

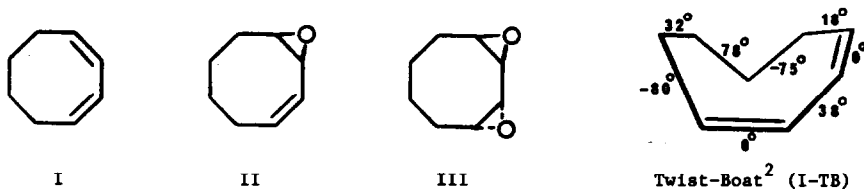
CONFORMATIONAL PROPERTIES OF CIS-CIS-1,3-CYCLOOCTADIENE
AND ITS EPOXIDES

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(Received in USA 6 March 1975; received in UK for publication 1 April 1975)

Cis-cis-1,3-cyclooctadiene (I) has a non-planar diene system, as shown by its ultraviolet spectrum.¹ A recent electron diffraction study has revealed an unsymmetrical twist-boat conformation for I in the gas phase.² The 60 MHz ¹H nmr spectrum of I shows a dynamic nmr effect



in the range of -80 to -130°, but unfortunately the low-temperature spectrum, because of its complexity, gives little conformational information.³ We now report the variable temperature ¹³C spectra of I and show that I exists in solution at low temperatures as a nearly equal mixture of two conformations, namely a twist-boat and a twist-boat-chair. The mono-epoxide (II)⁴ and the anti-di-epoxide (III)⁵ derived from I have torsional constraints similar to those of the parent diene. The ¹³C nmr spectral properties of II and III, in conjunction with the data on I, allow the conformations of these epoxides to be elucidated.

Carbon-13 nmr spectra⁶ of I are shown in Figure 1. Above about -50°, the spectrum shows two methine resonances (δ 131.9 and 126.4) and two methylene resonances (δ 28.5 and 23.6). The spectrum broadens below -50° and at -110° to -120° it consists of four sharp lines (δ 133.0, 126.4, 27.7

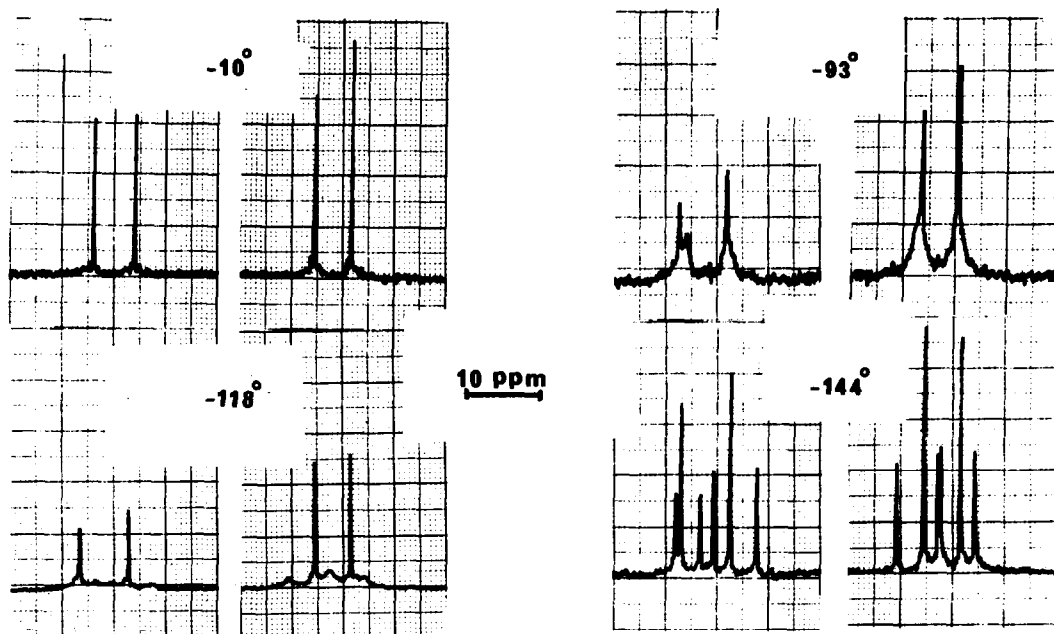


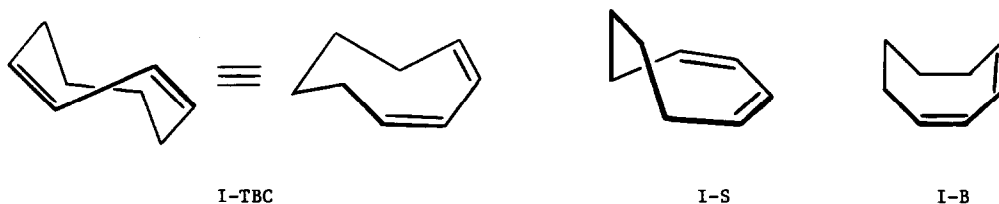
Figure 1. 63.1 MHz ^{13}C nmr spectra of 1,3-cyclooctadiene (I) in CH_2Cl_2 at various temperatures. Protons are noise decoupled. In each spectrum the peaks on the left arise from olefinic carbons and those on the right from methylene carbons. The four sharp peaks in the spectrum at -115° are assigned to a twist-boat-chair conformation (I-TBC).

and 22.7) surrounded by some very broad resonances. The sharp lines remain unchanged to at least -170° and are assigned to a twist-boat-chair (I-TBC)⁷ with C_2 symmetry. The broad resonances observed near -115° change as the temperature is lowered and give rise to a sharp 8-line spectrum (δ 134.1, 130.8, 128.9, 123.2, 31.3, 26.0, 25.4 and 20.8) below about -140° (Figure 1). We assign this spectrum to the twist-boat (I-TB), a conformation which lacks symmetry.

Although the ratio of I-TBC and I-TB may vary with temperature and phase, it seems unlikely that this can account completely for the difference between the present nmr data and the electron diffraction results.² It is conceivable that the electron diffraction data might fit I-TB with more or less I-TBC also present. If this is so, the structural parameters² deduced for I-TB may need to be modified.

Three conformational processes can be envisaged to occur in I: (1) a degenerate inter-conversion (pseudorotation) of I-TB with itself via the axial-symmetrical boat, I-B (process A);

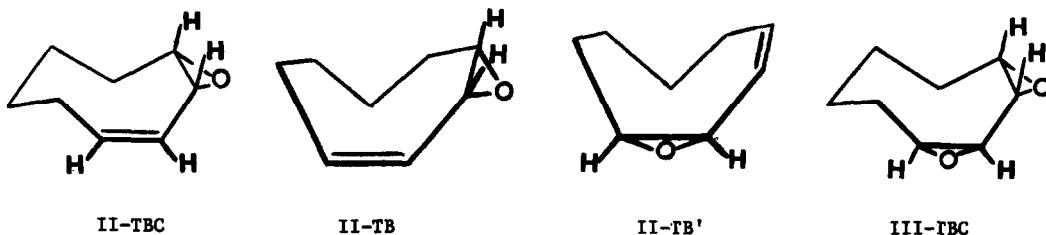
(2) a pseudorotation of I-TB via the plane-symmetrical form I-S (process B); and (3) a local ring inversion⁸ of I-TB to give I-TBC via an asymmetric transition state (process C). Both I-B and I-S are high-energy intermediates that are not appreciably populated.



Molecular models indicate that the barriers are probably in the order $A < B \approx C$.⁹ Thus we assign A to the dynamic nmr effect that collapses in a pair-wise fashion the spectral lines of I-TB in the temperature range -140° to -100° . The merging of the spectra of I-TB and I-TBC must arise from C. The free-energy barriers for A and C are calculated from the ^{13}C nmr changes to be 7.1 and 9.1 kcal/mol respectively. Process B also must occur since the proton spectrum³ above about -40° corresponds to a C_{2v} time-averaged symmetry, and the free-energy barrier for this is about 9 kcal/mol.¹⁰

1,3-Cyclooctadiene mono-epoxide (II) gives a ^{13}C nmr spectrum in CHFC_2 at -10° consisting of resonances at δ 136.3 and 123.1 ($\text{C}_{1,2}$), δ 58.9 and 54.4 ($\text{C}_{3,4}$) and at δ 29.6, 27.7, 25.5 and 25.5. The spectrum broadens below about -30° and, by about -95° , all the resonances have split into doublets with one component of each doublet sharp and the second component either sharp or more or less broad. This dynamic nmr effect corresponds to a ΔG^\ddagger of 9.5 kcal/mol. Below -100° , all the resonances become equally sharp and of similar intensities and no other changes take place down to -160° . At -123° , resonances occur at δ 136.9 (broad at -95°), 135.7, 123.6, 119.6 (broad at -95°), 59.3, 58.5, 55.0, 54.2, 31.5 (broad at -95°), 28.4, 28.0, 27.3, 26.4, 26.0 (very broad at -95°), 25.7, 22.2 (broad at -95°). We assign the sharp components of the sharp-broad pairs at -93° to a twist-boat-chair (II-TBC), in analogy with the spectrum of I. Since I-TBC in the diene has C_2 symmetry, only one exo mono-epoxide can exist (the endo mono-epoxide conformation suffers from large non-bonded repulsions). The broad components are assigned to two twist-boats which are interconverting with an intermediate rate constant at -93° . Since the broad components simply become sharp at lower temperatures, and the frequency changes in these resonances between -93° and -140° are small, the population ratio of the two twist-boats must be greater than 10:1 at -140° . The twist-boat conformation of the 1,3-diene can give two different exo mono-epoxides,

II-TB and II-TB', and molecular models show that one of these epoxides, namely II-TB', has more H-H non-bonded repulsions than the other and thus might be present only in minor amounts, in agreement with the deductions made above. $\Delta G^\ddagger(\text{II-TB}' \rightarrow \text{II-TB})$ is about 7.6 kcal/mol.



The cmr spectrum of the anti di-epoxide III in CH_2Cl_2 at -30° shows resonances at δ 57.3, 53.1, 29.4, and 23.6 and does not exhibit any dynamic nmr effect down to -170° . We therefore assign to III the twist-boat-chair conformation (III-TBC) in which both oxide rings are exo and the symmetry is C_2 . The twist-boat conformation of III cannot avoid having considerable H-H non-bonded repulsions, and not surprisingly is absent at low temperatures.

Acknowledgement: We thank the National Science Foundation for support of this work.

References and Footnotes

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5. M. Barrelle, A. Feugier, and M. Appar, Compt. Rend., 271, 519 (1970).
6. Spectra were measured on a superconducting-solenoid nmr spectrometer operating at a field of 59 kgauss.
7. The TBC form is geometrically rigid [cf. J. Dunitz and J. Waser, J. Amer. Chem. Soc., 94, 5645 (1972)] (in contrast to the TB form, which is more or less flexible) and was originally proposed by Braude.¹
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9. Strain-energy calculations have been reported for I-TBC, I-B and I-S, but not for other geometries of I, F. Zuccarello, G. Bueni, and G. Favini, J. Mol. Structure, 18, 295 (1973). In our opinion, the procedure and parameters used by these workers are far from optimum and we intend to carry out new calculations on I [cf. F. A. L. Anet and J. Krane, Tetrahedron Letters, 5029 (1973)].
10. An examination of the ^1H nmr spectra deuterated derivatives of I should be informative and is planned.