Journal of Fluorine Chemistry, 55 (1991) 163–167

Fluorine-19 NMR spectroscopy of polyhalonaphthalenes. Part III. A consideration of inter-ring SCSs in polychloropolyfluoronaphthalenes

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(Received June 8, 1991; accepted September 21, 1991)

Abstract

Substituent chemical shifts for the hypothetical replacement of fluorine atoms by chlorine atoms are considered for the ^{19}F shifts in a 'matrix' of data points from 21 compounds, from monochloroheptafluoro- to octafluoro-naphthalene. The use of inter-ring SCSs is investigated with an application to the heterologue, 2,4-dichloro-pentafluoroquinoline, where the ^{19}F shift predictions prove accurate and acceptable. A caution is given against using small SCSs in isolation to elucidate structures and assign peaks in the ^{19}F spectra of polyfluoropolycyclic aromatic compounds.

Introduction

In this note the SCSs (substituent chemical shifts for the hypothetical replacement of fluorine atoms by chlorine atoms) generated in recent reports, and their additivity, are considered. Nucleophilic fluoride dechlorination [1, 2] of octachloronaphthalene led to the identification of 18 new compounds in complicated mixtures via ^{19}F NMR spectroscopy [3, 4]. Integration, coupling constants and SCS additivity were the basis on which we assigned all the resonances in the ^{19}F spectra of the mixtures, thus elucidating the substitution geometry. One useful effect of SCSs is that the ^{19}F spectra can be subdivided into regions assigned to fluorines in specific structural positions. The SCSs (F to Cl), from the shift data in two previous papers, have already been calculated. We include three more known compounds, whose peaks were fortuitously identified in the ^{19}F spectra, in this consideration: 1- (21) and 2-chloroheptafluoronaphthalene (22) and octafluoronaphthalene (23). The numbering for compounds in this paper has been defined in previous papers in this series.

New SCSs are presented in Table 1 by refining the ^{19}F shifts (solvent $CDCl_3$) reported in Parts I and II and in Scheme 1. Scheme 1 presents the ^{19}F shifts of 21, 22 and 23 and relates them to those of compounds 12, 15, 16 and 17. This is an opportunity to follow SCS (F to Cl) variations in a large set or 'matrix' of synthetic compounds. Malinowski [5] has analysed in 1972 the additivity of ^{19}F shifts in polychloropolyfluorobenzenes (data of

0022-1139/91/$3.50

TABLE 1

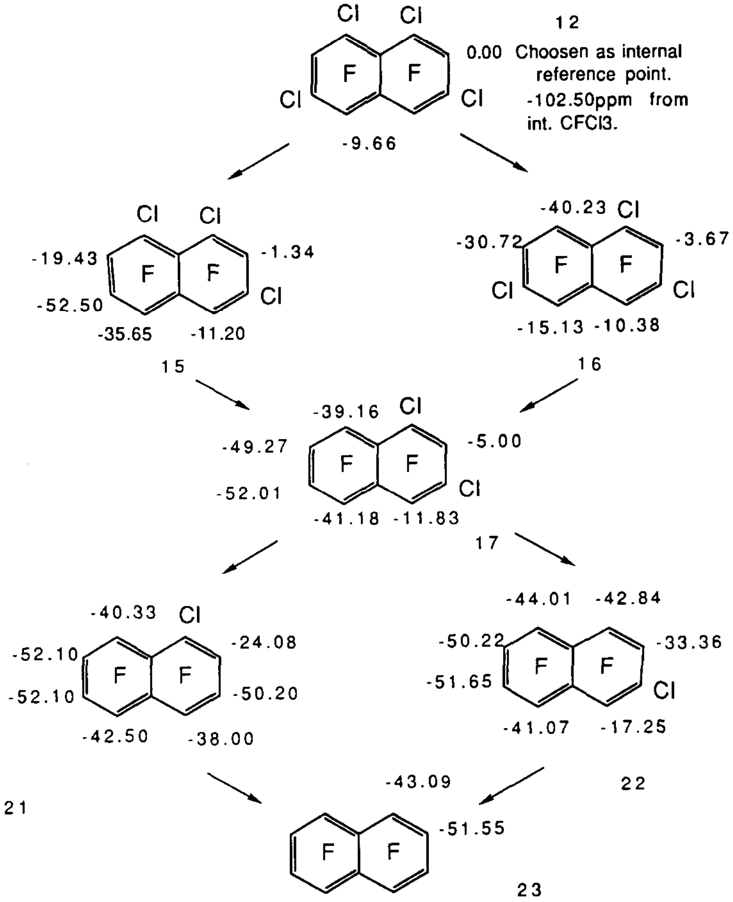
Substituent chemical shifts for the hypothetical replacement of fluorine by chlorine[a]

	^{19}F SCS values (for F to Cl substitution) (ppm)								
	A[b]	B	C	D	E	F	G	H	I
Site of change Compound		α 21–23[c]	β 22–23	α 19–22	β 19–21	α 17–22	β 17–21	α 18–21	β 20–22
β1 *ortho*	26		25.84		24.78		26.17		26.00
α2 *ortho*	30	27.47		27.50		28.36		31.40	
β3 *ortho*	18		18.19		19.89		19.08		18.44
β4 *meta*	3		0.25		1.11				−0.05
α3 *meta*	3	1.35		1.77				1.13	
β5	−1		−0.92				1.17		−1.15
α6	−1	−0.55		0.03		−0.34		−0.77	
β6	1.5		1.33		1.36		2.83		1.58
β7	0		0.12		0.30		0.09		
β8	2.5		1.39		2.25		1.32		1.55
α7	2.5	−0.55				0.95		−0.77	
α8 *peri*	7	2.76		4.79		4.85			
α4 *para*	5	5.09		5.91		5.42		5.33	
α5 *epi*	1	0.59				0.52		0.99	

[a] The values quoted 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.

[b] Column A. Average (±1 ppm) derived from inspection of SCS values in Part I.

[c] Octafluoronaphthalene in $CDCl_3$, F1 (−43.09), F2 (−51.55) (−145.59 and −154.05 ppm w.r.t. internal $CFCl_3$).
Compound 21: F4(−38.00), F5(−42.50), F8(−40.33), F2(−24.08), F3(−50.20), F6(−52.10), F7(−52.10).
Compound 22: F3(−33.36), F6(−50.22), F7(−51.65), F1(−17.25), F4(−42.84), F5(−44.01), F8(−41.07).



Scheme 1. Experimental ^{19}F chemical shifts (ppm) of compounds 12, 15, 16, 21, 22 and 23 in $CDCl_3$.

Boden *et al.* [6]) and calculated the errors in simple additivity (*i.e.* the pairwise terms). *Ortho*-disubstitution (two *ortho*-chlorines to a fluorine) led to the largest jump (+3.45 ppm) in the *ortho*-SCS values in circumstances where ±0.5 ppm was normal.

Because other spectroscopic techniques have proved less than useful (*e.g.* mass spectrometry, infrared spectroscopy, ^{13}C NMR spectroscopy), it was found necessary to examine the SCSs. Typically these samples were less than 10 mg and we relied upon a non-destructive spectroscopy, *i.e.* fluorine-NMR.

^{19}F substituent chemical shifts

SCSs were expected to be consistent throughout this sequence of compounds. In fact that expectation proved wrong and dramatic changes are visible in some elements or values listed in Parts I and II:

1. *Ortho-SCSs* can be divided into three systematic parts which are structurally distinct ($\alpha 2$, $\beta 1$ and $\beta 3$). $\alpha 2$- and $\beta 1$-SCSs form one group with a bond order of 1.66 whilst $\beta 3$ values form a separate group, with a bond order of 1.33, the difference attributable to variations in bond order (partial bond localisation [7]). A value of 21.69 ppm reported by Malinowski [5] for substituted benzenes (bond order 1.50) does not simply fit into this trend. A discontinuity was found in $\alpha 2$ here and values along Table 1 go 27.5 ppm, 27.5 ppm, 28.4 ppm, 31.4 ppm.
2. In part I, the *peri* $\alpha 8$-*SCS* values were 7 ± 1 ppm with an *ortho* chlorine to the monitor fluorine but 4 ± 1 ppm here with an *ortho* fluorine; the group next to the observation site is affecting the local SCS. This might be either a 'buttressing' effect (through-space) or an electronic effect (through-bond)
3. There are substantial changes in the *meta-SCSs*, the value depending on the juxtapositioned substituents. Furthermore, *meta*-substitution effects in chlorinated benzenes C_6Cl_5F to $C_4Cl_4F_2$ to $C_6Cl_3F_3$ in DMSO (our work) gave values of 2.8 and 4.0 ppm, somewhat larger than the 1.03 ppm noted in 1972 [5].
4. The *para-SCS* values are relatively static at 5.3 ± 0.2 ppm, *cf.* 6.22 ppm in ref. 5 and an unusual value of 5.9 ppm in Table 1.
5. In comparison, the range of $\beta 6$-*SCSs* (a seven-bond inter-ring SCS) is limited, 1.4–1.6 ppm, but surprisingly similar to the *meta* values [6].
6. $\alpha 6$-*SCSs* and $\beta 5$-*SCSs* for 15–19 appear to be small, negative and variable.

It would be unreliable to depend on the very small SCSs to assign the ^{19}F spectra and elucidate the structures of our 'matrix' of 21 compounds. It must be admitted that at the beginning of this work it was hoped that the inter-ring SCSs would be large enough and consistent enough for use in the analysis. In fact, inter-ring SCSs played a confimatory 'role' here. An example of the potential use of inter-ring SCSs follows.

An application of inter-ring SCSs to existing ^{19}F shift data

To illustrate the potential of inter-ring SCSs we chose the heterologue, heptafluoroquinoline and its disubstituted derivative 2,4-dichloro-pentafluoroquinoline whose ^{19}F shifts are known [8, 9]. ^{19}F shift predictions follow:

F3 $P + \beta 3 + \alpha 2 =$ $-161.9 + 19.1 + 27.5 = -115.3\ (-116.6)$
F5 $P + \beta 5 + \alpha 8 =$ $-147.0 + 1.2 + 2.7 = -143.1\ (-145.4)$
F6 $P + \beta 6 + \alpha 7 =$ $-156.2 + 2.8 - 0.5 = -153.9\ (-154.0)$
F7 $P + \beta 7 + \alpha 6 =$ $-152.6 + 0.1 - 0.5 = -153.2\ (-153.2)$
F8 $P + \beta 8 + \alpha 5 =$ $-149.8 + 1.3 + 0.6 = -147.9\ (148.6)$

where P is the ^{19}F shift in the parent compound. The SCSs are based on the shifts for compound 17, an ideal model for our system when referenced to compound 23 (columns G and B in practice). There is agreement between the predicted data and the experimental data in parentheses, especially for the remote F6 and F7 which provide a good test of our long-range inter-ring SCSs. The results prove that additivity to within ±0.2 ppm, via inter-ring shifts, is a viable proposition given accurate starting data and no interferring local effects. In brief, although one prediction has an error of −2.3 ppm, the average error is less than ±1.0 ppm, still accurate enough to apply to analogous heteroaromatics with a fair degree of confidence.

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