$\Delta\nu_{BH^+}$ values was made on the basis of eq 1 by expressing $\Delta\nu$ as a function of $\Delta\nu_B$, $H_0$, log $c_{H^+}$, $\Delta\nu_{BH^+}$, $\phi_e$ and p$K_{BH^+}$. The last three terms were varied by 1% increments until the best fit between calculated and experimental $\Delta\nu$ values was found through the least-squares analysis reported by Sillen.[23] The p$K_{BH^+}$ and $\phi_e$ values were computed as described elsewhere,[7,8] using the $H_0$ data obtained by interpolation of literature values at the appropriate temperature.[24] The somewhat larger than usual standard deviations found for $Me_2S$ p$K_{BH^+}$ values probably arise from the narrow range of acidity (about 2 $H_0$ units) in which protonation of this compound is complete.[7,8]

## References and Notes

(1) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899 (1966).
(2) L. P. Hammett, "Physical Organic Chemistry", 2nd ed, McGraw-Hill, New York, N.Y., 1970.
(3) E. M. Arnett and G. Scorrano, *Adv. Phys. Org. Chem.*, **13**, 83 (1976).
(4) E. M. Arnett and G. W. Mach, *J. Am. Chem. Soc.*, **86**, 2671 (1964).
(5) G. Scorrano, *Acc. Chem. Res.*, **6**, 132 (1973).
(6) J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley, New York, N.Y., 1975.
(7) (a) P. Bonvicini, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, *J. Am. Chem. Soc.*, **95**, 5960 (1973); (b) P. Bonvicini, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 2267 (1972).
(8) A. Levi, G. Modena, and G. Scorrano, *J. Am. Chem. Soc.*, **96**, 6585 (1974).
(9) C. H. Rochester, "Acidity Functions", Academic Press, New York, N.Y., 1970.
(10) M. Liler, "Reaction Mechanisms in Sulfuric Acid", Academic Press, New York, N.Y., 1971.
(11) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960).
(12) E. M. Arnett in "Proton-Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975.
(13) A complete list of $\Delta\nu$ and *I* values is reported in G. Perdoncin, Thesis, Padua, 1974. Ionization ratios may also be computed from data in Table II.
(14) A. Koeberg-Telder and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 226 (1975).
(15) E. J. King, "Acid-Base Equilibria", Pergamon Press, Oxford, 1965.
(16) F. M. Jones, III, and E. M. Arnett, *Prog. Phys. Org. Chem.*, 11, 263 (1974).
(17) J. W. Larson and L. G. Hepler in "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969.
(18) G. L. Bendazzoli, P. Palmieri, G. Gottarelli, I. Moretti, and G. Torre, *J. Am. Chem. Soc.*, **98**, 2659 (1976).
(19) P. D. Bolton, C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Am. Chem. Soc.*, **92**, 1567 (1970).
(20) S. Y. Lam and R. L. Benoit, *Can. J. Chem.*, **52**, 718 (1974), and references cited therein.
(21) M. J. Cook, N. L. Dassanayake, C. D. Johnson, A. R. Katritzky, and T. W. Toone, *J. Am. Chem. Soc.*, **97**, 760 (1975).
(22) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).
(23) L. G. Sillen, *Acta Chem. Scand.*, **18**, 1805 (1964), and previous papers.
(24) C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Am. Chem. Soc.*, **91**, 6654 (1969).

# Conformational Properties of *cis,cis*-1,4-Cyclooctadiene. Dynamic Nuclear Magnetic Resonance Spectroscopy and Iterative Strain-Energy Calculations

**Frank A. L. Anet* and Issa Yavari**

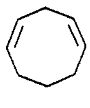
*Contribution No. 3769 from the Department of Chemistry,*
*University of California, Los Angeles, California 90024.*

*Received June 14, 1977*

**Abstract:** The $^1H$ and the natural abundance $^{13}C$ NMR spectra of *cis,cis*-1,4-cyclooctadiene have been measured from −10 to −180 °C. Dynamic NMR spectroscopy and iterative strain-energy calculations indicate that the compound exists in solution as a mixture of twist-boat (flexible) and boat-chair (relatively rigid) conformations having nearly the same energies. The calculated (strain energy) barrier for the interconversion of these two conformers was calculated to be 9.0 kcal/mol, in good agreement with the experimental (free energy) barrier of 8.0 kcal/mol. The present results are discussed in conjunction with previous experimental and theoretical data on 1,4-cyclooctadiene and related compounds.

In view of the success of dynamic NMR spectroscopy and iterative strain-energy calculations for investigating the conformational properties of *cis,cis*-1,3- and *cis,cis*-1,5-cyclooctadienes,[1,2] we have carried out corresponding investigations of the remaining *cis,cis*-cyclooctadiene, namely the 1,4 isomer,[3] and we now report these results. Dunitz and Waser[4] have pointed out that Dreiding molecular models of the 1,4-diene can exist as a rigid conformation or as a family of flexible conformations. However, the torsional, angle bending, and nonbonded potential energy contributions of real molecules are poorly reproduced by these molecular models, and therefore deductions based on such models may be misleading. Favini et al.[5] have published strain-energy calculations on 1,4-cyclooctadiene, but these authors used a simple procedure which does not minimize the energy by allowing the conformations to relax to their optimum geometries. Allinger et al.[6] have published force-field calculations on 1,4-cyclooctadiene but they did not consider the twist-boat conformation, which, as will be shown in this paper, is the lowest energy conformation of this molecule, nor did they consider conformational interconversion paths.

Although there is presently no published experimental data on the structure or conformational properties of 1,4-cyclooctadiene itself, several papers on dibenzo derivatives of this compound and its heterocyclic analogues have appeared recently.[7-9]



I

## Experimental Section

The *cis,cis*-1,4-cyclooctadiene was synthesized from the 1,3 isomer according to the method described by Moon and Ganz.[10] Its $^1H$ NMR spectrum in $CDCl_3$ at room temperature exhibits five absorption bands at $\delta$ (ppm) 1.39 (7-$CH_2$), 2.25 (6,8-$CH_2$), 2.74 (3-$CH_2$), 5.31 (1,5-CH), and 5.63 (2,4-CH). Irradiation of the band at $\delta$ 2.74 (3-$CH_2$) caused the quintet at $\delta$ 1.39 to become a doublet, and the rough quartet at $\delta$ 2.25 to become a doublet of triplets, proving the assignment given above for the olefinic protons. The $^{13}C$ NMR spectrum in $CDCl_3$ at room temperature shows five bands at $\delta$ (ppm) 23.3 (7-$^{13}CH_2$), 25.0 (6,8-$^{13}CH_2$), 29.7 (3-$^{13}CH_2$), 128.6 (1,5-$^{13}CH$), and 130.6 (2,4-$^{13}CH$). Selective irradiation with low power at each of the proton chemical shifts was carried out. In each case only a single $^{13}C$ resonance was observed as a sharp line, the other resonances being multiplets, thus giving directly the assignment shown above.

All NMR spectra were measured on a superconducting solenoid NMR spectrometer operating at 59 kG.[11,12] The proton noise-de-

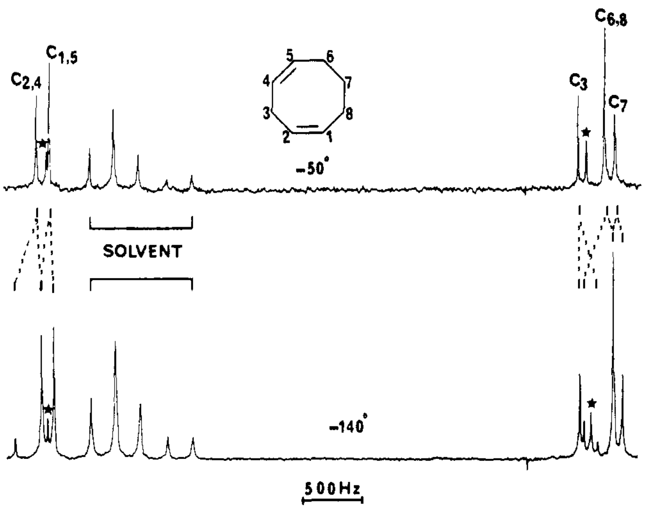


Figure 1. 63.1-MHz $^{13}C$ NMR spectra of *cis,cis*-1,4-cyclooctadiene in $CHFCl_2$-$CHF_2Cl$ (1:2) at −50 °C and −140 °C. In each spectrum the lines marked with stars belong to the 1,5 isomer.

coupled $^{13}C$ NMR spectra are Fourier transforms of accumulated free induction decays and were obtained with 8-mm tubes under the following conditions: 45° pulse angle, 8K data points, 11286-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 $CHFCl_2$-$CHF_2Cl$ (1:2) was used as the solvent. A fluorine line of the solvent was employed for lock purposes. The variable-temperature $^1H$ NMR spectra were obtained in a frequency sweep mode with $CHFCl_2$-$CHF_2Cl$ (1:2) as solvent. Tetramethylsilane was used as internal reference for both $^{13}C$ and $^1H$ 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 $^1H$ NMR spectra and to ±2 to 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. Strain-energy calculations were carried out on an IBM-360/91 computer at the Campus Computer Network of UCLA.

## Results and Discussion

Assignments of the $^1H$ and $^{13}C$ NMR spectra of 1,4-cyclooctadiene were made by selective decoupling experiments (see Experimental Section). The $^1H$ assignment confirms previous work[13] on the 100-MHz spectrum of this compound.

The $^1H$ NMR spectrum of 1,4-cyclooctadiene in $CHFCl_2$-$CHF_2Cl$ (1:2) remains essentially unchanged, apart from some general broadening, down to −160 °C. Further discussion of these spectra will be given after the presentation of the $^{13}C$ NMR data and of strain-energy calculations.

The $^{13}C$ NMR spectrum of 1,4-cyclooctadiene shows a clear dynamic NMR effect between −50 and −140 °C (Figures 1 and 2). The resonances are broad at about −100 °C and they split into doublets with intensity ratios of ~85:15 at lower temperatures. The splitting patterns given in Figure 1 are required for the calculated line shapes to fit the observed spectrum at −105 °C (Figure 2). These calculations were carried out with an equilibrium constant ($K$) of 0.176, a rate constant ($k$) of 130 $s^{-1}$, and the chemical shifts measured at −140 °C. Thus two conformations are present, and, at −105 °C, $\Delta G°$ is 0.58 ± 0.05 kcal/mol, and, from the absolute rate theory, $\Delta G^{\ddagger}$ is 8.0 ± 0.2 kcal/mol, where all known sources of errors are included.

We have not tried to calculate other activation parameters, such as $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$, because values of these parameters (unlike $\Delta G^{\ddagger}$) are very prone to systematic errors and are difficult to obtain with useful accuracies.[14] In a conformational process, which has first-order kinetics, and which occurs in a molecule of low symmetry and polarity, the value of $\Delta H^{\ddagger}$ should be close to that of $\Delta G^{\ddagger}$, and that of $\Delta S^{\ddagger}$ should be close to zero.[14] Similar relationships should hold for the corresponding thermodynamic parameters, $\Delta H°$, $\Delta G°$, and $\Delta S°$. With the assumption that $\Delta S°$ is within ±1 eu of zero, the equilibrium constant ($K$) at room temperature is calculated to be 0.4 ± 0.1, corresponding to a population ratio of ~70:30.

**Strain-Energy Calculations.** Strain-energy (force field or molecular mechanics)[15] calculations were carried out with Boyd's iterative computer program.[16] The parameters used for torsional and out-of-plane bending of a double bond were those of Ermer and Lifson;[17] all other parameters were those suggested by Boyd.[18] Calculations based on the Newton-Raphson procedure, as in the present instance, will converge to either an energy maximum or an energy minimum with respect to distortions corresponding to a normal mode of vibration. Ermer[19] has recently stressed the desirability of determining whether a given geometry obtained in a strain-energy calculation is a true (local) energy minimum with respect to any small distortion of the molecule. A test for a true (local) energy minimum can be made if the vibrational frequencies of the conformation are calculated, as all vibrational frequencies should be real for a true minimum. Since Boyd's program provides the vibrational frequencies as an optional feature, we have checked that all the minimum-energy conformations obtained in our strain-energy calculations have

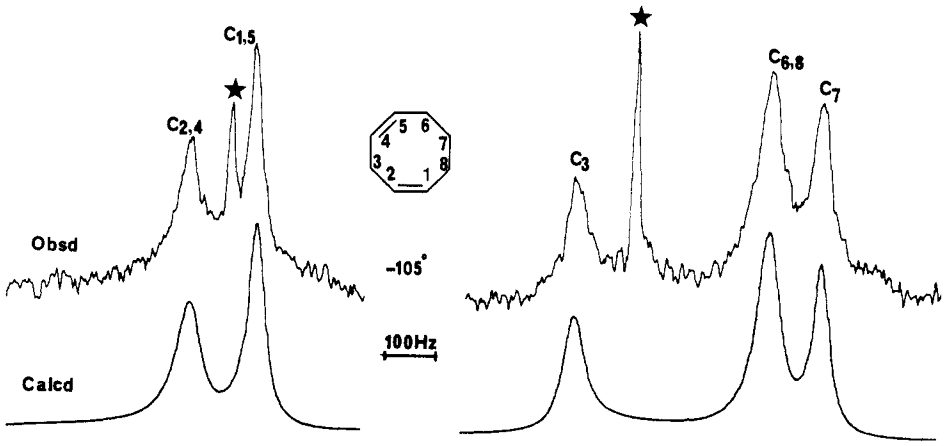


Figure 2. Experimental (top) and calculated (bottom) 63.1-MHz $^{13}C$ NMR spectrum of *cis,cis*-1,4-cyclooctadiene in $CHFCl_2$-$CHF_2Cl$ at −105 °C. The rate constant ($k$ = 130 $s^{-1}$) is given for the conversion of the twist-boat (major) to the boat-chair (minor) conformation. In the experimental spectrum, the peaks marked with stars belong to the 1,5 isomer.

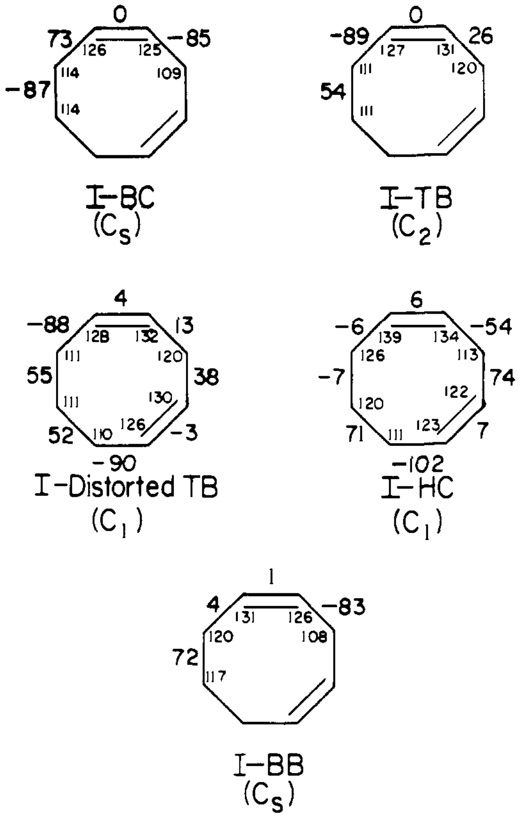


**Figure 3.** Torsional and internal angles in various geometries of *cis,cis*-1,4-cyclooctadiene.

$3N - 6$ real vibrational frequencies. For transition-state geometries, on the other hand, the criterion that must hold is that *one* and *only one* vibrational frequency be imaginary, and such a test has been applied to all conformational transition states in our calculations.

Approximate coordinates for the boat-chair (BC) or rigid[4] conformation were calculated by means of the program COORD[20] with input data obtained from a Dreiding-Fieser model. The computer calculated geometry of the boat-chair conformation resulting from the strain-energy calculations has $C_s$ symmetry and its torsional and internal angles are given in Figure 3.

The twist-boat (TB) or flexible[4] family of conformations of 1,4-cyclooctadiene was obtained by "driving"[15c,21,22] the C(6)-C(7) or C(7)-C(8) torsional angle of the boat-chair conformation by steps of 10 to 15° to give a smooth conformational change, as shown in Figure 4. The twist-boat family of conformations includes the axial-symmetrical twist-boat (TB, $C_2$) itself and a distorted twist-boat (DTB) which lacks symmetry (there are actually two distorted twist-boats when the molecule is labeled). The energy barrier separating these conformations is very small and the calculations are not accurate enough to determine meaningfully the precise energy surface in such situations. The torsional and internal angles for the twist-boat and distorted twist-boat conformations are given in Figure 3.

The transition state for the boat-chair to twist-boat process is the half-chair (HC) (Figures 3 and 4) and this has a relatively high strain energy, consistent with the rigidity of the boat-chair conformation in Dreiding molecular models.[4]

The driving process used in the calculations to change the boat-chair conformation to the twist-boat is not reversible.[23] If the reverse process is attempted, the twist-boat changes to its enantiomeric form (TB′) via the plane-symmetrical boat-boat (BB, $C_s$) geometery as the transition state (Figure 4). The calculated energy barrier separating the TB and TB′ conformations is relatively low (~3.8 kcal/mol), consistent with the flexibility of the family that includes the twist-boat, distorted twist-boat, and boat-boat forms in Dreiding molecular models.[4]

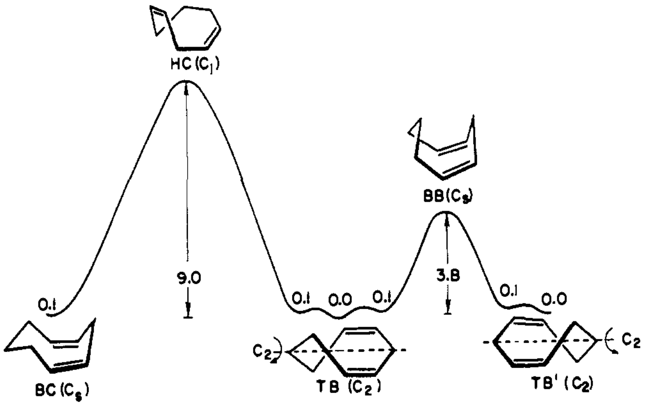


**Figure 4.** Results of iterative strain-energy calculations on *cis,cis*-1,4-cyclooctadiene. The energies are in units of kilocalories/mole.

Other possible driving modes for the conformational interconversions of 1,4-cyclooctadiene were also explored, but they were found to have much higher calculated strain energies than the corresponding paths shown in Figure 4.

Only a few comments need be made about the calculated structural and energy parameters of the various conformations and transition states shown in Figure 3 and in Table I. The boat-chair and the twist-boat conformations have almost the same strain energies for the bond-stretching and out-of-plane bending terms, and the amount of strain due to these terms is small. On the other hand, the strain-energy contributions arising from bond-angle bending and torsional effects are quite variable in these two conformations. The twist-boat has a higher strain energy for the bond-angle bending terms, whereas the torsional strain of the boat-chair conformation is higher than that of the twist-boat. An important difference between the boat-chair and the twist-boat (or distorted twist-boat) conformation concerns the internal angle $\theta_{234}$ of the isolated methylene group. This angle (109°) is compressed from its unstrained value (111°) in the boat-chair, but, in the twist-boat, the same angle (120°) is very much expanded. Internal bond angles in medium-ring compounds are usually larger than the unstrained value, a typical angle for saturated eight-membered rings being 114°,[24] and it is very unusual for such angles to have a value less than 111°. The internal angles of the olefinic carbons in the boat-chair are almost normal, whereas those of the C-2 and C-4 olefinic carbons in the twist-boat are quite expanded.

Because of the extremely low calculated barrier (which may not be real) separating the twist-boat and the distorted twist-boat, it is convenient to group these conformations together for the purpose of the subsequent discussion, and to label them as simply the twist-boat conformation. The strain-energy calculations show that there are only two low-energy conformations (neglecting enantiomeric forms) for 1,4-cyclooctadiene, and that the energy difference between them should be very small but that they should be separated by an energy barrier of 9.0 kcal/mol. Experimentally, the $^{13}C$ NMR data at low temperatures shows the presence of two conformations which have a free-energy difference of 0.5 kcal/mol, and which are separated by a free-energy barrier of 8.0 kcal/mol, in good agreement with the strain-energy calculations. Comparisons of strain-energy differences with free-energy differences should be valid in the present instance, because zero-point vibrational energy and entropy differences should be small. Although the symmetry numbers for the twist-boat and boat-chair are different, being 2 and 1, respectively, this effect

**Table I.** Calculated Strain Energies in Different Energy-Minima and Energy-Maxima Geometries of *cis,cis*-1,4-Cyclooctadiene

| | Strain-energy contributions, kcal/mol | | | | |
|---|---|---|---|---|---|
| | BC ($C_s$) | TB ($C_2$) | DTB ($C_1$) | HC ($C_1$) | BB ($C_s$) |
| Bond stretching (20 terms) | 0.25 | 0.31 | 0.31 | 0.50 | 0.48 |
| Bond-angle bending (36 terms) | 1.61 | 4.46 | 4.33 | 10.11 | 7.54 |
| Out-of-plane bending (8 terms) | 0.20 | 0.01 | 0.03 | 0.10 | 0.29 |
| Torsional strain (10 terms) | 7.72 | 3.63 | 3.87 | 6.68 | 3.49 |
| Nonbonded interactions (134 terms) | 2.42 | 3.68 | 3.68 | 3.61 | 4.11 |
| Total strain energy | 12.20 | 12.09 | 12.22 | 21.01 | 15.91 |

**Table II.** 63.1-MHz $^{13}$C NMR Chemical Shifts[a] of *cis,cis*-1,4-Cyclooctadiene

| Temp, °C | 7-$^{13}CH_2$ | 6,8-$^{13}CH_2$ | 3-$^{13}CH_2$ | 1,5-$^{13}$CH | 2,4-$^{13}$CH |
|---|---|---|---|---|---|
| −50 | 22.9 | 24.8 | 29.9 | 128.7 | 131.0 |
| −140 (TB) | 22.5 | 24.2 | 30.6 | 128.9 | 131.0 |
| −140 (BC) | 24.5 | 29.7 | 27.1 | 131.2 | 136.2 |

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

is cancelled by the fact that the former conformation is chiral and exists as a mixture of two enantiomeric forms, whereas the latter is achiral.

**Assignment of Conformations.** The $^1$H NMR spectrum of 1,4-cyclooctadiene, although virtually temperature independent, gives a valuable clue as to the nature of the major conformation of this compound. In the boat-chair conformation, each methylene group has anisochronous protons, and, at temperatures where the boat-chair is not taking part in a dynamic NMR effect, the $^1$NMR spectrum should exhibit *six* chemical shifts in the methylene region. The strain-energy calculations give a barrier of only 3.8 kcal/mol for the interconversion of the twist-boat and its mirror image, and it is therefore probable that the TB $\rightleftharpoons$ TB′ process will still be fast on the NMR time scale at −170 °C. The time-averaged symmetry will then be $C_{2v}$ for the twist-boat family and the $^1$H NMR spectrum of this conformational family will thus show only a single chemical shift for the geminal protons on C-6 and C-8. Also, the C-3 and C-7 methylene protons will each give rise to a single chemical shift by symmetry. Thus, the strain-energy calculations imply that the methylene-proton region of the twist-boat conformations should exhibit only *three* chemical shifts at all temperatures above −170 °C.

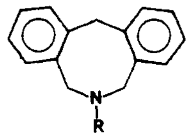
Since the $^1$H NMR spectrum of 1,4-cyclooctadiene does not change appreciably down to −170 °C, the major conformation is most probably the twist-boat. If only the twist-boat were populated, the $^1$H NMR spectrum would show no dynamic NMR effect; if a small population of the boat-chair is also present, some broadening of all the lines would be expected, the extent of the broadening being dependent on the chemical-shift differences between the two conformations. However, the bands of the various protons are already quite complex and broad because of coupling and dipole-dipole relaxation effects, and an additional small broadening due to a dynamic NMR effect would be difficult to detect. The presence of the boat-chair as a minor conformation might be directly visible at still lower temperature, when the exchange broadening has disappeared. However, the population of the boat-chair is low and the signals are expected to be more spread out than those in the twist-boat, and thus it is not surprising that the minor conformation could not be detected by $^1$H NMR. On the other hand, if the major conformation were the boat-chair, the $^1$H NMR spectrum would be understandable only provided that coincidences (or near coincidences) exist in the chemical shifts of the geminal proton in all three different methylene groups, a rather unlikely event.

Supporting evidence for the assignments made above can be obtained by a comparison of the chemical shifts in the twist-boat and boat-chair conformations (Table II). The chemical shifts of C-3 are particularly significant because of the very different environments of that carbon in the two conformations. C-3 lies along a $C_2$ axis in the twist-boat (or close to this in a distorted twist-boat), and thus it cannot be involved in shielding effects (e.g., a $\gamma$ or "vicinal gauche" effect).[25] In the boat-chair, on the other hand, C-3 is involved in $\gamma$ effects with C-6 and C-8, and thus it should be shielded by comparison with the same carbon in the twist-boat, as indeed is the case with assignment previously made (Table II). The magnitude of the shielding (3.5 ppm) is consistent with this effect. Other carbons also show pronounced shift differences in the two conformations, but these variations are not easy to interpret on the basis of empirical shift rules.[25]

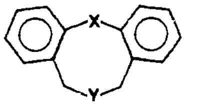
**Comparisons with Other Investigations.** Favini et al.[5] have calculated the strain energies of the boat-chair and a strongly distorted twist-boat and have found that the boat-chair was favored by either 1.3 or 7.1 kcal/mol, depending on the kind of nonbonded interactions used, but these authors did not optimize the geometries of these conformations. Allinger et al.[6] have applied iterative force-field calculations to 1,4-cyclooctadiene and have found that the boat-chair is the most stable conformation. However, they apparently did not investigate the axially symmetric twist-boat conformation, and they claimed that the boat-boat was an energy minimum, which surprised them. They state that distortion from $C_s$ symmetry led to an increase in the energy of the boat-boat, but this may have been the result of an insufficiently large distortion from the symmetrical geometry, as the energy profile is fairly flat in that region according to our calculations. We find that the twist-boat is 3.8 kcal/mol more stable than the boat-boat, and this difference is large enough for it to have at least the correct sign, in our opinion.

The conformational behavior of 1,4-cyclooctadiene can be contrasted to that of its dibenzo derivative,[9a] in which the boat-chair conformation is populated to the extent of 98% at room temperature, and where the boat-chair to twist-boat free-energy barrier is 14.9 kcal/mol.[26] The high barrier in the dibenzo series is reproduced by strain-energy calculations.[9a]

Pala et al.[7] were the first to observe dynamic $^1$H NMR effects in eight-membered rings which possess 1,4 unsaturation. They have discussed briefly the spectra of II (R = H, CN, or $CH_2Ph$) and pointed out that the NMR data indicates some rigidity in the eight-membered ring, but they did not propose any specific conformation for these compounds. No exchange rate constants or activation energy parameters were reported.



II



III

Fraser and coworkers[8] have applied dynamic $^1$H NMR spectroscopy to some *N*-alkyl derivatives of II. These compounds were found to exist in solution as mixtures of boat-chairs and "twist-boats" (see Appendix) in both the base and protonated states.[26] The barriers separating the two kinds of conformations are in the range of 16 to 18 kcal/mol, and are therefore similar to the corresponding barrier in dibenzo-1,4-cyclooctadiene.[9a]

X-ray diffraction data of the *N*-methyl and *N*-*tert*-butyl derivatives of II have recently been reported.[27] The azocine ring of the *N*-methyl derivative is found to have the rigid boat-chair conformation with approximately $C_s$ symmetry.[27a] The observed ring torsional angles are in good agreement with those calculated for the boat-chair conformation of 1,4-cyclooctadiene. On the other hand, the corresponding *N*-*tert*-butyl derivative of II is found to adopt a highly distorted twist-boat conformation in the crystalline state,[27b] with torsional angles about midway between those of the twist-boat and boat-boat geometries of 1,4-cyclooctadiene. However, it should be remembered that the geometry of a flexible conformation can be strongly affected by crystal packing effects and thus there may be appreciable differences between the solution and crystal conformations in such a case.

Ollis and coworkers[9b] have recently reported the temperature dependence of the $^1$H NMR spectra of a wide variety of heterocyclic analogues of dibenzo-1,4-cyclooctadiene, in which the C-3 and C-7 methylene groups were replaced by hetero substituents (e.g., O, S, $SO_2$, NR) (III). With two exceptions, all compounds were found to exist in solution as mixtures of boat-chairs and twist-boats with the former being the major conformation. The barriers separating these two families of conformations are in the range of 12 to 19 kcal/mol. Only the boat-chair is populated when $X = Y = SO_2$ and only the twist-boat is observed when $X = C{=}O$ with $Y = NCH_2Ph$. These authors were able to measure energy barriers (10 to 11 kcal/mol) for enantiomerization of the chiral twist-boat conformations in III ($X = Y = S$ and $X = O$, $Y = SO_2$).

## Conclusions

*cis,cis*-1,4-Cyclooctadiene exists as a mixture of two conformations, namely, a fairly rigid boat-chair, and a more or less flexible twist-boat, and in this regard it is similar to dibenzo-1,4-cyclooctadiene and many of its heterocyclic derivatives. However, the barriers to conformational processes are quite sensitive to the nature of substituents and to the presence or absence of fused benzene rings.

A knowledge of the conformation of 1,4-cyclooctadiene is of some importance for the interpretation of the photoelectron spectrum of this compound, since the interaction of the $\pi$ orbitals of the double bonds is mainly through space in the boat-chair, but should be largely by hyperconjugative interaction via the 3-methylene group in the twist-boat.[28] The two mechanisms have different signs of the interaction constants,[28] which unfortunately cannot be determined from the photoelectron spectrum. The observed splitting of 0.66 eV between the two lowest energy bands of 1,4-cyclooctadiene may well reflect superimposed splitting arising from both the boat-chair and twist-boat conformations, with interaction constants of similar magnitudes but of opposite signs.

**Acknowledgment.** This work was supported by the National Science Foundation.

## Appendix

**Nomenclature of 1,4-Cyclooctadiene Conformations.** Unfortunately, very different names have been used in the literature to describe the conformations of 1,4-cyclooctadiene and its analogues. The conformation termed the boat-chair in this paper and elsewhere[5,6,27a] has been named a crown[8a] (later changed to boat-chair[8b]) or a chair,[9] or simply left nameless and characterized as "rigid".[4] We strongly prefer the term boat-chair for reasons previously given.[8b]

For the twist-boat we are in agreement with Ollis and coworkers,[9] who use this term for the conformation with $C_2$ or near-$C_2$ symmetry. Other workers[8b,27b] have also used this name, but have applied it to conformations which are rather far from $C_2$ symmetry and it has been implied that the $C_2$ conformation is an energy barrier.[8b,26] It is, of course, difficult to assign meaningful names to more or less flexible conformations, because relatively large changes in geometry can result from small structural modifications.

The boat-boat name has been used previously, to describe a geometry assumed[5] or calculated[6] to be an energy minimum. Other workers[8b,9] have used the name boat for this geometry, and have considered it a transition state. We also find that this geometry, which we name the boat-boat, is a transition state.

Finally, the half-chair (I-HC) transition state is similar to the "TS1" geometry proposed by Ollis and co-workers[9] for dibenzo-1,4-cyclooctadiene.

**Supplementary Material Available:** A listing of the coordinates for all the atoms in five different geometries of *cis,cis*-1,4-cyclooctadiene (3 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) (a) F. A. L. Anet and I. Yavari, *Tetrahedron Lett.*, 1567–1570 (1975); (b) F. A. L. Anet and I. Yavari, unpublished work.

(2) F. A. L. Anet and L. Kozerski, *J. Am. Chem. Soc.*, **95**, 3407–3408 (1973); F. A. L. Anet and L. Kozerski, unpublished work.

(3) F. A. L. Anet and I. Yavari, paper presented at the 1975 Pacific Conference on Chemistry and Spectroscopy, North Hollywood, Calif., Oct 1975, Abstract N. 109.

(4) J. D. Dunitz and J. Waser, *J. Am. Chem. Soc.*, 94, 5645–5650 (1972).

(5) G. Favini, F. Zuccarello, and G. Buemi, *J. Mol. Struct.*, **3**, 385–394 (1969); F. Zuccarello, G. Buemi, and G. Favini, *ibid.*, **18**, 295–302 (1973).

(6) N. L. Allinger, J. F. Viskocil, Jr., U. Burkert, and Y. Yuh, *Tetrahedron*, **32**, 33–35 (1976).

(7) G. Pala, Mantegani, and E. Zugna, *Tetrahedron*, **26**, 1275–1279 (1970).

(8) (a) R. N. Renaud, R. B. Layton, and R. R. Fraser, *Can. J. Chem.*, **51**, 3380–3385 (1973); (b) R. R. Fraser, M. A. Razza, R. N. Renaud, and R. B. Layton, *Ibid.*, **53**, 167–176 (1975).

(9) (a) F. E. Elhadi, W. D. Ollis, and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, **15**, 224–225 (1976); (b) R. P. Gallantly, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 913–925 (1976).

(10) S. Moon and C. R. Ganz, *J. Org. Chem.*, **34**, 465–466 (1969); **35**, 1241–1250 (1970).

(11) F. A. L. Anet, V. J. Basus, C. H. Bradley, and A. K. Cheng, paper presented at the 12th Experimental Nuclear Magnetic Resonance Conference, Gainesville, Fla., Feb 1971.

(12) F. A. L. Anet and A. K. Cheng, *J. Am. Chem. Soc.*, **97**, 2420–2424 (1975).

(13) R. G. Salomon and N. El Sanadi, *J. Am. Chem. Soc.*, **97**, 6214–6221 (1975).

(14) F. A. L. Anet and R. Anet, "Dynamic Nuclear Magnetic Resonance Spectroscopy," L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, pp 543–619. If the two conformations have different symmetries a small entropy contribution from this effect will exist and can be easily calculated. Thus, a conformation with $C_s$ symmetry is achiral and has a symmetry number ($\sigma$) of 1, and there is no symmetry contribution to the entropy. A conformation with $C_2$ symmetry is chiral and exists as a mixture of enantiomeric forms, but also has $\sigma = 2$. In this case these effects cancel, so that again there is no symmetry correction to the entropy. Similar principles apply to transition states, except that transition states can be considered as having one degree of freedom less than energy minima.[16c] Thus, there is no entropy correction to proceed from a conformation which has $C_s$ symmetry to a chiral transition state with $C_1$ symmetry. In any case, entropy contributions due to a single symmetry element or due to the presence of chirality are small, being equal to $R \ln 2$ or 1.4 eu.

(15) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005–8025 (1973); C. Altona and D. H. Faber, *Top. Curr. Chem.*, **45**, 1–38 (1974); N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1–82 (1976); O. Ermer, *Struct. Bond.*, **27**, 161–211 (1976); A. Warshel in "Modern Theoretical Chemistry", Vol. 7, G. Segal, Ed., Plenum Press, New York, N.Y., in

press.

(16) (a) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574–2583 (1968); (b) S.-J. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *J. Am. Chem. Soc.*, **92**, 3109–3118 (1970); (c) K. B. Wiberg and R. H. Boyd, *ibid.*, **94**, 8426–8430 (1972).

(17) O. Ermer and S. Lifson, *J. Am. Chem. Soc.*, **95**, 4121–4132 (1973).

(18) The double-bond force-field parameters used in the present work have been used by us to calculate successfully known conformational properties of *trans*-cyclooctene, cyclohexene, and methylenecyclohexane. In some of our earlier work (F. A. L. Anet and L. Kozerski, unpublished work quoted in ref 14), we used double-bond force-field parameters provided by Professor R. H. Boyd. Although these parameters are satisfactory for many olefinic systems, they fail for very twisted olefins such as *trans*-cyclooctene.

(19) O. Ermer, *Tetrahedron*, **31**, 1849–1854 (1975).

(20) M. J. S. Dewar, *Fortschr. Chem. Forsch.*, **23**, 1–30 (1971).

(21) F. A. L. Anet and J. Krane, *Tetrahedron Lett.*, 5029–5032 (1973); F. A. L. Anet and I. Yavari, *Tetrahedron Lett.*, 4221–4224 (1975).

(22) In this process false torsional parameters are used to force one (or more than one) of the torsional angles to change in an appropriate direction, but all other parameters are left unchanged, and the true strain energy at the end is calculated with the correct torsional parameters.

(23) The boat–chair to twist–boat process is of course reversible in actuality. The computer-driven process follows the lowest energy path for any given constraint, and this does not necessarily lead to the lowest transition state (energy saddle point). It is possible to go from the twist-boat to the boat-chair conformation by "driving" *two* torsional angles, and this process *is* reversible.

(24) F. A. L. Anet, *Fortschr. Chem. Forsch.*, **45**, 169–220 (1974).

(25) G. J. Martin, M. L. Martin, and S. Odiot, *Org. Magn. Reson.*, **7**, 2–17 (1975).

(26) These authors[8b] deduced the presence of three different conformations for II (R = $CH_3$) in trifluoroacetic acid and assigned these forms to the boat-chair (*N*-methyl equatorial) and to two different so-called twist-boats (rather strongly distorted twist-boats in our terminology). However, the assigned barrier (17.5 kcal/mol) separating the latter two conformations is much too high for the proposed process and a better explanation of the results is that there are two boat-chairs, one with an axial and the other with an equatorial *N*-methyl group, and that the third conformation is either a twist-boat with approximately $C_2$ symmetry for the ring skeleton, or a more or less distorted twist-boat. In either case there should be rapid pseudorotation via the boat-boat[9] (with *N*-methyl group equatorial). Professor R. R. Fraser (personal communication) has informed us that he has reached similar conclusions.

(27) (a) A. D. Hardy and F. R. Ahmed, *Acta Crystallogr., Sect. B*, **30**, 1670–1673 (1974); (b) A. D. Hardy and F. R. Ahmed, *ibid.*, **30**, 1674–1677 (1974).

(28) C. Batich, P. Bischof, and E. Heilbronner, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 333–353 (1972/73).

# Kinetics of Dye Formation by Oxidative Coupling with a Micelle-Forming Coupler

**L. K. J. Tong* and M. C. Glesmann**

*Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650.* *Received March 9, 1977*

**Abstract:** Rates of dye formation by coupling between quinonediimines (QDI) and a micelle-forming $\alpha$-naphthol derivative have been measured. The results were found to fit a model which postulates that the QDIs rapidly distribute between the micelles and the aqueous region of the solution. Solubilization of QDIs favors dye formation and reduces side reactions which occur exclusively in the aqueous region. Partition coefficients and specific rates were obtained which showed that charges and hydrophobic characters of QDIs have large effects on the partition coefficient.

The image dyes of many color photographic systems are formed by the reaction of oxidized N,N-disubstituted *p*-phenylenediamines (QDI) and compounds with active methylene or methine groups known as couplers. The mechanism of this reaction has been studied in dilute aqueous solutions using substituted $\alpha$-naphthols and phenols of low molecular weight.[1] We have recently extended the study to include couplers which are simultaneously ballasted with hydrophobic groups and solubilized with ionizable groups. They are useful in photographic technology as incorporated couplers because their low mobility during development prevents diffusion causing interlayer contamination.[2] Such modifications, however, confer detergent-like properties to these molecules which profoundly alter their reaction kinetics. The latter is the subject of the present report.

We have compared the rate of dye formation between QDIs with various charges and an anionic micelle-forming coupler, 4-chloro-3′,5′-dicarboxy-*N*-octadecyl-1-hydroxy-2-naphthanilide (called coupler II in this report) with the rates of the same QDIs and a lower molecular weight analogous coupler (called coupler I). The structures of the compounds are shown in Chart I.

Differences in rate behavior of couplers I and II are apparent on examination of Figures 1 and 2. The results are interpreted by a model which postulates that (1) the QDI was rapidly distributed between the micellar and the aqueous region, and (2) the observed rate was the sum of two rates, one in each region. Similar models have been used by others to evaluate binding constants and micellar rate constants in systems where the surfactant was added to provide a micellar medium but did not take part directly in the reaction as in our system.[3,4] The use of a nonionic surfactant as a medium for the coupling reaction was published earlier by us.[5]

**Kinetic Model.** The kinetic data with micelle-forming coupler II (Figure 2) were obtained at concentrations above the critical micelle concentration (cmc). Interpretation of these kinetics should therefore take into account the possibility of reactions in the micellar region as well as in the continuous aqueous region. The proposed kinetic model assumes the distribution of QDI between these regions, with rates in each region determined by the respective reactant concentrations. Since the average micellar size is assumed constant, the ratio of micellar volume to surface is constant and the form of the kinetic expression will be the same whether the micellar reaction takes place at the surface or in the micellar interior. Further speculation as to the more detailed location of the reaction comes from the consideration of the kinetic parameters.

At concentrations above the cmc it is further assumed that, for a given pair of QDI and coupler, the concentration of monomeric coupler remains constant. Although aggregations are expected to depend somewhat on the structure of the QDI, the cmcs are probably of the same order of magnitude as the cmc measured using the cationic dye (see Table I).

Above the cmc we assume that the overall concentration of the coupler is

$$\overline{C} = C_1 + nC_n$$