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Conformational Study of 1,2-Cycloundecadiene by Dynamic NMR Spectroscopy and Computational Methods

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Solutions of 1,2-cycloundecadiene in propane were studied by low-temperature ^{13}C NMR spectroscopy. A total of 17 peaks were observed at −166.7 °C, corresponding to two conformations of similar populations, one of C_1 symmetry (11 peaks) and the other of C_2 symmetry. The line shapes show that the predominant pathway for exchange of the topomers (C_1 and C_1') of the C_1 conformation does not include the C_2 conformation. From the ^{13}C spectra, free-energy barriers of 8.38 ± 0.15, 9.45 ± 0.15, and 9.35 ± 0.15 kcal/mol were determined for the C_1 to C_1', ($C_1 + C_1'$) to C_2, and C_2 to ($C_1 + C_1'$) conversions, respectively, at −72.2 °C. The NMR results for this compound are discussed in terms of the conformations predicted by molecular mechanics calculations obtained with Allinger's MM3 program. Ab initio calculations of free energies are also reported at the HF/ 6-311G* level for 25 conformations.

Introduction

A combination of dynamic NMR spectroscopy and computational methods provides a useful way of studying the conformations of cyclic compounds. The structures of the possible stable conformations and their energies and symmetries can be obtained from the calculations; in favorable cases, dynamic NMR spectroscopy shows the number of conformations actually present at low temperatures, their relative free energies and populations, symmetries, and free-energy barriers to interconversion. The two CH_2 groups of allene are perpendicular to each other, and the 2-fold rotational axis perpendicular to the $C{=}C{=}C$ axis of this compound can be maintained in cyclic allenes[1] such as 1,2-cycloundecadiene, which would show six peaks in the low-temperature ^{13}C NMR spectra for each conformation of C_2 or time-averaged C_2 symmetry, and 11 peaks for each conformation of C_1 symmetry. We report here a conformational study of 1,2-cycloundecadiene by dynamic NMR spectroscopy and molecular mechanics and ab initio calculations.

Experimental Section

1,2-Cycloundecadiene (**1**)[5] was synthesized from *cis*- and *trans*-cyclodecenes by a procedure similar to the one described by Shea and Kim[6] for the synthesis of 1,2-cyclononadiene from cyclooctene.[7] Twenty grams of a 3:1 mixture of *cis*- and *trans*-cyclodecenes was added to 1.5 mL of ethanol, 73.1 g of bromoform, 29 mL of dichloromethane, 0.363 g of benzyltriethylammonium chloride, and 115.8 g of aqueous 50% sodium hydroxide solution, and the mixture was heated to 40−50 °C for 2 h with vigorous stirring, followed by stirring for 2 h at room temperature. Examination of the organic phase by ^{13}C NMR spectoscopy showed the presence of some unreacted cyclodecenes; additional bromoform, ethanol, benzyltriethylammonium chloride, and 50% sodium hydroxide were added, and the mixture was stirred vigorously at 40−50 °C for 2 h and stirred 2 h at room temperature. Water was added, and the dichloromethane layer was removed. The aqueous phase was extracted three times with dichloromethane, and the combined organic layers were washed with 5% hydrochloric acid and then water, dried over Drierite, and the solvent was evaporated. Excess bromoform was removed by heating under vacuum to yield 44.9 g of a *cis*- and *trans*-11,11-dibromobicyclo[8.1.0]undecane mixture. A ^{13}C NMR spectrum indicated a high level of purity (>98%) for the residue. One or both of the *gem*-bromocyclopropanes precipitated at −30 to −40 °C from a solution of 38.1 g of the dibromides in 19.1 mL of ether; an additional 10 mL of ether was added, and the temperature was raised to −2 to −5 °C while methyllithium (10 mL of a 1.4 M solution in ether) was added dropwise under argon with stirring. An additional 95.4 mL of methyllithium was added as the temperature was gradually decreased until a temperature of −30 to −40 °C was reached and maintained. After the addition was completed, the resulting solution was stirred at −30 to −40 °C for 1 h. The excess methyllithium was decomposed by adding water, and the reaction mixture was extracted with ether. The combined ether layers were washed with water, dried over Drierite, and concentrated on the rotary evaporator. Distillation under vacuum gave 12.7 g of 1, 2 -cycloundecadiene; the product was identified by its ^{13}C spectrum, which also established a high level of purity (≥99%).

A 30% solution of **1** in propane was prepared in a 5 mm thin-walled NMR tube and used to record ^{13}C spectra from room temperature to −90.0 °C. For lower temperatures, a 2% solution was used. A small amount of TMS was added as an internal reference to both solutions. *Caution*: high pressure. The sample tubes were stored and handled below 0 °C most of the time. Spectra were recorded on a General Electric Model

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[1] 1,2-Cyclononadiene has been studied by several methods[2−4] and exists as a mixture of a C_2 and a C_1 conformation.

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GN-300 wide-bore NMR spectrometer operating at 75.58 MHz for carbon. The ^{13}C spectra for **1** were obtained from $+17.8$ to -166.3 °C with a 5 mm dual probe. A pulse width of 8.0 μs, corresponding to a tip angle of 83°, was used. The pulse repetition period was 10 s at -166.3 °C, and 1 s at all other temperatures. A sweep width of $\pm$9600 Hz, data size of 32 K, 800−1200 pulses, and 3.0 Hz line broadening were used. Spinning was discontinued below about -120 °C. Because ejecting the sample at the lower temperatures was difficult, due to ice formation on the inner wall of the stack, the temperature calibrations were performed separately, using a copper−constantan thermocouple immersed in the same solvent contained in a nonspinning dummy sample tube and under conditions as nearly identical as possible. The emf's were measured with a Leeds and Northrup Model 8690-2 millivolt potentiometer. The uncertainty in the temperatures was estimated to be $\pm$2 °C.

The rate constants for the interconversion of conformations from the carbon spectra were obtained by total line shape matching on a PC using a DNMR simulation program,[8] and the free-energy barriers were obtained on an Apple computer with a program written by Newmark.[9]

The conformational space of **1** was searched with Allinger's MM3 program.[10] Kick sizes of 2.0 and 3.0 Å and several different numbers of pushes were used, and the results were combined. The conformations were visualized with Spartan 5.0.[11]

The geometries determined by the molecular mechanics program for the first 25 conformations of **1** according to strain energy were used as starting points for the ab initio calculations. The Gaussian 94 series of programs[12] was used for full geometry optimization, first at the HF/3-21G* level and then at the HF/6-311G* level. The optimized geometries were tested by frequency calculations, and free energies were obtained for -150 °C.

Results and Discussion

The ^{13}C spectrum of **1** at -25.0 °C shows the expected six signals at δ 204.13 (=C=), 93.71 (=CH), 29.61, 28.90, 26.18, and 24.68, relative to the carbons of internal TMS (Figure 1). A small amount of exchange broadening is apparent at this temperature, as indicated by the decreased height for two of the peaks in the CH$_2$ region. Further changes occur at lower temperatures, and by -166.3 °C, two peaks were found in the =C= region, which shows the presence of two conformations of similar populations. The spectrum for the =CH carbons at this temperature consists of three peaks, two of which are of equal intensity and correspond to a conformation of C_1 symmetry (**1A**). The third peak in this region is assigned to a conformation of C_2 (or time averaged C_2) symmetry (**1B**). The line shapes for the =C= and =CH regions at temperatures near -72.2 °C indicate that the high-frequency signal at -166.3 °C for the former region corresponds to the conformation of C_1 symmetry. The peaks for the C_1 conformation at -166.3 °C appear at δ 204.29, 94.21, 90.40, 34.21, 29.77, 28.46, 27.98, 26.79, 25.45, 24.72, and 24.23; the peaks at δ 201.50, 96.23, 31.41, 28.83, 24.01, and 19.91 were assigned to the C_2 conformation.

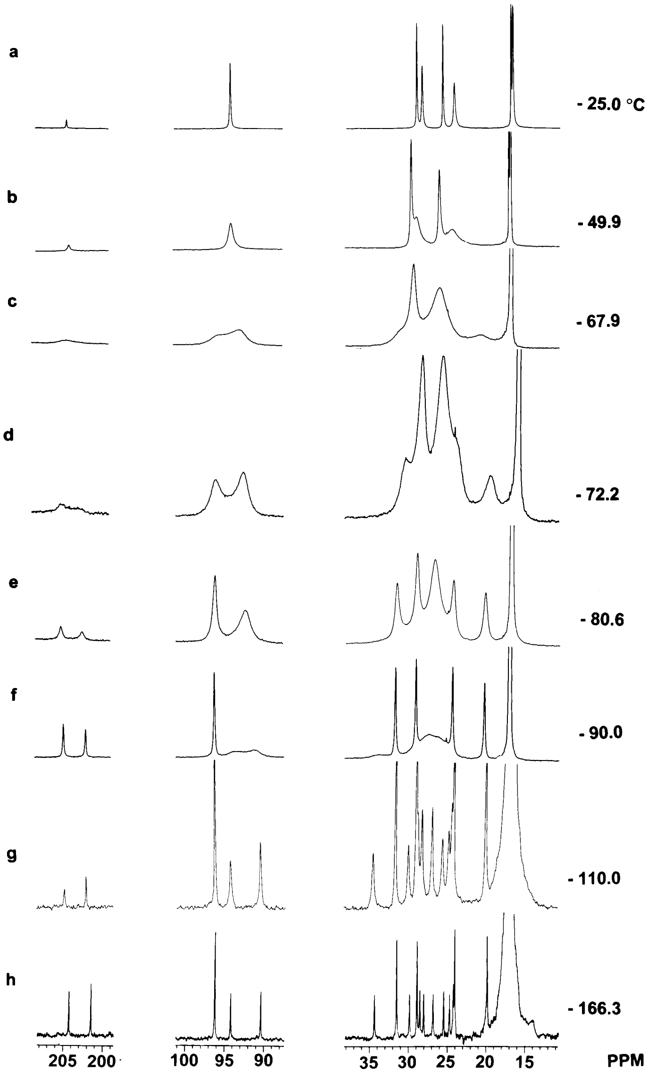
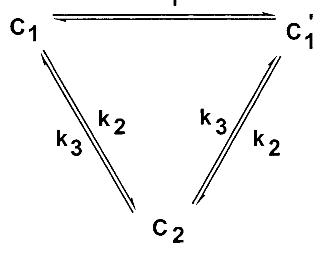


FIGURE 1. Low-temperature ^{13}C NMR spectra of 1,2-cycloundecadiene (**1**) in propane.

The line shapes for the =CH carbons at temperatures below -72.2 °C indicate that interconversion of the



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(8) Calculated spectra were obtained using program DNMR-SIM written by Hagele, G., Fuhler, R., Heinrich-Heine University, Dusseldorf Institute of Inorganic and Structural Chemistry, Dusseldorf, FRG, 1994.

(9) Free-energy barriers were calculated from the Eyring equation with a program written by Newmark: Newmark, R. A. *J. Chem. Educ.* **1983**, *60*, 45.

(10)) Version MM3 (2000) was used. This latest version of the MM3 program is available to academic users from the Quantum Chemistry Program Exchange and to commercial users from Tripose Associates, 1699 South Hanley St., St. Louis, MO 63144.

(11) Spartan version 5.10 from Wavefunction, Inc., Irvine, CA.

(12) Gaussian 94, Revision E.3: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; 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.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

TABLE 1. Actual Temperatures, Populations, Rate Constants for Interconversions, and Free-Energy Barriers for 1,2-Cycloundecadiene

T (°C)	pop. $C_1 + C_1'$	k_1 (s^{-1}) rate $C_1 \rightarrow C_1'$	k_2 (s^{-1}) rate $C_1 \rightarrow C_2$	k_3 (s^{-1}) rate $C_2 \rightarrow C_1$	$2k_3$ (s^{-1}) rate $C_2 \rightarrow (C_1 + C_1')$	$\Delta G^{\ddagger}$ $C_1 \rightarrow C_1'$	$\Delta G^{\ddagger}$ $(C_1 + C_1') \rightarrow C_2$	$\Delta G^{\ddagger}$ $C_2 \rightarrow (C_1 + C_1')$
−67.9	0.590	4200	483	348	696	8.45	9.34	9.19
−72.2	0.568	3140	215	141	282	8.38	9.45	9.35
−80.6	0.550	910	115	70.3	141	8.49	9.28	9.20
−90.0	0.525	480	35	19.3	38.6	8.29	9.24	9.21
−166.3	0.465							

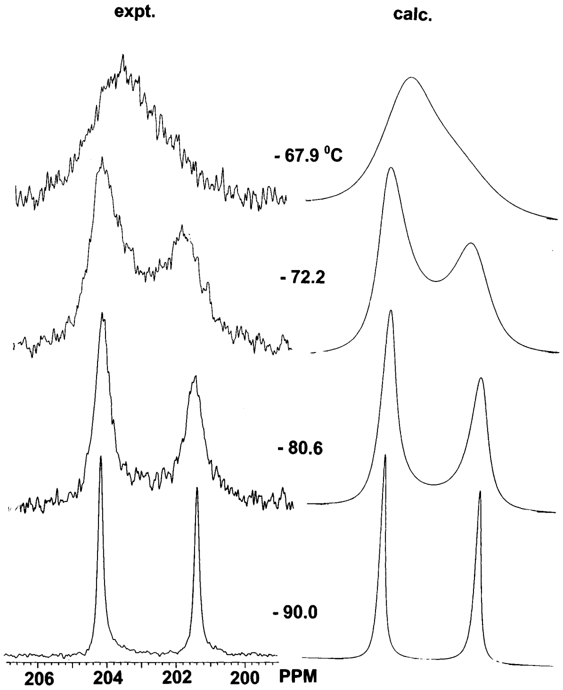

FIGURE 2. Experimental and calculated line shapes for the =C= carbons of 1,2-cycloundecadiene (**1**) at four temperatures.

topomers [13,14] of **1A** takes place predominantly (but not entirely) by a pathway that does not include **1B**. Calculated line shapes were based on the exchange scheme shown above, where C_1 and C_1' are the two topomers of **1A**.

From line shape matching of the =C= region, k_2 and $2k_3$ could be obtained, and these rate constants were used in the calculation of line shapes for the =CH region, along with values for k_1, which were determined from the latter calculations. Calculated and experimental line shapes for four temperatures are shown in Figures 2 and 3, and the rate constants and free-energy barriers are summarized in Table 1. For example, the populations of C_1, C_1', and C_2 at −72.2 °C were 0.284, 0.284, and 0.432 and k_2 and k_3 were 215 and 141 s^{-1}; the free-energy barrier for conversion of ($C_1 + C_1'$) to C_2 was calculated from the rate constant of 215 s^{-1} to be 9.45 kcal/mol, and the rate constant and free-energy barrier for the reverse process were 282 s^{-1} and 9.35 kcal/mol. As expected, k_1 is much higher (3140 s^{-1} at −72.2 °C) than k_2 and k_3 ; the free-energy barrier for interconversion of C_1 and C_1' was 8.38 kcal/mol.

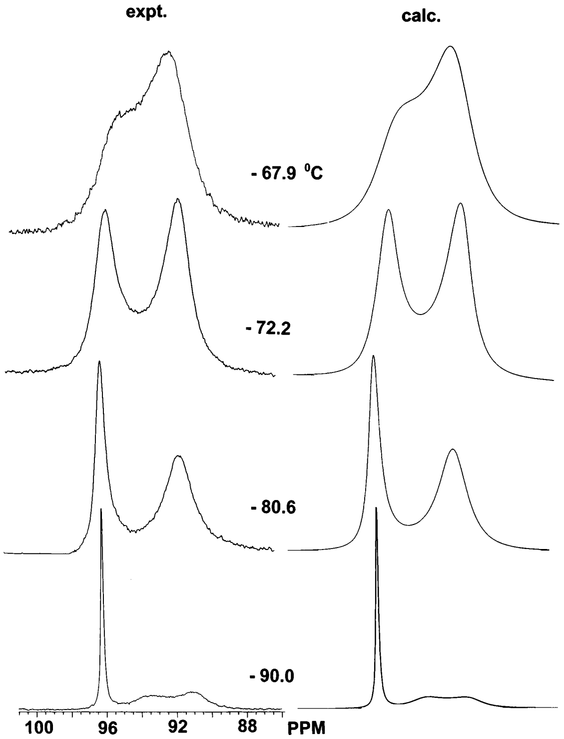

FIGURE 3. Experimental and calculated line shapes for the =CH carbons of 1,2-cycloundecadiene at four temperatures.

Structures calculated at the HF/6-311G* level for the first 10 conformations of **1** according to MM3 strain energies are shown in Figure 4. The symmetries and calculated strain energies and free energies according to MM3 for the 25 most stable conformations according to strain energy are listed in Table 2, and relative free energies from ab initio calculations at the HF/6-311G* level are also included. After optimization at the HF/6-311G* level, conformations **1g** and **1h** converged to a structure that closely resembled **1g**. Conformations **1x** and **1y** converged to the enantiomer of **1a**. 1,3-Symmetrically disubstituted allenes are chiral, and the enantiomers can be interconverted by rotation about the double bonds, but the barriers for this process are high. From the rate of racemization of 1,3-dimethylallene, the rotational barrier of the C=C bonds was determined[15] to be 46.17 kcal/mol for this compound.

The dihedral angles from MM3 and ab initio calculations are generally close for most of the conformations of Figure 4, except for $C_{11}C_1C_2C_3$ and $C_1C_2C_3C_4$, which are often very different. These dihedral angles depend on small distortions of the $C_1C_2C_3$ group from linearity, so perhaps the deviations are not surprising. The $C_1C_2C_3$

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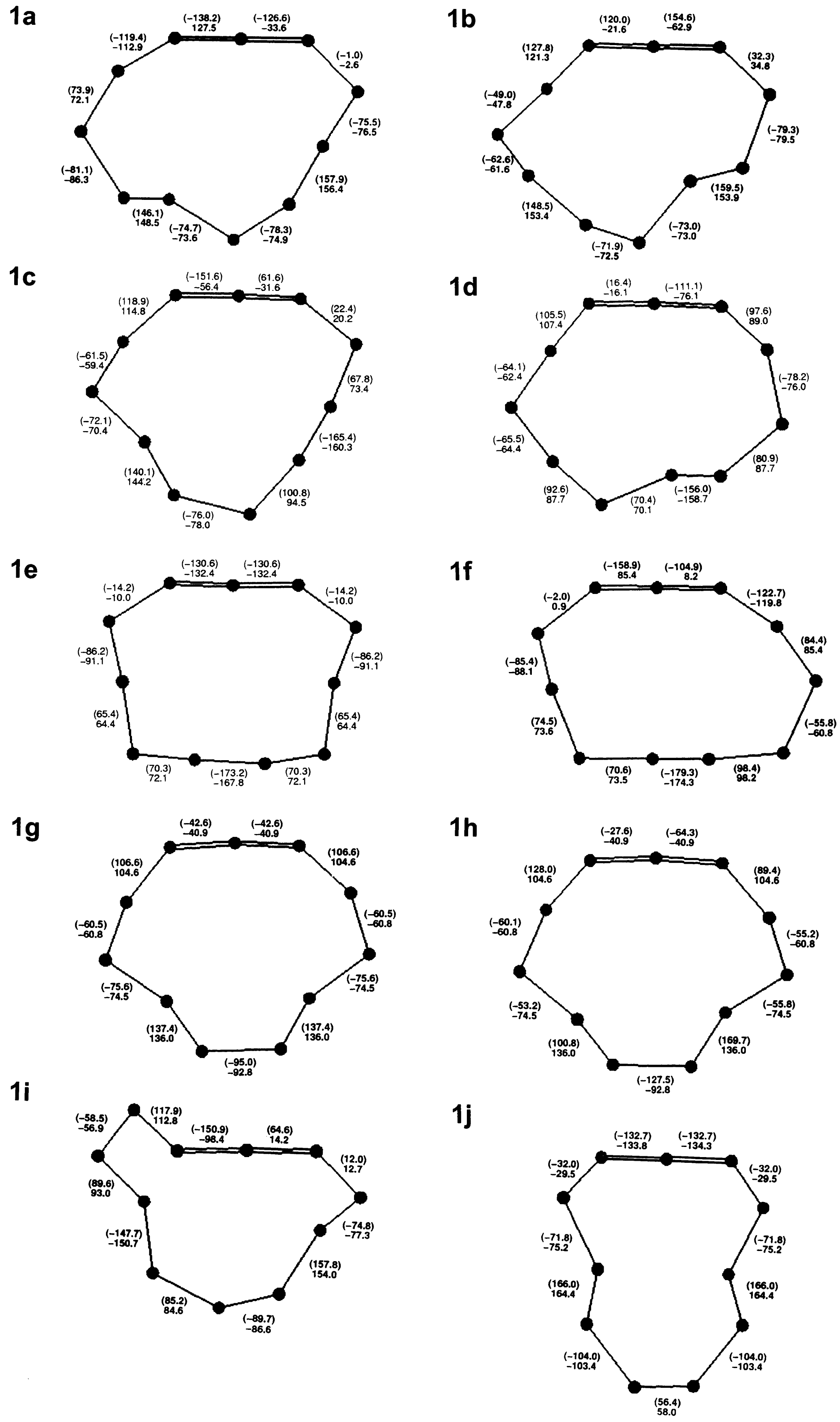
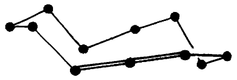


FIGURE 4. Conformations of 1,2-cycloundecadiene (**1**) in order of increasing MM3 strain energies. The numbers refer to CCCC dihedral angles. The values on top in parentheses are from MM3 and the lower numbers are from ab initio calculations at the HF/6-311G* level (used for the drawings).

TABLE 2. Relative Strain Energies[a] and Relative Free Energies[a] Calculated Using the Molecular Mechanics Force Field (MM3) and Relative Free Energies[b] and Low Frequencies[b] for Different Conformations of 1,2-Cycloundecadiene Calculated at the HF/6-311G* Level Using the Gaussian 94 Program

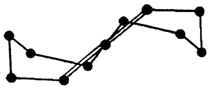
conformer	symmetry	relative strain energies (kcal/mol)	relative free energies[a] (kcal/mol) 25 °C	relative free energies[a] (kcal/mol) −166.3 °C	relative free energies[b] (kcal/mol) 25 °C	relative free energies[b] (kcal/mol) −166.3 °C	low frequencies[b] (cm^{-1})
1a	C_1	0.000	0.000	0.000	0.000	0.000	84.9256
1b	C_1	0.402	0.579	0.473	1.212	1.168	87.9764
1c	C_1	0.620	0.512	0.512	1.351	1.440	69.8268
1d	C_1	1.215	1.320	1.367	1.999	2.169	54.4559
1e	C_2	1.626	2.222	2.177	0.217	0.265	92.2170
1f	C_1	2.002	2.134	2.249	1.306	1.426	80.4187
1g	C_2	2.155	1.935	1.893	3.219	3.547	38.4844
1h	C_2	2.279	2.284	2.334	3.219	3.547	38.4846
1i	C_1	2.348	2.373	2.327	3.890	3.899	107.5399
1j	C_2	2.364	2.290	2.185	2.679	2.871	86.9023
1k	C_1	2.378	2.503	2.673	2.132	2.272	78.1287
1l	C_1	2.383	2.647	2.668	3.889	3.901	80.7804
1m	C_1	2.445	3.687	3.429	4.898	4.749	107.7798
1n	C_1	2.447	2.362	2.506	2.882	3.094	65.7568
1o	C_1	2.479	2.386	2.486	2.859	3.030	73.2783
1p	C_1	2.800	3.094	3.210	3.106	3.222	76.0551
1q	C_1	3.142	2.992	2.975	4.745	5.092	50.9557
1r	C_1	3.206	3.210	3.243	4.086	4.242	55.1516
1s	C_2	3.531	3.352	3.329	2.457	2.574	93.0544
1t	C_1	3.557	4.137	3.948	5.340	5.201	113.3284
1u	C_1	3.773	4.042	3.959	6.019	6.092	81.0494
1v	C_1	3.816	3.759	3.864	3.333	3.491	87.0930
1w	C_2	4.168	4.940	3.708	4.204	4.251	109.2182
1x	C_1	4.271	4.444	3.928	0.001	0.000	84.9593
1y	C_1	4.273	4.446	3.930	0.000	0.000	84.9257

1a



C_1

1e



C_2

bond angles for conformations **1a**−**j** are close to 180°, as expected (179.3, 179.4, 177.9, 176.9, 177.8, 179.4, 173.9, 173.9, 178.3, and 180.0°, respectively), and the corresponding $C_{11}C_1C_3C_4$ dihedral angles for these conformations are not far from 90° (93.9, −84.2, −87.0, −90.8, 96.5, 93.3, −79.4, −79.4, −83.8, and 91.9°).

On the basis of the ab initio calculations, the most likely structures are **1a** and **1e** for the C_1 and C_2 conformations **1A** and **1B**. Another view of these conformations is shown on the left. Several conformations (**1b**, **1c**, and **1f**) are close enough in free energy that they cannot be completely excluded.

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Supporting Information Available: The Cartesian coordinates and calculated energies for the 25 conformations of 1,2-cycloundecadiene at the HF/6-311G* level (Table 2) are provided. Cartesian coordinates for these conformations obtained with the MM3 force field and dihedral angles for conformations **1k**−**y** at the HF/6-311G* level are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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