Dynamic NMR Study of *trans*-Cyclodecene

Diwakar M. Pawar and Eric A. Noe*

Contribution from the Department of Chemistry, Jackson State University, Jackson, Mississippi 39217-0510

Received July 31, 1996⊗

Abstract: The slow-exchange ^{13}C spectrum of *trans*-cyclodecene at −154.9 °C shows eight peaks for the olefinic carbons, and these are interpreted in terms of five conformations. Three of the conformations are of C_1 symmetry, and two are of C_2 symmetry. Further evidence for the number of conformations and their symmetries came from a proton NMR spectrum of the olefinic hydrogens taken at −154.9 °C with decoupling the allylic hydrogens. Populations ranged from 3.0% to 37.6%, with the least-populated conformation having a free energy of 0.59 kcal/mol, relative to the most stable conformer. The conformations studied by Saunders and Jimenez-Vazquez using Allinger's MM3 force field are described, and the calculated strain energies and populations are discussed. Energies for six conformations were also obtained from *ab initio* calculations at the HF/6-311G* level.

The medium-ring *trans*-cycloalkenes have been of interest because of the molecular dissymmetry of these compounds, which was predicted by Blomquist et al.[1] and later confirmed experimentally by Cope and co-workers.[2] For example, isomers of *trans*-cyclooctene with rotations $[\alpha]_D^{25}$ of −458 and +440° were separated using diastereomeric platinum complexes. The (*R*)-configuration was later assigned to the levorotatory enantiomer.[3] Interconversion of enantiomers requires rotation of the double bond through the ring, and this motion is hindered by steric interactions with CH_2 groups across the ring. An activation energy for racemization of 35.6 kcal/mol was determined[4] from the changes in optical rotation at elevated temperatures. A lower barrier ($E_a = 20 \pm 2$ kcal/mol) was later obtained for racemization of *trans*-cyclononene, but optically active *trans*-cyclodecene could not be isolated.[5]

trans-Cyclodecene-*1,2,4,4,9,9*-d_6 was studied using low-temperature ^{1}H NMR spectroscopy by Binsch and Roberts.[6] These authors pointed out that the C_5-C_6 bond in *trans*-cyclooctene could be either parallel or crossed with respect to the carbon−carbon double bond and could constitute a second element of dissymmetry. Interconversion of enantiomers would require rotation of both the double bond and the C_5-C_6 bond through the ring, and either process alone results in a diastereomer. Recent strain-energy calculations using Allinger's MM3 force field predict[7] that the conformation of *trans*-cyclooctene with C_1-C_2 and C_5-C_6 parallel is 3.0 kcal/mol higher in strain energy than the conformation with these bonds crossed. For *trans*-cyclodecene, six conformations were considered.[6] In half of these, C_1-C_2 and C_6-C_7 were parallel and differed in the locations of C_4 and C_9, and in the other three conformations these bonds were crossed. Interconversion of conformations could be accomplished by rotation of the C_1-C_2 and C_6-C_7 bonds through the ring and flipping of C_4 and C_9.[8] The ^{1}H NMR spectrum for the allylic protons of the deuterated *trans*-cyclodecene was a singlet at room temperature and changed into an AB quartet by −74 °C. The changes were attributed to slowing the rate of rotation of the double bond through the ring, and an activation energy of 10.7 ± 0.3 kcal/mol was determined for the process. Further changes in the spectra of these protons were observed at lower temperatures, and by −164 °C two featureless, partially overlapping peaks with line widths of about 30 Hz were found. The finding of more than one process for the deuterated *trans*-cyclodecene rules out the possibility of a single C_2 conformation, such as one based on boat-chair-boat (BCB) cyclodecane or one based on twist-boat-chair-chair (TBCC) cyclodecane.

A low-temperature ^{19}F NMR study of 3,3-difluoro-*trans*-cyclodecene confirmed that more than one conformation is populated at lower temperatures.[11] By −30 °C, an AB quartet was also observed for this compound, and a free-energy barrier of 12.4 kcal/mol was determined for the difluoride, in reasonable agreement with the free-energy barrier for the deuterated *trans*-cyclodecene (12.0 kcal/mol).[12] At −148 °C, two AB quartets could be clearly identified, and smaller peaks indicated the presence of additional conformations, although the exact number could not be determined. Interpretation of the ^{19}F spectra was complicated by the observation of four peaks for each conformation at slow exchange, the broadening of the peaks by H-F couplings, and by the lower symmetry of the difluoride. For each C_1 conformation of *trans*-cyclodecene, there are two corresponding conformations of the difluoride.

We report here a low-temperature ^{13}C and ^{1}H NMR study of *trans*-cyclodecene (**1**). The molecular mechanics calculations of Saunders and Jimenez-Vazquez using Allinger's MM3 force field predict five conformations of **1** with measurable populations at −200 °C and are useful in indicating which conformations may be populated at low temperatures.[7] At the same time, the low-temperature NMR study provides an experimental check on some aspects of the molecular mechanics calculations for this complex system.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1996.

[1] Blomquist, A. T.; Liu, L. H.; Bohrer, J. C. *J. Am. Chem. Soc.* **1952**, *74*, 3643.

[2] Cope, A. C.; Ganellin, C. R.; Johnson, Jr., H. W.; Van Auken, T. V.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1963**, *85*, 3276.

[3] Cope, A. C.; Mehta, A. S. *J. Am. Chem. Soc.* **1964**, *86*, 5626.

[4] Cope, A. C.; Pawson, B. A. *J. Am. Chem. Soc.* **1965**, *87*, 3649.

[5] Cope, A. C.; Banholzer, K.; Keller, H.; Pawson, B. A.; Whang, J. J.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1965**, *87*, 3644.

[6] Binsch, G.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 5157.

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

[8] An alternative to rotation of C_6-C_7 through the ring has been described: Fanta, P. Private communication to Roberts, J. D. This process is shown in ref 9, p 64. For a description of conformational processes in medium ring cycloalkanes, see ref 10.

[9] Noe, E. A. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1971.

[10] Kolossvary, I. Guida, W. C. *J. Am. Chem. Soc.* **1993**, *115*, 2107.

[11] Noe, E. A.; Wheland, R. C.; Glazer, E. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 3488.

[12] This free-energy barrier is calculated from the reported[6] E_a and A values.

S0002-7863(96)02666-2 CCC: $12.00

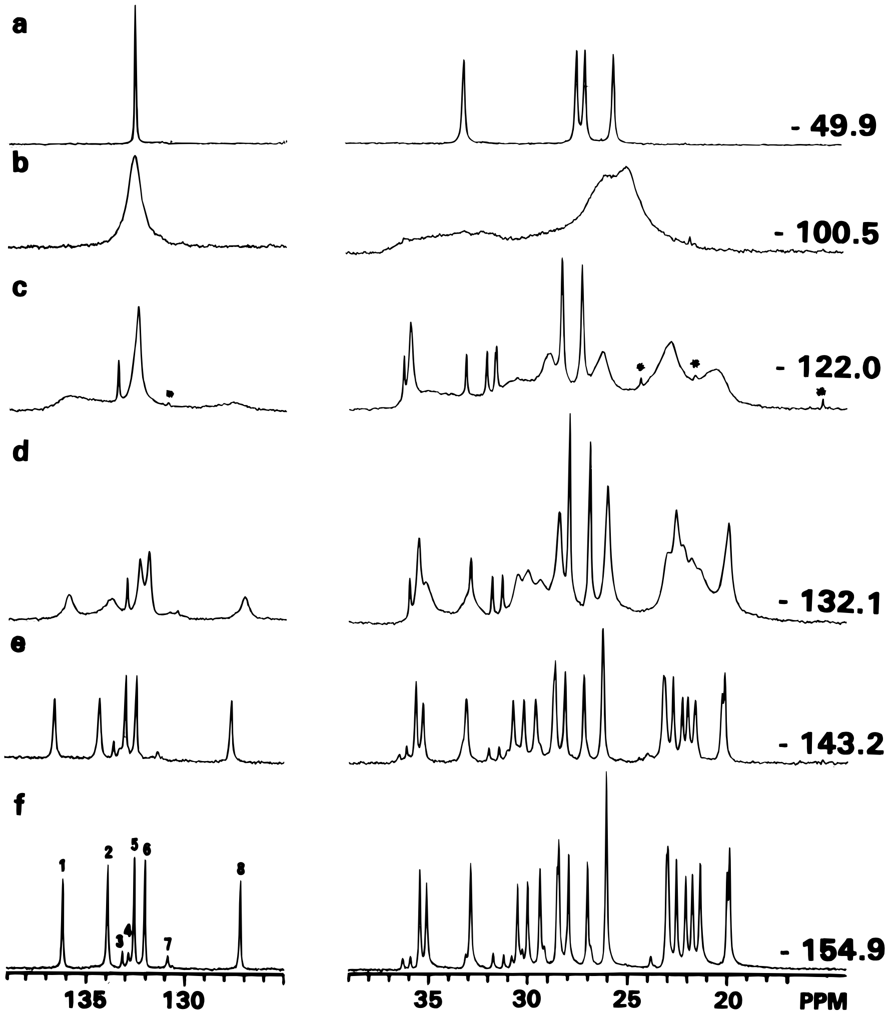


Figure 1. Low-temperature ^{13}C NMR spectra of *trans*-cyclodecene. The four asterisks for spectrum c mark the positions of small peaks believed to come from trace impurities in the solvents (see text).

Experimental Section

A mixture of *trans*- and *cis*-cyclodecene was purchased from Farchan Chemical Company, and the percentages of the two isomers were determined by ^{13}C NMR spectroscopy. The olefinic carbon signal at lower frequency (δ 130.0) was assigned to the cis isomer (72%), and the peak at δ 131.3 belonged to the trans isomer (28%), based on the chemical shift of a sample of pure *cis*-cyclodecene and on the general relationship[13] that *cis*-alkenes absorb at lower frequency than the corresponding *trans*-alkenes in the ^{13}C spectra of the olefinic carbons.

The *trans*-cyclodecene was separated from the cis isomer by a 16-stage counter current extraction,[14] as described by Binsch and Roberts.[6] Six grams of the mixture was separated into the components using twice the reported[6] amounts of reagents and solvents (40 mL of the equilibrated cyclohexane phase and 320 mL of the water, methanol, and silver nitrate solution for each extraction). From step 8 to step 16, the layers containing *cis*- and *trans*-cyclodecene were withdrawn, every other step, simultaneously from opposite ends. The combined phases containing the *trans*-cyclodecene were concentrated under vacuum using the rotary evaporator to about half the volume, poured into 1200 mL of concentrated ammonia and ice, and extracted five times with 600 mL portions of pentane. The combined pentane phases were dried over Drierite, and most of the pentane was removed by distillation. None of the cis isomer was detected by ^{13}C NMR spectroscopy. Small amounts of pentane and other impurities were removed by preparative gas chromatography using a 1/4 in. × 4 ft. column containing 20% carbowax 20M on 80/100 mesh chromosorb P. A column temperature of 86 °C was used, and 25 μL of concentrated *trans*-cyclodecene solution was injected each time. Two hundred microliters of pure *trans*-cyclodecene was isolated from the original 6 g of mixture. No impurities in the compound were detected by ^{13}C NMR spectroscopy for a solution in dichloromethane.

Several samples, using different lecture bottles of solvents, were used for the low-temperature spectra. For the spectra taken at −132.1, −139.0, and −154.9 °C, the solvent consisted of $CHClF_2$ and $CHCl_2F$ in a ratio of 3:1. Mixtures of $CHClF_2$, $CHCl_2F$, and CHF_3 in a ratio of 5:1:1 were used for the other temperatures.

A 5 mm thin-walled screw-cap tube from Wilmad Glass Company was used, and the sample temperature was maintained below 0 °C most of the time. A small amount of TMS was added to provide an internal reference for the ^{13}C and ^{1}H spectra, which were recorded on a General Electric model GN-300 wide-bore NMR spectrometer, operating at a frequency of 75.58 MHz for carbons and 300.52 MHz for protons. ^{13}C spectra were taken from 0 °C to −154.9 °C with a 5 mm dual probe, and spinning was discontinued below −120 °C. Up to 3000 acquisitions were used, with a sweep width of ±12 000 Hz, data size of 64 K, and 3.0 Hz line broadening to increase the signal-to-noise ratio, except for −154.9 °C, where the line broadening was 1 Hz. Several of the experimental parameters (sample concentration, pulse width, tip angle, and pulse-repitation period) differed at the various temperatures, and the values at each temperature are given in parentheses: −49.9 °C (10%, 14 μs, 124°, 7.0 s); −100.5 °C (12%, 14 μs, 124°, 7.0 s); −122.0 °C (15%, 6.8 μs, 60°, 2.0 s); −143.2 °C (15%, 8.0 μs, 71°, 2.0 s); −132.1, −139.0 and −154.9 °C (15%, 16 μs, 60°, 1.0 s). The last

---

[13] Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; John Wiley & Sons: New York, 1980; p 79.

[14] Craig, L. C.; Craig, D. Techniques of Organic Chemistry; Weissberger, A., Ed.; Interscience Publishers, Inc.: New York, NY, 1950; Vol. III, p 171.

three spectra were taken much later than the rest, and the pulse width for a 90° pulse had increased by this time. The use of a tip angle greater than 90° for the first two spectra was unintentional. The delay times are shorter than optimal for integration,[15] but this was necessary in order to obtain an adequate signal-to-noise ratio.

A ^{1}H NMR spectrum of the olefinic hydrogens was taken at -154.9 °C; 500 acquisitions were used, with a sweep width of ±5000 Hz, data size of 64 K, pulse width of 3.1 μs, tip angle of 45°, and pulse-repetition period of 1 s.

Because of the difficulty in ejecting the sample at the lower temperatures, the temperature calibration was performed separately, using a copper-constantan thermocouple immersed in the same solvents contained in a dummy sample tube and under conditions as nearly identical as possible. The emf's were measured using a Leeds and Northrup Model 8690-2 millivolt potentiometer.

Molecular mechanics calculations were done with Allinger's MM3 program, which was run using version 3.0 of Spartan. Gaussian 92[16] was used for the *ab initio* calculations. All force field or *ab initio* calculations were performed with a Silicon Graphics computer.

Results and Discussion

The proton-decoupled ^{13}C NMR spectrum of *trans*-cyclodecene at 0 °C consists of five sharp peaks, as a consequence of rapid equilibration of conformations, and shows the presence of a time-averaged axis of symmetry. The finding[6] of a single peak for the allylic hydrogens of *trans*-cyclodecene-*1,2,4,4,9,9*-d_6 at room temperature and an AB quartet by -74 °C is also consistent with rapid equilibration at the higher temperature and indicates that the compound possesses a time-averaged plane of symmetry at room temperature, which no longer exists by -74 °C. The ^{13}C spectrum shows slight broadening of the upfield signals by -49.9 °C (Figure 1), and large changes are observed at lower temperatures. The spectrum at -122.0 °C includes five sharp peaks at δ 133.5, 36.2, 33.1, 32.1, and 31.6, which are assigned to a conformation of C_2 symmetry[17] that is interconverting slowly on the NMR time scale with the other conformations. The spectrum at this temperature has several small peaks, marked by asterisks, which are believed to arise from traces of impurities. Not all of these peaks may be present or apparent for each temperature, as the solvent mixtures differ (some do not contain CF_3H), and different lecture bottles of solvents were used. Also, the small impurity peaks will be emphasized in spectra with very broad peaks of *trans*-cyclodecene, and signals from **1** may obscure the peaks at some temperatures. A short peak at δ 130.6 in the spectrum at -154.9 °C appears just upfield of peak number 7 of the compound and probably corresponds to the first of the impurity peaks at -122.0 °C. The second and fourth impurity peaks at -122.0 °C are absent at -154.9 °C.

Eight peaks are found for **1** in the olefinic carbon region at -154.9 °C, and these are assigned in Table 1 to three conformations of C_1 symmetry (peaks 1 and 8, 5 and 6, and 4 and 7), and two of C_2 symmetry (peaks 2 and 3). The finding of five major peaks (numbers 1, 2, 5, 6, and 8) in the olefinic region suggests that 20 peaks of similar intensity should exist in the CH_2 region of the spectrum, and these were found in a spectrum obtained from the same fid as was used for spectrum 1f of Figure 1, but processed without line broadening; it was assumed that the tall signal at δ 26.0 represents two chemical shifts which are too close to be resolved. Eleven of the 12 minor peaks expected in the CH_2 region were also detected in this spectrum processed without line broadening, although in a few cases substantial overlap with adjacent peaks occurred. Electronic integration[18] of the olefinic region of spectrum 1f gave the populations and free-energy differences of Table 1.

Table 1. Experimental Populations and Free Energies of *trans*-Cyclodecene Conformations at -154.9 °C

no.	symmetry/ peak numbers[a]	populations (%)	relative free energies (kcal/mol)
1	C_1 (5 + 6)	37.6	0.000
2	C_1 (1 + 8)	31.8	0.039
3	C_2 (2)	21.8	0.128
4	C_1 (4 + 7)	5.8	0.439
5	C_2 (3)	3.0	0.594

[a] Peak numbers refer to Figure 1f.

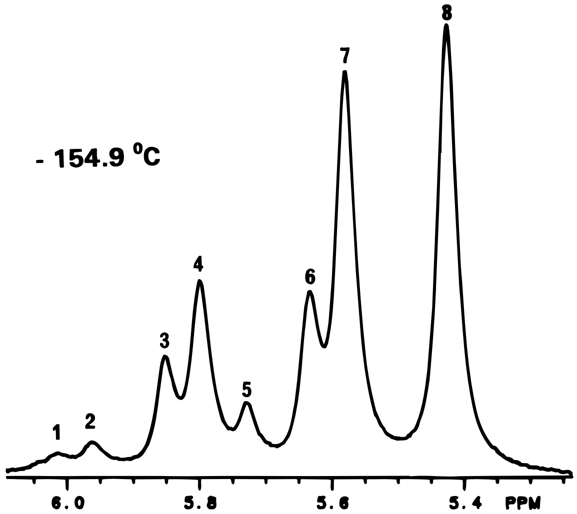


Figure 2. ^{1}H NMR spectrum of the olefinic hydrogens of *trans*-cyclodecene, taken with decoupling of the allylic hydrogens.

Assignment of pairs of peaks to C_1 conformations was based in part on the equal intensities for these signals, but it could be argued that they represent two C_2 conformations with nearly equal populations. The NMR spectra of the olefinic hydrogens, with decoupling of the adjacent allylic hydrogens, should distinguish between these possibilities if overlap of peaks does not occur. An AB quartet would be observable for each C_1 conformation, while two C_2 conformations would give rise to two single lines. The ^{1}H spectrum of **1** with decoupling of the allylic hydrogens is shown in Figure 2. Peaks 1 and 2 are separated by approximately 15 Hz and are assigned to the high-frequency half of the AB quartet for the minor C_1 conformation; the remaining half is assumed to be buried under other peaks of the spectrum. Signals 3, 4, and 6 of Figure 2 are assigned to the three peaks at highest frequency of an AB quartet from one of the two major C_1 conformations, and the separation of peaks 3 and 4 corresponds to a coupling constant of 15.5 Hz. Peak number 5 is assigned to the minor C_2 conformation, and the seventh peak has intensity from both the major C_2 conformation and the fourth peak of the major AB quartet. An additional major AB quartet is expected but not found, and, in

---

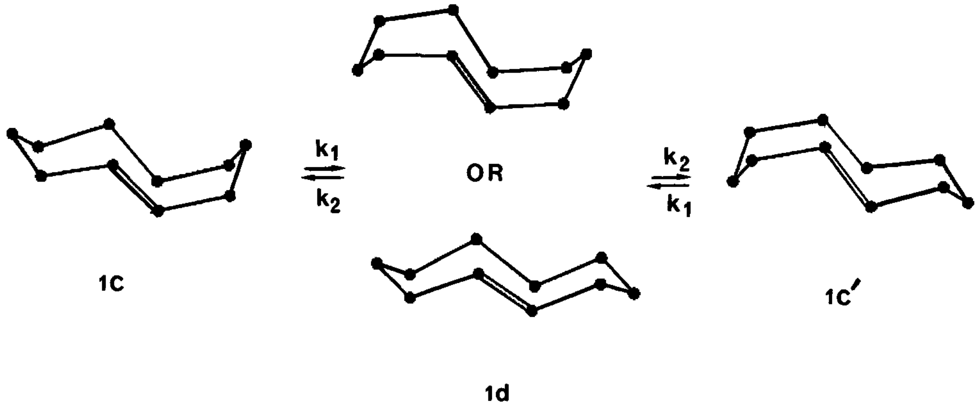
(15) Ideal conditions are a tip angle of 83° and a pulse − repetition period of 4.5 T_1: Traficante, D. D. *Concepts Magn. Reson.* **1992**, *4*, 153. See, also: Traficante, D. D.; Steward, L. R. *Concepts Magn. Reson.* **1994**, *6*, 131.

(16) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M.; Replogle, E. S.; Gomperts, R.; Anders, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*, Revision *A*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(17) The possibility that the symmetry is actually C_1, with conformational averaging to give a time-averaged C_2 symmetry, is not completely ruled out, but is considered unlikely. Accidental coincidence of chemical shifts for a C_1 conformation could also result in apparent C_2 symmetry, but coincidence for all five pairs of carbons is not expected.

(18) Peaks 4, 5, and 6 were integrated together. Peak 4 was assumed to have the same area as peak 7, and the area of 5 + 6 was obtained by subtracting this amount.

Scheme 1



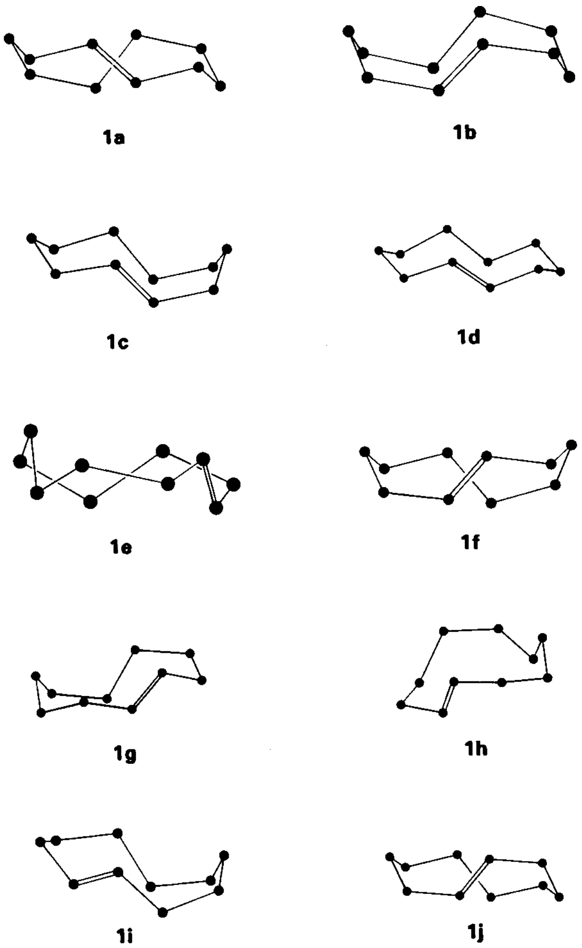


Figure 3. Conformations of *trans*-cyclodecene drawn in order of increasing strain energy according to the MM3 force field.[7]

order for the ^{1}H and ^{13}C results to match, it is necessary to assume that the chemical shift difference is small enough for the two hydrogens to give the appearance of a single line (peak number 8).

Molecular mechanics calculations by Saunders and Jimenez-Vazquez[7] using Allinger's MM3 force field predict five conformations with measurable populations at −200 °C, although two of these have C_1 symmetry and three are of C_2 symmetry, which is the reverse of our experimental results for −154.9 °C (three C_1 and two C_2 conformations). We have reproduced the strain energy calculations to obtain drawings for the ten conformations of Figure 3, which are shown in order of increasing strain energy. The calculated[19] symmetries, energies, and populations at −200 °C and 0 °C are shown in Table 2. Conformations **1b**−**d** are the conformations with parallel C_1-C_2 and C_6-C_7 bonds considered by Roberts and Binsch,[6] and conformations **1a**,**f**,**j** have these bonds crossed. Although conformation **1j** lacks a 2-fold rotational axis, the deviation from C_2 symmetry is small. Conformation **1b** resembles the BCB conformation of cyclodecane, which is the lowest-energy conformation of this compound, and **1a** and **1e** are both similar to the TBCC conformation of cyclodecane, with the double bond occupying different positions. A conformation corresponding to **1a** was found[20] by X-ray crystallography for a silver nitrate complex of **1** in the solid state. Although **1a** has the lowest strain energy according to MM3, the calculated population of this form at −200 °C is only 1.8%.[7]

Table 2. Symmetry, Strain Energies, Relative Strain Energies, and Populations of Different Conformations of *trans*-Cyclodecene, Predicted by Molecular Mechanics (MM3)[a]

conformer	symmetry	MM3 strain energies (kcal/mol)	relative MM3 strain energies (kcal/mol)	MM3 populations (%) 0.0 °C	MM3 populations (%) −200 °C
1a	C_2	22.147	0.000	4.6	1.8
1b	C_2	22.542	0.395	8.5	7.4
1c	C_1	22.602	0.455	32.6	50.5
1d	C_2	22.908	0.761	34.7	35.2
1e	C_1	23.302	1.155	15.1	5.1
1f	C_1	23.751	1.604	2.1	0.0
1g	C_1	24.077	1.930	1.1	0.0
1h	C_1	25.166	3.019	1.0	0.0
1i	C_1	25.419	3.272	0.1	0.0
1j	C_1	25.834	3.687	0.1	0.0

[a] Reference no. 7.

Ab initio calculations at the HF/6-311G* level were carried out for **1**, and the energies (electronic + vibrational) are summarized in Table 3. These calculations also predict that several low-energy conformations should exist for *trans*-cyclodecene.

The C_1 conformation **1c**, which resembles boat-chair-chair (BCC) cyclodecane, is calculated by MM3 to have the highest population (50.5% at −200 °C). Interconversion of olefinic carbon sites could occur through a C_2 conformation (**1d** or the mirror image of **1b**), as shown in Scheme 1. Peaks 1, 8, and 2 of the ^{13}C spectrum at −139.0 °C (Figure 4) appeared to be consistent with an exchanging system of this type, with the C_1 and C_2 conformations largely insulated from the others. An attempt to match the lineshape of these three peaks gave the calculated spectrum[21] shown in Figure 4c with k_1 and k_2 equal to 50.0 and 37.2 s^{-1}, and populations of 0.299 for **1c** or **1c′** and 0.402 for **1d** or the mirror image of **1b**. The barrier for

---

(19) Our version of Spartan does not allow calculation of free energies and populations. We thank Professor Saunders and Mr. Jimenez-Vazquez for sending a complete set of computations for **1**.

(20) Ganis, P.; Dunitz, J. D. *Helv. Chim. Acta* **1967**, *50*, 2379.

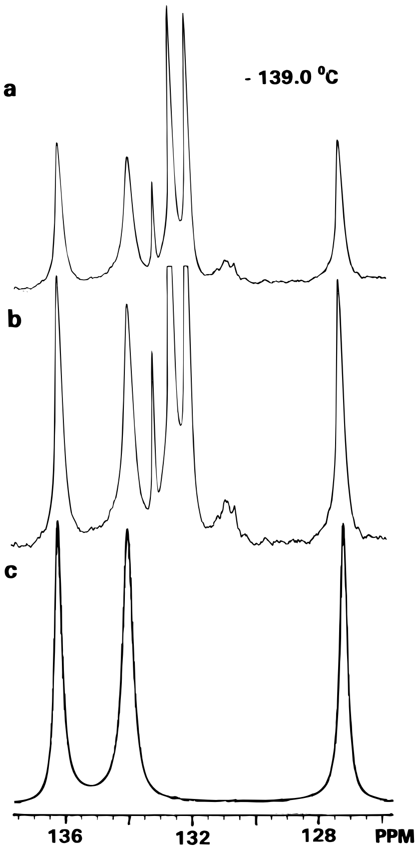


Figure 4. (a) ^{13}C spectrum of the olefinic carbons of **1** at −139.0 °C. (b) Same as (a) except expanded vertically; two peaks are offscale. (c) Calculated spectrum for three olefinic carbons of **1** at −139.0 °C; the three peaks correspond to peaks 1, 2, and 8 of Figure 1f.

conversion of the two topomers (**1c** + **1c′**) to **1d** or the mirror image of **1b** was calculated from the rate constant of 50.0 s^{-1} to be 6.6 kcal/mol, and the rate constant and barrier for the reverse process were 74.4 s^{-1} and 6.5 kcal/mol. The match between calculated and experimental spectra is not exact but may be close enough for these estimates of the barriers to be reasonable. The minor C_2 conformation (peak 3 of Figure 1) could then be **1a** of Figure 3. An alternative interpretation of peaks 1, 8, and 2 of Figure 1f in terms of conformations **1f** and **1a** or **1j** is possible, but the calculated populations of Table 2 for **1** at −200 °C are in better agreement with the interpretation above.[22]

Table 3. Energies and Relative Energies of *trans*-Cyclodecene from *ab Initio* Calculations at the HF/6-311G* Level

conformation[a]	energies (electronic + vibrational) (hartrees)	relative energies (electronic + vibrational) (kcal/mol)
1a	−389.479 629	0.000
1b	−389.476 378	2.040
1c	−389.477 932	1.065
1d	−389.478 701	0.582
1e	−389.478 786	0.529
1f	−389.474 840	3.005

[a] The numbering of conformations is the same as in Figure 3.

Conclusions

trans-Cyclodecene was shown to have five conformations present in observable amounts at −154.9 °C. Three of these are of C_1 symmetry and two are of C_2 symmetry. Force field calculations[7] predict five conformations at −200 °C, but the symmetries are reversed (2C_1 and 3C_2). A possible interpretation of three peaks of the slow-exchange spectrum of **1** in terms of conformations **1c** and **1d** (or **1b**) of Figure 3 was suggested. Free-energy barriers of 6.5 and 6.6 kcal/mol at −139.0 °C were estimated for interconversion of these conformations, which can be accomplished by flipping of carbons 4 and 9. A C_2 conformation interconverting slowly on the NMR time scale with the other conformations by −122 °C has been tentatively identified as conformation **1a** of Figure 3. Equilibration of **1a** with at least some of the other conformations requires rotation of the C6−C7 bond through the ring or an equivalent process. The process for *trans*-cyclodecene-*1,2,4,4,9,9*-d_6 with a free-energy barrier of 12.0 kcal/mol is probably rotation of the double bond through the ring, as suggested by the authors.[6]

Acknowledgment. We thank the National Science Foundation (EPSCoR-Grant No. EHR-91-08767) and the Department of Energy, Collaborative Research and Manpower Development Program Between JSU and AGMUS (Grant No. DE-FG05-86ER75274) for support of this work.

Supporting Information Available: Expanded ^{13}C spectrum of the CH_2 carbons of *trans*-cyclodecene at −154.9 °C (1 page). See any current masthead page for ordering and Internet access instructions.

JA962666S

---

(21) Calculated spectra were obtained using program DNMR-SIM, written by Hagele, G. and Fuhler, R., Heinrich-Heine University, Dusseldorf Institute of Inorganic and Structural Chemistry, Dusseldorf, FRG, 1994. We thank Mr. Ali Jabalameli of our department for acquiring this program from the internet and for installing the program on our computer.

(22) Ring conformations similar to **1c** or **1d** have been determined for the silver-nitrate adducts of several ten-membered ring sesquiterpenes: McClure, R. J.; Sim, G. A.; Coggon, P.; McPhail, A. T. *Chem. Commun.* **1970**, 128.