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1-Methyl-1-cyclohexyl Cations. Equilibria in Search of Structures

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Abstract: Solutions of the 1-methyl-1-cyclohexyl cation **1**, by four independent criteria, show unequivocal evidence for a populated equilibrium involving two different "structures" of this cation. One of these criteria makes use of a remarkably large new equilibrium isotope effect, a method that should have general structural use in other carbocation systems. Unfortunately, our previous assignment of a chair and twist-boat conformation for the structures does not accord with the new data. From an analysis of the ^{13}C and ^{1}H NMR shifts and K_H/K_D isotope effects for **1** and a series of ring-methylated analogues, it can be deduced that both structures are chair conformers and that one structure must involve extensive α-C–H hyperconjugation, while the other structure involves predominantly C–C hyperconjugation. The very existence of this type of isomerism in observable carbocations is unprecedented and has important implications for the field in general.

Several years ago we reported,[1] as part of a larger study, that the observable solution 1-methylcyclohexyl cation (**1**) appeared to exist as a populated equilibrium mixture of two isomers. We then assigned the structure of these equilibrium isomers to the chair and twist-boat conformers of **1** on the basis of some satisfactory chemical shift comparisons with model chair and twist-boat carbocations.

It is convenient at this point to schematically present a simplified version of our previous data (Figure 1) and our interpretation. In order to standarize descriptions, ring carbon atoms in a 1,3-orientation to the C$^+$ center are labeled β, protons on the α-carbon are α-hydrogens, etc. The structure with the low-field β-carbon ^{13}C shift was arbitrarily called **A** and that with the high-field β-carbon shift called **B**. Note that one never sees "direct" NMR evidence for an equilibrium, such as a "frozen-out" spectrum or even any indication of line broadening as one cools the solution; i.e., the temperature-dependent chemical shifts were the only evidence that one had the proposed populated equilibrium.

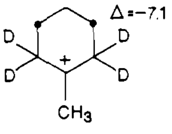
More recently, Lambert et al.,[2] with an eye to using such temperature shifts both to confirm the presence of a populated conformer equilibrium and then to treat the data quantitatively via a van't Hoff plot, looked at the temperature dependence of ^{13}C NMR peaks for a series of neutral cyclohexanes. They found that one can get very good van't Hoff plots in most of the cases studied, including situations where there cannot possibly be any conformational equilibrium, e.g., adamantane compounds, etc.

As also pointed out by Lambert, the fundamental problem in interpreting temperature-dependent ^{13}C NMR chemical shifts is to distinguish between "intrinsic" temperature-dependent shifts (caused by solution density changes, average bond length changes, etc.) and those that are the result of a rapid equilibrium of two or more structures, where averaged chemical shifts change because averaged populations of the individual isomers change with temperature. In the case of **1**, the large temperature-dependent chemical shifts involved only the β-carbons, and it was argued that such behavior would not be expected for "intrinsic shifts". Nevertheless, we found Lambert's results rather disquieting, and the purpose of the present paper was to obtain further (hopefully confirmatory) evidence that **1** did indeed exist as an equilibrium mixture of two "structures". Toward this end, we have used a number of approaches and have obtained convincing evidence that the original conclusion concerning the presence of an equilibrium was correct. However, as a result of this new work, and as our title indicates, we no longer believe that these equilibrium structures are ring conformational isomers.

Results and Discussion

I. Evidence That One Has a Populated Equilibrium. There are a number of pieces of evidence that show quite clearly that we indeed have a populated equilibrium.

(i) Isotopic Perturbation of an Existing Equilibrium.[3] The **1**-α-d_4 cation **2** shows a β-carbon ^{13}C shift that is 7.1 ppm (−95 °C) downfield from the same peak in **1**. This shift is nearly 2 orders of magnitude greater than that found for the intrinsic effects of two neighboring deuterium atoms, as found in cyclohexanone **3**, and is in any case in the *wrong* direction. The corresponding **1**-d_7 cation **4** has chemical shifts similar to **2**. A typical spectrum of a mixture of **1** and **2** is shown in Figure 2.



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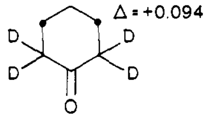

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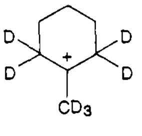

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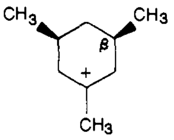
A similar result was found for the *cis*-1,3,5-trimethylcyclohexyl cations (**5**, **6**), where the total isotopic shift was 8.8 ppm downfield. This is also a cation system that shows evidence for a populated equilibrium (see later text). Finally, the 1,4,4-trimethylcyclohexyl cations (**7**, **8**) show only a very small shift on α-deuteriation (0.6 ppm at −100 °C). Cation **7**, as will be described subsequently, shows virtually no temperature dependence in the β-carbon chemical shift, and both this fact and the actual δ-position are consistent with only one populated isomer ($K > 50$). The overall conclusion therefore is that the large chemical shift changes in **1**–**2** and **5**–**6** are due to *isotope-derived equilibrium changes*, whereas in **7**–**8**, with no significant populated equilibrium, there is consequently no significant change. These data have been presented in graphic form in Figure 3.



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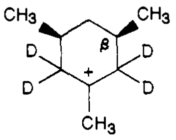

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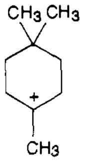

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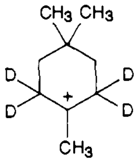

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(ii) A Study of Ring-Methylated 1-Methylcyclohexyl Cations. A series of ring-methylated (*t*-Bu in one case) 1-methylcyclohexyl cations were studied. The extra methyl groups were restricted to the 3-, 4-, and 5-positions of the ring (β and γ), since α-substitution would have lead to problems.[4] The new cations prepared, which included **5** and **7**, are listed in Table I. The ^{13}C β-carbon

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(1) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1978**, *100*, 1487.

(2) Lambert, J. B.; Vagenas, A. R.; Somani, S. *J. Am. Chem. Soc.* **1981**, *103*, 6398.

(3) For a recent example of the use of isotope perturbation in shifting carbocation conformational equilibria, see: Botkin, J. H.; Forsythe, D. A.; Sardella, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 2797.

(4) 1,2-Dimethylcyclohexyl cations undergo an extremely rapid 1,2 hydride shift that cannot be frozen out at any accessible temperature short of trying solid-state NMR techniques.

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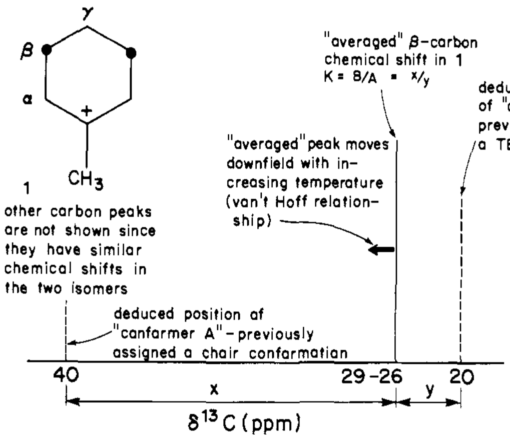


Figure 1. Simple schematic representation of the temperature-dependent ^{13}C peak for the β-carbon in **1** and a brief description of how these data were previously interpreted.

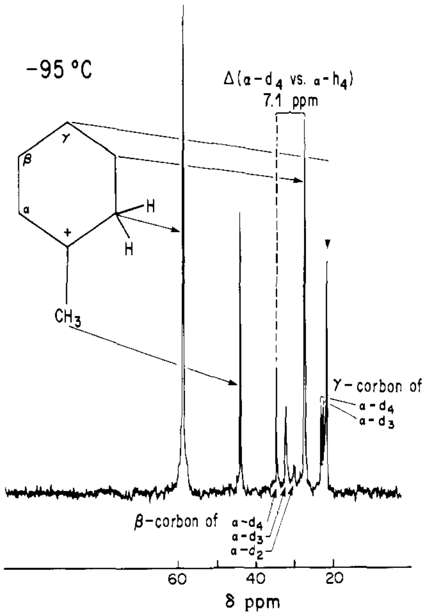


Figure 2. Decoupled ^{13}C NMR spectrum of equal amounts of the α-h_4 cation **1** and the α-d_4 cation **2**, where some of **2** has been allowed to scramble H and D atoms. Note that the α-carbon and the CH$_3$ carbon peaks have the same chemical shift in both structures, but the β-carbon peak and even the γ-carbons are different and are therefore "moved" when the equilibrium constant is changed. The C$^+$ carbon is not shown, but the α-d_4 vs α-h_4 shift is very small (ca. 0.4 ppm). All of the β-carbon peak positions are very temperature dependent.

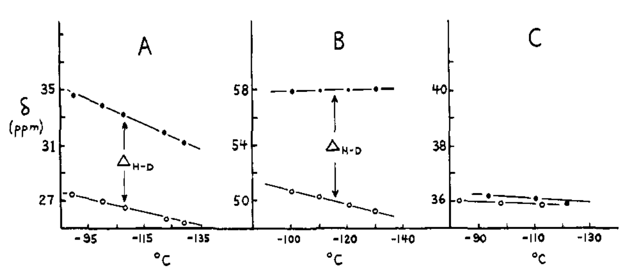
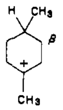
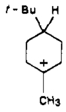
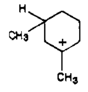
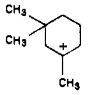
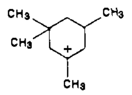
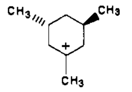


Figure 3. Temperature-dependent ^{13}C NMR chemical shifts for the β-carbons plotted as a function of the temperature: A, cations **1** (○) and **2** (●); B, cations **5** (○) and **6** (●); C, cations **7** (○) and **8** (●).

Table I. ^{13}C NMR Data for the β-Carbon(s) in Cations **5**, **7**, and **9**–**14**[a]

ion	β-^{13}C[b]	corrected shift[c]	temp, °C	temp-dependent β-^{13}C shift	shift on dec temp
 **9**	31.0	23.7	−91	no[d]	
 **10**	25.1	23.9	−91	no[d]	
7	36.6	23.9	−94	no[d]	
 **11**	39.5 (C3) 29.6 (C5)	33.3 31.9	−97	yes	downfield[e]
 **12**	46.5 (C3) 28.0 (C5)	37.0 32.0	−98	yes	downfield[e]
 **13**	56.6 (C3) 46.3 (C5)	48.0 43.3	−90	yes	downfield
 **14** (trans)	40.2	37.2	−115	yes	downfield
5 (cis)	50.6	44.0	−100	yes	downfield
1	25.7	25.7	−115	yes	downfield

[a] Remaining peaks are listed in the Experimental Section. [b] In δ, from internal CFCl$_3$ (δ 117.9). Some of these values are also medium dependent. [c] These corrected values (δ) were obtained as follows: Uncorrected value − (β-carbon shift of corresponding ketone peak −26.5), where δ 26.5 is the value for the parent cyclohexanone. Data for all ketones except 3,3-dimethylcyclohexanone were available.[18,19] The latter has peaks in CDCl$_3$ at δ 212.4 (C1), 54.9 (C2), 36.0 (C3), 37.9 (C4), 22.5 (C5), and 40.8 (C6). [d] There is a small downfield shift, with increasing temperature, but too little to really interpret. [e] The total shift is larger for the C3 carbon by a factor of ca. 3:2.

chemical shift position is shown, together with a "corrected" shift column. These latter "corrections" are based on those measured for the corresponding cyclohexanones and are the familiar ^{13}C correction factors. Thus, this corrected shift should give approximately a constant value if no equilibria are involved here. In fact, the extremes found are δ 23.7 for cation **9** vs δ 48.0 for cation **13**, with various in-between cases. This clearly favors an equilibrium argument, where, for example, cations **5** and **13** necessarily contain an even larger proportion of structure **A** than is the case with cation **1**.

(iii) Temperature Dependence of the β-Carbon Chemical Shifts. In the series of ring-methylated cyclohexyl cations (Table I), one finds two categories: (a) those with a high-field shift for the β-carbon ^{13}C peak and virtually no temperature dependence of the chemical shift; (b) those, like **1**, that have initially a lower field position for these β-carbons and where this peak always shifts to an even lower field with increasing temperature. This behavior is consistent with group (a) being virtually a single isomer (structure **B**, from Figure 1) and group (b) a populated equilibrium where ΔH favors structure **B** in all cases. We were initially disconcerted that this temperature shift was always in one direction but were able to predict[5] that the α-deuteriated cation **6** should show a reversed direction, and indeed this was the case (see Figure 3). In fact, cations **5** and **6**, which differ only in the isotopic substitution, *show an opposite temperature dependence for the β-carbon peak*, only explicable, surely, in terms of a populated equilibrium change. One also notes from Figure 3 that the temperature dependence of the β-carbons in **1** and **2** (or **1** and **3**) is quantitatively different. We show in a later section that such

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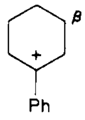
(5) The van't Hoff results (Table II) for cations **1** and **2** were obtained several years before the study of the ring-methylated cations was initiated. If one uses the same ΔΔH difference between **1** and **2** and applies this to **5**, the calculated ΔH for **6** is positive.

behavior is also uniquely consistent with a populated equilibrium argument. Finally, the β-carbon temperature shifts observed in this study (relative to internal $CFCl_3$) have values from about +400 to +800 or more, where these numbers are in units of 10^4 ppm/°C (see ref 2). In our experience with nonequilibrating cations, carbon intrinsic shifts do not usually exceed values of ±100.

(iv) Comparison of Data for the Corresponding 1-Methyl- and 1-Phenylcyclohexyl Cations. The ^{13}C NMR spectra of **1** and the 1-phenyl analogue **15** are anomalous in that the β-carbon in **15** is ca. 15 ppm downfield from the analogous peak in **1**. In other related carbocations such as the 1-methyl- and 1-phenylcycloheptyl or the corresponding cyclopentyl cations,[6] the corresponding β-carbons have very similar chemical shift values. We have found in this work that 1-phenylcyclohexyl cations involving ring methylation have β-carbon chemical shifts that are close to "normal" when one applies the previously mentioned ketone correction factors. Thus, cation **15** has a β-carbon shift of δ 42.0,[7] the 1-phenyl-*cis*-3,5-dimethylcyclohexyl cation (**16**) δ 50.5 (corrected δ 43.9), and the 1-phenyl-4-methylcyclohexyl cation (**17**) δ 46.8 (corrected δ 40.3), all these being measured at ca. -80 °C. These particular 1-phenyl cations were chosen because they are representative of the extreme behavior found in the 1-methyl series, as shown in Table I.



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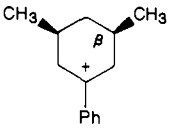

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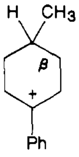

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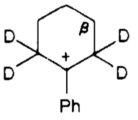

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The β-carbon chemical shifts for the 1-phenyl cations are not particularly temperature dependent, and also, the 1-phenylcyclohexyl cation (**15**) and the 1-phenylcyclohexyl-*2,2,6,6-d*$_4$ cation (**18**) have a β-carbon isotope shift of only 0.77 ppm (-80 °C), about 1 order of magnitude less than in the corresponding 1-methyl cations **1** and **2**. We conclude that the 1-phenyl cations **15–18** are basically interpretable in terms of a single structure.[8] These 1-phenyl cation results then emphasize the anomalous behavior of the 1-methyl analogues.

The above experiments leave us totally convinced that one is dealing with a populated equilibrium situation in **1**. At the very worst, one might offer some rationalization involving a very asymmetric single potential minimum, but we know of no precedent for the magnitude of the isotope shifts or the opposite temperature dependence seen for **5** and **6**. It is also clear that in all of the equilibrating cations studied here, the double minimum barrier must be very small (<5 kcal/mol), since in no case is NMR line broadening observed.

II. Quantitative Treatment of the Equilibrium Data (Van't Hoff Plots). The temperature dependence of an equilibrium constant can be used to obtain ΔH and ΔS, the enthalpy and entropy differences between the two equilibrium structures (van't Hoff plot). However, in order to calculate the individual K values [$K = (\delta_A(\beta) - \delta_{av}(\beta))/(\delta_{av}(\beta) - \delta_B(\beta))$], one needs estimates for the chemical shifts [$\delta_A(\beta)$, $\delta_B(\beta)$] of the frozen-out structures involved in the equilibrium. Of these four derived parameters, the $\delta_A(\beta)$ and $\delta_B(\beta)$ chemical shifts are of somewhat more interest to us than ΔH or ΔS because they are more directly useful in probing the unknown structures of **A** and **B**. All of the derived data are listed in Table II together with the similarly derived data for the ring-methylated systems. We also discuss in this table the detailed procedures used in arriving at the data.

Table II. Van't Hoff Plot Results

cation	derived low-field, β-carbon (**A**)[a]	high-field, β-carbon (**B**)	ΔH for $A \rightarrow B$,[b] cal/mol	ΔS for $\mathbf{A} \rightarrow \mathbf{B}$, eu	typical $K = [\mathbf{B}]/[\mathbf{A}]$[c] ($T$, °c)
1	60	23.5[d]	−1100	−2 ± 0.5	14.2 (−112.5)
2	60	23.5	−650	−2 ± 0.5	3.0 (−112.5)
5	70	30[e]	−250	−1.5 ± 0.5	0.98 (−110)
6	70	30	+50	−1.5 ± 0.5	0.43 (−110)
11	54	21	−650	−1.5 ± 0.5	3.1 (−108)
	75	27			
12	50	19.5	−550	−1.5 ± 0.5	2.9 (−113)
	80	33.0			

[a] It is difficult to estimate the uncertainty in these values. One starts out with potentially four variables in these van't Hoff plots, δ_A, δ_B, ΔH, and ΔS. The value for δ_B can be independently estimated (footnote *d*). The chemical shift data are simply not accurate enough to determine δ_A from "best-fit" plots, assuming this as one of the three remaining variables. One has, however, two further build-in factors, which must be made self-consistent. In the case of the α-d_4 vs α-h_4 data for cations **1–2** and **5–6**, one can safely assume that ΔS and δ_A will be essentially the same for both plots, even though the individual K data are quite different in each case. Thus, one has three unknowns to fit to two independent plots, as opposed to the original problem of four unknowns and one plot. In the case of cations **11** and **12**, one has two different chemical shifts to work with, each with a different temperature dependence, but K of course has to be the same at each temperature. This therefore also puts restrictions on the possible δ_A values. [b] The error range is estimated as ±20%. [c] These values are medium dependent. Most of this data is from solutions of the chloride in SbF_5–SO_2ClF. [d] This value is derived from the data for cations **7**, **9**, and **10**, which appear to be essentially pure structure **B**. [e] This and the following numbers are derived from the δ 23.5 value for **1** by using ketone corrections: estimate = 23.5 + (ketone δ-^{13}C shift − 26.5). See also footnote *c*, Table I.

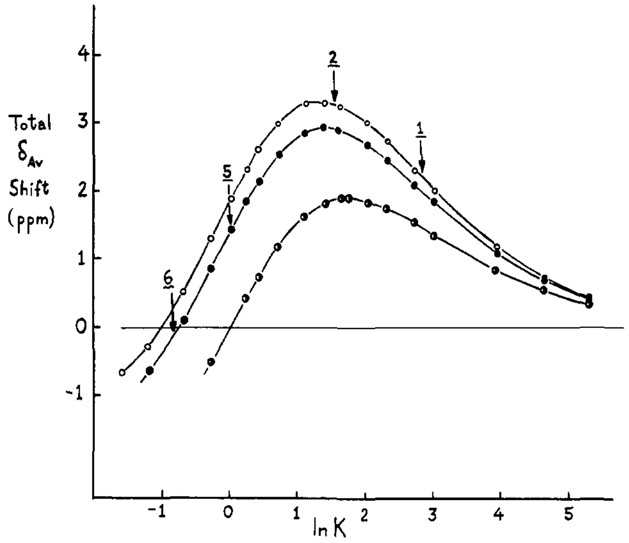

Figure 4. Calculated chemical shift vs temperature change for a rapidly equilibrating pair of structures A and B, given a δ_A–δ_B separation of 36.5 ppm and covering a 40 °C temperature range from −120 to −80 °C. The ln K value refers to the *lower* temperature end, i.e., −120 °C. This calculation is also shown for two cases where the $T\Delta S$ term increases the size of $-\Delta H$; i.e., ΔS is negative for $\mathrm{A} \rightleftarrows \mathrm{B}$ ($K = [\mathrm{B}]/[\mathrm{A}]$). $\Delta S = 0$ (◐), −1.5 (●), −2.0 eu (○). Shown also on this graph are the expected temperature dependencies for cations **1**, **2**, **5**, and 6. These quantitatively different shift predictions account very well for the differing δ vs T slopes shown in Figure 3, parts A and B (for cations **5** and **6**, one should have used a total separation of 40 ppm, but this will make a negligible difference).

It is pertinent at this point to show that the experimental results shown in Figure 3 (δ_{av} vs T results) can now be quantitatively rationalized. It can, for instance, be shown theoretically that the

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[6] For example, 1-phenyl- and 1-methylcycloheptyl cations show β-carbon ^{13}C shifts of δ 26.9 and 27.5, respectively. The corresponding cyclopentyl cations have δ 26.4 and 25.8.

[7] Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3161.

[8] Taken by themselves, the results for the 1-phenyl-1-cyclohexyl cations, in terms of both chemical shift positions and the temperatures dependence of these, appear normal. However, given the anomalous 1-methyl cation results, one can then see small effects in the 1-phenyl cations that show the same trends, although attenuated by a large factor, as one sees in the 1-methyl-1-cyclohexyl cation results. Thus, one should probably not view our results in strictly black and white terms.

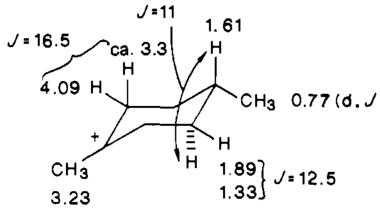
magnitude of a δ_{av} vs T relationship depends on three factors: (1) the chemical shift separation ($\delta_A - \delta_B = \Delta$) of the frozen-out peaks; (2) the numerical K values that happen to exist in the temperature range covered; (3) the ΔS value. In Figure 4, we show calculated plots of the predicted total δ_{av} shift for an arbitrary 40 °C temperature change and the Δ value taken from Table II. One notes that the experimental data in Figure 3 are quantitatively consistent with this Figure 4 plot; i.e., **2** has a larger δ_{av} vs T shift than **1**, **7** and **8** with large K are off-scale to the right (δ_{av} vs T is accordingly small), and **5** is positive, whereas **6** is slightly negative.

The ΔH and ΔS values obtained for the various equilibria shown in Table II exhibit some internal consistency when compared with **1**. Thus, a 3-methyl substituent favors the **A** structure (or disfavors **B**) by about 300 cal/mol, but a second 3-methyl substituent has virtually no further effect. Conversely, the 4-methyl substituents favor the **B** structure (or disfavor **A**). The ΔS values are small and quite similar in all cases.[9]

III. Possible Structures for Species A and B. In part I, we have shown *qualitatively* that **1** consists of two rapidly equilibrating structures, and in part II this was quantified to provide actual NMR δ-values for the β-carbons in both structures (as well as ΔH and ΔS data). As the title of the paper indicates, this information does not provide for much detailed insight into what these two structures might be. The new data obtained for $\delta_A(\beta)$ and $\delta_B(\beta)$ could still be consistent with a chair–twist-boat conformational equilibrium. Only the chair conformer would be at all consistent with the very low field shifts observed for structure A (extensive C–C hyperconjugation). The nonchair conformer would then have to be structure **B**, and this is quite consistent with a β-carbon shift of δ 23.5. The nonchair conformer would not have to be the previously proposed C_s twist-boat cation, and one might even consider a half-chair structure. However, several pieces of evidence indicate quite strongly that we are *not* dealing with a cyclohexane conformational equilibrium, as we in fact previously proposed:

1. Extensive molecular mechanics and MO calculations on **1** and on several of the ring-methylated derivatives fail to show any special stability for nonchair conformers.

2. The ^{1}H NMR spectrum of **9** (pure **B** isomer) has a well-resolved spectrum showing the typically large axial–axial coupling constants characteristic of a chair cyclohexane ring. This can be compared with the spectrum of **5** (ca. 1:1 **A** and **B** structures), where virtually identical coupling constants are obtained.



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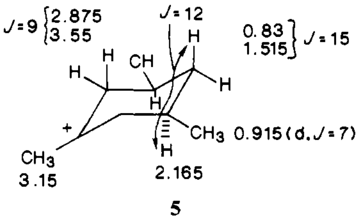

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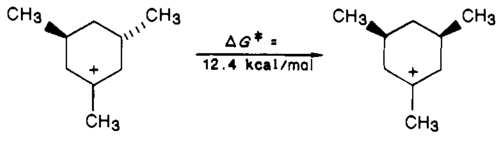
3. The *cis* and *trans*-1,3,5-trimethylcyclohexyl cations (**5** and **14**, respectively) are of definitive interest because the C_s twist-boat conformer of the trans isomer is particularly favorable (molecular mechanics calculations favor trans > cis by ~1 kcal/mol). If the cation **1** equilibrium were between a chair and C_s twist-boat structure, and if the twist-boat structure were, as implied, the more



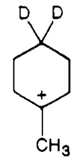
14 **5**

stable, then one would expect the thermochemistry to favor the *trans*-**14** over the *cis*-**5** isomer. Experimentally, just the opposite happens. Cation **14** is irreversibly transformed to **5**. This behavior is typical of a chair conformation, where equatorial, equatorial substituents are favored over axial, equatorial (molecular mechanics calculations give a 1.4 kcal/mol difference for the two chair ions).

4. None of the observed ΔH effects reported in Table II are consistent with a chair–twist-boat (or indeed any chair–nonchair) equilibrium, i.e., using the standard conformational analysis arguments based on the steric properties of a methyl group.

It therefore appears that *both* the A and **B** isomers have a basic chair cyclohexane structure. How then can one still have two distinct structures?

One valuable clue to the structures of **A** and **B** is provided by the equilibrium isotope data for **1–2** and **5–6**. The effect of the four α-deuterium atoms is almost certainly electronic rather than steric in origin. In order to be completely certain of this, we prepared the 4,4-dideuterio cation **19** and found that this cation behaves identically with the proton analogue **1**. In order for the four α-deuterium atoms to change the **B**/**A** equilibrium constant, the H/D isotope effect on the two structures must be markedly different. In fact, the data are consistent with a sizeable C_α–H hyperconjugation in structure **B** and a much smaller effect in A. Substituting four α-deuterium atoms then destabilizes **B** (a well-known effect[11]) and shifts the equilibrium toward **A**. There is even some indication that not all of the α-hydrogens are equally involved in this hyperconjugative delocalization.[12] One can also conclude that conformer **A** does not rely very heavily on C–H hyperconjugation, if at all,[13] but the very low field β-carbon



19

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[9] The origin of these ΔS values is not readily apparent, but could conceivably involve solvation changes (due to differential disorder) between the two structures; see also later discussion and ref 18.

[10] Gleicher, G. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 582.

[11] Numerous k_H/k_D ratios, generally giving a value >1, have been reported for solvolysis reactions in which the transition state resembles a carbocation and from which one concludes that α-C–H hyperconjugation stabilizes the carbocation more than the corresponding α-C–D interaction.

[12] The β-carbon peak position for the α-d_3, α-h_1 cation analogue of **2** can be seen easily (see Figure 2). The chemical shift position of this peak is consistent with the notion that the axial C–H(D) bonds are the ones mainly involved in hyperconjugative delocalization. On a simplistic level, one might have expected the single α-H to occupy the axial position and to perhaps cause a β-carbon shift halfway between **1** and **2**. In reality, the Boltzmann distribution will allow some equatorial α-H cation population (whose β-cation shift is probably similar to **2**). The overall effect is to produce a β-carbon shift for the α-d_3, α-h_1 cation about two-thirds of the distance between **1** and **2**.

[13] One can apply a Hess' law treatment of the equilibrium isotope data for **1–2** or **5–6**. This is derived as follows, with ΔH values, in calories, taken from Table II:

$$x\left\{\begin{array}{c} 1A \xrightleftharpoons{-1100} 1B \\ \\ 2A \xrightleftharpoons{-650} 2B \end{array}\right\}x + 450$$

The unknown here is x, but x must be relatively small if one compares these results with equilibrium isotope shifts of 137 ± 4 cal/mol per D atom as reported by: Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070. For example, if $x = 0$, the equilibrium isotope effect in **1–2** is 225 cal/mol per D atom if only two of the D atoms are involved (see ref 12) or 112 cal/mol per D atom if all four are equally involved. In other words, the numbers one obtains by assuming $x = 0$ are already quite large, and making x bigger simply makes matters worse.

chemical shift in A is consistent with extensive C_α–C_β hyperconjugation. Therefore, we believe that the two structures **A** and **B** are both chair conformations and that the C_α–H and C_α–C_β hyperconjugation operates as an *either/or* phenomenon rather than a mutually operational interaction (as one might expect for a single cation structure for **1**). The possible geometric consequences of this hyperconjugative dichotomy are difficult to probe since the cyclohexane ring is rather flexible, even within the consideration of a chair conformation. We therefore defer a detailed discussion of this to the following paper.

There is also some indication that the solvent and/or counterion may need to be included in the final structure description. The **B**/**A** equilibrium constant, as reported previously, is somewhat solvent and/or counterion dependent.[1] For example, with **1**, $K = [\mathbf{B}]/[\mathbf{A}] \approx 6.3$ in SbF_5–SO_2ClF with a chloride precursor of **1** (the counterion is likely a dimeric antimony species),[14] while in 4:1 FSO_3H–SbF_5 (SbF_5–FSO_3^- counterion, excess FSO_3H solvent) one finds $K \approx 3.4$, both measured at −40 °C ($\Delta\Delta G \sim$ 300 cal/mol). Similar magnitude differences in much more classic equilibria involving two different allyl cations have been reported.[15]

We have also noted several instances, e.g., with cation **11**, where one suddenly sees a "broadening" of the β-carbon peak as one progressively records ^{13}C NMR spectra at a series of higher and higher temperatures, starting at the very low temperature end first. This broadening is not reversible and appears to be due to some slow solution "phase change" occurring during the run. The end result of this is again a sharp but slightly shifted ^{13}C peak for the β-carbons, and we interpret the broadening as the net overlap of peaks from the slightly different environments that existed during the actual phase change. The β-carbon ^{13}C peaks are temperature dependent in both "phases", and the results are consistent therefore with a small equilibrium shift between the two phases. In any case, the total effect is rather minor, but another indication we believe of small differential solvation effects.

Conclusions

Several novel approaches have been developed in this work to decide whether temperature-dependent NMR chemical shifts are intrinsic or are brought about because the position of a rapidly averaged peak is sensitive to a shifting equilibrium constant. In particular, the isotopic perturbation approach allows one to both qualitatively confirm an equilibrium and to quantitatively treat the data in terms of a van't Hoff plot. In the case of the 1-methylcyclohexyl cation (**1**), we have confirmed that this cation exists as two rapidly equilibrating structures, as do a number (but not all) of ring-methylated analogues. These equilibrium structures are almost certainly not chair–twist-boat isomers, as previously proposed.[1] All evidence suggests that both structures are chair conformers.

Experimental Section

Preparation of Cations for ^{13}C and ^2D NMR Measurements. Procedure A. The alcohol (ca. 100 mg) dissolved in ca. 100–200 μL of $CFCl_3$ was added to ca. 2 mL of 1:1 SbF_5–FSO_3H diluted 1:4 (v/v) with SO_2ClF and contained in a 10-mm NMR tube. the acid mixture was kept at −120 °C during the addition of the alcohol.

Procedure B. The alcohol (ca. 100 mg) was converted in situ into the chloride, as previously described.[1] The $CFCl_3$ solution was concentrated to ca. 2 mL and a ^{13}C NMR spectrum obtained to verify that the chloride was pure. The solution was then further concentrated to ca. 200–300-μL volume and added to 1:4 (v/v) SbF_5 in SO_2ClF (−120 °C) or 1:3:1 SbF_5–SO_2ClF–SO_2F_2 (−135 °C), as above. For ^2H NMR spectra, about half the amount of alcohol was used in the preparation. As explained in the text, the β-^{13}C peaks are somewhat solvent dependent, and it is difficult to make duplicate solutions having exactly the same β-carbon shifts. Therefore, α-d_4 vs α-h_4 comparisons involved both cations in the same solution.

Procedure C. The alcohol (50–150 mg) dissolved in ca. 100–200 μL of $CFCl_3$ was added to ca. 2 mL of 4:1 FSO_3H–SbF_5 or to pure FSO_3H, contained in a 10-mm NMR tube. The addition temperature was between −50 and −80 °C.

^{13}C NMR Measurements. These were mostly performed on a Bruker WH-90 using previously described operational procedures.[1] Peak assignments, with the aid of off-resonance spectra, were relatively easy. In measuring temperature-dependent ^{13}C NMR spectra, the temperature control, digital resolution, and choice of reference are of concern. The reported temperatures are thought to be accurate to within ±1 °C, by the previously described calibration procedure. The digital resolution is ca. 2 Hz/data point, just about adequate considering the sizable shifts involved in this study (typically about 60 Hz). The reference in all cases is $CFCl_3$, taken as δ 117.9. The temperature dependence of the $CFCl_3$ peak is more than 1 order of magnitude less[18] than that of the β-carbon peaks studied here. A few of the ^{13}C NMR spectra were obtained on a Varian XL-200 instrument, with a few drops of CD_2Cl_2 as a lock and with the MLEV16 ^1H noise-decoupling sequence.

^1H NMR Measurements. Cation solutions were made up in 5-mm tubes with ca. 0.4 mL of solution and about 10 mg of alcohol. Spectra were run at 200 MHz on a Varian XL-200 instrument. Peaks were referenced with respect to external TMS in dimethyl-d_6 ether as a lock. A conversion factor of 0.15 was then subtracted from these shifts to convert to an external TMS–SO_2ClF reference (0.00).

^2D NMR Measurements. These were measured at 30.70 MHz with the above instrument and were run unlocked. Both ^1H coupled and decoupled spectra were obtained.

Details on the Cations. The 1-methyl, 1,3-dimethyl, and 1,4-dimethyl cations **1**, **11**, and **9** have been reported.[1,19,20] Cation **11** has ^{13}C peaks at δ 327.2 (C1), 64.9 (C2), 38.6 (C3), 28.9 and 30.7 (C4 and C5), 58.2 (C6), 43.9 (C1 methyl), 21.6 (C3 methyl) at −108 °C, procedure A. For ^1H spectral data on **9**, see the text. Data (^{13}C) for **11** and **9** were obtained over the temperature range −120 to −40 °C. At the highest temperature, **11**, **9**, and the 1,2-dimethyl isomer are present in their equilibrium concentrations, 8:4:1, respectively.

***cis*-1,3,5-Trimethyl-1-cyclohexyl cation (5)**: prepared by both procedures A and B. The ^1H spectral results are given in the text. ^{13}C peaks are at δ 318.6 (C1), 66.4 (C2, C6), 50.5 (C3, C5), 40.5 (C4), 42.9 (C1 methyl), 22.2 (C3, C5 methyls), −103 °C, procedure B. Cation **5** gave measurable spectra up to about −40 °C, although decomposition had set in. For the van't Hoff plots, spectra were recorded at seven temperatures from −133 to −43 °C.

***trans*-1,3,5-Trimethyl-1-cyclohexyl Cation (14).** The cation (procedure B) has ^{13}C peaks at δ 327.4 (C1), 65.3 (C2, C6), 39.9 (C3, C5), 35.8 (C4), 46.9 (C1 methyl), 21.4 (C3, C5 methyls), −123 °C. Spectra were obtained from −133 to −103 °C. At −103 °C, the first-order *trans*-**14** → *cis*-**5** rearrangement has $k = 3 \times 10^{-4}$ s^{-1}, $\Delta G^* = 12.4$ kcal/mol.

1-Methyl-4-*tert*-butyl-1-cyclohexyl Cation (10). The cation (procedure A) has ^{13}C peaks at δ 327.5 (C1), 58.8 (C2, C6), 25.1 (C3, C5), 43.2 (C4), 32.8 (C q of *t*-Bu), 43.2 (C1 methyl), 26.9 (methyls of *t*-Bu), −106 °C. Spectra were measured over the range −126 to −91 °C, where decomposition sets in.

1,3,3-Trimethyl-1-cyclohexyl Cation (12). The cation (procedure B) has ^{13}C peaks at δ 329.0 (C1), 69.7 (C2), 43.5 (C3), 35.0 (C4), 26.1 (C5), 58.6 (C6), 46.2 (C1 methyl), 29.1 (C3 methyls), −130 °C. Spectra were measured over the range −130 to −98 °C, where decomposition occurs.

1,4,4-Trimethyl-1-cyclohexyl cation (7): prepared by procedure A or B. The cation has ^{13}C peaks at δ 328.7 (C1), 56.4 (C2, C6), 35.8 (C3, C5), 29.5 (C4), 43.6 (C2 methyl), 27.3 (C4 methyls), −89 °C. Spectra were recorded over the range −83 to −113 °C.

1,3,3,5-Tetramethyl-1-cyclohexyl Cation (13). This cation (procedure B) has ^{13}C peaks at δ 70.2 (C2), 65.9 (C6), 56.6 (C3), 45.5 (C1 methyl or C4), 46.3 (double intensity), C5 and C4 (or C1 methyl), 32.6 (axial methyl at C3), 27.2 (equatorial methyl at C3), 22.5 (methyl at C5), −90 °C.

1-Phenyl-*cis*-3,5-dimethyl-1-cyclohexyl cation (16): prepared from the alcohol by procedure C. The cation has ^{13}C NMR peaks at δ 256.3 (C1), 52.7 (C2, C6), 50.5 (C3, C5), 43.8 (C4), 23.3 (methyls), 133.1 (meta), 137.7 (ipso), 140.6 (ortho), 155.0 (para), −80 °C. Spectra were obtained at 20 °C intervals from −40 to −80 °C. The β-carbons (C3 and C5) have a small $+45 \times 10^4$ ppm/°C temperature shift.

1-Phenyl-4-methyl-1-cyclohexyl cation (17): prepared from the alcohol by procedure C. The cation has ^{13}C NMR peaks at δ 262.8 (C1), 46.6 (C3, C5), 44.3 (C2, C6), 33.5 (C4), 19.0 (methyl), 133.4 (meta),

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138.5 (ipso), 140.9 (ortho), 156.0 (para), −80 °C. Spectra were obtained at 20 °C intervals from −20 to −100 °C. The β-carbons (C3 and C5) have a -130×10^4 ppm/°C temperature shift.

1-Phenyl-1-cyclohexyl Cation (15). This cation has been previously reported,[7] but no temperature data were measured. In our work, this cation was prepared by either procedure A or C. The β-carbons (C3 and C5) have a temperature dependence for the ^{13}C shifts of about -170×10^4 ppm/°C, over the range −40 to −100 °C.

Preparation of Deuteriated Cations 2, 4, 6, 8, 18, and 19. For the α-d_4-substituted cations **2**, **4**, 6, **8**, and **18**, the corresponding ketone was deuteriated in the α-position by a standard procedure[21] (two treatments). The corresponding alcohol was then prepared. The deuterium content of the ketones was analyzed by mass spectrometry and ^{2}D and ^{13}C NMR spectroscopy and corresponded to >95% D content in the α-position. The corresponding tertiary alcohols were also analyzed in a similar way (MS and ^{13}C NMR). The cyclohexanone-γ-d_2 needed for cation **18** was prepared by a modification of one of the several described routes.

Our synthesis started with 4-hydroxycyclohexanone, prepared from the diol by a modification of the literature procedure[22] (protecting one end as the tetrahydropyranyl ether rather than as an acetate). The synthesis proceeded

$$\text{4-hydroxycyclohexanone} \rightarrow \text{tetrahydropyranyl ether} \xrightarrow{\text{LiAlD}_4\ (99\%\ \text{D})}$$
$$\text{alcohol-}\gamma\text{-}d_1\text{-ether} \rightarrow \text{tosylate-}\gamma\text{-}d_1\text{-ether} \xrightarrow{\text{Superdeuteride}}$$
$$\text{cyclohexanol-}\gamma\text{-}d_2\text{-THP} \xrightarrow{[\text{H}^+]} \text{cyclohexanol-}\gamma\text{-}d_2 \xrightarrow[\text{oxidation}]{\text{Jones}}$$
$$\text{cyclohexanone-}\gamma\text{-d}_2$$

The reactions were standard procedures except for the Superdeuteride reduction, which followed a published procedure.[23] The overall yield on a 0.03-mol scale was ca. 15%. The ketone was analyzed by both ^{1}H (200-MHz) and ^{2}D (30.7-MHz) NMR spectroscopy, the former showing a γ-proton area at most 10% that of the α- and β-proton area and indicating a minimum of 60% γ-d_2 compound, the latter confirming no deuterium in the α-ring position. The corresponding methyl alcohol and chloride were prepared as described for the undeuteriated case. The alcohol showed C–D stretches at 2100, 2160, and 2190 cm^{-1} and the ^{13}C NMR of both alcohol and chloride showed only a weak multiplet for the γ-carbon.

The preparation of the deuteriated cations calls for some specific comment: Cations **2** and **4** have to be prepared at very low temperatures (ca. −135 °C) in order to prevent scrambling of the α-deuteriums into β- and γ-positions, which becomes rapid at about −100 °C. This scrambling was observed with both ^{2}D and ^{13}C NMR spectroscopy. No deuterium appears in the solvent peak, so all rearrangements are internal.

The β-carbon position in **2** or **4** is so sensitive that one can pick out peaks for α-d_3 and α-d_2 ions during this scrambling (see Figure 2). For quantitative measurement of the equilibrium isotope shifts, etc., solutions containing both **1** and **2** (1:1) or **1** and **4** (1:1) were prepared and the combined spectra measured. This eliminates solvent and temperature differentials, which inevitably occur in comparing separate runs. Spectra were run at six temperatures between −89 and −129 °C, above which the ^{13}C peak corresponding to **2** or **4** is lost. Cations **6** and **8** must also be prepared at very low temperatures, and the ^{13}C spectra were run (up to about −100 °C) singly, and as mixtures with their undeuteriated analogues, at a number of low temperatures. Cation **8**, although showing almost no change in the β-carbon position, does show a C$^+$ peak that is 2.9 ppm to lower field than in the undeuteriated **7**, an unusually large effect.[25] Cation **19** was prepared and handled as described for **2**. In this case, in the ^{13}C spectrum, the C4 peak is "missing", as expected. In the α-deuteriated ions, the C2,C6 peak is of low intensity and broad (C–D coupling). The 1-phenyl cation **18** is considerably more resistant to deuterium scrambling, and one can obtain spectra up to about −40 °C.

Molecular Mechanics Calculations. The program BIGSTRN, employing the Schleyer force field for cations,[10] was used. Equilibrium geometries for cations **1**, **5**, **9**, **11**, and **14** were calculated for all possible chair, boat, twist-boat, and five-carbon planar geometries. Some similar data have been published by Harris et al.[25] As expected, we found the C_s twist-boat isomer to be the best alternative to a chair, although the latter, in the best configuration, was the ground state in every case.

Molecular Orbital Calculations. The optimized geometries for cations **1**, **5**, and **10** were obtained by the MNDO semiempirical method.[26]

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Evidence for Equilibrating "Structures" in Unsymmetrical Tertiary 2-Adamantyl Cations. Possible Pyramidal Distortion of Observable Solution Carbocations

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Abstract: The observable tertiary carbocations 2,5-dimethyl-2-adamantyl and 2,4,4-trimethyl-2-adamantyl were prepared and the ^{13}C NMR spectra recorded over a wide range of temperatures and in several different solvent systems. Both the ^{13}C peak positions and the temperature dependence of these are consistent with both cations existing as a pair of rapidly equilibrating "structures". These structures involve enhanced C–C hyperconjugation on one face or the other of the 2-adamantyl framework and virtually require some nonplanarity at the C$^+$ center. We also believe that the cation structure must include the solvent and/or counterion in the description, but tight ion pairs, etc., are not thought to be involved; i.e., the effect is simply due to having a condensed phase. The 1-methyl-1-cyclohexyl cation also exists as a pair of rapidly equilibrating structures, which can now be seen to bear a close resemblance to the 2-adamantyl cation structures and are therefore also likely to be nonplanar at the C$^+$ center and to require the solvent and/or counterion in the overall description. Finally, we discuss some puzzling solvolysis results and rationalize the observations on the basis of our superacid structures.

2-Adamantane compounds (**1**) and various substituted analogues have been favored substrates for solvolysis studies,[1] partly because the molecules are rigid. Stable 2-R-2-adamantyl cations **2** have also been studied,[2] where R = methyl, ethyl, phenyl, or

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