Stereoisomerization of Perfluoro-(*N*-methyleneisopropylamine)

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RECENTLY we have recorded a broadening of the AB-type pattern of the ^{19}F nuclear magnetic resonance spectra of certain perfluoro-(*N*-methylene-alkylamines and -alkylenediamines).[1] We have investigated the temperature dependence of the ^{19}F n.m.r. spectrum of perfluoro-(*N*-methyleneisopropylamine), $(CF_3)_2CF{\cdot}N:CF_2$, and have established that the broadening results from rapid stereoisomerization about the C=N bond.

The equipment and techniques have been described previously[2] and $(CF_2)_2CF{\cdot}N:CF_2$ was prepared from perfluoro-2,3-diazabuta-1,3-diene and perfluoroisobutyryl fluoride.[1b]

At low temperatures (—42° and —63°) the spectrum shows an AB-type pattern centred at $37{\cdot}9 \pm 0{\cdot}05\phi^*$ corresponding to the $CF_2:N$ fluorine atoms, a complex doublet ($J = 4{\cdot}4$ c./sec.) at $80{\cdot}7\phi^*$. corresponding to the CF_3 groups and a doublet ($J = 24{\cdot}6 \pm 0{\cdot}6$ c./sec.) corresponding to the CF group. This spectrum, which is shown in Figure 1, indicates that the molecule does not isomerize rapidly (Figure 2a).

At higher temperatures, the AB-type pattern collapses into a single peak while the peak associated with the CF unit appears as a complex triplet (splitting = $14{\cdot}4 \pm 0{\cdot}2$ c./sec. at +78°). This spectrum indicates that rapid stereoisomerization is occurring about the C:N bond, rendering magnetically equivalent (on a time average) the fluorine atoms of the CF_2:N· group as shown in Figure 2b.

The results of line-width measurements at various temperatures are given in the Table. In all cases, the internal standard trichlorofluoromethane had a sharp peak. Errors quoted are standard deviations for the (averaged) numerical value listed.

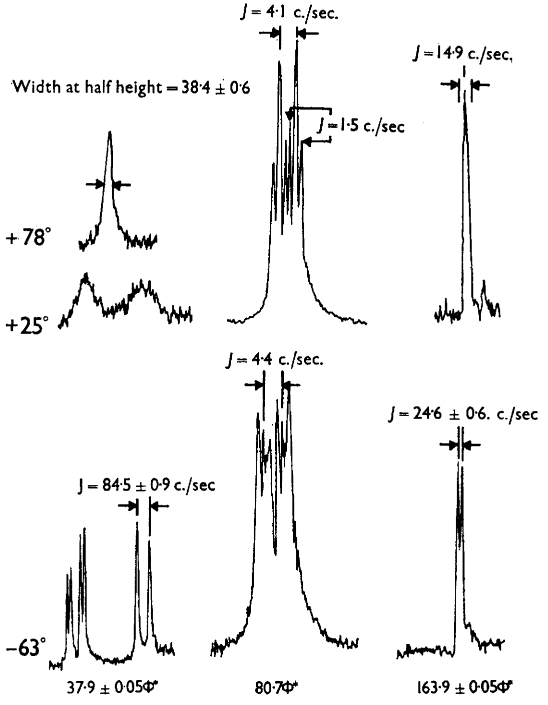
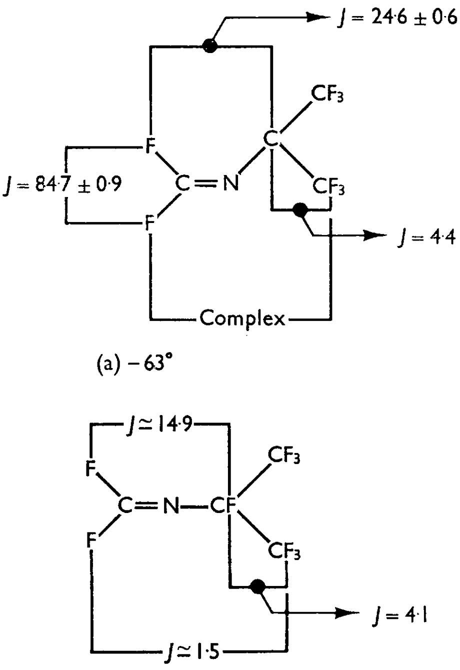


FIGURE 1



(a) −63°

(b) 25°

FIGURE 2

Rate constants, k_1, were calculated from measurements of peak width at half height and were based upon the chemical shifts as measured in the spectrum taken at −63°. At this temperature, the AB-type pattern centred at 37·9 ± 0·05ϕ^* was clearly resolved, the AB coupling constant being 84·5 ± 0·9 c./sec. and the shielding difference 10·94 ± 0·06ϕ^* (437·6 ± 2·5 c./sec. at 40·0 Mc./sec.). From the approximately linear plot of k_1 against $1/T$, the energy of activation ΔH^* is

TABLE

Free energy of activation for the stereoisomerization of perfluoro-(N-*methyleneisopropylamine*), *estimated from the temperature dependance of line-widths*

Temp.	ϕ^*[a] (p.p.m.)	w[b] (c./sec)	k_1,[c]	ΔG[d]
78°	38·82 ± 0·06	38·4 ± 0·6	7·83 × 10^3	15·2
74		44·6 ± 0·8	6·75 × 10^3	15·0
63		59·9 ± 0·8	5·0 × 10^3	14·7
56	38·4 ± 0·01	79·5 ± 7	3·9 × 10^3	14·4
52		106·5 ± 2·5	2·84 × 10^3	14·3
−42	32·44 ± 0·04[e]			
	43·22 ± 0·04[e]			
−63	32·16 ± 0·04[e]			
	43·14 ± 0·04[e]			

[a] At 10% conc. in $CFCl_3$ (see ref. 2b); [b] Line-width at half maximal height; [c] First-order rate constant for stereoisomerization; [d] From Eyring's equation; [e] By analysis of AB-type pattern, the centre of the pattern is at 37·9 ± 0·50 ϕ^*.

estimated as 11·0 kcal/mole, leading to $\Delta S^* = -10{\cdot}4$ e.u. at 25° from the Eyring equation. Andreades[3] has recently observed a similar isomerization about the C : N bond of perfluoro-(N-isopropylidineisopropylamine), $(CF_3)_2CF{\cdot}N{:}C(CF_3)_2$, for which he reported an activation energy of 13·0 ± 3·0 kcal/mole.

The mechanism of isomerization has not been deduced but it is noteworthy that rapid stereoisomerization about the C : N bond is not observed at room temperature in perfluoroalkylidine derivatives of normal perfluoroalkylamines. The ^{19}F n.m.r. spectra of such compounds show a typical AB-type pattern associated with the $CF_2{:}N$ group.[1,4] That the increased rate of isomerization observed in derivatives of the branched amines is caused by steric factors has yet to be established.

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