

This analysis of limiting ionic mobility demonstrates that a more refined equation is required. It suggests that the predicted values of B are grossly in error and that other effects besides dielectric and hydrodynamic frictional forces will probably have to be considered. However, the ability to unambiguously determine the numerical value of the hydrodynamic frictional coefficient as a function of solute size provides a better framework within which to evaluate the factors determining the mobility of ions.

Acknowledgments. This work was supported by National Science Foundation Grant ENG75-02029 A01. D.F.E. has an NIH Career Development Award 5K4-AM-12972.

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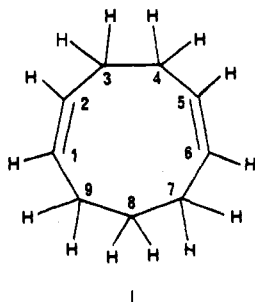
Conformational Properties of *cis,cis*-1,5-Cyclononadiene. Dynamic Nuclear Magnetic Resonance Spectroscopy and Iterative Force-Field Calculations

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Abstract: The 251-MHz ^1H and the 63.1-MHz ^{13}C NMR spectra of *cis,cis*-1,5-cyclononadiene (I) have been investigated over the temperature range from -5 to -170 °C. Unlike the ^{13}C spectrum, the ^1H spectrum of I shows a dynamic NMR effect in the vicinity of -60 °C. The NMR data are interpreted in terms of a pair of chiral chairlike conformations with C_2 symmetry. A free energy of activation (ΔG^\ddagger) of 10.3 ± 0.3 kcal/mol is calculated from the ^1H NMR data for the conformational enantiomerization of I. Iterative force-field calculations on I give results consistent with the NMR findings.

cis,cis-1,5-Cyclononadiene (I) is the most stable member of the isomeric cyclononadienes and is readily available by reduction of 1,2,6-cyclononatriene¹ with diimide² or metal-



ammonia,³ or by base catalyzed isomerization⁴ of 1,2-cyclononadiene.⁵ Palladium catalyzed rearrangement of bicyclo[6.1.0]non-4-ene also gives I in high yield.⁶ Several uses of I in organic⁷ and organometallic⁸ syntheses have been described.

Although there is presently no published experimental data on the structure or conformational properties of I itself, the temperature dependence of the ^1H NMR spectra of several heterocyclic analogues of dibenzo-1,5-cyclononadiene have recently been discussed by Ollis and Stoddart,⁹ who have also

carried out empirical force-field calculations on some of these molecules. The only published theoretical treatment of the conformations of I makes use of a simple procedure which does not minimize the energy by allowing the conformations to relax to their optimum geometries.¹⁰

The successful determination of the conformational features of *cis,cis*-1,5-cyclooctadiene (II) by ^1H and ^{13}C NMR spectroscopy¹¹ and iterative force-field calculations¹² prompted us to investigate the conformational properties of I, a molecule which can be considered as a higher homologue of II.

Experimental Section

cis,cis-1,5-Cyclononadiene was synthesized from 1,2-cyclononadiene⁵ by base catalyzed isomerization,⁴ and its ^{13}C NMR spectrum in CDCl_3 had bands at δ (ppm) 131.0 and 129.9 (olefinic ^{13}C), 28.7 (homoallylic ^{13}C), 26.7 and 24.4 (allylic ^{13}C).

All NMR spectra were measured on a superconducting solenoid spectrometer operating at 59 kG.^{13,14} The proton noise-decoupled ^{13}C NMR spectra are Fourier transforms of accumulated free induction decays and were obtained under the following conditions: 45° pulse angle, 8K data points, 11 013 Hz spectrum width, and an exponential broadening function corresponding to 4 Hz broadening. For variable temperature ^{13}C NMR spectra a mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ (1:1) was used as solvent and a fluorine line of the solvent was employed for lock purposes. The variable temperature proton NMR spectra were obtained in a frequency sweep mode with CH_2Cl_2 as the solvent.

Tetramethylsilane was used as an internal reference for both the ^{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. Force-field calculations were carried out on an IBM-360/91 computer at the Campus Computer Network of UCLA, with a slightly modified version¹⁵ of Boyd's MOLECULAR BUILDER IIA.¹⁶

Results and Discussion

NMR Spectra. The 63.1-MHz NMR spectrum of I was investigated in the temperature range from -5 to -180 °C, but no dynamic NMR effect was observed. The only conclusion that can be drawn is that one or more of the following features are present in I: (a) chemical shift coincidences, (b) low (ca. 4 kcal/mol) conformational energy barriers, or (c) conformational symmetry, namely, the presence of a molecular C_2 and/or C_s point group symmetry.

The 251-MHz ^1H NMR spectra of I at various temperatures are shown in Figure 1. At -5 °C the spectrum consists of multiplets at δ 1.5 (homoallylic protons), δ 2.0 (allylic protons), δ 5.4, and δ 5.7 (olefinic protons). The intensity ratio of the bands at δ 2.0 and δ 1.5 is 4:1, as expected. The shapes of the two olefinic resonances are quite different from one another, the higher-field signal being a sharp quartet (1:3:3:1), while the lower-field peak appears as a structureless broad absorption band. The analysis given below provides an explanation of these features and at the same time allows an assignment of the olefinic bands to be made. This analysis ignores all long-range coupling constants.

The protons on C-3 and C-4 have the same chemical shifts at room temperature, but they are not completely magnetically equivalent, because, for example, the proton on C-2 is unequally coupled to protons on C-3 and C-4. Furthermore, the protons on C-3 and C-4 are strongly coupled to one another and this should give rise to second-order effects in the splittings of H-2 (and H-5); i.e., the spectrum of H-2 and H-5 should be complex and thus might be expected to appear as an unresolved broad band.

On the other hand, the methylene protons on C-7 and C-9 are not coupled to one another, although they have the same chemical shifts. It is true that these protons are coupled to those on C-8, but this does not cause any second-order effects because the C-8 protons are chemically shifted from those on C-7 and C-9. Thus, the H-1 and H-6 protons should show relatively sharp lines, which should be analyzable according to the first-order splitting rules, i.e., they should be doublets of triplets, or if $J(\text{H}_1-\text{H}_2)$ and $J(\text{H}_1-\text{H}_6)$ are approximately equal, they should appear as a 1:3:3:1 quartet. We thus assign the lower-field broad olefinic band of I to H-2 and H-5, and the higher-field sharp quartet to H-1 and H-6.

At about -60 °C (Figure 1), the complex band arising from the allylic protons is appreciably broadened when compared with the same band in the spectrum measured at -5 °C, while the other resonances are unchanged. The allylic proton signal splits into several bands below about -80 °C. The spectrum does not change further down to -170 °C, which was the lowest temperature investigated.

The changes observed in the allylic proton band clearly are the result of a dynamic NMR effect, and not, for example, merely the result of temperature-dependent chemical shifts. The slow exchange spectrum observed at -100 °C can be interpreted in terms of two doublets, one widely and one narrowly spaced, as indicated in Figure 1. The small central doublet (splitting = 8 Hz) of the band of the allylic protons at this temperature is assumed to be a result of spin-spin coupling and not of chemical shifts.

Since the ^1H band of the homoallylic protons of I does not split at low temperatures, a conformation belonging to the C_2 point group is immediately consistent with this experimental

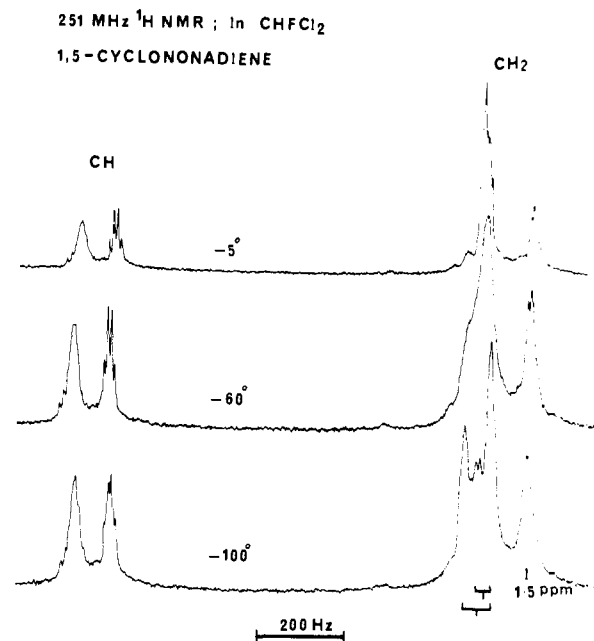


Figure 1. 251-MHz ^1H NMR spectra of *cis,cis*-1,5-cyclononadiene at various temperatures.

result. On the other hand, a conformation with C_s symmetry such as the boat-chair (see below), is expected to have quite different chemical shifts at low temperatures for the two homoallylic (H-8) protons. In any case, both the ^{13}C and ^1H NMR spectra of I give no indications that more than one kind of conformation is populated.

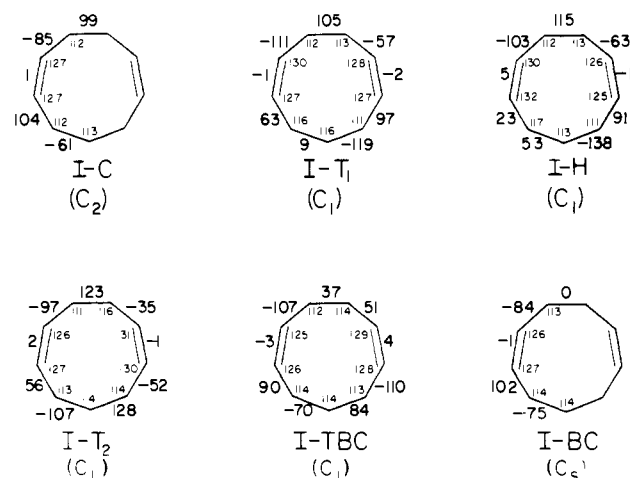
Although the allylic protons multiplet at -100 °C is too complex to be analyzed rigorously, considering the separation of the two outer components of the multiplet (see Figure 1) and using the expression,¹⁷ $k = \pi\Delta\nu/\sqrt{2}$, we calculate that the first-order rate constant (k) for site exchange of the diastereotopic allylic methylene protons in I is about 100 s^{-1} at -60 °C. Application of the absolute rate theory with a transmission coefficient of 1 gives a free-energy of activation (ΔG^\ddagger) of 10.3 ± 0.3 kcal/mol, where all known sources of errors are estimated and included. The experimental data available are not suitable for obtaining meaningful values of ΔH^\ddagger or ΔS^\ddagger , even though the errors in ΔG^\ddagger are not large.¹⁸

Empirical Force-Field Calculations. In the preceding section the dynamic NMR features of I were explored. Although that study yielded an energy barrier for the process corresponding to the site exchange of the diastereotopic allylic methylene protons, it was not possible to arrive at a completely unambiguous choice between the plane-symmetrical (achiral) boat-chair and the axial-symmetrical (chiral) conformations from the experimental data alone. In order to obtain more detailed information on the conformational-energy surface of I, we turned to empirical force-field (strain energy or molecular mechanics) calculations.¹⁹ Ground-state geometries and interconversion paths were computed as described previously for *cis,cis*-1,4-cyclooctadiene.¹⁵

Approximate coordinates for trial structures of the axial-symmetrical chair (I-C) and of the plane-symmetrical boat-chair (I-BC) geometries were calculated by means of the program COORD with torsional angles obtained from Dreiding-Fieser molecular models. Other conformational energy minima and energy maxima were explored by "driving" appropriate torsional angles starting from the boat-chair and I-C geometries.¹⁵ Altogether, six geometries were found important for a description of the conformational properties of I. There are three energy minima and three one-dimensional energy maxima (saddle points or transition states) as shown in Figure

Table I. Calculated Strain Energies in Different Energy-Minima and Energy-Maxima Geometries of *cis,cis*-1,5-Cyclononadiene

Strain-energy contributions, kcal/mol	I-C (C ₂)	I-T ₁ (C ₁)	I-H (C ₁)	I-T ₂ (C ₁)	I-TBC (C ₁)	I-BC (C _s)
Bond stretching	0.26	0.36	0.35	0.37	0.33	0.36
Bond-angle bending	1.50	2.85	4.05	3.81	2.46	1.75
Out-of-plane bending	0.00	0.00	0.01	0.01	0.02	0.00
Torsional strain	4.68	10.91	8.05	12.02	4.93	6.21
Nonbonded interactions	2.43	3.80	3.61	4.01	4.93	3.95
Total strain energy	8.87	17.91	16.07	20.22	11.21	12.27

**Figure 2.** Calculated torsional and internal angles in various geometries of *cis,cis*-1,5-cyclononadiene.

2. Calculated energy paths for conformational interconversion in I are given in Figure 3.

The axial-symmetrical conformation, which can be considered as an expanded chair form of 1,5-cyclooctadiene, is the ground state of I. The plane-symmetrical boat-chair (I-BC) is calculated to be 3.4 kcal/mol higher in energy than the ground state and it is found to be a transition state, not a true energy minimum. The presence of eclipsing strains in the C(3)-C(4) bond of the boat-chair is unfavorable, and a rotation about this bond gives an unsymmetrical form (twist-boat-chair, I-TBC or I-TBC') which is 1.1 cal/mol lower in energy than the symmetrical boat-chair itself. However, I-TBC is still 2.3 kcal/mol above I-C, and it is not expected to be populated in the temperature range investigated, unless the calculations are rather seriously in error.

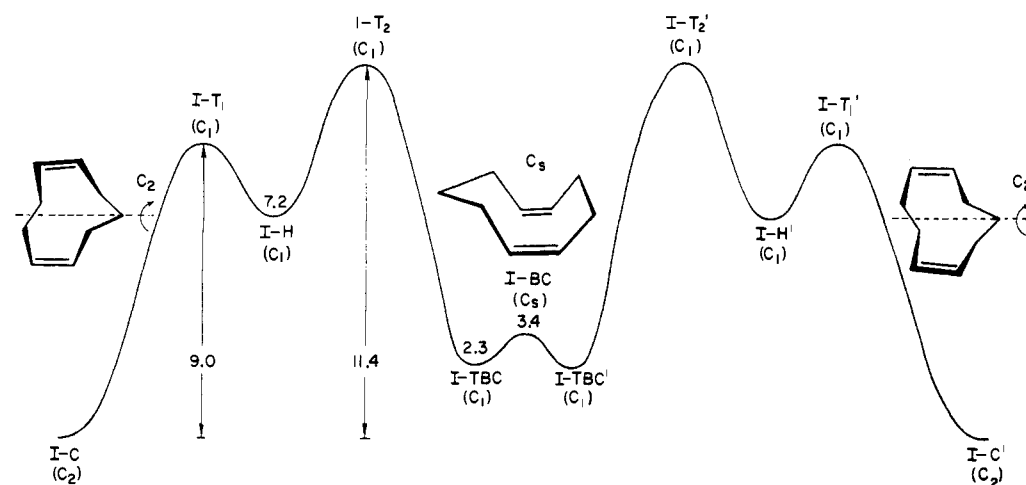
In order to calculate an energy barrier for the conformational enantiomerization of the chiral chair form, it is necessary

to change the signs of all the torsional angles. We chose to drive the C(7)-C(8) torsional angle of I-C from -61° to a corresponding positive value. In trying to do this, a high-energy conformation (I-H) was reached at a torsional angle of 53° , via a transition state (I-T₁) having a torsional angle of 9° (Figures 2 and 3). The transition state (I-T₁) for this process has a calculated strain energy which is 9.0 kcal/mol higher than that found for I-C.

The same high-energy conformation (I-H) was obtained by driving the C(3)-C(4) torsional angle of the boat-chair or twist-boat-chair and this process proceeds via transition state I-T₂ (see Figure 3). Since I-T₂ has 2.4 kcal/mol more strain energy than does I-T₁, it is the transition state for the interconversion of the chair to the boat chair family of conformations. Also, the transition states for chair enantiomerization (I-C \rightarrow I-C') are I-T₂ and I-T₂', as is clear from Figure 3. The calculated (strain-energy) barrier for the enantiomerization process is 11.4 kcal/mol, in good agreement with the experimental (free-energy) barrier of 10.3 kcal/mol.²⁰

A few comments need to be made regarding the calculated strain-energy contributions in various conformations and transition states of I given in Table I. All geometries have almost the same strain energies for the bond-stretching and out-of-plane bending terms, and the strains due to these terms are small. On the other hand, the strain-energy contributions arising from torsional effects are quite variable in these conformations and they are major contributors to the excess strain in the transition states I-T₁ and I-T₂.

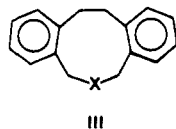
Other possible "driving" modes for the conformational interconversions of 1,5-cyclononadiene were explored, but they were found to have higher calculated strain energies than the paths shown in Figure 3. For example, the antisymmetrical driving of the C(7)-C(8) and C(8)-C(9) torsional angles in the boat-chair geometry maintains C_s symmetry and leads to a boat-boat form which is 10 kcal/mol above I-C. The energy barrier for this "process" is 15.3 kcal/mol and therefore this path does not contribute appreciably to enantiomerization of I-C.

**Figure 3.** Calculated potential energy profile for conformational enantiomerization of the chiral I-C conformation.

Pseudorotation of the boat-boat, described above, leads to an axial-symmetrical conformation, namely, the twist-boat-boat, which is 8 kcal/mol above I-C. The twist-boat-boat is separated from I-H by an energy barrier of 16.7 kcal/mol. Thus the boat-boat family of I can be neglected from the conformational point of view.

Comparison with Other Investigations. Favini et al.¹⁰ have reported the results of strain-energy calculations on three different geometries of *cis,cis*-1,5-cyclononadiene. These authors used a noniterative procedure, which gives the strain energy for fixed geometries. An axial-symmetrical conformation was found to have the lowest strain energy, although a plane-symmetrical form (the boat-chair) was only 1.4 kcal/mol higher in energy. Another plane-symmetrical form, namely, the boat-boat, was found to be 7.6 kcal/mol less stable than the lowest-energy conformation. No calculations of the transition states for conformational interconversions were attempted. The calculations of Favini et al. are in general agreement with our data, although there are significant differences in the bond angles of similar conformations in the two calculations.

Ollis and Stoddart⁹ were the first to observe dynamic ¹H NMR effects in a nine-membered ring which possesses 1,5 unsaturation. They investigated the conformational features of several heterocyclic analogues of dibenzo-1,5-cyclononadiene (III; X = NR, S, SO₂), and concluded that all compounds



exist in solution in axial-symmetrical (chiral) conformations similar to the conformation observed for the parent diene. The free-energy barriers for conformational enantiomerization were in the range of 9.8–13.7 kcal/mol.

Heavily substituted derivatives of 1,5-cyclononadiene occur as natural products,²¹ e.g., the nonadrienes, glauconic acid,²² and byssochlamic acid.²³ Several of these compounds have had their structures determined by X-ray diffraction studies,^{22,23} and all exist in twist-boat-chair conformations in the crystalline state. However, these compounds cannot be considered as models for the conformation of 1,5-cyclononadiene itself. Furthermore, crystal packing effects may cause the solution and the crystal conformations to have different energies.

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

Supplementary Material Available: a listing of the coordinates for all the atoms in six different geometries of *cis,cis*-1,5-cyclononadiene (3 pages). Ordering information is available on any current masthead page.

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