

The Structure of the Nonamethylcyclopentyl Cation

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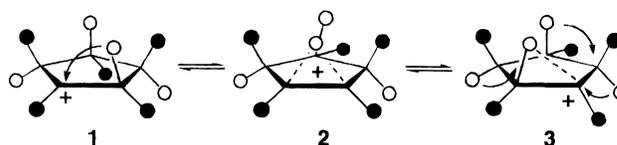
Abstract: The nonamethylcyclopentyl cation shows two types of methyl substituent in the NMR spectrum at low temperatures: four methyl groups undergo rapid circumambulatory migration with a barrier <2 kcal/mol while five methyl groups are fixed to ring carbons. The process that equalizes the two sets of methyls has a barrier of 7.0 kcal/mol. ¹³C NMR spectra of the (methyl-*d*₃)-octamethylcyclopentyl cation in SbF₅/SO₂ClF at -133 °C showed four ring carbons (2:2:5:1) indicating that the minimum structure is not symmetrically bridged. Quantum chemical calculations at HF/6-31G(d) and B3LYP/6-31G(d) levels revealed a minimum structure resembling a classical trivalent carbenium ion, but stabilized by hyperconjugation and partial bridging of two quasi-axial β-methyl groups. This bridging is related to the unique dynamic behavior of the title carbocation.

Introduction

The distinction between symmetrically bridged and rapidly equilibrating trivalent carbenium ions is often a challenging problem.¹ This kind of question has been effectively resolved for a number of structures using the isotopic perturbation method.² Experiments with deuterated isotopomers, for example, revealed the bicyclo[2.1.1]hexyl³ and norbornyl cations⁴ to be nonclassical, and the 2,3-dimethylbutyl⁵ and 1,2-dimethylcyclopentyl⁶ to be rapidly equilibrating classical structures.

A previous publication on the nonamethylcyclopentyl cation describes some extraordinary features.⁷ The ¹H NMR spectrum of this cation in superacid media (FSO₃H/SbF₅-SO₂ClF) consists of only a single peak at -90 °C (δ 1.86) indicating

Scheme 1



total scrambling of all methyl groups. When the solution was cooled, this peak split, and at -137 °C two peaks (δ 2.00 and 1.63) with relative intensities of 5:4 were recorded. Similar behavior was observed in the ¹³C NMR spectrum, where at -80 °C, the spectrum consists of one peak for the methyl groups at δ 25.24 and one peak at δ 110.88 corresponding to the ring carbons. In analogous fashion to the dynamic ¹H NMR spectrum, the methyl peaks split at lower temperature, and at -124 °C two signals appear at δ 23.57 and 28.17 with relative intensities 5:4. Line shape analysis yielded a barrier of 7.0 kcal/mol (ΔG[#], -120 °C) for their interconversion. Since the peak of the ring carbons did not broaden even at -135 °C, it was concluded that the barrier for methyl migration is lower than 2 kcal/mol. The simultaneous existence of a barrier of 7 kcal/mol for interchanging the two sets of four and five methyl groups and of a barrier of less than 2 kcal/mol for separately equilibrating all ring carbons and all the migrating methyls was explained by the exclusive migration of the trans located methyl groups. In this way, a bridged transition state or intermediate is displaced by approach of an adjacent methyl group from the opposite side of the ring. Repetition of this process results in a set of five methyl groups (●) which are fixed at ring carbons and of four methyl groups (○) which are following one another around the ring (Scheme 1). An analogous preference of trans-over cis-migrations has been observed for the degenerate hydride shifts in the *all-trans*- and *all-cis*-1,2,3,4,5-pentamethylcyclopentyl cation.⁸

These observations are inconsistent with the classically expected structure for this ion. A structure with a planar

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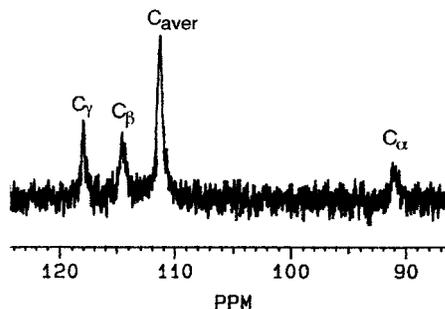


Figure 1. ^{13}C NMR spectrum of the ring carbons of the deuteriomethyl cation taken at -133°C .

arrangement of the ring carbons with one methyl in the plane of the ring on the tertiary cation center and four carbons above the plane of the ring and the other four symmetrically related to these and below the ring plane can be definitely ruled out. Not only can this structure be ruled out as a minimum energy structure, but it cannot be a low-energy transition state. It is a likely candidate for the transition state of the 7 kcal process.

Three possible minimum energy structures have been considered in accounting for the observed NMR spectra of the nonamethylcyclopentyl cation: a nonplanar classical and a partially bridged (e.g., **1**, **3**) or a symmetrically bridged (**2**) carbocation. To differentiate between these structures, we have now investigated the NMR spectra of the title cation in which one of the nine methyl groups was replaced by CD_3 . Calculations at HF/6-31G(d) and B3LYP/6-31G(d) levels of theory were also done to gain information about this ion.

Results and Discussion

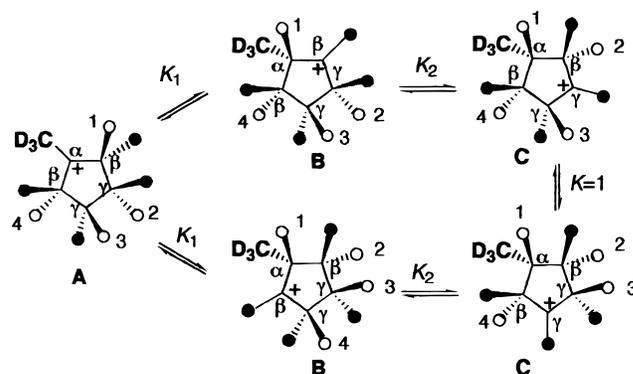
The (methyl- d_3)-octamethylcyclopentyl cation was prepared using a modified molecular beam method⁹ from (methyl- d_3)-octamethylcyclopentanol, as described in detail in the Experimental Section. The ^{13}C NMR spectrum obtained at -133°C shows four signals for the ring carbons due to the operation of equilibrium isotope effect (Figure 1). While the chemical shift of the most intensive peak (δ 111.22, relative intensity 5) is comparable to that of the all-protio compound, additional weaker peaks with relative intensities of 2:2:1 occur at δ 117.7, 114.4, and 90.9, respectively (referenced to *tert*-butyl cation, δ 47.6).

The equilibrium isotope effect (EIE)¹⁰ is mainly caused by the preference of deuterium to be at the position with large stretching and bending force constants and thus high zero-point energy. Thus, it is favorable for the C–D bond not to be involved in hyperconjugation, and the deuteromethyl group tends to be remote from the carbocation center.

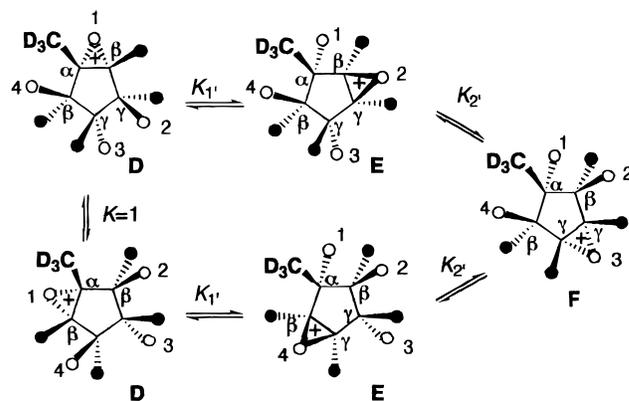
Since in the all-protio compound there are two types of methyl group which do not exchange at low temperature, there must be two sets of isomers of (methyl- d_3)-octamethylcyclopentyl cation that do not rapidly interconvert at -133°C : The isomers with the CD_3 group among the migrating (\circ , Scheme 1) and the isomers with the CD_3 group among the static methyl groups (\bullet , Scheme 1). In the first set of isomers (\circ , CD_3 migrating), all ring carbons share the positive charge equally, and the ring

Scheme 2

Case 1 (classical or semibridged minimum)



Case 2 (symmetrically bridged minimum)



carbons give rise to a single peak at δ 111.22, *i.e.* that appear at almost the same chemical shift as the nondeuterated analogue. In the second set of isomers, where CD_3 is one of the static methyl groups (\bullet), the unequal population of the different isomers (Scheme 2) due to the equilibrium isotope effect causes the splitting of the ring carbon absorption. It should be noted that the average of the chemical shifts of the small peaks $[(2 \times 117.7) + (2 \times 114.4) + 90.0]/5$ equals the chemical shift of the large peak (111).

Depending on the minimum energy structure, two splitting patterns of the ring carbons can be expected. If the minimum corresponds to **1** (or **3**), the EIE will reduce the population of structure **A** relative to that of **B** and **C** because CD_3 is directly attached to the carbocation center in **A**. As a consequence, the average positive charge at C_α will be smaller than that at C_β and C_γ , and C_α will become shielded while C_β and C_γ will become deshielded with respect to the averaged ring carbon (C_{aver}). In accord with this interpretation, two carbons (each with intensity 2) absorb downfield from C_{aver} , whereas one carbon (with intensity 1) absorbs upfield from C_{aver} (Figure 1).

If the minimum energy structure were the methyl-bridged species (**2**, Scheme 1), there would be one isomer (**D**) with CD_3 in the proximity of the carbocation center and two isomers (**E** and **F**) in which CD_3 is located at a formally uncharged ring carbon. Because of the EIE, the population of each isomer **D** should be lower than that of each isomer **E** and **F**. Since C_α is partially charged and C_γ is formally noncharged in both **D** isomers, a reduction of the population of **D** should result in an upfield shift of C_α and a downfield shift of C_γ . The analysis of the EIE on C_β is more complicated, since in each of the isomers **D** and **E**, one C_β is partially charged and the other C_β is formally noncharged, *i.e.*, in a first approximation, a change of the

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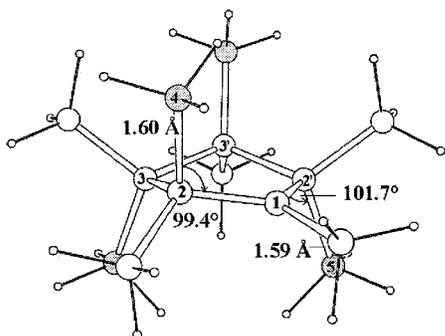


Figure 2. The optimized geometry on the B3LYP/6-31G(d) level of the nonamethylcyclopentyl cation (the migrating methyl groups are shaded).

population of isomers **D** and **E** would not affect δ_β significantly. In isomer **F**, however, both C_β atoms are formally uncharged, and an increase of the population of **F** due to the EIE should result in an upfield shift of C_β with respect to C_{aver} .

In summary, in the case of equilibrating structures $\mathbf{A} \rightleftharpoons \mathbf{B} \rightleftharpoons \mathbf{C}$ one would expect two downfield and one upfield ring carbon absorptions (2:2:1), while in the case of equilibrating structures $\mathbf{D} \rightleftharpoons \mathbf{E} \rightleftharpoons \mathbf{F}$ one would expect one ring carbon to absorb downfield and two ring carbons to absorb upfield with respect to C_{aver} . Figure 1 shows that the first case is experimentally observed, and a symmetrically bridged minimum structure can be ruled out.

To analyze the experimental findings in a quantitative manner, geometry optimization and frequency calculation for the nonamethylcyclopentyl cation was carried out at HF/6-31G(d) and B3LYP/6-31G(d) levels of theory, using the Gaussian 94 package.¹¹ The nonamethylcyclopentyl cation is a challenging case for the application of theoretical methods. To begin with, it has a relatively large number of atoms and adjustable structural parameters. To make optimizing particularly difficult, there are many methyl groups with low torsional barriers. With all the torsional degrees of freedom, it is very difficult to search over all conformational space for the lowest energy structures. This is true, whether one is searching for minima or transition states. In addition, the scrambling process we are searching for has a barrier of <2 kcal. It is not clear that the calculation level which can be achieved with this number of atoms using available computers and programs gives accurate enough results to get an appropriate energy, even if we could explore the energy surface thoroughly.

The new data presented in this paper come from introducing deuterium to break degeneracy and split NMR lines. Theoretical methods can be of substantial aid in evaluating these data. We can consider structures that must be close to the pathway for rearrangement and do *ab initio* calculations at a level high enough so that we expect that predicted isotope effects will be realistic.

The optimized DFT structure presented in Figure 2 shows a twisted cyclopentane ring which has C_1 symmetry. The positive charge is stabilized by β -CC hyperconjugation (C_2-C_6), resulting in a considerable reduction of the angle $C_4-C_2-C_1$ (99.4°)

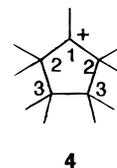
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Table 1. Calculated Chemical Shifts by the GIAO B3LYP/6-311G(d,p)//B3LYP/6-31G(d) Method (δ_{calc}) and the Corresponding Scaled Values (δ_{scaled}), Referenced to TMS

carbon atom	δ_{calc}	δ_{scaled}
1	347.7	339.7
2	87.4	76.4
2'	82.7	72.4
2 _{av}	(85.5) ^a	(74.4) ^a
3	60.1	27.5
3'	57.8	26.5
3 _{av}	(58.9) ^a	(27.0) ^a

^a Average between 2 and 2', or 3 and 3'.

and an elongation of the C_2-C_6 bond (1.60 Å). Analogously, the angle $C_5-C_2-C_1$ is reduced (101.7°), and the C_2-C_5 bond is elongated (1.59 Å), indicating that both quasi-axial β -methyl groups are partially bridging, and take part in hyperconjugative stabilization to a different extent.



To determine the equilibrium isotope effects (K_1 and K_2), let us consider the “frozen out” nonamethylcyclopentyl cation **4** with the chemical shifts δ_1 , δ_2 , and δ_3 that correspond to carbon atoms C_1 , C_2 , and C_3 , respectively. For the isotopomer in which CD_3 belongs to the set of migrating methyl groups (○) the averaged chemical shift of the ring carbons is given by eq 1:

$$\delta = \frac{\delta_1 + 2\delta_2 + 2\delta_3}{5} \quad (1)$$

If the CD_3 group is one of the static methyl groups, the ratio of the three energetically different structures **A**, **B**, and **C** (Scheme 1) is $1:2K_1:2K_1K_2$. Thus, the chemical shifts of the carbon atoms C_α , C_β , and C_γ can be obtained according to eqs 2–4:

$$\delta_\alpha = \frac{\delta_1 + 2\delta_2K_1 + 2\delta_3K_1K_2}{1 + K_1 + 2K_1K_2} = 90.9 \text{ ppm} \quad (2)$$

$$\delta_\beta = \frac{\delta_2 + (\delta_1 + \delta_3)K_1 + (\delta_2 + \delta_3)K_1K_2}{1 + K_1 + 2K_1K_2} = 114.4 \text{ ppm} \quad (3)$$

$$\delta_\gamma = \frac{\delta_3 + (\delta_2 + \delta_3)K_1 + (\delta_1 + \delta_2)K_1K_2}{1 + K_1 + 2K_1K_2} = 117.7 \text{ ppm} \quad (4)$$

To determine the equilibrium constants K_1 and K_2 , the ^{13}C shifts of the static carbocation **4** are needed. A method for predicting ^{13}C shifts of the carbocations with standard deviation as little as $|\Delta\delta_{\text{av}}| = 1.7$ ppm was presented recently.¹² It is based on the calculation of the NMR chemical shifts by the GIAO-B3LYP/6-311G(d,p) method using geometries optimized at the B3LYP/6-31G(d) level. The chemical shifts thus calculated (δ_{calc}) are then scaled by the equation $\delta_{\text{scaled}} = a\delta_{\text{calc}} + b$, using the parameters a and b given in ref 12 (Table 1). Because of the nonsymmetric nature of the minimum, different chemical shifts for C_2 and $C_{2'}$ as well as for C_3 and $C_{3'}$ were obtained

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Table 2. Experimental and Theoretical Equilibrium Isotope Effects ($-133\text{ }^{\circ}\text{C}$) Obtained for the (Methyl- d_3)-octamethylcyclopentyl Cation

isotope effect	experimental	theoretical	
		HF ^a	B3LYP ^b
K_1	1.65 ± 0.13	1.813	1.789
K_2	0.97 ± 0.08	1.015	1.033

^a The force constant matrix used as input to QUIVER was calculated at the HF/6-31G(d)//HF/6-31G(d) level. ^b The force constant used as input to QUIVER was calculated at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level.

(Figure 2). The average of the corresponding values was used for the following calculations.

Substituting the scaled chemical shifts (δ_{scaled}) given in Table 1 into eq 1 yields a theoretical averaged chemical shift for the ring carbons of δ 108.5. The excellent agreement with experiment (δ 110.1) demonstrates the reliability of the scaled chemical shifts presented in Table 1.

The δ_{scaled} of Table 1 were then substituted into eqs 2–4 yielding three linear equations with the two variables K_1 and K_1K_2 , from which the equilibrium constants $K_1 = 1.65 \pm 0.13$ and $K_2 = 0.97 \pm 0.08$ were derived. Structure **A** (Scheme 2) is thus found to be $\Delta G^{\circ}(-133\text{ }^{\circ}\text{C}) = 0.14$ kcal/mol less stable than **B** or **C**, which turned out to be almost equal in energy.

Equilibrium isotope effects can alternatively be derived by analysis of the theoretical vibrational frequencies. For that purpose, we have employed the program QUIVER,¹³ which uses the Cartesian force constant matrix produced by Gaussian to calculate the vibrational frequencies for the different isotopomers and the reduced isotopic partition function ratios (s_2/s_1)_f. The calculated equilibrium constants K_1 and K_2 nicely agree with the corresponding experimental values (Table 2).

Conclusion

NMR spectroscopic investigations and quantum chemical calculations agree that the nonamethylcyclopentyl cation possesses a minimum energy structure distorted from that expected for a classical trivalent carbenium ion. Strong hyperconjugative stabilization, i.e., partial bridging, from the two quasial axial methyl groups in the C_2 and C_2' positions is responsible for its unique properties, i.e. the splitting of the nine apparently equivalent methyl groups into two sets of four and five methyls. This 2-fold hyperconjugative stabilization is so strong that the circumambulatory migration of four methyls proceeds via the

bridged ion with an extremely low barrier (<2 kcal/mol), and the interconversion of all methyl groups is inhibited.

Experimental Section

Cation Sample Preparation. Cation samples were prepared by ionization of the corresponding alcohol prepared from octamethylcyclopentanone¹⁴ and CD_3Li in a modified molecular beam apparatus described in detail previously.⁹ Typically 25 mg of the sample was placed in a chamber of the apparatus. The glass chamber was then evacuated and placed into liquid nitrogen, and 0.2 mL of antimony pentafluoride (previously degassed) was distilled into the system cooled with liquid nitrogen over a period of about 15 min. The solvent (0.7 mL of SO_2ClF) was distilled into the chamber before and after the superacid distillation. Then, the frozen mixture was thawed slowly in a methanol/ethanol slush bath ($-120\text{ }^{\circ}\text{C}$). The obtained cation solution was frozen again in liquid nitrogen and evacuated, and 40 μL of *tert*-butyl chloride- d_9 was distilled into the chamber at high vacuum, followed by addition of the new portion of solvent (0.2 mL). The procedure of thawing was repeated, followed by pouring the sample into the precooled NMR tube, and sealing the tube which was immediately frozen in liquid nitrogen until analyzed.

NMR Spectra. ¹³C NMR spectra were recorded on a Bruker AM 500 spectrometer at 125.76 MHz. Cation samples were placed in a precooled NMR probe following temperature calibration with 1-chlorobutane.¹⁵ The *tert*-butyl cation was used as a reference for the peak position (δ 47.6 ppm) as well as for the lock signal. Spectrometer acquisition parameters were tailored according to the demands of the experiment. Typically, for recording the ring carbons of the (methyl- d_3)-octamethylcyclopentyl cation, the center of the frequency was positioned at δ 100 ppm, and ca. 10000 scans with digital resolution of 0.76 Hz/point (spectra with (SW) 12500 Hz) were collected.

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Supporting Information Available: Coordinates for optimized geometries of the title compound at the HF and DFT levels (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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