N-Chlorodifluoromethylenimine, CF_2=NCl

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Summary The simplest *N*-chloroperfluoroalkylenimine, CF_2=NCl, has been synthesised for the first time by thermolysis of the previously unknown *NN*-dichloroperhalogeno-alkylamine $CF_2Cl{\cdot}NCl_2$.

ALTHOUGH higher *N*-chloroperfluoroalkylenimines have been reported,[1,2] and isomers of CF_2=NCl are known,[3,4] the synthesis of this simplest *N*-chloroperfluoroalkylenimine was not accomplished until this work. In a novel dechlorination reaction, the new compound was isolated (>80%) from the thermolysis of $CF_2Cl{\cdot}NCl_2$.

$$CF_2Cl{\cdot}NCl_2 \xrightarrow[4\text{ hr.}]{100\text{–}150^\circ} CF_2{=}NCl + Cl_2$$

The free chlorine was removed from the imine by shaking with mercury at room temperature, and pure CF_2:NCl was then separated from trace amounts of $CF_3{\cdot}NCl_2$ and unreacted $CF_2Cl{\cdot}NCl_2$ by gas chromatography. No azo-compounds of the type RN=NR or azine compounds of the type R=N–N=R were observed in the thermolysis products.

The imine was characterised by its i.r., mass, and ^{19}F n.m.r. spectra and by elemental analysis. It has a boiling point of approximately 5°.

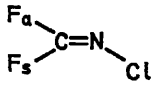
The very simple i.r. spectrum features bands at 1728 cm^{-1} (C=N stretch), 1322 and 981 cm^{-1} (CF_2 stretches), and 771 cm^{-1} (NCl stretch).

The mass spectrum of CF_2=NCl is tabulated below. Virtually all of the possible ions were observed in the cracking pattern, and their constitution corroborates the suggested isomer.

The ^{19}F n.m.r. spectrum consists of two doublets due to the spin coupling interaction of the magnetically non-equivalent *syn* and *anti* fluorines (ϕ_s + 40·2 p.p.m., ϕ_a + 61·3 p.p.m., J_{FF} = 69·0 Hz). Although both signals are relatively broad for fluorine resonances, the upfield signal attributed to the *anti* fluorine is broader, presumably because of the expected greater interaction with the nuclear quadrupole of the chlorine atom.[5]

Mass spectrum of CF_2=NCl

m/e	Assignment	*m/e*	Assignment
101	$CF_2N^{37}Cl^+$	51	$N^{37}Cl^+$
99	$CF_2N^{35}Cl^+$	50	CF_2^+
82	$CFN^{37}Cl^+$	49	$N^{35}Cl^+$
80	$CFN^{35}Cl^+$	45	CFN^+
64	CF_2N^+	37	$^{37}Cl^+$
63	$CN^{37}Cl^+$	35	$^{35}Cl^+$
61	$CN^{35}Cl^+$	31	CF^+
		26	CN^+



The precursor to CF_2=NCl, the dichloroamine $CF_2Cl{\cdot}NCl_2$, despite its direct preparation from the reaction of cyanogen chloride and chlorine monofluoride, was previously unknown.

$$ClC{\equiv}N + 2ClF \xrightarrow{25^\circ} CF_2Cl{\cdot}NCl_2\ (>90\%)$$

None of the intermediate imine CFCl=NCl was found in the reaction products even when a deficiency of ClF was used. This finding can be attributed to the greater reactivity of the imine when compared to the cyanide and has been observed in similar systems.[6] The clear, colourless, liquid $CF_2Cl{\cdot}NCl_2$ decomposes very slowly at room temperature to CF_2=NCl and Cl_2.

The compound was characterised by its i.r. and ^{19}F n.m.r. spectra, molecular weight (gas density), and by elemental analysis. The i.r. spectrum includes absorptions characteristic of C–F, C–N, and N–Cl bands, and the n.m.r. spectrum consists of a singlet at ϕ + 50·7 p.p.m.

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