Tertiary cyclohexyl cations. Definitive evidence for the existence of isomeric structures (hyperconjomers)

Arvi Rauk,[a] Ted S. Sorensen[a] and Paul von Ragué Schleyer[bc]

[a] *Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada*
[b] *Computational Chemistry Annex, University of Georgia, Athens, Georgia 30602-2555, USA*
[c] *Computer-Chemie-Centrum, Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany*

The 1-methyl-1-cyclohexyl cation **1** has previously been proposed to exist in superacid solution as a rapidly equilibrating pair of structures, one isomer involving C–C hyperconjugation, and a counterpart with axial C–H hyperconjugation (hyperconjomers). Using a combination of three techniques, which successfully compare theoretical results with experimental data, we have now obtained virtual proof for this concept. These three calculational procedures involve matching the experimental energy difference for the C–C and C–H hyperconjomers of **1**, together with the *cis*-3,5-dimethyl **2** and 4,4-dimethyl **3** analogs of **1**, to an accuracy of ±2 kJ mol^{-1} (solvation-simulation studies), a successful simulation of the α-d$_4$ equilibrium isotope effects for the **1**, **2** and **3** cation systems, and, finally, a close simulation of the average ^{13}C NMR spectra for mixtures of these C–C and C–H hyperconjomers in the **1**, **2** and **3** systems. These results have interesting implications for solvolysis studies of tertiary cyclohexyl systems, a full discussion of which is presented.

In an experimental low-temperature study[1,2] of the tertiary 1-methyl-1-cyclohexyl cation **1**, Sorensen has previously
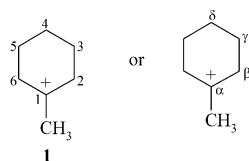

reported evidence that in superacid solutions there are actually two isomeric cation species in rapid equilibrium with each other. It was clear that both isomers were nominally 1-methyl-1-cyclohexyl cations, *i.e.* no skeletal rearrangements were involved in these two structures.

The evidence for this cationic equilibrium was initially based on temperature-dependent ^{13}C NMR chemical shifts,[2] later supplemented by studies involving C2–C6 deuterated isotopomers which showed that one isomer was destabilized much more than the other by this isotopic substitution.[1] It was also shown that the presence of remote methyl groups on the cyclohexane ring in **1**, *e.g.* 4,4-dimethyl or *cis*-3,5-dimethyl, had an appreciable effect on the position of the equilibrium constant involving their respective two cation structures.

Even at the very lowest temperatures accessible in superacid solution NMR studies (*ca.* −140 °C) there was no evidence that the rapid equilibrium between these two cation "isomers" could be frozen out on the NMR timescale, so that there were *no direct NMR data characterizing the individual isomers*, even though, as noted above, there was clear evidence that there were two species present. There was therefore "an equilibrium in search of structures".

In a previous publication it was proposed that the two isomers were both chair conformations of **1**, each involving a single hyperconjugation mode, with one isomer, **1CC**, distorted to maximize C$_{\beta-\gamma}$ hyperconjugation, the other, **1CH**, maximizing C$_\beta$–H$_{axial}$ hyperconjugation. An acute problem with this proposal at that time was the fact that MO calculations of **1**
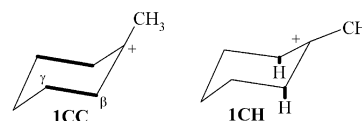
(only semi-empirical methods were feasible) gave only a single chair structure. However, it was argued that solvation and counterion effects might lead to an experimental situation that was not being well-modeled by the gas-phase calculations.

In a 1996 communication,[3] the present authors reported the results of high level *ab initio* calculations on **1**. In complete contrast to the semi-empirical level, two isomeric chair conformation structures were located, each having the hyperconjugation characteristics shown in **1CC** and **1CH** (these two structures being usefully referred to as hyperconjomers).† Furthermore, NMR chemical shift calculations on these two structures were in quite good agreement with the indirect estimates based on the experimental work.

The present paper is a full account of this theoretical work, but with a very important further result. The 1996 work reported gas-phase studies only, and these consistently showed that **1CC** was 1–3 kJ mol^{-1} (depending on the particular theoretical method) more stable than **1CH**, whereas the experimental results clearly showed **1CH** to be the dominant form in solution. The reason for this discrepancy was not known, but using the SCI-PCM solvation model in Gaussian 94, we now report that there is a significant differential solvation effect calculated for **1CC** *vs.* **1CH** such that **1CH** now becomes the preferred isomer. The optimized "solvated" structures of **1CC** and **1CH** are however essentially identical to the gas-phase geometries. As far as we are aware, this is the first time that differential

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† A term for isomeric carbocations involving some element of facially selective hyperconjugation. In the present case, the isomers involve C–H *vs.* C–C hyperconjugation, but cations **5CC** and **6CC**, which are briefly discussed in the paper, are examples of C–C *vs.* C–C hyperconjomers.

2CC   **2CH**

3CC   **3CH**
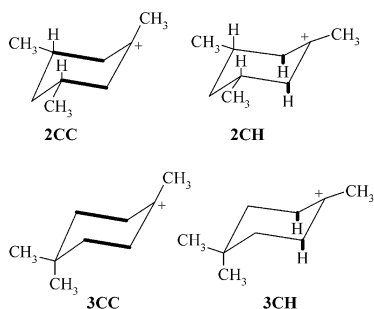
solvation effects have been successfully modeled for a carbocation equilibrium and this is discussed more fully later.

The present full paper also reports new computational results which confirm that these **CH** and **CC** isomers are also present in a number of ring-substituted derivatives of **1**. In the experimental study,[1] as mentioned, the addition of "remote" methyl substituents to the cation **1** skeleton was shown to cause sizeable changes to the **CH**–**CC** equilibrium constant, compared to the parent **1** system. The most divergent data were derived from the *cis*-1,3,5-trimethyl-1-cyclohexyl cation system **2**, and in the opposite direction, from the 1,4,4-trimethyl-1-cyclohexyl cation system **3**. The structures of the respective **2CH** and **2CC**, and **3CH** and **3CC** cations have been optimized both in the gas phase (except for **2CH**) and using the SCI-PCM solvation model. NMR chemical shifts have also been calculated so that one can obtain theoretical estimates of the **CH**–**CC** averaged ^{13}C NMR shifts.

β-d_4-Deuteration in the **1**, **2** and **3** cation systems has been shown[1] to cause large isotope-induced ^{13}C NMR chemical shift changes in the case of cation systems **1** and **2**, but not in the case of **3**. Using data from the energy calculations, frequency calculations, and calculated NMR chemical shifts, the experimental results can be very successfully modeled in terms of the existence of **CH** and **CC** hyperconjomers in each case.

The success of these theoretical studies, which are described in detail in the following sections, in closely modeling the solution behavior of cation systems **1**, **2** and **3** constitutes virtual proof for the existence of individual **CH** and **CC** hyperconjomers of 1-methyl-1-cyclohexyl cations.

Computational details

Calculations were performed with the Gaussian 94 suite of programs,[4a] the exception being the GIAO MP2/6-31G* NMR calculations which used the newly released Gaussian 98 version.[4b]

The SCI-PCM solvation model[5] at the B3LYP/6-31G** basis set level was used to compute optimized structures for **1CH** and **CC**, **2CH** and **CC**, and **3CH** and **CC**. A standardized value of 30.0 was used for the solvent relative permittivity (ε) (see Results section for discussion). The default value of 0.0004 was used for the isodensity surface, 974 points were used in the Special grid option and surface integrals were evaluated using the single center procedure. Single point energies were calculated for each cation using the SCI-PCM model and a B3LYP/6-311+G** basis set. Numerical frequencies were obtained for each structure at the B3LYP/6-31G** SCI-PCM level, confirming that all structures were minima (NIMAG = 0). Zero point vibrational energy values were corrected by a factor of 0.98.[6] Isotope effects were calculated for the 2,2,6,6-d_4 isotopomers of each of the above structures using the TDF program.[7] The NMR chemical shift calculations used the SCI-PCM optimized geometries but did not involve the solvation model (not available).

Results

In applying the SCI-PCM solvation model, based on the non-spherical cavity continuum model of Tomasi,[8] one requires a

Table 1 Calculated relative energies[a] for **CH** and **CC** carbocation isomers

	Gas phase		Solvation simulation		Differential solvation favoring **CH** isomer
	A^b	B^b	A_1^c	B_1^c	B^b
1CC	0.00	+0.71	6.0	7.0	6.3
1CH	0.33	0.00	0.00	0.00	
2CC	—	—	2.3	3.5	
2CH	[d]	[d]	0.00	0.00	
3CC	2.5	4.0	8.6	9.8	5.8
3CH	0.00	0.00	0.00	0.00	

[a] kJ mol^{-1}, relative to the most stable isomer = 0.0. [b] *A* method: B3LYP/6-31G** + 0.98 ZPVE, *B* method: B3LYP/6-311+G**//B3LYP/6-31G** + 0.98 ZPVE. [c] Basis sets and ZPVE as in [b] using the SCI-PCM method. Strictly speaking, the calculated solvation energies are free energies, but for the differential solvation energy between two ions in the same solvent, the entropy term specific to the gas-phase solvation process would effectively cancel, so that $\Delta\Delta H_{solv} \sim \Delta\Delta G_{solv}$. [d] A geometry optimization of this isomer was unsuccessful, giving instead an isomer of the **CC** form with the C1 methyl group rotated 60°.

solvent relative permittivity (ε) input parameter. The experimental data being modeled in the present calculations were obtained in a variety of solvents, but most of the low-temperature results involved SO$_2$ClF solvent, containing an excess of SbF$_5$. No literature data for the ε of SO$_2$ClF were found, but a value of 9.1 is reported[9] for the related SO$_2$Cl$_2$. Relative permittivities are slightly temperature dependent and given all this uncertainty, a value of ε = 30.0 was chosen for the present calculations. In part, we are also assuming that an excess of the strong Lewis acid SbF$_5$ would create a slightly more polar medium than that of the pure solvent.

In practice, the calculation results are not very dependent on ε values once one chooses a relatively high value such as 30.0. Doubling this to 60.0 in the calculations results in only small changes to the differential solvation values because the relative permittivity appears as an $\varepsilon - 1/\varepsilon$ factor in solvation theory. This fact could also explain why our previously reported experimental results[2] in FSO$_3$H solvent (ε = 120–150)[10] did not differ very much from the related SO$_2$ClF solvent data, even though it would now appear from the present work that a substantial differential solvation energy (**CH** isomer *vs.* **CC** isomer) is involved.

Calculated differential solvation energies

In Table 1 are shown the calculated relative energies for the cation systems **1**, **2** and **3**, in both their **CH** and **CC** isomeric forms, comparing in particular the differences between the gas-phase results and those using the solvation model. The comparison data for the *cis*-1,3,5-trimethyl system **2** are missing because we could not find a gas-phase energy minimum for the **CH** isomer. However this problem does not exist when the SCI-PCM solvation model is used.

The gas phase–solvation simulation data in Table 1 can be directly compared for the **1** and **3** systems, showing that solvation *differentially stabilizes the CH isomers by about 6 kJ mol^{-1}*. This computational area is still relatively unexplored but the magnitude of this result is quite significant, and this is discussed later. In comparisons with experimental data (Table 2), the solvation results now overestimate the experimental (solution) **CH** isomer stability by about 2 kJ mol^{-1}. However it should be kept in mind that Møller–Plesset-based theoretical methods show a somewhat larger gas-phase stabilization of the **CC** form of **1** (compared to **1CH**), which even after the differential solvation "correction", come out on the opposite side of the experimental results to those shown in Table 2. In either case the experimental *vs.* solvation model results are now within ±4 kJ mol^{-1}.

Structure comparisons—gas phase *vs.* solvation model

Structures for the gas-phase **1CC** and **1CH** cations have been published.[3] Comparison of the structures for gas-phase and solvated species shows that these are very similar in both cases. There is a slight reduction in the C2–C3 (C6–C5) bond from 1.604 to 1.596 Å in the solvated structure of **1CC**, this long carbon–carbon bond being the most important structural parameter characterizing this isomer. In **1CH**, the hyperconjugating C2–H$_{ax}$ (C6–H$_{ax}$) bond is almost unchanged (1.114 *vs.* 1.112 Å).

Similar comparative results are found for **2CC**, and for **3CH** and **3CC**, where the C2–C3 (C6–C5) bond is reduced from 1.616 to 1.606 Å in **2CC**, and from 1.602 to 1.592 Å in **3CC**, whereas **3CH** has C2-H$_{ax}$ (C6-H$_{ax}$) bonds which are virtually identical (1.112 Å) in the gas phase and solvation model.

Remote methyl substituent effects—calculated *vs.* experimental

As outlined in the Introduction, our previously reported experimental study[1] showed that the addition of remote methyl substituents to the cation **1** system brought about significant changes in the respective **CH**–**CC** equilibrium constants (assuming of course that the data were being correctly interpreted). Clearly, if one were able to model these substituent effect changes using MO theory, then this in itself would strengthen the original interpretation. As discussed in the Introduction, the *cis*-1,3,5- (**2**) and 1,4,4-trimethyl-1-cyclohexyl (**3**) cation systems were selected. The most meaningful comparison is that shown in column 4 of Table 2. Even though the individual calculated *vs.* experimental results differ in magnitude by *ca.* 2 kJ mol^{-1}, this difference is almost constant for the **1**, **2** and **3** sets, so that overall the substituent effects *per se* are being very well modeled by the calculations.

The opposing effect of the 4,4- and *cis*-3,5-dimethyl groups when added to the skeleton of **1** is of some interest. Using isodesmic reactions of the type

$$\textbf{2CC} + \text{cyclohexane} \longrightarrow \textbf{1CC} + \text{1,3-dimethylcyclohexane}$$

one finds that **2CC** is stabilized by methyl substituents (14.2 kJ mol^{-1}). This result is intuitively reasonable given the ability of CH$_3$ *vs.* H in stabilizing a positive charge on carbon. A related

Table 2 Comparison of experimental and calculated[a] (SCI-PCM solvation model) energy differences for the **CH** and **CC** isomers

Cation system	CC ⇌ CH		
	Calc. energy diff.	Experimental ΔH^b	$\Delta H_{calc.} - \Delta H_{exp.}$
1	−7.0	−4.6	−2.4
2	−3.5	−1.0	−2.5
3	−9.8	≥−7.5	−2.3

[a] Taken from Table 1. [b] Ref. 1.

evaluation of **2CH** was not possible since this structure was not found as a minimum in the gas-phase calculations (*vide infra*). In the 4,4-dimethyl case, the corresponding **3CC** is destabilized by 12.3 kJ mol^{-1} while **3CH** is stabilized by 8.58 kJ mol^{-1}. These individual numbers may be unreasonably large but the net effect is a destabilization of **3CC** by the substituents. This result is not readily predictable, but as discussed later, these observations (and the actual existence of isomeric **CH** and **CC** cyclohexyl cation structures) are potentially very relevant in the interpretation of solvolysis results involving cyclohexyl systems. The destabilization of **3CC** also agrees with results using remote methyl substituents in 2-methyl-2-adamantyl cation equilibria.

Relative entropies of the CC and CH isomers

The calculated internal entropy differences between the **CC** and **CH** isomers in the **1**, **2** and **3** series, using frequency data, are small and show no particular trends. However, the experimental data[1] for this same series, **CC** ⇌ **CH**, gives $\Delta S = -6$ to -8 J K^{-1} for each system.

In the original study no explanation was offered for the experimental ΔS observations, but the present calculations now offer a reasonable rationale. This is based on the fact that the calculations show the **CH** isomer to be more strongly solvated than the **CC** counterpart.

Larger solvation energies for a solute–solvent interaction should differentially reduce the entropy of the solvent system around the more highly solvated **CH** isomer because of a lowered randomness of this specific portion of the bulk solvent. This effect would be part of the *experimental* ΔS term associated with the **CC** ⇌ **CH** equilibrium process and we suggest that the measured ΔS of -6 to -8 J K^{-1} is mainly due to this factor (common to all three cation systems).

NMR chemical shift calculations

The ^{13}C NMR chemical shifts calculated for the six carbocations involved in this study are listed in Table 3. There is a close similarity between the individual carbon shifts in the **CH** and **CC** isomers, except for the C3–C5 chemical shifts, and to a lesser extent the C1 center. In the C3–C5 chemical shift comparison, the difference is an almost constant 30 ppm in the **1**, **2** and **3** series. This same large divergence was originally deduced from the experimental ^{13}C NMR results, and in fact was implicit in the original "two species" postulate, since one can only expect large chemical shift changes for a dynamically averaged signal, as a function of temperature, when the individual isomers have at least one quite divergent chemical shift value.

As noted in the Introduction, the **CC** ⇌ **CH** equilibrium could not be "frozen out", and so experimentally only a single set of average ^{13}C NMR chemical shifts can be obtained. In the case of the **1** and **2** systems, the dynamic populations of both the **CC** and **CH** isomers are significant, and so the averaged ^{13}C shift of the C3–C5 carbons does not closely correspond to that of either pure species. However, cation system **3** (even though

Table 3 Calculated ^{13}C chemical shifts[a] for the **CC** and **CH** isomers of the cation systems **1**, **2** and **3**

Cation	Carbon position (δ)					
	C1	C2–C6	C3–C5	C6	CH$_3$	Ring CH$_3$
1CC	317.47	60.52	56.27	27.38	43.76	
1CH	332.04	57.81	25.97	22.39	46.37	
2CC	304.78	67.51	66.28	42.17	42.58	25.78
2CH	330.71	64.45	36.54	38.67	46.89	22.81
3CC	323.64	57.49	66.45	35.63	44.44	25.91, 24.91
3CH	330.87	57.01	37.79	31.26	45.25	24.60, 30.78

[a] Relative to TMS $\delta = 0$, the absolute shielding for TMS = 207.12. In all calculations the GIAO MP2/6-31G* level was used, employing the SCI-PCM B3LYP/6-31G** optimized geometries as input.

dynamic) was deduced to overwhelmingly favor the **3CH** isomer, and if so the experimental ^{13}C NMR spectra for this cation can be compared to the calculated results for this single isomer, as is shown in Table 4. The agreement for all ^{13}C peaks is extremely good; on average the calculated results are 1.4 ppm larger δ than experiment, with the C3–C5 peak differing by 2 ppm. In contrast, calculated δ values for the C3–C5 peak of **3CC** differ by 31 ppm from the experimental value.

The calculated NMR chemical shifts in Table 4 were obtained with the GIAO-MP2 method, which in this case is much superior to uncorrelated methods, particularly with respect to the chemical shifts computed for the C3–C5 carbons in the **CC** isomers. The excellent agreement of calculated and experimental data for **3CH** also gives one confidence that the other cations in this series are being calculated to a similar precision.

Equilibrium isotope effects—calculated differential energy changes for d4-substitution at C2–C6 in the cations

In Table 5 are recorded the calculated differential energy changes brought about by d_4-substitution at C2 and C6 in the three cation systems. This isotopic substitution is calculated to produce a significant change in the relative enthalpies (or free energies) of the **CH** and **CC** isomeric pairs *in favor of the CC isomer*, a very similar 1.6–1.8 kJ mol⁻¹ in the **1–3** series. From related calculations in which other isotopomers are used, one can show that the main destabilization effect of the d_4-substitution involves the two axial hydrogens at C2–C6 in the **CH** isomer. These are the same hydrogens which are involved in the hyperconjugative delocalization which defines the **CH** isomers, and deuterium substitution of these would be expected to destabilize this isomer.

Modeling of the experimental NMR spectra—including equilibrium isotope effects

The combined data from Tables 2, 3 and 5 have been used to model the experimental ^{13}C NMR spectra of the **1**, **2** and **3** systems, and this result is shown in Fig. 1 for a temperature of 163 K.

The excellent overall theoretical *vs.* experimental agreement

Table 4 Comparison of calculated and experimental ^{13}C NMR shifts[a] for cation **3CH**

Carbon position	Experimental	Calc. for **3CH**	Calc. for **3CC**
C1	328.7	330.87	323.64
C2–C6	56.4	57.01	57.49
C3–C5	35.8	37.79	66.45
C6	29.5	31.26	35.63
CH₃ at C1	43.6	45.25	44.44
Ring CH₃[b]	27.3 (av.)	27.69 (av.)	25.41 (av.)

[a] δ (ppm). [b] Chair–chair interconversion is very fast in this system and is not being "frozen out".

shown in Fig. 1 for the **2** and **3** cation systems is highly dependent on getting three factors right: (1) the ^{13}C NMR shifts have to be correctly calculated; (2) the energy changes produced by *cis*-3,5- and 4,4-dimethyl substitution of **1** also have to be correctly calculated; and (3) the equilibrium isotope shifts (direction and magnitude) require a very specific frequency calculation result.

Factors (1) and (3) are actually very "structure specific" and we believe that the present theoretical modeling represents a *unique* fit of experimental *vs.* calculated results, and that it is nearly inconceivable that any other model would have fitted the combined experimental data.

Discussion

Differential solvation in carbocations

The area of experimental solution carbocations is rife with examples of isomeric carbocations in equilibrium with each other. A number of these systems have been calculated by high level MO methods (geometries, energies) and an enduring surprise has been the ability, using what amount to gas-phase models, to closely match the experimental (solution) energy differences. The "surprise" aspect arises because we
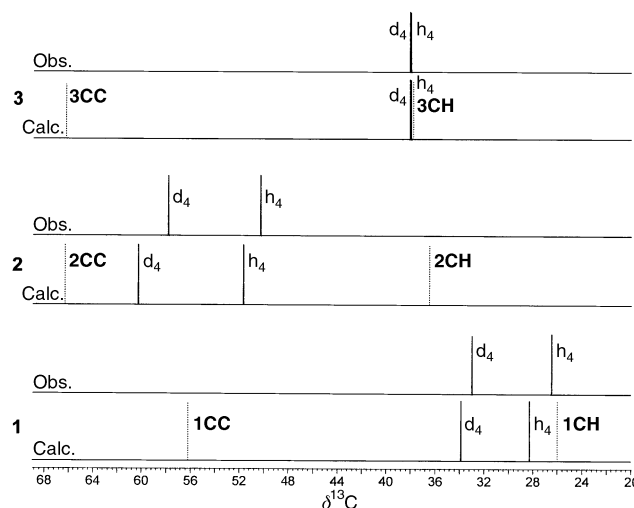

Fig. 1 Comparison of calculated and experimental averaged ^{13}C NMR shifts for the C3–C5 carbons of cation systems **1**, **2** and **3**, and their d_4-substituted analogs, at 163 K. The protocol used to generate this figure required the $\Delta H_{calc.} - \Delta H_{exp.}$ value from Table 2 to be set to zero for the parent system **1**. The corrected "calculated" data for **2** and **3** thus become −1.1 and −7.4 kJ mol⁻¹, respectively. The ΔG value for all three systems was derived by using the experimental ΔS value (**CC** ⇌ **CH**) of −7.3 J K⁻¹. Incremental ΔH changes for the d_4-cations were taken from Table 5, and ^{13}C NMR data from Table 3. The ^{13}C data for the d_4-cations have not been corrected for "intrinsic" isotope effects since these are known to be small compared with the large changes shown in Fig. 1. Calculated ^{13}C NMR shifts for the individual C3–C5 carbons in the **CC** and **CH** structures are also shown in the figure.

Table 5 Calculated enthalpy changes[a,b] (163 K) produced by d_4-deuteration at C2–C6 in the **CC** and **CH** isomers of cation systems **1**, **2** and **3**

Cation	ΔH (CC ⇌ CH)-h₄	ΔH (CC ⇌ CH)-d₄[c]	Isotope-induced $\Delta\Delta H$ change
1CC	7.1	5.1	2.0
1CH	0.00	0.00	
2CC	3.6	1.8	1.8
2CH	0.00	0.00	
3CC	10.3	8.3	2.0
3CH	0.00	0.00	

[a] In kJ mol⁻¹ using the SCI-PCM model with B3LYP/6-311+G**//B3LYP/6-31G** energy and 0.98 ZPVE and thermal data, from B3LYP/6-31G** frequencies. The data for the non-deuterated cations reported here are very similar to the ΔH values reported in Table 1, since the thermal correction differences are quite small. [b] Calculated for a temperature of 163 K, a mid-range temperature in the experimental work. [c] C2–C6-d_4 isomer.

know intuitively and experimentally [11] that individual gas-phase solvation energies of carbocations will be large numbers, and the probability that individual large solvation energies would totally cancel for a pair of cations seems low, particularly in cases where the cations have different modes of charge delocalization. Nevertheless, in examples such as the cyclobutyl–cyclopropylmethyl cation equilibrium, experimental (solution) and theoretical (gas-phase) measures of the equilibrium constant yield similar values. [12]
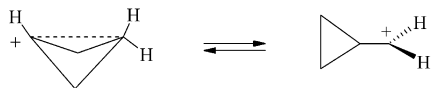
A related problem concerns the structure of experimental solution-phase carbocations *vs.* calculated (gas-phase) structures. In cases where flat potential energy surfaces are found using theory, one might expect that gas-phase transition-states and minima could be interchanged by solvation effects, particularly if the transition-state appeared to "concentrate" the cationic positive charge. However, a great many experimental solution-phase structures appear to be well described by gas-phase calculations [^{13}C NMR shift calculation comparisons (gas-phase) *vs.* experimental (solution) are invaluable in this regard].

The 2-norbornyl‡ cation provides a cogent example. It is calculated (gas-phase) to be a bridged structure, and all indications are that the experimental solution structure has essentially the same geometry. Schleyer *et al.* [13] have recently studied this cation using both gas-phase and solution-simulation theoretical methods, and found the "classical" structure to be stabilized by only 2 kJ mol⁻¹ by differential solvation compared to the bridged structure (charge equally on C1–C2), with the latter still the stable minimum species.

The differential solvation results described in the present study, an energy value of about 6 kJ mol⁻¹ favoring the **CH** isomers (Table 1), are surprisingly large in comparison with the 2-norbornyl cation case. Both **CH** and **CC** hyperconjomers have the charge concentrated at C1, but one can rationalize our results on the basis that the axial C2–C6 hydrogens (hyperconjugative charge delocalization) in the **CH** isomer are more accessible to the "solvent" than is the case for the more internal delocalization involved in the **CC** isomer. However, at present there have been very few solvation-simulation calculations involving carbocations, and more examples need to be studied before one attempts to reach definitive conclusions.

The results of our present study also suggest that solvation simulation can change the potential energy surface relative to that of the gas phase. A minimum could not be located for cation **2CH** as a gas-phase structure, whereas under the solvation-simulation conditions a minimum was easily located. The previously reported [3] transition-state energy (gas-phase) calculated for **1CC** ⇌ **1CH** is very small (<4 kJ mol⁻¹) measured from the less stable (gas-phase) **CH** isomer. Since the added 3,5-dimethyl groups further increase the **CC**–**CH** energy difference compared to **1**, it seems plausible that the gas-phase **2CH** minimum could disappear, in agreement with the calculated results.

Relevance of the results to S$_N$1 nucleophilic substitution reactions in cyclohexyl systems

The cyclohexane ring has been widely used in the study of nucleophilic substitution reactions, and in most tertiary cases these reactions involve an S$_N$1 mechanism. The intermediate cation in these reactions has been assumed to be a planar tertiary carbocation, with nucleophile capture taking place *via* an axial or equatorial approach, as illustrated.

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‡ The IUPAC name for 2-norbornyl is bicyclo[2.2.1]heptan-2-yl.
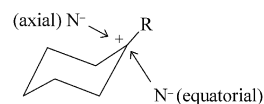
The steric requirements are obviously different for axial and equatorial attack, but in simple systems a rapid chair–chair interconversion of the product destroys any initial stereospecificity. Winstein and Holness [14] pioneered the use of the 4-*tert*-butylcyclohexane ring system as a way to lock a given chair conformation (although twist-boat conformations are a possible complication). [15] Subsequently, other "locking" procedures have been used. [16]

Solvolysis reaction mechanisms involve a number of factors, and the structure of the cation intermediates is only one issue, but on the basis of the results described in this paper, we suggest that previous S$_N$1 mechanistic interpretations of tertiary cyclohexyl systems may need to be re-evaluated. An examination of our **CC** and **CH** structures (geometry and electron distribution of the LUMO orbital, see ref. 3) shows that nucleophile capture in the **CC** isomer would occur from the equatorial face, and from the axial face for the **CH** isomer. These trajectories are *not* determined by steric effects *per se*, but by the electronic structure of the given cation.

A similar situation would also apply to the rate-determining formation of the S$_N$1 carbocation intermediate. Loss of an axial leaving group would lead to the **CH** hyperconjomer, while equatorial loss would give the **CC** structure. If the rate of **CC** ⇌ **CH** interconversion were slow with respect to nucleophile capture, one would get retention of configuration from either an axial or equatorial leaving group; conversely, rapid interconversion to a dominant hyperconjomer before nucleophile capture could lead to either predominant retention or inversion depending on which initial stereochemistry was present in the substance being solvolyzed, and on which hyperconjomer cation was the dominant species. This argument assumes of course that the **CC** and **CH** isomers would have identical nucleophile capture rates in an irreversible process.

The analysis offered above is similar to that which has been traditionally argued for various "nonclassical" carbocation intermediates. However, cyclohexyl systems have *not* to date been included in such definitions, and further, this system involves *two* "nonclassical" structures.

A key feature of the above analysis concerns the rate of hyperconjomer interconversion *vs.* nucleophile capture. A number of solvolysis rate studies have been carried out on tertiary cyclohexyl systems but in those cases where product studies have been done, a mixture of substitution products, and cyclohexenes from a presumed E1 elimination, are usually found. Further complicating this situation is the distinct possibility that cyclohexenes might be preferentially formed from a **CH** cation structure.

There are other indications, however, which suggest that solvolytically generated tertiary cyclohexyl hyperconjomers would interconvert rapidly relative to nucleophile capture. We base this prediction on the similarity in concept between the **CH** and **CC** hyperconjomers in cyclohexyl systems, and isomeric **CC** ⇌ **CC** hyperconjomers in tertiary 2-adamantyl systems, as illustrated below.
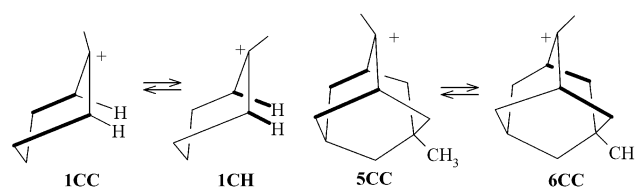
Whiting and co-workers have reported [17] solvolysis results for the 2,5-dimethyl-2-adamantyl system, and have shown that **4a** solvolysis gives predominant retention, while **4b** gives

predominant inversion. In a superacid study, and from computations, we find that cation **5CC** is the more stable hyperconjomer of the **5CC** $\rightleftharpoons$ **6CC** pair.

4a R' = CH₃, R = —O—⟨⟩—NO₂

4b R' = —O—⟨⟩—NO₂ , R = CH₃
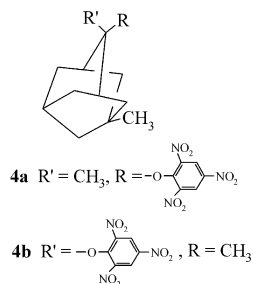
We interpret the solvolysis results in terms of each starting material, **4a** and **4b**, generating an individual hyperconjomer carbocation, **5CC** and **6CC**, respectively, which then both have time to equilibrate to the equilibrium population (favoring **5CC**) *before* nucleophile capture. We have also previously calculated the gas-phase transition-states for **1CH** $\rightleftharpoons$ **1CC** and for **5CC** $\rightleftharpoons$ **6CC**, and find similar size $\Delta E^{\ddagger}$ values in both cases (<4 kJ mol^{-1}). The structures of the hyperconjomers and transition-states from the **1** and **5**, **6** systems are so similar that we have no reason to doubt that they would have similar solvolytic behavior. However, the 2-adamantyl systems do not form adamantene E1 elimination products, and only minor amounts of 2-*exo*-methylene-5-methyladamantane are formed, allowing for reasonably clean solvolysis stereochemical results.

Finally, the rationalization offered in this section for the solvolysis of tertiary cyclohexyl systems would also imply that ring substituents such as the 4-*tert*-butyl group first used by Winstein *are not* without consequence at the C1 center, since this C4 substituent has already been shown in superacid studies to substantially enhance the **CH** hyperconjomer population in this cation system relative to the unsubstituted system **1**. Thus, any detailed comparison of the solvolytic behavior of the parent **1** system with that of the 4-*tert*-butyl-1-methyl system would be suspect.

Acknowledgements

References

1 R. P. Kirchen, K. Ranganayakulu and T. S. Sorensen, *J. Am. Chem. Soc.*, 1987, **109**, 7811.

2 R. P. Kirchen and T. S. Sorensen, *J. Am. Chem. Soc.*, 1978, **100**, 1487.

3 A. Rauk, T. S. Sorensen, C. Maerker, J. W. de M. Carneiro, S. Sieber and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1996, **118**, 3761.

4 (*a*) Gaussian 94 (Revision A.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1995; (*b*) Gaussian 98 (Revision A.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1998.

5 SCI-PCM Solvation Simulation. Users' Reference, Gaussian 94, p. 151 and refs. 155–157 therein.

6 A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502.

7 An implementation by A. Rauk of the harmonic oscillator–rigid rotator model, see D. A. McQuarrie, *Statistical Thermodynamics*, Harper and Row, New York, 1973.

8 (*a*) J. Tomasi and M. Persico, *Chem. Rev.*, 1994, **94**, 2027; (*b*) K. B. Wiberg, P. R. Rablen, D. J. Rush and T. A. Keith, *J. Am. Chem. Soc.*, 1995, **117**, 4261; (*c*) H. Castejon and K. B. Wiberg, *J. Am. Chem. Soc.*, 1999, **121**, 2139.

9 *Handbook of Chemistry and Physics*, 80th edn., CRC Press, New York, 1999–2000.

10 *Comprehensive Inorganic Chemistry*, vol. 2, Pergamon Press, Oxford, 1973, ch. 23, p. 850.

11 V. Gold, *J. Chem. Soc., Faraday Trans. 1*, 1972, 1611.

12 (*a*) J. S. Staral, I. Yavari, J. D. Roberts, G. K. S. Prakash, D. J. Donovan and G. A. Olah, *J. Am. Chem. Soc.*, 1978, **100**, 8016; (*b*) W. Koch, B. Liu and D. J. DeFrees, *J. Am. Chem. Soc.*, 1988, **110**, 7325; (*c*) M. Saunders, K. E. Laidig, K. B. Wiberg and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1988, **110**, 7652.

13 P. R. Schreiner, D. L. Severance, W. L. Jorgensen, P. von R. Schleyer and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1995, **117**, 2663.

14 S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 1955, **77**, 5562.

15 (*a*) V. J. Shiner, Jr. and J. G. Jewett, *J. Am. Chem. Soc.*, 1965, **87**, 1384; (*b*) W. H. Saunders, Jr. and J. T. Finley, *J. Am. Chem. Soc.*, 1965, **87**, 1385.

16 C. J. Coles and H. Maskill, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1083.

17 J. A. Bone, J. R. Pritt and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1447.