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# FLUORINE-19 NMR SPECTROSCOPY OF POLYCHLOROPOLYFLUORONAPHTHALENES. THE IDENTIFICATION OF FLUORINE EXCHANGE PRODUCTS

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## SUMMARY

Fluorine-19 NMR of the products of halogen exchange between octachloronaphthalene and caesium fluoride or potassium fluoride is reported. Twelve polychloropolyfluoronaphthalenes, although in complex mixtures and largely inseparable, could be identified by fluorine-19 NMR. One of the easily recognised parts of the fluorine NMR spectra was the ABX of 1,2,3,6,8-pentachloro-4,5,7-trifluoronaphthalene with a peri through-space F,F coupling of 95.8Hz. Initial exchange occurs at the 1-position in octachloronaphthalene and subsequent exchange occurs at the 3-position and/or at the 8-position. After four exchanges the dominant product was found to be 1,3,6,8-tetrachloro-2,4,5,7-tetrafluoronaphthalene in an experiment in aprotic solvent.

## INTRODUCTION

F-19 NMR measurements are reported for mixtures of polychloropolyfluoronaphthalenes in d-chloroform, the products of halogen exchange of octachloronaphthalene (1) with potassium fluoride or caesium fluoride with or without dipolar aprotic solvent. With one exception, these polyhalonaphthalenes could not be separated by partial crystallisation, column chromatography or sublimation although the composition of the mixtures could be radically changed. This paper describes an assignment of the F-19 NMR chemical shifts of the involatile polychloropolyfluoronaphthalenes whose empirical formulae are $C_{10}Cl_{8-n}F_n$ where n is 1 to 4.

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To check the method and to confirm the substituent chemical shifts the reaction mixtures from perchloro-benzene, -pyridine, -quinoline and -isoquinoline were exchanged in aprotic solvent, confirming the known chemistry and shifts[1,2]. For instance, treatment of hexachlorobenzene(**2**) with potassium fluoride or caesium fluoride in solution (DMSO, DMF, dimethylsulphone, sulpholane) at higher temperatures leads to all the expected intermediate products although 1,3,5-trichloro-2,4,6-trifluorobenzene is kinetically very stable and dominates the product distribution[1,2,3]. Similarly, treatment of highly chlorinated heterocycles at lower temperatures is known to give incomplete exchange[2].

Past glc studies[4] of the products of halogen exchange in polyhaloaromatics proved interesting, confirming known reactions, but unable to distinguish between the isomers produced. Here we identify, by NMR, many of the polychloropolyfluoronaphthalenes produced by heterogeneous halogen exchange reaction.

## REACTIONS

Complete replacement of all the chlorines in octachloronaphthalene can be achieved with anhydrous KF or CsF at 300-500°C. For incomplete reaction and to prepare polychloropolyfluoronaphthalenes, reactions were carried out in two ways, in dipolar aprotic solvent and without solvent:

(a) by heating 10 mg of (1) with 50 mg of anhydrous KF (or CsF) in 1 ml of sulpholane (5% d6-DMSO as lock) at 100-180°C in an NMR tube. The $^{19}F$ spectra were measured at 60°C. Cooling the solutions to ambient crystallised the more insoluble components i.e. monofluoro- and difluoro-isomers, whilst cooling the solutions to 10°C crystallised out most of the partially fluorinated components.

Attempts at separating these mixtures largely failed although some of the more volatile components ($n>4$) should be separable by glc. With repeat sublimations in vacuo it was possible to separate compound **12**, 1,3,6,8-tetrachloro-2,4,5,7-tetrafluoronaphthalene to >98% purity as determined by NMR (found, C 36.0%, H 0.1%, $M^+$ 336; $C_{10}Cl_4F_4$ requires C 35.7%, H 0.0% and M=336 for $C_{10}{}^{35}Cl_4F_4$ ). The mass spectrometric pattern confirmed the number of chlorine atoms in the molecule.

(b) by high temperature fluorine exchange in the absence of a solvent with a 10:1 molar excess of KF over (1) at 400°C in vacuo in one end of a Carius tube. Over a period of 24hours, product sublimed into the other end of the tube at room temperature. This involatile pyro-fraction represented a yield of <7% and, although complicated, contained mostly mono-, di- and trifluorinated products. An analysis of its F-19 spectrum is reported here. Less than 4% (mole fraction) of the material visible by F-19 NMR remained unidentified. The systematic names and molar percentage for **3**-**14** are as follows:

| | | |
|---|---|---|
| 3 | 1,2,3,6,8-pentachloro-4,5,7-trifluoronaphthalene | 5% |
| 4 | 1,2,3,5,7-pentachloro-4,6,8-trifluoronaphthalene | 2.5% |
| 5 | 1,2,3,4,5,7-hexachloro-6,8-difluoronaphthalene | 1.5% |
| 6 | 1,2,3,5,7,8-hexachloro-4,6-difluoronaphthalene | 4% |
| 7 | 1,2,3,5,6,8-hexachloro-4,7-difluoronaphthalene | 3% |
| 8 | 1,2,3,5,6,7-hexachloro-4,8-difluoronaphthalene | 7% |
| 9 | 1,2,3,6,7,8-hexachloro-4,5-difluoronaphthalene | 10.5% |
| 10 | 1,2,3,4,5,6,7-heptachloro-8-fluoronaphthalene | 49% |
| 11 | 1,2,3,4,5,6,8-heptachloro-7-fluoronaphthalene | 13% |
| 12 | 1,3,6,8-tetrachloro-2,4,5,7-tetrafluoronaphthalene | 2% |
| 13 | 1,3,5,7-tetrachloro-2,4,6,8-tetrafluoronaphthalene | trace |
| 14 | 2,3,6,7-tetrachloro-1,4,5,8-tetrafluoronaphthalene | trace |

## RESULTS AND F19 ASSIGNMENTS

Fluorine-19 NMR measurements were carried out at 84.675MHz on a Bruker HX90E spectrometer modified for FT operation. Samples were measured at low concentration in chloroform-d at 25°C; this provided the lock at 13.811MHz.

Free induction decays were measured into 8K channels and compounds are numbered in accordance with their appearance in this discussion.

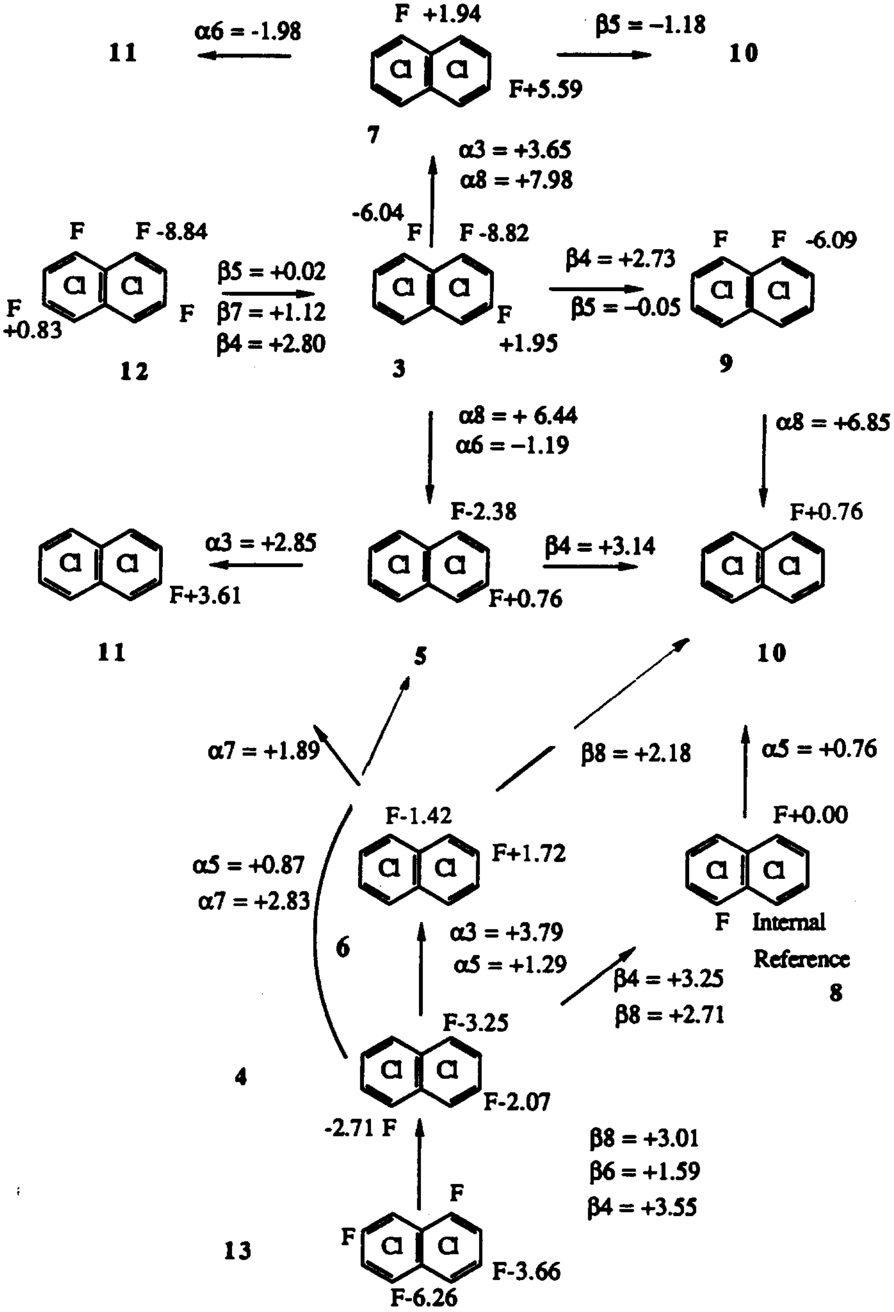
In analysing the F19 spectra there were two readily identifiable 3-spin systems, one displaying a peri fluorine-fluorine coupling and the other consisting of a triplet (-2ppm with respect to internal reference) and two doublets (-3ppm).

Pentachloro-4,5,7-trifluoronaphthalene **3** was identified by a peri-J(F,F) of 95.8 Hz and was a prominent component of most spectra. It could be distinguished from the 4,5,8-trifluoro-isomer on the basis that para F,F couplings are approximately 18 Hz in these systems[5] and from the 4,5,6-isomer on shift grounds (ortho fluorines would appear 20 ppm down frequency). Therefore we can identify **3** as 1,2,3,6,8-pentachloro-4,5,7--trifluoronaphthalene and assign it; meta-J(F,F) is 7 Hz. Compound **3** takes a pivotal role in the assignment logic in this paper and this is shown in Scheme A where we present the F-19 chemical shifts of compounds **3** to **13**. In that Scheme, the arrows indicate the hypothetical step-wise replacement of fluorine by chlorine and the related SCS values are for a particular disposition of the atom being substituted (i.e. $\alpha$ and $\beta$) and the site to which the observations relate. These SCS data are also presented in Table 1.

Pentachloro-4,6,8-trifluoronaphthalene **4**, the second trifluoro-derivative, gave a close sequence of peaks in the F19 spectrum at -2 to -4 ppm (overlapping in sulpholane). Like **3** it did not contain the 5,6 or 5,8-difluoro unit and the spectral assignment was consistent with the SCS in Table 1 and with F,F couplings [6].

There are two asymmetric difluoro-components with J = 7 Hz; these must be the 6,8- (**5**) and 4,6-(**6**)-difluoro derivatives. The other AX spectrum (J = 4 Hz) can be ascribed to **7**, the hexachloro-4,7-difluoronaphthalene (c.f. long range F,F coupling in [6]).

The sharp singlet from compound **8**, arbitrarily made the reference peak (0.0ppm) in Scheme A can now be assigned to hexachloro-4,8-difluoronaphthalene



SCHEME A. Fluorine chemical shifts and SCS for 3 to 13. The arrows indicate the hypothetical replacement of fluorine by chlorine and the SCS are quoted alongside these arrows. For the definition of SCS see footnote to Table 1.

TABLE 1

F19 Substituent Chemical Shifts for the Hypothetical Replacement of Fluorine by Chlorine in some Polyhalonaphthalenes

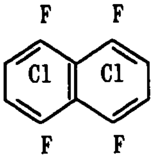
| | $^{19}F$ SCS (for F to Cl substitution)ppm | | | |
|---|---|---|---|---|
| | A | B | C | D |
| β1 ortho | +25.81 | +26.0 | | |
| α2 ortho | | +27.8 | | |
| β3 ortho | +18.27 | +18.6 | | |
| β4 meta | +1.08 | -0.6 | | 2.73 2.80 3.14 3.25 3.55 |
| α3 meta | | +1.2 | | 2.85 3.79 |
| β5 | -0.83 | -0.6 | <0.2 | -0.05 0.02 -1.18 |
| α6 | | -0.4 | | -1.19 -1.98 |
| β6 | +1.32 | +1.2 | +1.95 | 1.59 |
| β7 | <0.2 | -0.4 | -0.43 | 1.12 |
| β8 | +0.7 | +1.2 | +1.01 | 2.18 2.71 2.18 3.01 |
| α7 | | -0.4 | | 1.89 2.83 1.85 |
| α8 peri | | +3.7 | | 6.44 6.85 7.98 |
| α4 para | | +5.1 | | 5.59 |
| α5 epi | | +0.6 | | 0.76 1.29 0.87 |

| | |
|---|---|
| Column A. | SCS values for 2-chloroheptafluoronaphthalene derived during this work Upfrequency positive. |
| Column B. | Data for 1- and 2-chloroheptafluoronaphthalene from Kobrina *et al* [9]. |
| Column C. | Data from substitution work by Adcock *et al.* [12]. |
| Column D. | SCS from Scheme A in the text for $C_{10}Cl_{8-n}F_n$ where n is 1 to 4. |

Footnote. The values above are the substituent chemical shift changes (SCS in ppm) that occur when, hypothetically, a fluorine is replaced by a chlorine at the position of the Greek letter. α refers to position 1 in the ring system, and β to position 2. The number part of the symbol refers to the fluorine being observed.

(-102.50 ppm from ext. $CFCl_3$ or -102.89ppm from int. $CFCl_3$). The peri-fluorines in **3** appear well down frequency from the shifts of the difluoro-components, indicating a substantial peri SCS. Consequently, the singlet at -6.09 ppm (not surprisingly embraced by the arms of the peri F1 peaks of **3**) can be assigned to hexachloro-4,5-difluoronaphthalene **9** and, subsequently, the singlets for the mono-fluoro **10** and **11** can be assigned (see Scheme A).

Three symmetric tetrachlorotetrafluoronaphthalenes (**12**, **13** and **14**) have been identified and assigned. Their F-19 chemical shifts could be accurately predicted and the resultant SCS are acceptable in Table 1. The shift value for the unexpected **14** is -12.38ppm and it was always a very minor component in these mixtures. We do observe the intermediate compounds **8** and **9**.

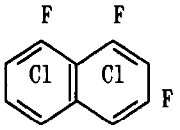


**(14)**

Table 1 presents the SCS (explicitly for the hypothetical replacement of fluorine by chlorine and the reverse of the chemical process) extracted from scheme A. The ortho SCS, $\alpha 2$-SCS and $\beta 1$-SCS, are grouped together whilst the $\beta 3$-SCS is found to be slightly lower in value, presumably due to partial bond localisation in these molecules.

It was initially felt that calculations of $^{19}F$ chemical shifts by the electric field method of Homer[7] would confirm our assignments. However, attempts by the Russians[8,9] to predict shifts in polyfluoronaphthalenes indicate that the $\beta$-fluorines can be calculated with an accuracy of ±3ppm whilst the $\alpha$-fluorines could only be predicted to ±15ppm. Obviously further calculations would be fruitless.

Polychloropolyfluoronaphthalenes hold out the promise of large steric interactions between peri substituents at C-4...C-5 and therefore with large through-space F1, F8 couplings. One through-space F-F coupling is reported; the peri F4.F5 coupling constant in **3** is 95.8Hz.



By comparison, the peri F,F coupling constant in octafluoronaphthalene [10,11] is 59.2Hz.

One implication of the above results is that a large peri F-F coupling should be found in hexachloro-4,5-difluoronaphthalene **9** and, if isolated, an inspection of the $^{13}C$ satellites of its fluorine spectrum should reveal couplings of approximately 100Hz. Because of overlap in the fluorine spectra of the mixtures studied here this did not prove possible.

Chemically, kinetic and thermodynamic effects are difficult to separate in such an experiment aimed at compound identification. It appears that initial fluoride exchange occurs at an $\alpha$-position and that subsequent exchange occurs either meta to the initial reaction site and/or at the adjacent peri position. Both secondary sites are two carbons from the initial site which would be expected from previous work on hexachlorobenzene. Thus after three exchanges, the predominant isomer is compound **3**. After four exchanges, the predominant isomer is compound **12** which, out of all the possible tetrachlorotetrafluoronaphthalenes isomers, could be isolated in the low temperature experiment in aprotic solvent. Overall, only three of the tetrachlorotetrafluoronaphthalene isomers have been observed. A reaction pathway which is typical of the dominant sequence of reactions is outlined below:

$$\begin{tikzcd}
 & & \mathbf{5} \arrow[dr] & & \\
\mathbf{1} \arrow[r] & \mathbf{10} \arrow[ur] \arrow[r] \arrow[dr] & \mathbf{9} \arrow[r] & \mathbf{3} \arrow[r] & \mathbf{12} \\
 & & \mathbf{7} \arrow[ur] & &
\end{tikzcd}$$

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