

NUCLEAR MAGNETIC RESONANCE  
AND CONFORMATIONAL ISOMERIZATION  
IN UNSATURATED CYCLOOCTANE DERIVATIVES\*

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The temperature dependence of the n.m.r. spectra of some saturated cyclooctane derivatives have been studied recently (1,2). The results have an important bearing on the conformations and the conformational processes which exist in these molecules. We now report some observations on unsaturated derivatives of cyclooctane.

The proton n.m.r. spectra (60 Mc/sec) of 5-t-butylcyclooctanone (I), cyclooctanone (II), cis-cyclooctene (III), cis-cis-1,3-cyclooctadiene (IV), and cis-cis-1,5-cyclooctadiene (V) were examined from room temperature down to about -150°. Compounds I and II were dissolved in  $\text{CHF}_2\text{Cl}$  and III, IV, and V in vinyl chloride. Compound V alone did not show a temperature-dependent spectrum. Fig. 1 shows spectra at various temperatures for compounds I to IV.

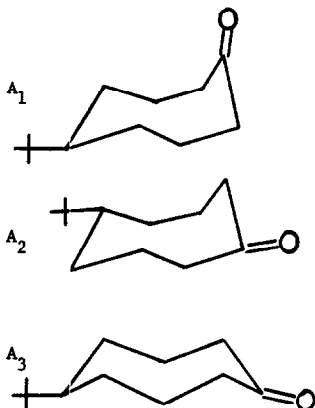
The spectrum of I at -120° shows the presence of two t-butyl bands of unequal intensities, and in this respect is very similar to that of t-butylcyclooctane (VI) (1). The temperature ranges at which the spectral changes take place are also very close for I and VI, so that it is tempting to assign a conformational picture to I similar to that of VI (1). If we do so, favorable conformations of I can be classified into two distinct sets, A and B. Some of these conformations are shown in the Table below. Interconversion between members of a given set is assumed to be rapid even at -150°, and takes place by a pseudorotation of the boat-chair (e.g.,  $A_1 \rightleftharpoons A_2$ ) and/or by a wagging of a C=O or  $\text{CH}_2$  group in the boat-chair to a stretched crown (e.g.,  $A_1 \rightleftharpoons A_3 \rightleftharpoons A_2$ ). Neither of these processes results in "ring inversion", i.e., a process which interconverts a member

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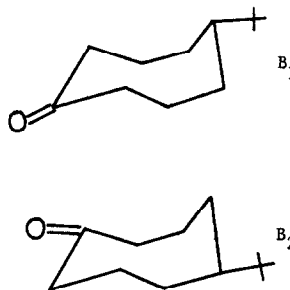
of set A to one of set B. Ring inversion can take place as indicated previously for cyclooctane (1), and when rapid enough, as at temperatures above  $-80^\circ$ , is responsible for the single line given by the t-butyl group. Below  $-120^\circ$ , ring inversion is slow on the n.m.r. time scale, and the t-butyl group gives two bands, one for molecules in set A and the other for molecules in set B.

TABLE

Typical Members of Set A



Typical Members of Set B



The n.m.r. spectrum of 4-t-butylcyclohexanone was found to be temperature-independent down to  $-145^\circ$ . This, coupled with previous arguments (1), shows that the phenomenon observed in I cannot be restricted rotation of the t-butyl group.

The presence of at least two different conformations for I is at variance with current views which hold that cyclooctanone and 5-p-chlorophenylcyclooctanone are conformationally pure (3), but are in agreement with an older view that these compounds exist as a mixture of two conformations (4). In our opinion, deductions (3) based on the similarity of the infrared spectra in the liquid and solid phases must be treated with reserve. In particular, the conclusion that this fact indicates conformational purity in both phases implies that solid solutions are absent. Many derivatives of cyclooctane have disordered structures in the solid phase (5), and it is known that cyclooctane forms solid solutions with adamantane and bicyclo[3, 3, 1]nonane (6). In addition, there is evidence (7) that chlorocyclohexane

crystallizes first into a modification containing both equatorial and axial forms and at lower temperatures undergoes a transition to a conformationally pure solid.

Cyclooctanone (II) shows spectral changes similar to those found in I (Fig. 1). The ring proton spectra of II are so complex that deductions of the number of conformations present is virtually impossible. However, there is no doubt that some molecular process, presumably ring inversion, is responsible for the changes in the spectrum of II observed around  $-120^{\circ}$ .

The n.m.r. spectra of cyclooctene (III) and 1,3-cyclooctadiene (IV) also show changes in the temperature range  $-100$  to  $-120$  and  $-85$  to  $-110^{\circ}$ , respectively (Fig. 1). These effects are presumably due to a slowing down of ring inversion, i.e., a process which averages the chemical shifts of the two protons on a methylene group in III or IV.

The lack of temperature dependence in the n.m.r. spectrum of V can be due to a low barrier to ring inversion. However, if the chemical shift between the protons in the methylene groups is small, the spectrum will be essentially independent of temperature, no matter what the barrier might be. Molecular models indicate that there should be an appreciable barrier to inversion in V. Reasonably large barriers to inversion are known to exist in derivatives of 1,3,5-cyclooctatriene (8) and cyclooctatetraene (9).

The great differences in the effects of unsaturation on the rates of ring inversion in the six- versus the eight-membered series are very striking. The coalescence temperature ( $T_c$ ) is lowered from about  $-60$  to  $-160^{\circ}$  on going from cyclohexane (10,11) to cyclohexene (11,12). The spectrum of cyclohexanone is not temperature dependent (13), but as mentioned above in connection with V, a definite conclusion about the rate of ring inversion cannot be drawn from this observation. Nevertheless, it is likely that inversion is indeed very fast (i.e.,  $T_c \ll -150^{\circ}$ ) in cyclohexanone. By contrast, cyclooctane, cyclooctene, and cyclooctanone have similar rates of ring inversion.

The syntheses of partially deuterated derivatives of I to V are planned to obtain further information on the conformation of these molecules.

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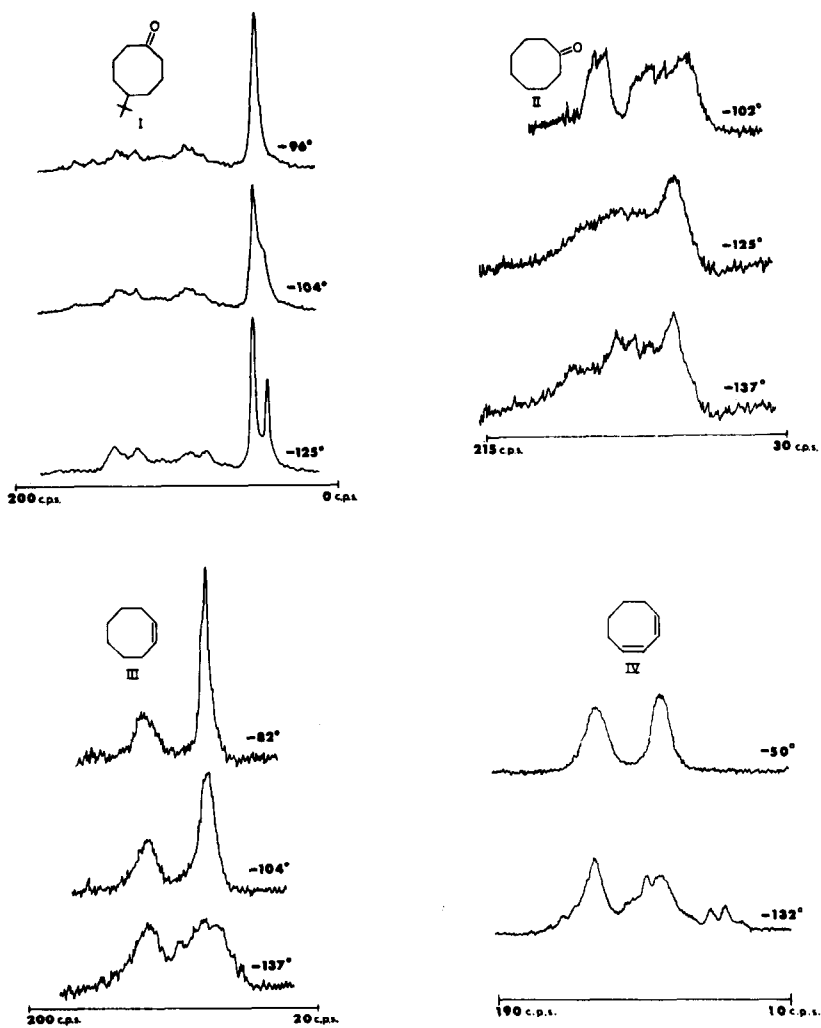


FIG. 1 N.m.r. spectra of compounds I to IV. The frequency scale is in c.p.s. downfield from tetramethylsilane.