Unusual Temperature-dependence of the ^{19}F Nuclear Magnetic Resonance Spectra of Compounds containing the –CF=N– Unit

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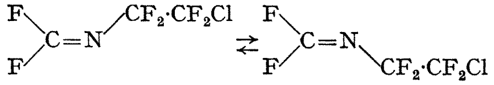
Summary The sharpening of the room-temperature spectrum due to C*F*=N– in $CF_3N{:}CF{\cdot}CF_2Cl$ as the temperature is lowered may be due to natural decoupling of ^{14}N–^{19}F coupling resulting from more effective quadrupolar relaxation of the nitrogen nucleus at the lower temperatures.

THE n.m.r. parameters (Table) of 4-chlorohexafluoro-2-azabut-1-ene (I) and 4-chlorohexafluoro-2-azabut-2-ene (II) were obtained by analysis on a first-order basis of the spectra. An AA′XX′ "deceptively simple"[1] spectrum is displayed by nuclei b and c of compound (I). The temperature markedly affects the AA′XX′ pattern, probably because of its influence on the relative populations of rotational isomers. Evidence of stereospecificity of F–F coupling is provided by the different values of J_{FF} between nuclei a and b in compound (I); one of the vinylic fluorines interacts strongly with the CF_2 (b) group (18·0 Hz.), while the other does not show any coupling. We have investigated the temperature-dependence of their ^{19}F n.m.r. spectra. At low temperatures, ^{19}F nuclei located near to a nitrogen atom give relatively sharp lines, as compared with broad absorptions observed at room temperature. This result can be interpreted, at least for compound (I), in terms of stereoisomerisation about the C=N bond:



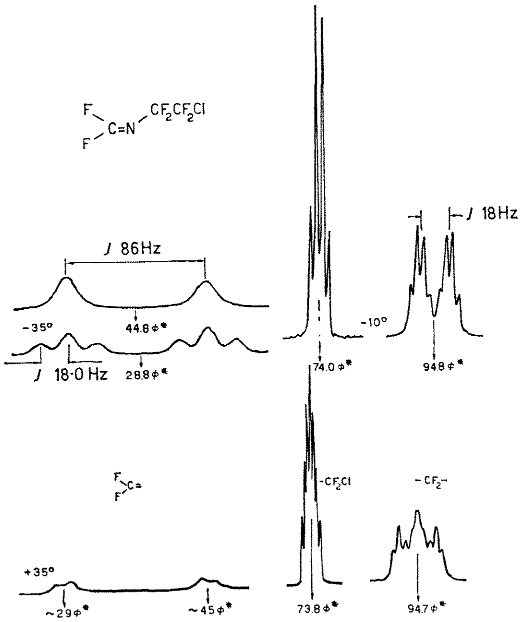
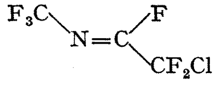
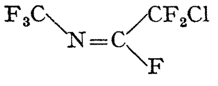


FIGURE 1. *The* ^{19}F *resonance spectrum at* 56·4 *MHz. of* $CF_2{=}\,NCF_2{\cdot}CF_2Cl$ *at room temperature and at* $-35°$.

The effects are particularly evident for the fluorine nuclei in $F_2C{=}N$–; at room temperature they give a very broad AB-type spectrum, which sharpens at lower temperatures ($-35°$) (Figure 1). However, it is difficult to invoke the same inversion process to rationalise the temperature-dependence of the n.m.r. spectrum of compound (II) (Figure 2). At room temperature, the –CF=N– absorption is a very broad band; when the temperature is lowered ($-70°$), splittings due to CF_3 and CF_2Cl groups appear. If the effect were due to a "freezing out" of the nitrogen inversion, signals related to the *syn*- and *anti*-stereoisomers should be observed at low temperatures.



syn



anti

The n.m.r. spectrum is compatible with the existence of only one isomer, probably the *syn*-isomer because of the $CF_3 \div CF$ coupling[2] (J 13·0 Hz.). We found no evidence of even a trace of the other isomer. This is in agreement with some literature data; n.m.r. spectra of compounds such as $CF_3N{=}CF{\cdot}CF_2{\cdot}CF_3$,[3,4] $CF_3N{=}CF{\cdot}CF_2{\cdot}CF_2{\cdot}CF_3$,[3-5] $CF_3N{=}CF{\cdot}CFCl{\cdot}CF_3$,[4] and $CF_2Cl{\cdot}CF_2N{=}CF{\cdot}CF_2Cl$,[6] for example, are consistent with the presence of only one isomerically pure product. In other cases,[2] such as $CF_3N{=}CF{\cdot}CF(CF_3)N{=}CF_2$ and $CF_3N{=}CF{\cdot}C(CF_3){=}NCF_3$, different geometrical isomeric forms were clearly distinguished in the n.m.r. spectrum. This shows that stereoisomerisation about the C=N bond for such compounds, at room temperature, is not at all rapid. As an alternative explanation, the temperature-dependence of the spectrum of (II) could be due to a natural decoupling of ^{14}N–^{19}F coupling due to a more effective quadrupolar relaxation of the nitrogen nucleus at lower temperatures. The molecular motion slows down on cooling and spin–lattice relaxation, arising from the fluctuating electric field gradient, becomes faster. This type of effect has been observed by Muetterties and Phillips[7] for ^{14}N–F and by Roberts[8] for ^{14}N–H in a number of amines. More recently, the same phenomenon has been observed in the D–H coupling of some deuteriated organic molecules.[9] If these considerations are valid for (II), they cannot be overlooked in the study of the rate of stereoisomerisation about the C=N bond. In addition, the free energy of activation, derived from temperature-dependence of line-width, of compounds such as $(CF_3)_2C{=}NCF(CF_3)_2$[10] or $(CF_3)_2CFN{=}CF_2$[11] must be considered an approximate estimate in view of a possible contribution of the ^{14}N quadrupole relaxation to the line-width of signals.

N.m.r. parameters for 4-*chlorohexafluoro*-2-*azabut*-1-*ene* (I) *and* 4-*chlorohexafluoro*-2-*azabut*-2-*ene* (II)

Compound		Chemical shift* (p.p.m. from $CFCl_3$)	Coupling constant* (Hz.)
	a	28·8	
$F_2C{=}N{-}CF_2{-}CF_2Cl$ (I)	a'^{0}	44·8	J_{ab} 18·0
a b c	b	94·8	$J_{a'b}$ *ca.* 0
	c	74·0	$J_{aa'}$ 86·0
	a	57·0	
$CF_3{-}N{=}CF{-}CF_2Cl$ (II)	b	32·4	J_{ab} 13·0
a b c	c	64·5	J_{bc} 7·0

* Measured at low temperature in $CFCl_3$ solution (*ca.* 20%) with an A 56/60 Varian spectrometer.

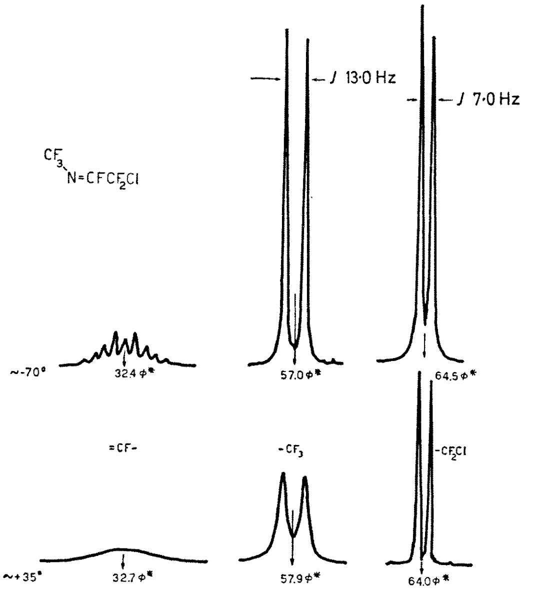


FIGURE 2. *The* ^{19}F *resonance spectrum at* 56·4 *MHz of* $CF_3N{=}CF{\cdot}CF_2Cl$ *at room temperature and at* −70°.

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