Nuclear Magnetic Resonance Studies of Fluorinated Heterocyclic Compounds: the Effect of Steric Hindrance on Inversion at Two Nitrogen Atoms

By PAUL OGDEN

(*Central Research Laboratories, Minnesota Mining and Manufacturing Company, 3M Center, St. Paul, Minnesota* 55101)

Summary The order of activation energy for nitrogen inversion is perfluoro-(3,4,5,6-tetrahydro-1,2-dimethylpyridazine) > perfluoro-(1,2-dimethyl-1,2-pyrazolidine) > perfluoro-(1,2-dimethyl-1,2-diazetidine), a reversal of predictions which is probably caused by steric effects.

ALTHOUGH inversion at two nitrogen atoms in a hydrocarbon heterocyclic compound has been investigated using ^1H n.m.r. spectroscopy,[1] no such study of fluorinated heterocyclic compounds using ^{19}F n.m.r. has been described. Primarily this is because fluorinated heterocyclic compounds containing adjacent nitrogen atoms bearing bulky substituents have not been available. However, I recently discovered a synthesis route to a series of such compounds[2] and here report some preliminary observations on the effect of steric hindrance upon inversion at the two nitrogen atoms in perfluoro-(1,2-dimethyl-1,2-diazetidine((I), -(1,2-dimethyl-1,2-pyrazolidine) (II), -(3,4,5,6-tetrahydro-1,2-dimethylpyridazine) (III) and -(2,3,5,6-tetrahydro-1,4-dimethyl-1,4-diazine) (IV).

At low temperatures the spectra of (I), (II), and (III) show well resolved AB-type patterns corresponding to the difluoromethylene groups (1) adjacent to the nitrogen atoms, while that of (IV) shows a quartet corresponding to the difluoromethylene groups. Upon raising the temperature, the AB patterns of (I) and (II) collapse [coalescence temperature (I) between −23°C and 17°, (II) between 30° and 44°] until at elevated temperatures they appear as complex single peaks. The spectra of (III) and (IV) do not change significantly when the sample temperature is raised to 100° (see Table for details).

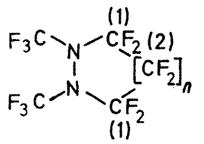
These results indicate that at elevated temperatures

^{19}F *N.m.r. data for perfluoro-*(1,2-*dimethyl*-1,2-*diazetidine*) (I), -(1,2-*dimethyl*-1,2-*pyrazolidine*) (II), -(3,4,5,6-*tetrahydro*-1,2-*dimethylpyridazine*) (III), *and* -2,3,5,6-*tetrahydro*-1,4-*dimethyl*-1,4-*diazine*) (IV), *at different temperatures*

Compound	Temp.	ϕ^* CF$_3$[a]	ϕ^* CF$_2$ (1)	ϕ^* CF$_2$ (2)
(I)	65°	67·43[b]	97·52 ± 0·04[c]	
(I)	−86	66·4 ± 0·03[d]	87·92 ± 0·03 103·92 ± 0·03 [e]	
(II)	84	63·62 ± 0·04[f]	99·59 ± 0·03[g]	126·4[h]
(II)	−58	63·77 ± 0·04[j]	90·0 ± 0·04 [k] 109·0 ± 0·04 [l]	128·03 ± 0·02[f]
(III)	100	58·1 ± 0·03[f]	91·25 117·75 [m]	128·25 137.15 [n]
(III)	−29	no appreciable change from above		
(IV)	23	52·8[o]	92·3[p]	
(IV)	−100	no appreciable change from above		

[a] The equipment and techniques have been described previously,[7] errors quoted are standard deviations for the (averaged) numerical value listed, taken from at least four measurements, other values are the average of two measurements. [b] Quintet, J 5·0 Hz. [c] Width at half maximal height ($W_{1/2}$) = 30·4 ± 0·3 Hz. [d] Doublet J 15·7 ± 0·5 Hz. [e] AB-type pattern centred at 95·92 ± 0·03 ϕ^*, J_{AB} 135 Hz., shielding difference = 16·0 ϕ^*. [f] Complex peak. [g] $W_{1/2}$ = 69·0 ± 1 0 Hz. [h] Seven-fold peak, J *ca.* 2·0 Hz. [j] Complex doublet, J 22·0 ± 1·5 Hz. [k] AB-type pattern centred at 99·5 ± 0·01 ϕ^*, J_{AB} 190 ± 2·0 Hz., shielding difference = 19·0 ± 0·04 ϕ^*. [l] Quartet, J 20·2 ± 0·7 Hz. [m] AB-type pattern centred at 104·5 ϕ^*, J_{AB} 215 Hz., shielding difference = 26·5 ϕ^*. [n] AB-type pattern centred at 132·7 ϕ^*, J_{AB} 265 Hz., shielding difference = 8·9 ϕ^*. [o] Quintet, J 12·6 Hz. [p] Quartet, J 12·6 Hz.

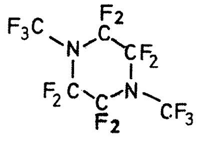
nitrogen inversion occurs in (I) and (II) (Fig. Ia and Ib). At lower temperatures the rate of inversion is sufficiently slowed that the spectra correspond to the "frozen" structures (Figure, c and d). The barrier to inversion is sufficiently high in (III), however, for the molecule to remain "frozen" at 100°, while in (IV) it is so low that rapid inversion continues at −100°.



(I) n = 0

(II) n = 1

(III) n = 2



(IV)

Inversion rates were calculated for (I) and (II) using line-width measurements, and from a plot of log k_1 against $1/T$, activation energies of 7·25 and 8·62 kcal./mole, respectively, were estimated. These values are somewhat lower than those previously reported for compounds which contain only one nitrogen atom, i.e. *ca.* 11·0 kcal./mole for perfluoro-oxazetidines,[3] 11·0 kcal./mole for $(CF_3)_2CF{-}N{=}CF_2$,[4] and 13·0 kcal./mole for $(CF_3)_2CF{-}N{=}C(CF_3)_2$.[5]

Nitrogen inversion has previously been described for perfluoro-heterocyclic compounds in which there are not two adjacent nitrogen atoms.[4] These, like their hydrocarbon analogues, show inversion to occur more readily in large rings than in smaller ones, where ring strain leads to a high barrier to inversion.[6] The results described here indicate that the reverse is true in the case of (I), (II), and (III).

That inversion is favoured for the smaller ring, (I), is probably due to increasing steric hindrance to inversion of the bulky trifluoromethyl groups as the C–N–N bond angle θ decreases (I) > (II) > (III). Such an explanation is clearly an oversimplification, ignoring effects such as ring puckering or inversion, but is supported by the fact that (IV), in which there is no steric hindrance, shows inversion even at −100°.

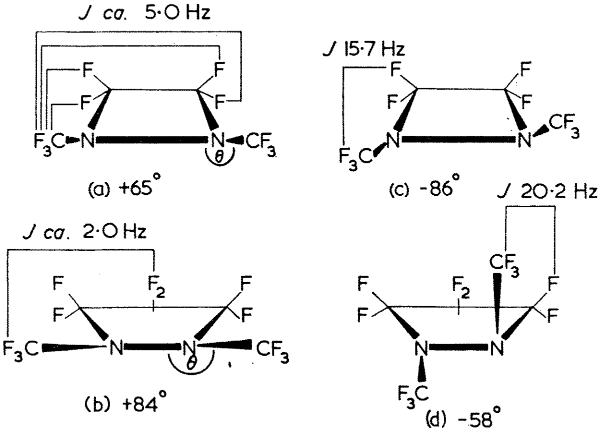


FIGURE. *Structural assignments* a, (I) *at* 65°; b, (II) *at* 84°; c, (I) *at* −85°; *and* d, (II) *at* −58°. c *and* d *represent the trans-isomer which is expected to be preferred.*

I thank Drs. J. J. McBrady and G. V. D. Tiers for many helpful discussions. This work was partially supported by a United States Air Force contract from Wright–Patterson Air Force Base.

(*Received, June* 19*th*, 1969; *Com.* 882.)

---

[1] J. E. Anderson and J. M. Lehn, *J. Amer. Chem. Soc.*, 1967, **89**, 81.

[2] P. H. Ogden, in preparation.

[3] J. Lee and K. C. Orrell, *Trans, Faraday Soc.*, 1965, **61**, 2342.

[4] P. H. Ogden and G. V. D. Tiers, *Chem. Comm.*, 1967, 527.

[5] S. Andreades, *J. Org. Chem.*, 1962, **27**, 4163.

[6] (a) For a recent review see J. P. Engstrom, *M.I.T. Seminars in Organic Chemistry*, Cambridge, Mass., 1st Semester 1965—66. p. 255; (b) A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 5023; (c) A. Lowenstein, F. D. Neumer, and J. D. Roberts, *ibid.*, 1960, **82**, 3599.

[7] (a) G. V. D. Tiers, *J. Phys. Chem.*, 1958, **62**, 1151; (b) G. Filipovich and G. V. D. Tiers, *ibid.*, 1959, **63**, 761.