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Conformational Study of Cyclodecane and Substituted Cyclodecanes by Dynamic NMR Spectroscopy and Computational Methods

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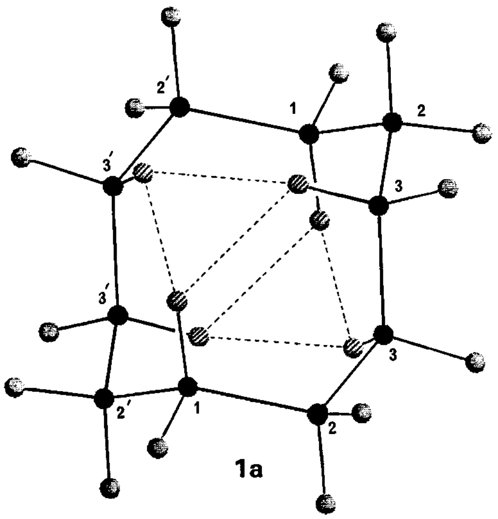
Abstract: Low-temperature ^{13}C NMR spectra of cyclodecane (**1**) showed the presence of a minor conformation, assigned to the twist-boat-chair-chair (TBCC), in addition to the expected boat-chair-boat (BCB). If only the TBCC and BCB conformations were assumed to be appreciably populated, then a free-energy difference between the two conformations of 0.73 ± 0.3 kcal/mol could be obtained from the five area measurements over a temperature range of −148.6 to −131.0 °C, with populations of 5.2 and 94.8% for the TBCC and BCB conformations at −146.1 °C. However, an alternative description of the conformations of **1** was suggested by the ab initio calculations, which predicted that the twist-boat-chair (TBC) and TBCC conformations have comparable free energies and populations. Equal amounts of TBCC and TBC would give populations of 5.2, 5.2, and 89.6% and relative free energies of 0.72, 0.72, and 0.00 kcal/mol for the TBCC, TBC, and BCB conformations at −146.1 °C, based on the experimental areas at this temperature. The experimental spectra could neither confirm nor disprove the presence of the TBC. Saunders' calculations of the strain energies of **1** using Allinger's MM3 program were reproduced to obtain a complete set of these parameters and drawings of the conformations, and free energies and populations were obtained at +25 and −171.1 °C. Free energies were also calculated at the HF/6-31G* and HF/6-311G* levels, and chemical shifts were obtained for three conformations at the HF/6-311G* level by the GIAO method. Chlorocyclodecane (**2**) was shown by ^{13}C and ^{1}H NMR spectroscopy to have three conformations at −165.5 °C. To aid in conformational assignments, the ^{13}C chemical shifts were calculated for all of the BCB and TBCC conformations of **2** using the GIAO method at the HF/6-311G* level. The free energies for each of the possible BCB, TBCC, and TBC conformations were also calculated using Allinger's MM3 program. From the line shape changes in the experimental ^{13}C NMR spectra, the free-energy barriers, a consideration of the X-ray structures of substituted cyclodecanes, and these calculated chemical shifts and free energies, the three conformations of **2** at −165.5 °C were suggested to be 2e BCB (31.2%), 2a BCB (14.9%), and a TBCC conformation (53.9%) (numbering as in Figure 1); the 2e and 2a BCB assignments could be reversed. Free-energy barriers for interconversion of BCB conformations of **2** at −159.8 °C were 5.4 ± 0.2 and 5.5 ± 0.2 kcal/mol, and the free-energy barriers at −120.9 °C for equilibration of the TBCC conformation with the rapidly interconverting BCB conformations were 7.07 ± 0.2 and 7.08 ± 0.2 kcal/mol. The ^{13}C NMR spectrum of cyclodecyl acetate (**3**) at −160.0 °C showed a similar pattern of chemical shifts and intensities for the substituted ring carbon.

The conformations of cyclodecane have been of interest for many years.[1] X-ray diffraction studies[1a] of a number of crystalline derivatives generally showed the conformation to be the BCB (**1a**), and this conformation has also been assigned to cyclodecane in the solid state by ^{13}C NMR spectroscopy[2a] and X-ray diffraction.[2b] The early force-field calculations[3−7] on cyclodecane included this conformation along with others, and these calculations also indicated the BCB to be of lowest energy. The initial studies by X-ray diffraction and molecular mechanics led to the perception[8] that the preference for the BCB in cyclodecane is comparable to the situation for the six-membered



1a

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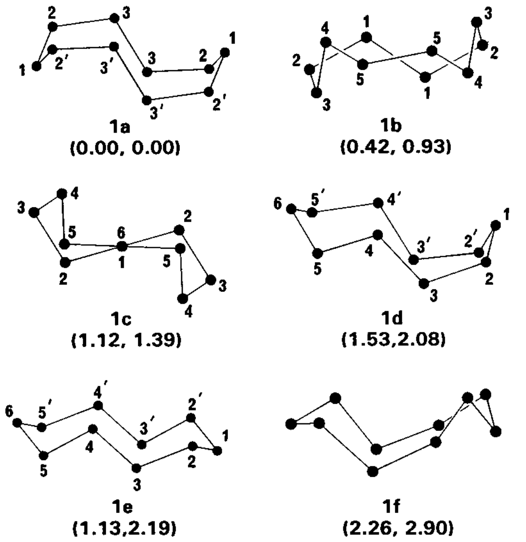

Figure 1. Strain energies of cyclodecane conformations, calculated by Saunders[16] using Allinger's MM2 and MM3 force fields. The structures are shown in order of increasing strain energy according to MM3 (second number in parentheses). For the TBC conformation, carbons 5 and 6 are in the front.

ring, where the chair conformation is found except in unusual circumstances.[9]

Two examples of substituted cyclodecanes with conformations other than BCB have been found by X-ray crystallography,[10,11] and in one case the departure from the usual ring conformation can be explained in terms of steric interactions. The 1a and 3a hydrogens of **1a** form two sets of three hydrogens with substantial nonbonded interactions, as shown in the diagram above, and these positions will be avoided if possible by substituents larger than hydrogen. Substitution of the ring by four methyl groups in a 1,1,5,5 relationship would place a methyl group in a highly strained intraanular position (1a or 3a), and the crystal structure of 4,4,8,8-tetramethylcyclodecanecarboxylic acid was determined[10] to examine the effects of this type of substitution. Initial results for the compound did not correspond to a reasonable structure, but the use of the apparent ring geometry as a starting point for force-field calculations of cyclodecane resulted in two conformations with relative strain energies of 2.1 kcal/mol (TBC, **1c** of Figure 1) and 3.1 kcal/mol (TBCC, **1b**). It was found that the X-ray diffraction data could be interpreted in terms of a 4:1 mixture of TBC and TBCC conformations randomly distributed in the crystal. More recently, the TBCC and BCB conformations have been found[11] in the crystals of *cis*-1,6-cyclodecanediol.

Cyclodecane has been studied in the gas phase at +130 °C by a combination of electron diffraction and molecular mechanics calculations.[12] Excellent agreement between the experimental intensity curve with a curve calculated for C_{2h} BCB cyclodecane was obtained, but significant differences between this structure and the X-ray structure were observed, leading the authors to suggest that other conformations may actually be populated. In an alternative interpretation[12] molecular mechanics was used to calculate the strain energies for the four most stable of these conformations. Populations were estimated by weighting the four theoretical curves to obtain the best match with the experimental data. In this way, the following composition was predicted: BCB, 49%; TBC, 35%; TBCC, 8%; and BCC (**1d**), 8%.

1,1-Difluorocyclodecane was studied in solution by ^{19}F NMR spectroscopy, and a single AB quartet was observed at slow exchange (−164 °C).[13] This result was interpreted in terms of the BCB conformation, with the fluorines at positions 2a and 2e, and the free-energy barrier was 5.7 kcal/mol. Proton NMR spectra for a 0.4% solution of cyclodecane in CF_2Cl_2 have been reported[14] for temperatures to −162 °C. Three broad, overlapping peaks were found at the lowest temperature. No discussion of the number or identity of possible conformations was made,[14] but a barrier of approximately 6 kcal/mol was estimated. ^{13}C NMR spectra for cyclodecane were obtained below room temperature,[14] but a limiting spectrum was not recorded because of the low solubility of the compound. A successful low-temperature ^{13}C NMR study of cyclodecane does not appear to have been reported in the primary literature, although the slow-exchange ^{13}C NMR spectrum of this compound has been described[15] as consisting of only 3 peaks for the BCB in a ratio of 4:4:2.

Later molecular mechanics calculations of strain energies by Saunders,[16] using both the MM2 and MM3 force fields of Allinger, appear to support the possibility that more than one conformation of cyclodecane could be populated. We have reproduced these calculations, and results for the first six conformations are shown in Figure 1. Although the steric energies are not directly related to populations, the low values for the TBCC, the TBC, and a slightly distorted BCC conformation indicated that the BCB may not be favored by as large a margin as previously believed. Barriers for interconversion of cyclodecane conformations also have been calculated recently using MM2.[17] For example, a barrier of 5.43 kcal/mol was found for conversion of TBCC to the distorted BCC by K3-kayaking.[17] BCB was reported[17] to be connected only to TBC, with a barrier of 6.38 kcal/mol for this K3-kayaking.

Allinger[18] has carried out a conformational search for cyclodecane using the MM4 force field, and a total of 10 conformations were found to have free energies within 3.2 kcal/mol of the lowest (TBCC) conformation. The BCB conformation was calculated to have a lower enthalpy than the TBCC conformation by 0.52 kcal/mol at room temperature, but the calculations indicated a free energy slightly higher for the BCB than for the TBCC at this temperature (by 0.14 kcal/mol). Most of the difference between the enthalpy and the free energy for the two conformations was attributed to the fact that the TBCC exists as a mixture of D and L forms, while unsubstituted BCB cyclodecane does not. MM4 calculations[18] at 298 K gave populations of 30% BCB, 37% TBCC, 12% of a C_1 conformation not considered by Hilderbrandt,[12] 10% TBC, and 11% of 6 additional conformations.

Cyclodecane possesses the common types of strain, including the transannular H···H repulsions noted above for **1a**, and the

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[15] Reference 1c, pp 50 and 208. On p 50, the ratio is given as 4:2:2.

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compound has been useful in refining the force fields used in molecular mechanics calculations.[18,19] The level of accuracy reached by the MM3 and MM4 programs is high enough that the results from these calculations suggested that further experimental studies of the conformations of **1** by NMR could be useful. No details (e.g., temperatures, solvent, chemical shifts, or signal-to-noise ratio) were described[15] for the early ^{13}C NMR study of cyclodecane, and it seemed possible that one or more additional conformations could be present and detected with the greater sensitivity of NMR spectrometers now available. The conformations of **1** have also been studied in this work using ab initio molecular orbital calculations. In addition, chlorocyclodecane and cyclodecyl acetate have been examined by dynamic NMR spectroscopy and computational methods. A low-temperature ESR study of the cyclodecylmethyl radical concluded[20] that two or three conformations were present, with the CH_2 group in an axial and one or two equatorial positions, but no dynamic NMR studies of substituted cyclodecanes have been described.

Experimental Section

Cyclodecane, listed as 98% pure, was purchased from Aldrich Chemical Co. and used as received. The actual level of purity was indicated to be greater than 99.5% by the room-temperature ^{13}C and ^{1}H NMR spectra. A 0.4% solution of **1** in CF_2Cl_2 was prepared in a 5-mm thin-walled screw-capped NMR tube. A small amount of tetramethylsilane was added for an internal reference. *Caution*: high pressure. The sample tube was stored and handled below 0 °C most of the time.

Spectra were recorded on a General Electric model GN-300 wide-bore NMR spectrometer operating at 75.58 MHz for ^{13}C and 300.52 MHz for ^{1}H. The ^{13}C NMR spectra for **1** were obtained from 18.2 to -171.1 °C with a 5-mm dual probe. A pulse width of 12.5 μs was used, corresponding to a tip angle of 45°, and the pulse repetition period was 1 s. The delay time was shorter than optimal for integration,[21] but this was necessary to obtain an adequate signal-to-noise ratio. From 2800 to 3200 acquisitions were used, with a sweep width of $\pm$12 500 Hz, data size of 64 K, and 3.0 Hz line broadening to increase the signal-to-noise ratio. Spinning was discontinued below about -120 °C. Area measurements in the temperature region -148.6 to -131.0 °C were made by a cut-and-weigh procedure.

Chlorocyclodecane (**2**) was purchased from Columbia Organics and used as received after checking for purity by ^{13}C NMR spectroscopy. It was studied as a 7% solution in a 2:1:1 mixture of $CHClF_2$, $CHCl_2F$, and CF_2Cl_2. ^{13}C NMR spectra were taken with 500 $\pm$ 100 acquisitions, a sweep width of $\pm$ 11 600 Hz, data size of 32 K, pulse width of 9.0 μs (80° tip angle), and pulse repetition period of 8 s, over a temperature range of -0.1 to -165.5 °C.

Cyclodecyl acetate (**3**) was synthesized by boiling a mixture of cyclodecanol (5.0 g) and acetic anhydride (13.1 g). Ether was added to the cooled mixture, and aqueous sodium hydroxide solution was used to remove excess anhydride and acetic acid. Cyclodecyl acetate was isolated by drying over Drierite, removing the ether, and distilling under reduced pressure. An 8% solution in 2:1:1 $CHClF_2$, $CHCl_2F$, CF_2Cl_2 was studied by ^{13}C NMR from $+0.1$ to -160.0 °C. The sweep width, number of acquisitions, data size, pulse width, tip angle, pulse repetition period, and line broadening were $\pm$ 10 500 Hz, 250 $\pm$ 50, 32 K, 4.2 μs, 45°, 6.0 s, and 3.0 Hz.

Because of the difficulty in ejecting the sample at the lower temperatures, the temperature calibrations were performed separately, using a copper−constantan thermocouple immersed in the same solvents contained in a nonspinning 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. The uncertainty in the temperatures was estimated to be $\pm$2 °C. The free-energy barriers obtained by dynamic NMR spectroscopy are not highly sensitive to the rate constant or the temperature.[22] For a process with a rate constant of 220 s^{-1} at -120.9 °C, a change in temperature of $\pm$2 °C raises or lowers the barrier of 7.07 kcal/mol by 0.10 kcal/mol. Temperatures were not rounded off to the nearest degree because this would have resulted in temperature changes of up to 0.5 °C, which would have had about $^1/_4$ the effect on the barrier of a 2 °C change.

The strain energies for **1**, calculated by Saunders,[16] were reproduced using Allinger's MM2 and MM3 programs built into Spartan.[23] An external MM3 program,[24] updated on January 1, 1994, and purchased from the Quantum Chemistry Program Exchange at Indiana University was used to obtain free energies for the conformations of **1** and **2**. 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.[25] For all five conformers, full geometry optimizations were done at the HF/6-31G* level; smaller basis sets were used initially. Results for these conformations were used as input for calculations at the HF/6-311G* level. Energy-minimized structures were characterized by calculation of harmonic vibrational frequencies at the same levels, and free energies were obtained. For the frequency calculations, the default scaling factor of 0.89 was used.

The gauge-including atomic orbitals (GIAO) method was employed to calculate isotropic absolute shielding constants (σ, in ppm) for the carbons of TMS, three conformations of **1**, and all of the possible BCB and TBCC conformations of **2**. 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.[25]

Results and Discussion

The ^{13}C NMR spectrum of **1** at $+18.2$ °C shows a single sharp peak at δ 26.10 (Figure 2). The spectrum is exchange-broadened by -120.1 °C, and at -131.0 °C two overlapping peaks are observed at δ 25.0 and 23.7, with line widths of 47 and 546 Hz, respectively. As the temperature is lowered further, the major signal decoalesces into three peaks at δ 28.4, 22.4, and 19.2 in a ratio of 2:2:1. From the number and relative intensities of the peaks, they are assigned to the BCB conformation (**1a**). Calculated chemical shifts (Table 1) permit assignment of these signals to carbons of types 2, 3, and 1, respectively; the assignment for C-1 is unambiguously confirmed by the intensity ratios. These ^{13}C assignments are in agreement with those made for **1a** in the solid state.[2a] The minor peak at -131.0 °C sharpens at first as the temperature is lowered and as the rate of exchange with the BCB conformation decreases and then broadens at still lower temperatures as interconversion of carbon positions within the conformation is slowed sufficiently on the NMR time scale. Slow exchange was not seen for the latter process. The total concentration of cyclodecane is 0.4%, and only 5.2% of this amount at -146.1 °C is due to

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[22] For a discussion of sources and magnitudes of errors in dynamic NMR spectroscopy, see: Raban, M.; Kost, D.; Carlson, E. H. *J. Chem. Soc. D* **1971**, 656.

[23] Spartan version 3.0 from Wavefunction, Inc., Irvine, CA.

[24] 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 South Hanley St., St. Louis, MO 63144.

[25] Gaussian 94: Rev. E. 2, Frisch M. J.; Trucks, G. W.; Gill, P. M. W.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Cheesman, J. R.; Gomperts, R.; Keith, T.; Petersson, G. A.; Montgomary, 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.

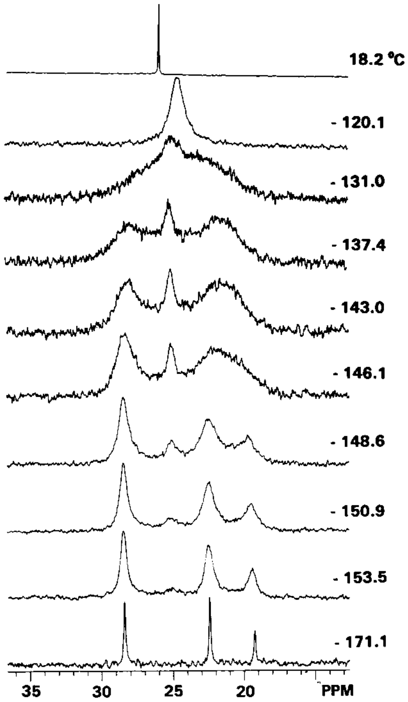

Figure 2. Low-temperature ^{13}C NMR spectra of cyclodecane.

Table 1. ^{13}C Chemical Shifts in PPM (δ) for the BCB, TBCC, and TBC Conformations of Cyclodecane. Calculated Chemical Shifts Are from ab Initio Calculations at the HF/6-311G* Level, Using the GIAO Method

carbon no.[a]	BCB conformation experimental[b]	BCB conformation calculated	TBCC conformation calculated	TBC conformation calculated
1	19.2	20.3	19.3	31.2
2	28.4	27.6	26.5	22.6
3	22.4	21.4	25.4	29.0
4			20.8	20.0
5			27.9	19.6
6				25.0

[a] Numbering of the ring carbons is shown in Figure 1. [b] At −171.1 °C.

the minor conformation. In addition, the peaks of the second conformation may still be exchange-broadened at −171.1 °C.

Calculated free energies for conformations of **1** at −171.1 °C by MM3 and ab initio methods (Tables 2 and 3) show that the observed minor conformation could be the TBCC (**1b**) or the TBC (**1c**). The line shape changes for **1** in Figure 2 suggest that the barriers to interconversion of **1a** with the second conformation are larger than the barrier to exchange of the BCB carbon positions. According to the pruned network of conformational interconversions of Kolossvary and Guida,[17] **1a** can interconvert only with **1c**. The low-temperature ^{13}C line shapes of **1** indicate that exchange of carbon positions in **1a** does not occur through conversion to the minor conformation, and the second conformation is then assigned to the TBCC. If only the TBCC and the BCB conformations are assumed to be appreciably populated, then a free-energy difference between the two conformations of 0.73 ± 0.3 kcal/mol could be obtained from the five area measurements over a temperature range of −148.6 to −131.0 °C. However, an alternative description of the conformations of **1** is suggested by the ab initio calculations of Table 3, which predict that the TBC and the TBCC conformations have comparable free energies and populations. If interconversion of the BCB and the TBC conformations provides the lowest-energy pathway for exchange of carbon positions within each of these conformations, then the TBC could be present in small amounts and not be detected in the low-temperature ^{13}C NMR spectra. At slow exchange, the TBC absorption would be divided among six peaks, each too low in intensity to be observed, and at higher temperatures, the line shapes of the broad signals would probably not be influenced enough by the presence of the TBC to make detection possible. Equal amounts of the TBCC and the TBC would give populations of 5.2, 5.2, and 89.6% and relative free energies of 0.72, 0.72, and 0.00 kcal/mol for the TBCC, TBC and BCB conformations at −146.1 °C, respectively, based on the experimental areas at this temperature. The experimental spectra neither confirm nor disprove the presence of the TBC conformation. Populations at −171.1 °C can be estimated as 2.7 and 97.3% by assuming that only the TBCC and the BCB conformations are present, separated by a constant free-energy difference of 0.73 kcal/mol. If equal amounts of the TBC and the TBCC are assumed, each separated from the BCB by a constant free-energy difference of 0.72 kcal/mol, then populations of 2.6, 2.6, and 94.7% would be predicted for −171.1 °C. On the basis of the contribution of Rln2 to the entropy of **1b** and **1c**, as a consequence of the presence of D and L forms, the free energy of either of these conformations would be expected to rise, relative to **1a**, as the temperature is lowered, and this effect is seen in the MM3 calculations of Table 2. However, the Gaussian 94 calculations (Table 3) do not include the Rln2 entropy term for **1b** or **1c**, resulting in calculated changes in relative free energies from +25 to −171.1 °C that are smaller than expected for **1a** and **1b** or for **1a** and **1c**. The free-energy difference between **1a** and **1b** would actually be expected to

Table 2. Relative Strain Energies,[a] Relative Free Energies, and Populations of Different Conformations of Cyclodecane, Calculated Using Allinger's MM3 Program[b]

		25 °C		−171.1 °C	
con-former	relative strain energies (kcal/mol)	relative free energies (kcal/mol)	popula-tions	relative free energies (kcal/mol)	popula-tions
1a	0.000	0.828	0.136	0.427	0.108
1b	0.930	0.000	0.546	0.000	0.885
1c	1.389	1.303	0.061	1.231	0.004
1d	2.079	1.007	0.100	1.315	0.002
1e	2.194	1.308	0.060	1.138	0.004
1f	2.890	1.196	0.073	1.585	0.000
1g	3.013	2.683	0.006	2.245	
1h	3.997	2.511	0.008	2.851	
1i	4.333	4.044	0.001	4.159	
1j	4.382	2.971	0.004	3.262	
1k	4.963	3.291	0.002	3.440	
1l	5.089	2.920	0.004	3.583	

[a] Previously calculated in ref 16. [b] Conformations are numbered according to increasing strain energy.

Table 3. Relative Free Energies of Cyclodecane Conformations from ab Initio Calculations at the HF/6-31G* and HF/6-311G* Levels[a]

	HF/6-31G*		HF/6-311G*	
conformer	relative free energies[b] at 25 °C	relative free energies at −171.1 °C	relative free energies at 25 °C	relative free energies at −171.1 °C
1a	0.000	0.000	0.000	0.000
1b	0.678	0.810	0.781	0.915
1c	0.767	0.819	0.815	0.868
1d	2.020	2.181	2.088	2.243
1e	2.120	2.319	2.204	2.395

[a] Conformations are numbered as in Figure 1. [b] Kcal/mol.

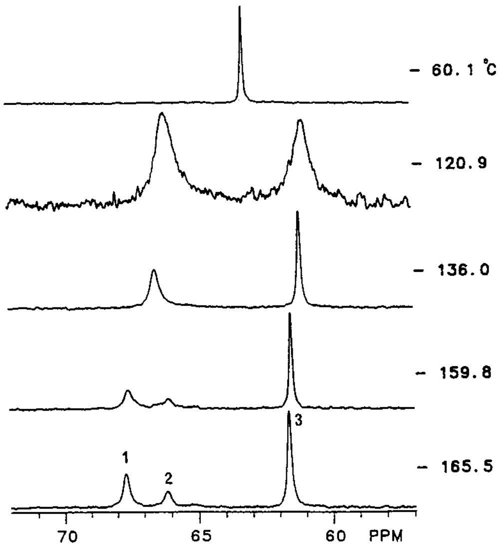

Figure 3. Low-temperature ^{13}C NMR spectra of the substituted ring carbon of chlorocyclodecane.

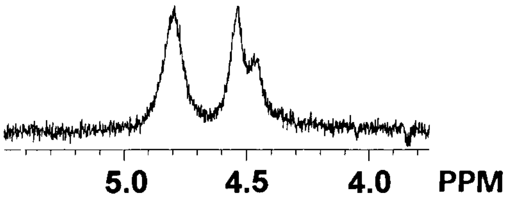

Figure 4. ^1H NMR spectrum of the methine proton of chlorocyclodecane at −165.5 °C, with decoupling of the adjacent protons.

increase slightly as the temperature is lowered to −171.1 °C from −146.1 °C.

Calculated chemical shifts for the five types of carbons of **1b** and six kinds of carbons for **1c** are given in Table 1. The average shifts for **1b** and **1c** are 24.0 and 23.9 ppm, respectively, and the experimental averaged shift of the minor conformation is 25.1 ppm at −146.1 °C. The calculated ^{13}C shifts of **1b** suggest that it should be possible to see at least some of its five peaks in the presence of **1a** if the signal-to-noise ratio is high enough and if slow exchange can be reached. These conditions were probably not met in an earlier ^{13}C NMR study[15] of cyclodecane, resulting in the conclusion[15] that only the BCB conformation is populated for **1**.

The ^{13}C NMR spectrum of chlorocyclodecane at −60.1 °C shows a single peak for the substituted carbon at δ 63.16, and by −120.9 °C the signal has decoalesced into two broad peaks at δ 60.95 and 66.12, with relative areas of 47.4 and 52.6%, respectively (Figure 3). By −165.5 °C, the signal at higher frequency has split into two peaks. The three chemical shifts at this temperature are δ 67.67, 66.14, and 61.63, and the populations are 31.2, 14.9, and 53.9%, respectively. The ^1H NMR spectrum of the methine proton, with decoupling of the adjacent hydrogens, also shows three peaks (Figure 4).

For cyclodecane, exchange between the BCB and the TBCC conformations first slowed as the temperature was lowered, followed by slowing of the exchange of the BCB carbon positions and then the TBCC carbon positons. The results for **2** show some similarity to **1** and are best interpreted in terms of a mixture of two BCB conformations, assigned to peaks 1 and 2 at −165.5 °C, and a TBCC conformation absorbing at the lowest frequency (peak no. 3).

Free-energy calculations for the possible BCB, TBCC, and TBC conformations of chlorocyclodecane using the MM3 program are summarized in Table 4. The TBC conformations are of higher energy and are not considered further here. Chemical shifts calculated for the substituted carbon of the BCB and the TBCC conformations of **2** (Table 5) provide support for the assignment of BCB conformations to peaks 1 and 2, since the calculated TBCC chemical shifts are all at substantially lower frequency than those found experimentally for peak no. 1. Assignment of peaks 1 and 2 to the 2e and 2a BCB conformations, respectively, gives the best match of calculated and experimental chemical shifts. However, axial hydrogens generally absorb at lower frequency than equatorial hydrogens,[26] and on this basis the chemical shifts of Figure 4 would predict the reverse assignments for peaks 1 and 2 of Figure 3. Of the two crystalline monosubstituted cyclodecanes studied by X-ray crystallography, cyclodecanol was found[27] to have the OH group in the 2e position of the BCB ring, and the NH_3^+ group of

Table 4. Relative Free Energies of the BCB, TBCC, and TBC Conformations of Chlorocyclodecane at −165.5 °C from MM3

relative free energies (kcal/mole)	BCB substituent position	TBCC substituent position	TBC substituent position
0.000		2a	
0.018		2e	
0.316		3e	
0.396	2e		
0.443	3e		
0.512	2a		
0.562	1e		
1.040		1e	
1.146		5e	
1.159			6
1.307		4e	
1.576			2e
1.727			3e
1.965			4e
1.985			5e
2.038			1
2.073			3a
2.319		5a	
6.436	1a		
8.016		1a	
8.219		4a	
8.987			2a
9.722		3a	
9.842			5a
11.358	3a		
12.127			4a

Table 5. ^{13}C NMR Chemical Shifts of the Substituted Ring Carbon of Chlorocyclodecane from ab Initio Calculations at the HF/6-311G* Level, Using the GIAO Method[a]

BCB substituent positions	chemical shifts (ppm, δ)	TBCC substituent positions	chemical shifts (ppm, δ)
1e	58.20	1a	60.50
2a	62.57	1e	56.81
2e	64.06	2e	61.64
3e	57.70	2a	61.87
		3e	62.83
		3a	61.53
		4e	57.97
		4a	61.01
		5e	62.04
		5a	62.25

[a] Ring carbons are numbered as in Figure 1.

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(26) Jensen, F. R.; Bushweller, C. H.; Beck, B. H. *J. Am. Chem. Soc.* **1969**, *91*, 344.

(27) Valente, E. J.; Pawar, D. M.; Noe, E. A. *Acta Crystallogr., Section C*, in press.

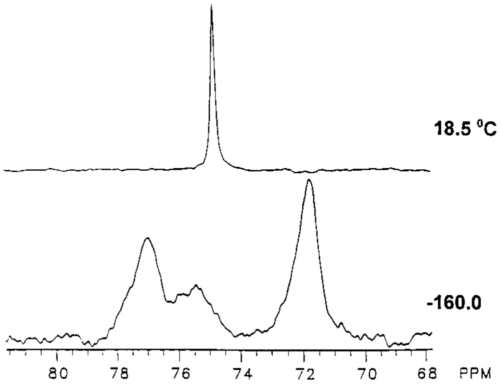

Figure 5. ^{13}C NMR spectra of cyclodecyl acetate.

cyclodecylamine hydrochloride sesquihydrate[28] was located at position 3e of the BCB. *trans*-1,6-Disubstituted cyclodecanes with both groups in the 3e,[29] 2e,[30,31] or 2a[29,32] positions of the BCB conformation are also known, but no examples of substitution at position 1e have been reported. The possibility that peak 1 or 2 of Figure 3 is associated with the 3e BCB is not excluded, but the calculated chemical shifts of Table 5 are in better agreement with the proposed assignments for this compound. The small calculated differences in free energies for several conformations of BCB and TBCC cyclodecane suggest the possibility that the positions occupied could change, depending on the group attached to the ring.

From the free energies of Table 4, the 2a and all of the conformations with the chlorine equatorial are possible for the TBCC conformation of **2**. The calculated chemical shifts for the 1e- and 4e-substituted conformations make these conformations less likely, but there is no firm basis to decide among the remaining four possibilities.

At −159.8 °C, exchange of the TBCC conformation of **2** with the BCB conformations is slow on the NMR time scale, and free-energy barriers of 5.4 ± 0.2 and 5.5 ± 0.2 kcal/mol for interconversion of 2a and 2e BCB chlorocyclodecane were calculated from the rate constants of 85.0 and 59.1 s^{-1}, which were obtained from complete line shape matching of this part of the spectrum. The similarity of these barriers to the barrier for exchange of 2a and 2e positions of 1,1-difluorocyclodecane (5.7 kcal/mol) provides some support for assignment of peaks 1 and 2 of the chloride to BCB conformations. By −120.9 °C, the BCB conformations of **2** are exchanging rapidly, and free-energy barriers of 7.07 ± 0.2 and 7.08 ± 0.2 kcal/mol were calculated from the rate constants of 220 and 211 s^{-1} for interconversion of BCB and TBCC conformations. The ^{13}C NMR spectrum (Figure 5) of the substituted ring carbon of cyclodecyl acetate at −160.0 °C shows a pattern of chemical shifts and intensities similar to that of **2**, although the signals are probably exchange-broadened, and three conformations are also populated for **3**.

Conclusions

The only observable ^{13}C peaks for cyclodecane at −171.1 °C were for the BCB conformation (**1a**), which can be identified by the 2:2:1 ratio of the areas for the three peaks. At temperatures between −131.0 and −154.0 °C, a peak for a minor conformation was visible and was assigned to the TBCC conformation on the basis of free energies estimated from MM3 and ab initio calculations, in addition to a consideration of the likely pathway for exchange of carbon positions in the BCB conformation. Because this exchange probably occurs by way of the TBC conformation, a small amount of the TBC, if present, would not be detected in the low-temperature ^{13}C NMR spectra. The free energy of **1b** relative to that of **1a** was found experimentally to be 0.73 kcal/mol at −146.1 °C, with the assumption that only these two conformations are present. If we assume equal amounts of **1b** and **1c**, the free-energy difference between **1a** and **1b** changes only slightly, to 0.72 kcal/mol.

Chlorocyclodecane (**2**) was found to have three conformations at −165.1 °C, with populations of 31.2, 14.9, and 53.9%. The major conformation (peak number 3 for the methine carbon of the slow-exchange ^{13}C NMR spectrum of Figure 3) was assigned to the TBCC ring conformation, and peaks 1 and 2 were assigned to BCB conformations, based on several considerations including the following: (1) The free-energy barriers of 5.4 and 5.5 kcal/mol separating the conformations associated with peaks 1 and 2 were close to the free-energy barrier of 5.7 kcal/mol for 1,1-difluorocyclodecane, which was assigned a BCB conformation.[13] If peaks 1 and 2 represented TBCC conformations, then lower barriers would have been expected, based on the results for cyclodecane. (2) The TBC conformations of **2** were calculated by MM3 to have free energies higher than those for the favorable TBCC or BCB conformations. (3) The chemical shifts for peaks 1 and 2 of **2** were at high frequency (δ 67.67 and 66.14). The chemical shift at the highest frequency calculated for this carbon was δ 64.06 for the 2e BCB conformation, which was then assigned to peak no. 1. The closest calculated chemical shift remaining for peak no. 2 of BCB **2** was at δ 62.57 for the 2a BCB conformation. However, as noted above, the experimental ^{1}H shifts of Figure 4 suggest the reverse assignments for peaks 1 and 2 of Figure 3.

The MM3 calculations indicate that a large number of TBCC and BCB conformations of **2** are of low energy, and other substituted cyclodecanes may have different conformational preferences, although the low-temperature spectra of cyclodecyl acetate (**3**) suggested an equilibrium for this compound similar to that of the chloride.

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