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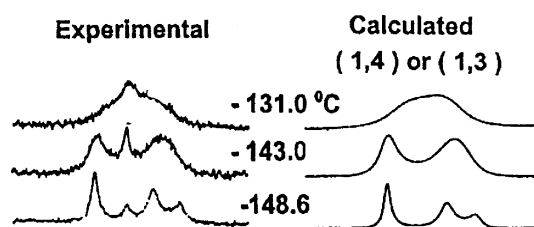
Interconversion of Carbon Sites in Boat-Chair-Boat Cyclodecane; Conformations of Chlorocyclodecane and Cyclodecyl Acetate

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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 $-137.4\text{ }^{\circ}\text{C}$. 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 study¹ 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,

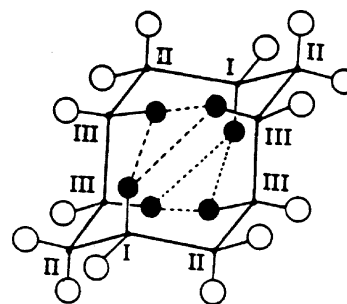


FIGURE 1. Boat-chair-boat cyclodecane (**1a**) showing extraannular (○) and intraannular (●) positions

suggested to be the twist-boat-chair-chair (TBCC, **1b**) was also found,¹ and calculations at the HF/6-311G* level predicted¹ free energies of 0.915 and 0.868 kcal/mol for the TBCC and the twist-boat-chair (TBC, **1c**) conformations at $-171.1\text{ }^{\circ}\text{C}$, relative to **1a**.

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 $25\text{ }^{\circ}\text{C}$.⁶

The ^{13}C NMR spectrum of cyclodecane shows three peaks at $-171.1\text{ }^{\circ}\text{C}$ for the three types of carbons (δ 28.4, 22.4 and

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(1) Pawar, D. M.; Smith, S. V.; Mark, H. L.; Odom, R. M.; Noe, E. A. *J. Am. Chem. Soc.* **1998**, *120*, 10715.

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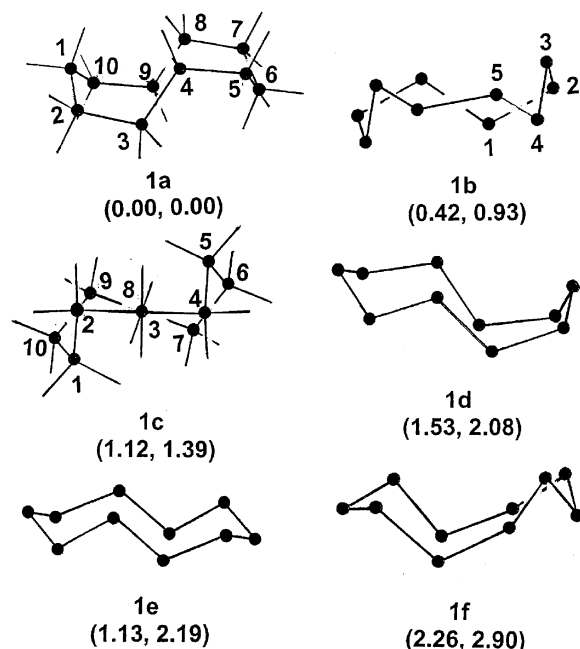


FIGURE 2. Low-energy conformations of cyclodecane. The numbers in parentheses are MM2 and MM3 strain energies calculated by Saunders.⁵

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

conformer	symmetry	MP2/6-311+G*			MM4
		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 made¹ on the basis of intensities and calculated chemical shifts. The corner carbons² (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 ¹⁹F 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 found⁹ for exchange of fluorine sites. An ¹H NMR study⁸ 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 ¹³C dynamic NMR study of interconversion of sites in BCB cyclodecane has not yet been described.

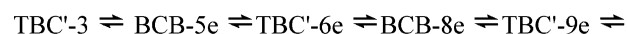
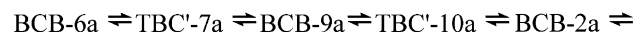
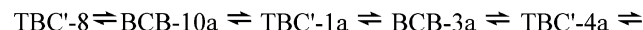
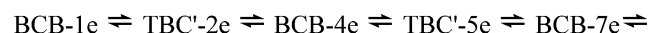
In this work, the previously reported¹ low-temperature ¹³C NMR spectra of **1** were used to obtain information about the

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 Dale² 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



The permutation scheme for this process (1,4 exchange) for calculation of ¹³C 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

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(13) The gNMR program can be purchased from Cherwell Scientific Publishing Limited, Oxford, Great Britain.

(7) Cyclononane: Anet, F. A. L.; Krane, J. *Isr. J. Chem.* **1980**, 20, 72. See also ref 8 (cyclododecane).

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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			

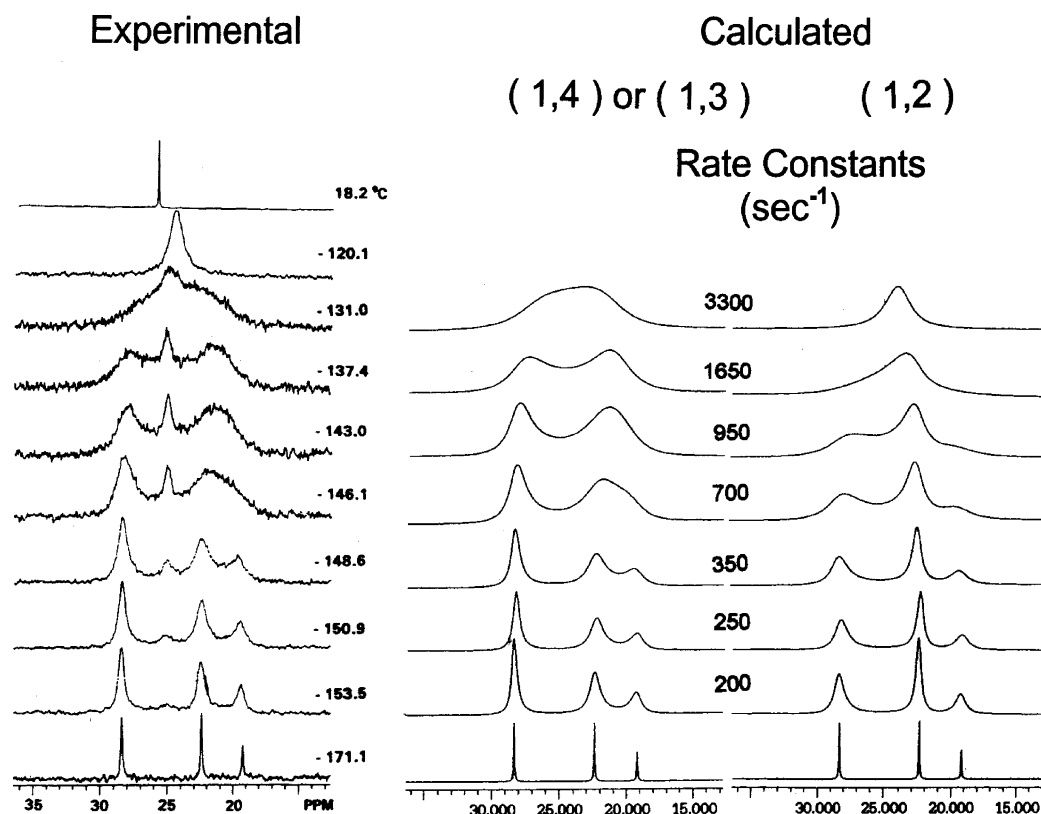
FIGURE 3. Experimental¹ and calculated line shapes for the carbons of cyclodecane (1) at several temperatures. The rate constants are for BCB → BCB.

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

<i>T</i> (°C)	BCB → BCB		BCB → TBC	
	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 energies⁶ 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-kayaking¹¹ and calculated a steric barrier of 6.37 kcal/mol for conversion of BCB to TBC. Wiberg⁶ 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

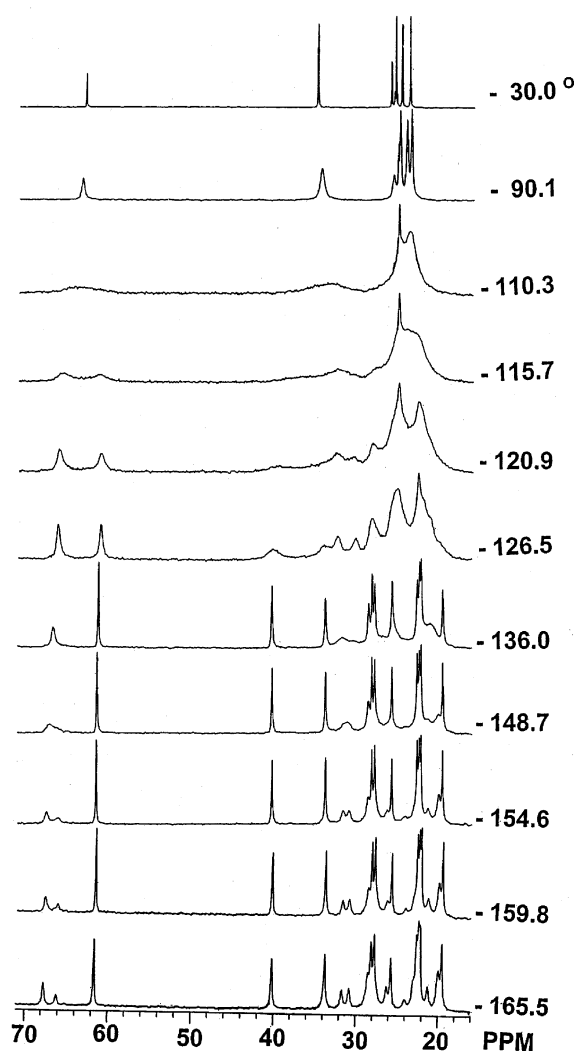


FIGURE 4. Low-temperature ^{13}C NMR spectra of chlorocyclodecane (2). A small impurity peak is apparent in some of the spectra and appears at δ 25.5 for -110.3°C .

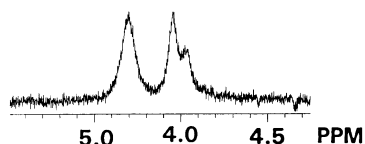


FIGURE 5. ^1H NMR spectrum of the methine proton of chlorocyclodecane at -165.5°C with decoupling of adjacent protons.¹

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

(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 reported¹ was obtained by computer matching and is too low.

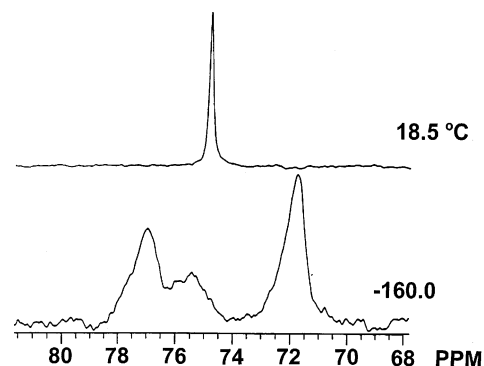


FIGURE 6. ^{13}C NMR spectra of the substituted carbon of cyclodecyl acetate (3).

the TBCC \rightarrow 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 authors¹¹ 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 barriers¹¹ for the BCB \rightarrow TBC and TBCC \rightarrow 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 spectrum¹⁶ 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 suggested¹ 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.

(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 C₂ and C₁₀, etc. of **2c** can also take place by way of the itinerary of Scheme 1, although different parts are involved than for **2a** \rightleftharpoons **2b** or **2c** \rightleftharpoons (**2a** + **2b**). Equilibration of these pairs of CH₂ carbons of **2c** can take place by way of the plane-symmetrical BCB Ie conformation (BCB Ie in Scheme 1), which is connected to BCB IIIe through the 2e or 9e TBC conformation. The full low-temperature ¹³C 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 CH₂ 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 \rightarrow BCB could be different than for equilibration of pairs of CH₂ 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 ¹³C spectra¹ 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 cyclodecanol¹⁸ and cyclodecylamine hydrochloride sesquihydrate¹⁹ 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-nitrophenylacetoxo group was recently found to occupy the IIIe position.²⁰

These assignments for **2** imply that the methine hydrogen chemical shifts¹ (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 ¹³C NMR spectrum¹ 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 ¹³C NMR spectrum of an 8% solution of cyclodecyl acetate in 2:1:1 CHClF₂/CHCl₂F/CF₂Cl₂ 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.

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Conclusions

Low-temperature ¹³C NMR spectra of BCB cyclodecane taken previously¹ 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 Guida¹¹ 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 itinerary¹² 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 ¹³C 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 ¹³C spectra of the substituted carbon of chlorocyclodecane showed peaks for three conformations (**2a,b,c**), which were suggested¹ to arise from the BCB IIe, BCB IIa, and a TBCC conformation. Corresponding assignments were suggested¹ 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 CH₂ region of the ¹³C spectra of **2c** indicated a similar barrier for exchange of C₂ and C₁₀, etc., as for **2c** \rightleftharpoons (**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 cyclodecanol¹⁸ and IIIe for cyclodecylamine hydrochloride sesquihydrate¹⁹), 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 ¹³C NMR spectra were used¹ in this report. The NMR spectral simulations for exchange of carbon sites were done with PC versions of the gNMR¹³ and MEXICO¹⁴ 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 ¹³C NMR spectra of chlorocyclodecane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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