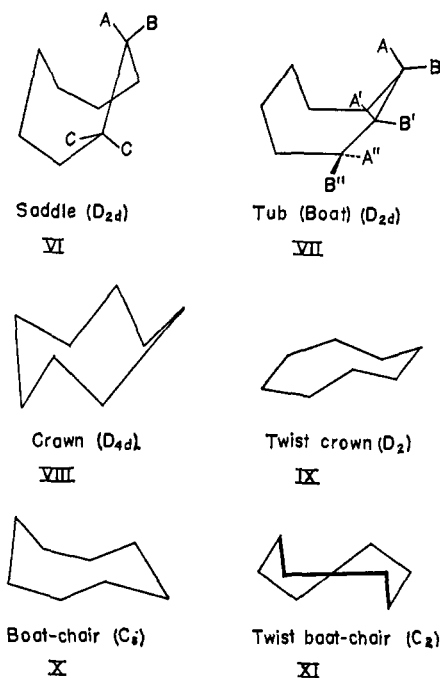


Communications to the Editor

Nuclear Magnetic Resonance Spectra and Conformations of Deuterated Cyclooctanes¹

Sir:

We wish to report the proton nmr spectra of perdeuteriocyclooctane-*cis*-1,2-*h*₂ (I), -*trans*-1,2-*h*₂ (II), and -1,1-*h*₂ (III). The results have an important bearing on the conformation(s) of cyclooctane, a subject of current interest.² Repeated exchanges of cyclooctane with deuterium oxide at 140° in the presence of palladium-charcoal yielded cyclooctene-*d*₁₄ (>99% D) (IV). Diimide³ reduction of IV gave I. Hydrobora-



tion⁴ of IV, followed by oxidation to the alcohol, conversion to the *p*-toluenesulfonate, and reduction of this ester with LiAlH_4 , gave II. Compound III should also be available from IV; it was actually prepared before the latter compound had been made, by a rather long route which started with cyclohexanone-*d*₁₀.⁵ All compounds were purified by preparative gas chromatography. The proton nmr spectra of I, II, and III were obtained at 60 Mcps with simultaneous irradiation at 9.2 Mcps to decouple deuterons (Figure 1). Chemical shifts and coupling constants are summarized in Table I. The results are in agreement with our previous work⁶ on $\text{C}_8\text{D}_{15}\text{H}$.

(1) This research was supported in part by National Science Foundation Grant No. GP3780.

(2) For a summary of all but very recent work on the subject, see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 4.

(3) R. S. Dewey and E. E. van Tamelen, *J. Am. Chem. Soc.*, **83**, 3729 (1961).

(4) H. C. Brown and G. Zweifel, *ibid.*, **81**, 247 (1959).

(5) The product obtained was an equimolecular mixture of C_8D_{16} and $\text{C}_8\text{D}_{14}\text{H}_2$, and it contained appreciable amounts of isotopic impurities having the partial structure, $-\text{CD}_2\text{CHDCD}_2-$ (Figure 1).

(6) F. A. L. Anet and J. S. Hartman, *J. Am. Chem. Soc.*, **85**, 1204 (1963). Because of isotopic impurities, deductions based on the spectrum of a compound related to I reported in this paper are ambiguous.

Table I. Chemical Shifts and Coupling Constants in Some Deuterated Cyclooctanes

Compd	Temp, °C	Chemical shifts, τ^a		Coupling constant, cps
I ^b	-50	8.53		
I ^b	-140	8.37	8.69	3.5
II ^c	-50	8.53		
II ^c	-140	8.37	8.69	
II ^c	-175	8.37	8.69	
III ^b	-50	8.51 (8.53) ^d		
III ^b	-140	8.35, 8.67 (8.37, 8.69) ^d		14.3

^aTMS = 10 ppm. ^b6% solution in vinyl chloride. ^c2% solution in vinyl chloride-difluorochloromethane (2:1). ^dStarred peaks in Figure 1. The isotope effect ($\text{CH}_2 \rightarrow \text{CHD}$) of +1.3 cps is normal.

The proposal⁷ that cyclooctane has the saddle conformation VI is at variance with the present results. There are three types of protons, A, B, and C, in the ratio 1:1:2. Even a chemical shift coincidence of A and B will not explain the spectra of II and III at -140°. The tub form (VII) can be ruled out because it predicts

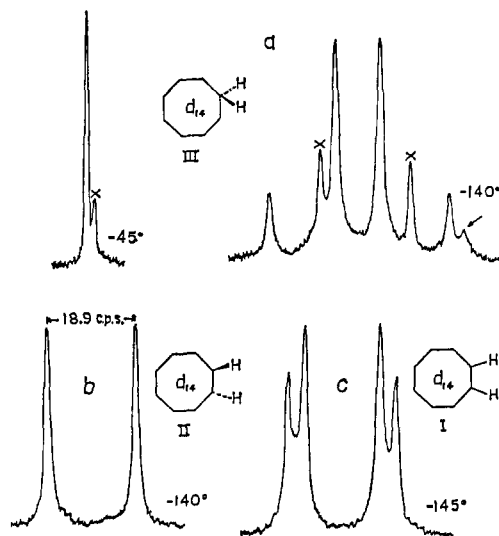


Figure 1. Proton nmr spectra (60 Mcps) (deuterons decoupled) of (a) III, (b) II, and (c) I at various temperatures. All spectra are shown on the same scale. The crosses indicate peaks due to isotopic impurities having the partial structure $-\text{CD}_2\text{CHDCD}_2-$. The arrow indicates a ^{13}C satellite of TMS.

that the spectrum of I should be a superposition of an AB spectrum (e.g., A'B'' or A''B') in VII) and a spectrum consisting of two unsplit lines (e.g., AA' and BB'). Twisted or distorted tubs⁸ are no better because, in order to obtain only two sets of protons, it is necessary to postulate an averaging process that is still very fast at -140°; the effective (averaged) symmetry is then the same as that of the tub form.

(7) J. Dale, I. Laszlo, and W. Ruland, *Proc. Chem. Soc.*, 1964, 190.

(8) Such conformations have been suggested by E. S. Glazer and J. D. Roberts for fluorinated cyclooctanes: J. D. Roberts, Abstracts of papers presented at the 19th National Organic Symposium of the American Chemical Society, Tempe, Ariz., June 1965.

The present results are consistent with the crown (D_{4d}) (VIII), or with the stretched (C_{2v}) or twisted (D_2) (IX) crown, provided that the latter two forms undergo rapid averaging which results in an effective D_{4d} symmetry.⁹ The boat-chair (X) is also in agreement with our data, again provided that some process is available to average the ten different protons of this form into two equal sets. One such process is pseudo-rotation.¹⁰ Another is a wagging¹¹ of a methylene group that results in the reversible formation of a crown. If the wagging process is fast at -140° , then a mixture of crown forms (*i.e.*, regular, stretched, or twisted) and boat-chair forms would have only two equal sets of protons at -140° . If pseudo-rotation is also fast, another conformation which can be included in this "mixture" is the twist boat-chair (XI) which is an intermediate in the pseudo-rotation itinerary of the boat-chair. It is significant that the calculations of Hendrickson^{9a} show that the five forms included in the "mixture" above are the five lowest energy forms of cyclooctane, and that these conformations are of closely similar energies.

The nmr spectra of methyl- and *t*-butylcyclooctane¹² and of 1,1-difluorocyclooctane¹³ rule out the crown forms as the exclusive¹⁴ conformations of these compounds.

All the evidence therefore points to the boat-chair and/or the twist boat-chair as being the major conformation(s) of cyclooctane.¹⁵

(9) Calculations strongly suggest that this should be so: (a) J. B. Hendrickson, *J. Am. Chem. Soc.*, **86**, 4854 (1964); (b) K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

(10) The statement^{9a} that the boat-chair cannot pseudo-rotate is not correct.

(11) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **87**, 3139 (1965). Wagging to give the saddle must not be fast at -140° as this leads to ring inversion.

(12) F. A. L. Anet and M. St. Jacques, *ibid.*, **88**, 2586 (1966).

(13) Two processes have been found in this system.⁸

(14) At least in cyclooctane and alkylcyclooctanes, a certain proportion (*e.g.*, up to 30%) of the crown forms in a "mixture" together with the boat-chair form would fit the data; indeed, the chemical shift of 0.315 ppm in cyclooctane at -140° fits best with such a model.

(15) An X-ray analysis, still not completely refined, shows that the conformation of crystalline cyclooctane-1,2-*trans*-dicarboxylic acid is clearly the boat-chair (J. D. Dunitz, personal communication).

(16) Holder of a National Research Council of Canada scholarship.

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Nuclear Magnetic Resonance Spectra and Conformations of Substituted Cyclooctanes¹

Sir:

The ability of large groups to fix the chair conformation in six-membered rings is well established.² Thus the nmr spectra of methylcyclohexane³ and *t*-butylcyclohexane (I) are temperature independent and show broad bands for the ring methylene protons. We now report that methylcyclooctane (II) and *t*-butylcyclooctane (III) have temperature-dependent spectra (Figures 1 and 2) and show relatively narrow methylene

(1) This research was supported in part by National Science Foundation Grant No. GP3780.

(2) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 2.

(3) N. Muller and W. C. Tosch, *J. Chem. Phys.*, **37**, 1167 (1962).

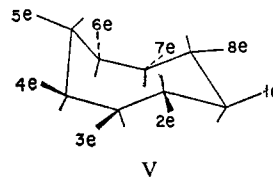
proton bands at room temperature. The same kind of behavior is also shown by the acetone of cyclooctane-*trans*-1,2-diol (IV) (Figure 3). Therefore, these compounds cannot exist exclusively or even largely in one conformation as do the cyclohexane analogs.

With both II and III the temperature-dependent spectral changes of the methylene protons take place at about -100 to -120° , while with IV the spectral changes take place at about -70 to -80° . The possibility that the two *t*-butyl bands in III at low temperatures are a result of restricted rotation about the bond linking the ring to the *t*-butyl group, which would be in agreement with the 2:1 intensity ratio, appears remote. The corresponding band in I remains unsplit down to -150° . Furthermore, restricted rotation does not explain the changes in the methylene proton band. The large splitting (0.23 ppm) of the *t*-butyl group in III at low temperatures is, however, remarkable, especially in comparison with the methyl band or II. As shown in Figure 1 the methyl group has a different shape at -25° than at -140° , but two distinct methyl bands are not seen; the chemical shift must then be less than about 0.04 ppm. The methyl bands in IV show no appreciable change with temperature, presumably because of a coincidence of chemical shifts in the low-temperature spectrum.

The results with II, III, and IV exclude a crown conformation for these compounds.⁴ In our opinion, the results are also inconsistent with a stretched crown or twisted crown. Although these forms have different equatorial sites where a large substituent can be placed, interconversion between these forms should be fast⁵ even at -150° ; otherwise cyclooctane-*d*₁₅ would show more than two lines at low temperatures. Also, the fact that the spectral changes in II and III occur at the same temperature as in cyclooctane itself strongly suggests that essentially the same kind of process is involved in these three compounds.

We have shown⁶ that the nmr spectra of various deuterated cyclooctanes are consistent with a boat-chair and/or twist boat-chair, where pseudo-rotation or a methylene wagging process is rapid at -140° , so that the time-average symmetry (at -140°), as far as nmr measurements are concerned, is the same as in the crown conformation.

For simplicity, we may consider just the boat-chair conformation (V). Although the various CH bonds



cannot be labeled as equatorial or axial with the same meaning that these terms are used in cyclohexane systems, it is nevertheless convenient to label those bonds in the general plane of the molecule as "equatorial";

(4) The temperature-dependent spectra would be consistent with the crown if the substituents could be axial to a considerable extent. This is unlikely in II, extremely unlikely in III, and impossible in IV.

(5) Theoretical calculations of the energies of the various crown forms show that interconversion between them should be extremely fast even at -200° (energy barrier <3 kcal/mole): (a) J. B. Hendrickson, *J. Am. Chem. Soc.*, **86**, 4854 (1964); (b) K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

(6) F. A. L. Anet and M. St. Jacques, *ibid.*, **88**, 2585 (1966).