JOC*Article*

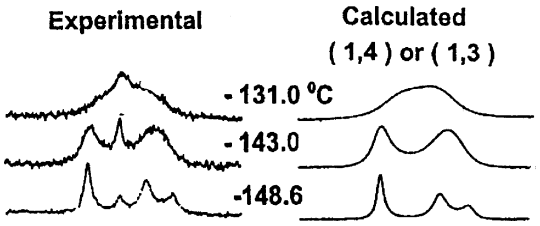
Interconversion of Carbon Sites in Boat-Chair-Boat Cyclodecane; Conformations of Chlorocyclodecane and Cyclodecyl Acetate

Diwakar M. Pawar,[†] Dalephine Cain,[†] Gurvinder Gill,[†] Alex D. Bain,[‡] Richard H. Sullivan,[†] and Eric A. Noe*[,†]

Department of Chemistry, Jackson State University, Jackson, Mississippi 39217-0510, and Department of Chemistry, McMaster University, Hamilton, ON, Canada L8S 4M1

ean12001@yahoo.com

Received June 16, 2006



Interconversion of carbon sites in boat-chair-boat (BCB) cyclodecane occurs by way of the twist-boat-chair (TBC) conformation, which predicts that C-1 exchanges with C-4, etc. The previously obtained low-temperature ^{13}C spectra could be matched by assuming (1,4) or (1,3) exchange, but not (1,2) exchange. A free-energy barrier of 5.54 kcal/mol was obtained for conversion of BCB to TBC at −137.4 °C. The major conformation of chlorocyclodecane and cyclodecyl acetate is assigned to the IIIe BCB.

Introduction

The major conformation of cyclodecane (**1**) at low-temperatures was found in a dynamic NMR study[1] to be the boat-chair-boat (BCB, **1a**), which corresponds to the rectangular diamond-lattice [2323] conformation according to Dale's nomenclature.[2]

The BCB (Figure 1) is the solid-state conformation of **1**[3] and the ring conformation of most of its solid derivatives.[4] This conformation has C_{2h} symmetry, resulting in three types of carbons in a ratio of 4:4:2; the plane of symmetry passes through the type I carbons, and the perpendicular axis bisects the bonds connecting the type III carbons.

A different view of **1a** is shown in Figure 2, which shows the first six conformers of **1** arranged in increasing order of MM3 strain energies.[5] Several percent of a second conformation, suggested to be the twist-boat-chair-chair (TBCC, **1b**) was also found,[1] and calculations at the HF/6-311G* level predicted[1] free energies of 0.915 and 0.868 kcal/mol for the TBCC and the twist-boat-chair (TBC, **1c**) conformations at −171.1 °C, relative to **1a**.

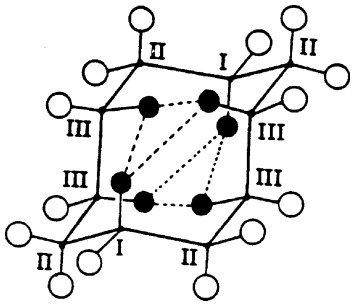


FIGURE 1. Boat−chair−boat cyclodecane (**1a**) showing extraannular (○) and intraannular (●) positions

Calculations for **1** using molecular mechanics (MM4) and ab initio calculations at the MP2/6-311+G* level (Table 1) predicted that the four lowest-energy conformers are within a 0.6 kcal/mol range in relative free energy at 25 °C.[6]

The ^{13}C NMR spectrum of cyclodecane shows three peaks at −171.1 °C for the three types of carbons (δ 28.4, 22.4 and

[†] Jackson State University.
[‡] McMaster University.

(1) Pawar, D. M.; Smith, S. V.; Mark, H. L.; Odom, R. M.; Noe, E. A. *J. Am. Chem. Soc.* **1998**, *120*, 10715.
(2) (a) Dale, J. *Acta Chem. Scand.* **1973**, *27*, 1130−1148. (b) Dale, J. *Stereochemistry and Conformational Analysis*; Verlag Chemie : New York, 1978.
(3) Shenhav, H.; Schaeffer, R. *Crystallogr. Struct. Commun.* **1981**, *10*, 1181.
(4) Dunitz, J. D. In *Perspectives in Structral Chemistry*; Dunitz, J. D., Ibers, J. A., Ed.; Wiley: New York, 1968; Vol. II.
(5) Saunders, M. J. *Comput. Chem.* **1991**, *12*, 645.
(6) Wiberg, K. B. *J. Org. Chem.* **2003**, *68*, 9322.

10.1021/jo061245i CCC: $37.00
Published on Web 12/05/2006

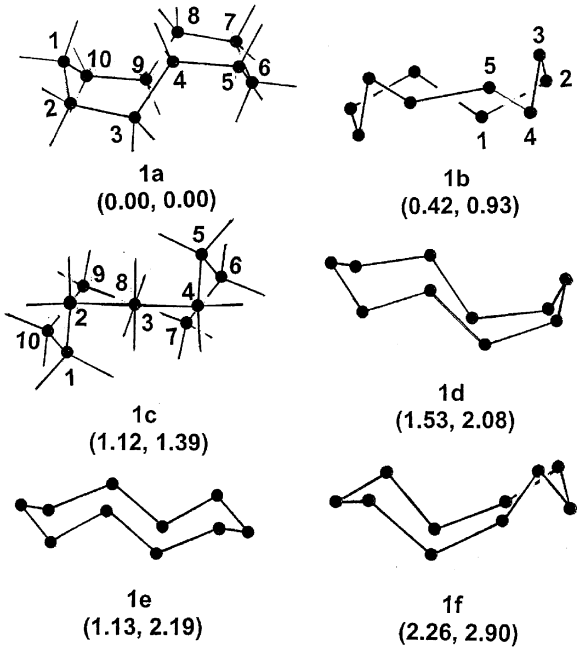


FIGURE 2. Low-energy conformations of cyclodecane. The numbers in parentheses are MM2 and MM3 strain energies calculated by Saunders.[5]

TABLE 1. Calculated Relative Energies for Conformations of Cyclodecane.[6]

		MP2/6-311+G*			MM4
conformer	symmetry	$H(0)_{rel}$[a]	G_{rel}[b]	population[b]	population[b]
1a (BCB)	C_{2h}	0.0	0.0	0.21	0.21
1b (TBCC)	C_2	0.4	−0.2	0.23	0.24
1c (TBC)	C_2	0.7	0.1	0.20	0.15
1d (BCC)	C_1	1.6	0.4	0.17	0.16
1e (CCC)	C_{2h}	1.6	1.3	0.10	0.13
1f	C_1	2.4	1.1	0.11	0.11

[a] $H(0)_{rel} = G_{rel}$ at 0 K. [b] G_{rel} and populations were calculated at 298 K.

19.2),[1] and assignments were made[1] on the basis of intensities and calculated chemical shifts. The corner carbons[2] (type II, Figure 1) absorb at lowest field, as found in other rings,[7] and the type I carbons absorb at highest field. The Ia and IIIa hydrogens of **1a** form two sets of three hydrogens which have substantial nonbonded interactions. These positions will be avoided by substituents larger than hydrogen, and the ^{19}F NMR spectrum of 1,1-difluorocyclodecane showed only a single AB quartet at low temperature,[9] which was consistent with a BCB conformation with fluorines at positions IIe and IIa. A free-energy barrier of 5.7 kcal/mol was found[9] for exchange of fluorine sites. An ^1H NMR study[8] of cyclodecane showed three broad peaks at −162 °C; no discussion of conformations was made, but an approximate barrier of 6 kcal/mol was obtained by an unspecified method. A detailed ^1H or ^{13}C dynamic NMR study of interconversion of sites in BCB cyclodecane has not yet been described.

In this work, the previously reported[1] low-temperature ^{13}C NMR spectra of **1** were used to obtain information about the pathway and barrier for exchange of carbon sites in **1a**. Also, the conformational assignment for the major conformation of chlorocyclodecane (**2**) is revised from TBCC to IIIe BCB, and a similar reassignment is made for cyclodecyl acetate (**3**).

Discussion

Because **1a** has perpendicular symmetry elements of opposite types (plane through atoms and axis through bonds), BCB cyclodecane pseudorotates with itself as a pseudorotation partner,[10] although the long chair conformation is an intermediate. This process would equilibrate the three types of carbons but is estimated to have a high barrier (24.6 kcal/mol).[10] Dale[2] and others[11,12] have noted that interconversion of BCB sites can be accomplished by exchange with the twist-boat-chair (TBC) conformation; in this process, the dihedral angle for a bond between a type II and type III carbon in **1a** goes to zero and then changes sign, leading to the TBC conformation. A similar process for the bond which is opposite the one that was changed then leads to a BCB conformation which has carbon 1 of the original conformation now occupying position 4. Repeated exchanges of this type result in complete equilibration of carbon sites, as shown in Scheme 1.[12]

SCHEME 1

BCB-1e ⇌ TBC'-2e ⇌ BCB-4e ⇌ TBC'-5e ⇌ BCB-7e⇌ TBC'-8⇌BCB-10a ⇌ TBC'-1a ⇌ BCB-3a ⇌ TBC'-4a ⇌ BCB-6a ⇌TBC'-7a ⇌BCB-9a⇌TBC'-10a ⇌BCB-2a ⇌ TBC'-3 ⇌ BCB-5e ⇌TBC'-6e ⇌BCB-8e ⇌TBC'-9e ⇌ BCB-1e ⇌ TBC'-2e ⇌ etc.

The permutation scheme for this process (1,4 exchange) for calculation of ^{13}C line shapes is shown below in Table 2, along with the corresponding schemes for (1,3) and (1,2) exchange.

Because the line shape program used initially in this work (gNMR)[13] could not accommodate 10 spins, and because the sequence of exchanges between types of carbons repeats after the first five, an approximate treatment using only five carbons was used. The simplified permutation schemes which were used are also shown in Table 2. Either (1,4) or (1,3) exchange gives the line shapes shown in Figure 3, which reproduce the general features of the BCB spectra. An additional peak near δ 25 in the experimental spectra is due to the TBCC conformation, which is not included in the calculations. The (1,2) exchange gives very different line shapes (Figure 3).

The rate constants used in the gNMR program and the associated free-energy barriers for the BCB to BCB conversions are summarized in Table 3. Because the intermediate TBC conformation can either go back to the original BCB or on to the next BCB conformation, the rate constants for the BCB to TBC conversion should be twice the values for BCB to BCB. The BCB → TBC rate constants and barriers are also shown in Table 3. At the lowest three temperatures in Table 3, the

(7) Cyclononane: Anet, F. A. L.; Krane, J. *Isr. J. Chem*. **1980**, *20*, 72. See also ref 8 (cyclododecane).
(8) Anet, F. A. L.; Cheng, A. K.; Wagner, J. J. *J. Am. Chem. Soc.* **1972**, *94*, 9250.
(9) Noe, E. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 2020.
(10) Hendrickson, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 7047.
(11) Kolossvary, I.; Guida, W. C. *J. Am. Chem. Soc.* **1993**, *115*, 2107.
(12) Cheng, A. K.-T. Doctoral thesis, University of California, Los Angeles, 1973.
(13) The gNMR program can be purchased from Cherwell Scientific Publishing Limited, Oxford, Great Britain.

TABLE 2. Permutation Schemes for Exchange of Carbon Sites in BCB Cyclodecane

full			simplified		
(1,4)	(1,3)	(1,2)	(1,4)	(1,3)	(1,2)
1,I → 4,III	1,I → 3,III	1,I → 2,II	1,I → 4,III	1,I → 3,III	1,I → 2,II
2,II → 5,II	2,II → 4,III	2,II → 3,III	2,II → 5,II	2,II → 4,III	2,II → 3,III
3,III → 6,I	3,III → 5,II	3,III → 4,III	3,III → 1,I	3,III → 5,II	3,III → 4,III
4,III → 7,II	4,III → 6,I	4,III → 5,II	4,III → 2,II	4,III → 1,I	4,III → 5,II
5,II → 8,III	5,II → 7,II	5,II → 6,I	5,II → 3,III	5,II → 2,II	5,II → 1,I
6,I → 9,III	6,I → 8,III	6,I → 7,II			
7,II → 10,II	7,II → 9,III	7,II → 8,III			
8,III → 1,I	8,III → 10,II	8,III → 9,III			
9,III → 2,II	9,III → 1,I	9,III → 10,II			
10,II → 3,III	10,II → 2,II	10,II → 1,I			

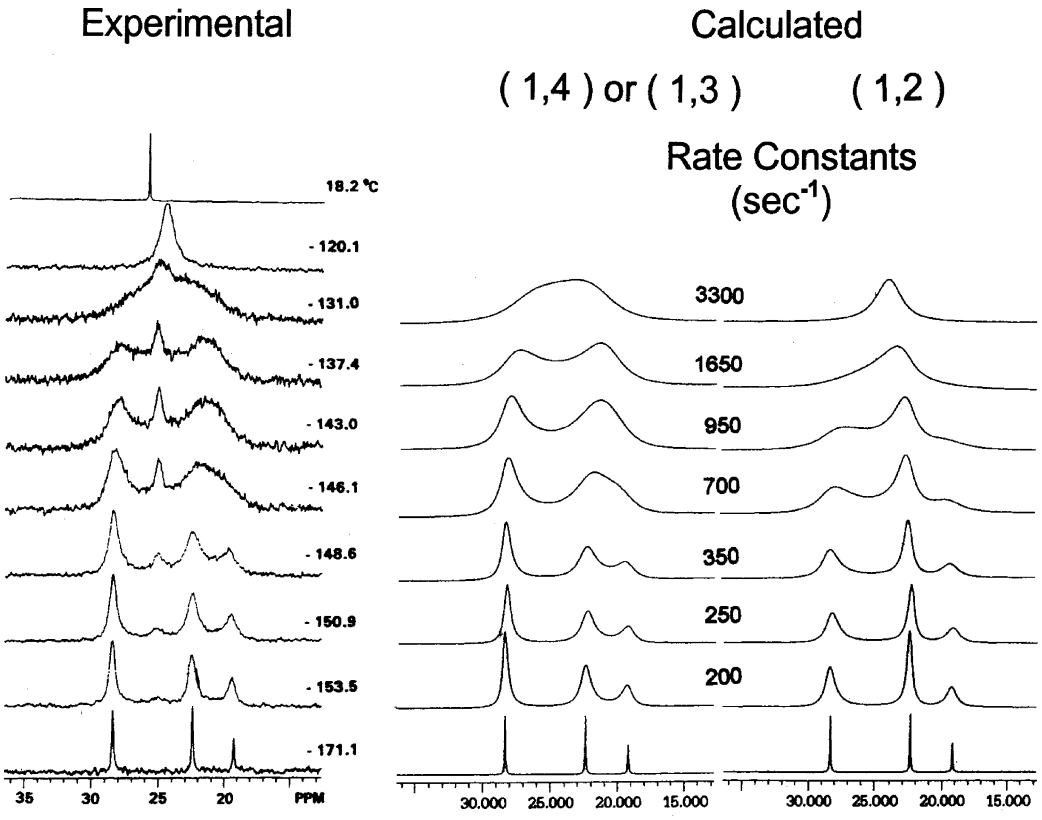


FIGURE 3. Experimental[1] and calculated line shapes for the carbons of cyclodecane (**1**) at several temperatures. The rate constants are for BCB → BCB.

TABLE 3. Rate Constants and Free-Energy Barriers for Interconversion of Carbon Sites in BCB Cyclodecane and for the BCB to TBC Conversion

	BCB → BCB		BCB → TBC	
T (°C)	rate constant (s^{-1})	free-energy barrier (kcal/mol)	rate constant (s^{-1})	free-energy barrier (kcal/mol)
−131.0	3300	5.82	6600	5.62
−137.4	1650	5.73	3300	5.54
−143.0	950	5.63	1900	5.45
−146.1	700	5.56	1400	5.39
−148.6	(350)	(5.62)	(700)	(5.45)
−150.9	(250)	(5.59)	(500)	(5.42)
−153.5	(200)	(5.52)	(400)	(5.36)

calculated line shapes for the middle and upfield BCB peaks were broader than in the experimental spectra, and the rate constants and barriers for these temperatures are considered to be less reliable. The greater broadening of the BCB peak at lowest field relative to the other two peaks, in comparison to predictions based on the calculated line shapes, may be due to the assumption in the calculations of a zero population for TBC, while the calculated energies[6] suggest the possibility of small populations for the TBC. The average of the remaining four barriers for BCB to BCB conversions (5.69 kcal/mol) is close to the value of 5.7 kcal/mol for 1,1-difluorocyclodecane.[8] Kolossvary and Guida,[11] in their extensive study by MM2 of the conformational interconversions of cyclodecane, concluded that, within their barrier window of 12 kcal/mol, the BCB equilibrated directly only with the TBC. The authors refer to the mode of the conversion as K3-kayaking[11] and calculated a steric barrier of 6.37 kcal/mol for conversion of BCB to TBC. Wiberg[6] calculated a free-energy barrier of 5.5 kcal/mol for this process, in good agreement with our experimental value of 5.54 kcal/mol at −137.4 °C.

The total line shape simulation calculations for **1a** were repeated with the MEXICO program,[14] which was modified to

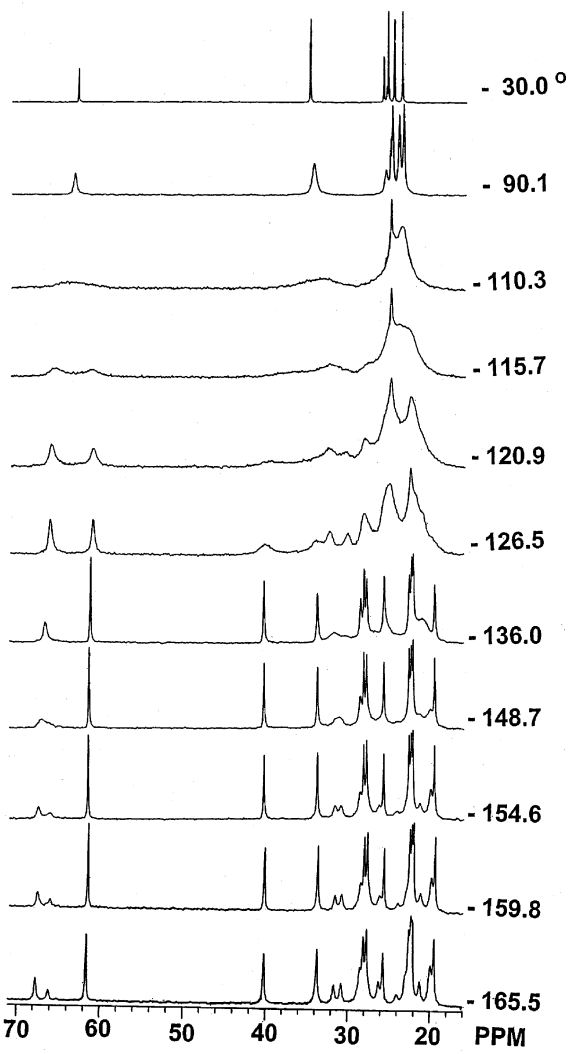


FIGURE 4. Low-temperature ^{13}C NMR spectra of chlorocyclodecane (**2**). A small impurity peak is apparent in some of the spectra and appears at δ 25.5 for −110.3 °C.

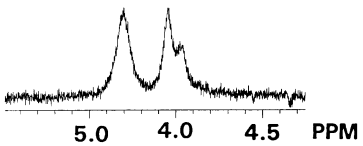


FIGURE 5. ^{1}H NMR spectrum of the methine proton of chlorocyclodecane at −165.5 °C with decoupling of adjadent protons.[1]

handle 10 spins. The line shapes from MEXICO using either 10 spins or the five-carbon approximation were indistinguishable from those of gNMR if the rate constants used were half the gNMR values. The factor of 2 may result from the MEXICO program's consideration of exchange with BCB conformations on either side of a given conformation.

From the line width of the TBCC peak at −131.0 °C (ca. 90 Hz),[15] a rate constant of 268 s^{-1} was estimated by subtracting the TMS line width (4.6 Hz) and multiplying by π. From this rate constant, a rough estimate of 6.5 kcal/mol was made for

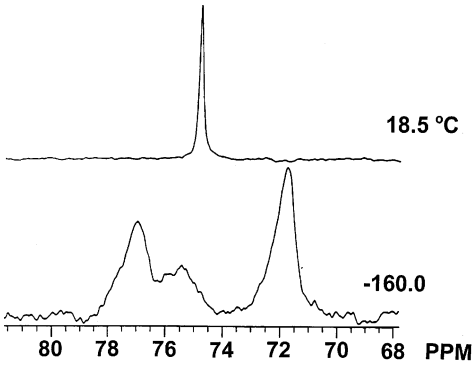


FIGURE 6. ^{13}C NMR spectra of the substituted carbon of cyclodecyl acetate (**3**).

the TBCC → BCB free-energy barrier. The populations at −131.0 °C (0.092 and 0.908) were used to estimate the rate constant and free-energy barrier for the reverse process (27.2 s^{-1} and 7.2 kcal/mol). As noted above, BCB should directly exchange only with the TBC according to the MM2 calculations of Kolossvary and Guida,[11] and the TBCC is expected to interconvert with the BCB by way of the TBC. These authors[11] show only three MSM (minimum−saddle point−minimum) triads including the TBC (numbers 14, 16, and 18 of their Table 2). Number 14 is the above-mentioned interconversion with BCB, and number 16 is for the conversion of TBC to conformation number 10 (in order of increasing MM2 steric energy), which has no further connections. Number 18 is for the TBCC to TBC conversion, and a steric barrier of 7.18 kcal/mol was predicted for this process; this will also be the overall barrier for the changing of TBCC into BCB. The steric barriers[11] for the BCB → TBC and TBCC → → BCB conversions are somewhat larger than the experimental free-energy barriers at low temperatures, but experiment and calculations both indicate a larger barrier for the latter process.

The ^{13}C NMR spectrum[16] of chlorocyclodecane (**2**, Figure 4) at −165.5 °C showed three peaks at δ 67.67, 66.14, and 61.63 for the carbon bonded to chlorine, which corresponded to three conformations, **2a**,**b**,**c**, with populations of 31.2, 14.9, and 53.9%, respectively. The two peaks at lowest field were assigned to the BCB IIe and IIa conformations, in part on the basis of calculated ^{13}C chemical shifts and MM3 free energies. This assignment is consistent with the expectation that corner carbons should absorb at lower field than non-corner carbons. They are interconverted with free-energy barriers of 5.4 and 5.5 kcal/mol, which are close to the free-energy barrier for BCB cyclodecane. The free-energy barriers to interconversion of (**2a** and **2b**) with **2c** were 7.07 and 7.08 kcal/mol, and partly based on these higher barriers, **2c** was suggested[1] to be a TBCC conformation. However, exchange of the IIe and IIa positions of **2** occurs by way of TBC conformations with chlorine replacing an isoclinal hydrogen of **1** (carbons 3 or 8 of TBC, Scheme 1), while exchange to give the IIIe conformation occurs by way of other TBC conformations (5e or 6e, Scheme 1), and there may also be higher barriers for the latter conversions. Thus, the larger barriers associated with **2c** do not necessarily indicate a different ring conformation.

(14) The MEXICO Suite of programs for NMR chemical exchange line shape calculation is available from Dr. Alex Bain at McMaster University.

(15) A linewidth of 47 Hz previously reported[1] was obtained by computer matching and is too low.

(16) Previously, only the spectra of the substituted carbon were considered. Full spectra which provide additional information are shown in Figure 4.

If **2c** is the IIIe BCB conformation, then equilibration of C_2 and C_{10}, etc. of **2c** can also take place by way of the itinerary of Scheme 1, although different parts are involved than for **2a** ⇌ **2b** or **2c** ⇌ (**2a** + **2b**). Equilibration of these pairs of CH_2 carbons of **2c** can take place by way of the plane-symmetrical BCB Ie conformation (BCB 1e in Scheme 1), which is connected to BCB IIIe through the 2e or 9e TBC conformation. The full low-temperature ^{13}C NMR spectra of **2** (Figure 4, −126.5 and −136.0 °C) show that all 10 peaks of the major conformation are visible by −136.0 °C. The line shape changes in this temperature region indicate that the barriers to equilibration of CH_2 carbons in **2c** are similar to the barriers to equilibration of **2c** with (**2a** + **2b**), although these barriers should not be identical, as discussed above. If the ring conformation of **2c** is TBCC, then the type of process for TBCC → → BCB could be different than for equilibration of pairs of CH_2 carbons, which can occur by pseudorotation with the BCC. The barrier to pseudorotation in unsubstituted TBCC cyclodecane is low, as implied by the low-temperature ^{13}C spectra[1] and calculated by Kolossvary and Guida,[17] but higher barriers could exist for this ring conformation of **2**. The line shapes for **2** at low temperatures could be interpreted in terms of BCB IIIe for **2c**, but a TBCC conformation cannot be ruled out on this basis. Additional support for BCB IIIe comes from the observation that monosubstituted cyclodecanes have not been observed in the solid state to have TBCC conformations, while solid cyclodecanol[18] and cyclodecylamine hydrochloride sesquihydrate[19] have been shown by X-ray crystallography to have the substituents in IIe and IIIe positions of the BCB, respectively. Similarly, in cyclodecyl-4-nitrophenylacetate, the 4-nitrophenylacetoxy group was recently found to occupy the IIIe position.[20]

These assignments for **2** imply that the methine hydrogen chemical shifts[1] (Figure 5) of this compound for **2c**, **2a**, and **2b** are about δ 4.7, 4.55, and 4.45, based on intensities, and correspond to hydrogens in the IIIa, IIa, and IIe positions, respectively.

The low-temperature ^{13}C NMR spectrum[1] in Figure 6 of the substituted carbon for cyclodecyl acetate (**3**) at −160.0 °C resembles the slow-exchange spectrum of chlorocyclodecane. At this temperature, the ^{13}C NMR spectrum of an 8% solution of cyclodecyl acetate in 2:1:1 $CHClF_2/CHCl_2F/CF_2Cl_2$ showed three peaks at δ 77.5, 76.0, and 72.3, corresponding to the IIe, IIa, and IIIe BCB conformations. The populations were determined to be 28.6%, 20.2%, and 51.2%, respectively.

(17) Steric barriers of 5.42 and 4.31 kcal/mol were calculated for interconversion of TBCC and TBC conformations.

(18) Valente, E. J.; Pawar, D. M.; Noe, E. A. *Acta Crystallogr., Sect. C* **1998**, *C54*, 1302.

(19) (a) Nowacki, W.; Mladeck, M. H. *Chimia* **1961**, *15*, 531. (b) Mladeck, M. H.; Nowacki, W. *Helv. Chim. Acta* **1964**, *47*, 1280.

(20) Fronczek, F.; Brown, J.; Pawar, D. M.; Noe, E. A. *Acta Crystallogr., Sect. C* **2006**, *C62*, o628.

Conclusions

Low-temperature ^{13}C NMR spectra of BCB cyclodecane taken previously[1] were matched by calculated spectra with the assumption of (1,4) exchange, in which a carbon moves from position 1 of the BCB to position 4, etc. Indistinguishable line shapes could also be obtained with (1,3) exchange, but this possibility could be eliminated on the basis of the following three points: (1) Kolossvary and Guida[11] concluded from their comprehensive study of interconversion of cyclodecane conformations that, within their barrier window of 12 kcal/mol, BCB cyclodecane exchanges only with the TBC. (2) Cheng's itinerary[12] for exchange of sites within the BCB and TBC (Scheme 1) shows that the exchange of BCB carbon positions is a (1,4) process. (3) Our free-energy barrier of 5.54 kcal/mol for the BCB to TBC conversion at −137.4 °C is in good agreement with Wiberg's free-energy barrier of 5.5 kcal/mol at 25 °C,[6] calculated at the MP2/6-311+G* level.

Small differences between the calculated and experimental ^{13}C spectra, which are noticeable at the lower temperatures may arise from the assumption for the calculated line shapes of a population of zero for the TBC.

The ^{13}C spectra of the substituted carbon of chlorocyclodecane showed peaks for three conformations (**2a**,**b**,**c**), which were suggested[1] to arise from the BCB IIe, BCB IIa, and a TBCC conformation. Corresponding assignments were suggested[1] for the three peaks of cyclodecyl acetate (3). In the present work, the major conformations (**2c** and **3c**) are revised from TBCC to BCB IIIe. Examination of the CH_2 region of the ^{13}C spectra of **2c** indicated a similar barrier for exchange of C_2 and C_{10}, etc., as for **2c** ⇌ (**2a** + **2b**), but a firm assignment for **2c** could not be made on this basis. Only BCB conformations have been found from X-ray studies of monosubstituted cyclodecanes (IIe for cyclodecanol[18] and IIIe for cyclodecylamine hydrochloride sesquihydrate[19]), and a BCB conformation is likely for **2c** and **3c**. An X-ray study of cyclodecyl 4-nitrophenylacetate, in which a methyl hydrogen of **3** is replaced by a 4-nitrophenyl group to produce a compound which is solid at room temperature, found the ring conformation to be BCB IIIe, which suggests that this will be the preferred conformation in solution, and by extension also for **2c** and **3c**.

Experimental Section and Calculations

Previously obtained low-temperature ^1H and ^{13}C NMR spectra were used[1] in this report. The NMR spectral simulations for exchange of carbon sites were done with PC versions of the gNMR[13] and MEXICO[14] programs.

Acknowledgment. We thank the National Science Foundation (NSF-CREST Grant No. HRD-9805465) for support of this work.

Supporting Information Available: Four expanded low-temperature ^{13}C NMR spectra of chlorocyclodecane. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061245I