Axial and Equatorial 1-Methyl-1-cyclohexyl Cation Isomers Both Have Chair Conformations but Differ in C−C and C−H Hyperconjugation Modes

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Remarkably, the 1-methyl-1-cyclohexyl cation **1** has two distinct isomers, both having chair conformations. Our first ^{13}C NMR observation of **1** in superacid media was unexceptional.[1] The spectrum had the hallmark of a "classical" carbocation, e.g., a very low-field $^{13}C^+$ resonance at δ 329.4 ppm. A similar $^{13}C^+$ chemical shift is the major defining feature of the *tert*-butyl cation, the planar, sp^2-hybridized tertiary classical carbocation prototype.[2] However, a more detailed ^{13}C NMR study of **1** revealed a marked temperature dependence: the C3−C5 (β) carbon chemical shift varied over several ppm.[1] Hence, two (or more) species, whose individual chemical shifts are quite different, must be in equilibrium. But what is the nature of these species?

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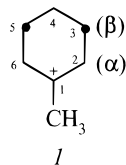
We first considered classical chair and twist-boat structures.[1] To fit the data, the twist-boat isomer had to be more stable than the chair form. However, the computed energies, calculated first at several semiempirical and later at *ab initio* MO levels, all gave the reverse order. Subsequent experiment results[3] could not be interpreted in terms of a twist-boat−chair conformer equilibrium either.
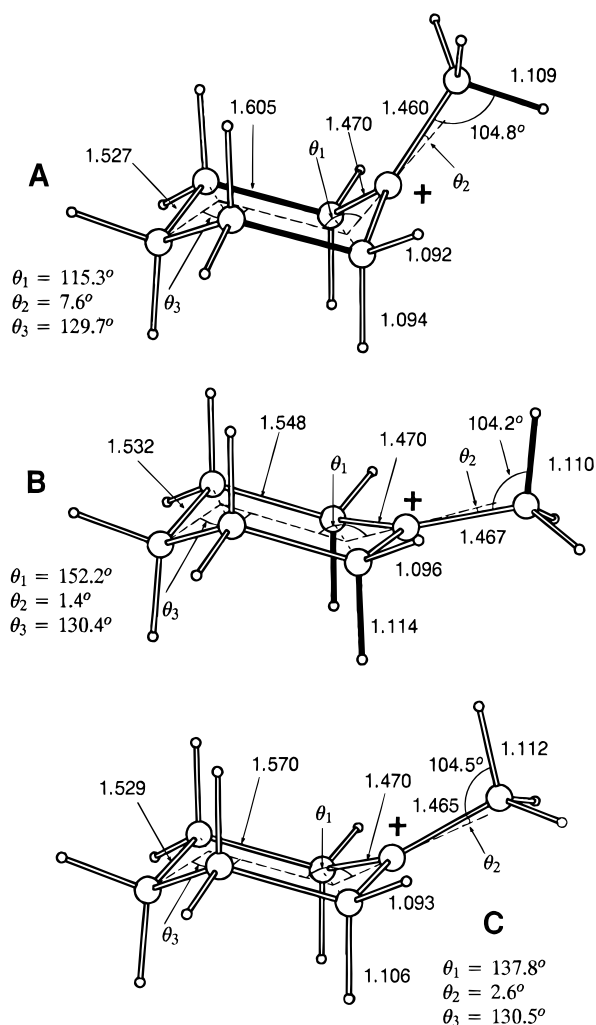
Consequently, we turned to the more radical possibility that the two isomers of **1** *both* had chair conformations but differed in having "axially" and "equatorially" oriented carbocation p-orbitals. These differing modes of pyramidal distortion might be due to counterion interactions[3,4] or to selective—and extensive—C−H and C−C hyperconjugation. However, these conclusions were only tentative. As no "frozen out" NMR data could be determined, recourse had to be made to indirect estimates of the β-^{13}C chemical shifts in the individual isomers.

We now report the results of an *ab initio* investigation which corroborate the isomeric *axial* vs *equatorial* cation picture nicely. Theoretical ^{13}C chemical shifts, computed at electron-correlated GIAO-MP2 levels,[5] agree well with the NMR data. The β-^{13}C chemical shift is particularly informative.

Figure 1. (A) Optimized geometry (Becke 3LYP/6-31G*) of the C−C hyperconjugated form **1** (**1** C−C). The bonds involved in hyperconjugation are shown in black. (B) Optimized geometry (Becke 3LYP/6-31G*) of the C−H hyperconjugated form **1** (**1** C−H) (bond designation as above). (C) Optimized geometry (Becke 3LYP/6-31G*) of the transition state connecting **1** C−C and **1** C−H.

Two very distinctive chair conformation minima of **1** were optimized at MP2/6-31G*[6] and at Becke 3LYP/6-31G*[7] (DFT) levels;[8] the geometries[9] of each isomer at both levels were quite similar (see Figure 1, where important bond lengths and angles are given). The equatorial cation, **1** C−C (Figure 1A), involves extensive C−C hyperconjugation characterized by long C2−C3 and C5−C6 bonds. Also note the larger degree of ring puckering and the inward distortion of the C^+ center, both of which facilitate C−C hyperconjugative interaction with the "vacant" p-orbital. In contrast, the axial cation isomer, **1** C−H (Figure 1B), features a flattened geometry, an opposite (small)

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

(2) Sieber, S.; Buzek, P.; Schleyer, P. v. R.; Koch, W.; Carneiro, J. W. de. M. *J. Am. Chem. Soc.* **1993,** *115,* 259.

(3) Kirchen, R. P.; Ranganayakulu, K.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987,** *109,* 7811.

(4) Finne, E. S.; Gunn, J. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987,** *109,* 7816.

(5) Gauss, J. *Chem. Phys. Lett.* **1992,** *191,* 614; *J. Chem. Phys.* **1993,** *99,* 3629. For a description of the GIAO approach, see: Ditchfield, R. *Mol. Phys.* **1974,** *27,* 789. Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990,** *112,* 851. For a recent application of GIAO-MP2 to carbocations, see: Sieber, S.; Schleyer, P. von R.; Gauss, J. *J. Am. Chem. Soc.* **1993,** *115,* 6987.

(6) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(7) Becke, A. D. *J. Chem. Phys.* **1993,** *98,* 5648.

(8) Several higher level single-point computations, e.g., MP4/6-31G*// MP2/6-31G*, were also carried out (see Table 2 of the supporting information for a listing of the energies obtained).

(9) See the supporting information for the geometry data for the two isomers of **1** at both levels of optimization.
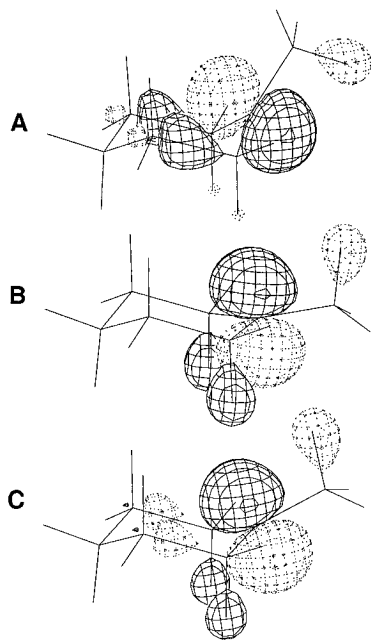
Figure 2. Plots of the LUMO orbital in the three structures shown in Figure 1.

pyramidal distortion, and lengthened axial C2−H and C6−H bonds. Clearly, C−H hyperconjugation is involved.[10] LUMO plots (Figure 2) also bring out the distinct differences between the C−C and C−H hyperconjugation modes.

Van't Hoff plots of NMR data of the 1-methyl-1-cyclohexyl cation **1**, as well as its isotopically labeled and methylated derivatives, indicated that the axial cation (**1** C−H) was ca. 1 kcal/mol more stable than **1** C−C. The theoretical energy difference between **1** C−H and **1** C−C varies somewhat from level to level but favors the latter (e.g., by 0.6 kcal/mol at B3LYP/6-31G* + ZPVE).[8] This insignificant discrepancy with experiment may be due to medium effects or insufficiencies in the theoretical levels employed.

The energy of the transition-state structure connecting **1** C−H and **1** C−C (Figure 1C), located at the Becke 3LYP/6-31G* level, is only 0.25 kcal/mol above **1** C−H (0.87 kcal/mol above **1** C−C)[12] (only a 4−5 kcal/mol upper limit could be estimated for the barrier from the −130° NMR data[1]). The TS geometry in Figure 1C is more in line with what one would expect for a classical 1-methyl-1-cyclohexyl cation than either the Figure 1A or 1B structures.

Other comparisons between the experimental and the computational results are satisfying. The GIAO-MP2/DZPDZ (TZPDZ) chemical shifts for the **1** C−C and **1** C−H isomers are given in Table 1. The experimentally derived β-^{13}C estimates are in good agreement with the computed values. Experimentally, 1α-D$_4$ substitution shifted the equilibrium

(10) The preferred hyperconjugative arrangement in these tertiary cations, with two interacting bonds on one C$^+$ cation face and one such bond on the other, also is found in the *tert*-butyl[2] and *tert*-pentyl[11] cations.

(11) Schleyer, P. von R.; Carneiro, J. W. de M.; Koch, W.; Forsythe, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3990.

(12) Nevertheless, both minima do support at least one vibrational level; for the frequency data for both the Becke 3LYP and MP2 calculations, see the supporting information.

Table 1. Calculated ^{13}C NMR Shifts[a] for the C−C and C−H Hyperconjugative Isomers of **1**,[b] Using the GIAO-MP2-Based Procedures[c] DZPDZ Basis Set (upper) and TZPDZ (lower)

	C1	C2−C6 (α)	C3−C5 (β)	C4	Me	exptl estimate C3−C5 (β)
C−C isomer	309.3	62.6	59.8[d]	28.1	42.4	
	322.4	64.9	62.2[d]	30.5	44.5	60[e]
C−H isomer	335.8	58.9	27.0	23.7	47.7	
	349.8	62.0	28.2	24.9	50.4	23.5[e]
experimental[f] at −88.5 °C	329.4	58.2	26.9	22.2	44.2	

a In δ ppm, relative to the calculated absolute shielding value for TMS of 205.720 (DZPDZ) and 198.89 (TZPDZ).[5] *b* Based on MP2/6-31G* geometries. *c* See ref 5 for descriptions of this method. See Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571 for a description of the DZPDZ and TZPDZ basis sets. *d* This calculated chemical shift is critically dependent on the level of theory used, and only the MP2-based procedures give these low-field values, e.g., IGLO/DZ gives δ 42.1 while GIAO-SCF/DZPDZ gives δ 42.5. See Table 3 of the supporting information for a complete listing of all of the NMR calculations. *e* Estimated from best fit van't Hoff plots[3] and guided by data from fixed geometry model systems.[1] *f* This temperature choice is arbitrary, but it was deduced (see *e*) that there was a 1:9.7 mixture of C−C and C−H isomers at this temperature. When the weighted averaged ^{13}C shifts for all carbons are calculated using the DZPDZ data in this table, the absolute deviation is a satisfying 3 ppm between experiment and theory.

population away from the **1** C−H isomer toward **1** C−C. The **1** C−H and **1** C−C ZPVE data can be used to compute the H/D isotope effect; the change in the equilibrium constant corresponds remarkably well to the experimental finding.[13]

In conclusion, the computational evidence confirms the postulated existence of two distinct chair conformers of the 1-methyl-1-cyclohexyl cation, **1** C−H and **1** C−C. Comparison of calcuated and experimental NMR chemical shifts confirms the somewhat greater stability of **1** C−H in superacid solution. While their interconversion barrier is small, these isomers should not be regarded as esoteric species. The manifestation of different hyperconjugation modes can be expected in other carbocations and in solvolysis transition states and may govern the preferred pathways for nucleophilic attack.

Supporting Information Available: Table 2, containing the calculated energies and ZPVE values for **1** C−C, **1** C−H, and the transition-state, for a range of computational levels; Table 3, containing details of all ^{13}C NMR computational results; the Z-matrices for the optimized geometries of both isomers at DFT and MP2 levels and the frequencies for each calculation (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) To be published later, together with data for other deuterated isotopomers of **1**.