

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.<sup>9</sup> 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.<sup>10</sup> Another is a wagging<sup>11</sup> of a methylene group that results in the reversible formation of a crown. If the wagging process is fast at  $-140^\circ$ , 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  $-140^\circ$ . 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<sup>9a</sup> 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*-butylcyclooctane<sup>12</sup> and of 1,1-difluorocyclooctane<sup>13</sup> rule out the crown forms as the exclusive<sup>14</sup> 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.<sup>15</sup>

(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<sup>9a</sup> 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  $-140^\circ$  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.<sup>8</sup>

(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  $-140^\circ$  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).

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## Nuclear Magnetic Resonance Spectra and Conformations of Substituted Cyclooctanes<sup>1</sup>

Sir:

The ability of large groups to fix the chair conformation in six-membered rings is well established.<sup>2</sup> Thus the nmr spectra of methylcyclohexane<sup>3</sup> 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).

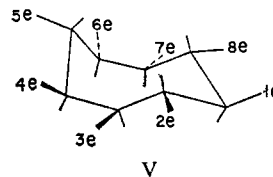
proton bands at room temperature. The same kind of behavior is also shown by the acetone of cyclooctane-*trans*-1,2-diol (IV) (Figure 3). Therefore, these compounds cannot exist exclusively or even largely in one conformation as do the cyclohexane analogs.

With both II and III the temperature-dependent spectral changes of the methylene protons take place at about  $-100$  to  $-120^\circ$ , while with IV the spectral changes take place at about  $-70$  to  $-80^\circ$ . 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  $-150^\circ$ . 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 of II. As shown in Figure 1 the methyl group has a different shape at  $-25^\circ$  than at  $-140^\circ$ , 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.<sup>4</sup> 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 fast<sup>5</sup> even at  $-150^\circ$ ; otherwise cyclooctane-*d*<sub>15</sub> 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 shown<sup>6</sup> 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  $-140^\circ$ , so that the time-average symmetry (at  $-140^\circ$ ), 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  $-200^\circ$  (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).

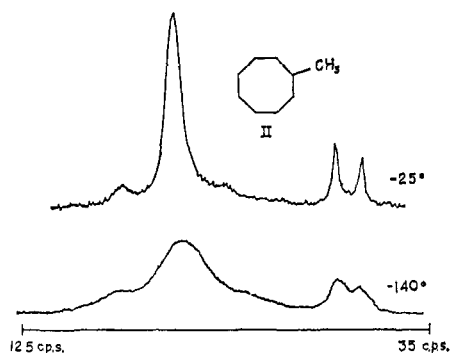


Figure 1. Proton nmr spectra (60 Mcps) of II, at various temperatures. The scale is in cycles per second downfield from tetramethylsilane.

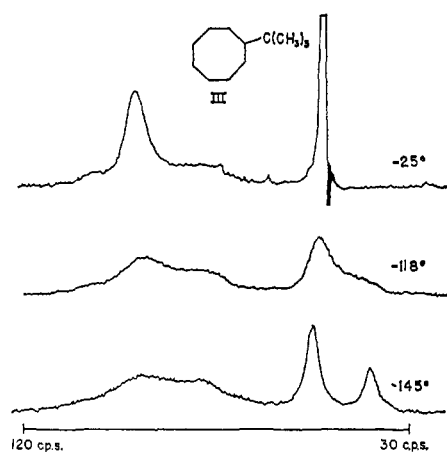


Figure 2. Proton nmr spectra (60 Mcps) of III at various temperatures. The scale is in cycles per second downfield from tetramethylsilane.

the others are then "axial." The eight "equatorial" bonds are shown in V.

The pseudo-rotation or wagging process mentioned above results in the formation of two sets of bonds: let set A be [1e, 2e, 3e, 4a, 5a, 6a, 7e, 8e]; then set B is [1a, 2a, 3a, 4e, 5e, 6e, 7a, 8a]. Only ring inversion will mix set A with set B. A large group can be accommodated in set A (positions 1e, 2e, 3e, 7e, or 8e) or in set B (positions 4e, 5e, or 6e). Therefore, the low-temperature nmr spectrum of an alkylcyclooctane should show two conformational isomers, even if the sole ring conformation is the boat-chair. Also it is possible to have two equatorial substituents on adjacent carbon atoms in either set A or set B, and therefore *trans* fusion to another ring also allows two conformational isomers to be present. It can also be seen that conversion of a group from set A to set B and *vice versa* is analogous to ring inversion in cyclooctane itself, except that it should lead, at high temperatures, to a relatively narrow band for the methylene protons instead of a single sharp line as with cyclooctane.<sup>7</sup>

Thus, the present evidence points to the boat-chair as the major conformation in cyclooctane and mono-substituted cyclooctanes. The assignment<sup>8</sup> of con-

(7) A mechanism for inversion which is satisfactory for II, III, and IV, as well as for cyclooctane itself, involves stretching out C<sub>3</sub> and C<sub>7</sub> in V to give a centrosymmetrical ring "conformation" (conformation V in ref 5a) as a transition state.

(8) N. L. Allinger and S. Greenberg, *J. Am. Chem. Soc.*, **84**, 2394 (1962).

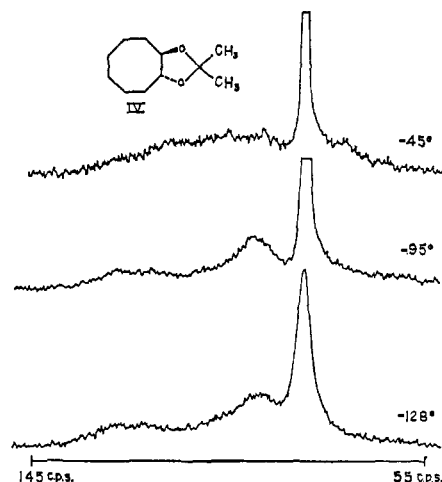


Figure 3. Proton nmr spectra (60 Mcps) of IV at various temperatures. The scale is in cycles per second downfield from tetramethylsilane.

figurations to the 5-*t*-butylcyclooctanols, made on the basis of a crown conformation, is therefore not convincing, but it is not easy to predict the relative proportions of boat-chair and crown forms for these compounds. Further work on the conformations of eight-membered rings is in progress.

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

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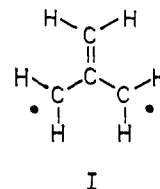
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### Trimethylenemethane

Sir:

Trimethylenemethane (I) is important in theoretical chemistry by virtue of the fact that the central carbon



atom of this molecule attains the maximum  $\pi$  bond order possible for any carbon atom.<sup>1</sup> The magnitude of the bond order thus obtained (4.732) is the base for numerous calculations of free valence indexes of carbon compounds. In addition, this molecule has been used as a model in theoretical calculations of negative spin density in triplet states<sup>2</sup> and in a comparison of different methods useful in theoretical calculations of the energies of  $\pi$  systems.<sup>3</sup>

(1) (a) W. E. Moffitt, footnote to C. A. Coulson, *J. Chim. Phys.*, **45**, 243 (1948); (b) W. Moffitt, *Trans. Faraday Soc.*, **45**, 373 (1949); (c) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952); (d) H. H. Greenwood, *Trans. Faraday Soc.*, **48**, 677 (1952); (e) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1961, p 56; (f) A. Streitwieser Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 43, 57.

(2) H. M. McConnell, *J. Chem. Phys.*, **35**, 1520 (1961); A. D. McLachlan, *Mol. Phys.*, **5**, 51 (1962).

(3) D. P. Chong and J. W. Linnett, *ibid.*, **8**, 541 (1964).