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FLUORINE-19 NMR SPECTROSCOPY OF POLYHALONAPHTHALENES. PART II POLYCHLOROPOLYFLUORONAPHTHALENES VIA NUCLEOPHILIC FLUORIDE DECHLORINATION

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SUMMARY

Six new polychloropolyfluoronaphthalenes have been identified by F-19 NMR whose empirical formulae are $C_{10}\ Cl_{8-n}\ F_n$ where n is 5 and 6 i.e. two trichloropentafluoronaphthalenes and four dichlorohexafluoronaphthalenes:-

1,3,8-trichloro-2,4,5,6,7-pentafluoronaphthalene,

1,3,6-trichloro-2,4,5,7,8-pentafluoronaphthalene,

1,3-dichloro-2,4,5,6,7,8-hexafluoronaphthalene,

1,8-dichloro-2,3,4,5,6,7-hexafluoronaphthalene,

1,6-dichloro-2,3,4,5,7,8-hexafluoronaphthalene and

2,7-dichloro-1,3,4,5,6,8-hexafluoronaphthalene.

In the partly fluorinated compounds such as 1,3,6,8-tetrachloro-2,4,5,7-tetrafluoronaphthalene, nucleophilic fluoride dechlorination occurs at both α and β positions. Initial substitution in octachloronaphthalene is more selective and occurs predominantly at the α-position; both subsequent exchanges occur at sites two carbons away from the initial site. The results support the idea that the transition state is stabilised by chlorine at the sites of electron density, ortho and para to the site of nucleophilic attack.

INTRODUCTION

In a recent paper[1] twelve polyhalonaphthalenes were identified and one compound isolated. These compounds, the products of exchange between octachloronaphthalene and fluoride ion, were in complex mixtures and largely

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inseparable. The pyro-product was investigated by F-19 NMR and it was found that 96% of the material could be identified as polychloropolyfluoro-naphthalenes, $C_{10}\ Cl_{8-n}\ F_n$, where n is 1 to 4. Indeed the reaction pathway is dominated by exchange at an α position in octachloronaphthalene with subsequent exchanges occurring two carbons away i.e.meta and/or peri sites. In other simple polychloroaromatic substrates, such as hexachlorobenzene, meta substitution similarly dominates the orienting effect of sequential substitutions. To explain the preferential production of 1,3,5-trichlorotrifluorobenzene in the exchange of hexachlorobenzene with KF in an autoclave it has been generalised[2,3] that ortho and para chlorines stabilise the energy of the intermediates of nucleophilic attack whilst ortho and para fluorines destabilise that energy. In this case it is the chlorines which so activate the molecule under extreme conditions (greater than $400^{o}C$).

In nucleophilic polysubstitution, the entering groups are electron rich relative to the leaving group and therefore gradually deactivate the molecule to subsequent nucleophilic attack by that particular nucleophile (see a recent review [4]). Work by Chambers, Williams et al.[5,6] on the analogous nucleophilic methoxy defluorination of polyfluoronaphthalenes (it must be emphasised polyFLUORO-compounds) showed that fluorine at a remote site has a negligible effect on the reaction rate(1/30th of an ortho or para effect) in comparison with hydrogen at that remote site. Nucleophilic attack is activated equally by ortho and meta fluorines in that case.

This paper describes an assignment of the F-19 NMR chemical shifts of the more volatile polychloropolyfluoronaphthalenes whose empirical formulae are $C_{10}\ Cl_{8-n}\ F_n$ where n is 5 and 6 i.e. two trichloropentafluoronaphthalenes and four dichlorohexafluoronaphthalenes. The availability of higher field spectrometers with higher sensitivity has increased markedly the number of products that can be identified by NMR.

The aim of this work was at least three fold: to identify more of the polychloropolyfluoronaphthalenes found in previous work; to expand the

methodology for identifying these polyhalonaphthalenes, especially for assigning the F-19 shifts; to strengthen our understanding of the process of halogen exchanges[2,3,7,8]. It is debatable whether these exchanges are heterogeneous or homogeneous under the selected conditions.

REACTIONS

To prepare mixtures of polychloropolyfluoronaphthalenes, an incomplete fluorination of octachloronaphthalene was carried out. High temperature fluorine exchange was carried out in the absence of a solvent with a 10:1 molar excess of KF over octachloronaphthalene at 420°C in vacuo in a Carius tube for 40 hours. The product was washed with water and extracted into diethylether, dried over $MgSO_4$, and the solvent evaporated, leaving a light yellow solid. Fractional sublimation in vacuo (0.4 τ) gave 10 fractions but did not lead to the successful isolation of any pure compounds. The early fractions contained the more volatile highly fluorinated compounds, while the middle fractions were rich in the tetrachlorotetrafluoronaphthalenes, and the later fractions were mixtures of compounds reported previously, mostly mono-, di- and trifluorinated products. For the sake of simplicity an analysis of the F-19 spectrum of partly-purified material (once sublimed) is reported here. The systematic names and molar percentage for three known compound (12, 21, 22) and six unknown compounds (15 to 20 where the numbering system follows on from part I) are as follows:

12	1,3,6,8-tetrachloro-2,4,5,7-tetrafluoronaphthalene	(6%)
15	1,3,8-trichloro-2,4,5,6,7-pentafluoronaphthalene	(10.5%)
16	1,3,6-trichloro-2,4,5,7,8-pentafluoronaphthalene	(8%)
17	1,3-dichloro-2,4,5,6,7,8-hexafluoronaphthalene	(16%)
18	1,8-dichloro-2,3,4,5,6,7-hexafluoronaphthalene	(13%)
19	1,6-dichloro-2,3,4,5,7,8-hexafluoronaphthalene	(10%)
20	2,7-dichloro-1,3,4,5,6,8-hexafluoronaphthalene	(5%)

21	1-chloroheptafluoronaphthalene	(14.5%)
22	2-chloroheptafluoronaphthalene	(9.5%)

Fluorine-19 NMR spectra were measured on a Bruker AC250 spectrometer at 235.36 MHz. Samples (<5mgs) were measured at low concentration in chloroform-d at 26^{o}C. Solubility was no longer a problem with these materials although the highly chlorinated naphthalenes[1] are less soluble . The peak chosen as the internal reference was the upfrequency peak of 1,3,6,8-tetrachloro-2,4,5,7-tetrafluoronaphthalene, compound 12 in the previous report[1]. The spectrum of the partly purified material was selected as the focus of this analysis; this spectrum is presented in two portions in the figures. It was estimated that greater than 94% (molar fraction) of the material available in this fraction had been identified. Some of the small peaks to the upfrequency end of the spectrum (Figure 1) can be assigned to compounds already identified, although, for the sake of clarity, these peaks were not marked. Several peaks remained unassigned and are marked with a U in Figs. 1 and 2 (possibly another symmetric dichlorohexafluoronaphthalene).

RESULTS AND F19 ASSIGNMENTS

Integrations were a basic tool in the diagnostic armory in the assignment of the F-19 spectrum of this mixture.

The initial thrust of this analysis targetted three peaks at the high frequency end of the spectral area (between -3 and -8ppm). allocating them compound numbers 15, 16 and 17. These pseudo-singlets were related by integration to three peri-peaks in the adjacent shift area (-8 to -13ppm). Initially these compounds were assumed to be 4-spin systems (tetrachloro-tetrafluoronaphthalenes) although subsequent analysis of the splitting patterns showed that they were 5- (15,16) and 6-spin (17) systems. It was possible to virtually assign all of the bands in the F-19 spectrum:

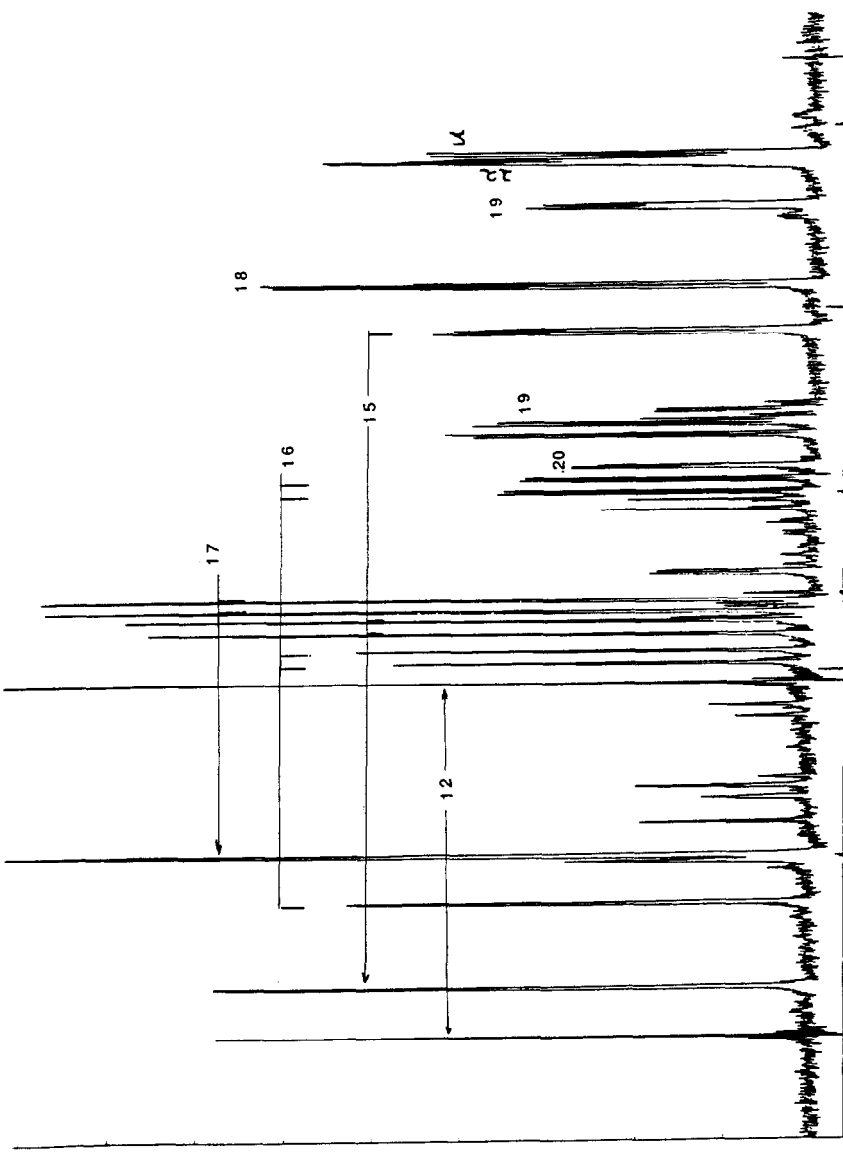


Fig. 1. Higher frequency portion of the F-19 spectrum of a typical mixture in d-chloroform. The numbers refer to the compounds described in the text.

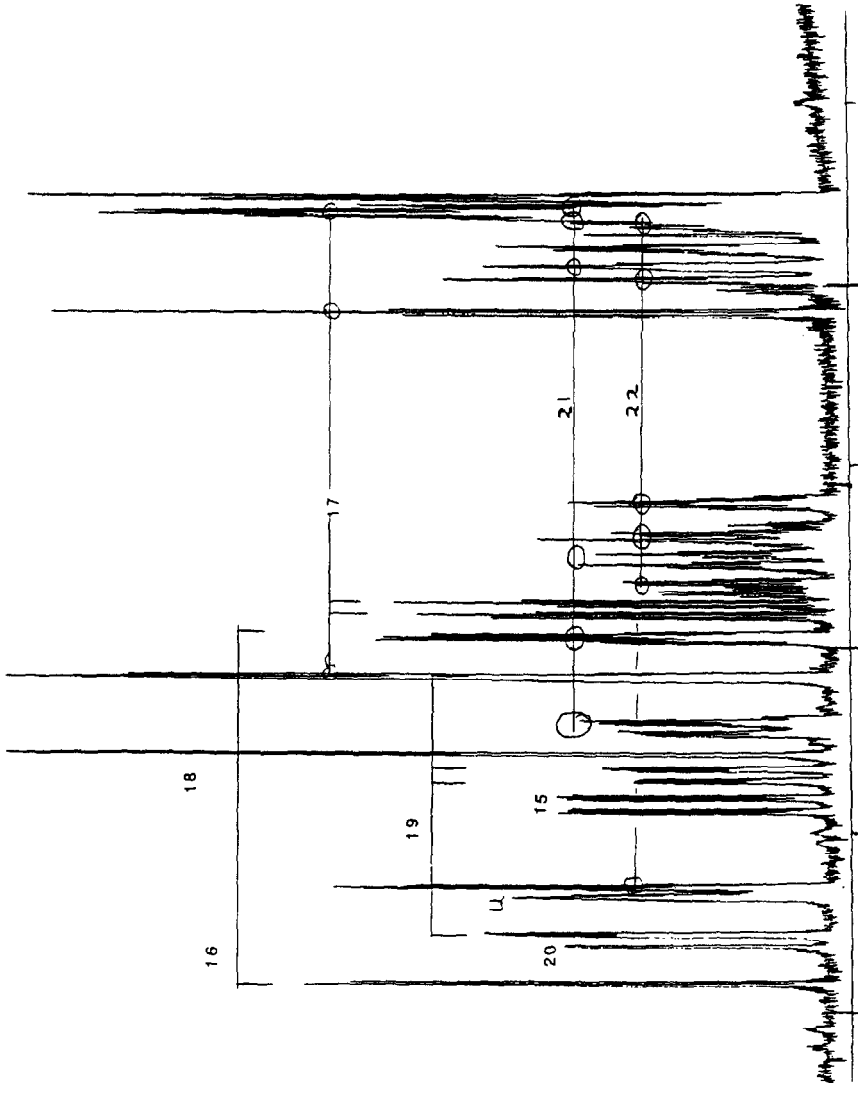


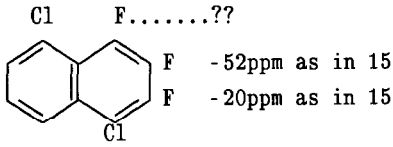
Fig. 2. Lower frequency portion of the F-19 spectrum of a typical mixture in d-chloroform. The numbers refer to the compounds described in the text.

(i) Compound **15**. The partner of the peri-band at -11ppm (obvious highest frequency doublet) was traced to -35ppm. Missing bands were found at -19 and -52ppm, identifying a trifluoro-unit where the fluorine atoms are contiguous and in one ring (see below). J(F,F)peri is 85.7Hz.

(ii) Compound **16**. A pair of peri-fluorines were found in the -10 to -20ppm range, implying that the adjacent nuclei are chlorines in both rings and that the molecule is asymmetric. J(F,F)peri is 81.4Hz.

(iii) Compound **17** was a minor component in the early sublimation fractions. Peri-partners could be identified at -11 and -41ppm, the splitting pattern of these was consistent with an asymmetric structure, totally fluorinated in one ring. Two distinct triplets were assigned at low frequency. J(F,F)peri is 69.8Hz.

A second phase in the analysis was the attempted interpretation of the five peaks between -19 and -25ppm where the peak at -19ppm had already been attributed to **15**. The next two peaks are labelled **18** and **19**. By comparison these peaks can be assigned to the F3 nuclei as shown in the contiguous trifluoro-subunit below:



In the same way the four peaks between -30 and -34ppm are assigned to peaks like F-1 in the above diagram i.e. with a peri chlorine and ortho fluorine. Compound **20** was identified later as giving 3 peaks of equal intensity, all at the same trace level and all indicating a symmetric molecule (no visible peri-splittings). However this product only exists at low levels and could not be unambiguously identified.

Most of the remaining peaks can now be attributed to the 1- and 2-chloroheptafluoronaphthalenes (**21** and **22**) where our shifts are in close agreement with those in the literature[9,10]. These compounds are marked in

Figs. 1 and 2 but the data is outside the limited scope of Schemes A and Table 1. Shift predictions via substituent chemical shifts are accurate to an estimated ±1ppm.

Table 1 presents the SCS(substituent chemical shift) for the hypothetical replacement of fluorine by chlorine (the reverse of the chemical process) with values calculated from Scheme A. Column A presents the average values derived by an inspection of part I. Subsequent columns contain the SCS for eight shift differences between compounds **12-15, 12-16, 16-17, 15-17, 15-18, 16-20, 15-19, 16-19.**

A third phase in this analysis was the recognition of eight distinct spectral areas that could each be attributed to a unique structural type or molecular subunit:

0 to -8ppm: F2 sandwiched by two chlorines atoms.

-10 to -18ppm: F1 with peri-fluorine and ortho-chlorine partners.

-18 to -25ppm: F2 with ortho-chlorine at C-1 and fluorine at C-3.

-30 to -32ppm: F2 with ortho-chlorine at C-3 and fluorine at C-1.

-39 to -41ppm: F1 with peri chlorine, ortho fluorine.

-35 to -39ppm: F1 with two adjacent fluorines and a para-chlorine.

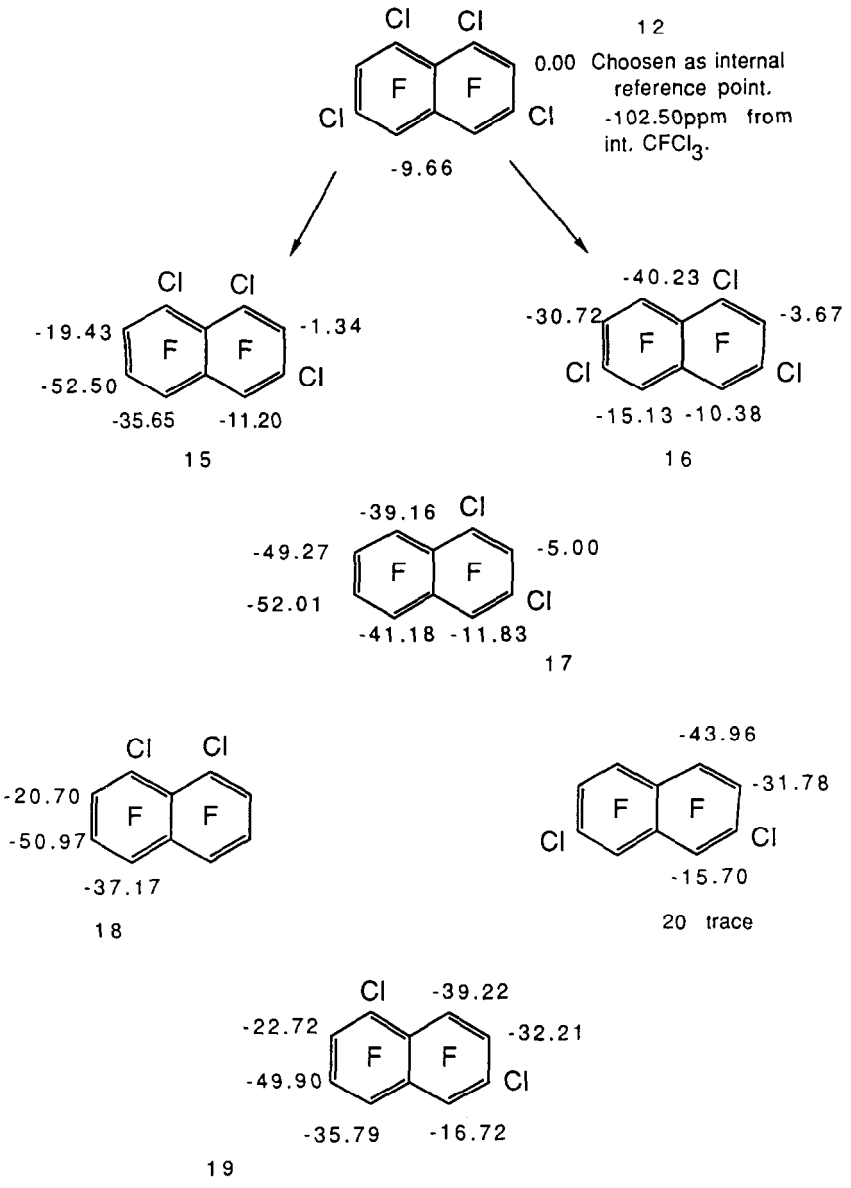
-41 to -45ppm: F1 in a fully fluorinated ring with a peri-fluorine.

-48 to -53ppm: F2 with two adjacent fluorines.

In a diagnostic sense this enabled us to check our results and provided a useful methodology for F19 shift assignment.

Nucleophilic Substitution

It is gratifying that the identified products are compounds which all fit into a simple set of chemical exchanges, leading to a high degree of confidence in these results. It is now possible to build up a picture of the likely reaction pathway for fluoride dechlorination:



Scheme A. Experimental Fluorine-19 Chemical Shifts (ppm) of Compounds 15 to 20 in $CDCl_3$.

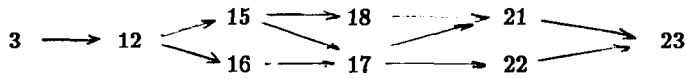
TABLE 1

F19 Substituent Chemical Shifts for the
Hypothetical Replacement of Fluorine by Chlorine.

	^{19}F SCS (for F to Cl substitution)ppm**								
	A*	B	C	D	E	F	G	H	I
Compounds		12-15	12-16	16-17	15-17	15-18	16-20	15-19	16-19
β1 ortho	26	25.99		26.05		25.97			25.41
α2 ortho	30		30.72		29.84		29.11	30.87	
β3 ortho	18	19.43		18.55		19.36			19.05
β4 meta	3			-1.07					
α3 meta	3				-0.49				
β5	-1								-1.01
α6	-1							-2.60	
β6	1.5	1.34		1.33		1.27			1.49
β7	0					-1.53			
β8	2.5	1.54		1.45		1.52			1.59
α7	2.5		3.67		3.66		1.06	3.29	
α8 peri	7						3.73		
α4 para	5		5.47		5.53		5.32	5.52	
α5 epi	1		0.72		0.63		0.57	0.15	

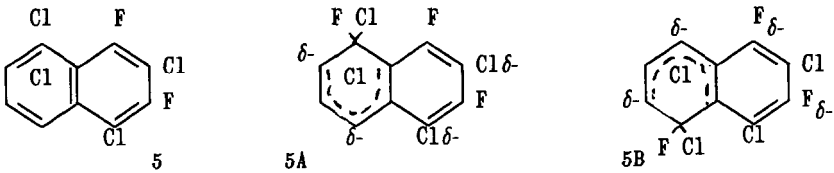
*Column A. Average values (±1ppm) derived from inspection of SCS in part I fo highly chlorinated naphthalenes.

** 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 α position (always position 1) or at the β position (always position 2). The above values are the shifts which occur at the 'numbered position' i.e. the monitored position.



where compound **3** was 1,2,3,6,8-pentachloro-4,5,7-trifluoronaphthalene. Compounds **3** and **12** become the nexus for these reactions, **12** going to both **15** and **16** via displacement at both *α* and *β* chlorines in **12**. The next exchange can also occur at any of the remaining chlorinated sites.

The conclusion in Part 1 was that the first exchange occurs predominantly at an *α*-site in octachloronaphthalene and subsequent exchanges occur two carbons away. The implication is that the orienting effect of a ortho and para chlorine on the intermediates is greater than the orienting effect of two ortho chlorines; the para orienting effect outweighs the ortho effect. This is in agreement with the nucleophilic dechlorination of heptachloroisoquinoline[3]. Chambers et al. found that the most reactive site to be the 1-position, adjacent to the ring nitrogen. Here, subsequent or secondary exchange is in the same ring, again analogous to the reaction with heptachloroisoquinoline[3]. The third site of substitution is the peri position in the remote ring, with the chlorines in both rings mopping up charge in the transition state:



thus favouring the orientation of attack as seen in 5A. These results support the simple conclusion that the intermediate states are stabilised by chlorine (ortho and para to nucleophilic attack) in the local ring. Some caution has to be applied in taking NMR 'snapshots' of these reactions and extrapolating

to reaction mechanisms when different solubilities or varying volatilities could affect the balance of compounds in our fraction.

Much of the diagnostic work is confirmed by recent F,F 2D COSY spectroscopy. Nowhere did we find anomalous F,F coupling constants.

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