(16) In general, the replacement of a methylene by a CO group in medium and large cycloalkanes is not expected to lead to significant conformational changes [see F. A. L. Anet, M. St. Jacques, P. Henrichs, A. Cheng, J. Krane, and L. Wong, *Tetrahedron*, **30**, 1629 (1974)].

(17) In a transition state of an elementary process the bond between the old and new corner atoms becomes eclipsed (Figure 1). This one-side bond is marked in italics in the name notation (underlined in Figure 3) and is associated with a torsional angle of 0°. This value is approximate and may vary by as much as 15° in particular cases.

(18) Our experience with the iterative force-field calculations of medium and large cycloalkanes (*e.g.*, *n* = 10, 12, 14, and 16) is that the (strain energy) barriers are generally ca. 1 kcal/mol higher than the experimental (free energy) barriers [F. A. L. Anet and T. N. Rawdah, *J. Am. Chem. Soc.*, in press; F. A. L. Anet and A. K. Cheng, *ibid.*, **97**, 2420 (1975)].

(19) A symmetrical [445] structure (torsional angles: −53, 171, −161, 49, 53, −148, 160, −148, 53, 49, −161, 171, and −53°) has a strain energy of

3.1 kcal/mol ($E_r$ = 0.90, $E_\Theta$ = 2.45, $E_\phi$ = 6.03, $E_{nb}$ = 6.93, and $E_T$ = 15.3) relative to that of the [13333] conformation.

(20) A [12534] conformation of cyclopentadecane (torsional angles: −57, 169, −176, 154, −72, −79, 139, −85, 139, 173, 153, −74, −71, 171, and −58°) has a strain energy of 5.2 kcal/mol ($E_r$ = 0.73, $E_\Theta$ = 1.81, $E_\phi$ = 7.82, $E_{nb}$ = 5.39, and $E_T$ = 15.8) relative to that of the [33333]. In Dale's calculations the [12534] conformation has a relative strain energy of 2.6 kcal/mol.

(21) The [33333] conformation has a symmetry number of 10 compared to only 2 for the [13443] and [14334], and 1 for the [13434] and [13353]. Therefore at 25 °C the conformations of cyclopentadecane with $C_1$ and $C_2$ symmetries are favored by entropy terms of ca. 1.4 and 1.0 kcal/mol, respectively, over the [33333] conformation with $D_5$ symmetry. These entropy terms result in relative free energy of 0.0, 0.2, 0.5, 0.5, and 0.8 kcal/mol for the [13443], [13434], [33333], [13353], and [14334] conformations, respectively.

# Conformations of *cis,cis*-1,3-Cyclooctadiene and Its Epoxides. Dynamic Nuclear Magnetic Resonance Spectroscopy and Iterative Force-Field Calculations

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**Abstract:** The 251-MHz $^1$H and the natural-abundance 63.1-MHz $^{13}$C NMR spectra of *cis,cis*-1,3-cyclooctadiene (I), *cis,cis*-1,3-cyclooctadiene monoepoxide (II), and *cis,cis*-1,3-cyclooctadiene *trans*-diepoxide (III) have been investigated over the temperature range of −10 to −170 °C. Compound I exists in solution as a nearly equal mixture of a symmetrical ($C_2$) twist-boat-chair (I-TBC) and an unsymmetrical twist-boat (I-TB) conformation. Two conformational processes affect the $^{13}$C NMR spectrum of I and the free-energy barriers are 7.2 and 9.0 kcal/mol. The lower energy process is a ring pseudorotation of the twist-boat and leads to a $C_2$ time-averaged symmetry, whereas the higher energy process is the interconversion of the two conformations. The $^1$H NMR spectra of I show complex and continuous changes from about −50 to −120 °C, and provide an upper limit of about 10 kcal/mol for the free-energy barrier for a third process which is required for I to achieve its maximum molecular symmetry of $C_{2v}$. Iterative force-field calculations on the conformations and conformational interconversion paths of I give results consistent with the NMR findings and define the conformations found experimentally. The $^{13}$C NMR spectra of II reveal that all three exo epoxides formally derived from the two conformations of I are present in solution. Two conformational processes, with free-energy barriers of 7.2 and 9.5 kcal/mol, occur in II. The lower energy process interconverts the two exo epoxides derived from the twist-boat, while the higher energy process is the interconversion of the twist-boat with the twist-boat-chair. The $^{13}$C NMR spectrum of III is found to be temperature independent and therefore a twist-boat-chair conformation with $C_2$ symmetry, similar to that of I-TBC, is proposed for this compound. The quite unequal populations of the two twist-boats of II and the absence of twist-boats of III is explained. Conformational implications of the current results for substituted derivatives of I and analogues of II and III are discussed.

## Introduction

*cis,cis*-1,3-Cyclooctadiene (I), which is the most stable cyclooctadiene isomer, can be obtained readily by isomerization of 1,5-cyclooctadiene.[1] On the basis of ultraviolet spectroscopy and the examination of molecular models, Braude[2] deduced that the diene system in I must be nonplanar with a torsional angle of about 40–45°; the conformation depicted in his paper corresponds to a twist-boat-chair in our nomenclature. Traetteberg has investigated the structure of I in the gas phase by electron diffraction and has reported[3] that the conformation is a twist-boat with a diene twist angle of 38°. Photoelectron spectroscopy on I has revealed a torsional angle of 59°.[4]

Early low-temperature 60-MHz $^1$H NMR spectra of I revealed the existence of a dynamic NMR effect at about −100 °C, but the complexity of the spectrum prevented a detailed analysis.[5] The olefinic proton coupling constants in I at room temperature correspond to a nonplanar diene moiety.[6]

Noniterative force-field calculations have been reported[7] for the twist-boat-chair, boat, and half-chair conformations of I. An iterative force-field calculation on the twist-boat-chair and twist-boat conformations of I has also been carried out,

and a comparison of the calculated and observed energy differences between I and its 1,4 and 1,5 isomers has been made.[8] No force-field calculations of the interconversion paths of the twist-boat and twist-boat-chair have been published.

Epoxidation of I gives a monoepoxide (II)[9] and, stereospecifically, a trans diepoxide (III).[10]



I            II            III
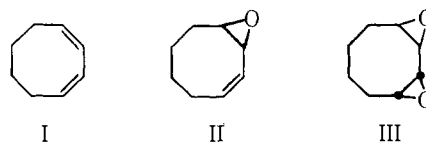
We now report $^1$H and $^{13}$C NMR data[11] and extensive force-field calculations on I and we show that the conformations of II and III can be deduced from their $^{13}$C NMR spectra and a consideration of the conformational relationships of II and III to I.

## Experimental Section

*cis,cis*-1,3-Cyclooctadiene[1] and its epoxides[9,10] were prepared by known procedures and the purity of the samples was checked by $^1$H and $^{13}$C NMR.
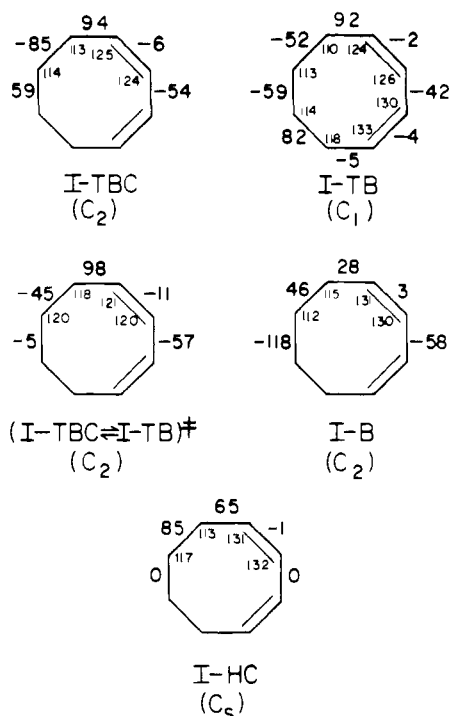
**Figure 1.** Calculated torsional and internal angles in different geometries of *cis,cis*-1,3-cyclooctadiene.



**Figure 2.** Calculated strain-energy profile for the conformational interconversion in *cis,cis*-1,3-cyclooctadiene.

All NMR spectra were measured on a superconducting solenoid NMR spectrometer operating at 59 kG.[12,13] The proton noise decoupled $^{13}$C NMR spectra are Fourier transforms of accumulated free induction decays and were obtained in 8-mm tubes under the following conditions: 45° pulse angle, 8K data points, 11 286-Hz spectrum width, and an exponential broadening function corresponding to a broadening of 4 Hz. For variable-temperature $^{13}$C NMR spectra a mixture of CHF$_2$Cl and CHFCl$_2$ (2:1) was used as the solvent. A fluorine line of the solvent was employed for lock purposes. The variable-temperature $^1$H NMR spectra were obtained in a frequency sweep mode with the same solvent as above. Tetramethylsilane was used as an internal reference for both the $^1$H and $^{13}$C NMR spectra. All temperatures were measured with a copper-constantan thermocouple situated in the probe a few centimeters below the sample, and should be accurate to ±1 °C for $^1$H NMR spectra and to ±2-3 °C for $^{13}$C NMR spectra.

Line-shape calculations were made with a Fortran program on the Data General Corp. Nova computer of the NMR spectrometer. Force-field calculations were carried out on an IBM-360/91 computer at the Campus Computer Network of UCLA, with a slightly modified version[14] of Boyd's MOLECULAR BUILDER IIA.[15] Atomic coordinates of the conformations calculated in this work are available from the authors.

## Results and Discussion

**Force-Field Calculations.** The strain energies of various molecular geometries of *cis,cis*-1,3-cyclooctadiene (1) were investigated by iterative force-field calculations,[16] with Boyd's computer program.[15] Two (energy-minimum) conformations, viz., the twist-boat-chair (I-TBC) and the twist-boat (I-TB), were found, in agreement with previous calculations.[7,8] Ring
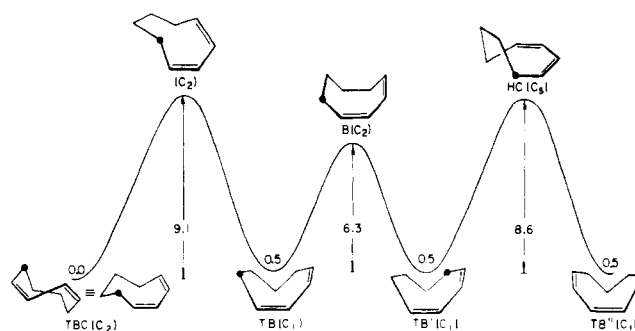
internal and torisonal angles for I-TBC and I-TB are shown in Figure 1, and strain-energy contributions to the total strain energy are given in Table I. The twist-boat conformation has some unusual internal angles. One C-CH$_2$-C angle has the value of 110° and is thus compressed from the unstrained value of 111° and is also much smaller than the usual C-CH$_2$-C angle (ca. 114°) in medium rings.[17] Also, one of the double bonds has greatly enlarged internal angles (130 and 133°), while the other double bond is normal. Both the I-TBC and I-TB have strongly twisted diene chromophores, the calculated twist angles being 54 and 42°, respectively.

The energy surface for interconversion of I-TBC and I-TB was investigated in detail by driving different torsional angles, as described previously,[14] and the results are summarized in Figure 2. There are three distinct and different transition states (not counting mirror images) which are required to describe the conformational dynamics in *cis,cis*-1,3-cyclooctadiene. The internal and torsional angles of these transition states are shown in Figure 1, and the strain-energy contributions to the total strains are listed in Table I.

The simplest conformational process, and the one with the lowest barrier, is the degenerate interconversion of the twist-boat conformation with itself via the boat (I-B) transition state. Because the boat has $C_2$ symmetry, this process, when fast, introduces a time-averaged $C_2$ axis of symmetry. A second, and higher energy, process undergone by the twist-boat conformation is also degenerate, and involves the half-chair (I-HC) transition state, which has $C_s$ symmetry. In this case, a time-averaged plane of symmetry results when the interconversion is fast. If both degenerate processes just considered are fast the time-averaged symmetry of the twist-boat conformation becomes $C_{2v}$, which is the maximum symmetry allowed by the chemical structure of *cis,cis*-1,3-cyclooctadiene. The twist-boat-chair, unlike the twist-boat, does not take part in any easy degenerate conformational process, but it can interconvert with the twist-boat via a transition state, (I-TBC $\rightleftharpoons$ I-TB)$^{\ddagger}$, which has $C_2$ symmetry. The strain-energy barrier separating I-TBC and I-TB is calculated to be substantially higher than the (boat) barrier separating the two twist-boat conformations.

Further discussion of these interconversions will be given in the next section in conjunction with dynamic NMR data.

The three transition states exhibit interesting geometrical differences. The boat and half-chair have strongly expanded

**Table I.** Calculated Strain Energies in Different Energy-Minima and Energy-Maxima Geometries of *cis,cis*-1,3-Cyclooctadiene (1)

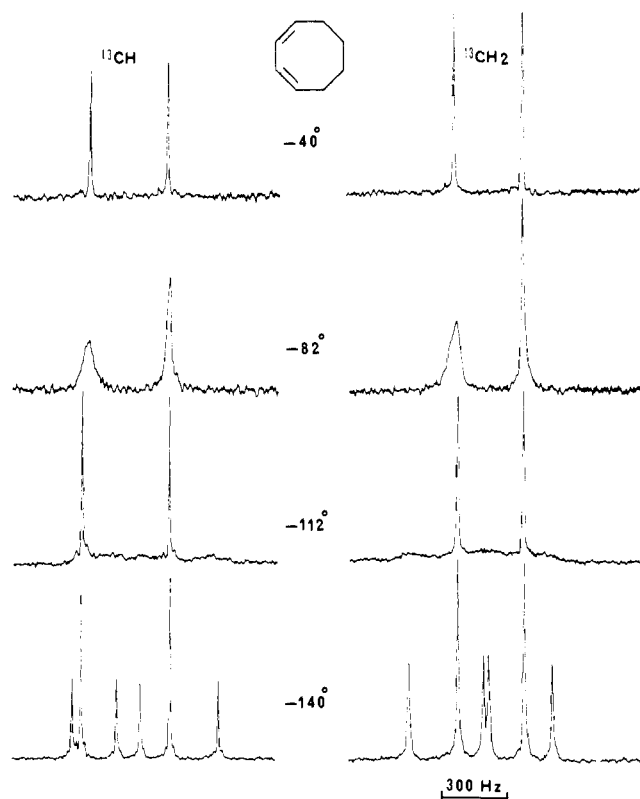| strain-energy contributions, kcal/mol | twist-boat-chair (I-TBC, $C_2$) | twist-boat (I-TB, $C_1$) | boat (I-B, $C_2$) | half-chair (I-HC, $C_s$) | (I-TBC $\rightleftharpoons$ I-TB)$^{\ddagger}$ ($C_2$) |
|---|---|---|---|---|---|
| bond stretching | 0.24 | 0.31 | 0.28 | 0.28 | 0.47 |
| bond-angle bending | 1.24 | 4.51 | 5.56 | 8.30 | 6.41 |
| out of plane bending | 0.06 | 0.04 | 0.01 | 0.00 | 0.17 |
| torsional strain | 2.24 | −0.60 | 3.94 | 3.54 | 3.98 |
| nonbonded interactions | 3.34 | 3.40 | 4.21 | 4.18 | 5.22 |
| total strain energy | 7.12 | 7.66 | 14.00 | 16.30 | 16.25 |

Figure 3. Natural-abundance 63.1-MHz $^{13}$C NMR spectra of *cis,cis*-1,3-cyclooctadiene at various temperatures.

**Table II.** Carbon-13 Resonances[a] in *cis,cis*-1,3-Cyclooctadiene (I)

| temp, °C | conformation | $^{13}CH_2$ | $^{13}CH$ |
|----------|--------------|-------------|-----------|
| −40 | TBC + TB[b] | 23.4, 28.5 | 126.5, 132.1 |
| −82 | TBC | 22.8, 27.6 | 126.3, 133.7 |
| −82 | TB | 23.0, 28.5 | 126.8, 132.7 |
| −140 | TBC | 22.8, 27.7 | 126.3, 133.0 |
| −140 | TB | 20.7, 25.4; | 123.2, 128.8; |
|      |    | 25.9, 31.3 | 130.8, 134.1 |

[a] In parts per million downfield from internal tetramethylsilane. [b] Averaged chemical shifts.

olefinic internal angles whereas the C–CH$_2$–C angles are more or less normal. By contrast, the transition state linking I-TBC and I-TB has distinctly reduced olefinic internal angles, but expanded C–CH$_2$–C angles. These results have a bearing on the barriers to be expected in substituted 1,3-cyclooctadienes, since substituents are expected to increase the energy required for angle expansion.

$^{13}$**C NMR Spectra of I.** Figure 3 shows $^{13}$C NMR spectra of 1,3-cyclooctadiene in the temperature range of −40 to −170 °C. Above about −40 °C, the spectrum consists of two methylene and two methine resonances (Table I). At −82 °C all four lines are broadened, but to quite different extents. The spectrum apparently exhibits just four sharp resonances of equal intensities at about −112 °C, but a careful examination reveals the presence of some very broad peaks which are hardly discernible from the base line. These broad peaks are more easily visible at either higher or lower temperatures.

These spectral changes can be most easily interpreted by first considering the spectrum at −140 °C. At this temperature, two sets of resonances can be distinguished: the first set consists of the four most intense lines in the spectrum, and the second set is made up of the remaining eight lines, all of which have similar intensities. The four lines of the first set can be assigned to a conformation which has $C_2$ symmetry, while the eight lines
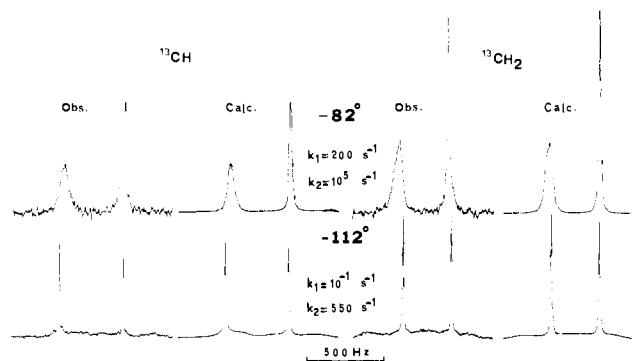


Figure 4. Observed and calculated $^{13}$C NMR spectra of *cis,cis*-1,3-cyclooctadiene at −82 and −112 °C.

**Table III.** Experimental and Theoretical Relative Energies[a] in *cis,cis*-1,3-Cyclooctadiene (I) and Its Monoepoxide (II)

| conformation | I exptl[b] | I calcd[c] | II exptl[b] |
|--------------|------------|------------|-------------|
| TBC | 0.0 | 0.0 | 0.1 |
| TB | 0.0 | 0.5 | 0.0[d] and 0.8[e] |
| (TBC ⇌ TB)[‡] | 9.0 | 9.1 | 9.9 |
| boat | 7.2 | 6.8 | 7.4 |
| half-chair | <10 | 9.1 | |

[a] In units of kilocalories/mole. [b] Free energies. [c] Strain energies. [d] II-TB1. [e] II-TB2.

of the second set can be simply explained if they belong to a single conformation lacking symmetry. From the previously presented force-field calculations, it is clear that the symmetrical conformation must be the twist-boat-chair (I-TBC), and the unsymmetrical one must be the twist-boat (I-TB). From the nearly equal intensities of the two sets of lines, the equilibrium constant for the interconversion of the two conformations must be close to unity and therefore $\Delta G°$ at −140 °C is zero.

As the temperature is raised above −140 °C, the eight lines of the twist-boat all broaden to the same extent, but the four lines of the twist-boat-chair remain very sharp. At −112 °C the twist-boat resonances are very broad. At −93 °C (not shown in Figure 3), four broad twist-boat resonances reappear at the midpoint of the doublets of the low-temperature spectrum and merge with the resonances of the twist-boat-chair at still higher temperatures.

The broadening process undergone by the twist-boat at about −120 to −110 °C cannot involve the twist-boat-chair, since the latter's resonances are sharp at these temperatures. From force-field calculations (Figure 2) it can be seen that the twist-boat conformation can pseudorotate more easily than it can interconvert with the twist-boat-chair. There are two pseudorotation paths and both should contribute to the line-shape changes observed in the twist-boat. However, since pseudorotation via the half-chair is 2.3 kcal/mol more difficult than that involving the boat, the former process can be neglected.

Line-shape calculations were carried out to fit the spectra at −82 and −112 °C (Figure 4). The following parameters were used: $\Delta G_1^‡$ (TBC ⇌ TB) = 9.0 ± 0.2 kcal/mol, $\Delta G_2^‡$ (TB ⇌ TB') = 7.2 ± 0.2 kcal/mol, $\Delta G°$ (TBC ⇌ TB) = 0, and the chemical shifts given in Table II. The values of $\Delta G°$, $\Delta G^‡$, and $\Delta G_2^‡$ are assumed to be independent of temperature, i.e., entropy effects are assumed to be negligible. These free-energy parameters agree well with the strain energies obtained in the force-field calculations (Table III), and this is also consistent with negligible entropy effects.

$^1$**H NMR Spectra of I.** The 251-MHz $^1$H NMR spectra of 1,3-cyclooctadiene at various temperatures are displayed in
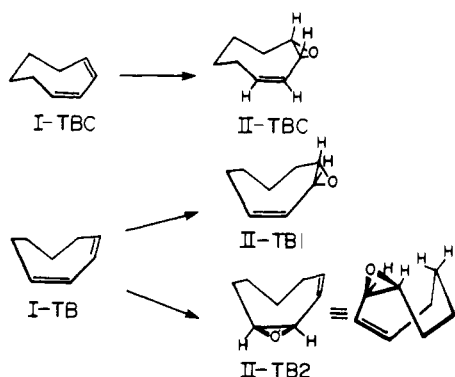
Scheme I





Figure 5. 251-MHz $^1$H NMR spectra of *cis,cis*-1,3-cyclooctadiene at various temperatures.

Figure 5. At −40 °C and above the spectrum is consistent with a time-averaged $C_{2v}$ symmetry, i.e., only two different types of methylene protons and two types of methine protons are observed. Below −50 °C the methylene region of the spectrum undergoes continuous and complex changes down to about −120 °C. The most noteworthy feature of the spectrum below −120 °C is the presence of an unusually high-field peak ($\delta$ 0.92 ppm). It is evident from this resonance, whose integrated intensity corresponds to about half a proton, that there are at least two different conformations present, in agreement with $^{13}$C NMR data. We assign the peak at $\delta$ 0.92 ppm to a proton which is strongly shielded as a result of being situated directly on the face of a double bond.[18] The twist-boat conformation has in fact such a unique proton as shown in IV.



IV
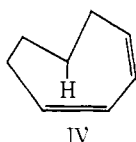
The two processes detected in the dynamic $^{13}$C NMR spectra must also cause line-shape changes in the $^1$H NMR spectra at low temperatures. However, the dynamic $^1$H NMR spectra are also affected by a third process, which introduces a time-averaged plane of symmetry and which has the half-chair as its transition state. Since the spectrum above about −40 °C is consistent with a time-averaged $C_{2v}$ symmetry, the $\Delta G^{\ddagger}$ for this third process must be less than 10 kcal/mol, but its precise value cannot be determined since the spectra are far too complex to be analyzable by line-shape methods.

**1,3-Cyclooctadiene Monoepoxide (II).** Because of the similar torsional rigidity of a double bond and a three-membered ring, any conformation of 1,3-cyclooctadiene epoxide can be considered as arising by the formal addition of an oxygen atom to a double bond in the twist-boat-chair or twist-boat conformation of cyclooctadiene. The conformations of the epoxide with the oxygen atom in an endo arrangement should be quite strained because of nonbonded repulsions, and can therefore be ignored. Thus, only the exo epoxide conformations are shown in Scheme I. Since the diene twist-boat-chair has $C_2$ symmetry, only a single twist-boat-chair exo epoxide conformation (II-TBC) can exist. The twist-boat, however, lacks symmetry and can therefore give rise to two different conformations (II-TB1 and II-TB2) with exo oxygen atoms. There should be a steric repulsion in TB2 between two inward-pointing hydrogen atoms, as shown in the drawing in Scheme I; this unfavorable interaction is absent in II-TB1. Thus, II might be expected to exist to a considerable extent in both the II-TBC and II-TB1 conformations and, probably to a minor extent, in the II-TB2 conformation. As will be shown below, the $^{13}$C NMR spectra of II can be well interpreted in terms of such a picture.

$^{13}$C NMR spectra of 1,3-cyclooctadiene monoepoxide (II) are shown in Figure 6. At −10 °C or above, the spectrum

consists of eight distinct lines, as required by the lack of chemical symmetry in II. The spectrum undergoes a number of changes between about −40 and −130 °C. At −140 °C and below the spectrum consists of 16 lines, which are approximately of equal intensities. There are thus two conformations of nearly the same free energies, and from the previous discussion, these must be II-TBC and II-TB1. On warming to −115 °C, five of the lines broaden to variable extents. At still higher temperatures, e.g., −90 °C, the broadened lines resharpen, and show distinctly different chemical shifts from those at lower temperature (Table IV). We assign this characteristic broadening and resharpening to a conformational process involving two very unequally populated conformations. From the previous discussion, and a consideration of the conformational barriers in 1,3-cyclooctadiene, the two conformations involved must be II-TB1 and II-TB2, with the latter conformation occurring only to a small extent. The broadening observed in a situation of this type depends on the chemical shift differences between exchanging nuclei in the two conformations, as well as on the population ratio, as given approximately by eq 1[19] where $\Delta_{1/2}^{max}$ is the maximum exchange broadening at half peak height, $p$ is the fractional population of the minor conformation, and $\delta$ is the chemical shift difference (in hertz) between the two conformations.

$$\Delta_{1/2}^{max} = p\delta \qquad (1)$$

Since no peaks of II-TB2 are visible at −140 °C, the population of II-TB2 at this temperature is clearly insufficient for direct detection with the signal to noise ratio shown in Figure 6, and is thus less than about 5%. This corresponds to a difference in $\Delta G°$ between II-TB1 and II-TB2 of about 0.8 kcal/mol or greater. The population of II-TB2 at −115 °C can be obtained provided that the chemical shift differences between II-TB1 and II-TB2 are known, which is unfortunately not the case. Among the most broadened resonances are those of the olefinic carbons and these must therefore have the largest chemical shift differences between II-TB1 and II-TB2. A typical large conformational chemical shift difference is of the
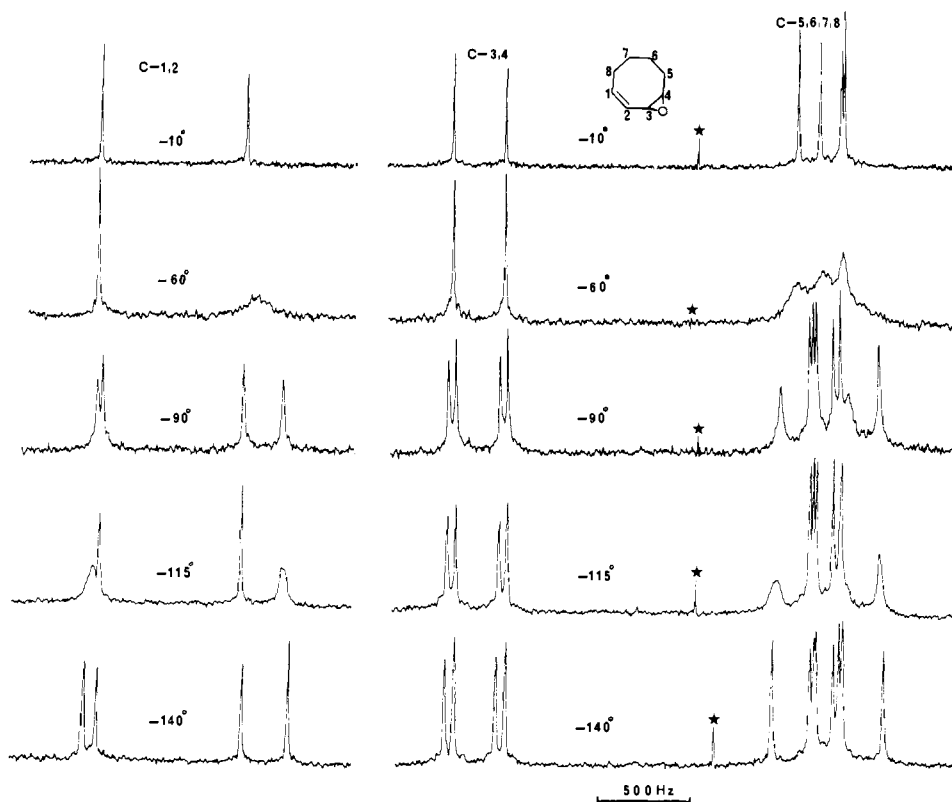
**Figure 6.** Natural-abundance 63.1-MHz $^{13}$C NMR spectra of *cis,cis*-1,3-cyclooctadiene monoepoxide at various temperatures. The lines marked with stars are beats.

**Table IV.** Carbon-13 Chemical Shifts[a] in 1,3-Cyclooctadiene Epoxides

| temp, °C | Conformation | CH$_2$ (sp$^3$) | CH (epoxide) | CH (double bond) |
|---|---|---|---|---|
| −10 | II-TBC + II-TB1 + II-TB2 | 25.7, 26.0, 27.8, 29.6 | 54.2, 58.6 | 123.0, 135.8 |
| −90 | II-TBC | 26.1, 26.7, 28.3, 28.6 | 54.7, 59.1 | 123.8, 135.7 |
| −90 | II-TB1 + II-TB2 | 22.8, 25.3, 28.1, 31.0 | 54.1, 58.5 | 120.4, 136.1 |
| −140 | II-TBC | 26.1, 26.6, 28.2, 28.5 | 54.8, 59.1 | 123.6, 135.8 |
| −140 | II-TB1 | 22.3, 25.8, 28.0, 31.7 | 54.0, 58.4 | 119.8, 136.9 |
| −30 | III | 23.6, 29.4 | 53.1, 57.3 | |

[a] In parts per million downfield from internal tetramethylsilane.

order 5–10 ppm. With this assumption, and the observed broadening of 30 Hz for either of the olefinic carbons, a population of 5–10% (at −115 °C) for II-TB2 can be deduced from eq 1. This corresponds to a $\Delta G°$ of 0.7–0.9 kcal/mol, in agreement with the previously obtained value. Another estimate of $\Delta G°$ can be obtained in the following way. The resonance frequencies of the twist-boat olefinic carbons, unlike those of the twist-boat-chair, change between −140 and −90 °C (Table IV). With the assumption that the chemical shifts of the carbons in II-TB1 and II-TB2 change by less than 0.2 ppm between these temperatures, a population of II-TB2 of 13 ± 2% at −90 °C can be calculated, and this corresponds to a $\Delta G°$ of 0.7 ± 0.1 kcal/mol. Thus, three different methods for estimating the $\Delta G°$ between II-TB1 and II-TB2 give a consistent value of 0.8 ± 0.2 kcal/mol.

Since the maximum in the exchange broadening of the olefinic carbons resonances is about 30 Hz and occurs at −115 °C, the rate constant for exchange at this temperature can be calculated by the equation[19]

$$k_1 + k_{-1} = 2\pi\delta \qquad (2)$$

where $k_1$ and $k_{-1}$ are the rate constants. With the conformational chemical shift difference of 5–10 ppm between the higher field olefinic carbons of II-TB1 and II-TB2, a value of $k_1 + k_{-1}$ of 2000–4000 s$^{-1}$ is obtained. At −115 °C, the

equilibrium constant is calculated to be about 13, and thus $k$ (II-TB1 to II-TB2) is 100–4000 s$^{-1}$ and $\Delta G^{\ddagger}$ is 7.4 ± 0.2 kcal/mol.

A second dynamic NMR effect is observed in the $^{13}$C spectrum of II at temperatures above −90 °C. This effect can be treated as one which effectively arises from an exchange process between two nearly equally populated sites. One of these sites is actually the weighted average of II-TB1 and II-TB2 (which are exchanging very rapidly at these temperatures), while the second site belongs to II-TBC. The observed broad resonance of the higher field olefinic carbon at −60 °C can be well simulated by a rate constant of 250 s$^{-1}$ ($\Delta G^{\ddagger}$ = 9.9 ± 0.2 kcal/mol) and population parameters obtained as described below. With the assumption of a temperature-independent $\Delta G°$ of 0.8 kcal/mol between II-TB1 and II-TB2, the ratio of these two conformations at −60 °C can be calculated to be 7:1. The ratio of II-TB1 to II-TBC at −140 °C is 1.2:1, corresponding to a $\Delta G°$ of 0.05 kcal/mol. If $\Delta G°$ is temperature independent, the ratio of II-TB1 to II-TBC becomes 1.1:1 at −60 °C.

The conformational free energies (including barriers) associated with 1,3-cyclooctadiene and its monoepoxide are listed in Table III and show great similarities.

**1,3-Cyclooctadiene *trans*-Diepoxide (III).** As with the monoepoxide, the diepoxide of 1 can be regarded as formally

arising by the addition of a second exo oxygen atom to the conformations of the monoepoxide. Such an addition to II-TBC, II-TB1, or II-TB2 leads exclusively to the trans isomer, which is indeed the stereochemistry of the 1,3-diepoxide.[10]

The addition of an exo oxygen atom to II-TBC leads to a sterically unhindered conformation of the diepoxide, whereas the addition of an exo oxygen to either II-TB1 or II-TB2 leads to a sterically crowded molecule, for the reason previously discussed with II-TB2. Thus, the diepoxide should exist predominantly in the twist-boat-chair, III-TBC.
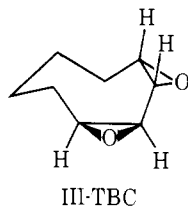


III-TBC

The ^{13}C NMR spectrum of III (Table IV) does not show any observable dynamic NMR effect from room temperature down to $-170$ °C. This result is consistent with the III-TBC conformation, which has $C_2$ symmetry. The population of twist-boat conformation of III is presumably too low to observe even by broadening effects, and is thus probably less than 1% at $-120$ °C. This means that in III the twist-boat-chair is at least 1.4 kcal/mol more stable than the twist-boat conformation.

## Conclusions

Force-field calculations in combination with ^{1}H and ^{13}C NMR spectroscopy unambiguously delineate both the static and dynamic conformational properties of *cis,cis*-1,3-cyclooctadiene and its epoxides. In the 1,3-diene, as also in *cis-cis*-1,4-[20] and *cis-cis*-1,5-cyclooctadienes,[21] there are two types of low-energy conformations, one of which is rigid when constructed from Dreiding molecular models, while the other is more or less flexible.[22] The interconversion of I-TB and I-TB' via I-B (Figure 2), which appears to be a strainless process on models, has in fact a barrier of 6–7 kcal/mol. On the other hand, I-TBC, which is "rigid" on models, requires only 9 kcal/mol for conversion to a twist-boat conformation. Thus, the distinction between rigid and flexible conformations is very much less in the real molecules than it appears to be when molecular models are examined, largely because models overemphasize angle distortion energies and completely neglect torsional strains.[23]

As we show in this paper, the conformations of the epoxides of 1,3-cyclooctadiene can be deduced from a knowledge of the conformational properties in the parent diene. The episulfides, imines (aziridines), and fused cyclopropane derivatives can be predicted to have similar conformational properties to the corresponding epoxide. The presence of *gem*-dimethyl sub-

stituents should alter the conformational picture from that in the parent diene in a fashion predictable by a consideration of the bulk of these groups and the geometrical data given in the present paper. Also, force-field calculations can be easily carried out on such compounds, in contrast to epoxides, etc. Benzo, dibenzo, 2-substituted, or 2,3-disubstituted *cis,cis*-1,3-cyclooctadiene, on the other hand, may behave rather differently, and conformational barriers in these compounds will probably be substantially higher than in the parent diene. The dibenzo derivative, for example, can be considered to be a ortho,ortho bridged biphenyl; thus the (conformational) barrier ($\Delta G^{\ddagger}$) to racemization of 23 kcal/mol in 1,2,3,4-dibenz-1,3-cyclooctadiene-6,7-dicarboxylic acid is not unexpected.[24]

## References and Notes

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