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The Nuclear Magnetic Resonance Spectrum and Conformation of Perfluorocyclo-octane

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The use of high-resolution n.m.r. spectroscopy in the investigation of conformation and conformational inversion of cyclic molecules is well established and a summary of such studies has recently been published. Some time ago² we examined the ¹⁹F spectrum of perfluorocyclo-octane in dilute solution in trichlorofluoromethane at 30·107 Mc./sec. At 33° c, the spectrum consists of a single sharp line 2·0 c./sec. wide at half-height.

Progressive lowering of sample temperature produces line-broadening followed by splitting into two signals of equal intensity separated by $25\cdot5$ c./sec., the low-field signal being broader. It was thought that the spectrum below $T_{\rm c}$ represented the separate signals from the "axially" and "equatorially" disposed nuclei of a regular crown conformation in which the differential broadening was attributed to dissimilar unresolved

spin-coupling patterns. By analogy with other cyclic fluorocarbons3 it was anticipated that the geminal fluorine coupling constant would be in the region of 280-300 c./sec., in which case the two observed signals would be the centre components of an AB-type quartet, the outer satellite lines of which would be too weak to be detected at this frequency and sensitivity.

We have recently examined the spectrum at 94.07 Mc./sec. and a more complex situation is The single peak at 120·1 p.p.m. broadens from 2.7 c./sec., at half-height, at 30° c to 74 c./sec. at -35° c, below which resolution into two peaks begins to occur. Further cooling produces sharpening and resolution of further peaks until at -70 ° c the spectrum consists of a well resolved AB quartet and a single sharp line, the integrated intensities of which are equal. Details of the spectrum are:

C(1), C(2), C(5), C(6) and C(3), C(4), C(7), C(8). It is not possible to assign the two parts of the spectrum between these sets, neither can the single signal be accounted for other than by accidental co-incidence, since in neither set is there a similarity of environment for both members of a CF_2 pair. A stable D_2 conformation has been proposed for cyclo-octane by Hendrickson who further suggested that pseudorotation occurs as a "ripple" which causes the ring to pass through an intermediate, less stable, C_{2v} (extended crown) form. A similar ripple in the perfluoro-analogue would produce a time-averaged configuration in which half the fluorine nuclei would retain a generally "axial" and half a generally "equatorial" disposition. This should result, at room temperature, in a spectrum consisting of an AB quartet centred on (118.6 + 120.8)/2 = 119.7 p.p.m. and (120.8 + 121.3)/2 = 121.05 p.p.m. but no such

$$\nu_{A} = + 118.6 \text{ p.p.m. from CF Cl}_{3}$$
 $\lambda_{B} = + 121.3$
 $\lambda_{AB} = 2.7 \text{ p.p.m.}$
 $\lambda_{AB} = 297 \text{ c./sec.}$
 $\lambda_{AB} = 297 \text{ c./sec.}$

These data predict, for the spectrum at 30·107 Mc./sec., the centre AB components as being 10.7 c./sec. apart about a position 27.1 c./sec. to low field of the single signal. It is clear, therefore, that the low-field peak observed in the earlier spectrum is, in fact, the unresolved AB pair. The calculated intensity of each outer satellite is less than 1% of that of the combined centre peak.

The structural implication of the spectrum is that the conformation of the "rigid" or slowly interconverting cyclo-octane ring is not that of a regular (D_{4d}) crown since such a structure would contain eight magnetically indistinguishable CF₂ groups. Rather, the configuration must be such that it contains two sets of magnetically, and hence sterically, distinguishable geminal pairs. This condition is met by distortion of the crown into a D_2 form containing two C_2 axes through the mid-points of, say C(1)-C(2) and C(5)-C(6), and C(3)-C(4) and C(7)-C(8), and a third C_2 axis perpendicular to the other two and passing through their point of intersection. This produces two sets of four equivalent geminal pairs on

distinction is shown, the observed single absorption at the mean position of the "rigid" spectrum indicating that each fluorine atom passes through each of the four environmental positions of the D_2 form. This can only mean that the molecule undergoes a more drastic distortion than a ripple and that inversion occurs.

In the earlier work we attempted² to assess ΔH and ΔS for the inversion process from linewidth and peak-separation measurements according to the method of Gutowsky and Holm.5 Since this treatment is only applicable where the spectrum is derived from, and divides into, two equivalent signals, such application to the present case, and the results quoted,6 are clearly invalid. It might have been possible to make a more reliable estimate of barrier height by applying the method of Heidberg et al.7 to the AB part of the high-frequency spectrum. Unfortunately, the near coincidence of the high-field centre component with the single signal prevents this being done with any accuracy.

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