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NUCLEAR MAGNETIC RESONANCE SPECTRA OF POLYFLUOROBUTA-1,3-DIENES. PART II [1]. VARIABLE TEMPERATURE STUDY OF TWO 2-AZABUTADIENES

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SUMMARY

The two perfluoro-azadienes $CF_2{=\!=}N.CR{=\!=}CF_2$ (R = CF_3 or CF_2Cl) show temperature dependent ^{19}F n.m.r. spectra, with non-equivalent fluorine nuclei of the $CF_2{=\!=}N$ portion at low temperatures, which coalesce due to inversion at the nitrogen at higher temperatures($\Delta G^{\ddagger} = 60$ kJ mol^{-1}). N.m.r. parameters have been obtained. One of the five-bond F-F coupling constants is much larger (ca. 24 Hz) than the remainder (0·5-5·5 Hz), possibly due to 'through-space' coupling of fluorines in the cis-skew conformation.

INTRODUCTION

Dynamic n.m.r. spectroscopy affords a convenient method for the study of rotation and inversion about carbon-nitrogen double bonds in imines [2]. A number of perfluoro-imines have been studied [3-5], and those containing $CF_2 = N$ groups show separate fluorines only at low temperatures. The availability of the two perfluoro-2-azabuta-1,3-dienes (I) and (II) prompted their investigation. It was of interest to see how they compared with non-conjugated imines, and what effect the nitrogen had upon the coupling constants of the perfluorobuta-1,3-diene system [1,6].

$CF_2{=}NCR{=}CF_2$ (I) $R{=}CF_3$, or (II) $R{=}CF_2Cl$

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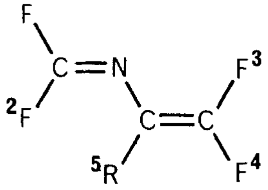
TABLE 1

^{19}F Chemical shifts of perfluoro-2-azabuta-1,3-dienes*



(I) R = CF_3

(II) R = CF_2Cl

Compound	Temperature °C	δ_1	δ_2	δ_3	δ_4	δ_5
(I)	-100	54·5	39·0	84·5	86·8	65·0
(I)	+75	48·0		84·5	86·8	64·5
(II)	-100	52·5	37·0	84·0	88·0	54·0
(II)	+75	44·0		84·5	88·4	52·5

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* In p.p.m. to high field of internal $CFCl_3$

RESULTS AND DISCUSSION

At ambient temperatures, the signal due to the fluorine nuclei of the $CF_2{=}N$ group in both compounds appeared as a very broad band ($\nu_{\frac{1}{2}}$ *ca.* 200 Hz), which sharpened when the temperature was raised, and separated upon cooling into two signals which were sharp below *ca.* -50°C, when the spectra were essentially first order. Appropriate coalescence behaviour was shown by certain lines in the remaining absorption bands as coupling to the $CF_2{:}N$ fluorines was averaged out. The parameters obtained are shown in Tables 1 - 3. The assignment of the fluorines of the $C{=}CF_2$group follows from the magnitude of the coupling constants, J_{35} and J_{45}, the *cis*-coupling having the larger value [7], and the assignment of the fluorines of the $CF_2{=}N$ group follows by analogy with other fluoro-imines of the type $CF_2{=}NR_F$, where the absorption to lower field is assigned to the fluorine *syn* to the side-chain because of the larger four-bond coupling to side-chain fluorines [3-5].

The derivation of the free energy of activation for stereoisomerization about the C=N bond from the coalescence of the $CF_2{=}N$ absorptions suffers from a possible contribution to line broadening arising from ^{14}N quadrupolar relaxation Coalescence behaviour in the remaining absorptions does not suffer from this disadvantage. They comprise X-portions of ABX_n sub-spectra, collapsing to A_2X_n sub-spectra. They contain pairs of lines separated by $|J_{AX} + J_{BX}|$ which remain sharp throughout the temperature range, and pairs, separated by $|J_{AX} - J_{BX}|$ in the first order limit, which coalesce to a single band. This coalescence may be treated as a simple two - site problem. The band system due to F-3 in compound (I) ($|J_{13}-J_{23}|$ = 24 Hz, T_c 0 ± 2°C) yielded $\Delta G^{\ddagger}$ 60±4 kJ mol^{-1}, and in compound (II) ($|J_{13} - J_{23}|$ = 21.4 Hz T_c -8 ± 2°C) also yielded $\Delta G^{\ddagger}$ 60 ± 4 kJ mol^{-1}. Very similar values were obtained from the coalescence behaviour of the $CF_2{=}N$ absorptions, indicating that quadrupolar relaxation does not make an important contribution to the line-widths.

TABLE 2

Coupling constant moduli (Hz) for $CF_2:NC(CF_3):CF_2$

Temperature °C	J_{12}	J_{13}	J_{23}	J_{14}	J_{24}	J_{15}	J_{25}	J_{34}	J_{35}	J_{45}
-100	68·0	1·8	24·0	5·1	5·1	0·5	2·0	25·0	8·6	24·8
-80	68·0	1·8	24·0	5·1	5·1	0·5	2·0	25·0	8·7	24·8
-60	68·0	2·0	24·5	5·1	5·1	0·5	2·8	26·7	9·0	24·8
-40	68·0	2·0	24·5	5·2	5·2	0·5	3·2	26·7	9·1	24·8
-20	*	*		5·4		1·6		27·0	9·2	24·6
0	*	12·8		5·4		2·0		27·6	9·3	24·4
10	*	12·7		5·5		2·2		27·8	9·4	24·3
33	*	12·4		5·6		2·4		28·0	9·6	24·2
75	*	11·7		5·7		2·6		28·4	10·0	24·2

* Unobtainable

TABLE 3

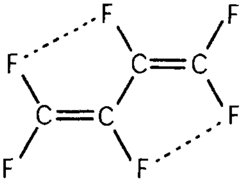
Coupling Constant moduli (Hz) for $CF_2:NC(CF_2Cl):CF_2$

Temperature °C	$\underline{J}_{12}$	$\underline{J}_{13}$	$\underline{J}_{23}$	$\underline{J}_{14}$	$\underline{J}_{24}$	$\underline{J}_{15}$	$\underline{J}_{25}$	$\underline{J}_{34}$	$\underline{J}_{35}$	$\underline{J}_{45}$
-90	69.0	1.6	23.0	3.4	5.5			24.6	6.2	34.4
-70	69.0	1.8	22.9	3.4	5.5	1.4	1.4	25.0	6.6	34.2
-50	69.0	1.7	23.2	3.4	5.5	1.4	1.4	26.2	6.8	34.4
-30	*	*		*		1.5		26.9	6.9	34.4
-10	*	12.4		4.7		1.6		27.4	7.0	34.4
10	*	12.4		4.7		1.6		27.6	7.4	34.4
33	*	12.4		4.9		1.7		28.4	7.5	34.4
50	*	12.4		4.9		1.9		29.0	7.8	34.4
75	*	12.4		4.9		2.1		30.0	7.8	34.4

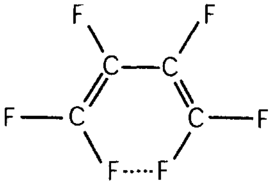
*Unobtainable

The broadening that CAVALLI and PICCARDI describe for the compound $CF_2N{=}CFCF_2Cl$ [5] may well be due to exchange between the *syn* isomer and a minor and undetected amount of *anti* isomer, rather than to the quadrupolar effects. The observed free energies of activation are very similar to the value reported for the compound $CF_2{=}N\ CF(CF_3)_2$ [4].

Buta-1,3-dienes may adopt three conformations, *s*-*trans*, *s*-*cis*, or skew, and in hexafluorobuta-1,3-diene, the *s*-*trans* conformation is destabilized by interactions of 1,3-fluorines (III) and the *s*-*cis* conformation by a 1,4-interaction (IV).

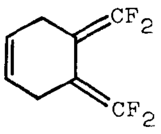


(III)

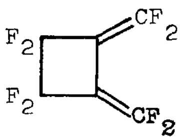


(IV)

An electron-diffraction study indicates that it adopts a *cis*-skew conformation with a dihedral angle of 47·4 ± 2·4° [8]. All the long-range five-bond coupling constants are positive, and the coupling constant corresponding to J_{23} of compounds (I) and (II) is more than twice as large as the remainder [1,6]. In the azadienes, the pairs of coupling constants J_{1x} and J_{2x} (x = 3-5) are of the same sign from the coalesence behaviour and are presumably positive. The only coupling constant which shows substantial temperature dependence is J_{34}, and in this it resembles the corresponding positive coupling constant in hexafluorobuta-1,3-diene. All this suggests that the azadienes also adopt a *cis*-skew conformation, and the larger magnitude of J_{23} may indicate that the dihedral angle is smaller, if it has 'through space' origin. Coupling constants of similar magnitude are seen in the dienes (V) and (VI) (31·4 and 23·2 Hz, respectively)



(V)



(VI)

which are forced to adopt a near *s-cis* arrangement [9].

The activation energy for stereoisomerization is not inconsistent with this since it resembles that of non-conjugated fluoro-imines. Imines appear to isomerize by planar inversion at the nitrogen [10]. This would result for the azadienes in conversion of a *cis*-skew to a *trans*-skew conformation. Since only one conformation is observed, subsequent or coincident rotation about the N-C single bond must be fast:

$$\begin{tikzcd}
\underline{\text{cis}}\text{-skew} \arrow[r, shift left, "\text{slow}"] \arrow[d, shift left, "\text{rot.}"] & \underline{\text{trans}}\text{-skew} \arrow[l, shift left, "\text{inv.}"] \arrow[d, shift left, "\text{fast}"] \\
\underline{\text{trans}}\text{-skew} \arrow[u, shift left, "\text{fast}"] \arrow[r, shift right, "\text{inv.}"'] & \underline{\text{cis}}\text{-skew} \arrow[l, shift right, "\text{slow}"'] \arrow[u, shift left, "\text{rot.}"]
\end{tikzcd}$$

EXPERIMENTAL

^{19}F n.m.r. spectra were recorded with a Perkin-Elmer R10 instrument operating at 56·46 MHz, and the chart calibration was checked by the side-band technique. A number were also recorded at 94·1 MHz using a Varian HA 100 instrument. Samples contained 10% trichlorofluoromethane.

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