4 to F-7 was therefore unambiguous and the coupling constants were consistent with those in 1, J(26) being present in 7, but not in 8 or 9.

The <sup>1</sup>H spectrum of **8** was a symmetrical multiplet (J = 5.5, 8.0, 9.8 Hz). Heteronuclear <sup>1</sup>H decoupling confirmed the expected *ortho* and *meta* H,F relationships.



The indene **10** was prepared independently<sup>17</sup> but its NMR spectrum is included for the sake of completeness. Both the <sup>19</sup>F and <sup>1</sup>H spectra are as expected. The <sup>1</sup>H NMR spectrum exhibits three multiplets (2:1:1) with J(AB) = 5.6 Hz. In the <sup>19</sup>F NMR spectrum interring SCS values are larger than expected, but this can be accounted for by changes in the measuring conditions.

Another fluoroindene which provides invaluable confirmatory NMR data, and has been unambiguously synthesized and characterized<sup>2</sup> is the heptafluoroindene **5**, obtained by the routes outlined below. Prior to these syntheses a mixture of the heptafluoroindenes **4** and **5** had been isolated as monosubstitution products from the reaction of **1** with the nucleophile sodium borohydride, the disubstitution product being the indene **6**, mentioned above. Substitution in the 5-membered ring was evident from the vinylic double bond, the absorption in the IR spectrum due to a CH=CF being at  $1670 \text{ cm}^{-1}$  for **4** and  $1640 \text{ cm}^{-1}$  for **5**.



The data obtained for compounds 4 and 5 are outlined in Tables 2 and 3. The important difference between their spectra is the presence of the large F-2/ F-6 coupling in 5 but not in the spectrum of 4. Peaks were assigned by assuming the inter-ring SCS to be small, and homonuclear decoupling confirmed the assignment of the couplings. Substitution in the vinyl positions leads to SCS of +24 and +28 ppm which is only slightly larger than similar ortho SCS ( $F \rightarrow H$ ) in aromatic systems. The mixture of heptafluoroindenes obtained by nucleophilic attack of borohydride on 1 gave a predominance of one product. NMR allows us to assign structure 4 to this product since its spectrum does not possess the large F-2/F-6 coupling. The minor product is 5, in disagreement with earlier ESCA work,<sup>4</sup> and recently conclusively confirmed with the unambiguous synthesis of pure 5 by the routes outlined above.

Nucleophiles initially attack octafluoroindene at a vinylic site in the 5-membered ring. Physical and spectroscopic data apart from NMR do not allow the differentiation of a 2- or a 3-substituted isomer; the large J(26), however, in the <sup>19</sup>F NMR spectrum of the 3-substituted isomer is diagnostic. This coupling has enabled an assignment to be made for the product of the reaction of **1** with methyllithium, and for the product on its reaction with sodium methoxide.<sup>2</sup>

The sole volatile product (2) from the reaction of methyllithium with 1 possessed an absorption in the IR spectrum at ~1700 cm<sup>-1</sup> (CF=CCH<sub>3</sub>), confirming vinylic substitution. In the <sup>19</sup>F NMR spectrum the intensity distortion in peaks attributed to F-4 and F-5 confirmed their *ortho* relationship, the *meta* related peaks being identified by  ${}^{4}J(FF)meta$ —an assignment confirmed by homonuclear decoupling. The band attributable to F-6 approximates to a pair of triplets (Fig. 2) and includes, in addition to the expected couplings, a 15 Hz splitting assigned to J(26) by analogy with 1. The <sup>1</sup>H NMR spectrum is a multiplet with



**Figure 2.** The <sup>19</sup>F NMR spectrum of a mixture of 3-methylheptafluoroindene (2) and 1-methylenehexafluoroindene (3) at 84.670 MHz.

splittings of 2.7, 2.7, 2.3 and 1.5 Hz and confirms the position of substitution in **2**. Chemical evidence conclusively proved the structure of **2** since it was the sole product of the pyrolysis of methylundecafluorotricyclo- $[5.2.2.0^{2.6}]$ undeca-2,5,8-triene (**15**) and dehydrofluorinated on pyrolysis to an asymmetric compound (**3**).

Structure	F-1	F-2	F-3	F-4	F-5	F-6	F-7	Measuring conditions
1	-124.62 -124.31	-158.05 -160.32	144.34 144.32	145.23 145.70	147.04 148.25	-151.74 -153.00	<b>138.1</b> 0 <b>139.3</b> 0	c.5% w/v <sup>ь</sup> c.50% w/v <sup>c</sup>
2 2	127.20 125.47	-147.71 -145.49	(2.06)	150.33 148.60	-151.68 -149.34	-158.30 -155.91	-143.49 -141.24	ط Major (75%) <sup>6</sup> component
3	(6.23)	-158.52	-150.55	-149.97	-154.73	-157.83	-143.48	Minor (25%) <sup>b</sup> component
5 5	<b>126.56</b> <b>128</b> .11	-133.09 -130.23	(5.53)	-145.32 c147.89	148.54 c147.89	155.31 158.13	139,97 135,83	ь Minor (30%) <sup>d</sup> component
4	-118.56	(5.28)	120.22	-146.49	-151.42	-153.93	-141.89	Major (70%) <sup>d</sup> component
6	121.08	(6.03 or 6.67)	(6.03 or 6.67)	145.39	-150.80	-155.38	-141.62	e
7	-125.30	-161.04	-144.23	-122.84	(6.87)	-128.65	-142.68	Minor (20%) <sup>5</sup> component
8	-125.30	-158.17	145.02	-149.41	-124.17	(6.87)	-116.28	Major (80%) <sup>b</sup> component
9	126.22	-161.56	-144.71	-127.29	(7.04)	(7.04)	-121.31	b
10	(3.41)	(6.55 or 6.88)	(6.55 or 6.88)	-148.15	-161.67	159.23	144.36	f
11	-121.73 -124.4	173.64 174.1	(4.1)	146.14 148.7	148.66 152.6	153.97 157.8	-140.93 144.3	g

Table 2. Chemical shifts (ppm upfield of CFCl<sub>3</sub>) of 1-11<sup>a</sup>

\* Proton chemical shifts in parentheses and referenced to internal TMS.

<sup>b</sup> CDCl<sub>3</sub> solvent, internal CFCl<sub>3</sub> reference, 84.67 MHz, 56.46 MHz, 40°C.

° CD<sub>3</sub>COCD<sub>3</sub>solvent, internal CFCI<sub>3</sub> reference, 84.67 MHz, 22 °C.

 $^{\rm d}$  Neat, external CFCl\_3 reference, 56.46 MHz, 40 °C. <sup>e</sup> Undiluted sample, internal CFCl<sub>3</sub> reference,

<sup>f</sup> CFCl<sub>3</sub> reference and solvent, 56.46 MHz, 40 °C.

<sup>9</sup> Ref. 12: pure compound, internal C<sub>6</sub>F<sub>6</sub>, 56.46 MHz.

## Table 3. Moduli of the coupling constants (Hz)

J	1	2	3	5	4	6	8	9	13A
12	10.8	12.9		12.2			11.5	10.8	
13	7.4	(2.7)ª			10.8		7.4	7.5	
14	2.9	2.6		1.5	3.5	2.4	3.1	3	0.6
15	0.9	c.0.5			0.4		0.8		2.3
16	0.7	c.0.5			0.8				1.1
17	4.3	4			4.4		4.2	4	25
23	9.8	(2.3)ª	5.0			(6.2) <sup>a</sup>	8.8	8.9	9.4
24	7.0	6	5.5	6.5			6.2	5. <del>9</del>	7.4
25	1.8		2				2.5		1.5
26	15.0	15.0	14.5	15					8.3
27	3.0		2				2.7	2.7	
34	8.5		6.0		11.9		8.8	9.3	7.57
35	0.7				0.4		0.4		0.8
36	4.9				4.4				3.9
37	11.7				11.7		12.0	12.0	8.0
45	18.1	17	20.0	20	18.3	19.0	20.0		
46	3.4	1.3	c.0.5	1.6	3.8	2.4	(5.5) <sup>a</sup>		
47	14.4	17	14.0	15.0	16.5	16.5	14.5	19	
56	15.3	15.0	17.0	14.6	14.8	15.8	(9.8) <sup>a</sup>		
57	7.7	6.8	5.0	6.5	6.8	5.8	8		
67	19.0	19.3	19.5	18.9	19.0	19.7	(8.0)ª		

<sup>a</sup> Parentheses include H,F and H,H coupling constants.

22 °C.

The <sup>19</sup>F NMR spectrum of a mixture of **2** and **3** is presented in Fig. 2. Six peaks of equal intensity were obtained for **3**. The penultimate upfield resonance (F-6) was a quartet coupled to the adjacent F-2 resonance. This, in conjunction with a low-field <sup>1</sup>H doublet [J(17) = 9.2 Hz], identified **3** as the only possibility. The dissimilar *meta* couplings, following the trend in **1** and **2**, supported this assignment and the lack of intensity distortion in the adjacent F-3 and F-4 peaks implied a small J(34), in agreement with the analysis of **1**.





Vinylic substitution in the methoxyheptafluoroindene obtained from the reaction of 1 with sodium methoxide was evident from an IR absorption at  $\sim 1700 \text{ cm}^{-1}$  (CF=COCH<sub>3</sub>). In the <sup>19</sup>F NMR spectrum the penultimate upfield peak determined the position of substitution, the F-6 quartet indicating a finite J(26) and showing the structure of **11** to be 3-methoxyheptafluoroindene. It was anticipated that the SCS for substitution of a fluorine atom by a methoxyl group would be small and negative, as found in trifluoroethenes,<sup>22</sup> and the present data bear out this prediction. The shift data are compatible with the unassigned values published by Karpov et al.<sup>12</sup> for 11 (Table 2); they also found J(12) to be 12.2 Hz and J(HF) to be 4.2 Hz, in accord with our measurements. Second-order effects in the <sup>19</sup>F spectrum of  $\mathbf{1}$  were



Figure 3. The <sup>19</sup>F NMR multiplets of octafluoroindene (upper spectra) and a first-order reconstruction of the multiplets (lower spectra) at 84.670 MHz.

minimized in  $d_6$ -acetone and linewidths of 0.35 Hz were obtained. The spectrum was analysed by firstorder methods and an unequivocal assignment of the splittings was made. This was confirmed by calculating the multiplet envelopes and their reconstruction (Fig. 3) illustrates the accuracy attained (better than  $\pm 0.1$  Hz). Each carbocyclic resonance was distinguished by two splittings of between 15 and 20 Hz, i.e. the typical range of  ${}^{3}J(FF)$ ortho and  ${}^{5}J(FF)$ para in monocyclic and bicyclic systems.

Coupling constants in the 5-membered ring were not helpful in establishing an assignment, although the following values were found in perfluorocyclopentene.<sup>19</sup>



However, for comparison we have recently analysed in detail the <sup>19</sup>F NMR spectrum of the following compound,



and the coupling constants are noted in the last column of Table 3 using the same numbering scheme as in **1**. These couplings are in general accord, except for the *peri* F,F and J(26)couplings, and provide some further support for our assignments.

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### REFERENCES

- 1. W. J. Feast and W. E. Preston, Tetrahedron 28, 2805 (1972).
- W. E. Preston, W. J. Feast and W. K. R. Musgrave, 5th European Fluorine Symposium, Aviemore, 1974; W. E. Preston, PhD Thesis, University of Durham (1972).
- R. E. Banks, A. C. Harrison and R. N. Haszeldine, J. Chem. Soc. C 2102 (1966).
- D. B. Adams, D. T. Clark, W. J. Feast, D. Kilcast, W. K. R. Musgrave and W. E. Preston, *Nature (London). Phys. Sci.* 239, 47 (1972).
- 5. R. J. Abraham. D. F. Wileman. G. R. Bedford and D. Greatbanks, Org. Magn. Reson. 4, 343 (1972).
- P. J. N. Brown and E. F. Mooney, *Tetrahedron* 23, 4047 (1967).
- G. M. Brooke, W. K. R. Musgrave and T. R. Thomas, J. Chem. Soc. C 3596 (1971).
- M. D. Castle, E. F. Mooney and R. G. Plevey, *Tetrahedron*, 24, 5457 (1968).
- 9. G. M. Brooke, B. S. Furniss and W. K. R. Musgrave, J. Chem. Soc. C 580 (1968).
- T. W. Bastock, A. E. Pedler and J. Tatlow, J. Fluorine Chem. 8, 11 (1976).
- 11. A. E. Pedler, J. C. Tatlow and A. J. Uff, Tetrahedron 25, 1597 (1969).
- V. M. Karpov, V. E. Platonov and G. Yakobson, *Izv. Sib. Otd.* Akad. Nauk SSSR Ser. Khim. Nauk 2, 124 (1974); V. M. Karpov, V. E. Platonov and G. Yakobson, *Izv. Akad. Nauk* SSSR Ser. Khim. 11, 2647 (1976) and 2, 375 (1976).
  W. J. Feast, R. R. Hughes and W. K. R. Musgrave, *J.*
- W. J. Feast, R. R. Hughes and W. K. R. Musgrave, J. Fluorine Chem. 10, 585 (1977).

- D. V. Gardener, J. F. W. McOmie, P. Albriktsen and R. K. Harris, J. Chem. Soc. C 1994 (1969).
- (a) D. Price, H. Suschitzky and D. Hollies, *J.C.S.* Chem. Soc. C 1967 (1969):

(b) R. A. Fletton, R. D. Lapper and L. F. Thomas. J. Chem. Soc. Chem Commun. 1049 (1969).

- R. S. Matthews, Org. Magn. Reson. 8, 240, 628 (1976); 9, 318 (1977).
- 17. G. M. Brooke, private communication.
- N. E. Akhmetova, N. G. Kostina, V. I. Mamatyak, A. A. Shtark and V. D. Steingarts, *Izv. Sib. Otd. Akad. Nauk SSSR* Ser. Khim. 6, 86 (1973).
- J. Feeney, L. H. Sutcliffe and S. M. Walker, *Trans. Faraday* Soc. 62, 2969 (1966).
- D. A. Burgess, I. D. Rae and J. D. Snell, Aust. J. Chem. 30, 543 (1977) and references therein.
- 21. R. S. Matthews, J. Magn. Reson. 29, 65 (1978).
- J. W. Emsley and L. Phillips, in *Progress in Nuclear Magne*tic Resonance, Vol. 8, ed. by J. W. Emsley, J. Feeney and L. H. Sutcliffe. Pergamon Press, Oxford (1972).
- 23. R. J. Abraham, D. B. Macdonald and E. S. Pepper, J. Am. Chem. Soc. 90, 147 (1968).

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