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A VARIABLE TEMPERATURE STUDY OF THE 19-F N.M.R. SPECTRUM OF PERFLUOROHEXAMETHYLTETRAZAN: NOVEL RESTRICTED ROTATION AND HINDERED INVERSION AT THE NITROGEN ATOMS [1]

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SUMMARY

At low temperatures, the ^{19}F n.m.r. spectrum of the tetrazan $(CF_3)_2NN(CF_3)N(CF_3)N(CF_3)_2$ shows the presence of two isomers with a free energy difference in stability $\Delta\underline{G}$ of 2.2 kJ mol^{-1}. Both isomers show three types of CF_3 group which coalesce at -15 °C to three systems of equal intensity ($\Delta\underline{G}^{\ddagger}$ 52 kJ mol^{-1}). At 40 °C the two signals assigned to the terminal CF_3 groups coalesce to a single band ($\Delta\underline{G}^{\ddagger}$ 65 kJ mol^{-1}).

The behaviour is discussed in terms of restricted inversion at the nitrogen atoms, and hindered rotation about the N-N bonds.

The hydrazines $(CF_3)_2NN(CF_3)NO$ and $(CF_3)_2NN(CF_3)NO_2$ have temperature independent spectra.

INTRODUCTION

The conformational behaviour of hydrazines, and their barriers to nitrogen inversion and rotation about the N-N bond have attracted much interest [2-4]. Their complex n.m.r. spectra have been variously interpreted in terms of hindered rotation and slow inversion, or of both processes. Of

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perfluoro-compounds, only three cyclic hydrazines have been studied [5]. The larger chemical shifts associated with ^{19}F n.m.r. spectroscopy makes easier study of such processes, and the behaviour of the hydrazine derivatives (I) to (III) are here described.

$$(CF_3)_2NN(CF_3)X \qquad X = \text{(I)}\ N(CF_3)N(CF_3)_2,\ \text{(II)}\ NO,\ \text{or (III)}\ NO_2$$

RESULTS AND DISCUSSION

At low temperatures, the tetrazan (I) showed the presence of unequal amounts of two components in its ^{19}F spectrum, each of which had three types of CF_3 group (see Fig. 1). Integration of the two high field bands (e and f) for the temperature range -100 to -40 °C and application of the Van't Hoff reaction isotherm yielded the thermodynamic parameters (at -90 °C):

$$\Delta\underline{G} = 2.2 \pm 0.2\ \text{kJ mol}^{-1},\ \Delta\underline{H} = 770 \pm 60\ \text{J mol}^{-1},\ \Delta\underline{S} = -8 \pm 4\ \text{J mol}^{-1}\ \text{K}^{-1}$$

At -15 °C, where, by extrapolation, the amounts of the two isomers were equal, the pairs of absorptions (see Fig. 1)

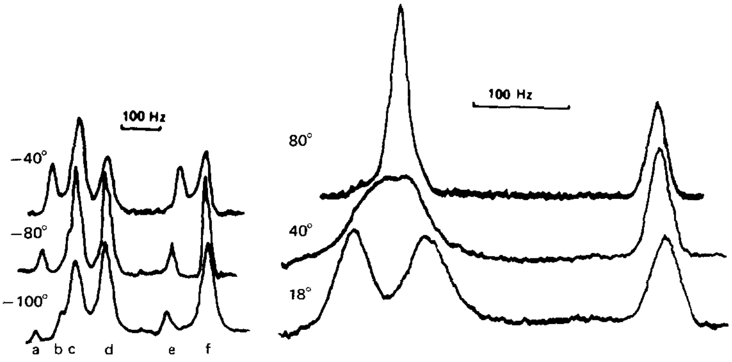


Fig. 1. Variable temperature ^{19}F n.m.r. spectra of the compound $(CF_3)_2NN(CF_3)N(CF_3)N(CF_3)_2$.

a and c, b and d, and e and f, had coalesced, and at -40 °C, further coalescence of the two low-field bands occurred, resulting at higher temperatures in two absorptions of relative intensity 2 : 1, assigned respectively to the terminal and the internal CF_3 groups.

There are a number of possible explanations for this behaviour. The two low temperature isomers could be dl and meso, either fixed in one conformation, or having free rotation about the N-N bonds. However, the averaging of these two isomers, but not of the non-equivalence of the terminal CF_3 groups, could only arise from inversion at a centre nitrogen and rotation through $2\pi/3$ of a terminal $(CF_3)_2N$ group (see Fig. 2). This would not result in the averaging of appropiate pairs of absorptions; instead the chemical shift difference for the terminal CF_3 groups after averaging would be only half the observed value.

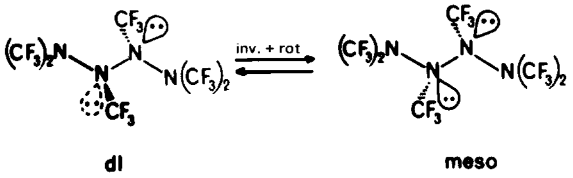
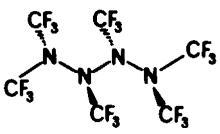
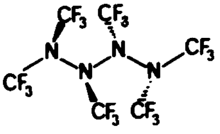


Fig. 2.

The following suggestions account entirely for the observed changes. At low temperatures, the tetrazan is fixed in two symmetrical conformers (IV) and (V) of the less crowded dl-isomer. Above the first coalescence temperature (-15 °C,



(IV)



(V)

$\Delta G^{\ddagger}$ = 52 kJ mol^{-1}, calculated from the equation rate $= \pi\delta/\sqrt{2}$ and the Eyring equation, assuming equal amounts of isomers), simultaneous rotation of the $(CF_3)_2N$ groups averages these, and at the second coalescence temperature (+40 °C, $\Delta G^{\ddagger}$ = 65 kJ mol^{-1}) inversion at the terminal nitrogens averages their CF_3 groups.

Theoretical calculations of the barrier to rotation about the N-N bond in hydrazine have produced figures similar to the lower of the above $\Delta G^{\ddagger}$ values [6], and the higher figure is at the upper end of a range we have observed for averaging of non-equivalent CF_3 groups in bistrifluoromethylamines [7].

In contrast to the above tetrazan, the N-nitroso and N-nitro-hydrazines (II) and (III) showed temperature independent spectra in the range -100 to +80 °C. Compound (II) showed absorptions of relative intensity 2 : 1 at 59.3 and 62.5 p.p.m. (to high field of internal $CFCl_3$), and (III) at 61.0 and 59.8 p.p.m. Here, the central nitrogen is much less crowded and probably planar, and the $(CF_3)_2N$ group either rotating freely or fixed in a symmetrical conformation.

EXPERIMENTAL

^{19}F n.m.r. spectra were obtained at 56.46 MHz using a Perkin-Elmer R10 instrument for samples 50% v/v in trichlorofluoromethane.

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REFERENCES

1 Reported in part at the 6th International Symposium on Fluorine Chemistry, Durham, July 1971, Abstract B34.

2 G.J. Bishop, B.J. Price and I.O. Sutherland, Chem. Comm., (1967) 672; B.H. Korsch and N.V. Riggs, Tetrahedron Letters, (1966) 5897.

3 J.E. Anderson and J.M. Lehn, Tetrahedron, 24 (1968) 123; S.F. Nelsen and G.R. Weisman, J. Amer. Chem. Soc., 98 (1976) 1842.

4 J.E. Anderson, D.L. Griffith and J.D. Roberts, J. Amer. Chem. Soc., 91 (1969) 6371; J.R. Fletcher and I.O. Sutherland, Chem. Comm., (1969) 706; M.J.S. Dewar and W.B. Jennings, Tetrahedron Letters, (1970) 339; M.J.S. Dewar and W.B. Jennings, J. Amer. Chem. Soc., 95 (1973) 1562.

5 P. Ogden, Chem. Comm., (1969) 1084.

6 See for example: A. Veillard, Theoret. chim. Acta, 5 (1966) 413; M.J.S. Dewar and M. Shanshal, J. Amer. Chem. Soc., 91 (1969) 3654.

7 M.G. Barlow and K.W. Cheung, Chem. Comm., (1969) 870.