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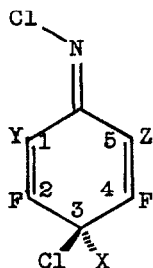
N-HALOGENO-COMPOUNDS. PART II [1]. N.M.R. DATA FOR  
POLYFLUOROCYCLOHEXADIENYLIDENEAMINES OBTAINED via N-  
CHLORINATION OF POLYFLUOROARYLAMINES

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SUMMARY

N.m.r. parameters for nine (I-IX) N-chloropolyfluorocyclohexa-2,5-dienylideneamines are reported and discussed; the magnitudes of the FF-coupling constants fall into the following ranges:



$$\begin{aligned} \underline{J}_{12} & 0-2.8; \underline{J}_{13}, \underline{J}_{35} & 6.0-6.8; \underline{J}_{14} < 1; \\ \underline{J}_{15} & 0-2.6; \underline{J}_{23}, \underline{J}_{34} & 25.5-27.2; \underline{J}_{24} & 0-6.0; \\ \underline{J}_{25} & 0-1.2; \underline{J}_{45} & 5.4-9.8 \text{ Hz} \end{aligned}$$

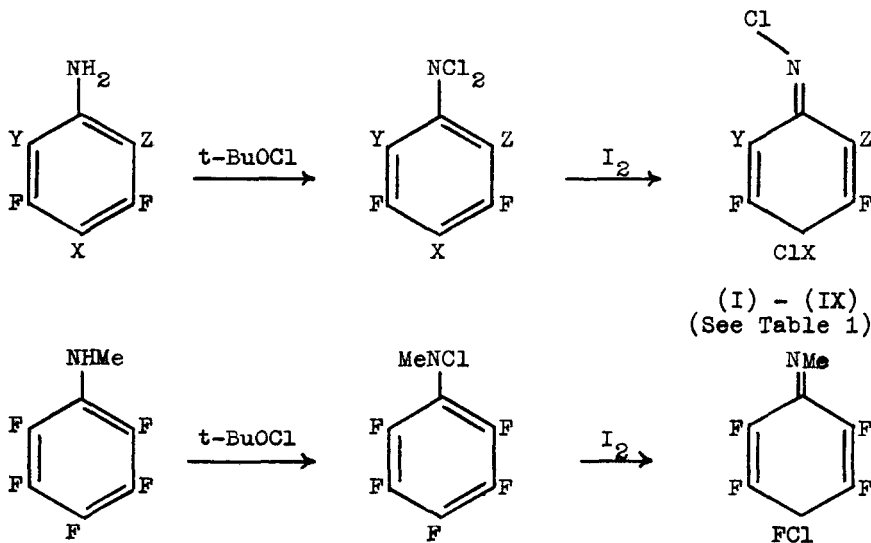
(I) X = Y = Z = F; (II) X = OMe, Y = Z = F; (III) X = CF<sub>3</sub>,  
Y = Z = F; (IV) X = Ph, Y = Z = F; (V) X = Cl, Y = Z = F;  
(VI) X = Br, Y = Z = F; (VII) X = Y = F, Z = Cl; (VIII) X = Y = F,  
Z = Br; (IX) X = Z = F, Y = H.

The spectra of N-methyl-4-chloropentafluorocyclohexa-2,5-dienylideneamine have also been analysed. All the imines examined are configurationally stable at the nitrogen atom.

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## INTRODUCTION

Electrophilic chlorination of 2,3,4,5,6-pentafluoroaniline with *t*-butyl hypochlorite yields NN-dichloropentafluoroaniline, which readily undergoes iodine-catalysed rearrangement to N,4-dichloropentafluorocyclohexa-2,5-dienylideneamine [1]. Application of this sequence [2] to seven other polyfluoroanilines and to N-methyl-2,3,4,5,6-pentafluoroaniline has provided the opportunity to carry out the first detailed  $^{19}\text{F}$  n.m.r. study of polyfluorocyclohexa-2,5-dienylideneamines.



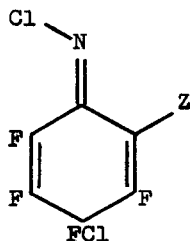
## RESULTS AND DISCUSSION

Chemical Shifts

$^{19}\text{F}$  Chemical shifts for compounds (I)-(X) are listed in Table 1. All the ring fluorines are non-equivalent owing to restricted rotation/inversion at nitrogen, so the correct assignments were not immediately obvious. The triplet of

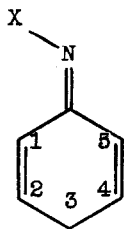
triplets arising from the  $\text{CFCl}$  group in compound (I) did not appear in the spectra of products (II)-(VI), and the two distinct coupling constants (26 and 6 Hz) allowed a pairing of the remaining four absorptions. The spectra of compounds (VII-IX), which lack one ring fluorine (labelled 1 or 5), each showed two large couplings with magnitudes ( $\gg 26$  Hz) indicating that this is the three-bond coupling. Assignments for the 4-fluorine in compounds (VII) and (VIII) and the 2-fluorine in (IX) were made following consideration of previous studies [3] on 1-substituted nonafluorocyclohexenes, which revealed that replacement of one olefinic fluorine in decafluorocyclohexene by chlorine/hydrogen or bromine causes the absorption of the other to suffer a downfield shift of about 30 or 39 p.p.m., respectively.

The halogeno-compounds (VII) and (VIII) each had an absorption at about 65 p.p.m., whereas the hydrogen-substituted compound (IX) has an absorption at 70.4 p.p.m., and the parent compound (I) had absorptions (at 64.6 and 70.2 p.p.m.) corresponding to both of these. The substituent should have only a small effect upon the chemical shift of the remote fluorine. Compounds (I)-(VI) all showed two absorptions separated by 5.6 p.p.m., which fall into two separate ranges of 53.2-64.6 and 59.0-70.2 p.p.m. These features, plus the reasonable assumption that compounds (VII) and (VIII) adopt conformation (XI) owing to the relative bulk of vinylic chlorine or bromine compared with fluorine [4], led to the assignments shown (Table 1) for  $\delta_2$  and  $\delta_4$ . The similarities of appropriate coupling constants and chemical shifts allowed the analyses for the N-chloro-compounds (I)-(IX) and the related N-methyl-compound (X) to be completed.



(XI) Z = Cl or Br

TABLE 1 \*

 $^{19}\text{F}$  Chemical Shifts<sup>a</sup>

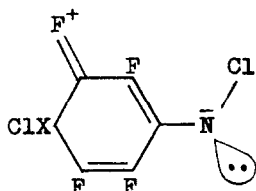
Number	Substituents <sup>b</sup>	$\delta_1$	$\delta_2$	$\delta_3$	$\delta_4$	$\delta_5$
(I) <sup>c</sup>	<u>N</u> -Cl, 3-Cl	71.6	64.6	35.1	70.2	72.8
(II) <sup>c</sup>	<u>N</u> -Cl, 3-Cl, 3-OMe	74.7	58.5	-	64.1	76.4
(III) <sup>c</sup>	<u>N</u> -Cl, 3-Cl, 3-CF <sub>3</sub>	66.2	56.5	(-5.4)	62.4	67.8
(IV) <sup>d</sup>	<u>N</u> -Cl, 3-Cl, 3-Ph	72.6	53.2	-	59.0	73.5
(V) <sup>e</sup>	<u>N</u> -Cl, 3,3-Cl <sub>2</sub>	73.1	58.0	-	63.6	74.3
(VI) <sup>f</sup>	<u>N</u> -Cl, 3-Cl, 3-Br	72.9	57.7	-	63.3	74.7
(VII) <sup>e</sup>	<u>N</u> -Cl, 3,5-Cl <sub>2</sub>	68.6	64.9	34.9	38.4	-
(VIII) <sup>f</sup>	<u>N</u> -Cl, 3-Cl, 5-Br	68.0	64.7	34.6	28.1	-
(IX) <sup>c</sup>	<u>N</u> -Cl, 1-H, 3-Cl	-	36.0	38.2	70.4	74.8
(X) <sup>c</sup>	<u>N</u> -Me, 3-Cl	72.1	74.8	31.7	76.9	74.0

<sup>a</sup> In p.p.m. to high field of external CF<sub>3</sub>CO<sub>2</sub>H; <sup>b</sup> other than fluorine; <sup>c</sup> neat liquid; <sup>d</sup> 25% w/v in CCl<sub>4</sub>; <sup>e</sup> 65:35 mixture of (V) and (VII); <sup>f</sup> 75:25 mixture of (VI) and (VIII).

The natures of the factors which affect  $^{19}\text{F}$  n.m.r. chemical shifts in non-aromatic polyfluoro-compounds are not well understood. Attempts have been made to account for changes brought about by nearby substituents in terms of their electric field effects [5], but these have not proved too successful,

\*The ring fluorines are numbered 1-5 for convenience; this does not correspond to the systematic nomenclature, which is, however, employed in the experimental section.

except possibly for halogen substituents. Replacement of the fluorine of the CFCl group in compound (I) by the substituents OMe, CF<sub>3</sub>, Ph, Cl, or Br clearly causes deshielding of both adjacent fluorine nuclei [2- and 4-F in (II)-(VI)]; furthermore in the set formed by (I) and its five 'derivatives',  $\delta_4 - \delta_2$  is remarkably constant (5.6, 5.6, 5.9, 5.8, 5.6, and 5.6 p.p.m., respectively), implying that electron withdrawal by nitrogen operates more effectively at the fluorine located in the 'syn' position as shown. The magnitude of  $\delta_4$  for compound (IX)



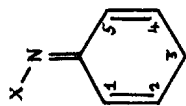
clearly indicates that the N-chlorine substituent lies syn with respect to the ring hydrogen.

The smallest range of olefinic fluorine chemical shifts was displayed by the N-methyl-compound (X), in which the least (overall) electron withdrawal from the ring fluorines occurred. When the sample under observation was heated, the spectrum (at 56.46 MHz) showed some loss of fine structure at 100°C and the bands had broadened, but not coalesced, at 140°C when decomposition began to occur. Thus the rate of site exchange of the N-methyl group which would average the chemical shift of the adjacent pair of fluorine nuclei is  $< 240 \text{ s}^{-1}$  (using the equation:  $\text{rate} = \pi\delta / \sqrt{2}$ , where the chemical shift difference  $\delta$  is 108 Hz) corresponding to a free energy of activation of  $> 83 \text{ kJ mol}^{-1}$  (using Eyring's equation, T 140°C).

### Coupling Constants

These were obtained for each of the ten compounds studied, and are listed in Table 2. Trends in the three-bond couplings of the two sets of olefinic fluorines parallel each other, with those involving nuclei syn to the N-chlorine some 5 Hz smaller in magnitude; a trend to larger values occurs as inductive withdrawal of electron density by the CClX group diminishes. Small values for similar cis-FF couplings have been noted previously [6]. The four-bond coupling constants

TABLE 2  
Coupling constants (Hz)<sup>a</sup>



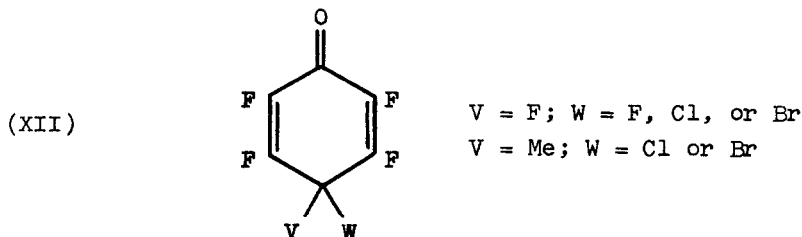
Compound	$ J_{12} $	$ J_{13} $	$ J_{14} $	$ J_{15} $	$ J_{23} $	$ J_{24} $	$ J_{25} $	$ J_{34} $	$ J_{35} $	$ J_{45} $	Others
(I)	1.2	6.0	0	2.6	26.2	4.2	1.2	25.9	6.0	6.3	
(II)	$\sim 2$	-	0	$< 1$	-	5.4	$< 1$	-	-	7.4	$J_{2H}$ , $J_{4H}$ 1.5
(III)	$< 1$	0	0	$< 1$	12.0	4.2	$< 1$	12.0	0	5.4	
(IV)	5.4	-	$< 1$	$\sim 1$	-	4.3	$\sim 1$	-	-	9.8	
(V)	$\sim 1.5$	-	0	$< 1$	-	6.0	$< 1$	-	-	6.8	
(VI)	2.8	-	$< 1$	$< 1$	-	4.8	$< 1$	-	-	7.5	
(VII)	$< 1$	6.0	$< 1$	-	26.8	$< 1$	-	29.0	-	-	
(VIII)	2.2	6.4	$< 1$	-	26.0	$< 1$	-	29.0	-	-	
(IX) <sup>b</sup>	(10.1)	(0.9)	(0.9)	(5.1)	27.2	1.6	$< 1$	25.5	6.8	5.9	
(X)	3.1	6.4	$< 1$	$\sim 1.4$	26.0	1.2	$< 1$	25.6	6.4	7.5	$J_{1H}$ 5.0, $J_{3H}$ 3.9, $J_{2H}$ , $J_{4H}$ 1.2

<sup>a</sup>Listed as  $< 1$  when they were not resolved in rather broad bands; and as 0 when not apparent in sharp, well-resolved bands. <sup>b</sup>Values in parentheses are HF-coupling constants.

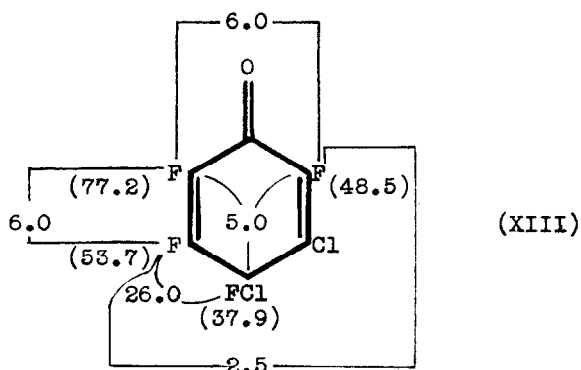
$\underline{J}_{13}$  and  $\underline{J}_{35}$  are fairly constant (6.0-6.4 Hz), as are the three-bond parameters  $\underline{J}_{23}$  and  $\underline{J}_{34}$  (25.5-27.2 Hz); the four-bond couplings  $\underline{J}_{24}$  are consistently larger than those ( $\underline{J}_{15}$ ) across the imine function but show no great variation with substituent. The five-bond coupling constants are small.

The four-bond HF-coupling  $\underline{J}_{15}$  in compound (IX) is notably larger in magnitude than the corresponding FF-coupling. In compound (X), the protons of the methyl group are strongly coupled to only one of the fluorines flanking the imine function, which indicates a syn disposition with coupling enjoying a 'through space contribution' [7]; the seven-bond coupling from  $\text{NCH}_3$  to  $\text{CFCl}$  ( $\underline{J}_{3H}$ ), which can only be through bond in nature, is remarkably large.

### Related Systems



A number of compounds directly related to the polyfluoro-cyclohexadienylideneamines (I)-(X), namely the cyclohexa-2,5-dienones (XII), have been studied recently by Russian investigators [8]. In those possessing a CFW group, the couplings arising from interaction of allylic with olefinic fluorine have magnitudes ( ${}^3\underline{J}$  21-26.5,  ${}^4\underline{J}$  4.5-10 Hz) similar to those of the corresponding couplings in the cyclohexadienylideneamines. All show deceptively simple AA'XX'-type sub-spectra for the olefinic fluorines ( $|\underline{J}| + |\underline{J}'| = 8-9$  Hz). We have examined the spectrum of 3,4-dichloro-2,4,5,6-tetrafluorocyclohexa-2,5-dienone (XIII) [1], which possesses the n.m.r. parameters shown (chemical shifts in parentheses). The olefinic coupling constant of 6 Hz is similar in magnitude to  $\underline{J}_{45}$  in the imines. The corresponding couplings for fluorinated p-benzoquinones lie in the range 4.5 - 5.6 Hz, but the four-bond couplings across the carbonyl group are smaller (0.3 - 1.7 Hz) [9].



## EXPERIMENTAL

### Spectroscopy

$^{19}\text{F}$  (at 94.1 MHz) and  $^1\text{H}$  (at 100 MHz) n.m.r. spectra were obtained using a Varian HA-100 instrument. Unless otherwise stated, the spectra were first-order and parameters were measured directly. Coupling constants, when quoted to two or three significant figures, are accurate to  $\pm 0.3$  Hz.

### Synthesis of N-substituted polyfluorocyclohexa-2,5-dienylideneamines

A small crystal of iodine was added to a stirred solution of the parent N-chlorinated polyfluoroarylamine [2] in AnalaR carbon tetrachloride. Solvent was removed from the product at 50-60 °C and water-pump pressure and the residue was purified by distillation or recrystallization. Details are listed in Table 3, and the results of elemental analysis of the products are as follows:

Q = Cl, X = CF<sub>3</sub>, Z = F

Found: C, 27.8; F, 44.0; N, 4.6.  
 Required: C, 27.8; F, 44.0; N, 4.6%.



TABLE 3  
Details of Syntheses



Q	X	Z	Starting material (g, mmol)	CCl <sub>4</sub> (cm <sup>3</sup> )	Temp., time (°C, min)	Product (g, mmol, %)
Cl	CF <sub>3</sub>	F	4.0, 13.2	5	30, 60	3.5, 11.6, 88 <sup>a</sup>
Cl	Ph	F	2.9, 9.35	20 <sup>b</sup>	20, 17 <sup>c</sup>	1.3, 4.2, 45 <sup>d</sup>
Cl	F	Cl } <sup>e</sup>	2.0, 7.4	25	60, 15	1.1, 4.1, 55 <sup>f</sup>
Cl	Cl	F				
Me	F	F	10.0, 43.2	30	20, 30 <sup>g</sup> then 60, 30	9.0, 39, 90 <sup>h</sup>
Cl	F	Br } <sup>i</sup>	2.0, 6.4	20	60, 10	0.9, 2.9, 45
Cl	Br	F				

<sup>a</sup>  $\lambda_{\text{max}}$  (film) 5.97 (CF=CF str.)  $\mu\text{m}$ . <sup>b</sup> Suspension. <sup>c</sup> The reaction was complete after 2 min.  
<sup>d</sup> M.p. 76 °C [after recrystallization from petroleum (b.p. 60-80 °C)];  $\lambda_{\text{max}}$  (mull) 5.79m,  
 5.97s (CF=CF str.)  $\mu\text{m}$ ;  $\lambda_{\text{max}}$  (hexane) 228 ( $\epsilon$  7,380), 267 ( $\epsilon$  37,400) nm. <sup>e</sup> Ca. 25:75 mixture  
 of 2- and 4-chloro isomers. <sup>f</sup> Pale-yellow oil, b.p. 72-74 °C at ca. 2 mmHg,  $\lambda_{\text{max}}$  (film) 5.85m,  
 5.98m (sh), 6.03s, 6.08s (C=C str.) shown to be a ca. 35:65 mixture of 2- and 4-chloro isomers by  
 n.m.r. <sup>g</sup> I.r. analysis of the reaction mixture after 30 min revealed that isomerization was  
 occurring only slowly at 20 °C. <sup>h</sup> Pale-yellow oil, b.p. 40-41 °C at ca. 2 mmHg,  $\lambda_{\text{max}}$  (film)  
 5.78w, 5.93s (CF=CF str.)  $\mu\text{m}$ ,  $\lambda_{\text{max}}$  (hexane) 232 ( $\epsilon$  12,540), 242 ( $\epsilon$  18,870) nm. <sup>i</sup> Ca. 25:75 <sup>g</sup>  
 mixture of 2- and 4-bromo isomers.

Q = Cl, X = Ph, Z = F

Found: C, 46.1; H, 1.7; Cl, 22.6; F, 24.5; N, 4.4.  
 Required: C, 46.5; H, 1.6; Cl, 22.9; F, 24.5; N, 4.5%.

Q = Cl, X = F, Z = Cl }  
Q = Cl, X = Cl, Z = F }

Found: C, 27.4; Cl, 39.5; F, 28.9; N, 5.7.  
 Required: C, 26.8; Cl, 39.7; F, 28.3; N, 5.2%.

Q = Me, X = Z = F

Found: C, 36.1; H, 1.5; Cl, 15.8; F, 40.7; N, 5.9.  
 Required: C, 36.3; H, 1.3; Cl, 15.3; F, 41.0; N, 6.0%.

Q = Cl, X = F, Z = Br }  
Q = Cl, X = Br, Z = F }

Found: C, 25.5; F, 25.0; N, 5.5.  
 Required: C, 23.0; F, 24.3; N, 4.5%.

N,4-Dichloropentafluorocyclohexa-2,5-dienylideneamine,  
N,4-dichloro-2,3,4,5-tetrafluorocyclohexa-2,5-dienylideneamine  
 and N,4-dichloro-2,3,5,6-tetrafluoro-4-methoxycyclohexa-2,5-  
 dienylideneamine were prepared as described elsewhere [1,2].

#### ACKNOWLEDGMENT

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