Journal of Fluorine Chemistry, 12 (1978) 35–44

Received: November 4, 1977

A VARIABLE TEMPERATURE STUDY OF THE 19-F N.M.R. SPECTRA OF SOME FLUOROALKYLHYDROXYLAMINES: CONFORMATIONAL CHANGES AT THE NITROGEN ATOM [1]

M.G. BARLOW* AND K.W. CHEUNG

Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD (U.K.)

SUMMARY

The fluoroalkylhydroxylamines (I) - (VII) have been examined by variable temperature 19-F n.m.r. spectroscopy, and free energies of activation obtained for the process which renders equivalent the fluorines of the CF_2N group in (I), and the trifluoromethyl groups of the $(CF_3)_2CFN$ group in (IV), and of the trifluoromethyl groups of the $(CF_3)_2N$ group nearest to the asymmetric carbon atom in (V) - (VII). The possible conformational processes at the nitrogen atom are discussed.

		$\Delta G^{\ddagger}$/kJ mol^{-1}
(I)	$(CF_3CF_2CF_2)_2NOCF_2CF_2CF_3$	72 ± 6
(II)	$CF_3CF_2CF_2N(CF_3)OCF_2CF_2CF_3$	
(III)	$CF_3CF_2CF_2N(CF_3)OCF_3$	
(IV)	$(CF_3)_2CFN(CF_3)OCF(CF_3)_2$	71 ± 4
(V)	$(CF_3)_2NOCH_2CHClON(CF_3)_2$	60 ± 4
(VI)	$(CF_3)_2NOCH_2CHFON(CF_3)_2$	59 ± 4
(VII)	$(CF_3)_2NOCF_2CHFON(CF_3)_2$	59 ± 4

The perfluorotrialkylhydroxylamines (II) - (IV) were prepared by photochemical reaction of a perfluoroalkyl iodide with a perfluoroalkyl nitroso compound.

* To whom enquiries should be addressed.

Since it was observed that some alkyl hydroxylamines show magnetic non-equivalence in their low temperature n.m.r. spectra [2,3] there has been a number of studies of conformational changes in such compounds. For cyclic derivatives [4,5] it is generally agreed that the changes are associated with hindered inversion at the nitrogen atom, but for acyclic compounds these have been variously ascribed to hindered inversion at the nitrogen atom [6,7] and to restricted rotation about the N—O bond [8,9] . The former explanation has received theoretical justification [10] .

RESULTS AND DISCUSION

In the hope of clarifying this problem, we have studied two types of fluoroalkylhydroxylamine: (i) tris-alkylhydroxylamines of the type $R_F^1R_F^2NOR_F^1$ (I) - (IV), where the presence of prochiral nuclei is associated with asymmetry at the nitrogen; and (ii) bis(NN-bistrifluoromethylaminoxy)ethanes (V) - (VII), where prochiral pairs of trifluoromethyl groups are associated with the presence of an asymmetric carbon atom.

$(CF_3CF_2CF_2)_2NOCF_2CF_2CF_3$ (I)

$CF_3CF_2CF_2N(CF_3)OCF_2CF_2CF_3$ (II)

$CF_3CF_2CF_2N(CF_3)OCF_3$ (III)

$(CF_3)_2CFN(CF_3)OCF(CF_3)_2$ (IV)

$(CF_3)_2NOCH_2CHClON(CF_3)_2$ (V)

$(CF_3)_2NOCH_2CHFON(CF_3)_2$ (VI)

$(CF_3)_2NOCF_2CHFON(CF_3)_2$ (VII)

$CF_3CF_2CF_2N[CF(CF_3)_2]OCF(CF_3)_2$ (VIII)

The hydroxylamines (II) - (IV) were prepared by the photochemical reaction of a perfluoroiodoalkane R_F^1I with a nitroso-compound R_F^2NO:

$$2R_F^1I + R_F^2NO \xrightarrow{u.v.} R_F^1R_F^2NOR_F^1$$

a route previously used to prepare compound (I) [3] . An attempt to prepare the hindered hydroxylamine (VIII) failed, and the product contained hydroxylamine (I), indicating C—N

bond cleavage. The hydroxylamines (V) - (VII) were prepared in this Department by the addition of bistrifluoromethylaminoxyl to the appropiate olefin [11].

The non-equivalence of the CF_2N fluorines of compound (I) has been described previously, and ascribed to hindered inversion at the nitrogen atom [3]. The AB-type absorption for these fluorines coalesced to a single absorption (T_c = 85 ± 2 °C), which further narrowed upon raising the temperature, suggesting that 14-N quadrupolar relaxation was contributing to the line-width. Other absorption bands also narrowed with increasing temperature. The hydroxylamines (II) and (III) showed little change in their spectra in the temperature range -90 to +180 °C, the absorption due to the CF_2N group remaining as a broad unresolved band throughout the range. Their chemical shifts to high field of internal $CFCl_3$ were as follows:

$CF_3\ CF_2\ CF_2\ N(CF_3)OCF_2CF_2CF_3$

83.5 128 100.7 66.7 91 131 83.5

$CF_3\ CF_2\ CF_2\ N(CF_3)OCF_3$

83.4 128.4 101.5 66.3 66.3

The failure to observe coalescence behaviour may well be due to a small chemical shift difference of the fluorines of the CF_2N group. The spectrum of hydroxylamine (IV) (see Fig. 1) showed absorptions due to non-equivalent CF_3 groups assigned to the $(CF_3)_2CFN$ group, with a chemical shift difference which decreased linearly with increasing temperature. These absorptions coalesced to a single absorption at 93 ± 2 °C (chemical shift difference 127 Hz by extrapolation). The absorptions of the $(CF_3)_2CFO$ group showed little change. The ambient temperature chemical shifts are as follows:

$(CF_3)_2\ CFN(CF_3)OCF\ (CF_3)_2$

73.2, 76.7 154.3 64.5 136.0 77.9

The three bisaminoxyethanes (V) - (VII) showed absorptions at low temperatures due to non-equivalent and coupled ($|J|$ = 10 Hz) CF_3 groups assigned to the $(CF_3)_2N$ group nearest to the

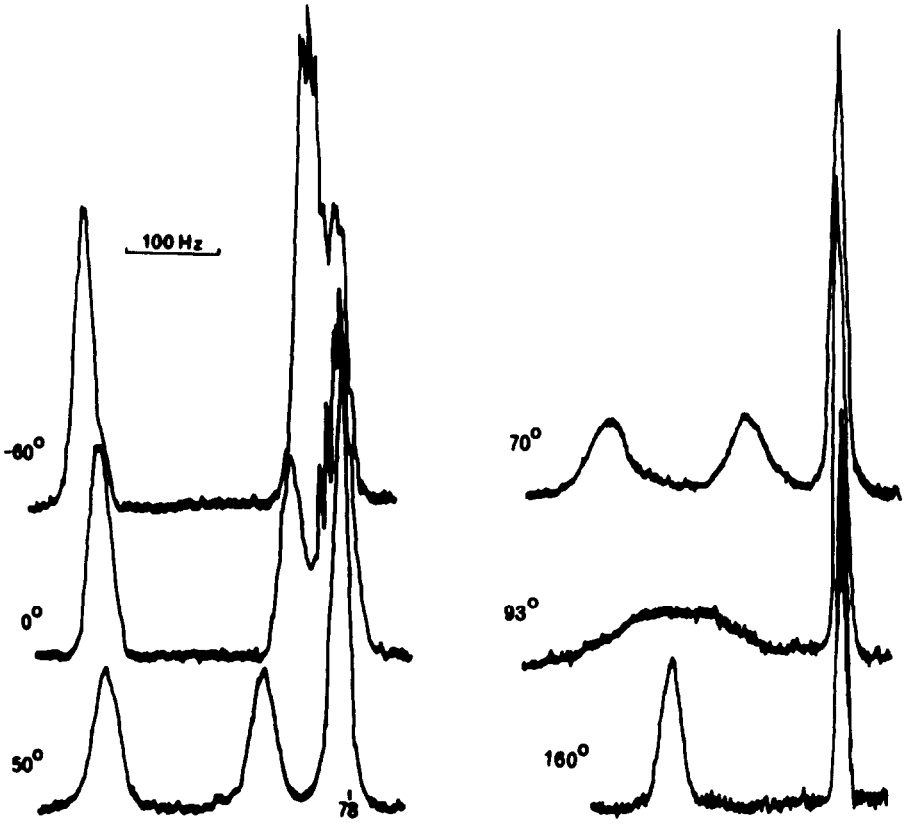


Fig. 1. The variable temperature 19-F n.m.r. spectrum of the CF_3-region of the hydroxylamine $(CF_3)_2CFN(CF_3)OCF(CF_3)_2$.

asymmetric carbon atom, whereas the other $(CF_3)_2N$ group showed no such non-equivalence. The bands coalesced to a single absorption at higher temperatures. This is illustrated in Fig. 2 where the CF_3-absorptions of compound (VI) are shown. Only the low-field absorption showed coupling to the fluorine nucleus of the adjacent CHF group. The spectral parameters obtained for this and the other compounds are shown below:

	$(CF_3)_2NOCHFCH_2ON(CF_3)_2$			at -50 °C
19-F	68.65 69.8	136.0	69.9	
1-H		5.68	4.17	(to low field of $SiMe_4$)

	$(CF_3)_2NOCHFCF_2ON(CF_3)$	at -50 °C
19-F	69.0, 70.1 } 143.8 91.3 68.6	
1-H	5.7	
	$(CF_3)_2NOCHClCH_2ON(CF_3)_2$	at -40 °C
19-F	67.6, 69.2 } 70.0	
1-H	5.91 4.35	

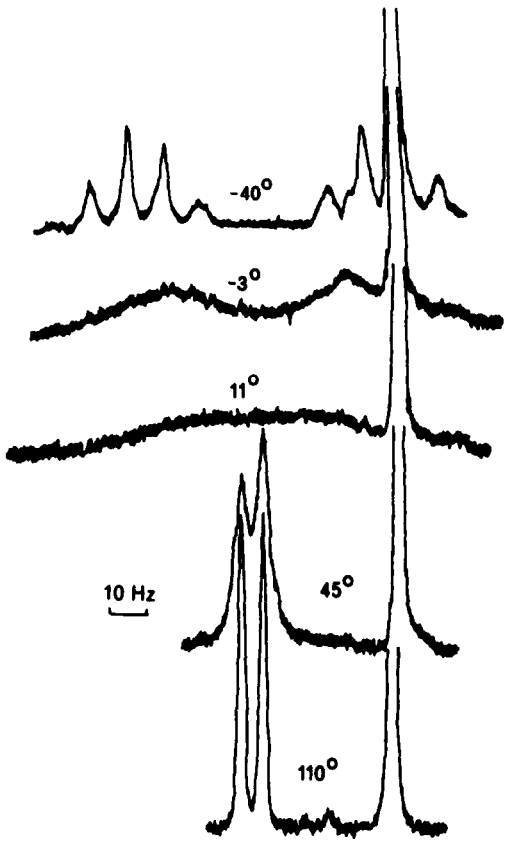


Fig. 2. The variable temperature 19-F n.m.r. spectrum of the CF_3-region of the hydroxylamine $(CF_3)_2NOCHFCH_2ON(CF_3)_2$.

TABLE

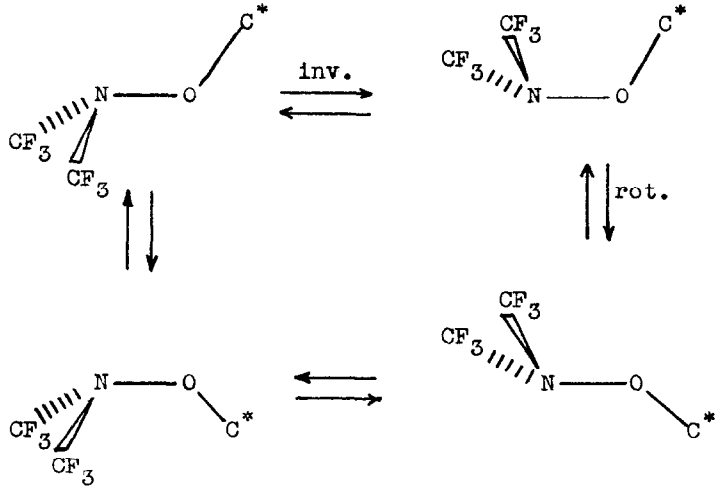
Rate constants and free energies of activation at the coalescence temperature (T_c) for some polyfluoroalkylhydroxylamines

Compound	T_c (°C)	$\delta\omega$/Hz [a]	k/s^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
(I)	79	247.4	708	72 ± 6 [b]
(IV)	93	127	225	71 ± 4 [c]
(V)	27	101	226	60 ± 4 [c]
	-3	9.6	62	56 ± 4
(VI)	11	67.1	149.5	59 ± 4 [c]
	-3	9.6	62	56 ± 4
(VII)	13	67.1	149.5	59 ± 4 [c]
	0	9.6	60	57 ± 4

[a] Either a chemical shift difference or a coupling constant; [b] Using the equation $k_c = \pi(\delta\omega^2 + 6J_{AB})^{\frac{1}{2}}/2^{\frac{1}{2}}$; and [c] Using the equation $k_c = \pi\delta\omega/2^{\frac{1}{2}}$.

The kinetic parameter obtained from the spectral changes are shown in the Table, where the free energies of activation for coalescence were obtained using the Eyring equation and a transmission coefficient of unity. The somewhat approximate figures do indicate that the process has an activation energy some 10 kJ mol^{-1} or so larger for the more hindered perfluoro-(trisalkylhydroxylamines). The figures for the bistrifluoromethylhydroxylamines are in turn, 4 kJ mol^{-1} or so larger than those reported for comparable non-fluorinated acyclic hydroxylamines.

The bistrifluoromethylhydroxylamines are the simpler case to consider. For coalescence of the CF_3-signals, both inversion at the nitrogen atom and rotation about the N—O bond must occur, and an alternative inversion rather than rotation at the oxygen atom would not result in equivalence. The same applies to the pair of CF_3 groups more remote from the asymmetric carbon, and the absence of observable non-equivalence is presumably a result of a small chemical shift difference.



For the hydroxylamines (I) and (IV), additional rotation about the C—N bonds is necessary, and this has been considered for (I) previously [3]. It has been argued that an apparent steric deceleration in compounds of the type $C_6H_5CH_2NR^1\text{-}OR^2$ (R^1 = i-Pr, R^2 = Me or R^1 = Me, R^2 = i-Pr) is evidence of a significant barrier to rotation about the N—O bond [8], since if inversion dominates the process, steric crowding, which is relieved in the transition state, should accelerate the process. However, unless they are of very different energies, the process of inversion and rotation will not occur in isolation, and the activation energies may well show a steric increase, even when nitrogen inversion is the dominant partner.

We have reported magnetic non-equivalence of trifluoromethyl groups in bistrifluoromethylalkylamines of the type $(CF_3)_2NCXYZ$ [12]. For the compound $(CF_3)_2NCHFCF_2Cl$, the free energy of activation (40 kJ mol^{-1}) for coalescence may be compared with those for compounds (V) - (VII). Introducing an oxygen atom, which may well reduce the crowding at the nitrogen somewhat, still raises the barrier by about 20 kJ mol^{-1}. Even if this difference is entirely due to N—O torsion, a substantial barrier remains to ascribe to nitrogen

inversion. The larger values for compounds (I) and (IV) then reflect an additional contribution to the barrier from C—N torsion.

EXPERIMENTAL

19-F N.m.r. spectra were obtained at 56.46 MHz for samples containing 50% v/v of trichlorofluoromethane using a Perkin-Elmer R10 instrument. The calibration of the built-in thermocouple of the variable-temperature probe was checked using methanol and temperatures are believed to be accurate to ± 1 °C. Mass spectra were recorded at 70 eV using an A.E.I. MS 2H instrument.

The nitroso-compounds were prepared by thermal decomposition of the appropiate acyl nitrite [13].

Preparation of perfluorotrialkylhydroxylamines

(a) From trifluoronitrosomethane and heptafluoro-1-iodopropane

Trifluoronitrosomethane (2.25 g, 22.6 mmol), heptafluoro-1-iodopropane (13.4 g, 45.2 mmol) and mercury (2 cm^3), sealed in a silica tube (300 cm^3) and irradiated with u.v. light from a Hanovia UVS 500 lamp at a distance of 200 mm for 6 h with shaking, gave a colourless fraction, b.p. 78 °C, identified by i.r. and n.m.r. spectroscopy, and mass spectrometry as perfluoro-*N*-methyl-*O*,*N*-di-n-propylhydroxylamine (nc) (6.75 g, 15.4 mmol, 68%)(Found: C, 19.5; F, 73.8; N, 3.1%; $M^{+\cdot}$, 437. $C_7F_{17}NO$ requires C, 19.2; F, 73.9; N, 3.2%; *M*, 437).

(b) From heptafluoro-1-nitrosopropane and trifluoroiodomethane

In a similar manner, heptafluoro-1-nitrosopropane (4.5 g, 22.6 mmol) and trifluoroiodomethane (9.05 g, 45.2 mmol) gave perfluoro-*O*,*N*-dimethyl-*N*-n-propylhydroxylamine (nc) (4.72 g, 14.0 mmol, 62%)(Found: C, 17.5; F, 73.6; N, 4.0%; $M^{+\cdot}$, 337. $C_5F_{13}NO$ requires C, 17.8; F, 73.3; N, 4.2%; *M*, 337) as a colourless liquid, b.p. 34 °C.

(c) From trifluoronitrosomethane and heptafluoro-2-iodopropane

In a similar manner, trifluoronitrosomethane (2.25 g, 22.5 mmol) and heptafluoro-2-iodopropane (13.4 g, 45.2 mmol) gave perfluoro-N-methyl-O,N-di-isopropylhydroxylamine (nc) 5.55 g, 12.7 mmol, 56%) (Found: C, 19.4; F, 73.9; N, 3.1%; $M^{+\cdot}$, 437. $C_7F_{17}NO$ requires C, 19.2; F, 73.9; N, 3.2%; M, 437) b.p. 45 °C

(d) From heptafluoro-1-nitrosopropane and heptafluoro-2-iodopropane

Heptafluoro-1-nitrosopropane (4.5 g, 22.6 mmol) and heptafluoro-2-iodopropane (13.4 g, 45.2 mmol) gave a fraction, b.p. 126-128 °C, the 19-F n.m.r. spectrum of which indicated the presence of perfluoro-tri-n-propylhydroxylamine and other unidentified components, which could not be separated by g.l.c.

We thank Professor R.N Haszeldine, and Drs. R.E. Banks and B. Justin for the gift of samples of bistrifluoromethyl-hydroxylamines.

REFERENCES

1 Reported in part at the 6th International Symposium on Fluorine Chemistry, Durham, July 1971, Abstract B34.
2 D.L. Griffith and J.D. Roberts, J. Amer. Chem. Soc., 87 (1965) 4089.
3 R.E. Banks, M.G. Barlow, R.N. Haszeldine and M.K. McCreath, J. Chem. Soc., (1965) 7203.
4 W.D. Emmons, J. Amer. Chem. Soc., 79 (1957) 5739; S.J. Brois, ibid., 90 (1968) 506; F.G. Riddell, J.M. Lehn and J. Wagner, Chem. Commun. (1968) 1403.
5 J. Lee and K.G. Orrell, Trans. Faraday Soc., 61 (1965) 2342.
6 D.L. Griffith, B.L. Olson and J.D. Roberts, J. Amer. Chem. Soc., 93 (1971) 1648.
7 J.R. Fletcher and I.O. Sutherland, Chem. Commun., (1970) 687.

8 M. Raban and G.W.J. Kenney, Tetrahedron Lett., (1969) 1295.
9 B.J. Price and I.O. Sutherland, Chem. Commun., (1967) 1070.
10 D. Kost and M. Raban, J. Org. Chem., 41 (1976) 1748.
11 R.E. Banks, R.N. Haszeldine and B. Justin, unpublished results.
12 M.G. Barlow and K.W. Cheung, Chem. Commun., (1969) 870.
13 R.E. Banks, M.G. Barlow, R.N. Haszeldine and M.K. McCreath, J. Chem. Soc. (C), (1966) 1350.