Conformational Studies of *cis*-Cyclodecene and *cis*-Cyclodecene Oxide by Dynamic NMR Spectroscopy and Computational Methods

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Abstract: Each of the five ^{13}C signals of *cis*-cyclodecene (**1**) splits into two peaks of equal intensity at lower temperatures, with a free-energy barrier of 6.64 kcal/mol for the process at −139.7 °C. The ^{1}H NMR spectrum of the allylic protons shows decoalescence at −36.4 °C, and a free-energy barrier of 10.9 kcal/mol was determined at this temperature. The MM3 strain-energy calculations of Saunders and Jimenez-Vazquez were reproduced to obtain drawings of these conformations, and relative free energies for **1** at −152.7 °C were calculated using this program. A single conformation of C_1 symmetry resembling boat−chair−boat (BCB) cyclodecane was predicted by these calculations and by ab initio calculations at the HF/6-311G* level. ^{13}C chemical shifts for the preferred conformation of **1** were calculated at the HF/6-311G* level using the GIAO method. *cis*-Cyclodecene oxide (**2**) also shows decoalescence in the ^{13}C spectrum, with $\Delta G^{\ddagger} = 7.4$ kcal/mol at −125.4 °C. The epoxide has a time-averaged plane of symmetry at room temperature, which no longer exists at −152.6 °C. Similarly, the lower barrier of 6.64 kcal/mol for **1** is suggested to be associated with a process which gives the compound a time-averaged plane of symmetry when it is rapid on the NMR time scale.

Introduction and Background

The medium-ring epoxides generally react with nucleophiles under acidic conditions by transannular pathways because backside attack on the three-membered ring is blocked by the CH_2 groups on the opposite side of the ring.[1] Treatment of *cis*-cyclodecene with performic acid, followed by hydrolysis of the formate esters,[1] gave a mixture of 2-cyclodecen-1-ol, *cis*-1,6-cyclodecanediol,[2] and two isomeric compounds of formula $C_{10}H_{18}O_2$ which were not assigned structures, but were believed to be bicyclic ethers. None of the *trans*-1,2-diol that would normally be expected was isolated.

A conformation resembling boat−chair−boat (BCB) cyclodecane was found[3] in an X-ray diffraction study of the silver nitrate adduct of *cis*-cyclodecene (**1**) and provides a possible geometry for both **1** and *cis*-cyclodecene oxide (**2**). Free energies at − 200 °C and strain energies for **1** calculated[4] using Allinger's MM3 program predict that this conformation is the only one significantly populated. This is in contrast to *trans*-cyclodecene, which was predicted[4] by MM3 to have five conformations populated at −200 °C, and five were found at −154.9 °C by dynamic NMR spectroscopy,[5] although the number of C_1 and C_2 conformations differed in the experimental and computational work (3 and 2 vs 2 and 3). In the present work, dynamic NMR spectroscopy was used to obtain information about the conformations present for **1** and **2** at low temperatures. In addition, free energies for different conformations of **1** at −152.7 °C were calculated at the HF/6-311G* level to compare with those from MM3. The experimental work also provides free-energy barriers to conformational processes for both compounds.

Experimental and Methods Section

cis-Cyclodecene was purchased from Fluka Chemicals, New Jersey, and used as received. The purity of the compound was checked by taking the ^{13}C and ^{1}H NMR spectra at room temperature. *cis*-Cyclodecene oxide was synthesized by treatment of **1** with *m*-chloroperbenzoic acid in methylene chloride solvent,[6] and the purity was established by the room-temperature ^{13}C and ^{1}H NMR spectra.

NMR samples were prepared in 5 mm thin-walled screw-capped NMR tubes. For **1**, 1% solutions in CF_2Cl_2 or propene were used, and for **2**, a 5% solution in a 2:1:1 mixture of $CHClF_2$, $CHCl_2F$, and CF_2Cl_2 was prepared. A small amount of TMS was added to each sample for an internal reference. ***Caution:*** high pressure.

Spectra were recorded with a General Electric Model GN-300 wide-bore NMR spectrometer operating at 75.58 MHz for ^{13}C and 300.54 MHz for ^{1}H. For the carbon spectra, the tip angle, pulse repetition period, sweep width, block size, and number of acquisitions were 83°, 6.0−10.0 s, ±10417 or ±11100, 64 K (**1**) or 32 K (**2**), and 200−800. A line broadening of 3.0 Hz was used to increase the signal-to-noise ratio. Spinning of the sample was discontinued below about −120 °C. Because of the difficulty in ejecting the sample at lower temperatures, the temperature calibration was performed separately, using a copper−constantan thermocouple immersed in the same solvents contained in a nonspinning dummy tube and under conditions as nearly identical as possible. The emf's were measured using a Leeds and Northrup Model 8690-2 millivolt potentiometer. The uncertainties in the temperatures and barriers are estimated to be ±2 °C and ±0.2 kcal/mol.

The rate constant of 465 s^{-1} for **1** at −36.4 °C (^{1}H spectrum) was obtained by multiplying the separation of the multiplets at −70 °C by 2.22. The other rate constants for **1** and **2** were determined by line

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[1] Solvolysis of *cis*- and *trans*-cyclodecene oxides by aqueous formic acid: Prelog, V.; Schenker, K. *Helv. Chim. Acta* **1952**, *35*, 2044.

[2] Ermer, O.; Vincent, B. R.; Dunitz, J. D. *Isr. J. Chem.* **1989**, *29*, 137.

[3] Ermer, O.; Eser, H.; Dunitz, J. D. *Helv. Chim. Acta* **1971**, *54*, 2469.

[4] Saunders, M.; Jimenez-Vazquez, H. A. *J. Comput. Chem.* **1993**, *14*, 330.

[5] Pawar, D. M.; Noe, E. A. *J. Am. Chem. Soc.* **1996**, *118*, 12821.

[6] Servis, K. L.; Noe, E. A. *J. Am. Chem. Soc.* **1973**, *95*, 171.

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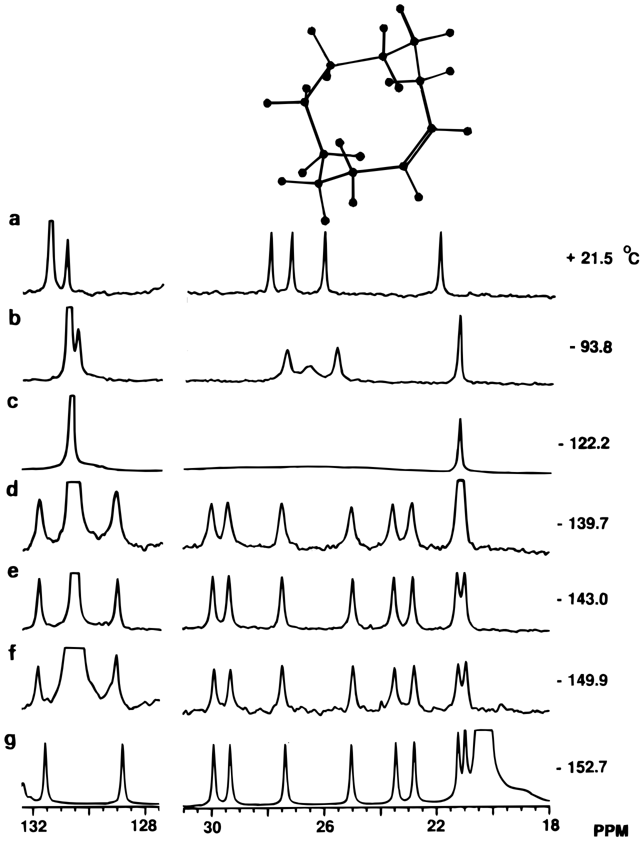

Figure 1. Low-temperature ^{13}C NMR spectra of *cis*-cyclodecene. The solvent was CF_2Cl_2 for spectra a−f and propene for spectrum g.

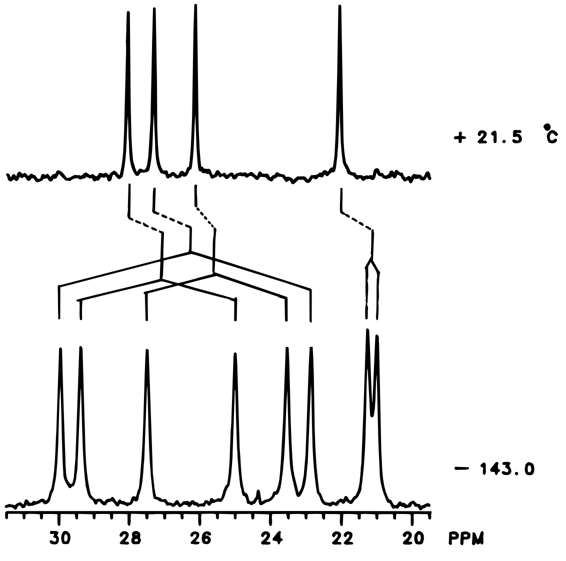

Figure 2. Correlation of room-temperature and slow-exchange ^{13}C shifts for the methylene carbons of *cis*-cyclodecene in CF_2Cl_2.

shape matching using an Apple computer and a two-site exchange program written by R. A. Newmark.[7]

The strain energies for **1** calculated by Saunders[4] were reproduced using Allinger's MM3 program built into Spartan.[8] An external MM3 program[9] was used to obtain free energies for the conformations of **1**. The geometries determined for the first five conformations of **1** according to MM3 strain energies were used as starting points for the ab initio calculations, using the Gaussian 94 series of programs.[10] For all five conformations, full geometry optimizations were done at the HF/6-311G* level; smaller basis sets were used initially. Energy-minimized structures were characterized by calculation of harmonic vibrational frequencies at the same level, and free energies were obtained. For the frequency calculations, the default scaling factor of 0.89 was used.

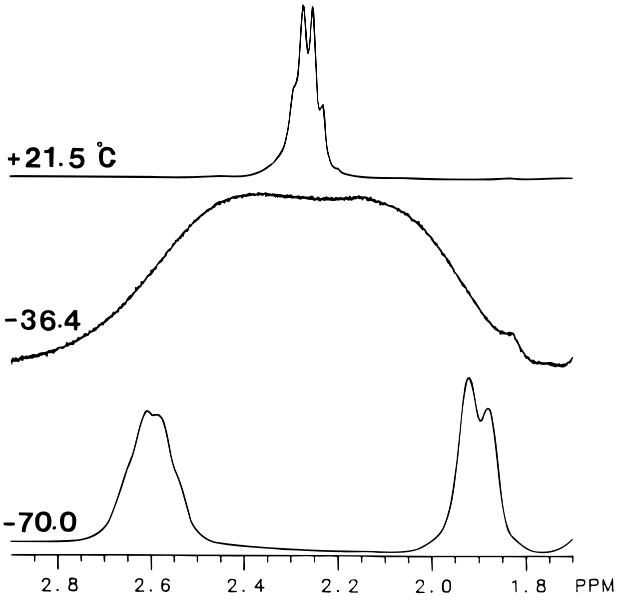

Figure 3. ^{1}H NMR spectra of *cis*-cyclodecene in CF_2Cl_2.

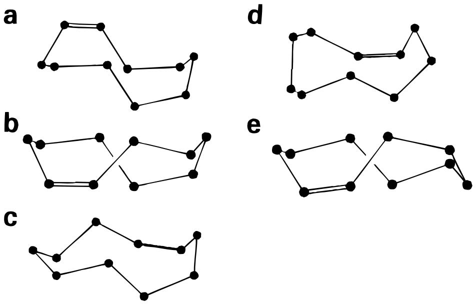

Figure 4. Conformations of *cis*-cyclodecene in order of increasing MM3 strain energies.

The conformational space of **2** was searched using Sybyl,[11] a molecular mechanics program also built into Spartan. The geometry of the single conformation produced by this search was used as the starting point for the external MM3 program, and a drawing of the structure obtained in this way is shown in the next section with the ^{13}C spectra of **2**.

The gauge-including atomic orbitals (GIAO) method was employed to calculate isotropic absolute shielding constants (σ, ppm) for the carbons of TMS and the lowest-energy conformation of **1**. Subtraction gave the calculated chemical shifts, relative to TMS. These calculations were done at the HF/6-311G* level using the Gaussian 94 series of programs.[10]

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(7) Newmark, R. A. *J. Chem. Educ.* **1983**, *60*, 45.

(8) Spartan version 3.0 from Wavefunction, Inc., Irvine, CA.

(9) Version MM3(94) was used. The latest version of the MM3 program, which is referred to as MM3(96), is available to academic users from the Quantum Chemistry Program Exchange and to commercial users from Tripos Associates, 1699 S. Hanley St., St. Louis, MO 63144.

(10) Gaussian 94, Rev. E2: Frisch, M. J.; Trucks, G. W.; Gill, P. M. W.; Johnson, B. G.; Schelegel, H. B.; Robb, M. A.; Cheesman, J. R.; Gomperts, R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, J. V. O.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Fox, D. J.; Head-Gordon, M.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Defrees, D. J.; Baker, J.; Stewart, J. J.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.

(11) Clark, M.; Cramer III, R. D.; van Opdensch, N. *J. Comput. Chem.* **1989**, *10*, 982. The Sybyl force field is marketed by Tripos, Inc.

Table 1. Strain Energies and Relative Strain Energies from MM3 for *cis*-Cyclodecene (**1**),[a] Free Energies and Relative Free Energies for **1** at −152.7 °C from MM3 and ab Initio Calculations at the HF/6-311G* Level, and Populations of Conformations of **1** at −152.7 °C Calculated Using the ab Initio Relative Free Energies

	MM3 calculations				ab initio calculations		
conformer[b]	strain energy (kcal/mol)	realtive strain energy (kcal/mol)	free energy (kcal/mol)	relative free energy (kcal/mol)	free energy (Hartree)	relative free energy (kcal/mol)	population
1a	19.9065	0.00	173.346	0.00	−388.9682	0.00	1.00
1b	22.6824	2.78	175.523	2.18	−388.9634	3.02	0.00
1c	23.0519	3.15	175.705	2.36	−388.9638	2.76	0.00
1d	23.3062	3.40	176.126	2.78	−388.9621	3.85	0.00
1e	23.6289	3.72	176.091	2.75	−388.9607	4.73	0.00

[a] See ref 4. [b] Numbering of conformations is shown in Figure 1.

Results and Discussion

The ^{13}C spectrum of **1** dissolved in CF_2Cl_2 shows five sharp peaks at +21.5 °C, and each of these decoalesces into two peaks of equal intensity by −149.9 °C (Figure 1). The two CH_2 carbon peaks at lowest frequency at −143.0 °C are associated with the lowest-frequency peak at +21.5 °C. For assignment of the six other CH_2 peaks at slow exchange to the three remaining peaks at room temperature, six measurements of the averaged shifts for these three carbons were made at temperatures to −100 °C and were extrapolated to −143.0 °C, and then compared with the possible averages of the six slow-exchange peaks. Broadening of the middle peak before the outer two shows that the chemical shift difference for the two corresponding peaks at slow exchange is larger in this case. Correlations made in this way are shown in Figure 2.

The two ^{13}C signals at lowest frequency coalesce at −139.7 °C, and a free-energy barrier of 6.64 kcal/mol was determined from the rate constant of 36.9 s^{-1} at this temperature. The solubility of *cis*-cyclodecene is low in CF_2Cl_2, and some precipitation may be occurring at −149.9 °C (Figure 1f). A better slow-exchange spectrum, shown in Figure 1g, could be obtained for a 1% solution in propene.

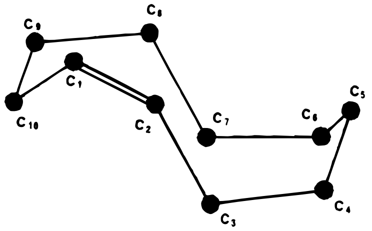
The effects of a second process with a higher barrier are observable in the NMR spectra of the allylic hydrogens of **1** (Figure 3). From the rate constant of 465 s^{-1} at −36.4 °C, a free-energy barrier of 10.9 kcal/mol was determined.

The finding of 10 ^{13}C peaks of equal intensity for **1** at slow exchange indicates the presence of a single C_1 conformation, and is consistent with conformation **1a** of Figure 4. A similar conformation has been found[3] by X-ray diffraction for a silver nitrate adduct of **1**. The strain energies according to MM3 for the first five conformations of **1** in order of increasing strain energy are listed in Table 1, along with the corresponding free energies at −152.7 °C from MM3 and ab initio calculations at the HF/6-311G* level. Both sets of free energies support the existence of a single conformation, **1a**, for *cis*-cyclodecene.

Calculated and experimental chemical shifts for the 10 carbons of **1a** are shown in Chart 1. The chemical shifts for the alkene carbons are too large by several parts per million, but the calculated and experimental shift differences for these two carbons are similar (2.28 vs 2.79 ppm).

The ^{13}C spectra of *cis*-cyclodecene oxide (**2**) also show five peaks at room temperature and 10 peaks of equal intensity at −156.2 °C (Figure 5). The slow-exchange spectrum is consistent with a C_1 conformation similar to **1a** for the alkene. The rate constant and free-energy barrier for interconversion of carbon positions in **2** were 34.5 s^{-1} and 7.4 kcal/mol at −125.4 °C, the coalescence temperature for the carbons at highest frequency, which are part of the three-membered ring. Although *cis*-cyclodecene can have both a time-averaged plane and axis of symmetry, the epoxide **2** can have only a time-averaged plane, and the changes observed at low temperatures in the ^{13}C spectra correspond to loss of this plane. The free-energy barrier of 6.64 kcal/mol from the carbon spectra of **1** is closer to the barrier for **2** than the barrier determined from the proton NMR spectra (10.9 kcal/mol), and this lower barrier of **1** may also correspond to a process which results in a time-averaged plane of symmetry.

Chart 1



^{13}C Chemical Shifts (δ, in ppm) :

	C1		C2
Expt. alkene carbons 21.5 ^0C (ave.)		130.74	
Expt. alkene carbons -149.9 ^0C	129.09		131.88
Cal. HF/6-311G* (GIAO)	133.52		135.80

Expt. ring carbons at -149.9 ^0C, in order of increasing chemical shifts : (20.96; 21.25; 22.82; 23.50; 24.96; 27.47; 29.33, 29.92)

Cal. HF/6-311G* (GIAO) : (C3, 25.76; C4, 28.28; C5, 20.77; C6, 28.34; C7, 21.47; C8, 20.13; C9, 24.84, C10, 22.81)

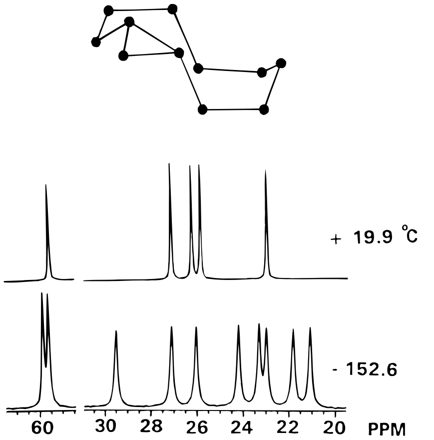


Figure 5. ^{13}C NMR spectra of *cis*-cyclodecene oxide in 2:1:1 $CHClF_2-CHCl_2F-CF_2Cl_2$.

Acknowledgment. We thank the National Science Foundation (EPSCoR Grant No. EHR-91-08767) for support of this work and the Mississippi Center for Supercomputing Research for a generous amount of time on the Cray Y-MP supercomputer. Some calculations were done using the molecular modeling laboratory at Jackson State University, supported by the Army High Performance Computing Research Center.

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